ELECTRONIC SPECTRA AND STRUCTURE OF SOME ELECTROACTIVE ORGANOTRANSITION METAL COMPLEXES

by

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INTRODUCTION

During the past two decades, the field of organometallic chemistry has grown very rapidly. Both experimental and theoretical investigations in this area of chemistry continue to proliferate. Initially, the interest in this branch of chemistry stemmed from the novelty of direct linkage between a metal atom or ion, usually in a low formal oxidation state, and a carbon atom. Such a linkage had previously been considered by chemists as unlikely or impossible. Subsequent investigations, however, have disclosed that many organometallic compounds possess considerable industrial and biological, as well as fundamental chemical significance.[1-8] As a result of this disclosure, extensive activity has been directed toward the electronic structural elucidation of organometallic and organometalloidal compounds.[7-10] Organometallic carbonyl and nitrosyl compounds have been especially amenable to electronic structural studies because of the considerable stability that both the CO and NO molecules impart to complexes possessing a metal in a low formal oxidation state.[11,12] In addition, coordinated nitrosyl and carbonyl groups exhibit pronounced sensitivity toward changes in electronic charge density around the metal to which they are bonded. This sensitivity is manifested in alterations of the metal-nitrogen, nitrogen-oxygen, metal-carbon, and carbon-oxygen stretching frequencies.[13,14] Consequently, infrared spectroscopy has been a valuable physical technique for probing the electronic structure of carbonyl- and nitrosyl-containing organometallic complexes.

In theory, replacement of one or more carbonyls or nitrosyls in a complex by other ligands enables ascertainment of certain properties of the new ligand in addition to providing bonding information on the metal-carbonyl or metal-nitrosyl moiety. The technique of monitoring changes in the remaining carbonyl and nitrosyl stretching frequencies as a function of the replacing ligand has been used to assess base-strengths,[15-17] π-acceptor capacities,[18,19] modes of bonding and electronic charge distribution mechanisms[20-22] for a variety of ligands. Inherent in such an approach is the introduction of steric, geometric, and electronic factors which are not readily identified and evaluated. A more direct approach to the study of electronic structures of and modes of electronic charge distribution in substituted metal carbonyls and nitrosyls is electrochemical alteration of charge distribution. The reversible electrochemical reduction of organotransition metal carbonyls and nitrosyls to radical anions and, in some cases, to singlet-state dianions and the reversible oxidation to radical cations perturb the electronic structures without, generally, producing steric or geometric changes. Electrochemically generated organotransition metal radical anions, dianions, and radical cations representative of octahedral, trigonal bipyramidal, and tetrahedral geometry have been studied by infrared, electron spin resonance, nuclear magnetic resonance, and Mössbauer spectroscopy.[23-25] Each of these tools has provided significant insight into the electronic structures of the electroactive organotransition metal species, but, not without leaving a number of germane questions unanswered.

An important spectroscopic tool which has not previously been employed in the study of the electronic structures of electroactive organotransition metal species is electronic absorption spectroscopy.

Indeed, a relative dearth of electronic spectral information has existed for many of the neutral presursor molecules.

The procurement and analysis of electronic absorption spectra of both neutral presurosrs and electrolyzed organotransition metal complexes would be expected to provide a complementary adjunct to the spectroscopic results previously reported. Such an investigation might also be expected to provide answers to some of the questions left unanswered by the preceding studies. For these reasons, the investigation reported in this dissertation was undertaken. Electronic absorption spectra for complexes of two distinct geometries have been obtained and analyzed. Thus, presentation is made in two parts. The major part, Part I, will deal with diimine Group VI-B metal tetracarbonyls (octahedral geometry); Part II will deal briefly with diiminedinitrosyliron(0) complexes (tetrahedral geometry). (Full names and abbreviations for all the complexes involved in this work are listed in Appendix A).

PART I

THE OCTAHEDRAL CASE:

DIIMINE DERIVATIVES OF

GROUP VI-B METAL HEXACARBONYLS

INTRODUCTION

The electronic structures and modes of bonding in transition metal carbonyl complexes are of considerable theoretical interest to chemists because of the tendency for carbon monoxide to form complexes with metals in very low formal oxidation states. These complexes are generally considered to be stabilized through synergistic bonding between the carbon monoxide molecule and the low-valent metal. The bonding between the carbon and oxygen atoms in carbon monoxide consists of a σ-bonding molecular orbital and a pair of degenerate π-bonding molecular orbitals (Appendix B).[26] In addition, lone pairs of electrons occupy non-bonding molecular orbitals on both the oxygen and carbon atoms, the latter being the donor pair used in forming σ-bonds with transition metals. The lowest unoccupied molecular orbitals are the doubly degenerate π-antibonding orbitals. Formation of the dative σ-bond between carbon monoxide and the metal results in the accumulation of an intolerably high charge density on the metal. This situation is alleviated through the overlap of filled metal d-orbitals, of appropriate symmetry, with the π-antibonding orbitals of the carbon monoxide. Delocalization of electronic charge density from the filled metal d-π orbitals into the CO-π^* orbitals increases the attractive potential of the metal, giving rise to enhanced d-orbital sigma bonding. The increased participation of CO-σ orbitals, in turn, produces an expansion of the metal orbitals, especially the d orbitals, thereby augmenting overlap with the antibonding π-orbitals of CO.[27] The electronic structures of unsubstituted Group VI-B metal carbonyls have been thoroughly studied and are apparently well understood.[27-31]

Successive replacement of CO in Group VI-B hexacarbonyls by other ligands, L, to produce complexes of the general stoichiometry, $L_nM(CO)_{6-n}$, is readily achieved.[11] When carbon monoxide is replaced by a ligand (hereinafter, the term "ligand" refers specifically to a non-carbonyl ligand) possessing π-acceptor capacity, the ligand competes with the remaining carbonyls for metal d-π orbital interaction. Consequently, a ligand which is a poorer π-acceptor than carbon monoxide should enable the filled metal d-π orbitals to overlap more effectively with the π^* orbitals of the carbonyls. The net result of this interaction is a flow of electronic charge toward the carbonyls. Entry of charge into the CO-π^* orbitals via the metal d-π orbitals should diminish the formal C-O bond order and, hence, decrease the C-O stretching frequencies. This π-mode of charge transmission must be anisotropic in nature. The C-O stretching force constants (k_2) for carbonyls positioned <u>cis</u> to π-acceptor ligands are expected to be influenced approximately twice as much as the force constants (k_1) for those carbonyls located <u>trans</u> to a ligand in both mono- and disubstituted complexes. Semiquantitative estimates of the degree of π-bonding between a ligand and Group VI-B metals have been made from observed changes in these force constants, which have been derived from an approximate force field in which only pure C-O stretching modes and non-mechanical coupling of these modes are considered.[19,32] Such estimates are predicated upon the assumption that the observed force constant changes result almost entirely from changes in the M-C-O π-bonds.

It has, however, been argued that any change of electronic density in the M-CO σ-bond will also influence the C-O stretching frequencies and force constants.[15,21] Increased negative charge on the metal, such as would result through σ-donation from a coordinated ligand, renders the metal less acidic toward CO σ-donation. Consequent weakening of the M-CO σ-bond results in a decrease of the C-O bond order and, hence, leads to a decrease in the C-O stretching force constants. This σ-only mode of charge distribution is postulated to be anisotropic in nature, with the stretching force constants of the carbonyls cis to a ligand being affected to a greater extent than those trans to a ligand. Thus, a σ-mechanism of charge transmission can also provide a plausible rationalization for observed decreases of C-O stretching force constants as ligands, whether potential π-acceptors or not, are substituted for carbonyls.

Finally, a combination of σ- and π-modes of charge distribution has also been advanced to account for the observed changes in carbonyl stretching force constants as ligands are substituted for carbonyls.[21,22] According to this point of view, σ-donation by the ligand to the metal results in an increase in negative charge on the metal. This increase in charge on the metal raises the energies of the d-π orbitals, facilitating enhanced overlap with CO-π^* orbitals and leads to a decrease in C-O force constants. In terms of the combination σ-π

mechanism of charge distribution in monosubstituted Group VI-B metal carbonyls, the force constant change for CO molecules cis to a ligand is given by $\Delta k_2 = \Delta\sigma + \Delta\pi$ where $\Delta\sigma$ and $\Delta\pi$ represent the σ and π contributions, respectively, to the overall force constant change. The change in the CO trans to the ligand, is then, given by $\Delta k_1 = \Delta\sigma + 2\Delta\pi$. For a cis-disubstituted complex or for $L_2M(CO)_4$, where L_2 is a bidentate ligand such as a diimine, these relationships become $\Delta k_1 = \Delta\sigma + \Delta\pi$ and $\Delta k_2 = \Delta\sigma + 2\Delta\pi$.

Obviously, all three of these charge transmission mechanisms, all of which are ultimately based on carbonyl stretching force constant changes derived from a "Cotton-Kraihanzel" force field, cannot be generally valid. Consequently, the mechanism of charge distribution in substituted Group VI-B metal carbonyls, through which has been established relative donor-acceptor capacities for a number of series of ligands, has been and, apparently, remains a source of controversy.[33]

The three preceding arguments have been based upon data obtained through ligand variation. Attempts to determine the mechanism involved in charge transmission on such a basis suffers from the disadvantage that, in producing the changes in carbonyl stretching frequencies which are to be analyzed and interpreted in terms of the bonding, additional changes such as steric factors, geometrical factors, electronegativities, and polarizabilities have been introduced. These additional changes are neither easily revealed nor readily assessed and they will almost assuredly affect the net bonding scheme so that only a cumulative result is obtained. Recognizing these inherent deficiencies, Dessy and Wieczorek,[23,34] have investigated carbonyl force constant changes between several neutral complexes and their corresponding electrochemically generated radical anions. The conclusions reached in these studies have been based upon the premise that the reversible electrochemical reduction of an organotransition metal carbonyl results in the addition of an electron to the lowest unoccupied molecular orbital of the neutral complex without producing steric or geometric alterations requiring evaluation. Accordingly, the influence experienced by the carbonyls is solely, or more nearly so than in the case of a ligand change, due to the manner in which the central metal atom accepts and transmits charge density.

In the case of (2,2'-bipy)M$(CO)_4$ where M is a Group VI-B metal, these investigators have found that the change in carbonyl stretching force constants (Δk_1) for carbonyls <u>trans</u> to the 2,2'-bipyridyl is greater than the change in the force constants (Δk_2) for the carbonyls located <u>cis</u> to the ligand. (Relevant data for these complexes are shown in Appendix C). This change in force constants is consistent with an anisotropic σ-mechanism of charge distribution. Electron spin resonance measurements on the radical anion of 2,2'-bipyridyl and on the radical anion of (2,2'-bipy)Mo$(CO)_4$ indicate that the hyperfine coupling constants (obtained by successful computer simulation of the esr spectra) at corresponding positions in the diimine are quite similar. Thus, it has been concluded that the reducing electron enters a predominantly ligand-based molecular orbital and that some of the charge due to this electron is subsequently disseminated to and through the metal to the carbonyls by an anisotropic σ-only mechanism.

Dessy and Charkoudian[24,35] have arrived at similar conclusions for diacetyldianil derivatives of Group VI-B hexacarbonyls. (Relevant data are shown in Appendix C). In this case, the complexes form stable singlet-state dianions as well as stable radical anions. The dianions, being diamagnetic, are amenable to nmr investigation. Evaluation of the chemical shifts for the diacetyldianil aromatic protons shows that only one percent of the reductive charge resides on the ortho- and para-carbons. For the corresponding radical anions, it has been found that approximately 22% of the unpaired spin density resides at these same positions. Thus, the second important conclusion derived from this study is that spin and charge density are distinct and separable phenomena.

The last two investigations described in the preceding paragraphs either raise or do not unequivocally answer several important questions, e.g., (1) Do electrons actually enter ligand-based molecular orbitals when tetracarbonyldiimine Group VI-B metal complexes are reduced? (2) Is charge disseminated by a σ-only mechanism in systems containing ligands, such as diimines, which can and do form π-bonds to transition metals in certain instances? (3) Is the concept of spin and charge separation, based upon two differently charged species, a valid concept?

In an effort to answer some of these questions in a less equivocal manner and anticipating that such an investigation would provide additional insight into the electronic structures of diimine derivatives of Group VI-B metal hexacarbonyls, the electronic spectral studies reported in this part of the dissertation were undertaken.

EXPERIMENTAL

Electrochemical Studies

All electrochemical work and preparations of electroactive samples used in obtaining electronic, esr, and infrared spectra were performed in a dry box (Vacuum Atmospheres Dry-Lab Train) employing an argon atmosphere controlled to not more than about 2 ppm water vapor and oxygen.

Controlled-potential electrolyses, polarographic measurements, and cyclic voltammetry were conducted in a standard H-type cell. The anodic compartment of the cell was 35 mm in diameter, 47 mm high, and fitted with a standard taper joint into which was sealed a platinum wire serving as electrical contact with a mercury pool at the bottom of the compartment. The cathodic sector of the cell, 35 mm in diameter and 60 mm high, possessed three outer standard taper joints at the top, had a platinum wire sealed into the side near the base, and was fitted with an exit stopcock at the base. The standard taper joints accommodated the reference, the hanging-drop, and the dropping mercury electrodes while the platinum wire provided electrical contact with a stirred mercury pool at the bottom of the compartment during controlled-potential electrolyses. A medium porosity glass frit, 25 mm in diameter, separated the two compartments.

The electrolysis cell used in preparing samples for infrared investigation consisted of two concentric compartments connected electrically by a 20 mm medium porosity glass frit. The outer compartment, which held the test solution and supporting electrolyte, was 45 mm in diameter, 57 mm high and had a platinum wire pinchsealed into the base to provide electrical contact with the mercury pool. The inner compartment was 25 mm in diameter, 44 mm high, and fitted with a standard taper joint into which was the placed the counter electrode. This counter electrode consisted of a platinum wire sealed into glass and spot welded to a platinum disk 13 mm in diameter.

The reference electrode consisted of two compartments separated by a glass frit. The upper compartment contained a sealed-in, 20-gauge silver wire immersed in a reference solution of 1 X 10^{-3} M silver perchlorate and 0.1 M tetrabutylammonium perchlorate in 1,2-dimethoxyethane. The lower portion, also possessing a glass frit at the bottom, contained 0.1 M tetrabutylammonium perchlorate in 1,2-dimethoxyethane which served as a salt bridge between the Ag/Ag^{+} reference and the test solution in the cathodic compartment.

Polarograms were recorded using a Metrohm Polarecord E-261 in conjunction with a Sargent Model A iR compensator. The capillary used for the dropping mercury electrode had a drop time of about two seconds.

Cyclic voltammetric data were obtained employing a unit based on standard operational amplifier circuitry.[36] The unit which was employed allowed independent variation of the anodic and cathodic limits, the mid-potentials, and the scan frequencies. The voltammograms were recorded on a Moseley 2D-2XY recorder. The hanging-drop electrode consisted of a standard capillary tube attached to a microsyringe head.

All controlled-potential electrolyses were carried out at a stirred mercury pool and employed electrical circuits based on standard operational amplifier design.[36] Coulometry was performed by graphical integration of current-vs-time plots of the electrolyses.

Large scale reductions for infrared analyses were conducted with two Kepco CK 60-0.5 power supplies wired in a master-slave configuration. A Heath voltage reference source was used to offset the summing point of the master unit, thus setting the controlled potential, $E_{ref} - E_{test}$, for electrolysis at the large mercury pool in the cathode compartment. Current passed during the electrolysis was monitored by a small dropping resistor in series with the working electrodes, the iR drop being fed into a Yellowsprings recorder. After the current had dropped to the residual level, the exhaustively reduced material was syringed into the infrared cell.

Infrared Spectra

The infrared spectra for most of the neutral and reduced tetracarbonyldiimine Group VI-B metal complexes, for which electronic spectral data have been obtained, have been reported previously.[34,35] Only the infrared spectra of neutral and reduced (1,10-phen)$M(CO)_4$ (M = Cr, Mo, W), (4,7-ϕ_2-1,10-phen)$Cr(CO)_4$, (4,4'-ϕ_2-2,2'-bipy)$Cr(CO)_4$, and (dibenzyldianil)$Cr(CO)_4$ have been obtained and analyzed in this work. The neutral, radical anion, and dianion spectra for these complexes were taken on approximately 0.02 M solutions in 1,2-dimethoxyethane and in the presence of supporting electrolyte. Infrared spectra were recorded on a Perkin-Elmer Model 621 double beam spectrophotometer. The reference cell, in all instances, contained only solvent and supporting electrolyte, thus removing these components from the recorded spectra. The cells, purchased from Barnes Engineering Co., employed Teflon spacers (0.1 mm thick), gaskets, and "O" rings to achieve an air-tight seal. Syringe-barrel receptacles, capable of being tightly stoppered with Teflon plugs, were mounted on the cell frame to facilitate syringing of samples in the dry box. Irtran-2 type windows were used in the cells.

The infrared data were analyzed using a Fortran IV program written by G. W. Dulaney and described elsewhere.[34]

Electron Spin Resonance Measurements

Electron spin resonance measurements were made on all radical anion samples for which electronic absorption spectra were recorded. However, this physical method has not been used as an electronic structural tool in the present investigation. It has, rather, been simply used as a routine device to monitor the formation of radical anions. The esr spectra of most of the radical anions for which electronic spectra have been obtained have been reported previously.[34,35] All measurements were made on a Varian E-3 Spectrometer equipped with a variable temperature accessory.

Electronic Absorption Spectra

Ultraviolet, visible, and near-infrared electronic absorption spectra were recorded on a Cary 14 Spectrophotometer. All spectra were recorded on 1,2-dimethoxyethane solutions containing solute concentrations of about 2.5×10^{-4} M for ultraviolet and visible spectra and about 1×10^{-3} M for near infrared spectra. Matched quartz cells of either 0.1 or 1 mm path length were employed for measurements made in the ultraviolet region, whereas matched quartz cells of 1 cm path length were used for the visible and the near-infrared measurements.

Two methods were employed to obtain electronic spectra of reduced free diimine ligands and reduced tetracarbonyldiimine Group VI-B metal complexes. The former were reduced chemically with potassium metal and the latter were reduced electrochemically. Electrochemical reductions were carried out as described in the section entitled "Electrochemical Studies." First, polarograms were run between 0.0 volt D.C. and about -3.6 volts D.C. (the reduction potential for supporting electrolyte). Then, cyclic voltammograms were obtained to ascertain reversibility of the reductive and oxidative processes, after which the substrates were exhaustively reduced at a potential corresponding to the top of the diffusion current waves indicated in the polarograms. At the conclusion of an exhaustive controlled-potential electrolysis, the solution of reduced substrate (and tetrabutylammonium perchlorate, which does not absorb in the spectral regions investigated) was removed from the electrolysis cell with a meticulously cleaned hypodermic syringe and introduced into a clean cell apparatus, designed as shown schematically in Figure 1a.

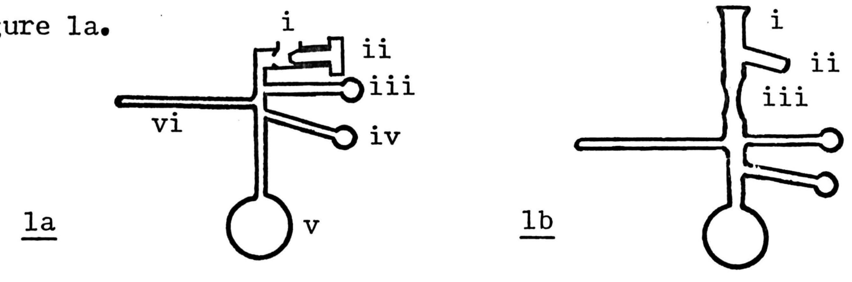


Figure 1. Spectral Cell Designs. 1a: i. entry port; ii. high-vacuum valve (Teflon-to-glass seal); iii. 1 mm pathlength quartz cell; iv. 1 cm pathlength quartz cell; v. 25 ml volumetric flask; vi. 2 mm-i.d. quartz tube for esr measurements. 1b: i. 14/35 outer joint for vacuum-line attachment; ii. side-arm for potassium; iii. constriction for sealing.

The closed cell was then removed from the dry box and an esr spectrum recorded. Following the esr measurement, an electronic sbsorption spectrum between 2,000 and 20,000 Å was obtained. After obtaining the electronic absorption spectrum, an esr spectrum was again recorded to insure minimal loss of radical anion or dianion during the recording of the electronic absorption spectrum. After this had been accomplished, the reduced sample was oxidized, a polarogram was run on the oxidized sample and compared to the original neutral sample. Finally, an electronic absorption spectrum was run on the oxidized sample and compared to that of the neutral complex. Unless the polarogram and electronic absorption spectrum of the oxidized and neutral species were coincident, or nearly so, the spectrum of the reduced species was rejected.

Despite rigorous controlled-potential electrolysis, there is always danger of radical anion loss between the time when the electrolysis is curtailed and the time when the electronic spectrum is actually taken and there is no way to judge, with certainty, the amount of loss. The criteria that have been used in ascertaining whether a given spectrum is acceptable are 1) no discernible loss of radical anion and 2) at least a threefold replication of the spectrum in terms of band position. Even then, there remains some uncertainty in the actual concentration of radical anion or dianion present in solution. Consequently, considerable uncertainty exists in measured molar absorptivities and oscillator strengths for radical anions and dianions.

The electronic spectra of reduced ligands were obtained after the ligands were reduced by vacuum line technique. The solvent, 1,2-dimethoxyethane, was predried over calcium hydride and distilled from lithium aluminum hydride, after which it was thoroughly degassed by bubbling argon through it for approximately twenty minutes. In the dry box, two 500 ml round bottom flasks, fitted with high-vacuum stopcocks, were charged with about 5 g of sodium-potassium alloy. These flasks, one of which contained the solvent prepared as described above, were then transferred to a vacuum line. After bulb-to-bulb distillation from one flask to the second and thorough degassing, the solvent was used for the preparation of chemically reduced ligands.

The chemically reduced species were then prepared as follows. Into a specially constructed cell assembly, shown schematically in Figure 1b, was placed, via a long, narrow funnel, a pre-weighed quantity of substrate. The assembly was then transferred to the dry box. Clean, dried potassium metal was then introduced into a side arm, after which the cell and contents (under a positive pressure of Ar) were transferred from the dry box to a vacuum line. There a potassium mirror was deposited just below the constriction by application of a relatively low temperature flame and, then, about 25 ml of solvent were bulb-to-bulb distilled over the sample. The tube containing frozen solvent, sample, and potassium mirror was then sealed off from the upper portion of the assembly. Dissolution of the sample and subsequent contact of this solution with the potassium mirror generated the radical anion species. Because virtually all the ligands investigated formed singlet state dianions, as well as radical anions, it was necessary to monitor the formation of both. This was done by a combination of esr and electronic spectral measurements. In general, as the contact time with a potassium mirror increased, the intensity of an esr signal and certain spectral bands increased until the concentration of dianion became appreciable. By following the growth in intensity of new bands and the disappearance of other bands in the electronic spectra taken in time increments with the esr measurements, it was possible to sort out neutral, radical anion, and dianion bands.

To insure that ion-pairing influences on the electronic spectra were minimal, the electronic spectra of electrochemically reduced 1,10-phenanthroline (tetrabutylammonium gegenion) and chemically reduced 1,10-phenanthroline (potassium gegenion) were compared. The spectra were identical in terms of band positions. However, as expected, the intensities of the bands in the spectrum of the electrochemically reduced ligand were consistently lower than the intensities of the corresponding bands in the spectrum of the chemically reduced ligand. This is undoubtedly due to the greater loss of reduced species, either through decomposition or oxidation, involved in the electrochemical technique.

The majority of the electronic spectra presented in this work have been traced full scale, photoreduced, and presented as absorbance vs. wavelength plots. However, those for which Self-Consistent Field Molecular Orbital Calculations have been performed are presented as molar absorptivity vs. energy plots. Conversion of these spectra from absorbance vs. wavelength to molar absorptivity vs. energy plots has been effected on a Digital Equipment Corporation PDP-8I "in house" computer with peripheral photoelectric curve follower and line plotter. The program used for these conversions, originally written by Dr. T. Abeles and modified by Mr. C. Titus of the V.P.I.&S.U. Chemistry Department, is shown in Appendix D.

Chemicals

1,2-Dimethoxyethane (Ansul 21) was predried over calcium hydride and then distilled from lithium aluminum hydride under an argon atmosphere. The solvent was then degassed with argon and used immediately, except as described in the preceding section.

Tetrabutylammonium perchlorate (TBAP) was purchased from G. Frederick Smith Chemical Company and dried in an Abderhalden drying pistol at the boiling point of xylene and 0.1 mm Hg using P_2O_5 as desiccant.

The triply distilled mercury employed in the electrochemical measurements was obtained from Eastern Smelting and Refining Company and used as obtained.

Electrochemical-grade silver perchlorate, which was used to prepare electrochemical reference solutions, was obtained from Ventron Chemical Company and used as obtained.

1,10-Phenanthroline and all substituted phenanthrolines, except 5-nitro-1,10-phenanthroline, were obtained from G. Frederick Smith Chemical Company. 5-Nitro-1,10-phenanthroline was prepared according to the method of G. F. Smith and F. W. Cagle.[37] This method involves the direct nitration of 1,10-phenanthroline with concentrated nitric acid in the presence of oleum. 1,10-Phenanthroline and most of its methyl derivatives readily form hydrates and are usually commercially obtained as such. These hydrated diimines were recrystallized 2-3 times from freshly distilled, predried benzene and stored in a vacuum desiccator over concentrated H_2SO_4. Only anhydrous ligands were used in obtaining electronic spectra of neutral and reduced diimines.

2,2'-Bipyridyl, its methyl and phenyl derivatives, and 2,2'-biquinolyl were purchased from Columbia Chemical Company and recrystallized from dry benzene before use.

Diacetyldianil, the methyl and methoxy derivatives of diacetyldianil, and benzildianil were all prepared in essentially the same manner.[38,39] An appropriate aniline and either 1,2-butanedione or benzil were combined in a condensation reaction. In the preparation of diacetyldianil, approximately 0.1 mole of 1,2-butanedione, excess aniline, and about 1 g of $ZnCl_2$ catalyst were placed in a one-necked, 500 ml boiling flask fitted with a Dean-Stark assembly and refluxed at ca. 200^{o}C for 3-4 hours. After refluxing for this period, excess aniline was removed in a rotary evaporator and the resulting diacetyldianil was recrystallized from absolute ethanol at -10^{o}C. Benzildianil was prepared in the same manner, except that benzil was used, rather than 1,2-butanedione. The substituted diacetyldianils were also prepared in this way except that toluene was used as the reflux solvent.

All tetracarbonyldiimine Group VI-B metal complexes, except (4,7-ϕ_2-1,10-phen)$Cr(CO)_4$, (4,4'-ϕ_2-2,2'-bipy)$Cr(CO)_4$, and (benzildianil)$Cr(CO)_4$ were prepared according to the method of Abel, Bennett, and Wilkinson.[40] The (4,7-ϕ_2-1,10-phen)$Cr(CO)_4$, (4,4'-ϕ_2-2,2'-bipy)$Cr(CO)_4$, and (benzildianil)$Cr(CO)_4$ were successfully synthesized by the photolytic method described by Angelici and Graham.[41]

All ligands and complexes employed in this investigation gave acceptable elemental analyses (within 0.3%) for carbon, hydrogen, and nitrogen. The analyses were performed by the Analytical Services Division of the V.P.I.&S.U. Chemistry Department.

RESULTS AND DISCUSSION

Electrochemical Studies

Tetracarbonyldiimine Group VI-B metal complexes containing ligands characterized by extensive electronic delocalization will, in general, reversibly form radical anions by the addition of an electron to the energetically lowest-lying molecular orbital in which a vacancy exists. The reductive formation of these radical anions is both voltammetrically and chemically reversible for all complexes studied. The kinetic stabilities of the resulting radical anions, as qualitatively judged by the apparent rate of decomposition, vary considerably from one diimine series to another. 1,10-Phenanthroline and methyl substituted 1,10-phenanthroline tetracarbonyl complexes undergo one-electron reductions (at the top of the first polarographic wave) to form radical anions which are very unstable relative to the other diimine complexes studied in the present investigation. The reduced 2,2'-bipyridyl and 2,2'-biquinolyl complexes appear to be of intermediate stability, while the reduced dianil complexes are definitely the most stable of the reduced diimine complexes studied.

Significantly, the phenanthroline and bipyridyl ligands, themselves, will undergo chemical reduction to form relatively stable, singlet-state dianions, as well as radical anions. However, only when electronic delocalization is extended by phenyl substitution will the complexes form dianions. Conversely, in the dianil series, the ligands, by themselves, form neither stable radical anions nor dianions. The complexes, however, form both. These differences in behavior surely must be a reflection of a difference in bonding between the ligand and the metal in these ostensibly similar complexes.

Polarographic half-wave reduction potentials for phenanthroline and substituted phenanthroline complexes are shown in Table I. Half-wave reduction potentials for other diimine complexes, not previously reported, are listed in Table II. All complexes studied undergo clean, reversible, one-electron reductions at the top of the first polarographic wave.

Even a cursory inspection of the first half-wave potentials listed, particularly in Table I, discloses the fact that, in general, substitution of electron-releasing methyl groups into the diimine portion of the complexes produces cathodic shifts in the reduction potentials relative to the unsubstituted complexes. Conversely, substitution of phenyl groups into the ligands, produces anodic shifts of the half-wave potentials relative to the unsubstituted complexes. Similarly, for a homologous series of complexes, wherein the only change is a variation of the central metal atom, anodic shifts of the half-wave potentials occur as the metal is varied from Cr to Mo to W.

These shifts in reductive half-wave potentials for the complexes parallel the changes in half-wave potentials for the ligands, themselves, as similar substitutions are made. Substitution of methyl groups into aromatic molecules, in general, results in cathodic shifts of reduction half-wave potentials, whereas, substitution of phenyl groups produces anodic shifts in these potentials.[42-45] As the nitrogen atoms in the heterocyclic ligands become more electronegative with respect to adjacent aromatic carbon atoms, the eigenvalues of the lowest unoccupied

TABLE I

POLAROGRAPHIC HALF-WAVE POTENTIALS:[a]

PHENANTHROLINE COMPLEXES[b]

COMPLEX	$E_{\frac{1}{2}}^{(1)}$	$E_{\frac{1}{2}}^{(2)}$
(1,10-Phen)Cr$(CO)_4$	-2.24	-2.78
(1,10-Phen)Mo$(CO)_4$	-2.17	-2.70
(1,10-Phen)W$(CO)_4$	-2.08	-2.63
(5-(CH_3)-1,10-phen)Cr$(CO)_4$	-2.26	-2.72
(5,6-$(CH_3)_2$-1,10-phen)Cr$(CO)_4$	-2.31	-2.80
(4,7-$(CH_3)_2$-1,10-phen)Cr$(CO)_4$	-2.35	-2.85
(2,9-$(CH_3)_2$-1,10-phen)Cr$(CO)_4$	-2.25	-2.71
(2,9-$(CH_3)_2$-1,10-phen)Mo$(CO)_4$	-2.21	-2.66
(2,9-$(CH_3)_2$-1,10-phen)W$(CO)_4$	-2.12	-2.59
(3,4,7,8-$(CH_3)_2$-1,10-phen)Cr$(CO)_4$	-2.40	-2.92
(4,7-$(\phi)_2$-1,10-phen)Cr$(CO)_4$	-2.11	-2.53

[a]Measured in volts ($\pm$ 0.01) with reference to 1 X 10^{-3} M Ag^+/Ag, in 1,2-dimethoxyethane, with TBAP as supporting electrolyte.

[b]All complexes undergo both chemically and voltammetrically reversible one-electron reductions at the top of the first wave. Reduction at the top of the second wave is voltammetrically reversible for all complexes, but chemically reversible for (4,7-$(\phi)_2$-1,10-phen)Cr$(CO)_4$ only.

TABLE II

POLAROGRAPHIC HALF-WAVE POTENTIALS:[a]

BIPYRIDYL, BIQUINOLYL, DIANIL COMPLEXES

COMPLEX	$E_{\frac{1}{2}}^{(1)}$	$E_{\frac{1}{2}}^{(2)}$	
$(2,2'\text{-Bipy})Cr(CO)_4$	-2.25[b]	-2.79	(C.I.,V.R.)[c]
$(2,2'\text{-Bipy})Mo(CO)_4$	-2.17	-2.71	(C.I.,V.R.)
$(2,2'\text{-Bipy})W(CO)_4$	-2.10	-2.69	(C.I.,V.R.)
$(4,4'\text{-}(\phi)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$	-2.14	-2.52	(C.R.,V.R.)
$(4,4'\text{-}(\phi)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$	-2.05	-2.54	(C.R.,V.R.)
$(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$	-1.84	-2.33	(C.I.,V.R.)
$(2,2'\text{-Biquin})Cr(CO)_4$	-1.77	-2.28	(C.R.,V.R.)
$(\text{Benzilanil})Cr(CO)_4$	-1.67	-2.18	(C.R.,V.R.)
$(\underline{p}\text{-}(CH_3O)\text{diacetylanil})Cr(CO)_4$	-2.00	-2.47	(C.R.,V.R.)
$(\underline{p}\text{-}(CH_3)\text{diacetylanil})Cr(CO)_4$	-2.01	-2.40	(C.R.,V.R.)

[a]Measured in volts (± 0.01) with reference to 1 X 10^{-3} M Ag^+/Ag, in 1,2-dimethoxyethane, with TBAP as supporting electrolyte.

[b]One-electron reductions at the top of the first wave are chemically and voltammetrically reversible for all complexes.

[c]C.I. = chemically irreversible; V.R. = voltammetrically reversible; C.R. = chemically reversible.

molecular orbitals are decreased, causing anodic shifts in the half-wave potentials.[45] For the unsubstituted hexacarbonyls, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, the calculated charges on the metal are respectively +0.42, +0.45, +0.59.[27] Although the charges on the corresponding metals in the tetracarbonyl complexes are not expected to be the same, the trend for the three metals is expected to be similar. As the charge on the metal increases, the metal becomes more acidic toward the nitrogen lone pair electrons, electronic charge density on the nitrogens is thereby lowered, and the electronegativity of the nitrogens toward adjacent aromatic carbons is enhanced. The observed variation in half-wave potentials as the central metal atom is changed is, thus, readily explicable in terms of an inductive sigma influence by the metal on the ligand nitrogen atoms.

The shifts in half-wave reduction potentials discussed in the preceding paragraphs can all be explained in terms of ligand reductions and the observed trends provide the first evidence, presented in this work, that reductive electrons enter predominantly ligand-based molecular orbitals. If reductive electrons do, indeed, enter ligand molecular orbitals, the question of which orbitals are involved immediately arises. Any electrochemical data providing information germane to this question should also provide evidence on the existence of π-bonding between diimine and metal in the tetracarbonyl complexes and, thus, indirectly, provide evidence concerning the mode of charge transmission to the carbonyls in these complexes. The series of methyl substituted phenanthroline complexes is the only series for which sufficient electrochemical data, from which to extract clues regarding the ligand molecular orbital involved in reduction, have been obtained.

1,10-Phenanthroline contains fourteen π-electrons so that the highest filled, non-degenerate π-molecular orbital is π_7. Thus, when this molecule is reduced to the radical anion, the reductive electron is expected to enter π_8, the lowest unoccupied molecular orbital of the molecule. In the tetracarbonyl complexes, if the metal engages in π-bonding to the phenanthroline ligand, π_8 is reasonably expected to be involved in the synergistic bonding. Consequently, the lowest unoccupied molecular orbital of the ligand, in this case, must be π_9. If π_8 is the lowest unoccupied molecular orbital in the tetracarbonyl complexes, a positive correlation should exist between the energy of π_8 and the corresponding $E_{\frac{1}{2}}^{(1)}$ value. On the other hand, if π_8 is involved in back-bonding, a positive correlation should exist between π_9 and $E_{\frac{1}{2}}^{(1)}$.

A plot of $E_{\frac{1}{2}}^{(1)}$ values, for the methyl substituted phenanthroline tetracarbonyl complexes of chromium versus calculated eigenvalues of π_8 and π_9 (tabulated in Table III) is shown in Figure 2. The eigenvalues have been obtained from P.P.P. Self-Consistent Field Molecular Orbital calculations, which will be discussed subsequently. The empirical parameters employed in these calculations, with the exception of α_N, the coulomb integral for nitrogen, and α_X, the coulomb integral for the aromatic carbon to which a methyl group is bonded, are those parameters which provided the best agreement between the calculated spectrum and the experimentally observed spectrum for 1,10-phenanthroline. The value of α_N has been decreased in these calculations from -3.225 eV (used for 1,10-phenanthroline) to -4.085 eV to account for the sigma withdrawal of charge from the nitrogen, brought about by coordination to chromium.

TABLE III

CALCULATED EIGENVALUES of the LOWEST

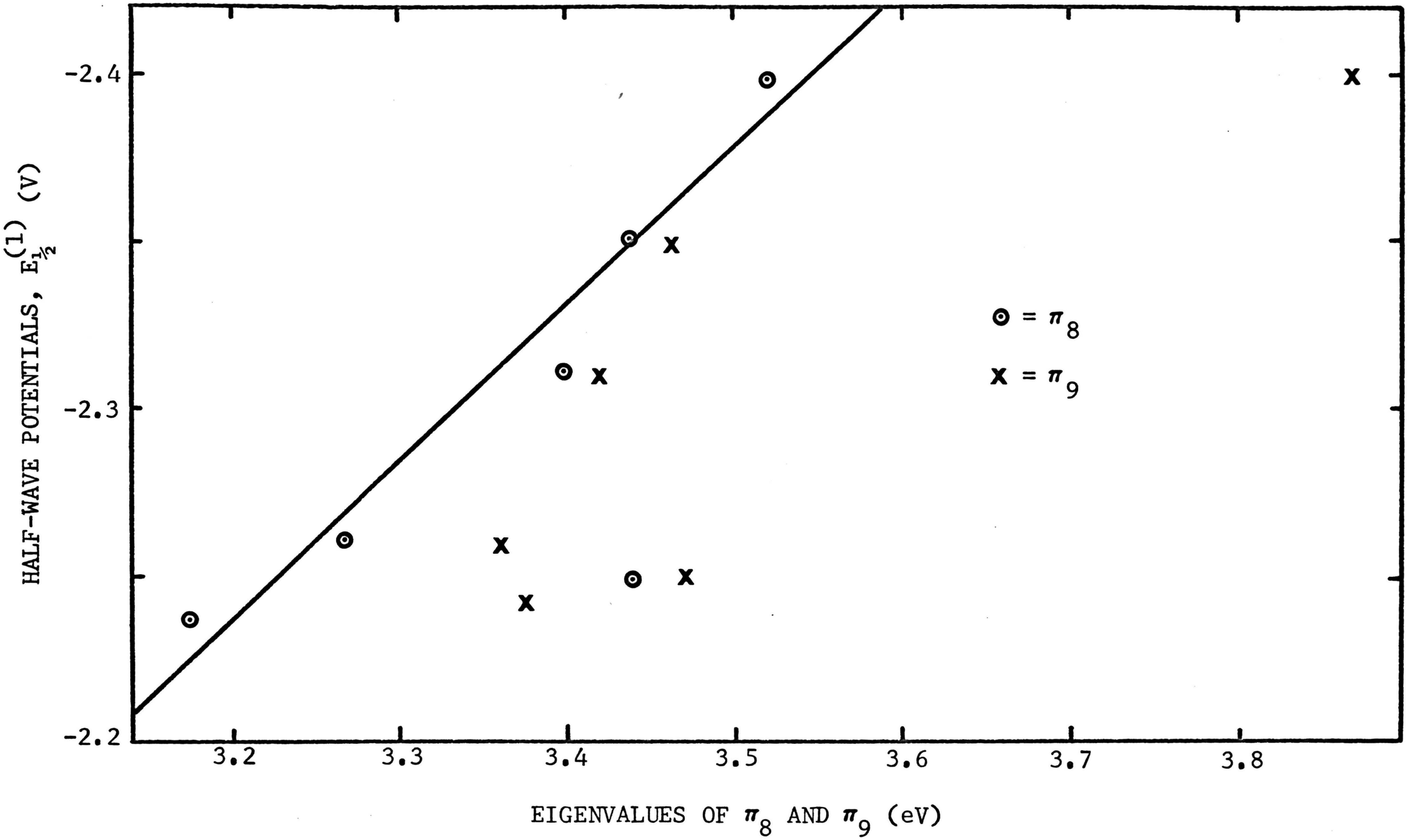
ENERGY VIRTUAL ORBITALS in METHYL SUBSTITUTED PHENANTHROLINES[a]

COMPOUND	π_8	π_9
1,10-Phenanthroline	3.16[b]	3.38[b]
5-Methyl-1,10-Phenanthroline	3.27	3.36
5,6-Dimethyl-1,10-Phenanthroline	3.40	3.41
4,7-Dimethyl-1,10-Phenanthroline	3.44	3.60
2,9-Dimethyl-1,10-Phenanthroline	3.44	3.47
3,4,7,8-Tetramethyl-1,10-Phenanthroline	3.52	3.88

[a]Pariser-Parr-Pople(P.P.P.) Eigenvalues obtained from S.C.F.-M.O. calculations employing the following parameters: $\alpha_N = \alpha_C + 1.9\beta_{CC}$; $\alpha_X = \alpha_C - 0.59\beta_{CC}$;[45] $\beta_{CC} = -2.15$ eV;

$\beta_{CN} = -2.40$ eV; $\gamma_{CC} = 11.13$ eV[46]; $\gamma_{NN} = 12.34$ eV[46]

[b]In electron volts (eV).



