Analogy to pyrrole association[29,30] and local dipole-dipole considerations favor **5** as does the fact (Table V) that in 7-methylindole the solvent shift of the 2-proton resonance is exceptionally high and that of the 7-proton is somewhat low. This may be rationalized by orientation **5** if the mutual repulsion of the adjacent 7-methyl groups would force them further from, and the 2 positions closer to, the aromatic rings of the adjacent indole molecule in the complex. A similarly convenient rationalization for **4** is not available.

Further information on the preferred orientation of indole complexes may be available from studies of substituted derivatives similar to those in the purine series.[37]

Experimental Section

Equipment. The nmr spectra were taken at 38 ± 2° on a Varian Associates A-60 spectrometer operating at 60 Mcps. Chemical shifts were obtained from precalibrated chart paper with the internal tetramethylsilane reference signal set at τ 10.00. The calibration was checked frequently with a chloroform–tetramethylsilane standard. A variable-temperature probe regulated with a Varian V-6040 variable-temperature controller was used for the temperature studies.

Infrared spectra were taken on a Perkin-Elmer 421 grating spectrophotometer. Band positions were checked against the 1028, 1603, and 3083 cm^{-1} absorption bonds of a polystyrene film.

All melting points (corrected) were determined on a Thomas-Hoover capillary melting point apparatus.

Solvents. Tetrahydrofuran was stored over potassium hydroxide and distilled immediately before use from lithium aluminum hydride. Dioxane, dimethoxymethane, 1,2-dimethoxyethane, and diethyl ether were distilled from sodium. Dimethyl sulfoxide was treated with molecular sieves and then vacuum distilled. Carbon tetrachloride was of reagent quality and stored in dark bottles.

Indoles. With two exceptions noted below the indoles used in this study were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. Indole, mp 52–53° (lit.[66] 52–53°), 2-methylindole, mp 59–61° (lit.[67] 62°), 3-methylindole, mp 94–96° (lit.[67] 96.5°), 7-methylindole, mp 81–83° (lit.[67] 85°), and 2,7-dimethylindole, mp picrate 154–155° (lit.[67] 156.5°), were used without further purification. 5-Methylindole, mp 58–60° (lit.[67] 59.5°), and 2,5-dimethylindole, mp 114–115° (lit.[67] 115°), were sublimed before use. 1-Methylindole was prepared by the method of Potts and Saxton[68] and purified by elution from a neutral alumina column with high-boiling petroleum ether (bp 60–90°). 2,6-Dimethylindole was prepared by the method of Marion and Oldfield[67] and purified by sublimation, mp 85–86° (lit.[67] 88.5°), mp picrate 137–138° (lit.[67] 138.5°).

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Nuclear Magnetic Resonance Studies of Diquat, Paraquat, and Their Charge-Transfer Complexes[1]

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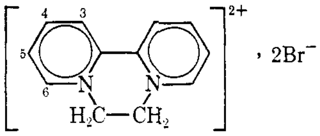
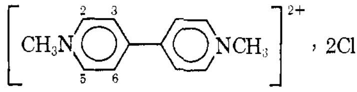
Abstract: The proton magnetic resonance spectra of two quaternary pyridinium salts, diquat (I) and paraquat (II), in D_2O solution have been reported. A complete analysis of the spectra has been carried out, and the coupling constants and the chemical shifts for various protons are reported. These studies have indicated a strong tendency for ion association of these cations with electron-donating anions. Iodide and ferrocyanide ions form charge-transfer-type complexes with diquat and paraquat, while ferricyanide ions form an outer-sphere-type ion pair. The association constant for the ion association has been measured using nuclear magnetic resonance and absorption spectrophotometry. The results obtained by the two methods are in good agreement.

Diquat (I) and paraquat (II), also known by the name viologens, are employed as herbicides.[3] In solution they form free radicals, either by the action of sunlight or by the presence of reducing agents. They also form charge-transfer complexes in the presence of various anions. The formation of free radicals and charge-transfer complexes plays an important role in determining their biological activity.[4] The electron spin resonance spectra[5,6] of the diquat and paraquat free radicals and a preliminary investigation of the charge-transfer complexes of paraquat and potassium ferrocyanide have been reported.[7] In this paper we



