the ground configuration with locally excited configurations, which have bearing on the origin of the dispersion force. Naturally it is probable that the binding energy due to the dispersion force can be larger than the binding energy associated with the charge-transfer interaction. But we must consider that the contribution of the charge-transfer interaction is of significant importance in the intermolecular binding, at least in the case of TCNE complexes of naphthalene and pyrene, if the binding energy due to the charge-transfer interaction is about 6 kcal/mole as theoretically estimated in the present study.

Studies on Complexes. XII. Charge-Transfer Interactions of Aromatic Hydrocarbon and Azahydrocarbon Acceptors[1]

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Abstract: The strong donor properties of tetrakis(dimethylamino)ethylene (TMAE) are determined by its interactions with π acceptors. Colors of *n*-hexane solutions of this donor with pyrene, anthracene, and perylene are ascribed to intermolecular charge-transfer transitions, where the hydrocarbons function as electron acceptors. Azahydrocarbons similarly produce colors and are stronger acceptors. All association constants for complex formation with the tetraaminoethylene are close to zero, and this is ascribed to the bulk of the TMAE molecule. From these studies and from the published literature, a "perpendicular with a wobble" structure is proposed for TMAE, in which thermally accessible vibrations of the $(CH_3)_2N$ groups occur about a position perpendicular to the $N_2C{=}CN_2$ plane. An earlier proposal that a charge-transfer interaction occurs between the methylbenzenes and anthracene is reinterpreted.

A well-established property of the aromatic hydrocarbons is their Lewis base or electron donor character. As a criterion of this donor strength, their ionization potentials,[2,3] particularly for the highly condensed members, appear low within the series of the numerous measurements[3] for neutral organic molecules. Properties associated with low ionization potentials (I_d), they also exhibit; thus they may be oxidized electrochemically with moderate ease,[4] and they function as strong donors in forming molecular complexes. On oxidation they yield radical cations[5] and they are chemically reactive toward acceptor molecules.

A theoretical rationalization of this donor character comes from the energies of the highest filled π-molecular orbitals, which correspond at least approximately to ionization potentials. On the other hand, from the energies of their lowest unfilled orbitals, which correspond to electron affinities (E_a), weak electron-accepting properties have been predicted. Thus increases in electron affinities with decreasing ionization potential have been proposed[6] so that the sum $I_d + E_a$ is a constant. Moreover, it has been suggested[7] that I_d and E_a expressed as dependencies of the energy of the lowest transitions should be symmetrical about the work function for graphite.

Evidence for accepting properties comes from polarographic reduction potentials[8] and the detection of radical anions.[5,9] Gas-phase, electron-scavenging experiments have been reported in direct, pioneering measurements of electron affinities.[10]

Neutral acceptor–donor interaction as spectral evidence of hydrocarbon acceptor properties has not been presented,[11] and the conclusions of the one study[12] in this area on complexes of condensed aromatics such as anthracene with the methylbenzenes is criticized below.

The energy $h\nu_{CT}$ of the maximum of the charge-transfer transition has been related[13] to a donor ionization

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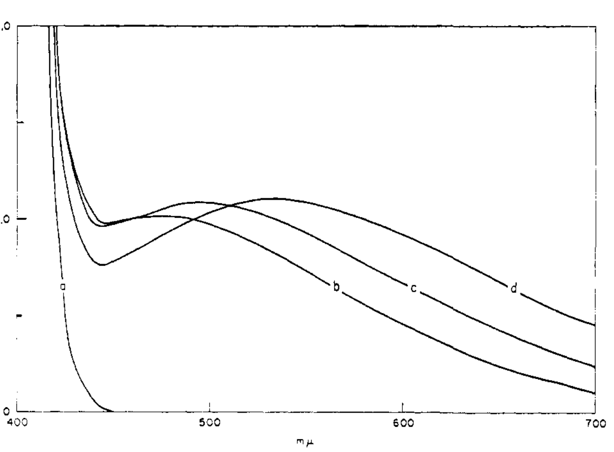


Figure 1. Spectra of TMAE–nitrobenzene systems in *n*-hexane. Absorptions of 1-cm cells of 1.00 *M* TMAE: a, alone; b, with 0.0198 *M* *p*-nitroanisole; c, with 0.0231 *M* nitrobenzene; and d, with 0.0203 *M* *p*-chloronitrobenzene.