<u>Figure 2.</u> Plot of methyl phenanthroline complex $E_{1/2}^{(1)}$ values vs. calculated eigenvalues of lowest energy virtual orbitals.

A purely inductive model has been employed for the methyl group by raising the value of α_X from -2.51 eV, for the unsubstituted ligand carbon atoms, to +1.26 eV for each methyl group substituted into the ligand.

It is seen that a reasonably good correlation exists between the $E_{\frac{1}{2}}^{(1)}$ values and the calculated eigenvalues of π_8, but not with the eigenvalues of π_9. (Presumably, the 2,9-dimethyl-1,10-phenanthroline complex deviates from the correlation line because of steric interference between the trans carbonyls and the methyl groups). This positive correlation between the $E_{\frac{1}{2}}^{(1)}$ values and the energies of π_8 suggests that reductive electrons enter π_8, not π_9, of the phenanthroline ligand in the tetracarbonyl complexes of chromium and, in addition, suggests the lack of π-bonding between metal and diimine in these complexes.

Infrared Spectra

Organometallic compounds of the general formula $L_2M(CO)_4$, wherein L_2 represents two identical cis monodentate ligands or a single symmetrical bidentate ligand, have C_{2v} symmetry and, on the basis of theoretical group analysis, should show four infrared-active carbonyl stretching vibrations. These stretching vibrations arise from B_1, B_2, and two A_1 normal modes of vibration. Assignment of these modes to the observed frequencies for the $L_2M(CO)_4$ class of compounds has been made by Cotton and Kraihanzel.[19,32] Figure 3 shows these four absorptions labeled for the spectrum of neutral (1,10-phen)$Cr(CO)_4$. Also included in Figure 3 are the infrared spectra, in the carbonyl region, for neutral molecule and radical anion of (1,10-phen)$Cr(CO)_4$, neutral and radical anion spectra for (1,10-phen)$Mo(CO)_4$, and neutral and radical anion spectra for (1,10-phen)$W(CO)_4$. Tables IVa, IVb, and IVc list the carbonyl absorption frequencies for the six species whose spectra are shown in Figure 3. Tables IVd, IVe, and IVf give the carbonyl stretching frequencies for the neutral and reduced (radical anion and dianion) phenyl substituted compounds, (4,7-$(\phi)_2$-1,10-phen)$Cr(CO)_4$, (4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$, and (benzilanil)$Cr(CO)_4$, respectively. Force constants have been calculated from the observed frequencies and are shown in Tables Va - Vf. The results in these latter tables employ the following notation:

k_1 = force constant between C and O atoms of a carbonyl trans to a ligand (a general, structural formula is shown in Appendix C). The unit of k is millidynes/Angstrom (md/Å).

k_2 = force constant between C and O atoms of a carbonyl group cis to a ligand and trans to another carbonyl group.

k_i = interaction force constant between two carbonyl groups.

$\Delta k = k_{neutral} - k_{reduced}$.

<u>Figure 3.</u> Infrared spectra of tetracarbonyl-1,10-phenanthroline Group VI-B metal neutral complexes and corresponding radical anions at 1.0 X 10^{-2} M concentration in 1,2-dimethoxyethane.

(A) Chromium Complex; ——— neutral, ----radical anion

(B) Molybdenum Complex; ——— neutral, -----radical anion

(C) Tungsten Complex; ——— neutral, ----radical anion

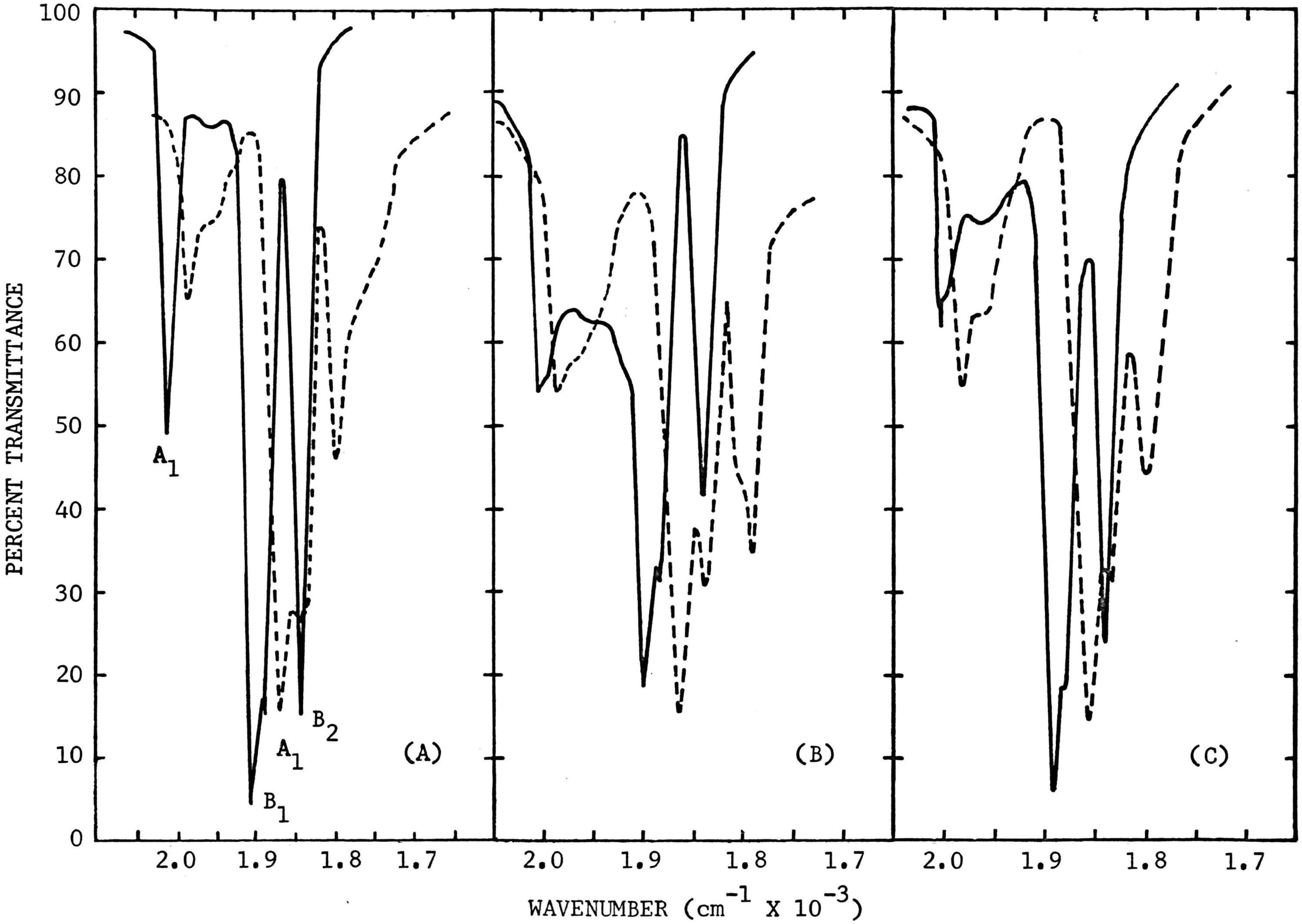


Figure 3. Infrared spectra of tetracarbonyl-1,10-phenanthroline Group VI-B metal neutral complexes and corresponding radical anions.

TABLE IVa

INFRARED ASSIGNMENTS FOR (1,10-Phen)$Cr(CO)_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})
A_1	2012	1986
B_1	1902	1869
A_1	1889	1845
A_2	1842	1797

TABLE IVb

INFRARED ASSIGNMENTS FOR (1,10-Phen)$Mo(CO)_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})
A_1	2010	1984
B_1	1900	1866
A_1	1885	1842
A_2	1840	1796

TABLE IVc

INFRARED ASSIGNMENTS FOR (1,10-Phen)$W(CO)_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})
A_1	2002	1980
B_1	1890	1857
A_1	1882	1835
A_2	1838	1797

TABLE IVd

INFRARED ASSIGNMENTS FOR (4,7-(ϕ)$_2$-1,10-Phen)Cr(CO)$_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})	DIANION (cm^{-1})
A_1	2005	1988	1988
B_1	1902	1872	1870
A_1	1890	1846	1840
B_2	1842	1807	1800

TABLE IVe

INFRARED ASSIGNMENTS FOR (4,4'-(ϕ)$_2$-2,2'-Bipy)Cr(CO)$_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})	DIANION (cm^{-1})
A_1	2002	1975	1960
B_1	1898	1860	1858
A_1	1878	1835	1835
B_2	1840	1792	1775

TABLE IVf

INFRARED ASSIGNMENTS FOR (Benzilanil)Cr(CO)$_4$

ASSIGNMENT	NEUTRAL (cm^{-1})	RADICAL ANION (cm^{-1})	DIANION (cm^{-1})
A_1	2000	1965	1942
B_1	1915	1850	1806
A_1	1910	1835	1764
B_2	1870	1783	1720

TABLE Va

CARBONYL FORCE CONSTANTS (md/Å) FOR (1,10-Phen)Cr(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk
k_1	14.19	13.59	0.60
k_2	15.23	14.63	0.60
k_i	0.39	0.39	0.0

TABLE Vb

CARBONYL FORCE CONSTANTS (md/Å) FOR (1,10-Phen)Mo(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk
k_1	14.16	13.58	0.58
k_2	15.17	14.58	0.59
k_i	0.38	0.38	0.0

TABLE Vc

CARBONYL FORCE CONSTANTS (md/Å) FOR (1,10-Phen)W(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk
k_1	14.09	13.52	0.57
k_2	15.12	14.57	0.55
k_i	0.39	0.39	0.0

TABLE Vd

CARBONYL FORCE CONSTANTS (md/Å) FOR (4,7-(φ)$_2$-1,10-Phen)Cr(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk	DIANION	Δk
k_1	14.19	13.68	0.51	13.64	0.55
k_2	15.16	14.56	0.60	14.56	0.60
k_i	0.37	0.36	0.01	0.37	0.0

TABLE Ve

CARBONYL FORCE CONSTANTS (md/Å) FOR (4,4'-(φ)$_2$-2,2'-Bipy)Cr(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk	DIANION	Δk
k_1	14.09	13.46	0.63	13.26	0.83
k_2	15.17	14.56	0.58	14.45	0.72
k_i	0.36	0.38	-0.02	0.37	-0.02

TABLE Vf

CARBONYL FORCE CONSTANTS (md/Å) FOR (Benzilanil)Cr(CO)$_4$

	NEUTRAL	RADICAL ANION	Δk	DIANION	Δk
k_1	14.58	13.37	1.21	12.38	2.20
k_2	15.11	14.39	0.72	14.08	1.03
k_i	0.29	0.39	-0.10	0.45	-0.16

An examination of the tables reveals that the value of k_2, the force constant for carbonyls <u>cis</u> to a ligand, exceeds k_1, the force constant for the carbonyls situated <u>trans</u> to a ligand, for any given species. This appears to be general, having been observed for a large number of carbonyl complexes of the general type $L_2M(CO)_4$, and according to Cotton and Kraihanzel,[19] is to be expected.

Somewhat unexpected in the present investigation is the observation that the changes in k_1 and k_2 between neutral and reduced species are equal within experimental error (± 0.08 — ± 0.12 md/Å),[22] for the phenanthroline, phenyl substituted phenanthroline, and phenyl substituted bipyridyl complexes. This behavior has also been observed when comparing the force constants of neutral Group VI-B metal phenanthroline complexes to the corresponding neutral, ethylenediamine complexes.[15,47] (Interestingly, these same studies show $\Delta k_2 = 2\Delta k_1$ for the force constant changes between the 2,9-$(CH_3)_2$-1,10-phenanthroline complexes and the ethylenediamine complexes!) However, this equality in Δk_1 and Δk_2 is in contrast to observed changes in the force constants for the ostensibly similar bipyridyl and diacetyldianil systems (Appendix C). For these latter two series of complexes, $\Delta k_1 > \Delta k_2$ in all cases. Because a pi-only mechanism of charge transmission predicts $\Delta k_2 = 2\Delta k_1$, as does a combination sigma-pi mechanism, it has been concluded that an anisotropic sigma-only mode of charge distribution is operative in the bipyridyl and diacetyldinail complexes.[34,35] The results obtained in the present investigation are also inconsistent with a pi-only mechanism of charge dispersal and, if, indeed, a combination sigma-pi mechanism demands that $\Delta k_2 = 2\Delta k_1$, the results for the phenanthroline, phenyl substituted phenanthroline, and phenyl substituted bipyridyl complexes can be rationalized only in terms of an isotropic sigma mechanism.

In the case of (benzilanil)$Cr(CO)_4$, the changes in force constants are similar to the changes observed for the diacetyldianil complexes. Figure 4 illustrates the fact that, although both k_1 and k_2 are diminished by successive reductions to radical anion and dianion, k_1 is affected appreciably more than is k_2. In fact, Δk_1 is roughly twice Δk_2. These results, too, are inconsistent with a pi-only, or a combination sigma-pi transmission of charge density. The observed data can be rationalized, in terms of presently existing theories, only on the basis of a directional sigma mechanism.

Two additional points of significance are also revealed as one examines the force constant changes listed in Tables Va - Vf. Like the bipyridyl and diacetyldianil complexes studied previously, $\Delta k_1 > \Delta k_2$ for the (benzilanil)$Cr(CO)_4$ species. However, the actual magnitudes of the changes are strikingly larger for the dianil species than for the bipyridyl and phenanthroline series. In addition, from Figure 4, it is seen that the change in force constants describes a clean, linear progression for the dianil complexes. Obviously, both cis and trans carbonyls in the dianil complexes are influenced to a much greater extent by reduction than are the carbonyls in the phenanthroline and bipyridyl complexes. Furthermore, this influence occurs to about the same extent in going from neutral to radical anion as in going from radical anion to dianion. Conversely, reduction of the phenyl substituted phenanthroline and phenyl substituted bipyridyl complexes

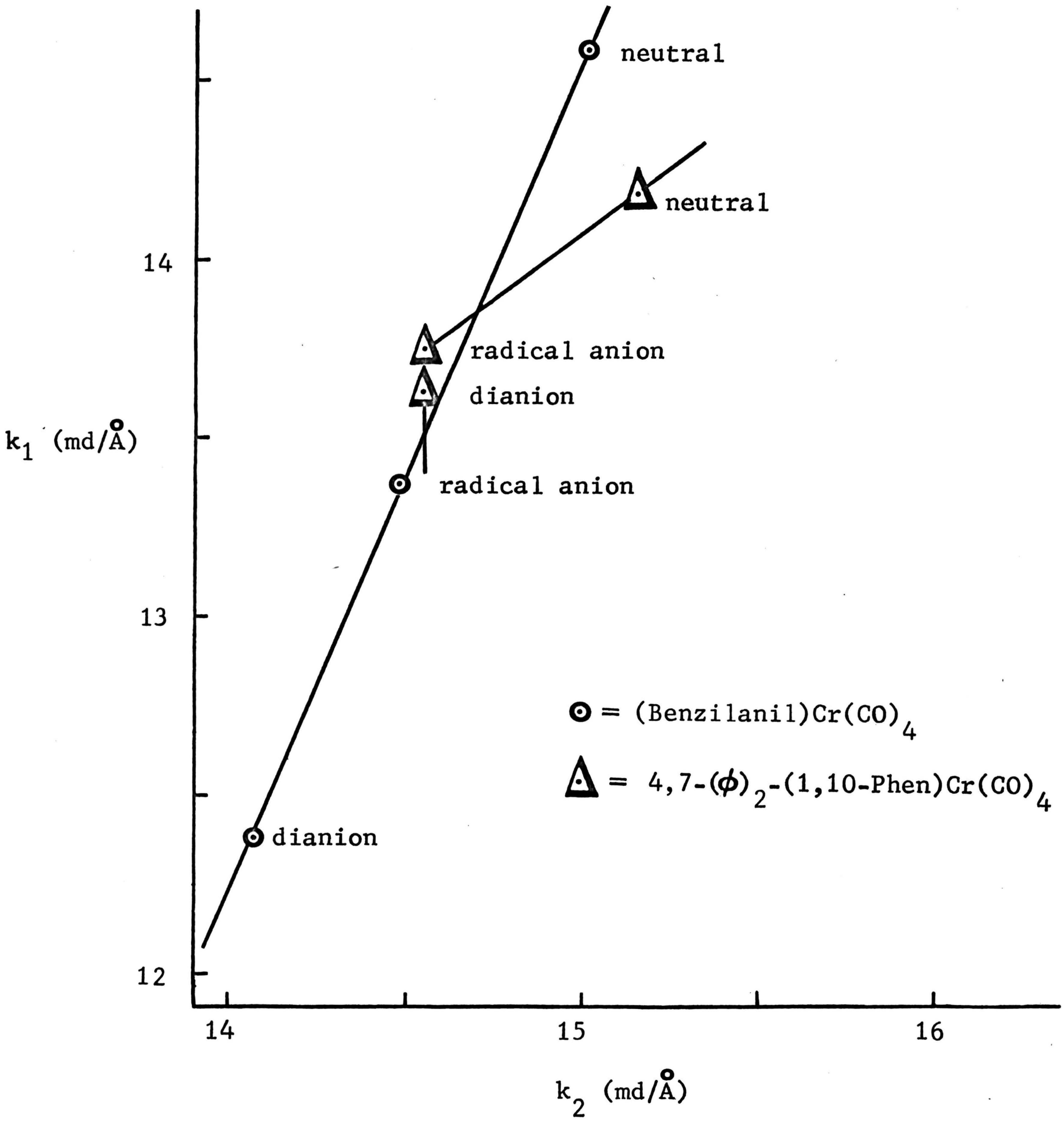


Figure 4. Plot of k_1 versus k_2 for (Benzilanil)$Cr(CO)_4$ and 4,7-$(\phi)_2$-(1,10-Phenanthroline)$Cr(CO)_4$ neutral and reduced species.

to the dianion produces only very slight additional changes in the force constants from the radical anion values. Thus, for these complexes, charge migration to the carbonyls seems to have approached a maximum with formation of the radical anions.

Apparently, in the case of phenyl substituted phenanthroline and bipyridyl complexes, the addition of a second election produces no additional increase in basicity of the ligand, if, indeed, reductive electrons do enter primarily ligand-based molecular orbitals with the resulting charge dispersed by a sigma-only mechanism. Immediately raised is the question of why the dianil complexes, in which charge is, presumably, also disseminated by a sigma-only mechanism, do not behave similarly.

Electronic spectral evidence, to be presented, suggests that very considerable back-bonding between metal and diimine exists in the benzildianil and diacetyldianil complexes. On the other hand, evidence indicating the lack of back-bonding between a Group VI-B metal and 1,10-phenanthroline will also be presented. With this evidence in mind, it is difficult to understand why a sigma-only mechanism of charge transfer should be involved in both types of complexes -- one in which metal-ligand π-bonding exists and one in which it does not exist.

It may well be that the approach to establishing charge distribution mechanisms and inferring π-bonding interactions in substituted organometallic carbonyl complexes on the basis of carbonyl force constant changes, alone, is of seriously questionable validity. In fact, the calculation of force constants employing a "Cotton-Kraihanzel" force field has indeed been challenged as being over simplified.[21,47,48]

Electronic Absorption Spectra

Neutral Ligand Spectra. As far as can be ascertained, the electronic absorption spectra of electrochemically reduced tetracarbonyldiimine Group VI-B metal complexes have not previously been investigated. For the most part, very little electronic spectral information has been obtained for the neutral complexes. Before discussing the electronic spectra of the reduced complexes, it is desirable to characterize the electronic spectra of the neutral complexes as unequivocally as possible.

Essentially four types of band structures are discernible in the spectra of substituted carbonyl complexes. These are intraligand ($\pi \rightarrow \pi^*$) transitions, metal-to-metal bands (subsequently referred to as "d-d" type bands despite the fact that extensive mixing of non-d-orbitals with d-orbitals undoubtedly occurs in these highly delocalized, covalently bonded molecules), and two types of charge transfer bands, metal-to-carbonyl ($M \rightarrow \pi^*_{CO}$) and either metal-to-ligand ($M \rightarrow \pi^*_L$) or ligand-to-metal ($\pi_L \rightarrow M^*$) transitions.

The metal-ligand charge transfer bands in most transition metal complexes appear in the visible region of the spectrum and are characterized by relatively high molar absorptivities. These band types are usually observed in complexes possessing metal ions of relatively high oxidizing or reducing capacity. For example, in the tris-(1,10-phenanthroline)iron(II,III) complexes, a metal-to-ligand charge transfer obtains in the ferrous complex, whereas a ligand-to-metal charge transfer is displayed by the ferric complex.[49] It is thought that these transitions are true charge transfer transitions, i.e., that a transfer of an electron between the metal and the ligand actually occurs. As used in the present discussion, the term "charge transfer" will be used in reference to an electronic transition between molecular orbitals predominantly metal in character and those predominantly ligand in character. In the highly delocalized systems under investigation, the metal is present in a very low oxidation state, formally zero in the neutral complexes. Consequently, it is entirely reasonable to dispense with any consideration of ligand-to-metal charge transfer bands. Thus, the ensuing discussion will focus on metal-to-ligand and metal-to-carbonyl charge transfer, d-d, and intraligand bands.

The intraligand bands in the spectra of the complexes are most suitably identified by comparing the electronic spectra of the ligands to the spectra of the complexes. Electronic absorption spectra of neutral phenanthroline and "bipyridyl-like" ligands are shown in Figures 5-8. (Figures 7 and 8 also respectively display the radical anion spectra for 2,2'-bipyridyl and 1,10-phenanthroline between 8,000 and 50,000 cm^{-1}). The ultraviolet spectra of these heterocyclic diimines characteristically exhibit two distinct bands of relatively high intensity with lower intensity transitions appearing as shoulders on the long wavelength side of the low energy band and on the short wavelength side of the higher energy band. Band positions of these bands for 2,2'-bipyridyl, 1,10-phenanthroline, and methyl substituted phenanthrolines are listed in Table VI.

Although the electronic spectra of many of the diimines included in this study have previously been discussed,[50-54,66] the majority of these discussions have been presented in conjunction with studies of

Figure 5. Electronic absorption spectra of neutral phenanthroline ligands. All the spectra were recorded with 1 mm pathlength cells in 1,2-dimethoxyethane at the indicated concentrations.

A)

	Compound	Conc.
———	1,10-Phenanthroline	1.5×10^{-4} M
·····	5-Methyl-1,10-phenanthroline	2.0×10^{-4} M
-----	5,6-Dimethyl-1,10-phenanthroline	3.2×10^{-4} M
-·-·-	4,7-Dimethyl-1,10-phenanthroline	3.0×10^{-4} M

B)

	Compound	Conc.
———	2,9-Dimethyl-1,10-phenanthroline	3.2×10^{-4} M
·····	5-Nitro-1,10-phenanthroline	3.0×10^{-4} M
-----	3,4,7,8-Tetramethyl-1,10-phenanthroline	2.5×10^{-4} M
-·-·-	4,7-Diphenyl-1,10-phenanthroline	3.3×10^{-4} M

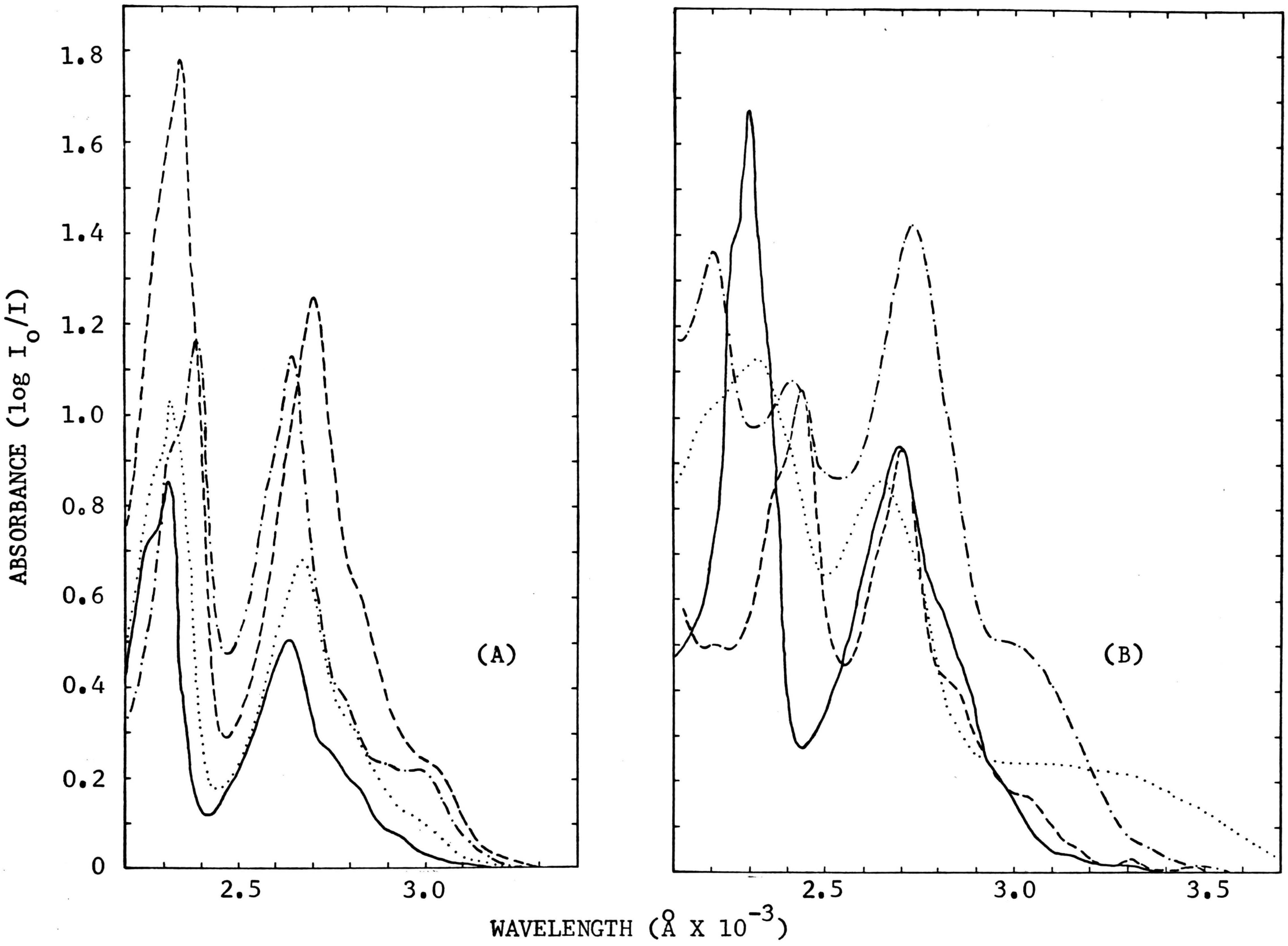


Figure 5. Electronic absorption spectra of neutral phenanthroline ligands.

<u>Figure 6.</u> Electronic absorption spectra of neutral "bipyridyl-like" diimines. All the spectra were recorded with 1 mm pathlength cells in 1,2-dimethoxyethane at the indicated concentrations.

	Compound	Conc.
————	2,2'-Bipyridyl	3.0×10^{-4} M
·······	4,4'-Dimethyl-2,2'-bipyridyl	4.0×10^{-4} M
-------	2,2'-Biquinolyl	1.0×10^{-4} M
-·-·-·-	4,4'-Diphenyl-2,2'-bipyridyl	1.2×10^{-4} M
—····—	Di-2-pyridyl ketone	5.0×10^{-4} M

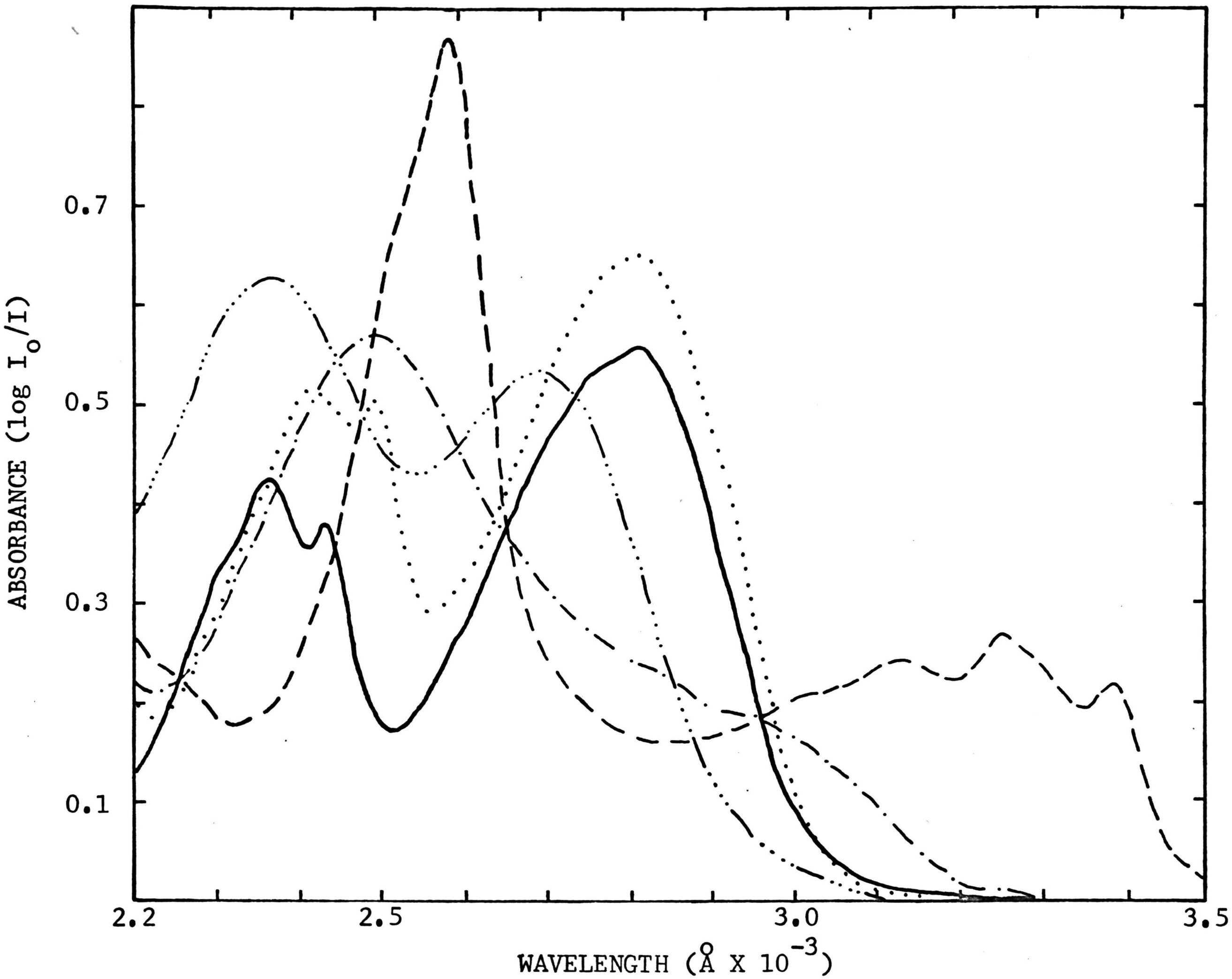


Figure 6. Electronic absorption spectra of neutral "bipyridyl-like" diimines.

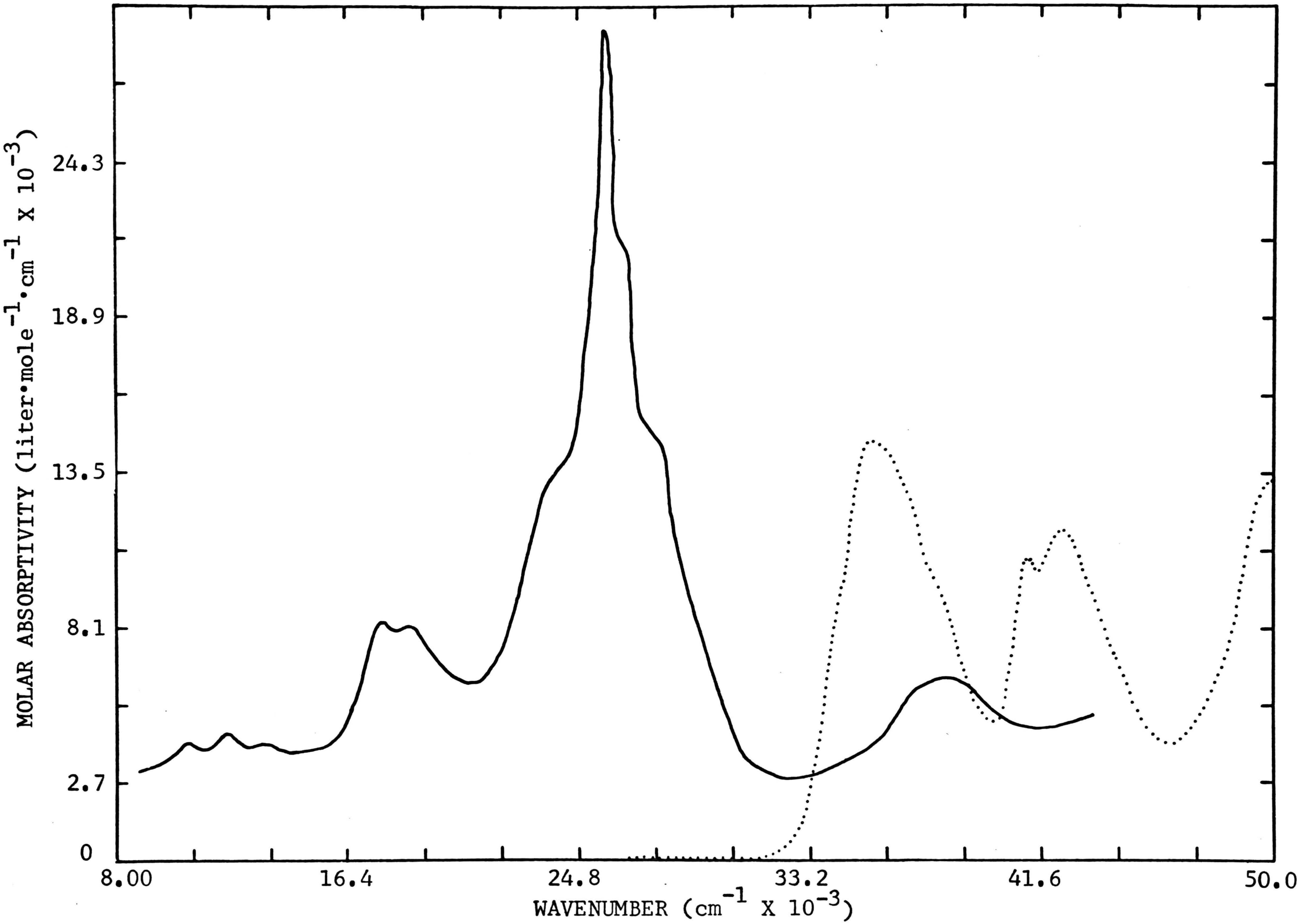


Figure 7. Electronic absorption spectra of neutral (•••) 2,2'-bipyridyl and its radical anion (——).

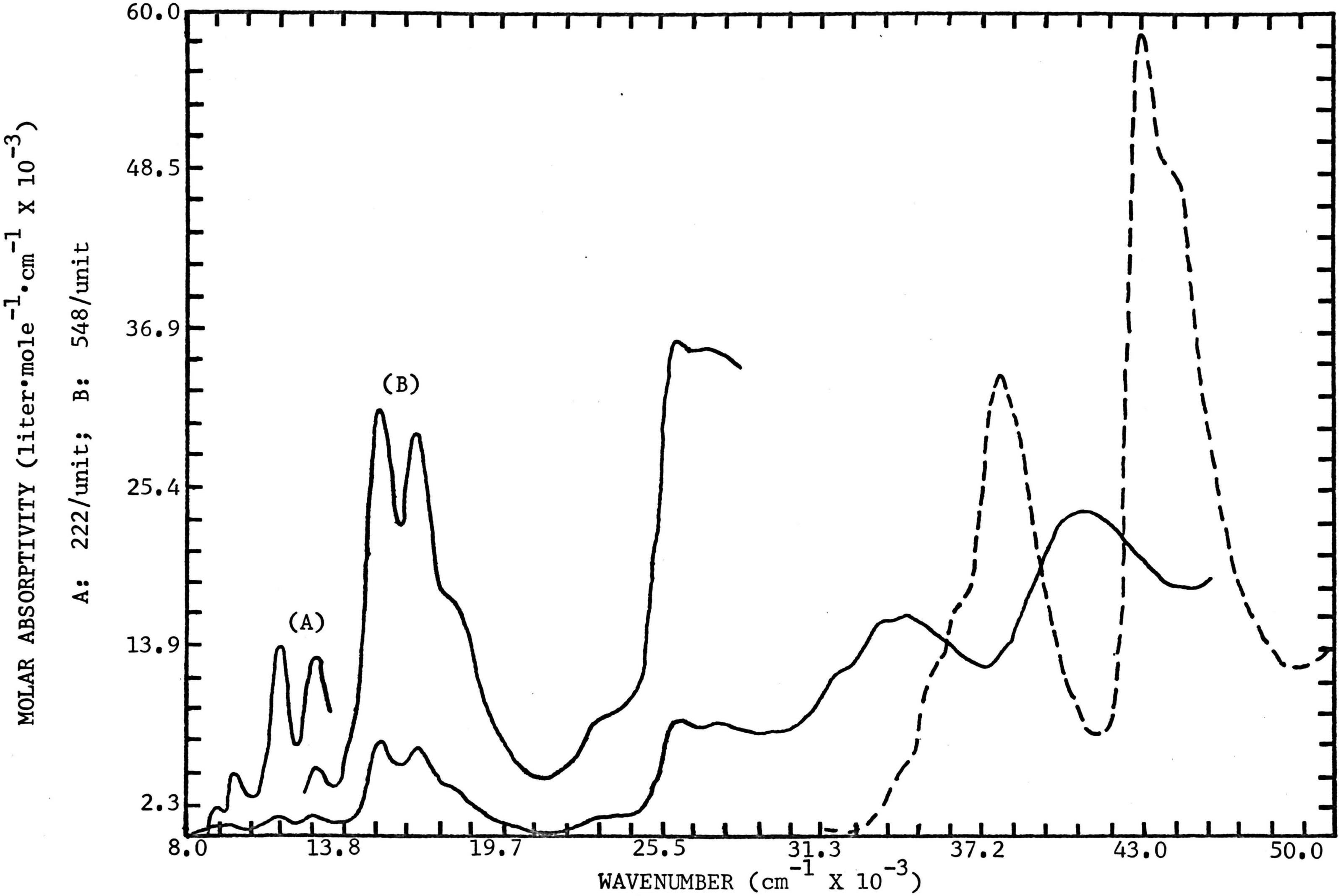


Figure 8. Electronic absorption spectra of 1,10-phenanthroline (----) and 1,10-phenanthroline radical anion (——).