(I)
diquat



(II)
paraquat

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(1) (a) Research supported by U. S. Public Health Service Grant No. EH-00040-04. (b) Presented in part at the 23rd Northwest Regional Meeting of the Amerian Chemical Society, Portland, Ore., 1968.
(2) (a) Oregon State University. (b) To whom reprints request should be made. (c) Varian Associates.
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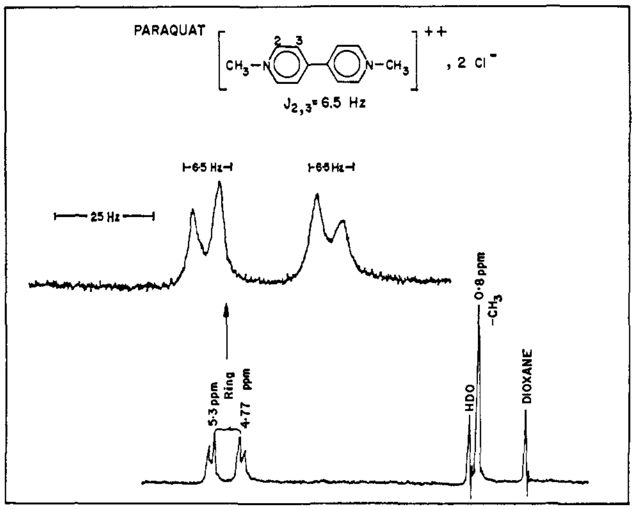

Figure 1. Proton magnetic resonance spectrum of paraquat in D_2O at 60 MHz (dioxane internal standard).

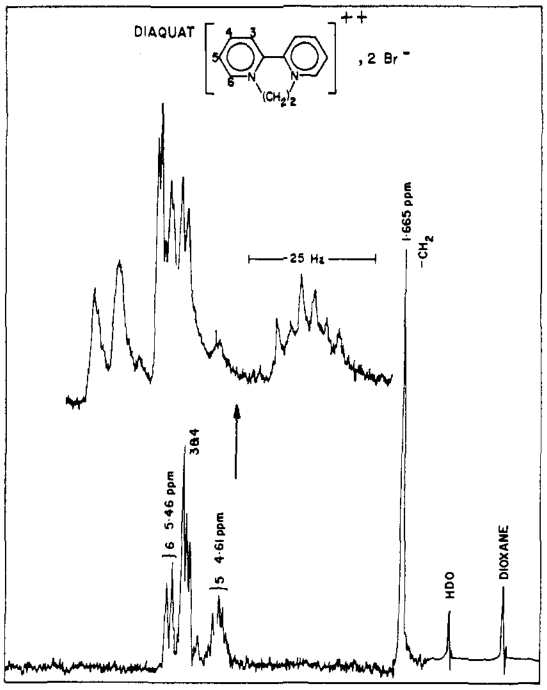

Figure 2. Proton magnetic resonance spectrum of diquat in D_2O at 60 MHz (dioxane internal standard).

shall present data on the proton magnetic resonance and absorption spectra of diquat and paraquat and their charge-transfer complexes. Some work also is reported on the charge-transfer complexes using absorption spectrophotometry.

Experimental Section

Materials. Reagent grade diquat and paraquat were supplied by Chevron Chemical Company, Richmond, Calif. Other chemicals employed also were of reagent grade. Salt solutions of known concentration were prepared in either D_2O or H_2O.

Apparatus and Technique. Nuclear magnetic resonance (nmr) spectra were recorded using a Varian A-60 spectrometer. Chemical shifts were measured using dioxane as an internal standard and were accurate to ±0.1 Hz. A 220-MHz spectrum diquat, recorded on a Varian HR-220 spectrometer, was used to analyze the ring proton region of the spectrum. Some nmr measurements and spin decoupling experiments were also carried out using a Varian HA-100 spectrometer.

Absorption measurements in the ultraviolet and visible region were performed on a Cary Model 11 spectrophotometer.