potential I_d and an acceptor electron affinity E_a by the proposed relation

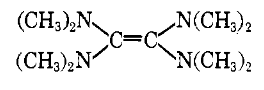
$$h\nu_{CT} = I_d - E_a + G_1 - G_0 + X_1 - X_0 \qquad (1)$$

G_1 and G_0 are the interaction energies between donor and acceptor in the dative state and in the ground state, and $X_1 - X_0$ is the resonance energy of interaction between the two states. For consideration of a series of closely related compounds, eq 1 can be simplified to

$$h\nu_{CT} = I_d - E_a + \text{constant} \qquad (2)$$

although such an expression should have its limitations.[13] It is sufficient for the present purposes that detectable transitions with the weak acceptor hydrocarbons should be expected only with a donor of very low ionization potential.

Candidates for such a donor are the peraminoethylenes as tetrakis(dimethylamino)ethylene (TMAE) (I) and bis(1,3-diethylimidazolinylidene-2) (II), and indeed *n*-hexane solutions of naphthalene, phenanthrene, triphenylene, pyrene, anthracene, and perylene with TMAE were found to be yellow. As a measure of its donor strength, the polarographic oxidation potential[14] of TMAE in acetonitrile containing 0.1 *M* tetraalkylammonium perchlorate is −0.75 v, which may be compared[15] with the quite strong donors N,N,N′,N′-tetramethyl-*p*-phenylenediamine at 0.06 v, and dimethylaniline at 0.69 v. Colored solutions, arising presumably from acceptor–donor interactions, have been reported for TMAE with acrylonitrile[18] (orange), nitrobenzene[18] (violet), dichloromethane[19] (yellow), chloroform[19] (orange), and carbon tetrachloride[19] (red). Absorption of an oxygen–TMAE system[20] occurs at 450 mμ and a mixture with hexafluorobenzene is red. On the other hand, complexes with the common electron acceptors tetracyanoethylene[21] and *sym*-trinitrobenzene[18] are paramagnetic and unstable.



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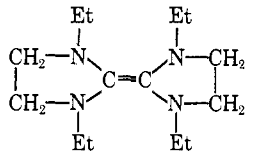

II

In this article, interactions of TMAE with the *para*-substituted nitrobenzenes, as examples of weak but customary acceptors, are first examined to clarify the complexing properties of the base. The colors with pyrene, anthracene, and perylene are examined more closely and are compared with the azahydrocarbons pyridine, pyrazine, acridine, and phenazine. Interactions of donor II are also examined.

Experimental Section

The source and the handling of the highly reactive TMAE have been described elsewhere.[20] A small sample of bis(1,3-diethylimidazolinylidene-2), also from the Du Pont Central Research Department, had deteriorated slightly during repeated laboratory use. Precautions in its handling were identical with those for TMAE, and only the most certain experimental results for this compound are reported.

Matheson Coleman and Bell Spectroquality Reagent *n*-hexane was used throughout as a solvent system. This was left overnight in contact with freshly dried molecular sieve 4A and was decanted, distilled, and stored prior to use in polythene, sealed, screw-capped bottles. Dry nitrogen was bubbled through the solvent for 2 hr, and the system was equilibrated in a nitrogen drybox atmosphere for at least 2 days. All runs were prepared from 500 ml of 1 *M* TMAE from a stock solution. Preparation of this stock sample, when there was a briefer deaeration and no initial equilibration in the drybox, produced a just noticeable deepening of the yellow of the solution compared with the base itself, and after 1 hr this became turbid and slowly cleared to the original TMAE color by depositing a small amount of precipitate.

Good commercial samples of pyrazine, *s*-triazine, *p*-nitrotoluene, *p*-fluoronitrobenzene, and *p*-bromonitrobenzene were used without further purification, apart from the equilibration of the pyrazine sample with the atmosphere of the drybox. Pyrene, anthracene, and phenazine were crystallized twice from ethanol; *p*-chloronitrobenzene and acridine, twice from ethanol water; *p*-nitroanisole, twice from methanol-water; and perylene, twice from benzene. All compounds had melting points and analyses, where examined, in accordance with literature values. Good commercial grades of nitrobenzenes and pyridine were distilled, the latter after it had stood over molecular sieve 4A overnight.