TABLE VI

ELECTRONIC SPECTRA OF 1,10-PHENANTHROLINE, METHYL SUBSTITUTED PHENANTHROLINES AND 2,2'-BIPYRIDYL

Compound	$\pi \rightarrow \pi^*$ Absorption Bands[a]					
1,10-Phenanthroline	2930(sh)[b]	2800(sh)	2750(sh)	2635 (33700)[c]	2320 (57000)	2260(sh)
5-Methyl-1,10-phenanthroline	2980(sh)	2850(sh)	2790(sh)	2660 (34000)	2330 (51750)	2280(sh)
5,6-Dimethyl-1,10-phenanthroline	3000(sh)	--	2840(sh)	2700 (39400)	2360 (55600)	2300(sh)
4,7-Dimethyl-1,10-phenanthroline	2990	2880(sh)	2780(sh)	2750 (37700)	2390 (38800)	2330(sh)
2,9-Dimethyl-1,10-phenanthroline	3080(sh)	2950(sh)	2810(sh)	2690 (29400)	2290 (52200)	2260(sh)
3,4,7,8-Tetramethyl-1,10-phenanthroline	3300	3020(sh)	2830(sh)	2700 (37200)	2430 (42400)	2350(sh)
2,2'-Bipyridyl	2820 (16000)	2630(sh)	2430 (11000)	2360 (12140)	2260	

[a] In Angstroms (Å)

[b] sh = shoulder

[c] Molar absorptivities of principal bands are shown in parantheses immediately below the wavelengths.

classical transition metal complexes or in terms of simple Hückel Molecular Orbital Theory. Recognizing the limitations imposed on the Hückel Theory by the omission of interelectronic repulsions, the electronic spectra of 1,10-phenanthroline, methyl substituted phenanthrolines, and 2,2'-bipyridyl are herein discussed in terms of P.P.P.[55,56] Self-Consistent Field Molecular Orbital calculations including configuration interaction (S.C.F.-C.I.; Appendix B). These calculations do attempt to include explicit interelectronic repulsions.

For a planar, aromatic hydrocarbon containing 2m conjugated atoms in the pi-system, the highest occupied molecular orbitals (HOMO's) and lowest unoccupied molecular orbitals (LUMO's), all of which will be non-degenerate for a molecule having C_{2v} symmetry, may be depicted as shown schematically in Figure 9. Also shown are the possible one electron transitions between these orbitals.

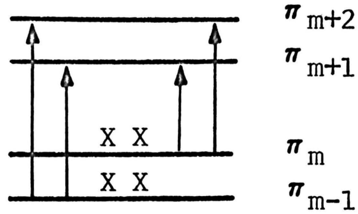


Figure 9. Pi-molecular orbitals and electronic transitions for a molecule having non-degenerate orbitals.

In the Clar spectral nomenclature system,[57,58] configurational mixing of the medium energy excitations $\pi_{m-1} \rightarrow \pi_{m+1}$ and $\pi_m \rightarrow \pi_{m+2}$ gives rise to a low intensity band (α) and a high intensity band (β), generally at lower and higher energies, respectively, than the p-band, which is the lowest energy band of moderate intensity. In addition, the high energy excitation, $\pi_{m-1} \rightarrow \pi_{m+2}$, which mixes to some extent with the $\pi_m \rightarrow \pi_{m+1}$ transition, is usually referred to as the β'-band.

On the basis of Hückel Theory, the bands in neutral 1,10-phenanthroline have been assigned to these transitions.[54,66] The low energy band in the 2900 Å region has been assigned as the weak α-band, the band between 2700 Å and 2900 Å has been assigned as the p-band, and the intense bands at 2635 Å and 2320 Å have been assigned as the β'- and β-bands respectively. These band assignments are in fair agreement with the more complete and more accurate results obtained from S.C.F.-C.I. calculations.

Singlet spectra for 1,10-phenanthroline, calculated by the S.C.F.-C.I. method, using a configuration interaction matrix of order 21, are listed in Table VII. The empirical parameters employed in the various calculations are also shown in this table. All the calculations performed on 1,10-phenanthroline were based on the molecular geometry shown in Figure 10.

A perusal of Table VII indicates that calculation number 11 yields the spectrum providing the best overall fit to the experimental spectrum. The calculated energies for the highest and lowest energy bands are somewhat low in energy; however, the calculated wavelengths of the most intense bands are in excellent agreement with those of the experimental spectrum. Band assignments for 1,10-phenanthroline, based on this calculation, are compiled in Table VIII. All of the indicated transitions are fully allowed and are polarized in the plane of the molecule. Transitions 1, 4, and 6 are short-axis polarized and transitions 2, 3, and 5 are long-axis polarized. The $n \rightarrow \pi^*$ band, which is perpendicularly polarized and forbidden, is not observed in the spectrum.

TABLE VII

CALCULATED SINGLET SPECTRA FOR 1,10-PHENANTHROLINE

Calc. No.	α_N	β_{CC}	β_{CN}	γ_{CC}	γ_{NN}	Calculated Wavelengths (Å)
	Parameters (eV)					
1[53]	-2.46	-2.39	-2.58	11.13	12.85	3130, 2840, 2460, 2380, 2210, 2160
2	-3.59	-2.39	-2.58	11.13	12.83	3100, 2870, 2550, 2450, 2160, 2120
3	-4.78	-2.39	-2.58	11.13	12.83	3120, 2910, 2650, 2530, 2120, 2100
4[59]	-3.59	-2.39	-2.74	11.13	12.83	3060, 2860, 2490, 2410, 2130, 2110
5[60]	-3.66	-2.44	-2.44	11.13	12.34	3110, 2870, 2610, 2490, 2140, 2100
6[61]	-3.59	-2.39	-2.58	11.13	13.46	3100, 2860, 2520, 2420, 2170, 2120
7[62]	-3.59	-2.39	-2.58	11.00	12.83	3110, 2880, 2550, 2450, 2160, 2120
8[63]	-2.50	-2.50	-2.58	11.13	12.34	3050, 2780, 2433, 2361, 2152, 2096
9	-1.88	-2.50	-2.58	11.13	12.34	3053, 2768, 2387, 2323, 2188, 2111
10	-3.15	-2.10	-2.40	11.13	12.34	3420, 3120, 2780, 2640, 2350, 2310
11	-3.23	-2.15	-2.40	11.13	12.34	3370, 3080, 2760, 2620, 2320, 2280
12	-3.30	-2.20	-2.40	11.13	12.34	3320, 3040, 2730, 2600, 2290, 2240
13	-3.45	-2.30	-2.40	11.13	12.34	3230, 2970, 2680, 2560, 2230, 2180

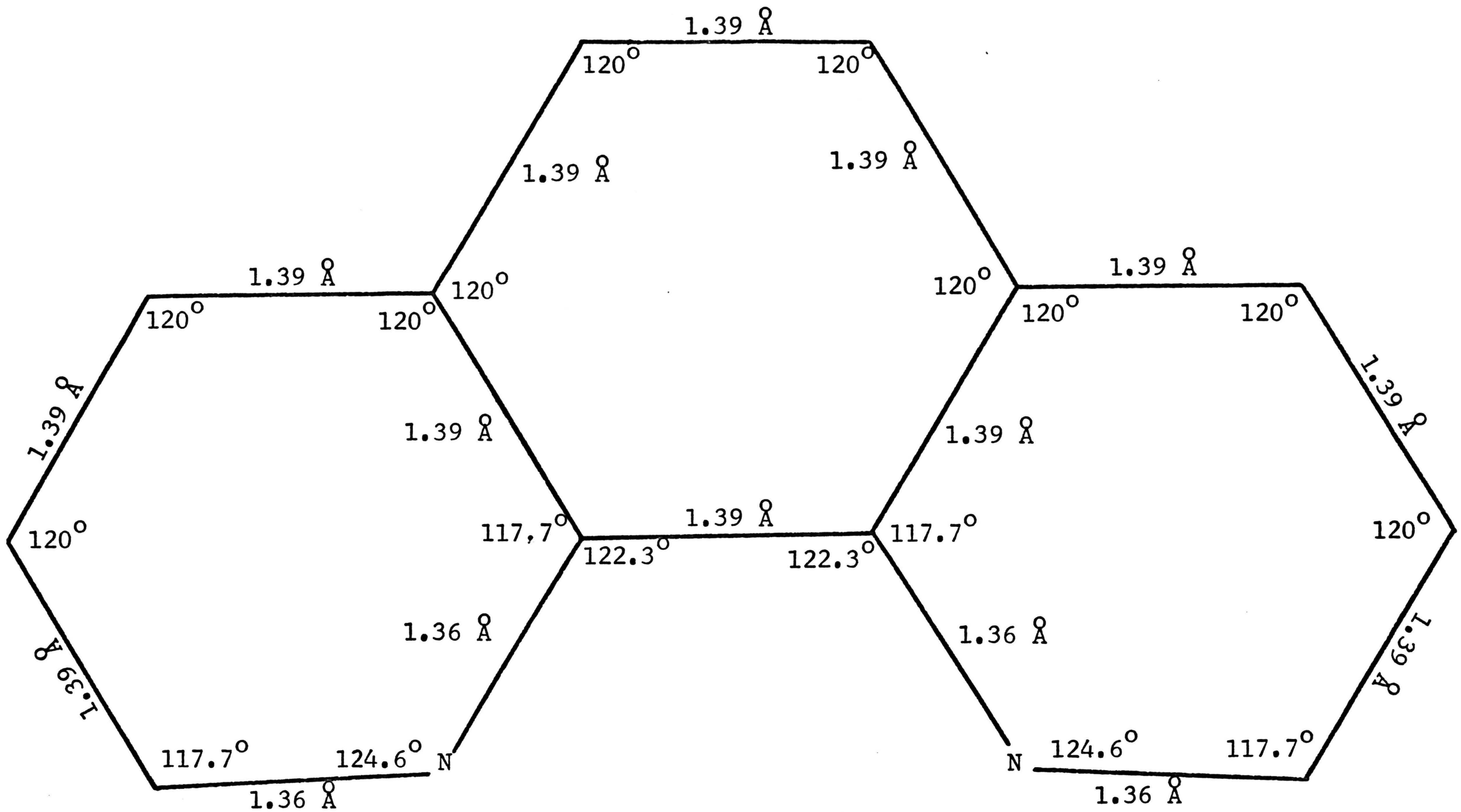


Figure 10. Molecular geometry of 1,10-phenanthroline.[64]

TABLE VIII

ELECTRONIC SPECTRAL ASSIGNMENTS FOR 1,10-PHENANTHROLINE

	Bands Exp.(Å)	Bands Calc.(Å)	Calculated Oscillator Strengths	Band Assignments[a]	State Notation
1)	2930	3370	0.0034	$\pi_7 \rightarrow \pi_9$ $\pi_6 \rightarrow \pi_8$	$^1A_1$
2)	2800	3080	0.348	$\pi_7 \rightarrow \pi_8$	$^1B_1$
3)	2750	2760	0.320	$\pi_6 \rightarrow \pi_9$	$^1B_1$
4)	2635	2620	0.652	$\pi_6 \rightarrow \pi_8$ $\pi_7 \rightarrow \pi_{10}$	$^1A_1$
5)	2320	2320	1.06	$\pi_6 \rightarrow \pi_9$ $\pi_5 \rightarrow \pi_8$ $\pi_7 \rightarrow \pi_{11}$ $\pi_4 \rightarrow \pi_9$ $\pi_6 \rightarrow \pi_{10}$	$^1B_1$
6)	2260	2280	0.714	$\pi_7 \rightarrow \pi_{10}$	$^1A_1$

[a]Only those excitations contributing near 50% or more to the configurational wave functions are shown.

Employing essentially the same set of parameters as used in the above calculation, the electronic spectra of methyl substituted phenanthrolines and 2,2'-bipyridyl have also been calculated. The results are listed in Table IX. As indicated previously, a purely inductive model has been used to account for the perturbational influence of the methyl groups. By comparing the calculated spectra with the experimental spectra, it is seen that agreement is, in general, reasonably good for the methyl substituted phenanthrolines. Although the calculated spectrum of 2,2'-bipyridyl is not quite so good as the calculated spectra for the phenanthrolines, it is to be noted that the calculation is based on a planar model (using the same bond lengths and bond angles as in 1,10-phenanthroline except that the "essential single bond" joining the two rings is assumed to have a length of 1.52 Å). Since 2,2'-bipyridyl is likely non-planar in solution,[53] agreement between a spectrum calculated from a planar model and an experimentally obtained spectrum can hardly be expected to be excellent. The agreement, on the other hand, is sufficiently good to suggest that non-planarity is not extensive.

Spectra of Neutral Complexes. Electronic absorption spectra of neutral tetracarbonyl bipyridyl, phenanthroline, and biquinolyl Group VI-B metal complexes are presented in Figures 11-15. Some of the bands in the spectra of a few of these complexes have been previously discussed and tentatively assigned.[65] The assignments made in the present work, based upon a far more extensive set of data, establish the nature of the electronic transitions involved in these diimine complexes with a considerably greater degree of certainty.

TABLE IX

CALCULATED SPECTRA OF METHYL SUBSTITUTED PHENANTHROLINES AND 2,2'-BIPYRIDYL

Compound	Calculated $\pi \rightarrow \pi^*$ Bands[a]				
5-Methyl-1,10-phenanthroline	3200	2850	2750	2340	2280
5,6-Dimethyl-1,10-phenanthroline	3320	2850	2840	2380	2300
4,7-Dimethyl-1,10-phenanthroline	3040	2700	2560	2320	2280
2,9-Dimethyl-1,10-phenanthroline	3080	2860	2660	2259	2251
3,4,7,8-Tetramethyl-1,10-phenanthroline	3070	2770	2610	2370	2260
2,2'-Bipyridyl	2820	2730	2320	2180	2090

[a]In Angstroms (Å). Parameters Employed:
$\alpha_N = -4.09$ eV, $\alpha_X = +1.26$ eV (for phenanthrolines), $\beta_{CC} = -2.15$ eV, $\beta_{CN} = -2.40$ eV, $\gamma_{CC} = 11.13$ eV, $\gamma_{NN} = 12.34$ eV.

Figure 11. Electronic spectra of neutral (2,2'-bipy)M$(CO)_4$ complexes in 1,2-dimethoxyethane.

M	A		B	
	conc.,	cell	conc.,	cell
—— Cr	3.0×10^{-4} M,	1 mm;	1.5×10^{-4} M,	1 cm
•••• Mo	2.5×10^{-4} M,	1 mm;	1.9×10^{-4} M,	1 mm
-•-• W	3.6×10^{-4} M,	1 mm;	1.0×10^{-3} M,	1 mm

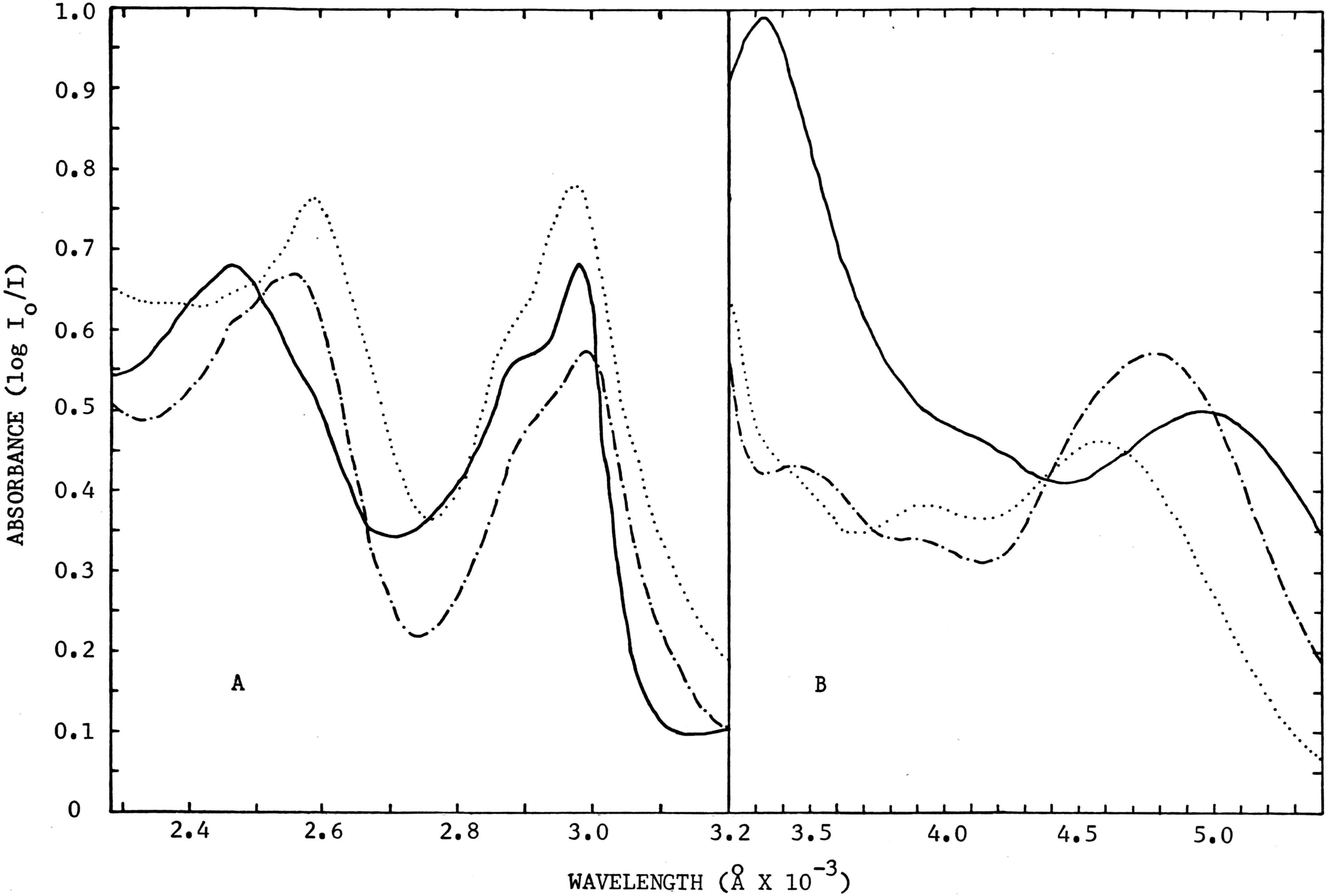
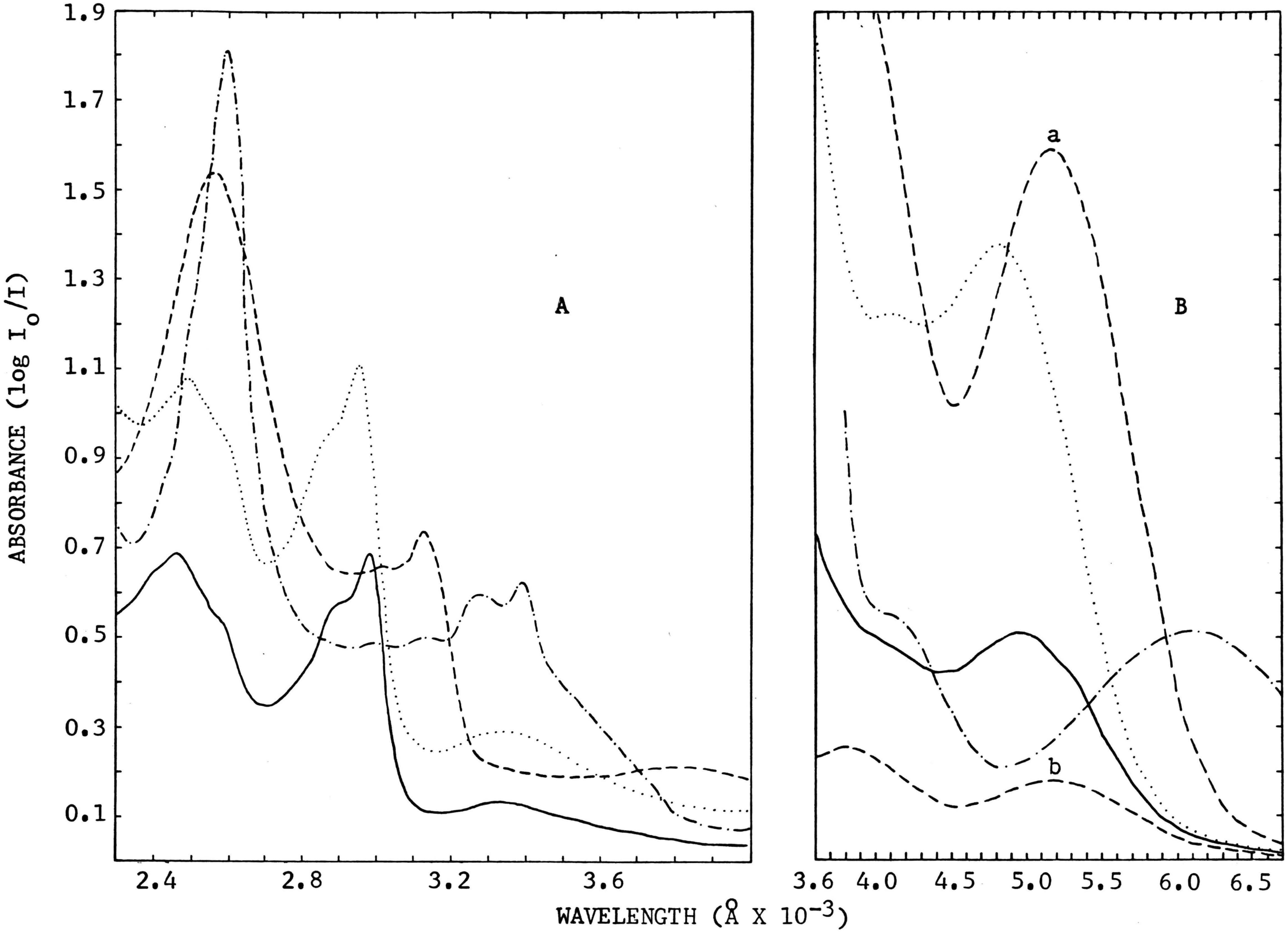


Figure 11. Electronic spectra of neutral (2,2'-bipy)M$(CO)_4$ complexes.

Figure 12. Electronic spectra of neutral "bipyridyl-like" tetracarbonyl complexes of chromium in 1,2-dimethoxyethane.

	A) Complex	Conc.	Cell
——	(2,2'-Bipy)$Cr(CO)_4$:	3.0×10^{-4} M,	1 mm
....	(4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$:	3.0×10^{-4} M,	1 mm
----	(4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$:	2.7×10^{-4} M,	1 mm
-.-.	(2,2'-Biquin)$Cr(CO)_4$:	4.0×10^{-4} M,	1 mm

	B) Complex	Conc.	Cell
——	(2,2'-Bipy)$Cr(CO)_4$:	1.5×10^{-4} M,	1 cm
....	(4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$:	3.0×10^{-4} M,	1 cm
----	(4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$:	2.7×10^{-4} M,	a = 1 cm b = 1 mm
-.-.	(2,2'-Biquin)$Cr(CO)_4$:	4.0×10^{-4} M,	1 cm



<u>Figure 12.</u> Electronic spectra of neutral "bipyridyl-like" tetracarbonyl complexes of chromium.

<u>Figure 13.</u> Electronic spectra of (1,10-phen)$M(CO)_4$ in 1,2-dimethoxyethane.

	M	(A) Conc.	Cell	(B) Conc.	Cell
——	Cr	1.9×10^{-4} M,	1 mm;	1.7×10^{-4} M,	1 cm
····	Mo	2.5×10^{-4} M,	1 mm;	2.4×10^{-4} M,	1 cm
		(a)4.3×10^{-4} M,	1 mm		
-·-·	W	1.7×10^{-4} M,	1 mm;	2.7×10^{-4} M,	1 cm
		(b)4.8×10^{-4} M,	1 mm		

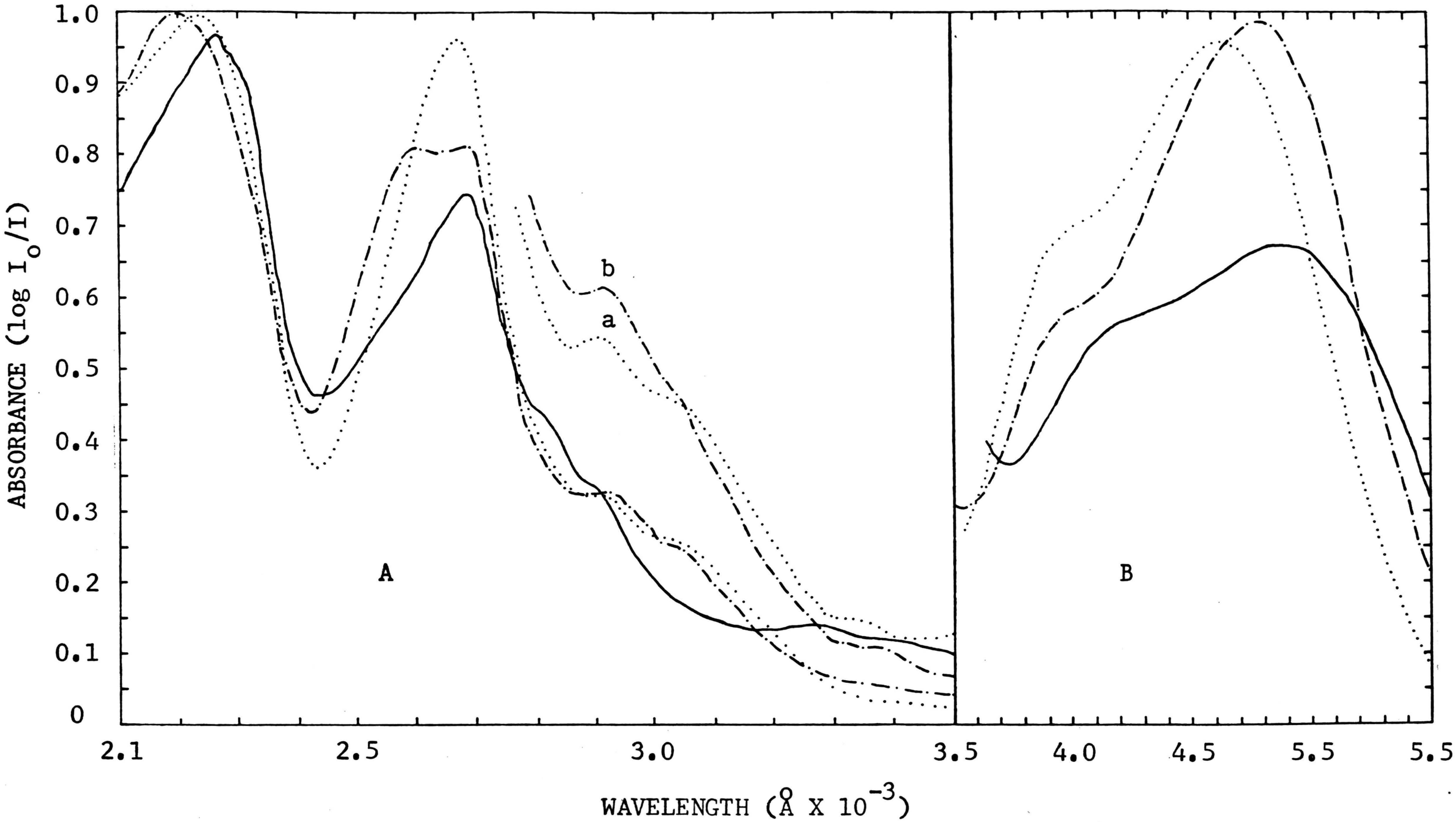


Figure 13. Electronic spectra of (1,10-phen)$M(CO)_4$ in 1,2-dimethoxyethane.

Figure 14. Electronic spectra of neutral 1,10-phenanthroline and methyl-substituted 1,10-phenanthroline tetracarbonyl chromium (0) complexes in 1,2-dimethoxyethane.

A)	Complex	Conc.	Cell
————	(1,10-Phen)Cr(CO)$_4$:	1.9 X 10^{-4} M,	1 mm
········	(5-(CH$_3$)-1,10-phen)Cr(CO)$_4$:	2.5 X 10^{-4} M,	1 mm
--------	(5,6-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	2.5 X 10^{-4} M,	1 mm
-·-·-·-·	(4,7-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	4.0 X 10^{-4} M,	1 mm
—···—	(2,9-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	2.8 X 10^{-4} M,	1 mm

B)	Complex	Conc.	Cell
————	(1,10-Phen)Cr(CO)$_4$:	1.9 X 10^{-4} M,	1 cm
········	(5-(CH$_3$)-1,10-phen)Cr(CO)$_4$:	1.0 X 10^{-3} M,	1 mm
--------	(5,6-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	2.5 X 10^{-4} M,	1 cm
-·-·-·-·	(4,7-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	4.0 X 10^{-4} M,	1 cm
—···—	(2,9-(CH$_3$)$_2$-1,10-phen)Cr(CO)$_4$:	2,8 X 10^{-4} M,	1 cm

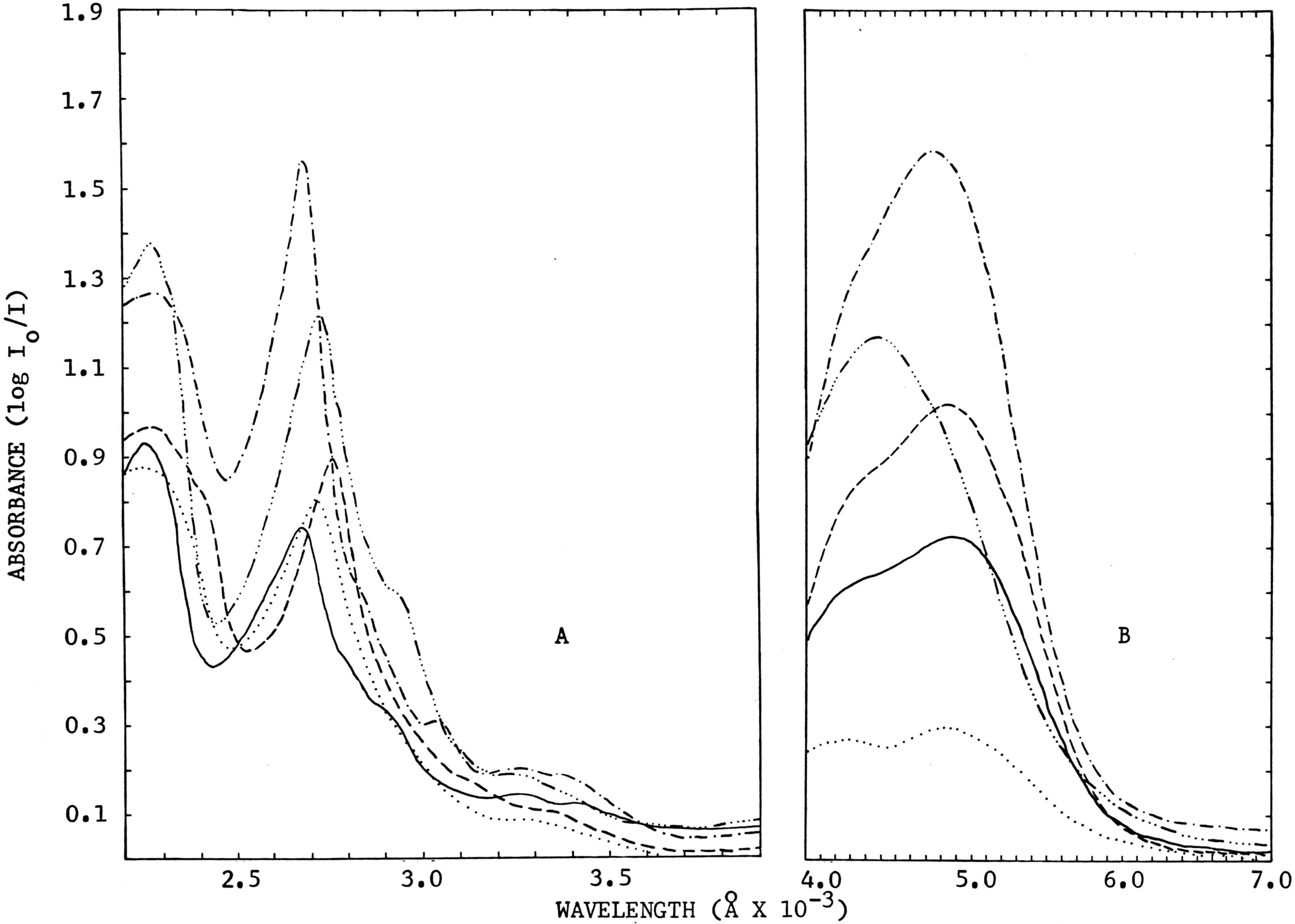


Figure 14. Electronic spectra of neutral 1,10-phenanthroline and methyl substituted 1,10-phenanthroline tetracarbonyl chromium(0) complexes.

Figure 15. Electronic spectra of neutral substituted phenanthroline tetracarbonyl chromium (0) complexes in 1,2-dimethoxyethane.

	A) Complex	Conc.	Cell
——	(5-(NO_2)-1,10-phen)$Cr(CO)_4$:	4.0×10^{-4} M,	1 mm
••••	(3,4,7,8-$(CH_3)_4$-1,10-phen)$Cr(CO)_4$:	2.9×10^{-4} M,	1 mm
----	(4,7-$(\phi)_2$-1,10-phen)$Cr(CO)_4$:	3.0×10^{-4} M,	1 mm

	B) Complex	Conc.	Cell
——	(5-(NO_2)-1,10-phen)$Cr(CO)_4$:	4.0×10^{-4} M,	1 cm
••••	(3,4,7,8-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$:	1.0×10^{-4} M,	1 mm
----	(4,7-$(\phi)_2$-1,10-phen)$Cr(CO)_4$:	3.0×10^{-4} M,	1 cm

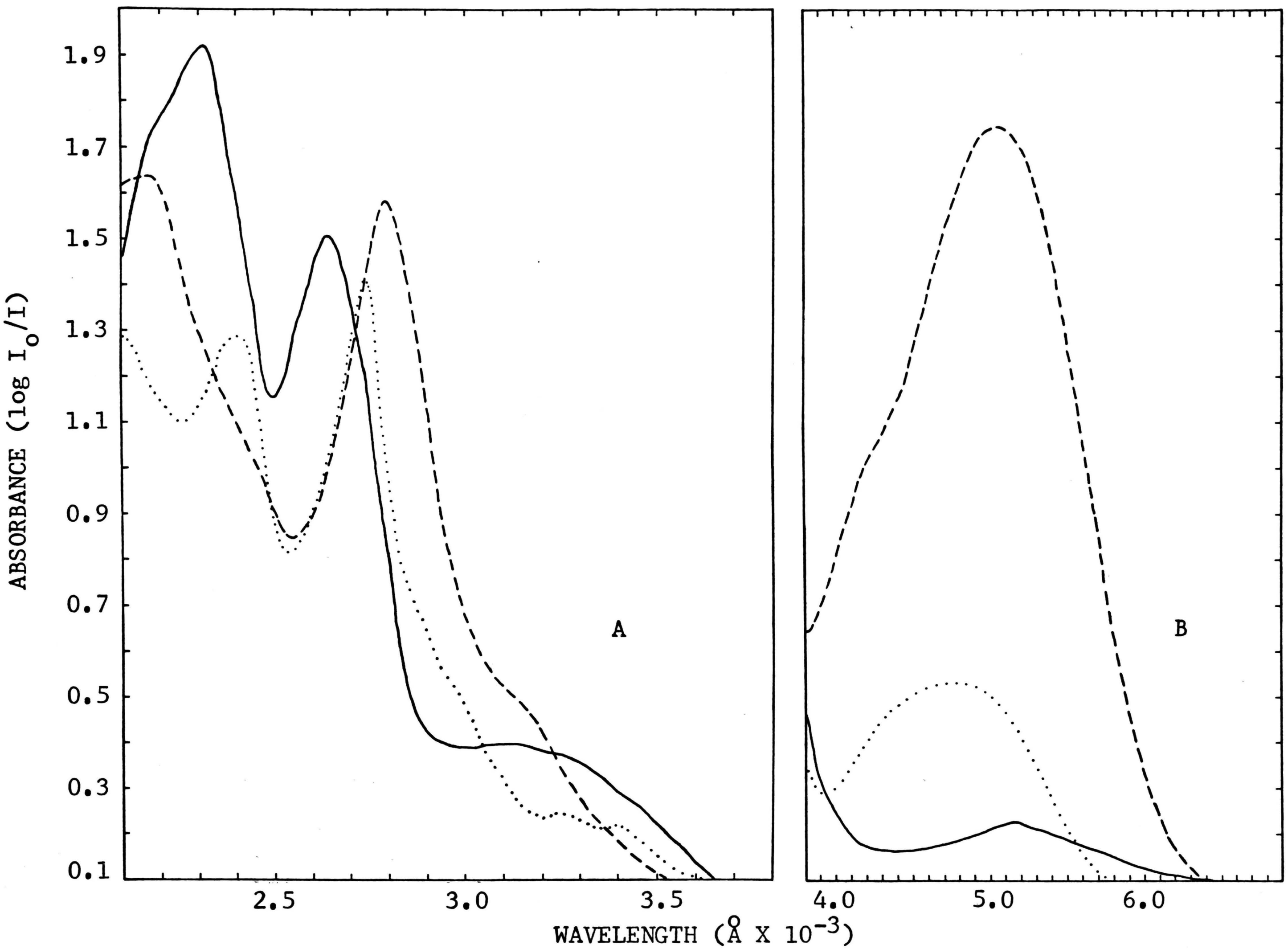


Figure 15. Electronic spectra of neutral substituted phenanthroline tetracarbonyl chromium(0) complexes.