Results and Discussion

Analysis of the Spectra. The nmr spectra of diquat and paraquat in D_2O are shown in Figures 1 and 2. One common feature of the spectrum of both compounds is that the lines are relatively broad. The $-CH_3$ protons in paraquat and the $-CH_2$ protons in diquat could be readily assigned. These peaks are at 0.80 and 1.67 ppm, respectively, low field from internal dioxane as standard. Broadening of the lines in the nmr spectra of diquat and paraquat probably is caused partly by the presence of the quadrupole moment in the ^{14}N nucleus[8] and partly due to long-range spin coupling between the protons in the N-methyl and NCH_2 groups and the aromatic protons. The ring proton spectrum of paraquat gives two broad doublets of equal spacing at 5.30 and 4.77 ppm, respectively, from internal dioxane as standard. This indicates that there are two sets of equivalent ring protons (protons 2,6 and 3,5). The presence of an NCH_3 group and the couplings $|J_{N-H}|$ and J_{CH_3-H} should cause a broadening in the multiplet corresponding to protons 2 and 6. Protons 3 and 5 should be at low field due to the presence of the aromatic ring at position 4. Since the multiplet at 4.77 ppm is broader than the one at 5.30 ppm we may then assign the multiplets at 4.77 and 5.3 ppm to protons 2,6 and 3,5, respectively. The splitting is approximately equal to the coupling constant $|J_{2,3}| = 6.5$ Hz. This can be compared to the value of 5.96 Hz for aqueous pyridinium ion[9] (99% protonated pyridine). The line widths were too broad to show observable splittings due to 2,5 or 3,6 coupling.

The ring proton spectrum of diquat was more complex. From the structure of the compound one should expect four different sets of peaks. The 60-MHz spectrum (Figure 2) shows a doublet at 5.46 ppm, a six-line pattern at 4.60 ppm, and a complex pattern between these two lines. The doublet at 5.46 ppm may be assigned to the proton 6 and the six-line pattern to proton 5 by analogy to the spectrum of 2,2′-bipyridine.[10,11] The remaining lines are due to protons 3 and 4. It has been suggested that the proton 3 position is more susceptible to the environment than the other[11] and consequently there is a considerable overlap between the lines due to protons 3 and 4. However, the proton magnetic resonance spectrum at 220 MHz completely separated these two multiplets (Figure 3). The complete spectrum at 220 MHz is very similar in shape to that of 2,2′-bipyridine[10] and the proton spectrum due to protons 3 and 4 shows a doublet which further splits into two lines and triplet which again splits into two. The doublet then can be assigned to proton 3 and the triplet to proton 4.

The coupling constants between two protons adjacent to carbon atoms should be much greater than for remote protons. Hence, one should expect the principal splittings to be a doublet for protons 6 and 3 and a

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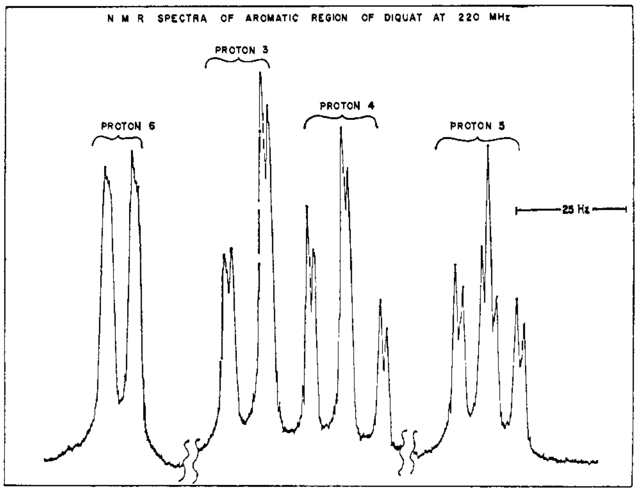

Figure 3. Proton magnetic resonance spectrum (ring proton) of diquat at 220 MHz.

triplet or quartet (depending on the coupling constant magnitude) for protons 4 and 5. The doublet due to proton 6 gives a coupling constant $|J_{5,6}| = 5.0$ Hz; the doublet due to proton 3 gives $|J_{3,4}| = 7.5$ Hz. This accounts for all the principal coupling constants.

This nmr assignment is confirmed further by the spin-decoupling experiment. By irradiating proton 6 the six-line pattern of proton 5 collapses to two lines. Similarly, by irradiating proton 5 the doublet of proton 6 collapses to a singlet. The origin of all the splittings is shown in Figure 4, and the values of various coupling constants and chemical shifts are summarized as follows: $|J_{3,4}| = 8.0$ Hz, $|J_{5,6}| = 6.0$ Hz, $|J_{4,5}| = 7.5$ Hz, $|J_{3,5}| = 1.5$ Hz, $|J_{4,6}| = 1.25$ Hz; δCH_2 1.67 ppm, $\delta 5$ 4.61 ppm, $\delta 6$ 5.46 ppm, $\delta 3$ 5.223 ppm, $\delta 4$ 5.127 ppm.