Initial examinations were performed in test tubes open to the atmosphere, using a 1 *M* TMAE solution stored under nitrogen. Under this condition the colors of solutions deteriorated in about a day. Solutions for final runs were prepared in the drybox and were conveyed directly to 1- or 5-cm cells. Tests were made on blank absorptions of the cells, the stability of sealed TMAE samples they contained, and on the applicability of the Beer–Lambert law to the base solutions. Small corrections, where necessary, were applied for the cell absorptions, and the solutions were found to be stable. Deviations from the law, if any, were not sufficient to interfere with experiment, although a precise examination at the concentrations used was difficult, because of the steepness of the base absorption. Unit activity coefficients were assumed for all solutions. If deviations did occur, they were not apparent from the plots.

All spectra were measured in a Cary Model 11 spectrophotometer mainly on the 0–1 absorbance scale, at an ambient temperature of 24 ± 1°. Accuracy is considered to be limited by readout and by the precision of setting the scale to zero. The latter was checked repeatedly throughout the experiment. The results were processed by means of a weighted least-squares analysis based on the assumption that the variance in the absorbance was a constant, independent of A. For plots as shown in Figure 3 below, the weights of the points were thus in the ratio A^4.

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(14) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964).

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(16) A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4130 (1964).

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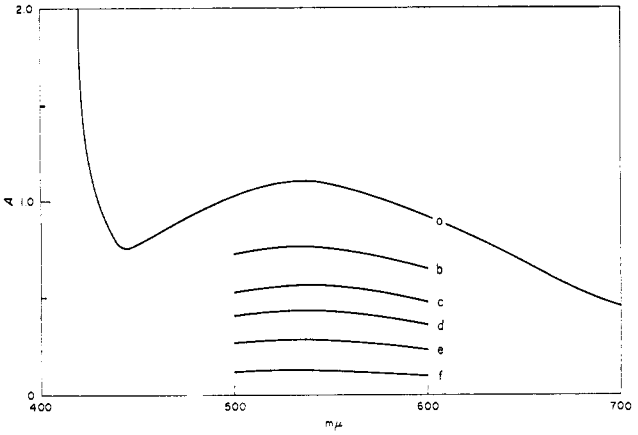

Figure 2. Effect of dilution on spectra. Absorptions of 1-cm cells of 1.00 *M* TMAE with 0.0231 *M* *p*-chloronitobenzene at dilutions a, 1.0; b, 1.2; c, 1.4; d, 1.6; e, 2.0; and f, 3.0.

Results

Of a number of TMAE systems examined, those acceptors producing spectra sufficiently stable for a 3-hr experiment are presented here. Indeed the colors of the solutions of Figures 1 and 5–8, as well as those of donor II, were stable under nitrogen in diffuse daylight for at least 2 months.

A series of *para*-substituted nitrobenzenes were tested by adding a 1.00 *M* TMAE solution stored under nitrogen to the compound open to the atmosphere. Absorption maxima are shown in Table I together with the stabilities. On this basis, the spectra as displayed in Figure 1 of the red, magenta, and violet colors with nitroanisole, nitrobenzene, and chloronitrobenzene, respectively, were examined more closely. For example, Figure 2 shows the TMAE chloronitrobenzene absorption together with the changes produced by successive dilutions. Of particular note, when the volume of the solution was doubled, the absorbance decreased to a quarter of its original value, whereas when the volume was trebled it decreased to a ninth.

Table I. Absorption Maxima of TMAE with *p*-Nitrobenzenes in *n*-Hexane at 25°

Substituent	Absorption, mμ	Stability[a]
Methoxy	474	S
Methyl	482	U
Hydrogen	493	S
Fluoro	511	U
Chloro	533	S
Bromo	536	S

[a] U, unstable, 10% or more change in the maximum within 10 min; S, stable.

The plots of Figure 3 are based on a rearrangement of an equation proposed by Cilento and Sanioto[22]

$$\frac{1}{vA} = \frac{v}{Km_a m_d \epsilon} + \frac{1}{m_a \epsilon} \tag{3}$$

Here, m_a and m_d are the number of gram moles of acceptor and donor, respectively ($m_d >> m_a$), dissolved in volume v liters, to give an absorbance A at the absorption maximum, for a 1-cm light path (v and A variables). K and ϵ are the association constant and molar absorptivity, respectively, for complex formation. The lines of the data (weighted by A^4) shown in the plots are given in Table II. Also shown are estimates of the K values and a measure of the reliability of the lines. The acridine plots were obtained from the spectra shown in Figure 4.