The ultraviolet spectra (2000 - 4000 Å) of all the phenanthroline, bipyridyl, and biquinolyl complexes exhibit bands clearly associated with the ligands. Comparing the spectra of the ligands to the ultraviolet spectra of the corresponding complexes indicates that the ligand $\pi \rightarrow \pi^*$ transitions undergo small, although significant, energy changes, but do not undergo structural modification when the ligands become complexed. The nature of the shifts experienced by the intraligand bands in the 1,10-phenanthroline series of complexes is especially revealing.

In the 1,10-phenanthroline spectrum, the two most intense bands ($\beta'$and β) occur at 2310 Å and 2635 Å. When 1,10-phenanthroline becomes complexed to a Group VI-B metal in the tetracarbonyl complexes, the 2310 Å band is shifted hypsochromically to about 2250 Å while the 2635 Å band is shifted bathochromically to about 2690 Å. These shifts are in precisely the same direction energetically and to virtually the same extent as the shifts experienced by these bands when 1,10-phenanthroline is monoprotonated.[66]

To be sure, both protonation and metal coordination of 1,10-phenanthroline produces inductive withdrawal of electronic charge density from the diimine nitrogens, rendering the nitrogens more electronegative toward adjacent aromatic carbons. Such an effect is theoretically treated in terms of an increase in the value of the nitrogen coulomb integrals. Both Hückel and S.C.F. calculations predict that an increase in the coulombic increment for nitrogen should result in a hypsochromic shift of the β'-band and a bathochromic shift of the β-band. This is precisely the behavior observed in the ultraviolet spectra of monoprotonated 1,10-phenanthroline and the (1,10-phen)M$(CO)_4$ complexes.

S.C.F.-C.I. calculated electronic transitions corresponding to increasing coulombic increments are tabulated in Table X and plotted in Figure 16. Also included in Figure 16 are the experimentally observed β- and β'-bands for 1,10-phenanthroline, monoprotonated 1,10-phenanthroline, and the (1,10-phen)M$(CO)_4$ complexes.

From the preceding discussion and the data included in Table X, as well as Figure 16, it is clear that the ultraviolet spectra of the (1,10-phen)M$(CO)_4$ complexes are readily explicable in terms of perturbations to the 1,10-phenanthroline spectrum brought about by sigma coordination. The similarity between the spectrum of monoprotonated phenanthroline, which obviously involves no π-bonding between the proton and phenanthroline, and the spectra of the (1,10-phen)M$(CO)_4$ complexes, thus, provides additional strong evidence to support the contention that no back-bonding exists between phenanthroline and metal in the (1,10-phen)M$(CO)_4$ complexes.

The similarity between the spectrum of the monoprotonated ligand and the ultraviolet spectra of the corresponding Group VI-B tetracarbonyl complexes is also readily apparent when the ligand is 2,2'-bipyridyl. The principal absorption bands for monoprotonated 2,2'-bipyridyl have been reported[66] at 3180 Å, 2985 Å, 2564 Å, and 2475 Å. All of these transitions occur at lower energies than the corresponding bands in the free ligand (2820 Å, 2630 Å, 2430 Å, and 2360 Å for 2,2'-bipyridyl in 1,2-dimethoxyethane) and at energies comparable to the ultraviolet bands for the complexes (e.g., 2980 Å,

TABLE X

CALCULATED ELECTRONIC SPECTRA OF 1,10-PHENANTHROLINE

WITH INCREASING NITROGEN COULOMBIC INCREMENTS[a]

h_N	Calculated Wavelengths (Å)					
				β	β'	
0.75	3420	3040	2630	2500	2390	2340
1.00	3410	3050	2670	2540	2370	2330
1.50	3370	3080	2760	2620	2320	2280
1.80	3379	3118	2838	2698	2286	2279
2.00	3380	3120	2850	2710	2280	2260

[a]Parameters employed in the S.C.F.-C.I. calculations:

$\alpha_N = h_N \beta_{CC}$ eV; $\beta_{CC} = -2.15$ eV; $\beta_{CN} = -2.40$ eV; $\gamma_{CC} = 11.13$ eV; $\gamma_{NN} = 12.13$ eV

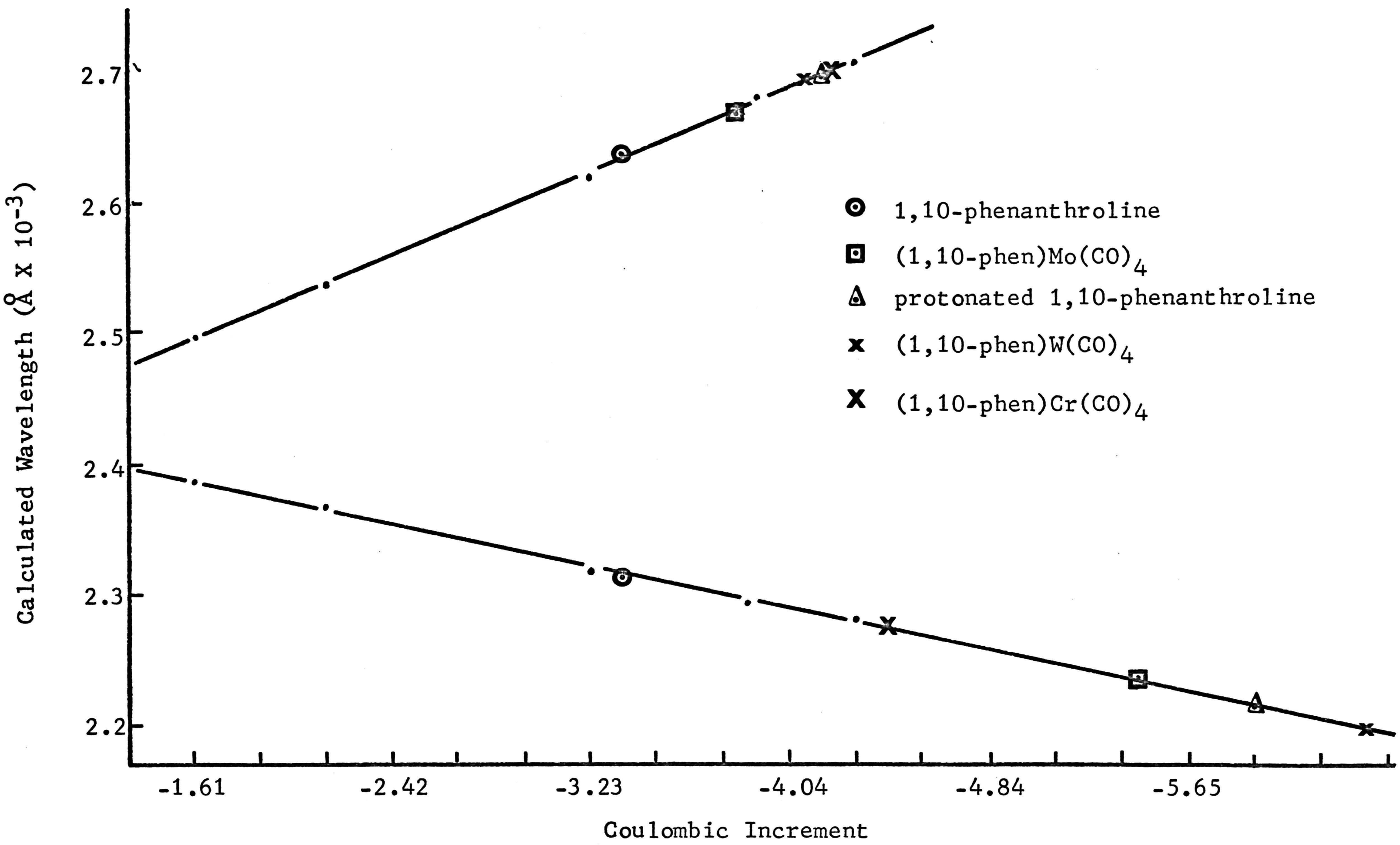


Figure 16. Plot of calculated β and β' transitions versus increasing coulombic increment.

2900 Å, about 2550 Å, and 2440 Å for the chromium complex in 1,2-dimethoxyethane). In a manner analogous to the phenanthroline system, S.C.F.-C.I. calculations, based on a cis planar model and employing the parameters shown in Table IX, predict this observed behavior. All bands in the calculated spectra are shifted bathochromically with increasing coulombic increments on the nitrogens. The calculations indicate that the lowest energy transition ($\pi_6 \rightarrow \pi_7$; $^1B_1$ symmetry) is long-axis (x axis) polarized, as is the band near 2500 Å ($\pi_6 \rightarrow \pi_9$; $^1B_1$ symmetry). The next-to-lowest energy band and the highest energy band (both are $^1A_1$ states arising from configurational mixing of $\pi_6 \rightarrow \pi_8$ and $\pi_5 \rightarrow \pi_7$ transitions) are short-axis (z axis) polarized and, therefore, are predicted to be of lower intensity than the $^1B_1$ states. These predicted relative intensities are, indeed, observed in the spectra of the complexes and the monoprotonated species. Therefore, as with the phenanthroline complexes, on the basis of the resemblance between the spectrum of the monoprotonated 2,2'-bipyridyl and the ultraviolet spectra of the group VI-B tetracarbonyl complexes of 2,2'-bipyridyl, pi-bonding between metal and diimine is inferred to be absent or of insignificant magnitude.

Thus, it is seen that the ultraviolet spectra of the heterocyclic diimine Group VI-B tetracarbonyl complexes are essentially dominated by intraligand $\pi \rightarrow \pi^*$ transitions and that these transitions correspond to perturbed transitions of the free ligands. At lower energies (longer wavelengths), most of the heterocyclic diimine complexes included in this study exhibit four additional, lower intensity bands. Two of these bands appear in the vicinity between 3000 Å and 3400 Å, one between

3900 Å and 4400 Å, and one between about 4500 Å and 5200 Å. The intensities of all of these bands are high, indicating that these are probably allowed transitions. The band appearing between about 4500 Å and 5200 Å is the lowest energy band which has been detected; none of the neutral diimine Group VI-B tetracarbonyl complexes exhibit any absorption in the near infrared region of the spectrum.

The colorless Group VI-B metal hexacarbonyls, of course, show no absorption bands in the visible spectral region. Consequently, the transitions appearing in the visible spectrum for the diimine tetracarbonyl complexes are suspected of being either metal-to-ligand charge transfer bands ($M \rightarrow \pi^*_L$) or "d-d" and metal-to-carbonyl charge transfers ($M \rightarrow \pi^*_{CO}$) which have undergone bathochromic shifts relative to these bands in the parent hexacarbonyls. The hexacarbonyls exhibit high intensity absorptions at 2700-3100 Å, which have been assigned as fully allowed $M \rightarrow \pi^*_{CO}$ charge transfer bands.[27] At slightly lower energies (3100-3300 Å), the hexacarbonyls display absorption bands having molar absorptivities of about 2000. These bands have been assigned as spin-allowed "d-d" bands, which have gained intensity by their close proximity to the fully allowed $M \rightarrow \pi^*_{CO}$ bands.[27] Both of these "d-d" and $M \rightarrow \pi^*_{CO}$ bands are expected to undergo bathochromic shifts upon replacement of one or more CO molecules by poorer π-acceptor ligands. A molecule which is a poorer π-acceptor than CO will have a tendency, as a result of sigma-donation, to increase electronic charge density on the metal. To be sure, some of this charge density will be removed by enhanced π-bonding between the metal and the remaining carbonyls; however, a net increase in negative charge on the metal very likely results. This is especially true when the ligand which replaces the CO(s) engages in no π-bonding with the metal. An increase in negative charge on the metal destabilizes the occupied d-orbitals and consequently results in a diminution of the energy separation between them and the corresponding antibonding orbitals. Thus, the absorption bands in the vicinity of 3000-3400 Å and those in the region of 3900 Å to 4400 Å in the spectra of the tetracarbonyl complexes are reasonably assigned as $M \rightarrow \pi^*_{CO}$ and "d-d" bands respectively. Saito[65] has similarly assigned the transitions occurring at approximately these energies for ethylenediamine, propylenediamine, and trimethylenediamine Group VI-B tetracarbonyl complexes. These latter assignments have been based on the band shifts with variation of ligand as well as central metal. Tabulation of the "d-d" and $M \rightarrow \pi^*_{CO}$ bands for the ethylenediamine (en) and trimethylenediamine (tn) complexes, along with some of the diimine complexes reported in this study, is made in Table XI. Trimethylenediamine is apparently lower in the spectrochemical series than ethylenediamine (in the tetracyanocobaltate(III) complexes, which are isoelectronic with the tetracarbonylchromium(0) complexes, the established d-d band occurs at lower energy for the trimethylenediamine complex). Consequently, for a given Group VI-B metal, the d-d band for the trimethylenediamine tetracarbonyl complex should occur at a lower energy than for the ethylenediamine complex. This is, indeed, observed to be the case with the band assigned as a "d-d" transition. Similarly, 1,10-phenanthroline and 2,2'-bipyridyl are stronger field ligands than ethylenediamine or trimethylenediamine and should, therefore, cause the "d-d" band to occur at higher energies for a given metal and this is also

TABLE XI

BAND POSITIONS (Å) OF "d-d" AND LOWEST ENERGY $M \rightarrow \pi^*_{CO}$ TRANSITIONS IN SOME DIAMINE AND DIIMINE COMPLEXES

Complex	"d-d"	$M \rightarrow \pi^*_{CO}$ (1)
$(en)Cr(CO)_4$ [a,b]	4240	3370
$(en)Mo(CO)_4$ [b]	3950	3060
$(en)W(CO)_4$ [b]	3970	3010
$(tn)Cr(CO)_4$ [a,b]	4350	3370
$(tn)Mo(CO)_4$ [b]	4010	3010
$(tn)W(CO)_4$ [b]	4050	2980
$(1,10\text{-phen})Cr(CO)_4$	4150(sh)[c]	3400
$(1,10\text{-phen})Mo(CO)_4$	3940(sh)	3350(sh)
$(1,10\text{-phen})W(CO)_4$	3960(sh)	3380(sh)
$(4,7\text{-}(CH_3)_2\text{-}1,10\text{-phen})Cr(CO)_4$	4150(sh)	3400
$(4,7\text{-}(\phi)_2\text{-}1,10\text{-phen})Cr(CO)_4$	4150(sh)	--
$(2,2'\text{-bipy})Cr(CO)_4$	4100(sh)	3350
$(2,2'\text{-bipy})Mo(CO)_4$	3950	3450(sh)
$(2,2'\text{-bipy})W(CO)_4$	3950(sh)	3470
$(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$	4100(sh)	3350

[a]en = ethylenediamine; tn = trimethylenediamine

[b]Reference 65

[c]sh = shoulder

observed to be the case. A general characteristic of d-d type bands is that they undergo hypsochromic shifts corresponding to increased ligand field splitting with a change in congeners from first row transition metals to second or third row transition metals. Inspection of Table XI reveals that, for the four series listed, the "d-d" band does, indeed, undergo a hypsochromic shift when the central metal atom is changed from chromium to molybdenum. The anticipated increase in energy of the "d-d" transition between molybdenum and tungsten is not observed, very possibly because the transition under consideration is not a pure d-d band. Also of interest is the observation that the wavelength of the d-d band remains essentially constant as various substitutions are made in the diimine. Apparently, the effects of substitution remain localized on the ligand or those effects on the metal wrought by substitution are disseminated to the carbonyls. It is important to note that the variations discussed for the "d-d" band are not observed in the other bands of the spectra.

The remaining band, which occurs around 5000 Å, in the spectra of the aromatic diimine complexes is conspicuously absent in the spectra of the aliphatic diamine complexes. This band is, thus, very likely a metal-to-ligand charge transfer band. Such bands are commonly observed in this region for many "classical" transition metal complexes containing 2,2'-bipyridyl or 1,10-phenanthroline. The hypsochromic shifts in this band from the chromium complexes to the molybdenum and tungsten complexes are readily explicable, if, indeed, this band is a $M \rightarrow \pi_L^*$ transition. The position of this type of band is known to be rather sensitive to the charge on the metal. The higher positive charge on molybdenum and tungsten, as discussed previously, renders a metal-to-ligand charge transfer energetically more difficult and the transition has been shifted hypsochromically with respect to the chromium complex. This behavior is also observed and similarly rationalized for the spectra of the (2,2'-bipy)M$(CO)_4$ complexes.

Additional evidence indicating that this band is, indeed, a $M \rightarrow \pi_L^*$ band has been obtained by substitutionally perturbing the diimine ring systems. The effects of ring substitution in heterocyclic diimine transition metal complexes, particularly by methyl groups, on charge transfer bands have been rather extensively studied.[49,67] These investigations have focused on the substitutional influence of methyl groups upon charge transfer bands in ferrous, ferric, and cuprous 1,10-phenanthroline and 2,2'-bipyridyl complexes. In the case of the tris(1,10-phenanthroline)iron(II) complexes, wherein the charge transfer band in the visible region is a metal-to-ligand charge transfer, methyl substitution into the 4, 5, 6, 7 positions of the aromatic rings all produce hypsochromic shifts of the $M \rightarrow \pi_L^*$ band. The 2,9-dimethyl-1,10-phenanthroline complex does not form, presumably because of steric hindrance. However, in the case of bis(1,10-phenanthroline)copper(II) complexes, the 2,9-dimethyl complex does form and also produces a strong hypsochromic shift of the $M \rightarrow \pi_L^*$ band.

Band positions for the transition referred to as the $M \rightarrow \pi_L^*$ band in the diimine Group VI-B tetracarbonyl complexes are listed in Table XII for several substituted complexes. It is seen by inspecting Table XII that the same trends, as observed for the substituted diimine iron(II) and copper(II) complexes, are observed for the substituted diimine

TABLE XII

BAND POSITIONS (Å) OF $M \rightarrow \pi^*_L$ AND $M \rightarrow \pi^*_{CO}$ (1)

IN SUBSTITUTED 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDYL

CHROMIUM TETRACARBONYL COMPLEXES

Complex	$M \rightarrow \pi^*_L$	$M \rightarrow \pi^*_{CO}$ (1)
(1,10-Phen)$Cr(CO)_4$	4880	3400
(5-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$	4850	3370
(5,6-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$	4825	3360
(4,7-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$	4750	3370
(2,9-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$	4350	3250
(3,4,7,8-$(CH_3)_4$-1,10-phen)$Cr(CO)_4$	4580	3390
(5-(NO_2)-1,10-phen)$Cr(CO)_4$	5150	a
(4,7-$(\phi)_2$-1,10-phen)$Cr(CO)_4$	5100	a
(2,2'-Bipy)$Cr(CO)_4$	4970	3340
(4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$	4820	3330
(4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$	5180	3850

[a]Band position uncertain.

chromium tetracarbonyl complexes. Substitution by electron releasing groups results in hypsochromic shifts, relative to the unsubstituted parent complex, of the metal-to-ligand charge transfer band and electron withdrawing groups shift the bands bathochromically. Two points may be noted here. First, the shift produced by one methyl group in the 5 position is 25-30 Å. The shift produced by placing an additional methyl group in the equivalent 6 position is an additional 25 Å. Thus, it appears that the shifts produced by methyl groups in equivalent positions are additive. Secondly, it is noted that disubstitution of methyl groups in positions closer to the nitrogens produces larger hypsochromic shifts, so that apparently the effects of methyl substitution are attenuated with increasing distance from the base site and the metal atom. Both of these observations are consistent with the hypothesis that the predominant cause of these shifts is an inductive electron release by the methyl groups. In accordance with arguments presented by Coulson and Longuett-Higgins,[68,69] the inductive electron release has raised the energies of both the pi bonding and antibonding levels in the ligand.

These shifts parallel the pK_a changes in the neutral ligands. Angelici[15] has studied the effects of substituted phenanthrolines on the carbonyl stretching frequencies and found that methyl substituents decrease the stretching frequencies and electron withdrawing substituents increase them, the trends paralleling the shifts described for the metal-to-ligand charge transfer bands. This certainly implies a change in the electron density on the carbonyls resulting from stabilization or destabilization of the d-π levels through enhanced or diminished back-bonding with the carbonyls. In this context, it is pointed out that the bands assigned as metal-to-carbonyl charge transfer bands also appear to undergo hypsochromic shifts when methyl groups are substituted into the diimine ring. Unfortunately, because of the rather broad nature of these bands and their relatively low intensity compared to the much more intense, contiguous intraligand bands, the exact positions of some of these bands, particularly those which appear as shoulders, are not known with certainty. Clearly, a distinct trend paralleling the pK_a's of the ligands is not observed despite the anticipation of such a trend. Except for the 2,9-dimethyl-1,10-phenanthroline complex, the hypsochromic shifts in the $M \rightarrow \pi^*_{CO}$ bands are rather small and occur to roughly the same extent for the methyl substituted complexes.

Evidence suggesting which antibonding orbital in the phenanthroline complexes is involved in the $M \rightarrow \pi^*_L$ band is obtained by comparing the energies of this band to the first reductive half-wave potentials of the complexes. These latter have been shown to correlate reasonably with calculated energies of π_8, the first virtual orbital of free 1,10-phenanthroline and its methyl derivatives. A plot of experimentally obtained energies of the $M \rightarrow \pi^*_L$ band versus $E^{(1)}_{\frac{1}{2}}$ values is shown in Figure 17. Although a perfect straight-line plot is not obtained, the plot is sufficiently close to being linear so as to indicate a direct correlation between the metal-to-ligand charge transfer energy and the first reductive half-wave potentials of the phenanthroline complexes. Having earlier established the existence of a positive correlation between these first reductive half-wave potentials and the energies of the first virtual orbitals in the ligands, it is clear that a positive

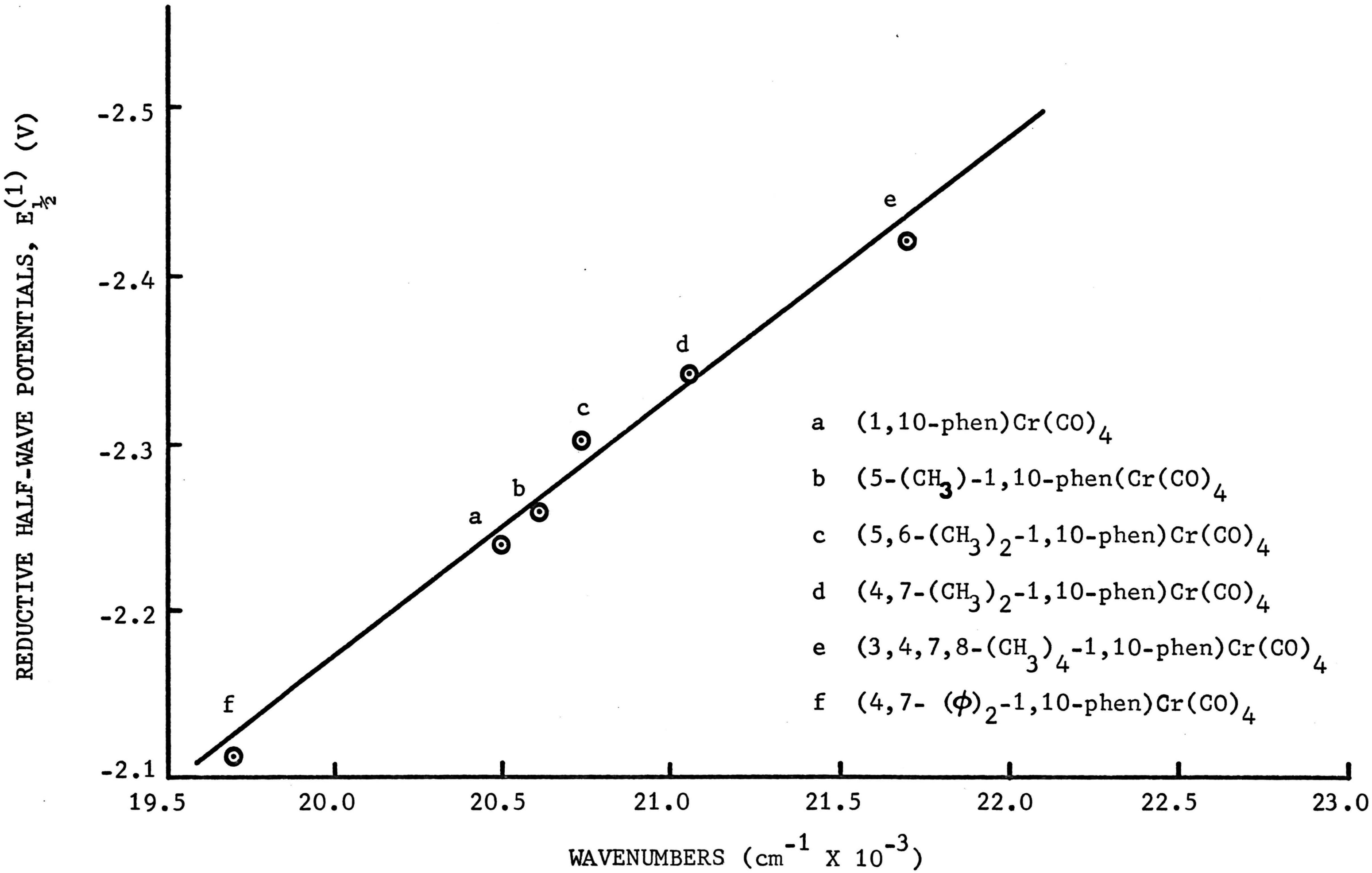


Figure 17. Plot of Reductive Half-Wave Potentials, $E_{\frac{1}{2}}^{(1)}$, versus Energies of $M \rightarrow \pi_L^*$ Bands in Phenanthroline Complexes.

correlation exists between the energies of the $M \rightarrow \pi_L^*$ bands and the energies of the first virtual orbitals. The conclusion to be drawn from these observations is that the lowest energy absorption band in the electronic spectra of the (1,10-phen)M$(CO)_4$ complexes involves a transition between a molecular orbital, predominantly metal in character, to π_8 of the ligand. In turn, such a conclusion implies that the electron added to these complexes in forming the radical anions must enter π_8 of the ligands.

Electronic absorption spectra of some neutral diazabutadiene tetracarbonyl complexes of chromium and molybdenum are shown in Figures 18 and 19. Of the spectra included in these figures, only that of (diacetylanil)Mo$(CO)_4$ has been previously reported. The spectra of (diacetylanil)Mo$(CO)_4$ and several closely related molybdenum diazabutadiene complexes have been studied and discussed by Dieck, Bock, and Renk.[70-72] These investigators have assigned the lowest energy transitions of the spectra as metal-to-ligand charge transfers. The band assignments have been made on the basis of a bonding model involving extensive back-bonding between filled metal d-orbitals and the two lowest energy virtual orbitals of the diazabutadiene moieties (the qualitative molecular orbital scheme published by these investigators is included in Appendix B for reference. Although carbonyl contributions to ϕ_1 through ϕ_4 are not explicitly included, their inclusion, particularly in ϕ_1 and ϕ_3, is to be assumed). That the lowest energy band ($\phi_2 \rightarrow \phi_3$) is, indeed, a metal-to-ligand charge transfer band is indicated by the shifts which this band undergoes with substitution into the diazabutadiene moiety and with a change in central metal. As is seen in Figure 18,

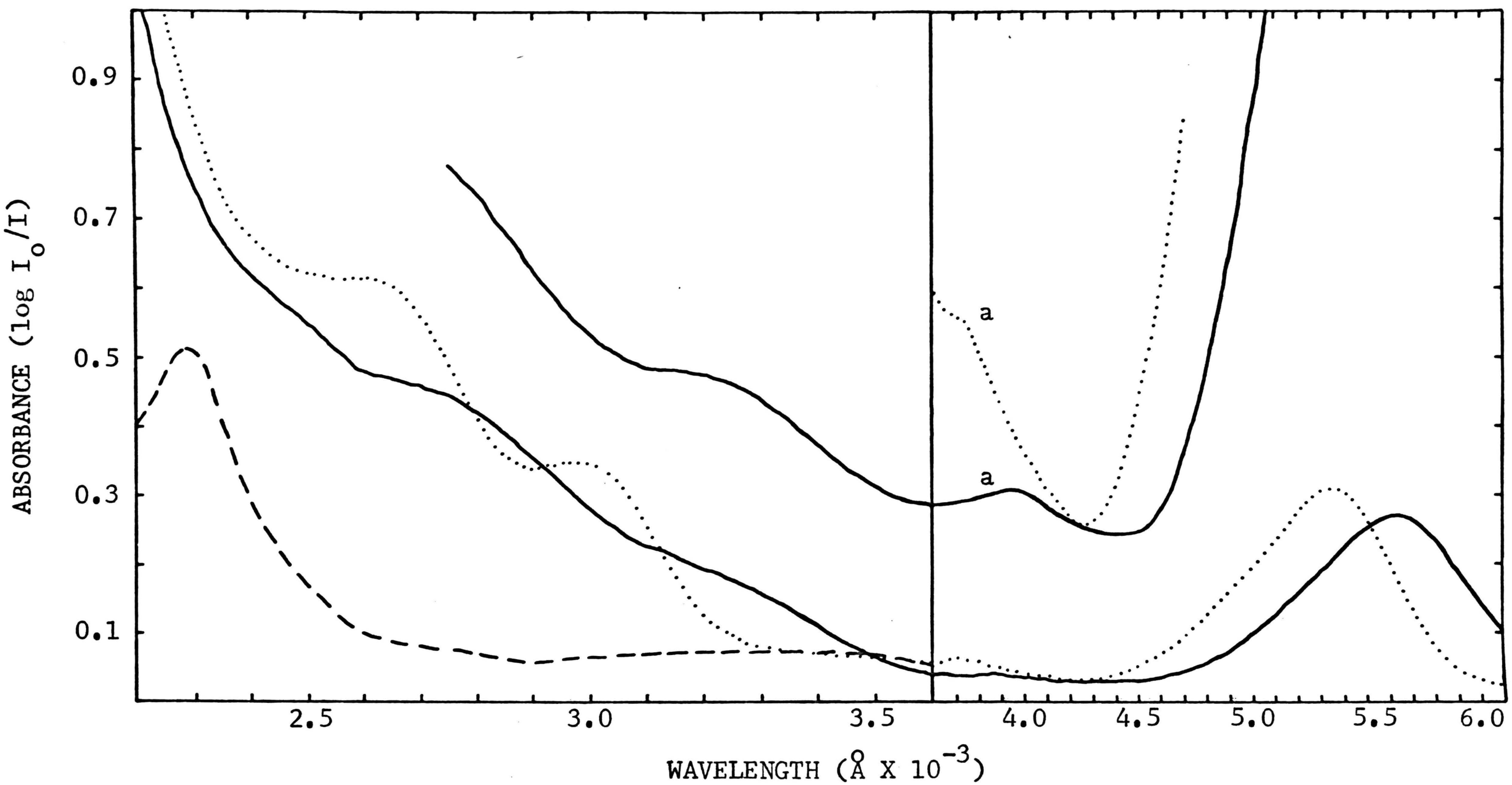


Figure 18. Electronic spectra of diacetyldianil, (diacetylanil)$Cr(CO)_4$, and (diacetylanil) $Mo(CO)_4$ in 1,2-dimethoxyethane.

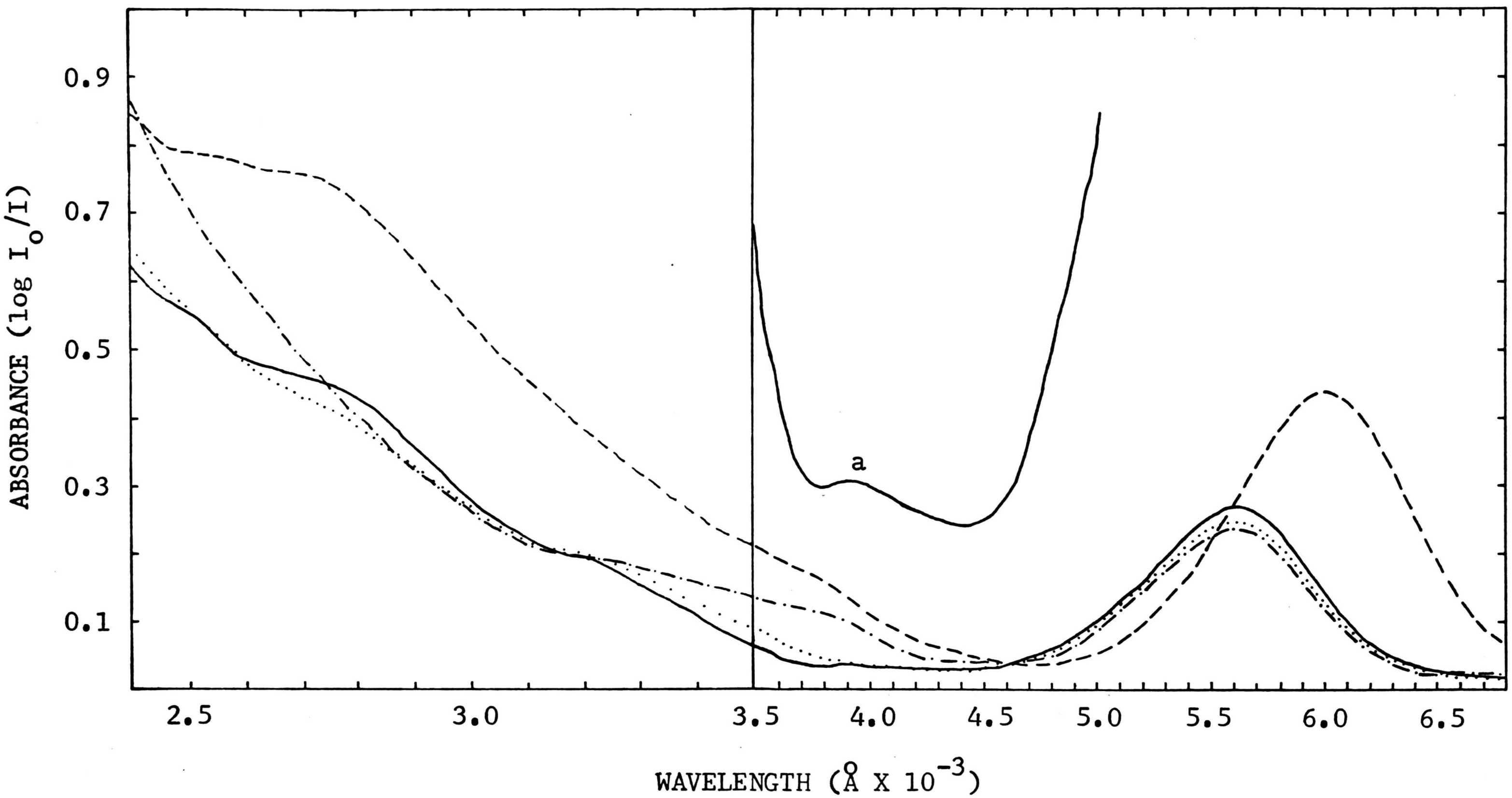
——— Chromium; 2.5 X 10^{-4} M; 1 mm cell (a = 1 cm cell)

•••• Molybdenum; 2.5 X 10^{-4} M; 1 mm cell (a = 1 cm cell)

---- Diacetyldinail; 1.1 X 10^{-4} M; 1 mm cell

Figure 19. Electronic spectra of tetracarbonyl"anil"chromium(0) complexes in 1,2-dimethoxyethane.

	Complex	Conc.	Cell
——	(Diacetylanil)Cr$(CO)_4$	2.5 X 10^{-4} M	1 mm a = 1 cm
••••	(p-CH_3-diacetylanil)Cr$(CO)_4$	2.5 X 10^{-4} M	1 mm
-•-•	(p-CH_3O-diacetylanil)Cr$(CO)_4$	2.5 X 10^{-4} M	1 mm
----	(Benzilanil)Cr$(CO)_4$	4.7 X 10^{-4} M	1 mm



<u>Figure 19.</u> Electronic spectra of tetracarbonyl"anil"chromium(0) complexes.

the band centered around 5500 Å undergoes a hypsochromic shift when chromium is replaced by molybdenum. As with the other diimine complexes involved in this study, this behavior is to be expected on the basis of enhanced stabilization of d-orbitals in changing from chromium to molybdenum. Similarly, as observed in Figure 19, replacement of electron releasing methyl groups in the 2, 3 positions of diacetyldianil by electron withdrawing phenyl groups produces the expected bathochromic shift. The same types of shifts are also reported by Dieck and Bock for a number of other substituted diazabutadiene complexes.

Interestingly, substitution into the diacetyldianil phenyl rings by such groups as methoxy and methyl is observed to have negligible influence upon not only the lowest energy transition, but essentially on all the transitions. This observation suggests that the N-phenyl groups are poorly conjugated with the diazabutadiene skeleton.

Electronic Spectra of Reduced Species. The electronic absorption spectra of reduced 2,2'-bipyridyl, (2,2'-bipy)M$(CO)_4$, 4,4'-dimethyl-2,2'-bipyridyl, (4,4'-$(CH_3)_2$-2,2'-bipy)Cr$(CO)_4$, 4,4'-diphenyl-2,2'-bipyridyl, (4,4'-$(\phi)_2$-2,2'-bipy)Cr,Mo$(CO)_4$, 2,2'-biquinolyl, and (2,2'-biquin)Cr$(CO)_4$ are shown in Figures 20 - 27. The spectrum of the radical anion of 2,2'-bipyridyl, which was shown in Figure 7 and is included in Figures 20 and 21 for comparison purposes, has been reported and interpreted by König and Kremer.[73] These investigators have obtained the spectrum of the radical anion in dioxane between 5000 and 50,000 cm^{-1}. Spectral assignments have been made on the basis of both Hückel and S.C.F. calculations. The band system which displays a

Figure 20. Ultraviolet (A) and visible (B) spectra of the radical anions of 2,2'-bipyridyl and (2,2'-bipy)M$(CO)_4$ in 1,2-dimethoxyethane.