Ion Association and Formation of Charge-Transfer Complexes. During the course of investigation it was noticed that the color of diquat or paraquat solution depended on the nature of the anion present in the solution. For example, Cl^- ion gave a colorless solution, while the solutions were light yellow, yellow, and dark blue in the presence of Br^-, I^-, and $Fe(CN)_6{}^{4-}$ ions, respectively. Early studies of Nakahara and Wang[7] indicated that paraquat showed distinct changes in the absorption maximum in the presence of various anions. Chloride ion gave maxima at 260 and 377 mμ; bromide gave maxima at 265 and 387 mμ; and iodide gave maxima at 277, 285, and 575 mμ. In contrast ferrocyanide, with a deep purple color, showed a distinct peak at about 600 mμ. Since neither the paraquat nor the iodide or ferrocyanide ions give any appreciable absorption in this region, the absorption at the longer wavelengths was attributed to formation of charge-transfer complexes. Formation of the charge-transfer complex is favored by the ability of diquat and paraquat to serve as good electron acceptors.[3] Since iodide and ferrocyanide ions are good electron donors, they form charge-transfer complexes through ion association with diquat and paraquat.

The studies of Nakahara and Wang[7] showed that two types of complexes were formed in a mixture of paraquat and ferrocyanide. A 1:1 complex of paraquat and ferrocyanide was the main species, while at higher concentrations of paraquat, a 2:1 complex formation was achieved. In the present study, diquat also formed distinct charge-transfer bands in the presence of I^- and $Fe(CN)_6{}^{4-}$ ions. No charge-transfer bands were noticed with the paramagnetic ferricyanide ion.

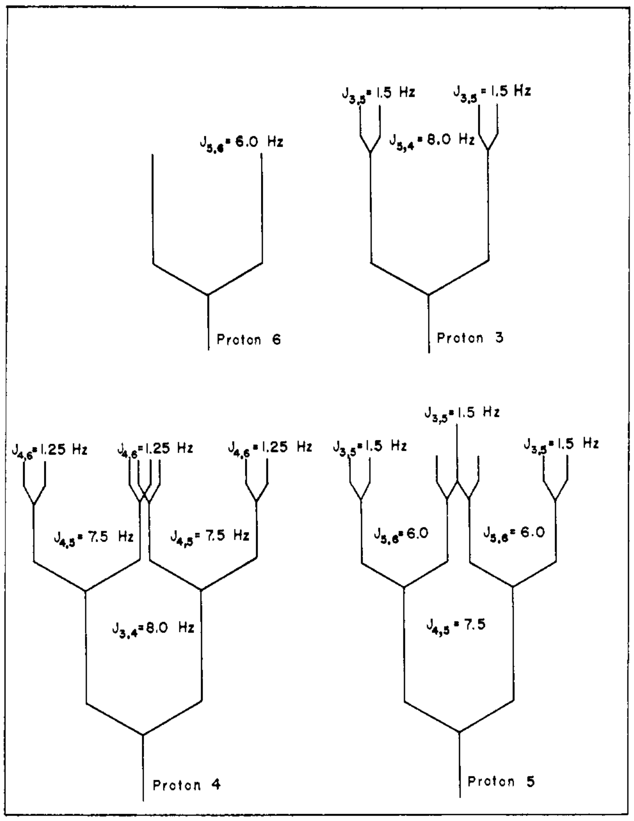

Figure 4. Diagram showing spin–spin splitting patterns of the ring protons in diquat.

We have been able to calculate the equilibrium constant for the diquat–ferrocyanide complex using absorption data. The absorption spectra of ferrocyanide-diquat charge-transfer complex is shown in Figure 5. The absorption peak is broad and shows a maximum at 575 mμ for all molar ratio solutions. The composition of the ferrocyanide–diquat charge-transfer complex was found to be a 1:1 ratio by the method of continuous variation (Figure 5).