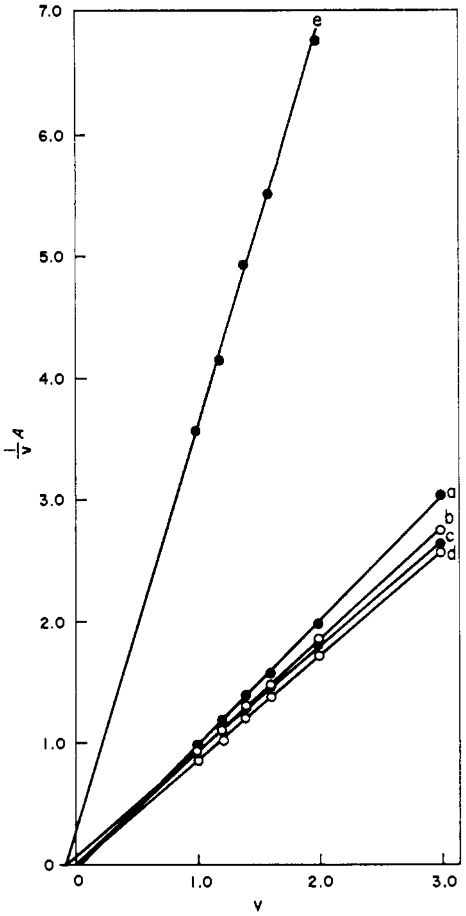

Figure 3. Dilution plots of the absorption maxima for 1-cm cells of TMAE with a, *p*-nitroanisole; b, nitrobenzene; c, *p*-chloronitrobenzene at the initial concentrations of Figure 1; and d, with acridine at the concentrations of Figure 4. (e) Plot for 5-cm cells for the system of initial concentration of 1.00 *M* TMAE with 1.98 × 10^{-3} *M* phenazine.

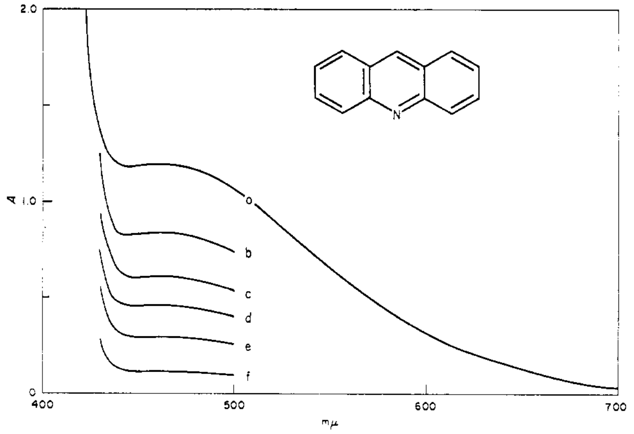

Figure 4. Absorption of 1-cm cells of 1.00 *M* TMAE with 0.020 *M* acridine at dilutions a, 1.0; b, 1.2; c, 1.4; d, 1.6; e, 2.0; and f, 3.0.

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(22) G. Cilento and D. L. Sanioto, *Z. Physik. Chem.* (Leipzig), **223**, 333 (1963).

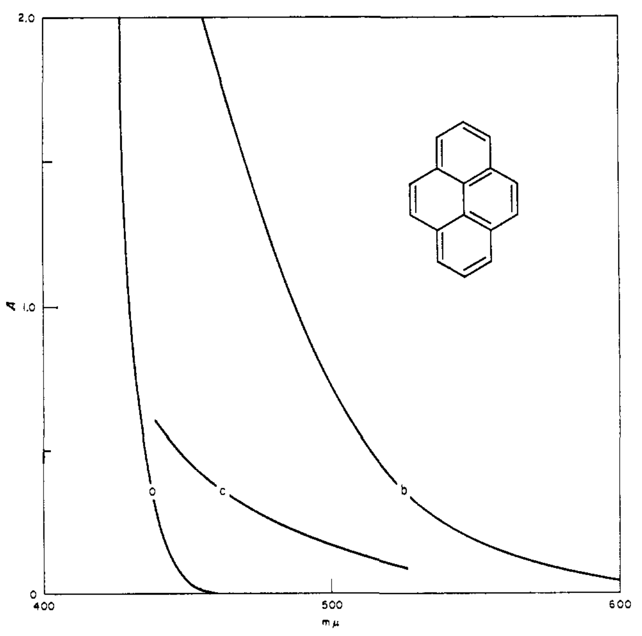

Figure 5. TMAE–pyrene system in *n*-hexane. Absorption of 5-cm cells of a, 1.00 *M* TMAE; b, with 0.0101 *M* pyrene; c, solution b at dilution 2.2.