	Compound	Concentration	Cell
———	2,2'-Bipyridyl	A: 5.4 X 10^{-4} M	1 mm
		B: 1.4 X 10^{-4} M	1 cm
------	(2,2'-Bipy)Cr$(CO)_4$	A: 3.7 X 10^{-4} M	1 mm
		B: 3.7 X 10^{-4} M	1 cm
······	(2,2'-Bipy)Mo$(CO)_4$	A: a - 2.2 X 10^{-4} M	1 mm
		b - 1.9 X 10^{-3} M	1 mm
		B: 2.2 X 10^{-4} M	1 cm
—··—	(2,2'-Bipy)W$(CO)_4$	A: 2.6 X 10^{-4} M	1 mm
		B: 2.6 X 10^{-4} M	1 cm

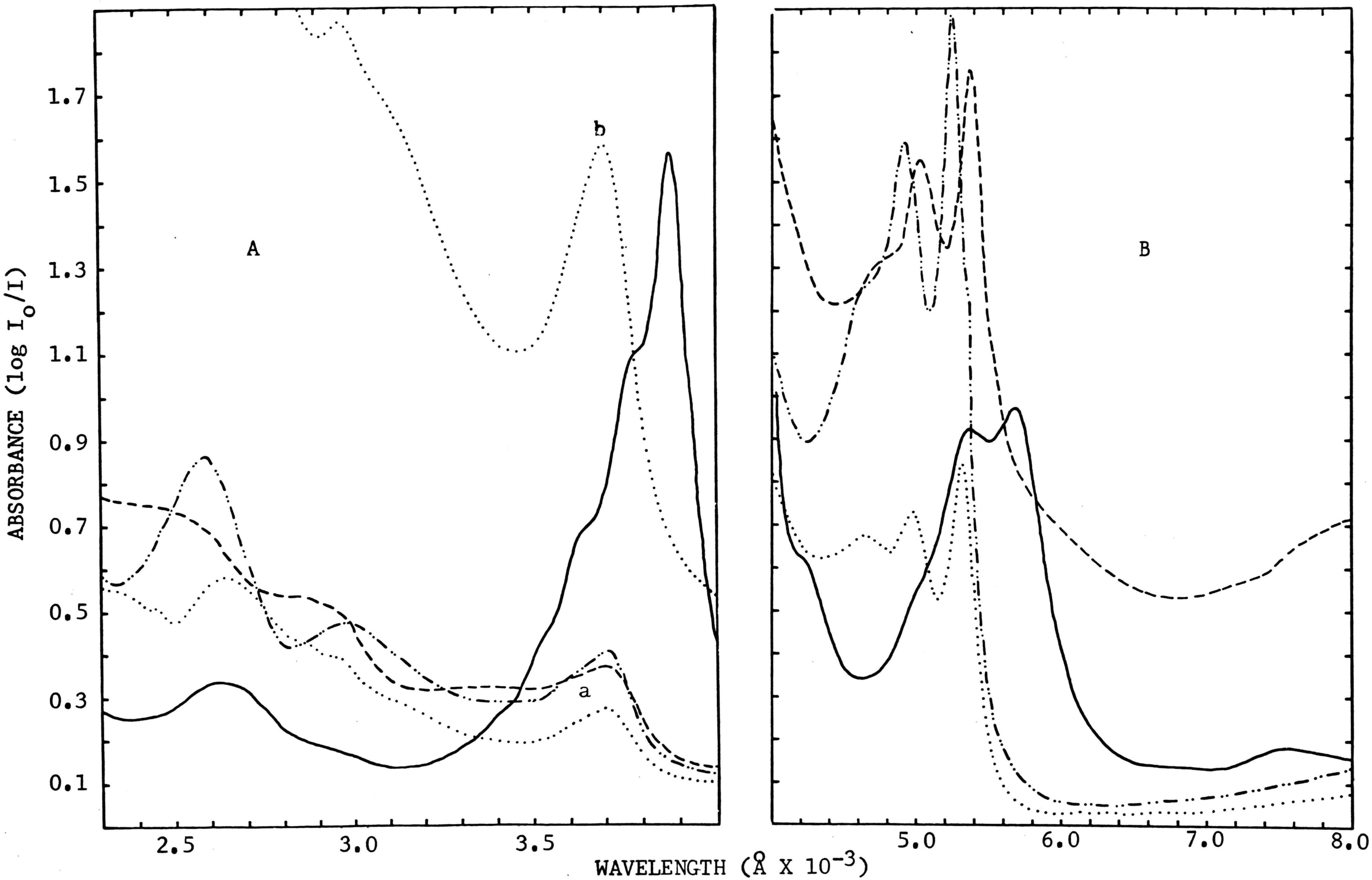


Figure 20. Ultraviolet and visible spectra of the radical anions of 2,2'-bipyridyl and (2,2'-bipy)$M(CO)_4$, M = Cr, Mo, W.

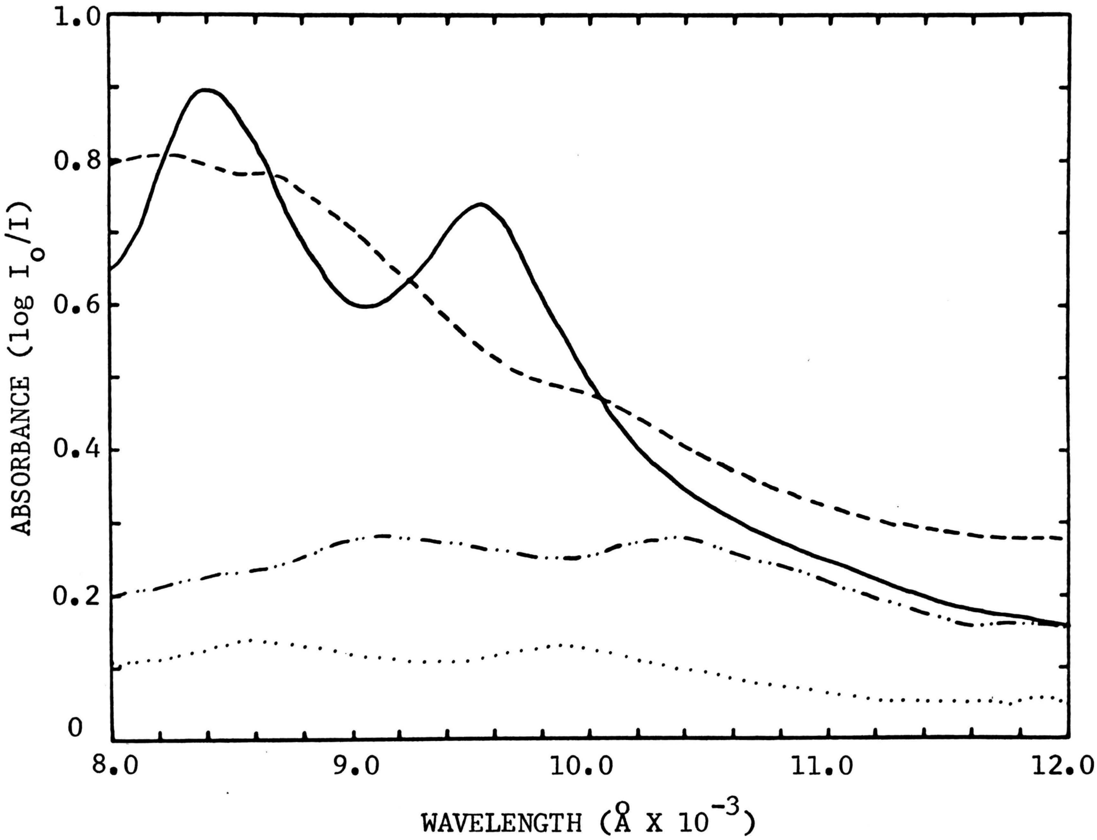


Figure 21. Near infrared spectra of the radical anions of 2,2'-bipyridyl (——; 6.3 X 10^{-4} M; 1 cm cell), (2,2'-bipy)$Cr(CO)_4$ (----; 3.7 X 10^{-4} M; 1 cm cell), (2,2'-bipy)$Mo(CO)_4$ (••••; 2.2 X 10^{-4} M; 1 cm cell), and (2,2'-bipy)$W(CO)_4$(—••—; 2.6 X 10^{-4} M; 1 cm cell) in 1,2-dimethoxyethane.

Figure 22. Electronic spectra of the radical anions of 4,4'-dimethyl-2,2'-bipyridyl and (4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$ in 1,2-dimethoxyethane.

——— 4,4'-Dimethyl-2,2'-bipyridyl

A: 7.7×10^{-4} M; 1 mm

B,C: 7.7×10^{-4} M; 1 cm

---- (4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$

A: a - 3.0×10^{-4} M; 1 mm

b - 1.2×10^{-3} M; 1 mm

B: 1.2×10^{-3} M; 1 mm

C: 1.2×10^{-3} M; 1 cm

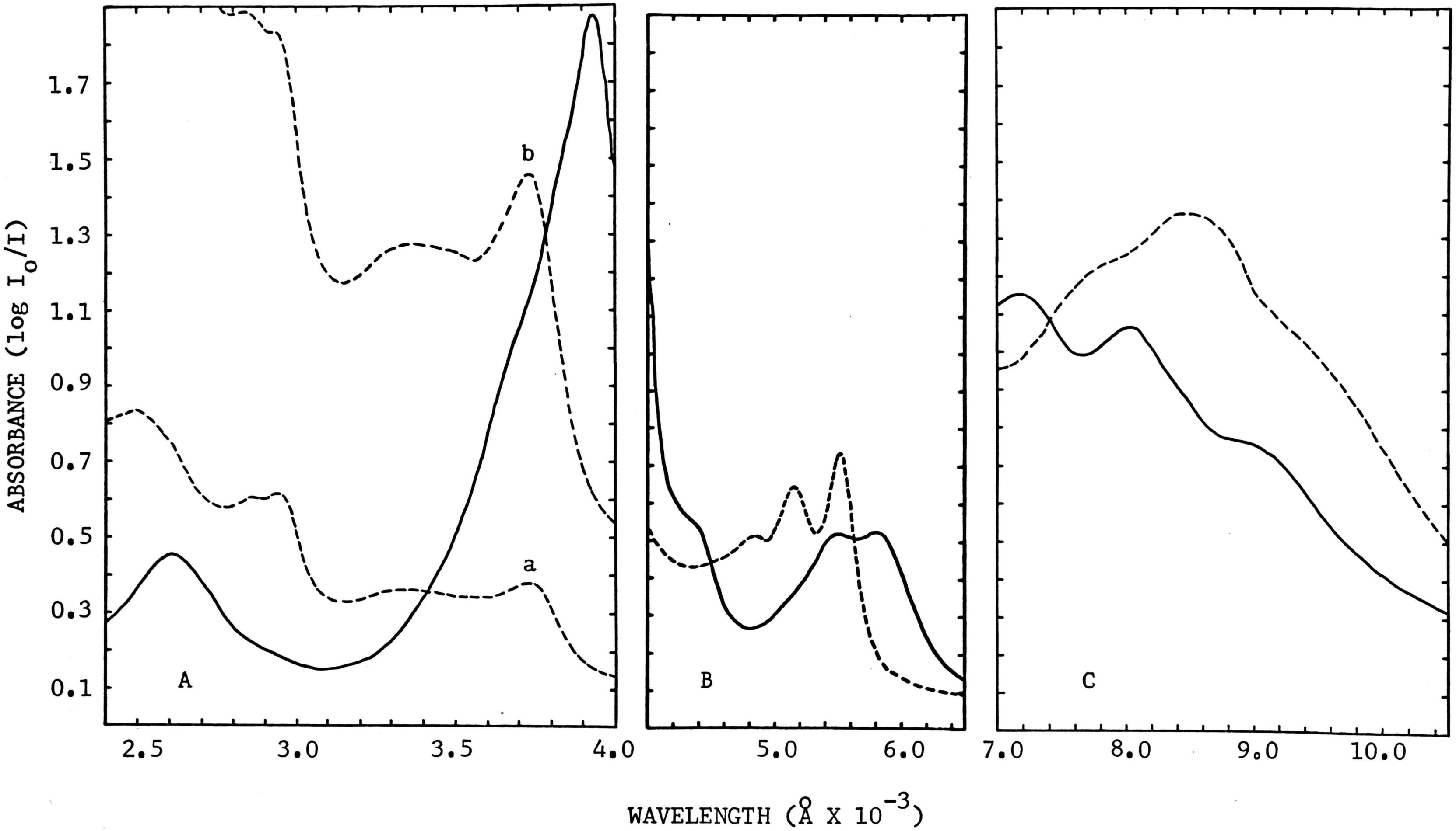


Figure 22. Electronic spectra of the radical anions of 4,4'-dimethyl-2,2'-bipyridyl (——) and (4,4'-$(CH_3)_2$-2,2'-bipy)$Cr(CO)_4$ (----).

Figure 23. Ultraviolet (A) and visible (B) spectra of radical anions and dianions of 4,4'-diphenyl-2,2'-bipyridyl and (4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$ in 1,2-dimethoxyethane.

Species	Concentration	Cell
4,4'-Diphenyl-2,2'-bipyridyl		
——— radical anion	A: 1.0×10^{-4} M	1 mm
	a - concentration unknown	
	B: 8.4×10^{-5} M	1 cm
······ dianion	A: 3.0×10^{-4} M	1 mm
	B: 1.1×10^{-3} M	1 mm
(4,4'-$(\phi)_2$-2,2'-bipy)$Cr(CO)_4$		
------ radical anion	A: a - 5.2×10^{-4} M	1 mm
	b - 5.2×10^{-4} M	0.1 mm
	B: 5.2×10^{-4} M	1 mm
-·-·-· dianion	A: 4.0×10^{-4} M	1 mm
	B: 4.0×10^{-4} M	1 mm

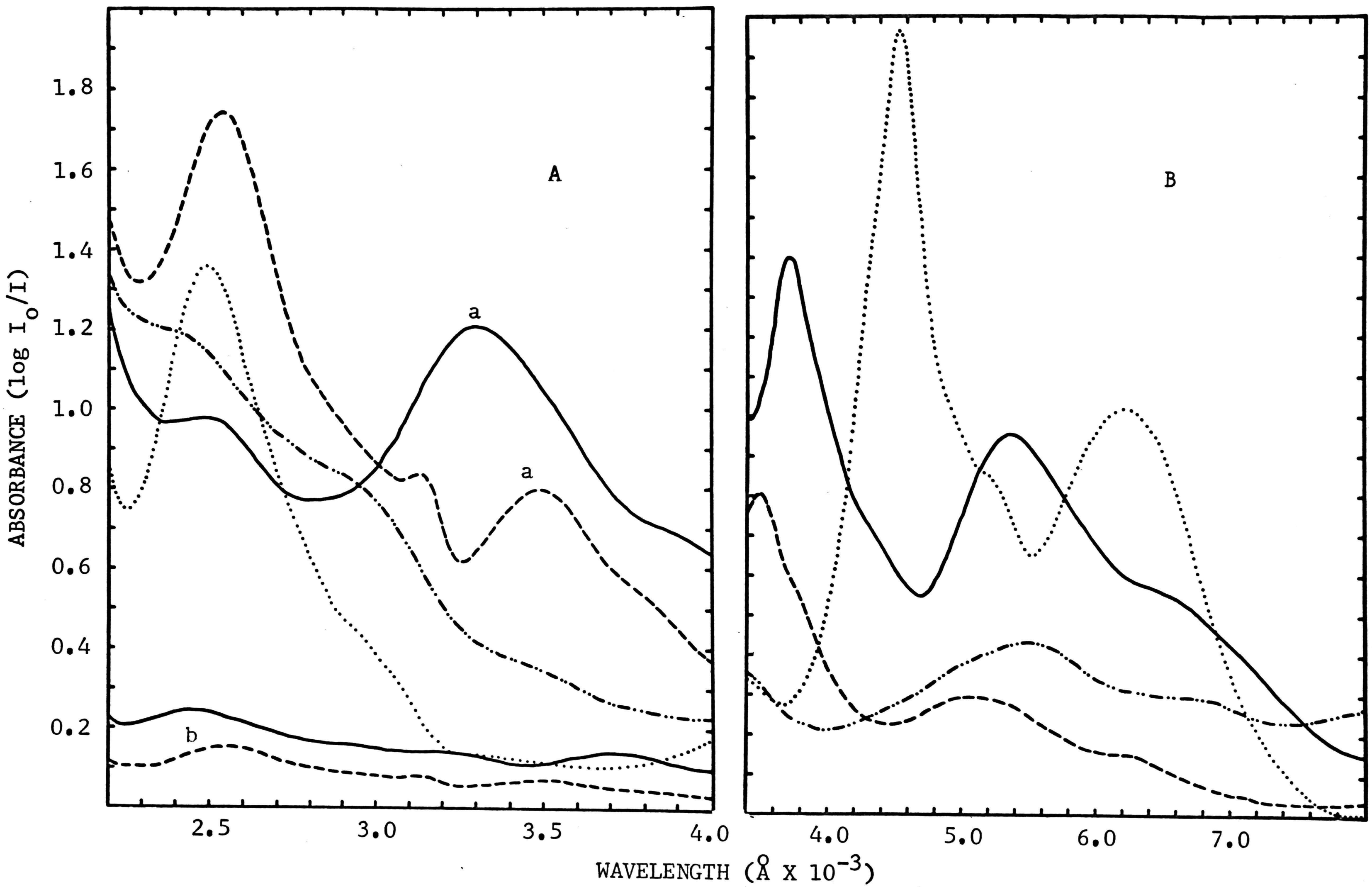


Figure 23. Ultraviolet and visible spectra of radical anions and dianions of 4,4'-diphenyl-2,2'-bipyridyl and (4,4'-(ϕ)$_2$-2,2'-bipy)Cr(CO)$_4$.

Figure 24. Ultraviolet (A) and visible (B) spectra of neutral and reduced (4,4'-(ϕ)$_2$-2,2'-bipy)Mo(CO)$_4$ in 1,2-dimethoxyethane.

Species		Concentration	Cell
——	neutral	A: a - 6.9 X 10^{-4} M	1 mm
		b - 3.4 X 10^{-4} M	1 mm
		B: 3.1 X 10^{-4} M	1 cm
....	radical anion	A: 1.0 X 10^{-3} M	0.1 mm
		B: 1.0 X 10^{-3} M	1 mm
----	dianion	A: 1.0 X 10^{-3} M	0.1 mm
		B: 1.0 X 10^{-3} M	1 mm

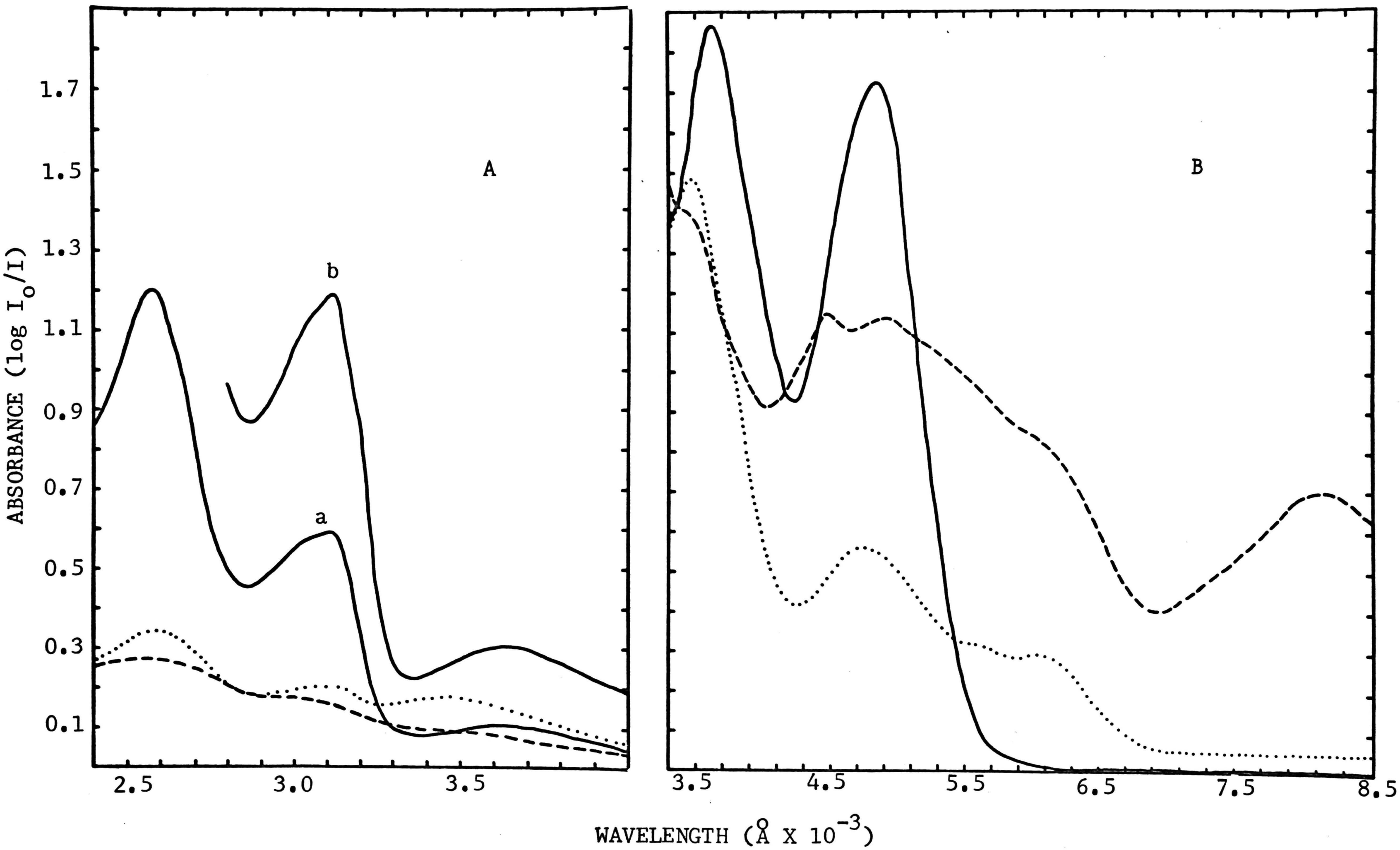


Figure 24. Ultraviolet and visible spectra of neutral and reduced $(4,4'-(\phi)_2-2,2'-bipy)Mo(CO)_4$.

Figure 25. Near infrared spectra of the radical anions of 4,4'-diphenyl-2,2'-bipyridyl (——, 8.4 X 10^{-5} M, 1 cm cell), (4,4'-(ϕ)$_2$-2,2'-bipy)Cr(CO)$_4$ (----, 5.2 X 10^{-4} M, 1 cm cell), and (4,4'-(ϕ)$_2$-2,2'-bipy)Mo(CO)$_4$ (····, 1 X 10^{-3} M, 1 cm cell) in 1,2-dimethoxyethane.

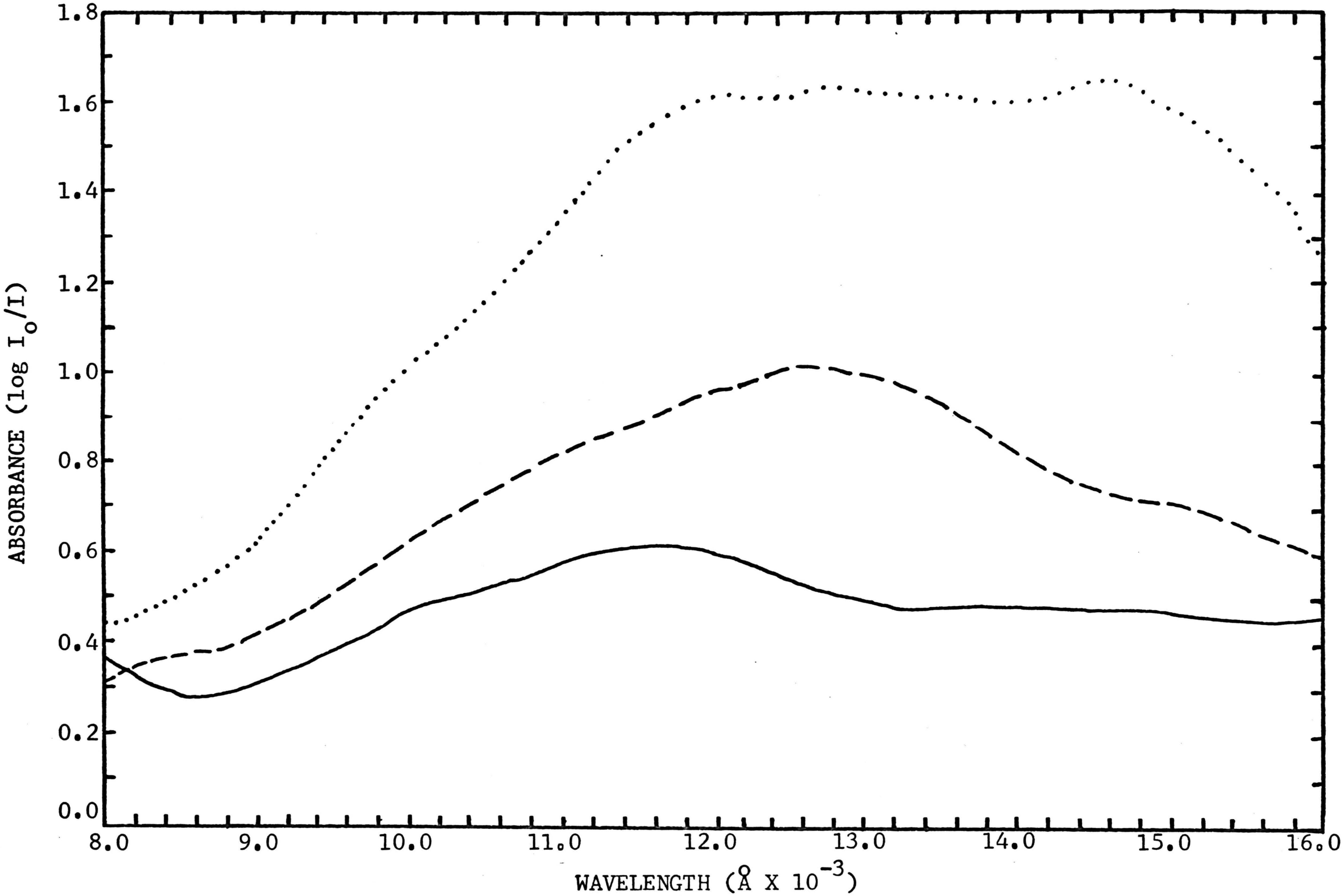


Figure 25. Near infrared spectra of the radical anions of 4,4'-diphenyl-2,2'-biypridyl and (4,4'-$(\phi)_2$-2,2'-bipy)$M(CO)_4$, M = Cr, Mo.

Figure 26. Ultraviolet (A) and visible spectra (B) of reduced 2,2'-biquinolyl and (2,2'-biquin)$Cr(CO)_4$ in 1,2-dimethoxyethane.

Species		Concentration	Cell
2,2'-Biquinolyl			
——— radical anion	A:	2.8×10^{-4} M	1 mm
	B:	2.8×10^{-4} M	1 mm
---- dianion	A:	4.2×10^{-4} M	1 mm
	B:	4.2×10^{-4} M	1 mm
(2,2'-Biquin)$Cr(CO)_4$			
•••• radical anion	A:	9×10^{-4} M	1 mm
	B:	9×10^{-4} M	1 mm
-••- dianion	A:	7×10^{-4} M	1 mm
	B:	7×10^{-4} M	1 mm

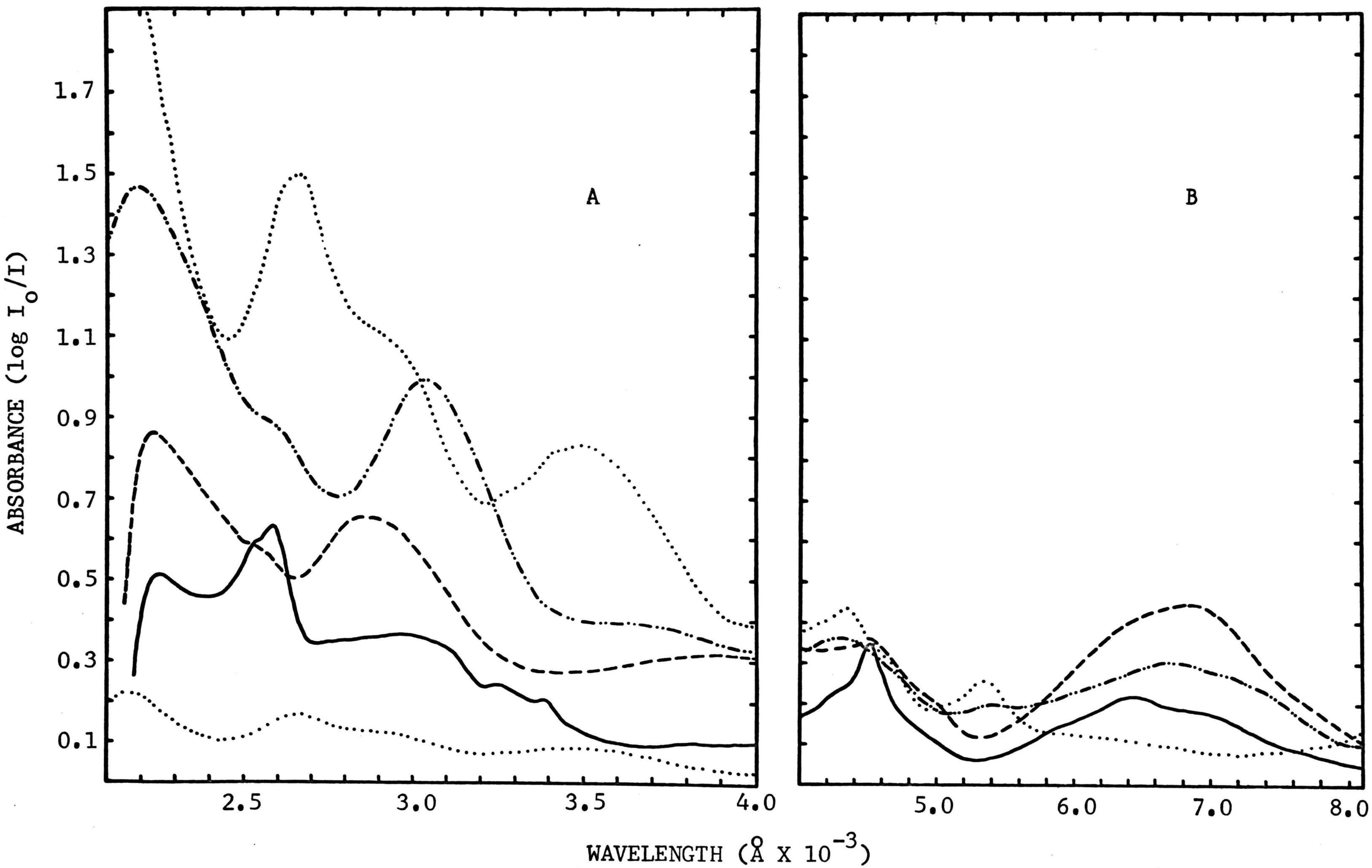


Figure 26. Ultraviolet and visible spectra of reduced 2,2'-biquinolyl and (2,2'-biquin)$Cr(CO)_4$.

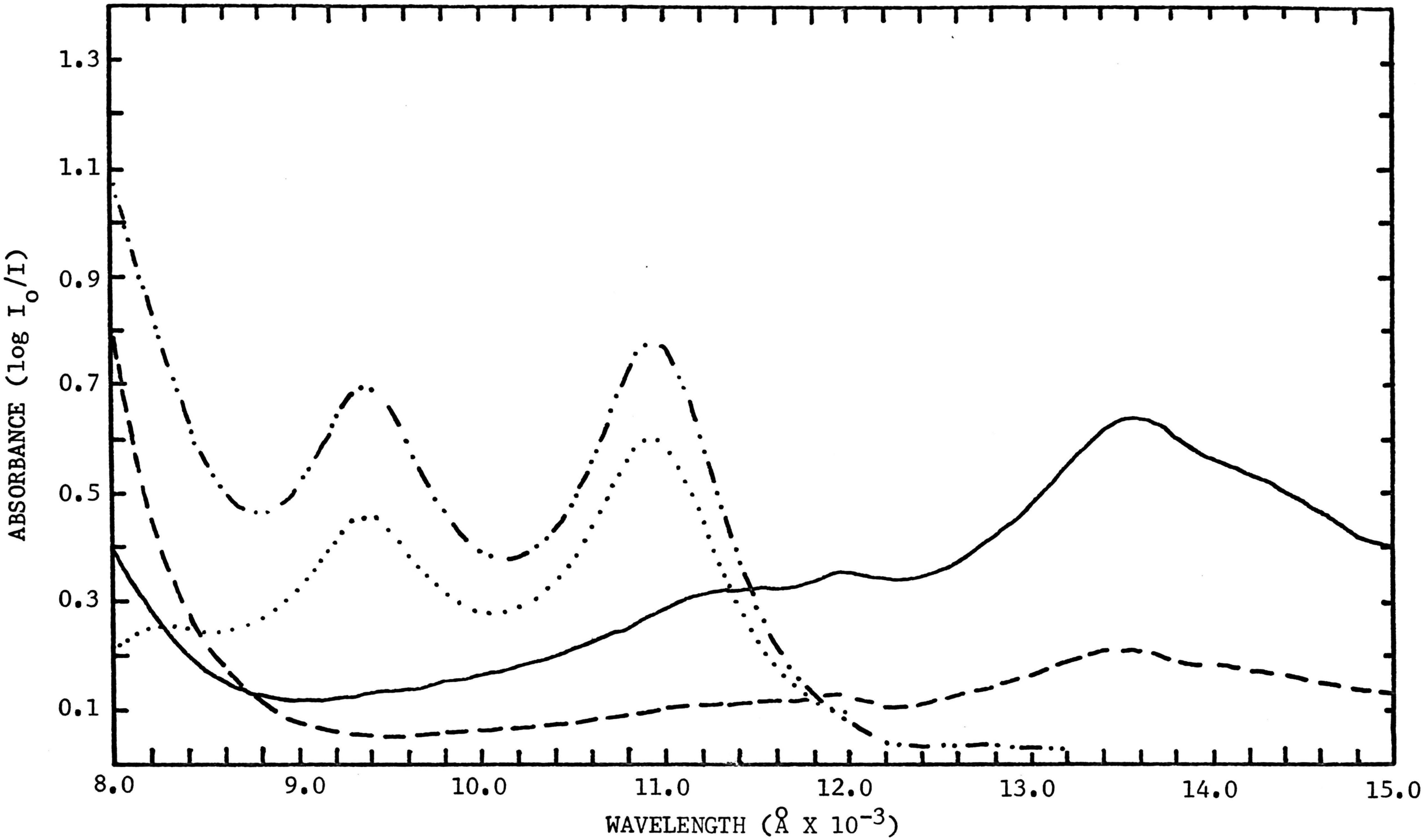


Figure 27. Near infrared spectra of reduced 2,2'-biquinolyl (—— radical anion, 3.6 X 10^{-4} M, 1 cm cell; ---- dianion, 3.6 X 10^{-4} M, 1 cm cell), and (2,2'-biquin)$Cr(CO)_4$ (···· radical anion, 9 X 10^{-4} M, 1 cm cell; -··- dianion, 7 X 10^{-4} M, 1 cm cell) in 1,2-dimethoxyethane.

considerable amount of vibrational structure and which is centered at about 12,000 cm^{-1} (8330 Å) is assigned as a combination of $\pi_7 \rightarrow \pi_8$ and $\pi_7 \rightarrow \pi_9$ transitions (the reported C.I. value for these two transitions are 7750 and 9400 cm^{-1}, respectively). The bands in the visible spectrum near 18000 cm^{-1} (5600 Å) are considered to arise primarily from the $\pi_7 \rightarrow \pi_{10}$ excitation. Occurring in the 27000 cm^{-1} (3700 Å) region is an intense band envelope, which reportedly includes the $\pi_6 \rightarrow \pi_7$, $\pi_7 \rightarrow \pi_{11}$, and $\pi_7 \rightarrow \pi_{12}$ transitions. The high energy bands occurring at approximately 35000 cm^{-1} (2900 Å) and 38000 cm^{-1} (2630 Å) are, according to König and Kremer, due to the $\pi_6 \rightarrow \pi_9$ transition and configurational mixing of the excited configurations $\pi_6 \rightarrow \pi_9$ and $\pi_6 \rightarrow \pi_8$, respectively.

The spectra of the 2,2'-bipyridyl radical anion reported in the present investigation were, of course, obtained in 1,2-dimethoxyethane. Radical anion spectra obtained in the two solvents, dioxane and 1,2-dimethoxyethane, correspond closely in terms of both band positions and intensities. Open-shell S.C.F.-C.I. (restricted Hartree-Fock) calculations, using the same empirical parameters that were employed in the closed-shell calculations (Tables VII and IX) have been performed for the 2,2'-bipyridyl radical anion. The calculated highest energy transitions, agree with those reported by König and Kremer. However, the three lowest energy bands do not agree. Employment of the parameters $\alpha_N = \alpha_C + 1.8\,\beta_{CC}$, $\beta_{CC} = -2.15$ eV, $\beta_{CN} = -2.40$ eV, $\gamma_{CC} = 11.13$ eV, and $\gamma_{NN} = 12.34$ eV leads to calculated transition energies of 4700 cm^{-1} for the $\pi_7 \rightarrow \pi_8$ transition, 5000 cm^{-1} for the $\pi_7 \rightarrow \pi_9$ transition, and 9000 cm^{-1} for the $\pi_7 \rightarrow \pi_{10}$ transition. These particular calculations yield theoretical radical anion spin densities (Experimental:[23,74] $\rho_N = 0.106$, $\rho_3 = \rho_6 = 0.022$, $\rho_4 = 0.203$, $\rho_5 = 0.044$; Theoretical: $\rho_N = 0.103$, $\rho_3 = -0.045$, $\rho_4 = 0.142$, $\rho_5 = 0.051$, $\rho_6 = 0.0197$), which are in much better agreement with the experimental values than are the theoretical values reported by König and Kremer. Nevertheless, the two low energy bands at 4700 cm^{-1} and 5000 cm^{-1} have not been experimentally observed. Consequently, there is, at this point, no sound basis for taking exception to the assignments made by König and Kremer. The important point, of significance to the present investigation, is that all of the S.C.F. calculations indicate that the low energy electronic absorptions in the visible and near infrared regions have their origin in π_7, the LUMO for the neutral molecule and the HOMO for the radical anion.

If one compares the electronic spectrum of the 2,2'-bipyridyl radical anion to the electronic spectra of the radical anions of (2,2'-bipy)$M(CO)_4$, one notes the striking similarity in band structures and band positions, particularly in the visible and near infrared regions. Two prominent bands are present in the visible spectra of both the reduced ligand and the reduced complexes. These bands, at about 5000-5400 Å for the reduced complexes and at about 5600 Å for the reduced ligand, are undoubtedly intraligand bands (either $\pi_7 \rightarrow \pi_{10}$ or $\pi_7 \rightarrow \pi_{11}$ transitions), which have been modified in energy by complexation of the ligand to a Group VI-B metal. At longer wavelengths (7000 - 10,500 Å) both the ligand radical anion and the complex radical anions exhibit three bands, which may also be attributed to intraligand $\pi \rightarrow \pi^*$ transitions. On the basis of the similarity between the ligand radical anion spectrum and the complex radical anion spectra there is little doubt, indeed, that the electron added during reduction enters the ligand molecular orbital, π_7.

In addition to the two prominent bands in the 5000-5400 Å region of the complex radical anion spectra, there appears a strong shoulder on the high energy side of the two-band structure. This band, which does not appear in the spectrum of the ligand radical anion, is very likely the $M \rightarrow \pi^*_L$ charge transfer band. The band is seen to be shifted hypsochromically, relative to the neutral complex, by about 1100 cm^{-1}. This shift is roughly the same as was seen to occur with methyl substitution and is considerably smaller than one might expect if the full charge due to the reductive electron was localized in the same ligand orbital involved in the $M \rightarrow \pi^*_L$ excitation.

Looking at the near ultraviolet spectra of the complex radical anions, one also notes the similarity to the spectrum of the ligand radical anion. The intense absorption at about 3700 Å in the spectra of the complexes corresponds to the ligand radical anion transition which has been assigned as essentially the $\pi_6 \rightarrow \pi_7$ absorption. Although the fate of the $M \rightarrow \pi^*_{CO}$ band is not clear in the spectrum of the radical anion of the chromium complex, the spectrum of the Mo complex and, to a lesser extent, the tungsten complex reveals a strong hypsochromic shift in this band from about 3400 Å to near 3100 Å. This is a shift of almost 3000 cm^{-1}, a much larger shift than produced by methyl substitution.

The relatively small shift in the $M \rightarrow \pi^*_L$ transition coupled with the much larger shift in the $M \rightarrow \pi^*_{CO}$ band upon reduction suggests that a goodly amount of the charge due to the reductive electron is, indeed, transmitted from the ligand to the carbonyls. Unfortunately, it is not possible, from the essentially qualitative analysis used in the present investigation, to ascertain the actual amount of charge which has been disseminated.