Equilibrium in the above system could be represented as

$$C^{2+}(H_2O)_x + A^{-n}(H_2O)_y \rightleftharpoons C^{2+}(H_2O)_zA^{-n} \qquad (1)$$

where x and y are the hydration number of the cation and the anion, respectively; z is the number of water layers present between the anion and the cation during the ion association (in the case of ferrocyanide charge-transfer complex $z = 0$, since we assume that there is direct interaction between the cation and the anion), C is the cation, A represents the anion; and n is the valency of the anion (in ferrocyanide case $n = 4$). Therefore, equilibrium for ferrocyanide–diquat complexes may be written as

$$C^{2+} + A^{4-} \overset{K_1}{\rightleftharpoons} CA^{2-} \qquad (2)$$

where K_1 represents the equilibrium constant for the 1:1 charge-transfer complex. This also could be

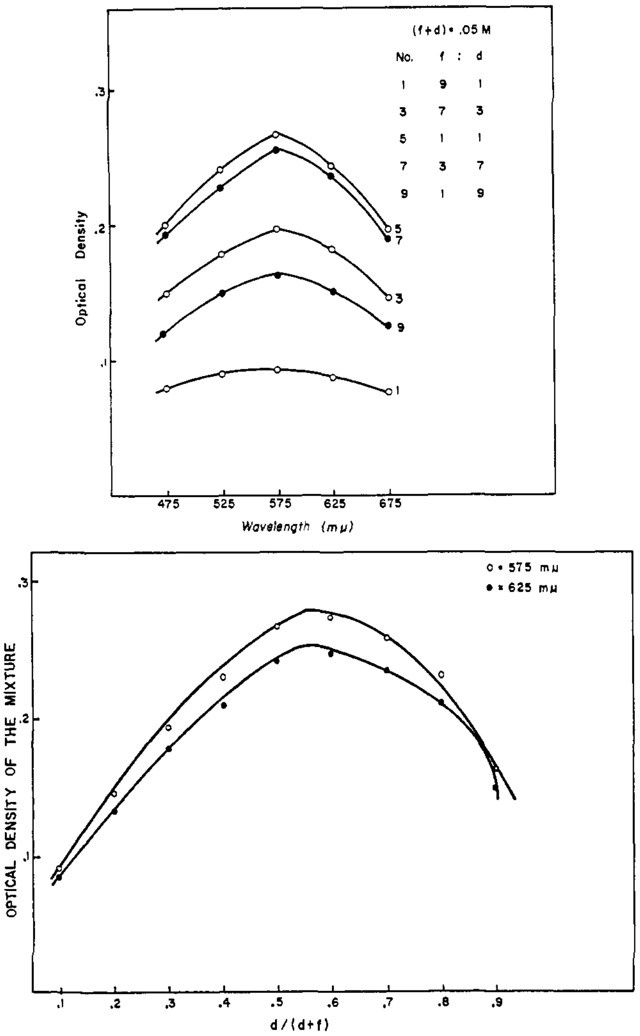

Figure 5. (a, top) Absorption spectra of diquat-ferrocyanide charge-transfer complex. (b, bottom) Graph showing 1:1 molar ratio for diquat-ferrocyanide complex using the method of continuous variation.

represented by the well-known Benesi and Hildebrand equation[12] as

$$\frac{fl}{(\mathrm{OD})} = \frac{1}{\epsilon}\left(1 + \frac{1}{K_1 d}\right) \tag{3}$$

where OD is the optical density of the complex, ϵ is the extinction coefficient, f and d are the concentrations of ferrocyanide and diquat, respectively, and l is the path length of the cell. It has been assumed that the concentration of the complex is negligible as compared to the concentration of the reactants and that K_1 represents the equilibrium in terms of concentration rather than activity. A plot of $f/(\mathrm{OD})$ against $1/d$ gave a resonably straight line. The value of K_1 was determined to be 29 ± 3 mol^{-1} from the slope and intercept of this line. This value is somewhat smaller than that for the paraquat-ferrocyanide complex[7] which is 52 mol^{-1}.

Proton magnetic resonance studied with diquat and paraquat showed strong evidence of ion association. The chemical shift of various protons in diquat and paraquat was influenced by the addition of I^-, $\mathrm{Fe(CN)_6}^{4-}$, and $\mathrm{Fe(CN)_6}^{3-}$ ions. Chemical shift changes for CH_2 and the ring proton (number 6) in diquat and CH_3 and ring protons (number 2 and 3) for paraquat in the presence of increasing concentration of I^-, $\mathrm{Fe(CN)_6}^{4-}$, and $\mathrm{Fe(CN)_6}^{3-}$ ions are shown in Figure 6. It is interesting to note that the presence of I^- and $\mathrm{K_4Fe(CN)_6}^{4-}$ ions causes a small low-field shift while the paramagnetic ferricyanide ions induce a high-field shift. These results can be compared with the work of Larsen and Wahl[13] who observed similar chemical-shift changes for the proton resonance spectrum of tetramethylammonium ion in the presence of I^-, $\mathrm{Fe(CN)_6}^{3-}$, $\mathrm{Fe(CN)_6}^{4-}$ ions. However, the chemical shift changes for ferricyanide ion exhibit some additional