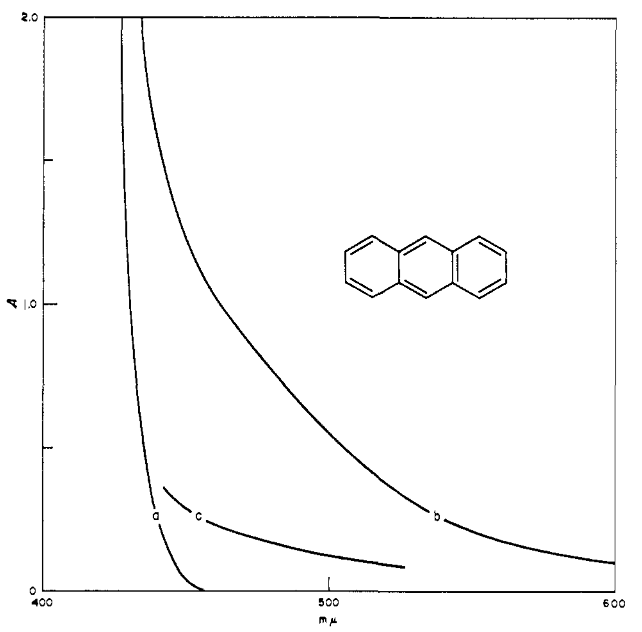

Figure 6. TMAE–anthracene system in *n*-hexane. Absorption of 5-cm cells of a, 1.00 *M* TMAE; b with 4.15 × 10^{-3} *M* anthracene; c, solution b at dilution 2.2.

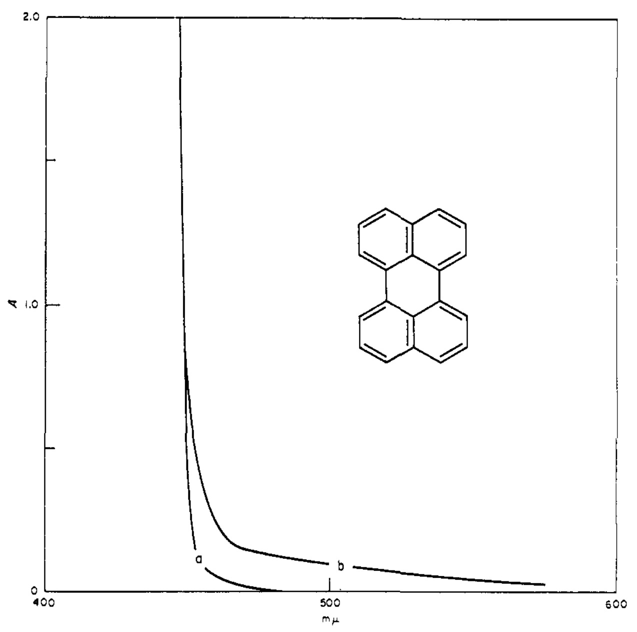

Figure 7. TMAE–perylene system in *n*-hexane. Absorption of 5-cm cells of a, 1.67 × 10^{-4} *M* perylene; b, with 1.00 *M* TMAE.