Strong spectral similarity between reduced ligand and reduced Group VI-B metal tetracarbonyl complexes is also observed for the substituted 2,2'-bipyridyl and the 2,2'-biquinolyl complexes shown in Figures 22 - 27. Certainly, such behavior is expected for methyl substituted complexes. However, substitution of phenyl groups into the bipyridyl molecule might be expected to lower the energy of the ligand LUMO and thereby facilitate back-bonding from the metal, assuming that phenyl substitution does not alter the essential character, i.e., symmetry, of the LUMO. Inspection of the spectra shown in Figures 23-25 indicates that reduction of the $(4,4'-(\phi)_2-2,2'\text{-bipy})Cr,Mo(CO)_4$ complexes, like the methyl substituted complexes, results in the addition of electron(s) to a ligand molecular orbital and not to a molecular orbital delocalized over the entire complex.

Electronic absorption spectra of reduced 1,10-phenanthroline, reduced $(1,10\text{-phen})M(CO)_4$ complexes, reduced methyl substituted 1,10-phenanthrolines, and reduced methyl substituted 1,10-phenanthroline chromium tetracarbonyl complexes are displayed in Figures 28-32. A comparison of the spectrum of the radical anion of 1,10-phenanthroline with the spectra of the radical anions of the corresponding Group VI-B metal tetracarbonyls discloses, as was observed to be the case in the 2,2'-bipyridyl series, a dramatic similarity between band positions and

Figure 28. Ultraviolet (A) and visible (B) electronic spectra of the radical anions of 1,10-phenanthroline and (1,10-phen)M$(CO)_4$ in 1,2-dimethoxyethane.

	Anion	Concentration	Cell
——	1,10-Phenanthroline	A: 2.2×10^{-4} M	1 mm
		B: 2.2×10^{-4} M	1 cm
----	(1,10-Phen)Cr$(CO)_4$	A: a - 2.2×10^{-4} M	1 mm
		b - 5.0×10^{-4} M	1 mm
		B: a - 3.2×10^{-4} M	1 mm
		b - 3.2×10^{-4} M	1 cm
....	(1,10-Phen)Mo$(CO)_4$	A: 3.5×10^{-4} M	1 mm
		B: a - 1.2×10^{-3} M	1 mm
		b - 3.5×10^{-4} M	1 cm
-...	(1,10-Phen)W$(CO)_4$	A: 1×10^{-3} M	0.1 mm
		B: 1×10^{-3} M	1 mm

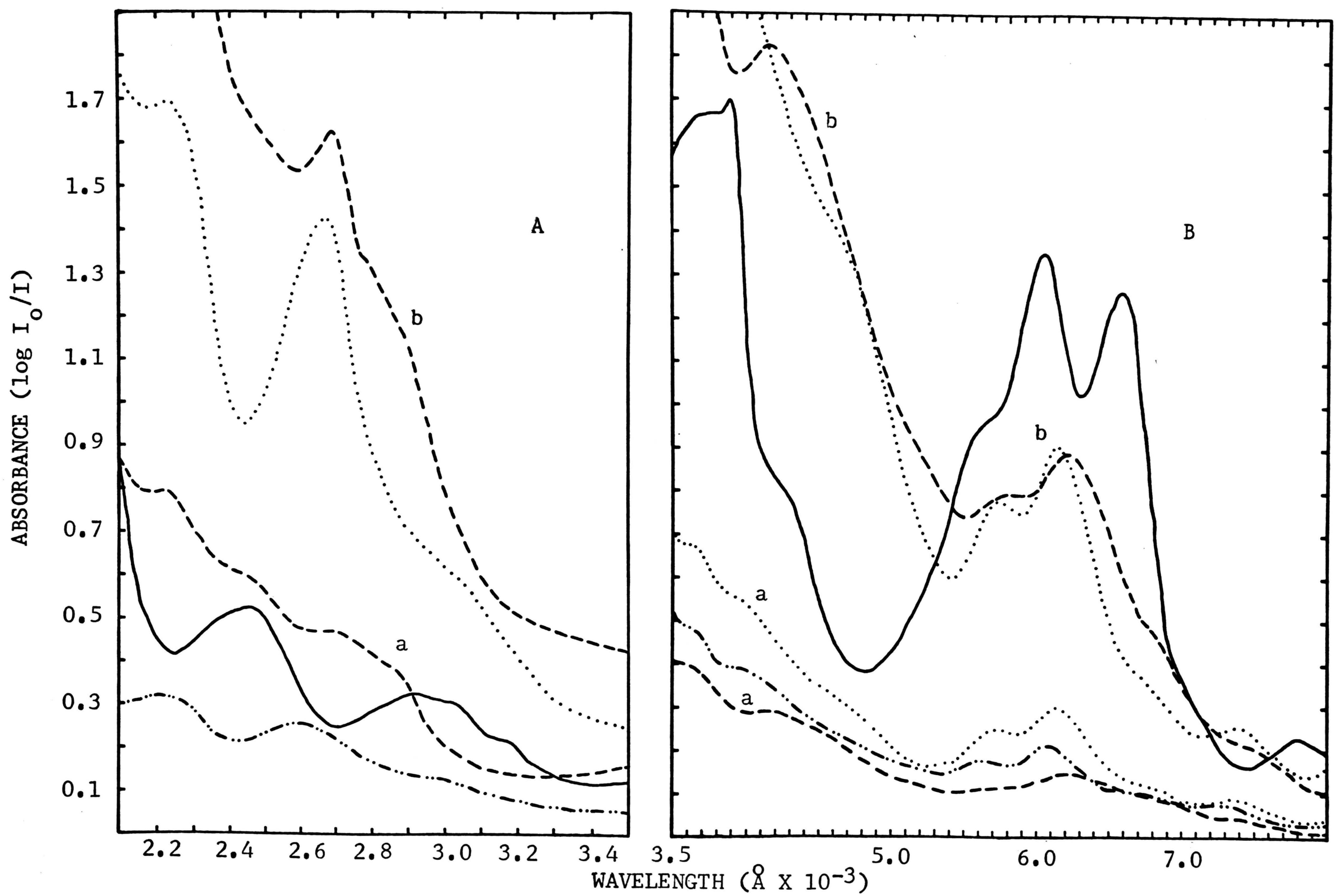


Figure 28. Ultraviolet and visible electronic spectra of the radical anions of 1,10-phenanthroline and (1,10-phen)$M(CO)_4$.

Figure 29. Near infrared electronic absorption spectra of the radical anions of 1,10-phenanthroline and (1,10-phen)$M(CO)_4$ in 1,2-dimethoxyethane using 1 cm cells.

	Anion		Concentration
——	1,10-Phenanthroline		2.2×10^{-4} M
----	(1,10-Phen)$Cr(CO)_4$	A:	9.1×10^{-4} M
		B:	1×10^{-2} M
••••	(1,10-Phen)$Mo(CO)_4$	A:	1.1×10^{-3} M
		B:	1×10^{-2} M
-••-	(1,10-Phen)$W(CO)_4$	A:	1.2×10^{-3} M
		B:	1×10^{-2} M

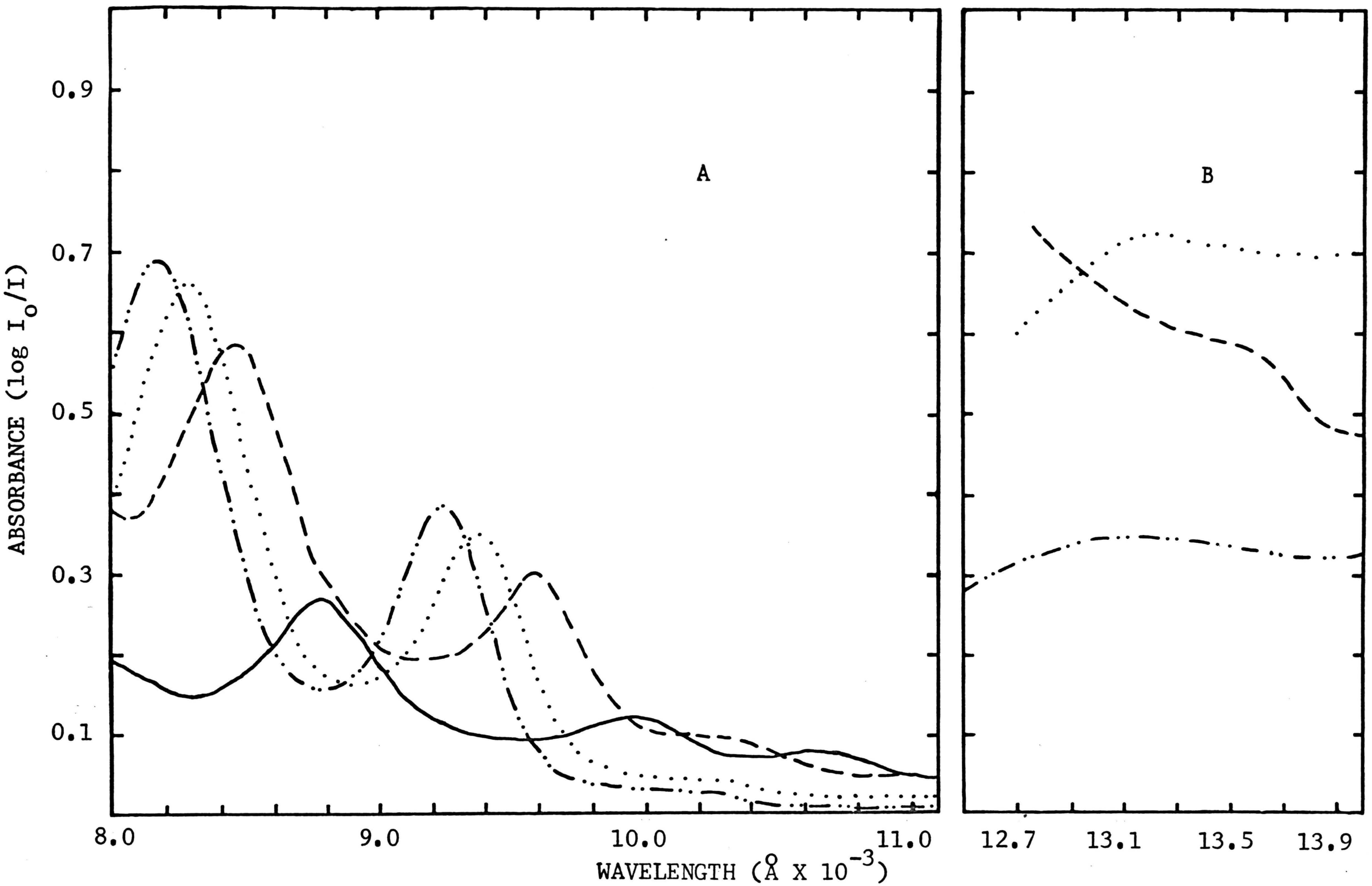


Figure 29. Near infrared spectra of the radical anions of 1,10-phenanthroline and (1,10-phen)$M(CO)_4$.

Figure 30. Ultraviolet spectra of the radical anions of methyl substituted 1,10-phenanthrolines and corresponding chromium tetracarbonyl complexes in 1,2-dimethoxyethane.

	Anion	Conc.	Cell
——	5-Methyl-1,10-phenanthroline	2.1×10^{-4} M	a - 1 mm b - 1 cm
....	5,6-Dimethyl-1,10-phenanthroline	3.5×10^{-4} M	1 mm
----	$(5\text{-}CH_3\text{-}1,10\text{-phen})Cr(CO)_4$	a - 3×10^{-4} M b - 1×10^{-3} M	1 mm 1 mm
-...	$(5,6\text{-}(CH_3)_2\text{-}1,10\text{-phen})Cr(CO)_4$	a - 2.5×10^{-4} M b - 1×10^{-3} M	1 mm 1 mm

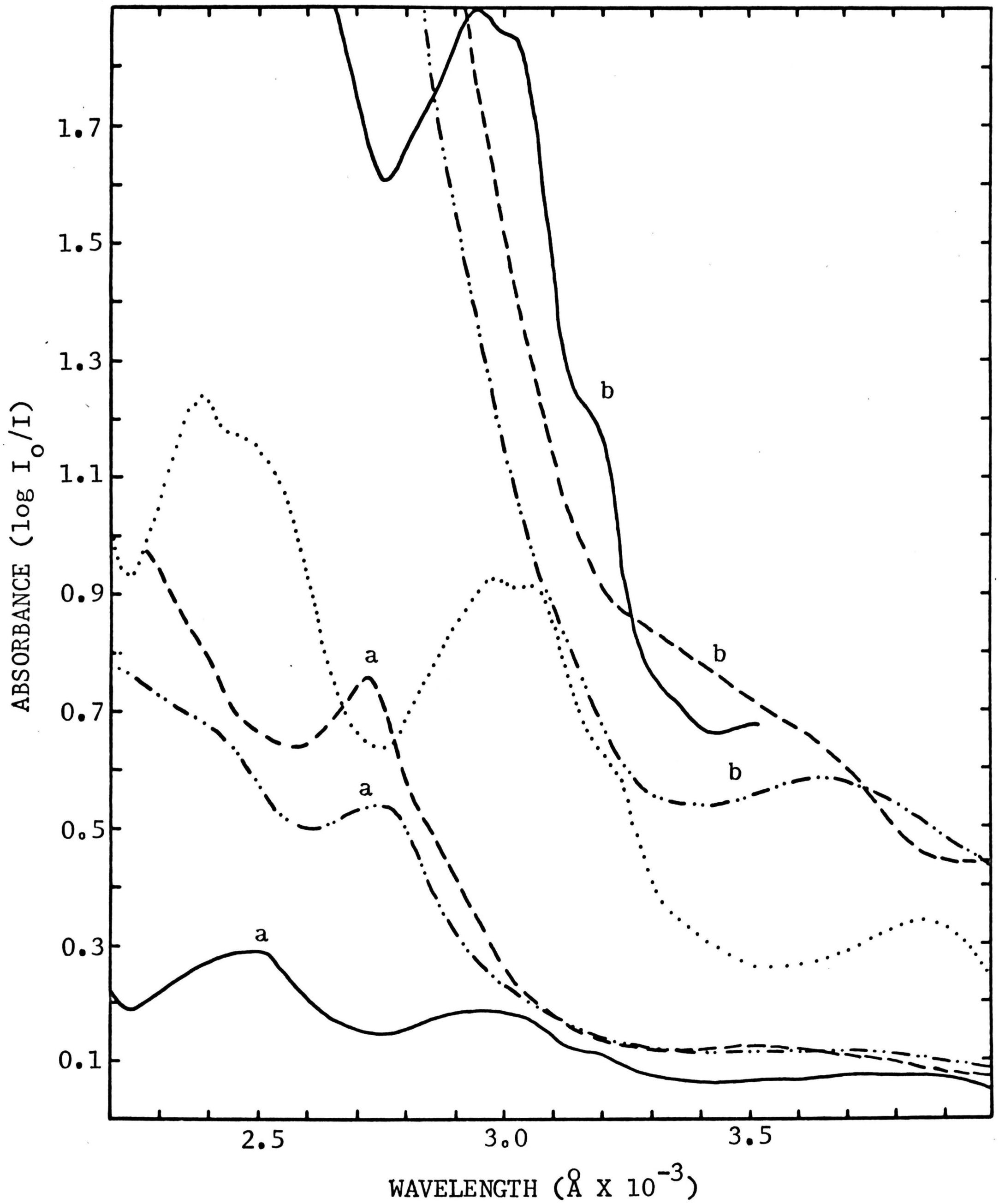


Figure 30. Ultraviolet spectra of the radical anions of methyl substituted 1,10-phenanthrolines and corresponding chromium tetracarbonyl complexes.

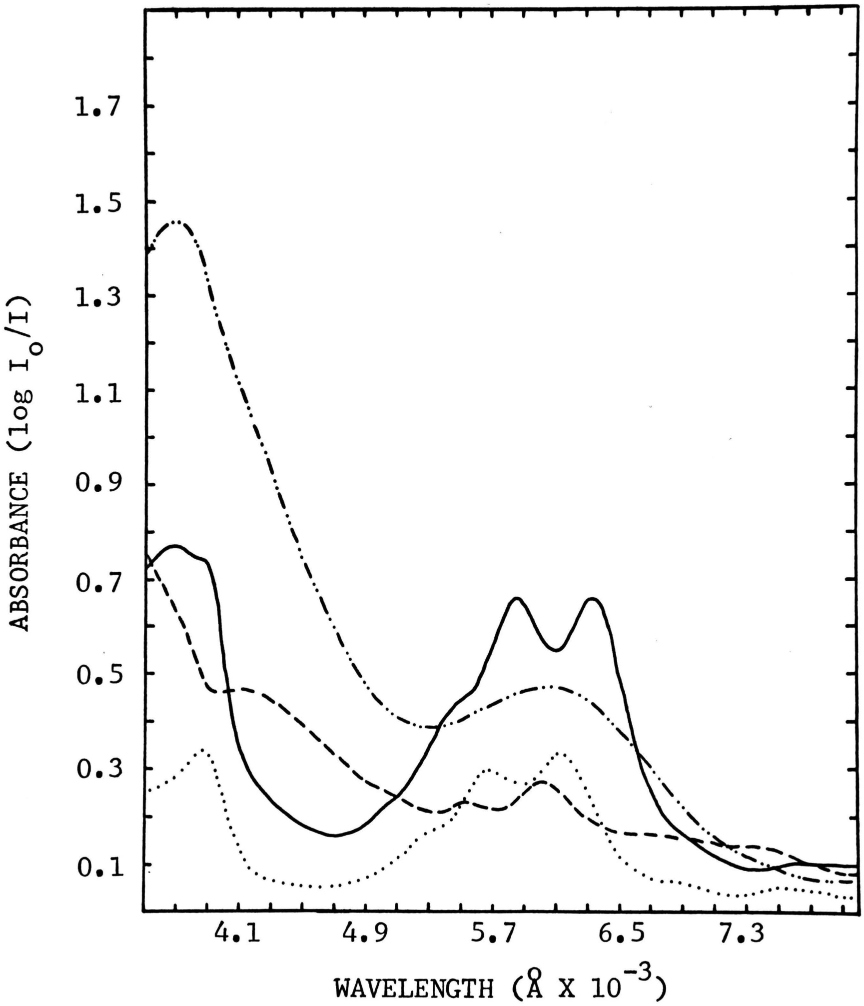


Figure 31. Visible spectra of the radical anions of methyl substituted 1,10-phenanthrolines and corresponding chromium tetracarbonyl complexes in 1,2-dimethoxyethane.

	Anion	Conc.	Cell
——	5-Methyl-1,10-phenanthroline	2.1 X 10^{-4} M	1 cm
••••	5,6-Dimethyl-1,10-phenanthroline	3.5 X 10^{-4} M	1 mm
----	(5-(CH_3)-1,10-phen)Cr$(CO)_4$	1 X 10^{-3} M	1 mm
-•--	(5,6-$(CH_3)_2$-1,10-phen)Cr$(CO)_4$	2.5 X 10^{-4} M	1 cm

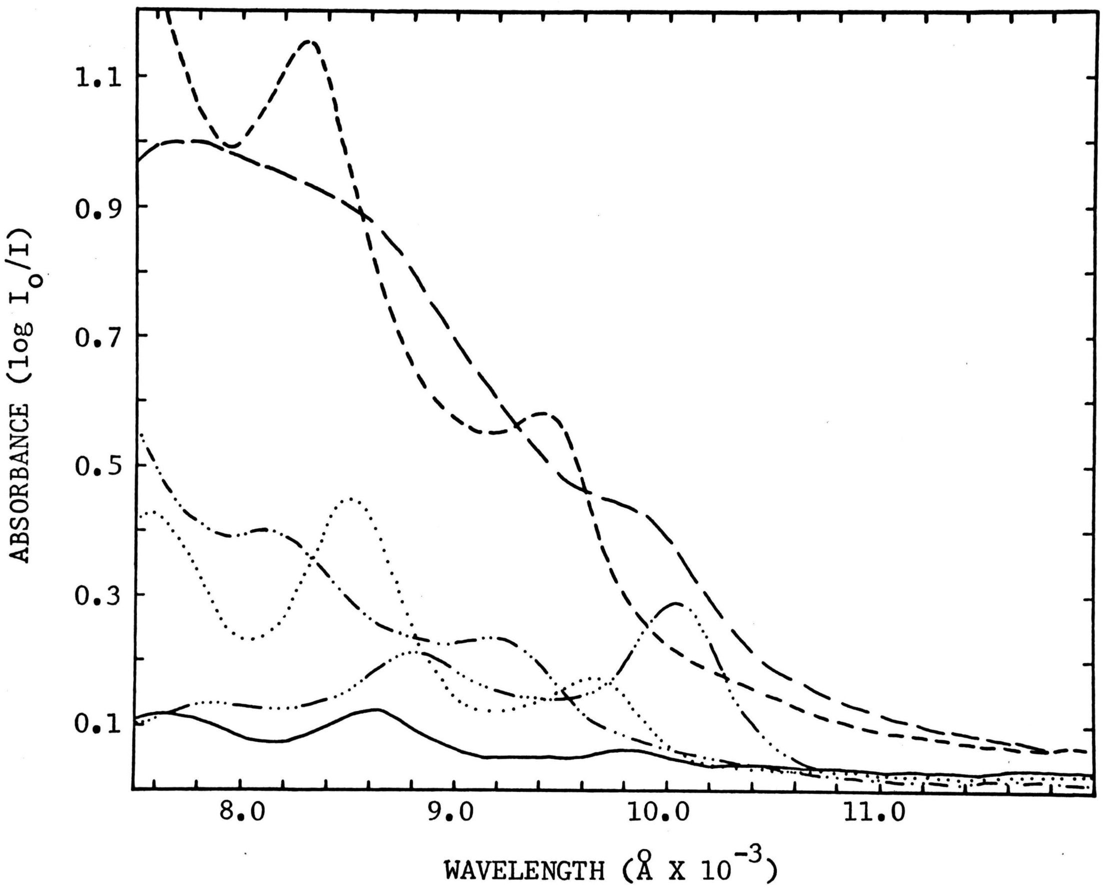


Figure 32. Near infrared spectra of the radical anions of methyl substituted 1,10-phenanthrolines and corresponding chromium tetracarbonyl complexes recorded in 1,2-dimethoxyethane with 1 cm cells.

	Anion	Conc.
———	5-Methyl-1,10-phenanthroline	2.1×10^{-4} M
••••••	5,6-Dimethyl-1,10-phenanthroline	3.5×10^{-4} M
—••••	4,7-Dimethyl-1,10-phenanthroline	?
------	$(5\text{-}(CH_3)\text{-}1,10\text{-phen})Cr(CO)_4$	1×10^{-3} M
—•—	$(5,6\text{-}(CH_3)_2\text{-}1,10\text{-phen})Cr(CO)_4$	2.5×10^{-4} M
— —	$(4,7\text{-}(CH_3)_2\text{-}1,10\text{-phen})Cr(CO)_4$	?

band structures. This is especially evident in the low energy visible and near infrared regions. The absorptions in these areas for both reduced ligand and reduced complexes, are, without doubt, intraligand absorptions.

Open-shell S.C.F.-C.I. calculations have been performed on the phenanthroline radical anion, using essentially the same empirical parameters as in the closed-shell calculations (Table VII). The closest fit between the experimental and calculated doublet spectrum has been obtained with the following set of parameters: α_N = -1.61 eV, β_{CC} = -2.15 eV, β_{CN} = -2.40 eV, γ_{CC} = 11.13 eV, and γ_{NN} = 12.34 eV. Band assignments, eigenvalues, C.I. coefficients, and calculated dipole strengths for the calculated doublet spectrum are listed in Table XIII. Again, as with the calculated doublet spectrum of the bipyridyl radical anion, the predicted lowest energy transition has not been detected experimentally. The energies of the other calculated transitions are, however, in sufficiently close agreement with the energies of observed bands to allow one to conclude that the low energy visible and near infrared transitions, in both ligand and complex spectra, originate from π_8. Thus, one may conclude that it is 1,10-phenanthroline, not the overall complex, that is actually being reduced in the electrochemical reduction of (1,10-phen)$M(CO)_4$ complexes. In turn, rather compelling evidence once again points to the absence of back-bonding between metal and phenanthroline in the (1,10-phen)$M(CO)_4$ complexes.

One additional point of significance has been obtained from the various open-shell calculations. The calculated charge densities on the nitrogens of the 1,10-phenanthroline radical anion are consistently

TABLE XIII

CALCULATED DOUBLET SPECTRUM OF 1,10-PHENANTHROLINE

Band Assignment[a]	C.I. Coefficient	C.I. Eigenvalue[b]	Dipole Strength (Å^2)	Experimental Energy[b]
8 $\rightarrow$ 9	0.969	4.45	0.11	--
8 $\rightarrow$ 10	0.950	11.6	0.70	11.5
8 $\rightarrow$ 11	0.917	15.3	0.21] $\rightarrow$	16.1
8 $\rightarrow$ 12	0.911	18.8	0.30]	
7 $\rightarrow$ 8	0.811	21.0	0.78] $\rightarrow$	25.5
8 $\rightarrow$ 13	0.736	24.9	0.13]	
5 $\rightarrow$ 8	0.412] $\rightarrow$	30.2	0.097] $\rightarrow$	31.8
7 $\rightarrow$ 9(1)[c]	0.627]			
6 $\rightarrow$ 8(1)[c]	0.576] $\rightarrow$	30.9	0.003]	
7 $\rightarrow$ 9(2)[c]	0.347]			
6 $\rightarrow$ 9(1)[c]	0.705	33.3	0.57	33.6
6 $\rightarrow$ 9(2)[c]	0.616	39.2	0.43] $\rightarrow$	40.7
6 $\rightarrow$ 8(2)[c]	0.408] $\rightarrow$	41.0	0.24]	
7 $\rightarrow$ 9(3)[c]	0.571]			

[a] $8 = \pi_8$, etc.

[b] Units of 1000 cm^{-1}.

[c] The excited state configurations 7 $\rightarrow$ 9(1), 7 $\rightarrow$ 9(2), and 7 $\rightarrow$ 9(3) are linear combinations (doublets) of the configurational functions resulting from the excitation 7 $\rightarrow$ 9. The configurations 6 $\rightarrow$ 9(1 and 2) and 6 $\rightarrow$ 8(1 and 2) are similarly defined.

lower than those of the 2,2'-bipyridyl radical anion (charge densities of 1.14 for the nitrogens of 1,10-phenanthroline anion and of 1.40 for the nitrogens of 2,2'-bipyridyl anion have been obtained from the calculations discussed herein). Since there exists no back-bonding between metal and diimine in either the phenanthroline or bipyridyl complexes of Group VI-B tetracarbonyls, the larger charge density on the bipyridyl radical anion might reasonably account, in part at least, for the greater stability of the bipyridyl complex radical anions.

In addition to the intraligand absorptions in the near infrared spectra of the complex radical anions, an additional, very low intensity absorption appears between 13,000 and 14,000 Å. This band is observed in the spectrum of each of the complex radical anions but not in the ligand radical anion spectrum. The difference in energy between the $M \rightarrow \pi^*_L$ (π_8) and $M \rightarrow \pi^*_{CO}$ charge transfer bands of the neutral complexes is roughly 8000 cm^{-1} (12,500 Å). Thus, this band appearing in the 13,000 Å region of the complex radical anion spectra is very likely a transition from π_8 of the ligand to "π^*_{CO}" (this molecular orbital is not, of course, a pure CO antibonding π orbital. It is the antibonding orbital corresponding to a bonding molecular orbital formed by the overlap of filled metal d-orbitals and pure antibonding π-orbitals of the CO).

The relative hypsochromic shifts in the $M \rightarrow \pi^*_L$ and $M \rightarrow \pi^*_{CO}$ transitions that were observed in the bipyridyl series are also seen in the phenanthroline series. Specifically, for (1,10-phen)$Cr(CO)_4$, the $M \rightarrow \pi^*_L$ band at 4880 Å in the neutral complex appears to undergo virtually no shift when the complex is reduced. This band is apparently present as a shoulder at about 4800 Å in the spectrum of the radical anion. On the other hand, the $M \rightarrow \pi^*_{CO}$ transition, which occurs at about 3400 Å in the spectrum of the neutral complex is shifted into the region of 2900 Å in the spectrum of the radical anion. Similar behavior is also observed for the molybdenum and tungsten complexes. These are especially dramatic shifts in the $M \rightarrow \pi^*_{CO}$ charge transfer bands -- shifts on the order of 4000-5000 cm^{-1} versus a change of only about 500-1500 cm^{-1} for the $M \rightarrow \pi^*_L$ charge transfer bands. These results may be compared with the shifts produced by methyl substitution. Methyl substitution in the neutral chromium complexes produced shifts in the $M \rightarrow \pi^*_L$ band of about 1000 cm^{-1}. At the same time, very small shifts of about 500 cm^{-1} were observed for the $M \rightarrow \pi^*_{CO}$ transitions. The corresponding changes in the CO stretching frequencies[15] are between 0 and 10 cm^{-1}, small changes, indeed. In the case of the radical anions it is observed that the $M \rightarrow \pi^*_L$ bands shift by roughly the same magnitude as for the neutral methylated phenanthroline complexes, yet the $M \rightarrow \pi^*_{CO}$ bands undergo shifts of about 4000-5000 cm^{-1} and the corresponding stretching frequencies change by 30-40 cm^{-1}. This very strongly suggests, in a manner similar to the bipyridyl complexes, that, even though the reductive electron enters a ligand based molecular orbital during the course of reduction, a substantial portion of the charge due to that electron is disseminated through the N-M sigma bond and into the d $\pi-\pi^*_{CO}$ molecular orbitals.

Methyl substituted phenanthroline chromium complexes behave much like the unsubstituted parent complexes. As expected, the similarity in band positions and band structures between the spectra of the reduced ligands and the spectra of the corresponding reduced complexes indicates that the reductive electron enters π_8 of the ligand.

Electronic spectra of reduced dianil complexes are shown in Figures 33 and 34. These spectra are relatively simple compared to the bipyridyl and phenanthroline analogs and are consistent with the qualitative bonding scheme advanced by Dieck and Bock.[72] The electronic transition occurring at 5640 Å in the spectrum of neutral (diacetyl-anil)$Cr(CO)_4$ (at 5380 Å for the molybdenum complex) has been assigned as the $\phi_2 \rightarrow \phi_3$ transition. This transition is seen to be shifted hypsochromically to 5370 Å when the chromium complex is reduced to the radical anion (5320 Å for the molybdenum radical anion). In addition to the hypsochromic shifts seen for this band, the intensity of the band is diminished by roughly one-half upon formation of the radical anions for both chromium and molybdenum complexes. Furthermore, upon addition of the second electron to form the dianion, this band disappears from the spectra of both complexes as one would expect if both reductive electrons entered ϕ_3.

As the $\phi_2 \rightarrow \phi_3$ transition loses intensity and shifts hypsochromically, the higher energy band, at 3900 Å for the chromium complex and at about 3750 Å for the molybdenum complex, also undergoes hypsochromic shifts, but gains rather than loses intensity. Such behavior means that this transition, which has not been previously assigned, cannot be assigned as a $\phi_1 \rightarrow \phi_3$ transition. The $\phi_1 \rightarrow \phi_3$ transition is expected to behave in a manner similar to the $\phi_2 \rightarrow \phi_3$ transition and may well be included with the $\phi_2 \rightarrow \phi_3$ band under the 5640 Å envelope. That two bands may be under this envelope is suggested by the

Figure 33. Electronic absorption spectra of reduced (diacetylanil)$Cr(CO)_4$ and (diacetylanil)$Mo(CO)_4$ complexes in 1,2-dimethoxyethane.

	Anion	Concentration	Cell
(Diacetylanil)$Cr(CO)_4$			
——	radical anion	A: 9×10^{-4} M	a - 0.1 mm
		B: 9×10^{-4} M	b - 1 mm
....	dianion	A: 2.7×10^{-4} M	1 mm
		B: 2.7×10^{-4} M	1 mm
(Diacetylanil)$Mo(CO)_4$			
----	radical anion	A: 2.9×10^{-4} M	1 mm
		B: 1.1×10^{-3} M	1 mm
-..-	dianion	A: 1.7×10^{-4} M	1 mm
		B: 8.4×10^{-4} M	1 mm

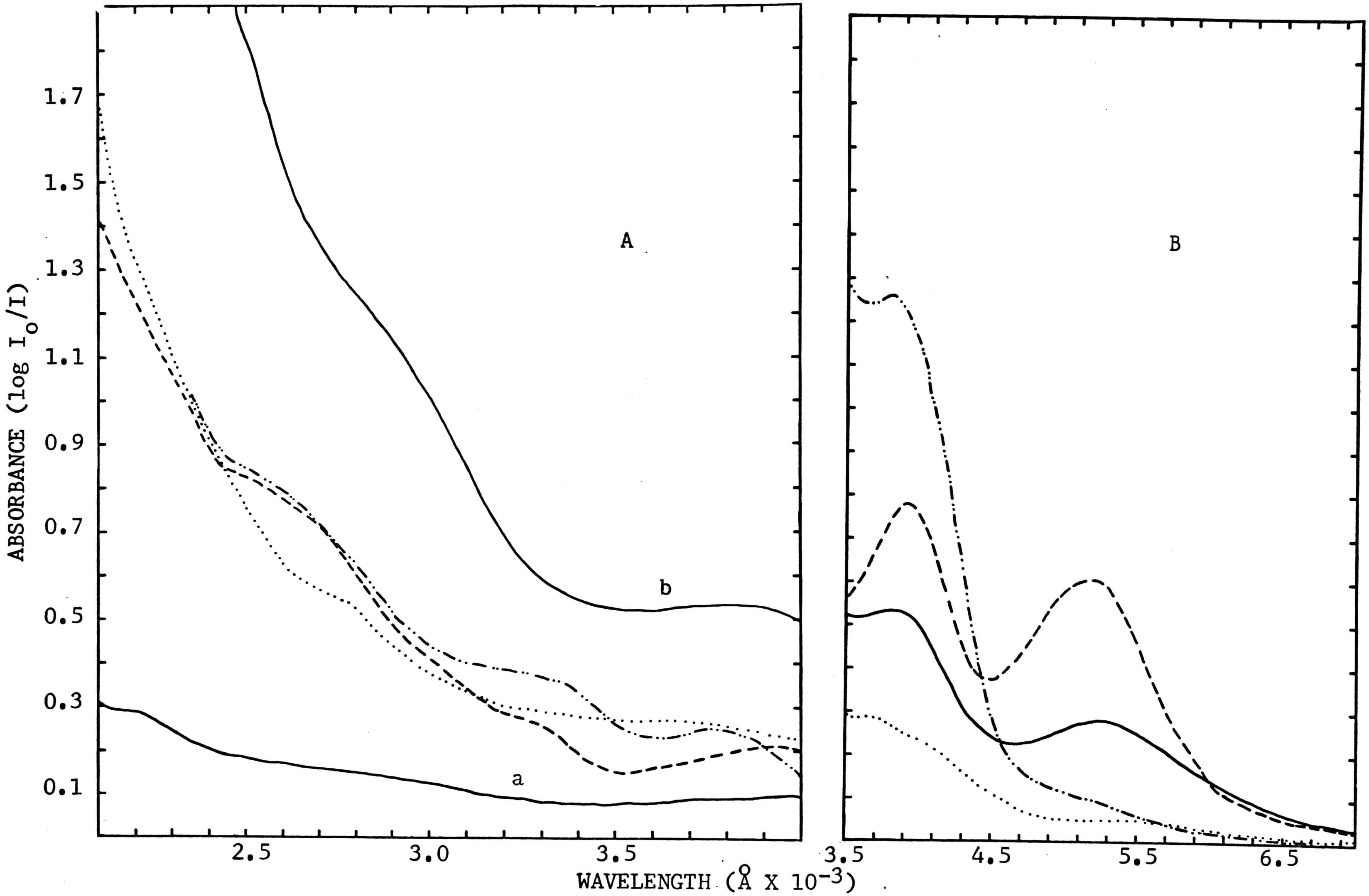


Figure 33. Electronic absorption spectra of reduced (diacetylanil)$Cr(CO)_4$ and (diacetylanil)-$Mo(CO)_4$ complexes.

Figure 34. Electronic absorption spectra of neutral and reduced (benzilanil)$Cr(CO)_4$ recorded in 1,2-dimethoxyethane with 1 mm cells.

Species		Conc.
····· neutral		4.6×10^{-4} M
——— radical anion	A:	4.6×10^{-4} M
	B:	4.6×10^{-4} M
----- dianion	A:	2.4×10^{-4} M
	B:	1×10^{-3} M

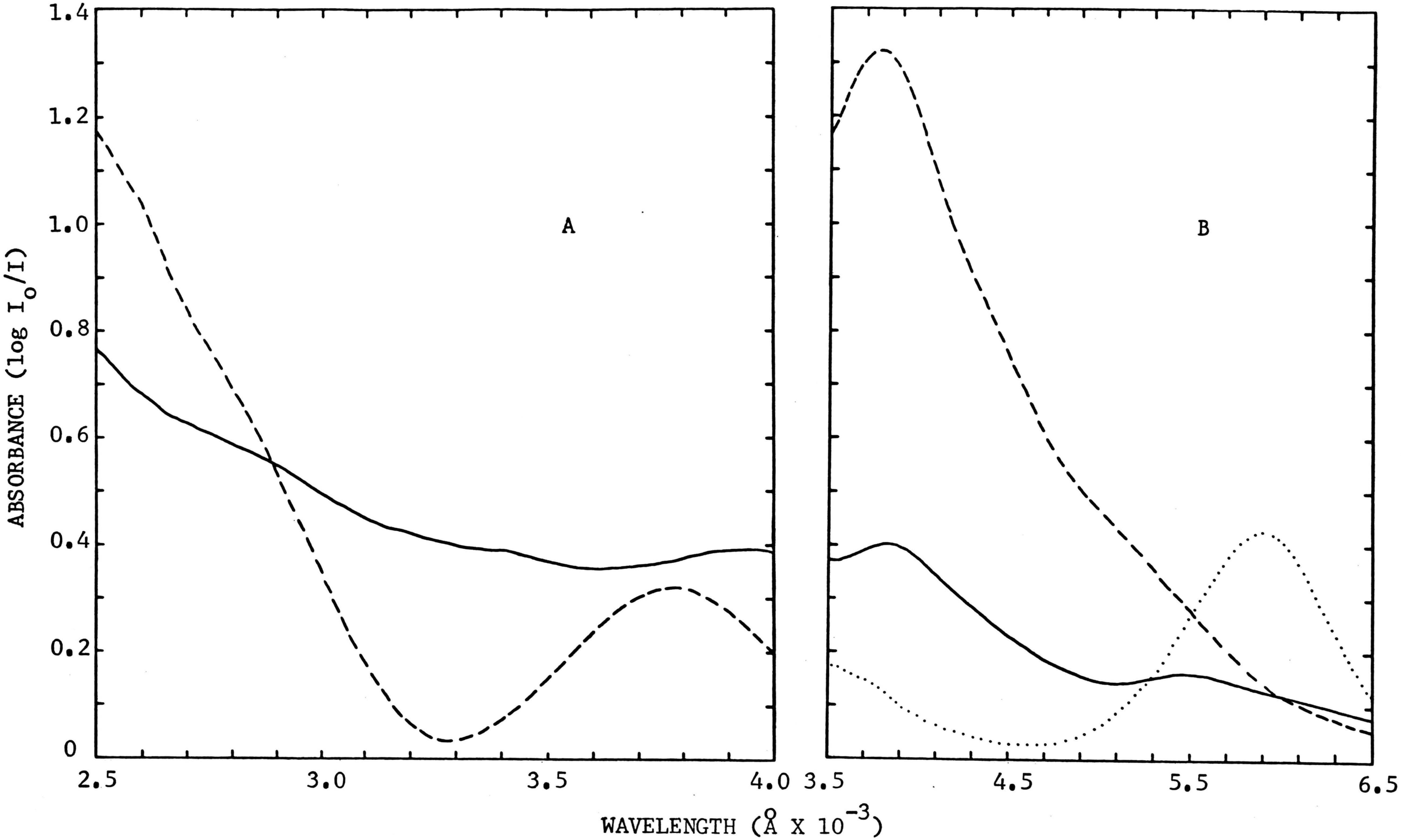


Figure 34. Electronic absorption spectra of neutral and reduced (benzilanil)$Cr(CO)_4$.

slight dissymmetry of the band envelope, which is clearly seen in the visible spectra of the radical anions. A $\phi_2 \rightarrow \phi_4$ assignment is also untenable. Such an assignment would mean that the energy separation between ϕ_3 and ϕ_4 is on the order of 7800 cm^{-1} ($E_{\phi 2 \rightarrow 4} - E_{\phi 2 \rightarrow 3}$). If this was true, occupation of ϕ_3 by an electron in the radical anion, would be expected to lead to a new transition, $\phi_3 \rightarrow \phi_4$, having energy of roughly 7800 cm^{-1} (12,800 Å). No bands have been observed in the near infrared region, even with concentrations as high as 0.01 - 0.1 M, for any of the "anil" species. Thus, the 3900 Å band in the chromium complex of diacetyldianil (at 3750 Å for the molybdenum complex) is assigned as the $\phi_1 \rightarrow \phi_4$ transition.