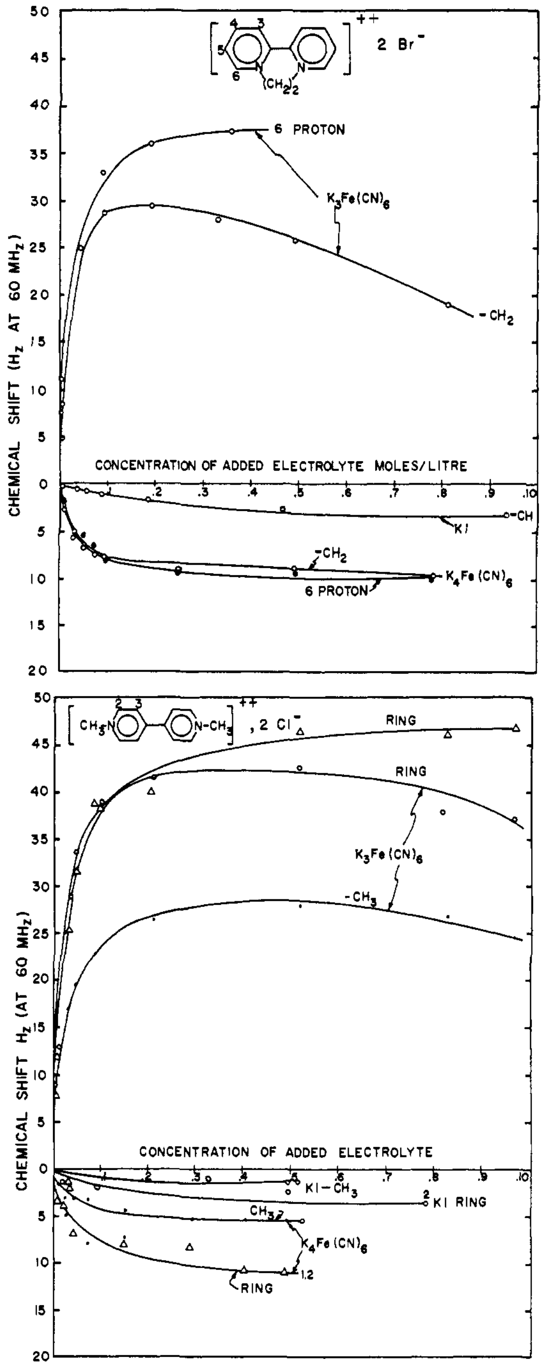

Figure 6. (a, top) Chemical-shift changes for protons in diquat by the addition of various anions. (b, bottom) Chemical-shift changes for protons in paraquat by the addition of various anions.

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features. As may be seen from Figure 6, the chemical shift of $-CH_2$ and $-CH_3$ protons in paraquat and diquat initially increases with increasing ferricyanide concentration. At higher concentration of ferricyanide, however, the chemical shift begins to decrease.

According to equilibrium 1, in these systems two different types of ion association can take place: the outer-sphere-type ion association (when $z > 0$) and the inner sphere type (when $z = 0$). In the inner-sphere ion association there is a direct contact between anion and cation. The presence of a charge-transfer band indicates a direct interaction between I^-, $Fe(CN)_6^{4-}$ ions, and diquat or paraquat cations. Hence, we can conclude that the small low-field shift is due to formation of inner-sphere-type ion pair. During this ion association process there are some changes in the electrical field of the proton in the cation that causes this low-field shift.[14,15]

Paramagnetic ions such as $Fe(CN)_6^{3-}$ can cause two types of chemical-shift changes. One type of shift results from the hyperfine contact interaction[16] arising from the σ overlap of the Fe^{3+} t_{2g} orbital having an unpaired electron with the proton of the cation. This contribution can be expressed as

$$\delta c = A_i \frac{\gamma_e}{\gamma_h} \frac{g\beta(S + 1)}{3kT} \qquad (4)$$

where δc is the chemical shift, A_i the hyperfine interaction constant, γ_e and γ_h the gyromagnetic ratio of the electron and the proton, respectively, S the spin of the electron, β the Bohr magneton, k the Boltzmann constant, and T the absolute temperature. The second type of shift is called the pseudo-contact interaction[17] that arises due to anisotropy in the electronic g tensor, and could be represented as