Figure 34 indicates that the (benzilanil)$Cr(CO)_4$ complex behaves very much like the diacetyldianil complexes when it is reduced successively to radical anion and dianion. Like the diacetyldianil complexes, the spectra of the neutral and reduced species may be rationalized in terms of a bonding model involving π-bonding between filled metal d-π orbitals and empty diimine virtual orbitals.

CONCLUSIONS

The preceding results and discussion on the electronic spectra and electronic structures of diimine Group VI-B metal tetracarbonyl complexes allow several inportant conclusions to be drawn. These are perhaps most readily presented by answering the questions raised in the introductory discussion.

In response to the question of whether electrons actually enter ligand-based molecular orbitals when tetracarbonyl diimine Group VI-B metal complexes are reduced, an unequivocal yes can now be given. Electrochemical data coupled with the electronic spectra of the neutral complexes, esr data previously reported,[23,24] and electronic spectra of the complex radical anions all provide evidence indicating that reductive electrons enter pure ligand orbitals in the phenanthroline and bipyridyl complexes and a molecular orbital predominantly ligand in character in the diazabutadiene complexes. Furthermore, infrared data, electrochemical half-wave potential data, and electronic spectra of both neutral and reduced complexes, in conjunction with S.C.F. calculations, indicate that the ligand molecular orbital involved in the reduction of the bipyridyl and phenanthroline complexes is the first virtual orbital of the ligand. This, of course, implies the nonexistence of π-bonding between phenanthroline or bipyridyl and a Group VI-B metal in the corresponding tetracarbonyl complexes. Although the individual pieces of evidence, by themselves, may not be rigorously conclusive, when they are viewed *in toto*, there can be very little doubt that neither phenanthroline nor bipyridyl engage in backbonding to the metals in these particular complexes. This is an important result, in view of the fact that at least three investigators[70,72,75] have explicitly and unequivocally stated that all diimine four-center pi systems, which would, of course, include the 1,10-phenanthrolines and 2,2'-bipyridyls, will engage in pi-bonding to metals in octahedral complexes. To be sure, 2,2'-bipyridyl and 1,10-phenanthroline can and do π-bond to metals in certain complexes such as tris-(diimine)iron (II), as has been convincingly demonstrated.[50,51,67] However, from the results obtained in the present study, the extrapolation of the behavior of a given ligand in one complex to another complex is clearly dangerous and is a pitfall that can be avoided by experimentally establishing the properties of the ligand <u>in</u> the complex under investigation.

Cotton and Kraihanzel[19] have simply assumed the existence of π-bonding between 2,2'-bipyridyl and chromium in (2,2'-bipy)$Cr(CO)_4$ and then compared the carbonyl force constants for this complex to those of (ethylenediamine)$Cr(CO)_4$, in which there is assumed to be no back-bonding between diamine and metal. The experimentally observed change in force constants is $\Delta k_2 \cong 2\Delta k_1$, in agreement with the changes predicted for a pi-only mode of charge transfer from the bipyridyl to the carbonyls. The results of the present investigation, however, clearly show that a pi-only mechanism of charge transfer cannot be operative in (2,2'-bipy)$Cr(CO)_4$ or in (1,10-phen)$Cr(CO)_4$. This answers, in part, at least, the question of whether charge is disseminated by a σ-only mechanism in systems containing ligands capable of π-bonding to metals. Transmission of charge from 1,10-phenanthroline and 2,2'-bipyridyl to the central metal does, indeed, occur by a σ-only mechanism.

Unfortunately, the results of the present investigation do not provide any evidence concerning the mode of charge transmission from the metal to the carbonyl groups.

The results of the present study cast a large shadow of doubt on the validity of using changes in carbonyl force constants to infer degrees of π-bonding and mechanisms of charge distribution in substituted carbonyl complexes of Group VI-B metals. It is unreasonable to argue that the (2,2'-bipy)$Cr(CO)_4$ radical anion, in which π-bonding between ligand and metal is absent, and the (diacetylanil)$Cr(CO)_4$ radical anion, in which π-bonding between ligand and metal is present, both employ an anisotropic σ-only mechanism of charge distribution.

Finally, in answer to the last question raised in the introduction, supporting evidence indicating that spin and charge densities may, indeed, be separated in the radical anions of tetracarbonyl diimine Group VI-B metal complexes has been obtained. Unfortunately, the actual charge and spin densities have not been obtained for the complex radical anions and only these values would provide an unequivocal measure of the separation.

PART II

THE TETRAHEDRAL CASE:

DIIMINE DERIVATIVES OF

DICARBONYLDINITROSYLIRON(0)

INTRODUCTION

After having rather extensively investigated the electronic spectral characteristics of reduced octahedral diimine Group VI-B tetracarbonyl complexes, extension of the study to a second geometry, such as tetrahedral, seemed desirable. Recognizing that 1,10-phenanthroline and 2,2'-bipyridyl are both capable of functioning as pi-acceptors, one may reasonably inquire whether the lack of pi-bonding between these ligands and a low valent metal is unique to octahedral Group VI-B metal complexes.

1,10-Phenanthroline and 2,2'-bipyridyl derivatives of tetrahedral $Fe(NO)_2(CO)_2$ were selected for this study because electrochemical, esr, infrared, and Mössbauer investigations have been conducted on these neutral and electrolyzed derivatives.[35] The results obtained in these latter studies lead to conclusions which are similar to those reached for the octahedral systems - namely, that reductive electrons enter primarily ligand based molecular orbitals and that oxidative electrons are removed from orbitals predominantly metal in character. Of primary concern, in the present investigation, is a confirmation of these conclusions, if possible, and ascertainment of the existence or non-existence of pi-bonding between diimine and metal.

The nitric oxide molecule behaves as a coordinating ligand in a manner similar to carbon monoxide, except that it is usually considered to be a three electron donor and to coordinate as the nitrosonium ion, NO^+, rather than the neutral molecule. The ground state configuration of the NO molecule may be written as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1$ in simple molecular orbital parlance. Hence, coordination to a metal as the NO^+ (in which the antibonding 2π electron has been transferred) enables establishment of synergistic coupling to the metal. This, of course, stabilizes the low-valent metal. However, in the (1,10-phen)-$Fe(NO)_2$ and (2,2'-bipy)$Fe(NO)_2$, it is noted that only two strong pi-acceptors are coordinated to the metal (compared with four CO's in the octahedral complexes). Thus, it is of interest, to ask whether these two ligands are sufficiently strong pi-acceptors to allow the formation of a stable complex without the diimines also engaging in pi-bonding.

EXPERIMENTAL

Electrochemical Studies, Electron Spin Resonance Measurements, and Electronic Spectra

Because the electrochemical properties of the complexes included in this part of the dissertation were previously investigated,[35] polarograms were recorded only as a check on sample purity and completeness of controlled-potential electrolyses. These electrochemical experiments were conducted in the same manner as described in the experimental section of Part I. Again, as in Part 1, esr measurements were routinely run on all electrolyzed solutions to assure the presence of radical anions in reduced solutions and radical cations in oxidized solutions. Electronic spectral measurements were made as described in the experimental section of Part I. All sample preparations, including 1,2-dimethoxyethane solutions of neutral complexes, which are oxygen and water sensitive, were carried out in an argon atmosphere (Vacuum Atmospheres Dry-Lab Train).

Chemicals

The 1,2-Dimethoxyethane, supporting electrolyte (TBAP), mercury, and electrochemical reference solutions were all prepared as completely described in Part I. The (1,10-phen)$Fe(NO)_2$ and (2,2'-bipy)$Fe(NO)_2$ complexes and their derivatives were synthesized from $Fe(NO)_2(CO)_2$ and the corresponding ligands.[35] The $Fe(NO)_2(CO)_2$ was prepared according to the method discussed by King.[76] All complexes were analyzed for C, H, and N (Analytical Services Division, Department of Chemistry, V.P.I.&S.U.) and yielded acceptable ($\pm$ 0.3%) elemental analyses.

RESULTS AND DISCUSSIONS

All of the iron dinitrosyl complexes included in Part II undergo clean, reversible, one-electron reductions to radical anions. Unlike the octahedral Group VI-B metal tetracarbonyl complexes, the iron dinitrosyl complexes also undergo chemically and electrochemically reversible, one-electron oxidations to radical cations. Thus, three distinct charge states for each of these complexes may be investigated.

Electronic Spectra of Neutral Complexes

As in the case of the octahedral complexes, the electronic spectra of the neutral tetrahedral complexes will be considered first, with the electronic spectra of the oxidized and reduced species then being compared to the netural spectra. In the tetrahedral series not even the neutral complex spectra have been previously considered.

Electronic spectra of neutral (1,10-phen)$Fe(NO)_2$, methyl substituted 1,10-phenanthroline iron dinitrosyl, (2,2'-bipy)$Fe(NO)_2$, and bipyridine-like diimine iron dinitrosyl complexes are shown in Figures 35 - 37. Inspection of these spectra indicates that, as was seen to be the case in the spectra of the octahedral complexes, the high energy ultraviolet region is dominated by intraligand $\pi \rightarrow \pi^*$ transitions. The ultraviolet spectrum of (1,10-phen)$Fe(NO)_2$ shows that the β'-band of 1,10-phenanthroline has been shifted hypsochromically and the β —band has undergone a bathochromic shift in precisely the same manner as was noted for the 1,10-phenanthroline Group VI-B metal tetracarbonyl complexes. Similarly, the intraligand bands of 2,2'-bipyridyl are observed to be shifted bathochromically upon formation of (2,2'-bipy)$Fe(NO)_2$. This behavior is also analogous to the octahedral complexes.

Figure 35. Ultraviolet (A) and visible (B) electronic spectra of neutral (1,10-phen)$Fe(NO)_2$ and neutral, substituted phenanthroline iron dinitrosyl complexes in 1,2-dimethoxyethane.

	Complex	Concentration	Cell
———	(1,10-Phen)$Fe(NO)_2$	A: 1.4×10^{-3} M	1 mm
		B: 8.6×10^{-4} M	1 cm
—··—	(5-CH_3-1,10-phen)$Fe(NO)_2$	A: 1.2×10^{-3} M	1 mm
		B: 1.2×10^{-3} M	1 cm
—·—	(5,6-$(CH_3)_2$-1,10-phen)$Fe(NO)_2$	A-a: 3.7×10^{-4} M	1 mm
		b: 3.7×10^{-4} M	1 cm
		B: 3.7×10^{-4} M	1 cm
······	(4,7-$(CH_3)_2$-1,10-phen)$Fe(NO)_2$	A: 7.4×10^{-4} M	1 mm
		B: 7.4×10^{-4} M	1 cm
— —	(2,9-$(CH_3)_2$-1,10-phen)$Fe(NO)_2$	A: 4.5×10^{-4} M	1 mm
		B: 4.5×10^{-4} M	1 cm
------	(5-ϕ-1,10-phen)$Fe(NO)_2$	A: 6.9×10^{-4} M	1 mm
		B: 6.9×10^{-4} M	1 cm
--····	1,10-Phenanthroline	A: 1.5×10^{-4} M	1 mm

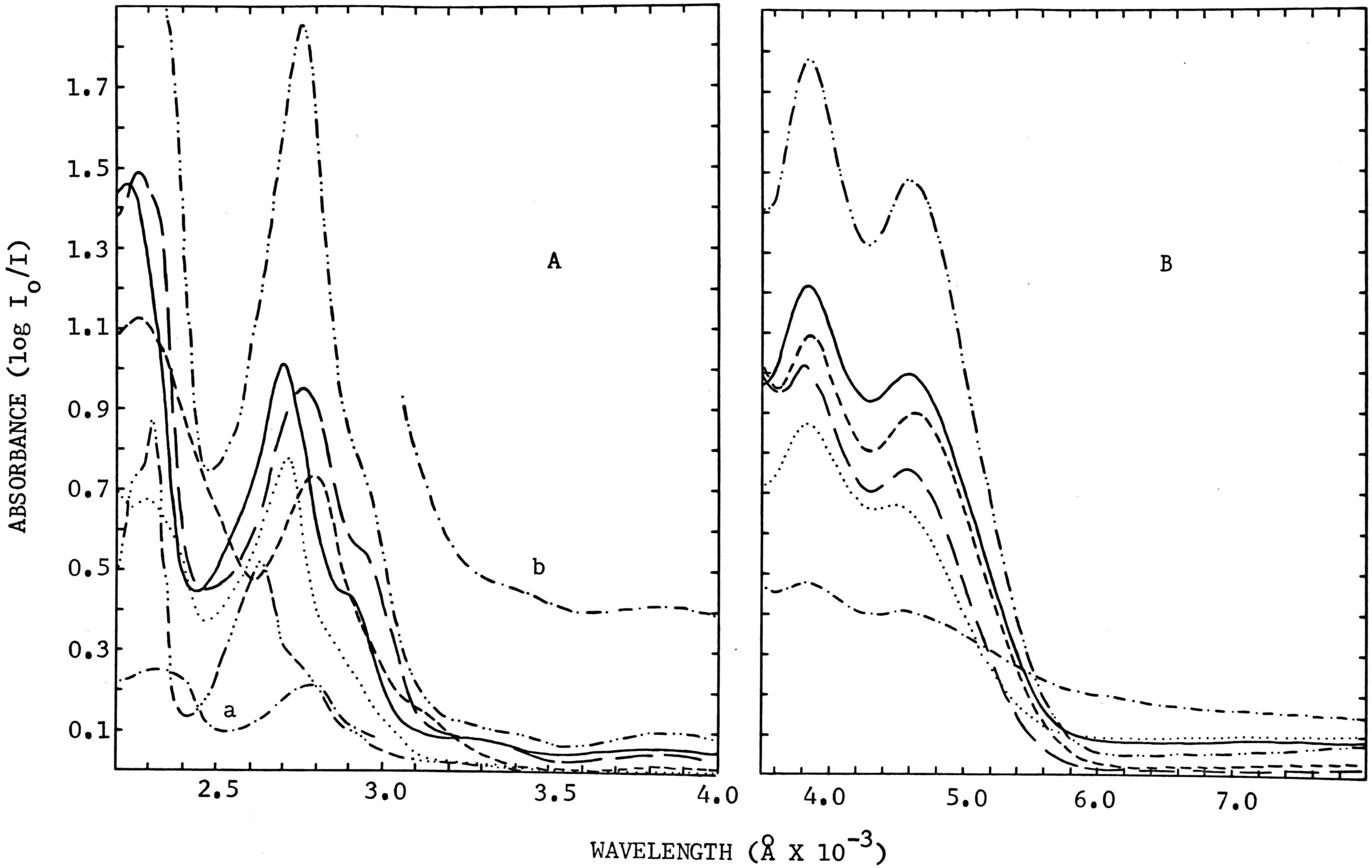


Figure 35. Ultraviolet (A) and visible (B) electronic spectra of neutral (1,10-phen)-$Fe(NO)_2$ and neutral, substituted phenanthroline iron dinitrosyl complexes.

Figure 36. Ultraviolet (A) and visible (B) electronic spectra of neutral (2,2'-bipy)$Fe(NO)_2$ and neutral "bipyridyl-like" diimine $Fe(NO)_2$ complexes in 1,2-dimethoxyethane.

	Complex	Concentration	Cell
———	(2,2'-Bipy)$Fe(NO)_2$	A-a 3.0×10^{-4} M	1 mm
		b 3.0×10^{-4} M	1 cm
		B: 2.7×10^{-4} M	1 cm
-----	(4,4'-$(CH_3)_2$-2,2'-bipy)$Fe(NO)_2$	A: 6.5×10^{-4} M	1 mm
		B: 5.3×10^{-4} M	1 cm
·····	(4,4'-$(\phi)_2$-2,2'-bipy)$Fe(NO)_2$	A: 1×10^{-3} M	1 mm
		B: 1×10^{-3} M	1 cm
— —	(2,2'-Biquin)$Fe(NO)_2$	A: 4.6×10^{-4} M	1 mm
		B: 4.6×10^{-4} M	1 cm
—•—	(Di-2-py-ketone)$Fe(NO)_2$	A: 4.8×10^{-4} M	1 mm
		B: 4.8×10^{-4} M	1 cm

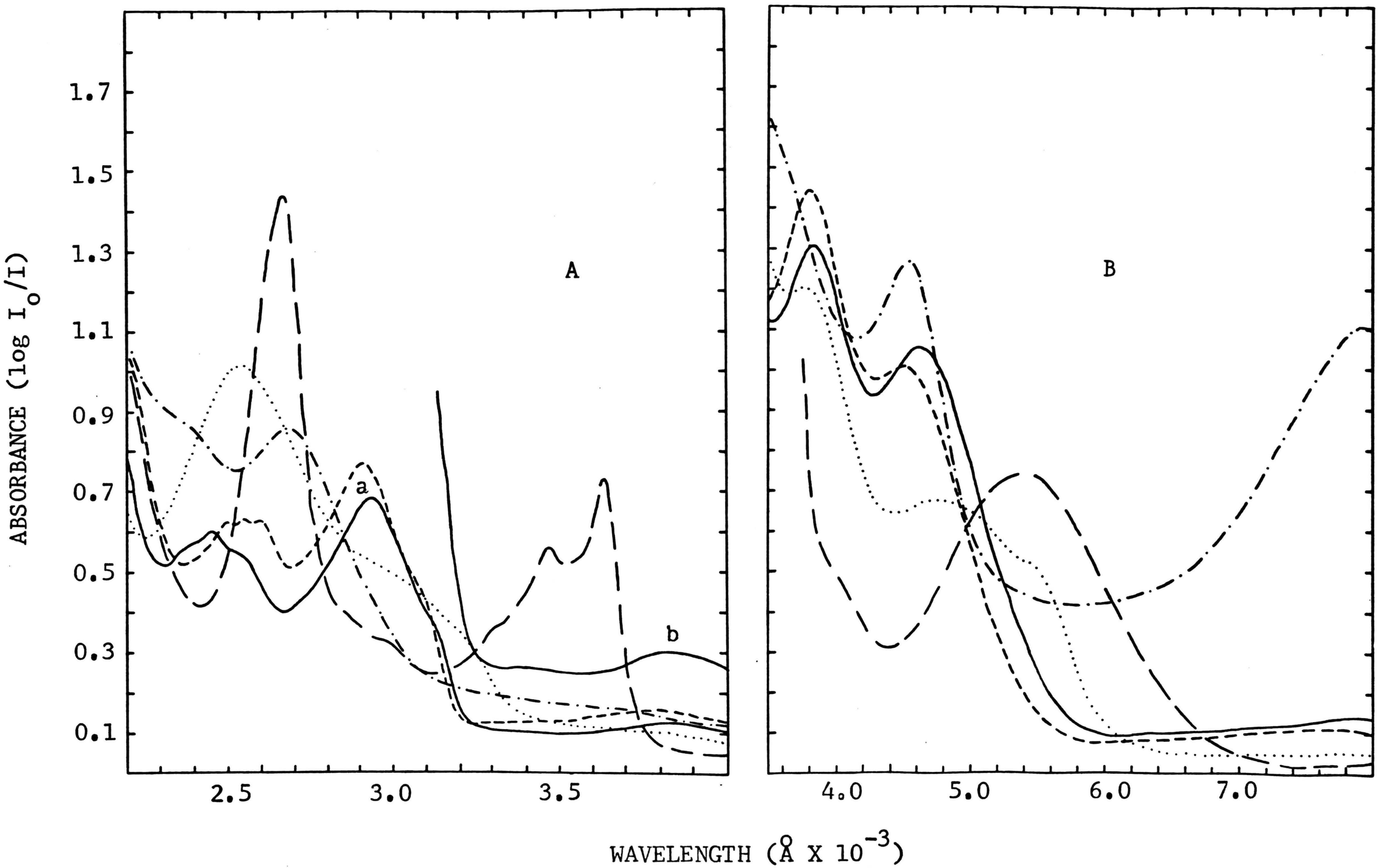


Figure 36. Ultraviolet (A) and visible (B) electronic spectra of neutral (2,2'-bipy)-$Fe(NO)_2$ and neutral "bipyridyl-like" diimine $Fe(NO)_2$ complexes.

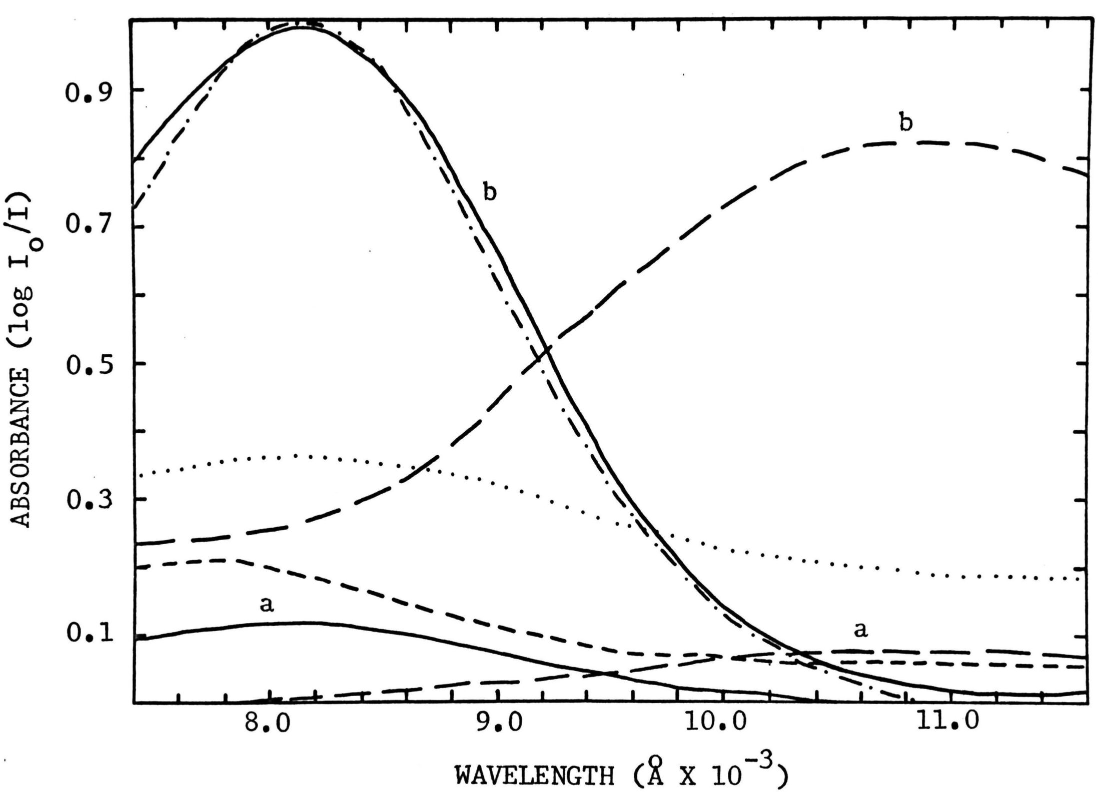


Figure 37. Near infrared spectra of neutral (2,2'-bipy)Fe$(NO)_2$ and neutral "bipyridyl-like" diimine Fe$(NO)_2$ complexes recorded in 1,2-dimethoxyethane using 1 cm cells.

	Complex	Concentration
———	(2,2'-Bipy)Fe$(NO)_2$	a - 2.7 X 10^{-4} M b - 2.7 x 10^{-3} M
-----	(4,4'-$(CH_3)_2$-2,2'-bipy)Fe$(NO)_2$	6.5 X 10^{-4} M
•••••	(4,4'-$(\phi)_2$-2,2'-bipy)Fe$(NO)_2$	3.3 X 10^{-4} M
— —	(2,2'-Biquin)Fe$(NO)_2$	a - 4.6 X 10^{-4} M b - 4.5 X 10^{-3} M
-•-•-	(Di-2-py-ketone)Fe$(NO)_2$	4.4 X 10^{-4} M

At longer wavelengths, the neutral diimine iron dinitrosyl complexes display four absorption bands. These occur at approximately 3400 Å, 3850 Å, 4600 Å, and 8200 Å. It is observed that the energies of the two bands in the 3400 Å and 3850 Å region are essentially unchanged by substitutions into the parent 1,10-phenanthroline and 2,2'-bipyridyl ligands. On the basis of the observation and the similarity in band positions to the $M \rightarrow \pi^*_{CO}$ and "d-d" transitions in the octahedral complexes, these bands might tentatively be assigned as $M \rightarrow \pi^*_{NO}$ and "d-d" transitions. Unfortunately, the presently available data do not allow confident assignment of these two bands. Although unequivocal assignments of these two bands would be essential to a full elucidation of the electronic structure of the iron dinitrosyl complexes, such assignments are of minor relevance to the present study.

The two bands near 4600 Å and 8200 Å (shown only for the bipyridyl complexes) behave, toward substitution into the diimines, in the manner expected for $M \rightarrow \pi^*_L$ charge transfer excitations. Although the band shifts are much less dramatic than were the corresponding shifts in the spectra of the octahedral complexes, close inspection of Figures 35 - 37 reveals that both bands are shifted hypsochromically by substitution of electron-releasing methyl groups into the diimine and bathochromically by phenyl substitution into the diimines. Since the band near 8200 Å is absent from the spectra of the neutral octahedral complexes involving the same ligands, it does not appear that the two low energy absorptions originate from the same molecular orbital. If this assumption is correct, one must conclude that the two highest energy, occupied molecular orbitals have substantial metal character. Furthermore, if these latter assignments are correct, one predicts that when the complexes are reduced, an electron will enter a ligand-based molecular orbital (or one substantially ligand in character) and when the complexes are oxidized an electron will be removed from a molecular orbital primarily metal in character.

Electronic Spectra of Electrolyzed Complexes

The electronic spectra of oxidized and reduced (1,10-phen)$Fe(NO)_2$, (2,2'-bipy)$Fe(NO)_2$, and (4,4'-$(CH_3)_2$-2,2'-bipy)$Fe(NO)_2$ are presented, along with spectra of the neutral complexes and of the reduced ligands for comparison, in Figures 38 - 42. Of primary concern to the present discussion are the spectra in the low energy visible and near infrared regions. Again, as with the octahedral species, the similarities in band positions between reduced ligands and reduced complexes in these regions are striking. The two-band structure near 6000 Å and the three-band structure near 8500 Å are both clearly seen in the radical anion spectra of the ligands and the complexes. These two distinctive band structures were considered in the octahedral species as diagnostic of ligand reduction. In addition, the presence of these band structures indicates that the ligand LUMO is also the complex LUMO. This, in turn, implies the non-existence of back-bonding between iron and the diimines under consideration.

As expected, the electronic spectra of the radical cations are quite similar to the spectra of the corresponding neutral complexes. The spectra of the cations do, however, show at least one band, in the

Figure 38. Ultraviolet (A) and visible (B) spectra of neutral and electrolyzed (2,2'-bipy)$Fe(NO)_2$ in 1,2-dimethoxyethane.

	Species	Concentration	Cell
——	neutral	A: 3.0 X 10^{-4} M	1 mm
		B: 2.7 X 10^{-4} M	1 cm
···	radical cation	A-a: 8.7 X 10^{-4} M	1 mm
		b: 4.7 X 10^{-3} M	1 mm
		B: 8.7 X 10^{-4} M	1 cm
---	complex radical anion	A: 1.6 X 10^{-3} M	1 mm
		B: 8.8 X 10^{-4} M	1 cm
-·-	ligand radical anion	A: 5.4 X 10^{-4} M	1 mm
		B: 1.4 X 10^{-4} M	1 cm

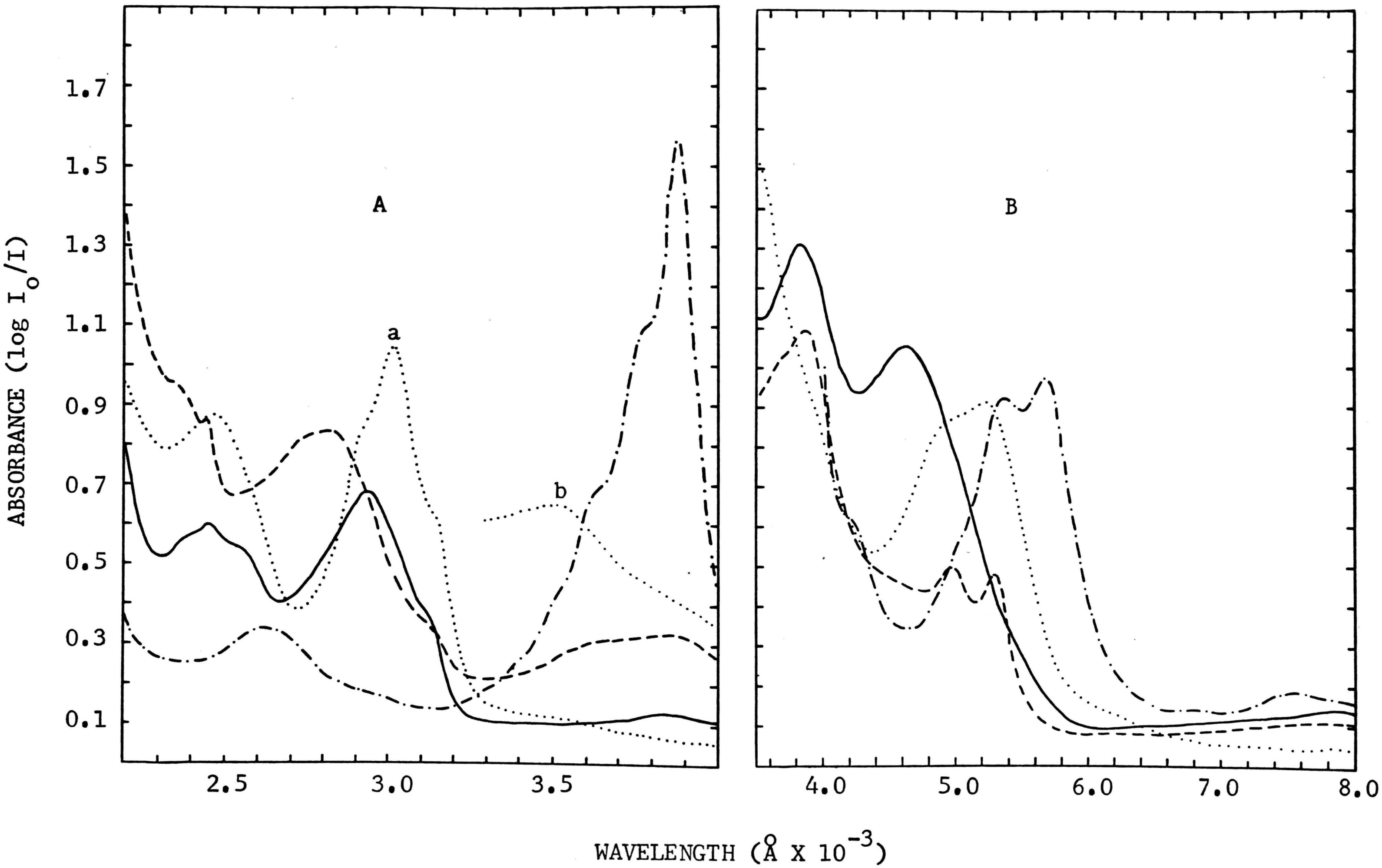


Figure 38. Ultraviolet (A) and visible (B) spectra of neutral and electrolyzed (2,2'-bipy)Fe$(NO)_2$.

Figure 39. Near infrared spectra of neutral and electrolyzed (2,2'-bipy)$Fe(NO)_2$ recorded in 1,2-dimethoxyethane in 1 cm cells.

	Species	Concentration
———	neutral	a: 2.7 X 10^{-4} M b: 2.6 X 10^{-3} M
•••	radical cation	a: 8.7 X 10^{-4} M b: 8.7 X 10^{-3} M
---	complex radical anion	2.4 X 10^{-3} M
-•-	ligand radical anion	6.3 X 10^{-4} M

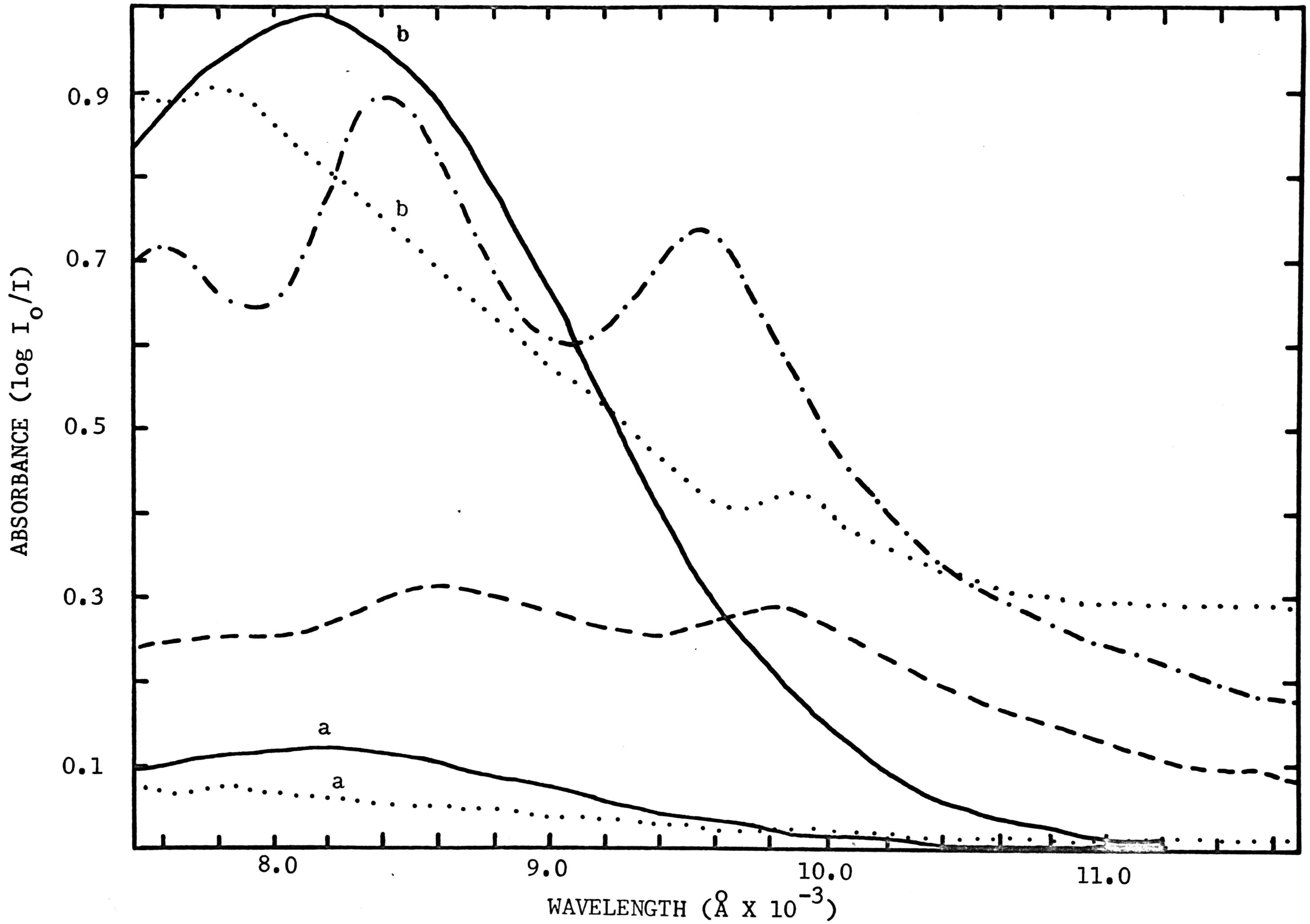
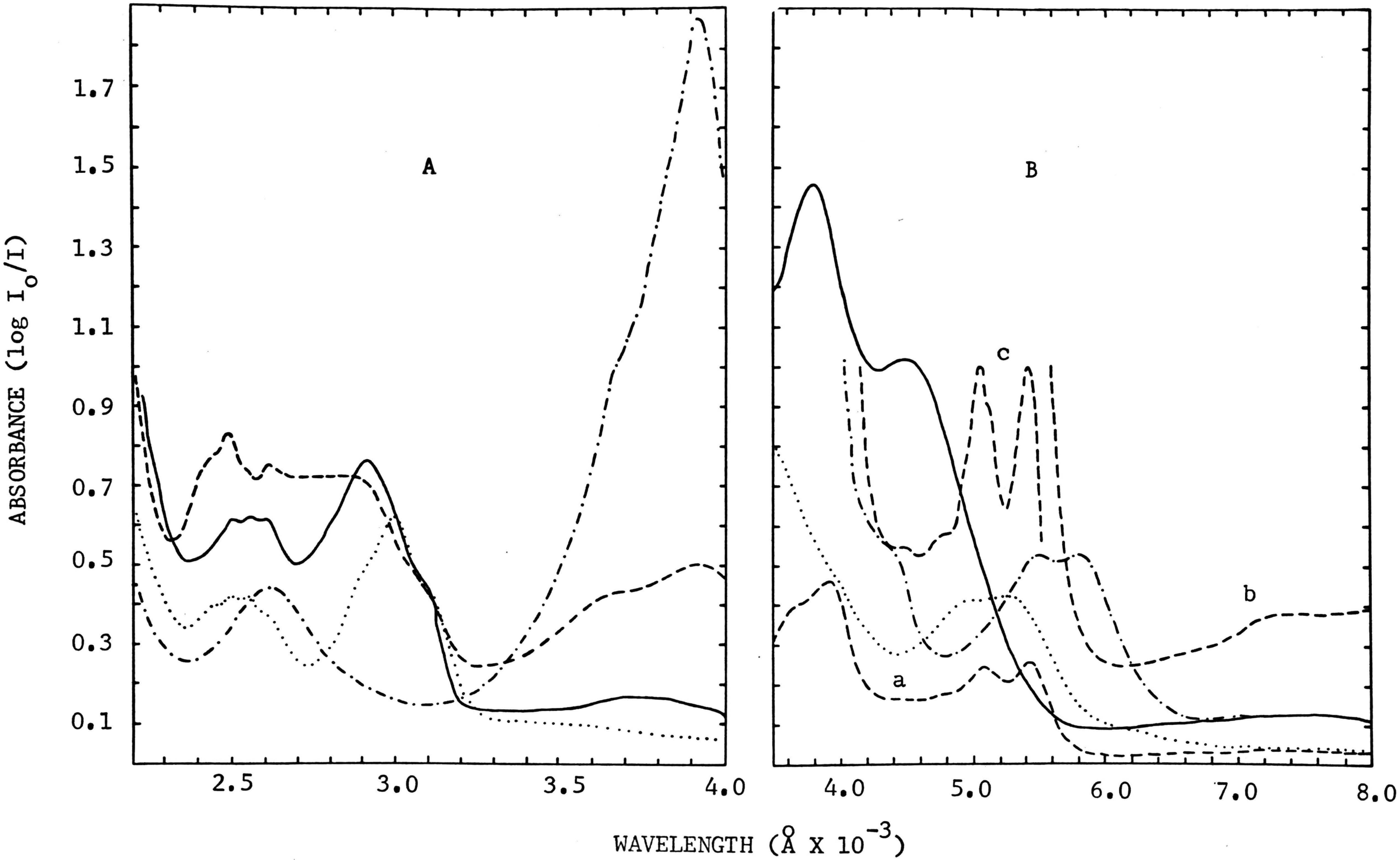


Figure 39. Near infrared spectra of neutral and electrolyzed (2,2'-bipy)Fe$(NO)_2$.