$$\delta pc = \frac{\beta^2 S(S + 1)(3 \cos^2 X_i - 1)}{27 r_1{}^3 kT} \times (g_{\parallel} + 2g_{\perp})(g_{\parallel} - g_{\perp}) \qquad (5)$$

where r_1 is the distance between the anion and the proton in the cation and X_i is the angle between the radius vector r_1 and the crystal field axis of the paramagnetic anion. The above equation is good only in the cases $Tie \gg \tau$ where Tie is the spin–lattice relaxation time of the electron and τ is the characteristic correlation time of the tumbling motion. However, if $\tau \gg Tie$ the expression for the pseudo-contact term becomes

$$\delta pc = \frac{\beta^2 S(S + 1)(3 \cos^2 X_i - 1)}{45 r_1{}^3 kT} \times (3g_{\parallel}{}^2 - g_{\parallel} g_{\perp} + 4g_{\perp}{}^2) \qquad (6)$$

The higher field shift obtained in the proton magnetic resonance spectra of diquat and paraquat in the presence of ferricyanide ion can be explained in terms of pseudo-contact interaction. We believe that during the ion-association process there are always a few water molecules present between the ferricyanide ion and the cation. Consequently, there is little direct interaction between the cation and the anion. In such a scheme, the hyperfine interaction term which contributes toward the chemical shift is very small. However, Larsen and Wahl,[13] LaMar,[18] and Walker and Drago[19] have also explained that during several ion-association processes the contribution due to hyperfine contact term is small when a paramagnetic ion is present. The question then arises why does the chemical shift begin to decrease after a certain concentration of diquat or paraquat is reached? A decrease in the chemical shift might be explained by assuming that at higher concentrations there is formation of some inner-sphere-type ion pairs. Consequently, as the concentration of ferricyanide ion increases, the contribution of the hyperfine interaction (which is opposite in sign) due to the direct interaction of cations and anions also increases, causing the chemical shift to decrease.

Chemical shift data also can be used to calculate the equilibrium constant K_1 for the ion association. Since chemical-shift changes were measured for a very dilute solution of diquat or paraquat as compared to the anion, it could be assumed that a 1:1 complex is the dominant species in the solution. The observed chemical shift δo, therefore, can be represented as an average of the chemical shifts of the ion pair δp and the free cation $\delta \alpha$ as

$$\delta o = \frac{[C^{2+}]}{[C^{2+} + CA^{-n+2}]}\delta\alpha + \frac{[CA^{-n+2}]}{[C^{2+} + CA^{-n+2}]} \qquad (7)$$

If we assume that the concentration of $CA^{-n+2} \ll A^{-n}$ or C^{2+}, which seems reasonable because low concentrations of diquat or paraquat have been employed, eq 8 could be derived.[20] Hence, from the

$$\frac{[A^{-n}]}{(\delta o - \delta\alpha)} = \frac{[A^{-n}]}{(\delta p - \delta\alpha)} + \frac{1}{K_1(\delta p - \delta\alpha)} \qquad (8)$$

intercept and slope of the line obtained by plotting $[A^{-n}]/(\delta o - \delta\alpha)$ against $[A^{-n}]$, K_1 and $(\delta p - \delta\alpha)$ can be obtained. The K_1 obtained by the above method is in terms of concentration rather than activity. We have neglected the concentration of the ion pair formed by the anion and its salt, *i.e.*, $K^+Fe(CN)_6^{4-}$, $K^+Fe(CN)_6^{3-}$, K^+I^- as compared to the main ion-pair complex. Further, in the evaluation of K_1 for the ferricyanide complex only the chemical shift values at the initial concentration are used. The values of K_1 and δp obtained in this manner are given in Table I. The small chemical shift observed for the I^- ion prevented the

Table I. Association Constant and Chemical Shift for the Ion Pair for Various Systems

System	Association Constant, K_1, mol^{-1} Nmr	Association Constant, K_1, mol^{-1} Absorption	Chemical Shift $(\delta p - \delta\alpha)$ of ring proton, Hz
Diquat + $K_3Fe(CN)_6$	29		+38
Diquat + $K_4Fe(CN)_6$	37	30	−11
Paraquat + $K_3Fe(CN)_6$	31		+37
Paraquat + $K_4Fe(CN)_6$	57	52[a]	−8

[a] See ref 7.