Figure 40. Ultraviolet (A) and visible (B) electronic spectra of neutral and electrolyzed $(4,4'-(CH_3)_2-2,2'-bipy)Fe(NO)_2$ in 1,2-dimethoxyethane.

	Species	Concentration	Cell
——	neutral	A: 6.7×10^{-4} M	1 mm
		B: 5.3×10^{-4} M	1 cm
••••	radical cation	A: 5.3×10^{-4} M	1 mm
		B: 5.3×10^{-4} M	1 cm
----	complex radical anion	A: 6.7×10^{-4} M	1 mm
		B: a - 6.7×10^{-4} M	1 mm
		b - 6.7×10^{-4} M	1 cm
		c - 3.4×10^{-4} M	1 cm
-•-•	ligand radical anion	A: 7.7×10^{-4} M	1 mm
		B: 7.7×10^{-3} M	1 mm



<u>Figure 40.</u> Ultraviolet (A) and visible (B) electronic spectra of neutral and electrolyzed (4,4'-$(CH_3)_2$-2,2'-bipy)$Fe(NO)_2$.

Figure 41. Ultraviolet (A) and visible (B) spectra of neutral and electrolyzed (1,10-phen)$Fe(NO)_2$ in 1,2-dimethoxyethane.

	Species	Concentration	Cell
——	neutral	A: 8.6×10^{-4} M	1 mm
		B: 1.4×10^{-3} M	1 cm
···	radical cation	A: 8.6×10^{-4} M	1 mm
		B: 8.6×10^{-4} M	1 cm
---	radical anion	A: 1.4×10^{-3} M	1 mm
		B: a - 1.4×10^{-3} M	1 mm
		b - 1.4×10^{-3} M	1 cm

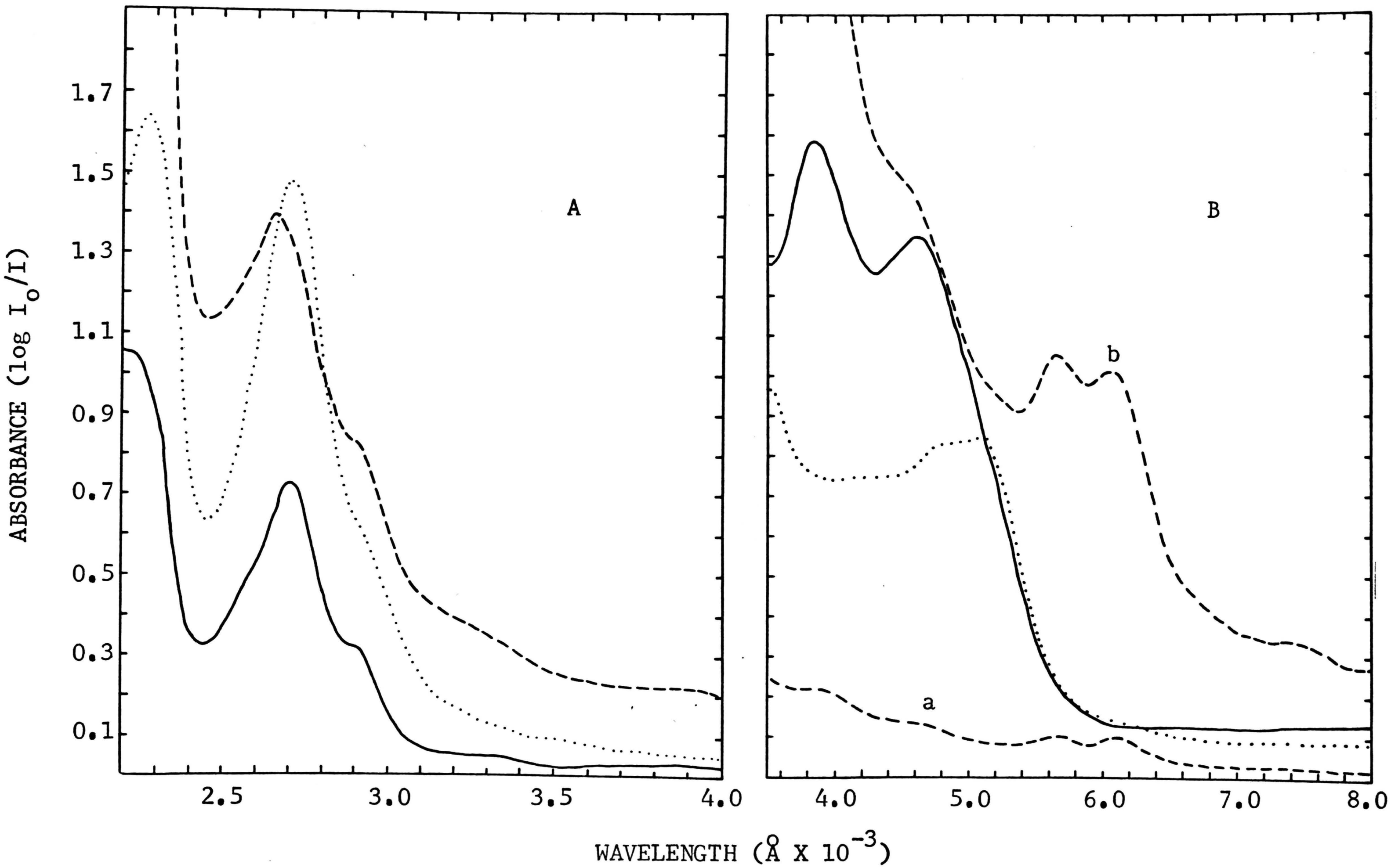


Figure 41. Ultraviolet (A) and visible (B) electronic spectra of neutral and electrolyzed (1,10-phen)$Fe(NO)_2$.

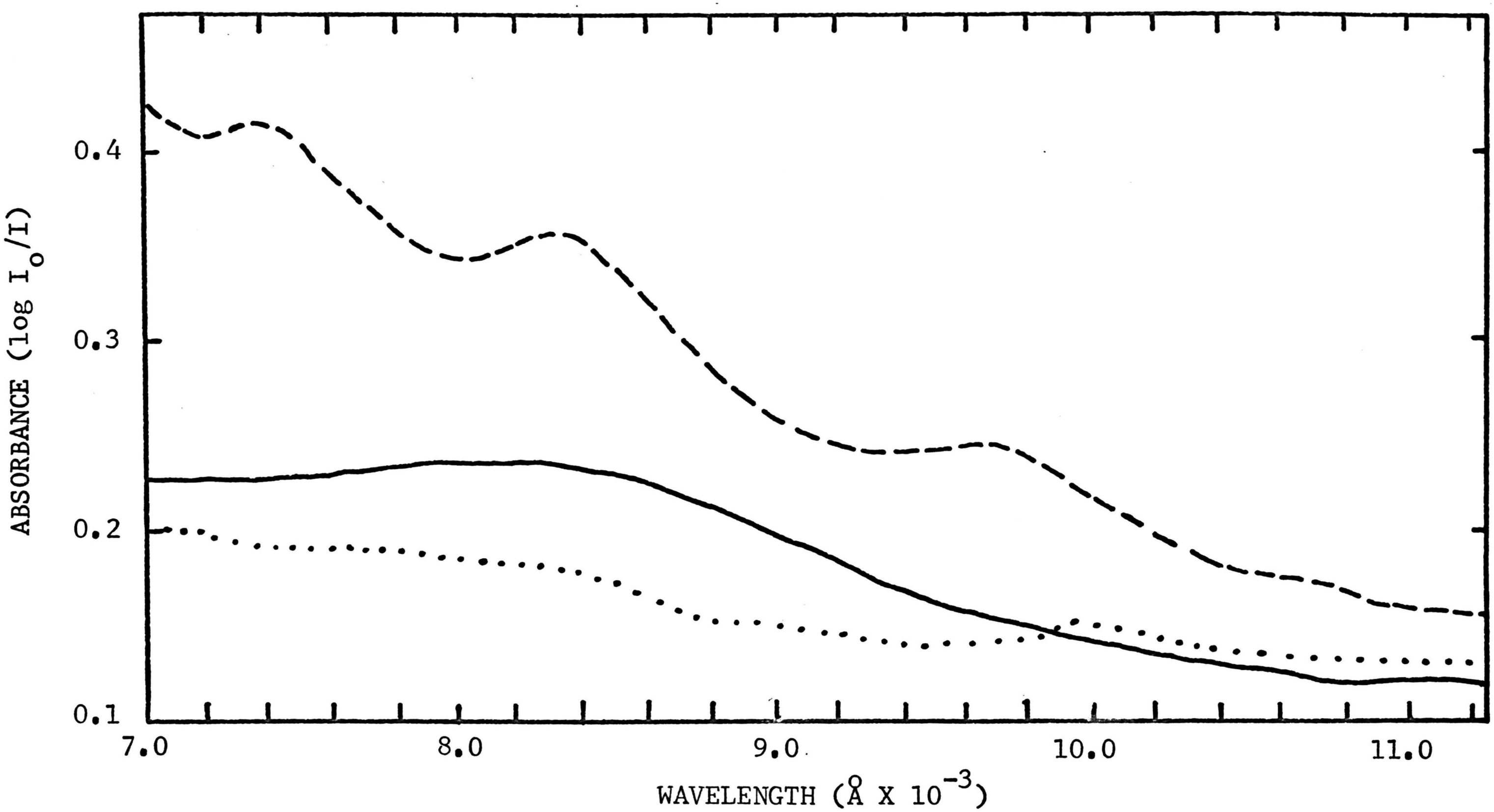


Figure 42. Near infrared spectra of neutral (1,10-phen)$Fe(NO)_2$ (——; 2 X 10^{-3} M; 1 cm cell), the radical cation of (1,10-phen)$Fe(NO)_2$ (•••; 8.4 X 10^{-4} M; 1 cm cell), and the radical anion of (1,10-phen)$Fe(NO)_2$ (---; 2 X 10^{-3} M; 1 cm cell) in 1,2-dimethoxyethane.

vicinity of 10,000 Å, which is not present in the spectra of the neutral complexes. This band is very likely due to a transition between the penultimate HOMO and the, now, half-occupied HOMO of the radical cation. In the neutral complexes, the difference in energy between the two lowest energy absorptions, which have been assigned as metal-to-ligand charge transfers is roughly 9500 cm^{-1} or about 10,500 Å.

CONCLUSIONS

The results of the spectroscopic studies on the tetrahedral complexes lead to conclusions very similar to those derived from analogous studies on the octahedral complexes. Diimine iron dinitrosyl complexes, wherein the diimine is 1,10-phenanthroline or 2,2'-bipyridyl, are reduced to radical anions in which the reductive electron has entered a ligand molecular orbital (π_7 for 2,2'-bipyridyl and π_8 for 1,10-phenanthroline). Thus, one concludes that pi-bonding between iron and diimine in non-existent in these tetrahedral complexes also. Apparently, then, non-existence of back-bonding from metal to 2,2'-bipyridyl or 1,10-phenanthroline is not restricted to octahedral tetracarbonyl complexes of Group VI-B metals.

Finally, although the evidence is by no means as compelling as the evidence leading to the above conclusions, one can probably quite safely conclude that the HOMO of these tetrahedral complexes does possess very considerable metal character.

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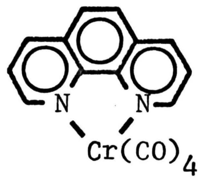
APPENDIX

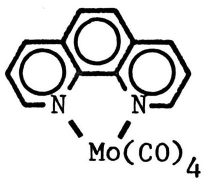
APPENDIX A

NOMENCLATURE AND ABBREVIATIONS OF COMPLEXES

1. 

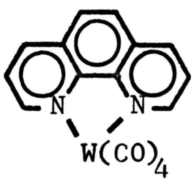
Tetracarbonyl-1,10-phenanthroline-chromium(0)

(1,10-phen)$Cr(CO)_4$

2. 

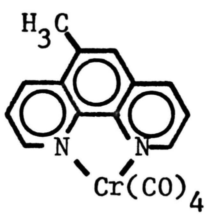
Tetracarbonyl-1,10-phenanthroline-molybdenum(0)

(1,10-phen)$Mo(CO)_4$

3. 

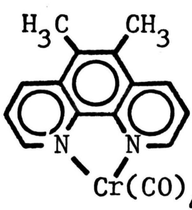
Tetracarbonyl-1,10-phenanthroline-tungsten(0)

(1,10-phen)$W(CO)_4$

4. 

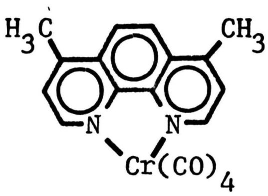
Tetracarbonyl-5-methyl-1,10-phenanthrolinechromium(0)

(5-(CH_3)-1,10-phen)$Cr(CO)_4$

5. 

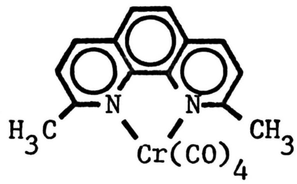
Tetracarbonyl-5,6-dimethyl-1,10-phenanthrolinechromium(0)

(5,6-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$

6. 

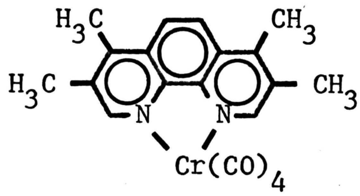
Tetracarbonyl-4,7-dimethyl-1,10-phenanthrolinechromium(0)

(4,7-$(CH_3)_2$-1,10-phen)$Cr(CO)_4$

7. 

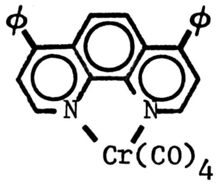
Tetracarbonyl-2,9-dimethyl-1,10-phenanthrolinechromium(0)

$(2,9\text{-}(CH_3)_2\text{-}1,10\text{-phen})Cr(CO)_4$

8. 

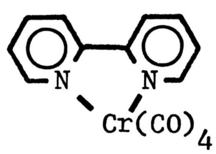
Tetracarbonyl-3,4,7,8-tetramethyl-1,10-phenanthrolinechromium(0)

$(3,4,7,8\text{-}(CH_3)_4\text{-}1,10\text{-phen})Cr(CO)_4$

9. 

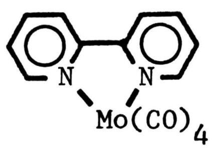
Tetracarbonyl-4,7-diphenyl-1,10-phenanthrolinechromium(0)

$(4,7\text{-}(\phi)_2\text{-}1,10\text{-phen})Cr(CO)_4$

10. 

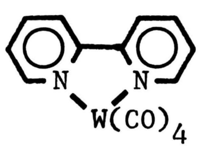
Tetracarbonyl-2,2'-bipyridylchromium(0)

$(2,2'\text{-bipy})Cr(CO)_4$

11. 

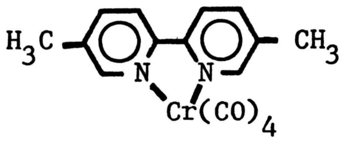
Tetracarbonyl-2,2'-bipyridylmolybdenum(0)

$(2,2'\text{-bipy})Mo(CO)_4$

12. 

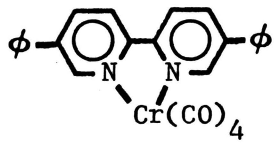
Tetracarbonyl-2,2'-bipyridyltungsten(0)

$(2,2'\text{-bipy})W(CO)_4$

13. 

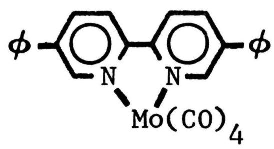
Tetracarbonyl-4,4'-dimethyl-2,2'-bipyridylchromium(0)

$(4,4'\text{-}(CH_3)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$

14. 

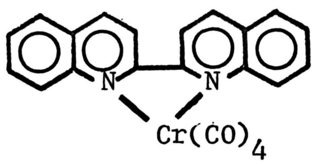
Tetracarbonyl-4,4'-diphenyl-2,2'-bipyridylchromium(0)

$(4,4'\text{-}(\phi)_2\text{-}2,2'\text{-bipy})Cr(CO)_4$

15. 

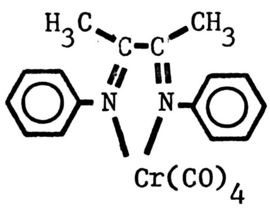
Tetracarbonyl-4,4'-diphenyl-2,2'-bipyridylmolybdenum(0)

$(4,4'\text{-}(\phi)_2\text{-}2,2'\text{-bipy})Mo(CO)_4$

16. 

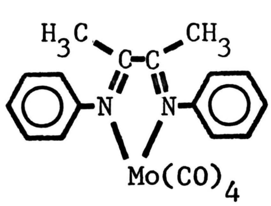
Tetracarbonyl-2,2'-biquinolylchromium(0)

$(2,2'\text{-biquin})Cr(CO)_4$

17. 

Tetracarbonyl-2,3-bis(phenylimino)-butanechromium(0)

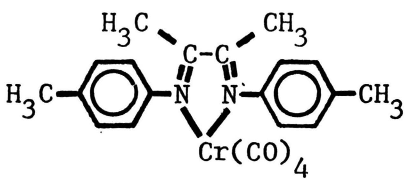
$(\text{diacetylanil})Cr(CO)_4$

18. 

Tetracarbonyl-2,3-bis(phenylimino)-butanemolybdenum(0)

$(\text{diacetylanil})Mo(CO)_4$

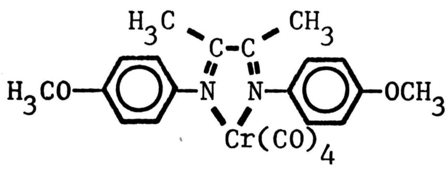
19.



Tetracarbonyl-2,3-bis(*p*-tolylinimo)-butanechromium(0)

(*p*-(CH_3)-diacetylanil)$Cr(CO)_4$

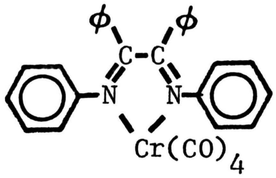
20.



Tetracarbonyl-2,3-bis(*p*-anisylimino)-butanechromium(0)

(*p*-(CH_3O)-diacetylanil)$Cr(CO)_4$

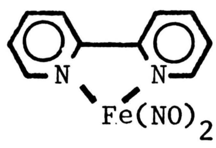
21.



Tetracarbonyl-1,2-diphenyl-1,2-bis(phenylimino)ethanechromium(0)

(benzilanil)$Cr(CO)_4$

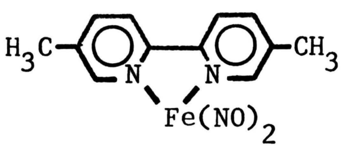
22.



Dinitrosyl-2,2'-bipyridyliron(0)

(2,2'-bipy)$Fe(NO)_2$

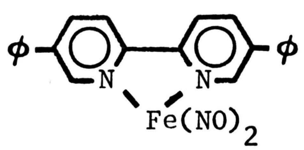
23.



Dinitrosyl-4,4'-dimethyl-2,2'-bipyridyliron(0)

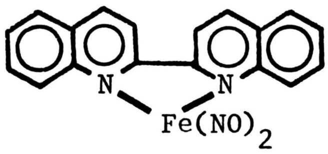
(4,4'-$(CH_3)_2$-2,2'-bipy)$Fe(NO)_2$

24.



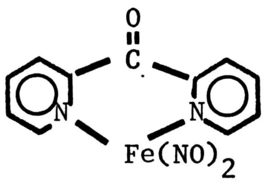
Dinitrosyl-4,4'-diphenyl-2,2'-bipyridyliron(0)

(4,4'-$(\phi)_2$-2,2'-bipy)$Fe(NO)_2$

25. 

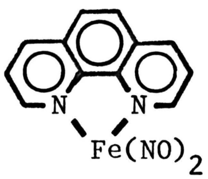
Dinitrosyl-2,2'-biquinolyliron(0)

(2,2'-biquin)Fe$(NO)_2$

26. 

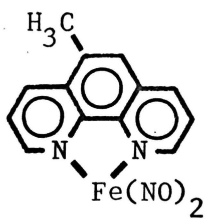
Dinitrosyl-di-2-pyridylketoneiron(0)

(di-2-py-ketone)Fe$(NO)_2$

27. 

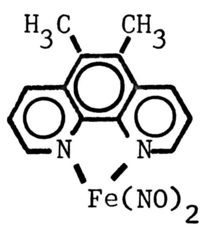
Dinitrosyl-1,10-phenanthrolineiron(0)

(1,10-phen)Fe$(NO)_2$

28. 

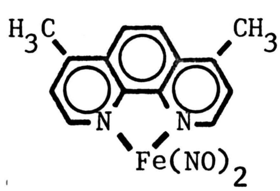
Dinitrosyl-5-methyl-1,10-phenanthroline-iron(0)

(5-(CH_3)-1,10-phen)Fe$(NO)_2$

29. 

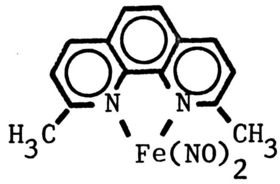
Dinitrosyl-5,6-dimethyl-1,10-phenanthrolineiron(0)

(5,6-$(CH_3)_2$-1,10-phen)Fe$(NO)_2$

30. 

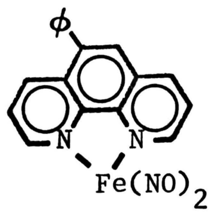
Dinitrosyl-4,7-dimethyl-1,10-phenanthrolineiron(0)

(4,7-$(CH_3)_2$-1,10-phen)Fe$(NO)_2$

31. 

Dinitrosyl-2,9-dimethyl-1,10-phenanthrolineiron(0)

(2,9-$(CH_3)_2$-1,10-phen)$Fe(NO)_2$

32. 

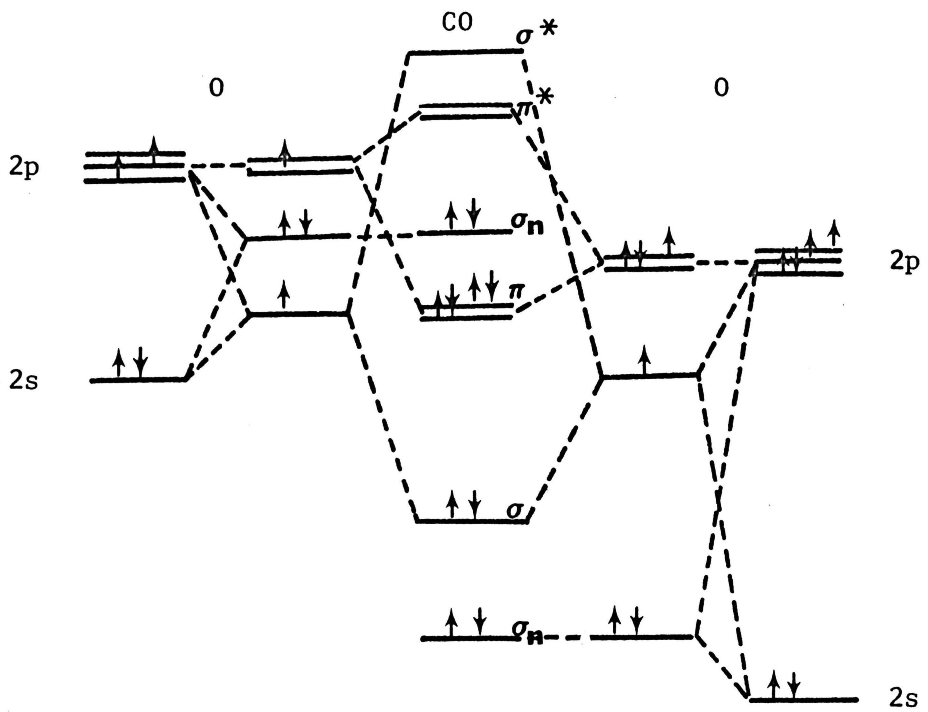
Dinitrosyl-5-phenyl-1,10-phenanthrolineiron(0)

(5-(ϕ)-1,10-phen)$Fe(NO)_2$

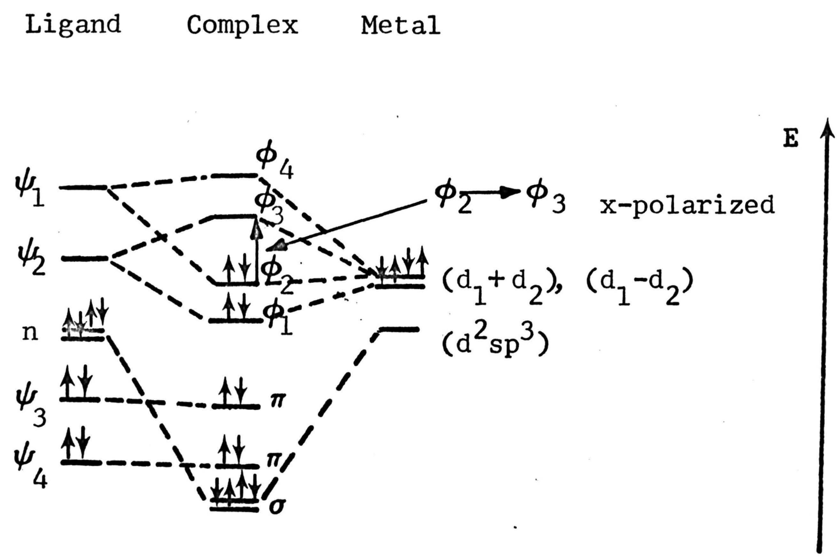
APPENDIX B

MOLECULAR ORBITAL ASPECTS

I. Qualitative Molecular Orbital Scheme for Carbon Monoxide.[26]



II. Qualitative Molecular Orbital Scheme for Diacetyldianil Complexes.[72]



III. Pariser-Parr-Pople (PPP) Self-Consistent Field Molecular Orbital (SCF-MO) Calculations.

The PPP-SCF method, which has been used to calculate singlet spectra for 1,10-phenanthroline, methyl substituted 1,10-phenanthrolines, and 2,2'-bipyridyl, has been thoroughly discussed in a number of texts,[46,61] and will be only briefly outlined here.

This method, like the Hückel method and variations thereof, begins by approximating the pi-molecular orbitals, ψ_i, as linear combinations of atomic pi-orbitals,

$$\psi_i = \sum_{\mu} C_{i\mu} \chi_{\mu} .$$

The eigenvalues, E_i, are obtained as solutions to the secular determinant

$$\left| F_{\mu\nu} - E_i S_{\mu\nu} \right| = 0,$$

and are approximations to the orbital ionization potentials. The $F_{\mu\nu}$ integrals are elements of the Fock matrix, F.

$$F_{\mu\mu} = H^{core}_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu} \langle \chi_{\mu}\chi_{\mu} | \frac{1}{r_{12}} | \chi_{\mu}\chi_{\mu} \rangle + \sum_{\mu \neq \nu} P \langle \chi_{\mu}\chi_{\nu} | \frac{1}{r_{12}} | \chi_{\mu}\chi_{\nu} \rangle$$

$$F_{\mu\nu} = H^{core}_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \langle \chi_{\mu}\chi_{\nu} | \frac{1}{r_{12}} | \chi_{\mu}\chi_{\nu} \rangle$$

$$S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle = \delta_{\mu\nu}$$

$H^{core}_{\mu\mu}$, $H^{core}_{\mu\nu}$, $P_{\mu\mu}$, $P_{\mu\nu}$ are the diagonal and off-diagonal elements of the core Hamiltonian matrix, H, and the density matrix, P, respectively, where

$$P_{\mu\mu} = 2 \sum_{i} C_{i\mu} C_{i\mu} .$$

The integrals $H_{\mu\mu}^{core}$ and $H_{\mu\nu}^{core}$ are generally given the symbols α_{μ} and $\beta_{\mu\nu}$ and referred to as the coulomb and resonance integrals respectively. These integrals have been assigned various semi-empirical values based on valence state ionization potential data.

The integrals $<\chi_{\mu}\chi_{\mu}\left|\frac{1}{r_{12}}\right|\chi_{\mu}\chi_{\mu}>$ and $<\chi_{\mu}\chi_{\nu}\left|\frac{1}{r_{12}}\right|\chi_{\mu}\chi_{\nu}>$ are one- and two-center repulsion integrals, respectively, and are generally abbreviated as $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$. The one-center repulsion integrals, $\gamma_{\mu\mu}$, have been assigned values of $I_{\mu} - A_{\mu}$ where I_{μ} is the valence state ionization potential of μ and A is the electron affinity of μ. The two-center repulsion integrals, $\gamma_{\mu\nu}$, were computed by the Matago-Nishimoto[46] approximation,

$$\gamma_{\mu\nu} = \frac{1}{R_{\mu\nu} + [2/(\gamma_{\mu\mu} + \gamma_{\nu\nu})]}$$

where $R_{\mu\nu}$ is the interatomic distance in Å.

Thus, the method entails selection of $P_{\mu\nu}$ values (usually obtained from preliminary Hückel calculations), α_{μ}, $\beta_{\mu\nu}$, and $\gamma_{\mu\mu}$ values. These values are then used to calculate the $F_{\mu\nu}$ elements, the secular determinant is solved, and a new set of $P_{\mu\nu}$ values are obtained. This process is then repeated (iterated) until self-consistency is achieved.

The SCF-MO method may be extended to open-shell systems (e.g., radical anions). In the present work, restricted Hartree-Fock calculations[46] within the zero differential overlap approximation have been performed. In this approach, the problem is separated into two pseudo-eigenvalue problems, one involving all the closed-shell molecular orbitals and the other involving the partial occupied molecular orbital(s). Individual Fock operators are constructed for the closed- and open-shell portions and are then combined to give a total F matrix similar to that discussed previously. Just as in the closed-shell SCF-MO theory, the mechanics of obtaining an answer is to first choose a trial form for the wave function, construct the starting F matrix, obtain the eigenvectors, reconstruct a new F matrix, and continue iteratively until self-consistency is obtained.

APPENDIX C

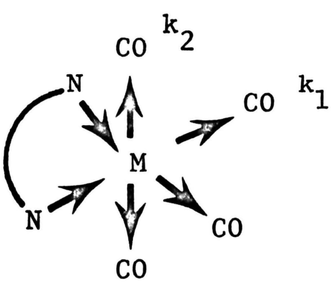
RELEVANT INFRARED, ESR, AND

NMR RESULTS FROM PREVIOUS STUDIES[34,35]

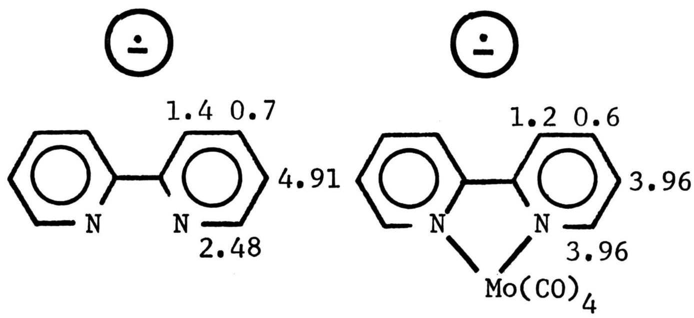
I. Bipyridyl Results:[34]

FORCE CONSTANTS FOR BIPYRIDYL $M(CO)_4$

M	k	Neutral	Reduced	Δk
Cr	k_1	14.03	13.53	0.50
	k_2	15.20	14.86	0.34
	k_i	0.40	0.40	0.00
Mo	k_1	14.09	13.43	0.66
	k_2	15.15	14.80	0.35
	k_i	0.42	0.38	0.04
W	k_1	14.07	13.38	0.69
	k_2	15.16	14.68	0.48
	k_i	0.41	0.41	0.00



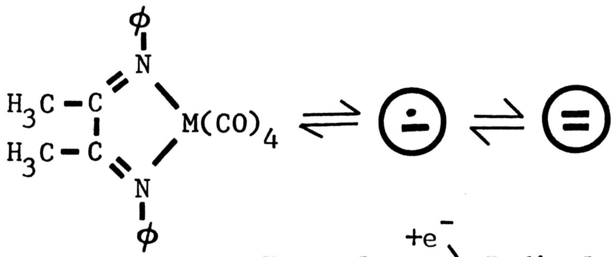
Hyperfine-coupling Constants



Ligand Radical Anion

Complex Radical Anion

II. Diacetyldianil Results:[35]



Neutral $\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$ Radical Anion $\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$ Dianion

ESR Results:

radical anion

$$a_H^{(1)} = Q_{CH}^{H} \rho_C \qquad Q_{CH}^{H} = -23 \text{ G}$$

$a_N = 5.08$ G, $a_{H_o} = 5.08$ G, $a_{H_p} = 5.08$ G,

$a_{CH_3} = 0.48$ G, $a_{H_m} = 0.48$ G

NMR Results:

dianion

$$\Delta\delta_r^{(2)} = -Kq_r$$

$$\Delta\delta_{r(o,p)} = 0.10 \text{ ppm}$$

IR Results:

Force Constants (md/Å) for Diacetylanil

k	Neutral	Radical Anion	Δk	Dianion	Δk
k_1	14.42	13.41	1.01	12.76	1.66
k_2	15.14	14.53	0.61	14.31	0.83
k_i	0.36	0.40	-0.04	0.45	-0.09

(1) a = hyperfine-coupling constants in gauss

H_o = ortho proton on N-phenyl rings

(2) δ = chemical shift in ppm

K = empirical constant of proportionality, approximately 10 ppm

q_r = charge density at r

APPENDIX D

"FOCAL" COMPUTER PROGRAM FOR CONVERTING

ELECTRONIC SPECTRA FROM

ABSORBANCE VS. WAVELENGTH TO ABSORBTIVITY VS. WAVENUMBER[1]

```
C-8K MODV 11-219

Ø1.Ø5 S K=Ø
Ø1.Ø6 TYPE "PUT FIRST SET OF PARAS IN HS READER"!

Ø2.Ø1 ASK "MAX ABS" AF,!
Ø2.Ø2 SET SF=AF/5ØØ
Ø2.1Ø ASK "READY"TA,!
Ø2.2Ø IF (TA-ØWAIT)2.3,2.1,2.1
Ø2.3Ø * A C,P,MI,MA,NP,!
Ø2.31 *
Ø2.4Ø S IN=(MA-MI)/NP
Ø2.5Ø TYPE "INCREMENT IS",IN,"A"!
Ø2.6Ø TYPE " PUT Y DATA IN HS READER?!
Ø2.7Ø ASK "READY"TB,!
Ø2.8Ø IF (TB-ØWAIT)2.9,2.7,2.7
Ø2.89 T "  ",!!!
Ø2.9Ø * F I=1,1,NP/2+.5; D 3.Ø
Ø2.91 *
Ø2.94 F I = 1,2,NP/2+.5; D 4.Ø
Ø2.95 S K = NP/2
Ø2.96 GOTO 2.90

Ø3.1Ø ASK Y(I)
Ø3.21 SET Y(I)=(Y(I)*SF)/(C*P)
Ø3.3Ø S X(I)=1Ø↑8/<MI+IN*(I+K-1)>

Ø4.1Ø TYPE X(I),Y(I),"    "X(I+1),Y(I+1),!

Ø5.Ø5 * F I=1,1,NP/2+.5; D 3.Ø
Ø5.Ø6 *
Ø5.1Ø F I=1,2,(NP/2)+.5; D 4.Ø
Ø5.15 Q
*
```

[1]Written by T. P. Abeles and C. Titus.

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ELECTRONIC SPECTRA AND STRUCTURE

OF SOME ELECTROACTIVE ORGANOTRANSITION

METAL COMPLEXES

by

Leo A. Bares

(ABSTRACT)

The electronic structures of several carbonyl and nitrosyl organometallic complexes having octahedral and tetrahedral geometry have been investigated by a combination of electrochemical and spectroscopic methods. A fruitful approach to the study of the electronic structures of substituted metal carbonyls and nitrosyls has been to perturb the electronic structures by reversible, electrochemical oxidation and/or reduction of the complexes and then to study the resulting electroactive species by appropriate spectroscopic tools.

Thirty-two diimine Group VI-B metal tetracarbonyl and diimine dinitrosyliron(0) complexes have been studied. The general approach has been to electrochemically generate radical anions and, where possible, radical cations and singlet state dianions of the complexes followed by esr, infrared, and electronic spectral investigation of the resulting species. Primary emphasis has been placed on the use of the latter tool.

Diimine derivatives of Group VI-B metal carbonyls form stable radical anions and, in some cases, e.g., diacetyldianil, 4,4'-diphenyl-2,2'-bipyridyl, and 4,7-diphenyl-1,10-phenanthroline derivatives, stable

singlet state dianions are formed. None of these complexes, however, form stable radical cations. On the other hand, diiminedinitrosyl-iron(0) complexes form radical cations, as well as the other charged states.

Infrared force constant analyses and electronic absorption spectra, in which band assignments have been made primarily by ligand-substitutional perturbations, indicate that reductive charge enters non-carbonyl and non-nitrosyl ligand-based molecular orbitals. Much of this charge density, but not spin density, is subsequently disseminated through the metal to the carbonyls by a directional sigma mechanism.

Electronic spectral studies indicate that, despite the fact that 1,10-phenanthroline and 2,2'-bipyridyl are generally considered as π-acceptors, these ligands engage in no back-bonding from the Group VI-B metals in the tetracarbonyl complexes nor from iron in the dinitrosyl-iron(0) complexes. On the other hand, extensive back-bonding occurs in the diacetyldianil Group VI-B metal tetracarbonyl complexes.

The conclusions reached in these studies indicate that the sigma framework is as important, or more important, than the pi-structure in determining the electronic properties of substituted carbonyl complexes. In addition, it has been concluded, rather dramatically, that it is, indeed, dangerous to extrapolate the properties of a given ligand from one type of complex to another, ostensibly similar, complex.