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calculation of K_1 for the iodide charge-transfer complex.

Values of K_1 determined on a basis of chemical shift are only accurate to ±20%. The K_1 for the ferrocyanide charge-transfer complex, however, has been determined from both absorbancy and nmr data and the results have been found to be in good agreement (Table I).

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Stereochemistry of Trityl Compounds. V. Resolution of Phenylbiphenylyl-α-naphthylcarbinol[1,2]

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Abstract: A new method has been developed for the resolution of (+)- and (−)-phenylbiphenylyl-α-naphthylcarbinol. The alcohols had been partially resolved by Wallis.[8] (±)-Ar_3COH was converted to (±)-$\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$ by alkylation of ethyl glycolate with Ar_3CCl followed by saponification. (−)-$\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$ was separated as the brucine salt and (+)-$\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$ was separated as the cinchonidine salt. Each enantiomeric acid was converted to the corresponding amide by aminolysis of its methyl ester. The usual medium for the Hofmann rearrangement (bromine in methanolic sodium methoxide) was shown to cleave the trityl ether linkage of the amide affording trityl methyl ether. However, treatment of the N-haloamide, $\text{Ar}_3\text{COCH}_2\text{CONHCl}$, previously prepared in benzene using *t*-butyl hypochlorite, with methanolic sodium methoxide led to Hofmann rearrangement. The expected carbamate was cleaved under the reaction conditions to Ar_3COH. (−)-$\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$ gave optically pure (+)-Ar_3COH and (+)-$\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$ gave optically pure (−)-Ar_3COH. The C–O bond at the asymmetric center remained intact throughout the degradation procedure. Wallis' resolution was repeated and shown to have an optical yield of *ca.* 60%. His product was brought to optical purity by fractional crystallization. An attempted resolution of phenyl-*p*-chlorophenylbiphenylylcarbinol according to the new method was unsuccessful.

Preliminary to stereochemical studies of the mechanisms of substitution of trityl (triarylmethyl) derivatives, it was desirable to have a source of an optically pure triarylcarbinol. Satisfactory methods of resolution have been reported for all types of alkyl and arylalkyl secondary[4,5] and tertiary[6,7] carbinols except for the triarylcarbinols.[8,9] Wallis[8] obtained (+)-phenylbiphenylyl-α-naphthylcarbinol [(+)-Ar_3COH] by treating (−)-phenylbiphenylyl-α-naphthylmethylthioglycolic acid [(−)-$\text{Ar}_3\text{CSCH}_2\text{CO}_2\text{H}$] with silver nitrate in aqueous acetone (reaction 1). Although no experimental evidence was available regarding the optical purity of (+)-Ar_3COH, Wallis' method was termed unsatisfactory,[4] probably because the method entailed a cleavage reaction of unknown stereospecificity at the asymmetric center.

$$(-)\text{-Ar}_3\text{CSCH}_2\text{CO}_2\text{H} + \text{AgNO}_3 \xrightarrow[\text{acetone}]{66\%} (+)\text{-Ar}_3\text{COH} \quad (1)$$

Most alcohol resolutions have depended on fractional crystallization of a mixture of diastereomeric amine salts of the hemiphthalate ester.[5] Kenyon's early attempt to resolve a trityl alcohol failed because the hemiphthalate ester could not be prepared.[10] This problem has now been solved.[11] More recently, an effort was made to prepare an optically active trityl alcohol by nitrous acid deamination of the corresponding amine.[10] The product showed no optical activity. After our work was in progress, Thaker and Dave reported the resolution of phenyl-*p*-tolyl-α-naphthylcarbinol by the hemiphthalate method.[12]

Because disproportionation of hemiphthalate salts is a known complication in alcohol resolutions[5] and because the trityl ester linkage is known to be labile,[13] we decided to employ the more stable ether linkage at the asymmetric center. The simplest such compound for the formation of diastereomeric amine salts is an ether of glycolic acid, $\text{Ar}_3\text{COCH}_2\text{CO}_2\text{H}$. This type of compound was attractive because it appeared possible to use the Hofmann rearrangement[14] to convert the amide of

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(2) These results were reported in preliminary form: B. L. Murr, *J. Am. Chem. Soc.*, **85**, 2866 (1963). For the preceeding paper in this series see B. L. Murr and L. W. Feller, *ibid.*, **90**, 2966 (1968).

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