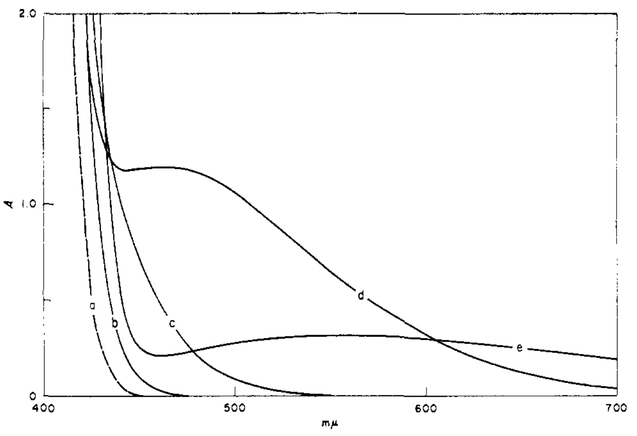

Figure 8. Spectra of TMAE–azahydrocarbon systems in *n*-hexane. Absorption of 1-cm cells of a, 1.00 *M* TMAE; b, 0.92 *M* TMAE with 1.00 *M* pyridine; c, 1.00 *M* with 0.0510 *M* pyrazine; d, 1.00 *M* TMAE with 0.020 *M* acridine; and e, 5-cm cells of 1.00 *M* TMAE with 1.98 × 10^{-3} *M* (phenazine).

The addition of pyrene, anthracene, and perylene to the donor solution produced distinct yellow colors, and these were associated with the spectra of Figures 5–7. In no case were maxima observed, and, because of the strong absorption of the donor below 430 mμ at the high concentrations and long path length of the experiment, a search for such maxima was not attempted. The effect of diluting the pyrene and anthracene solutions is also shown in Figures 5 and 6.

With the azahydrocarbons, TMAE produced pale yellow (pyridine), deep yellow (pyrazine), orange (acridine), and very pale blue (phenazine) solutions. Figure 8 shows the spectra and Figure 3 the absorption changes on dilution. An open-air, test-tube examination of *s*-triazine as an acceptor produced a bright yellow color similar to the pyrazine system but, unlike the latter, deteriorated to a cloudy colorless solution within 10 min.

Table II

	$1/vA$	Association constant,[a] l. mole^{-1}	10^2SD[b]
Nitroanisole	$1.016v - 0.067$	-0.066	2
Nitrobenzene	$0.907v + 0.006$	$+0.007$	1
Chloronitrobenzene	$0.849v + 0.064$	$+0.075$	2
Acridine	$0.853v - 0.019$	-0.022	2
Phenazine	$3.222v + 0.335$	$+0.104$	3

[a] Abscissa intercept calculated from the lines is $-Km_d$, where m_d in each case is 1.00. [b] Weighted, standard deviation of the ordinate residuals to the nearest 0.01.

For systems of sufficient solubility, nitrobenzene, pyrazine, and pyridine, examination of the absorptions for constant combined donor plus acceptor concentrations, but of varying ratios, produced the plots of Figure 9.

The observation[23] that solutions of TMAE with a product of its oxidation,[24] tetramethylurea, are a deeper yellow than the base solution alone is relevant to spectral work on this reactive molecule. A spectrum was observed similar to, but much weaker than, the pyridine system at 1 M concentration of both the base and the urea. On dilution it decreased more rapidly than predicted from Beer's law. Thus a weak charge-transfer absorption is observed even in this system, although its intensity, particularly for the concentrations and oxygen-free conditions of experiment, is certainly too small to interfere with the reported spectra. Moreover, the experimental conditions are likely to preclude contamination by other oxidation products.

Discussion

Stable colors, not present in either component separately, were formed immediately as the solutions were prepared at room temperature. Moreover, they disappeared on dilution much more rapidly than expected for Beer's law. The positions of maximum absorption for the nitrobenzene series followed the substituent constant. The spectra are thus ascribed to charge-transfer transitions, and their wavelengths are rationalized in terms of a TMAE donor molecule of very low ionization potential (about a volt above the ionization potential of sodium) and the relative electron affinities of the other components acting as acceptors. The facts above and the solvent used must preclude significant ion formation.

On the other hand, the small K values, which necessitate high component concentrations to produce color, are unusual. They are all very close to zero and are distributed on either side of the origin. Estimates of ϵ are not quoted. They can be seen from the equations of the lines to have large positive and large negative values.

The significance of small K measurements derived from customary spectrophotometric relations has been criticized.[25] A "conspiracy" of experimental errors obscures the derived K and ϵ values, so that little reliance can be placed upon them. A similar analysis of eq 3 with regard to errors in absorbance measurement alone gives an identical result. A small experimental K should be expected even for an acceptor–donor pair that exhibits no energy of interaction, but can allow charge-transfer transitions between loose, contact partners.[26] For a complex in solution, where competitive solvation of the donor, acceptor, and complex species occurs, an equilibrium study underestimates K, whatever its units of measurement,[27] and even negative values should be possible. The design of the experiment was to employ an inert, neutral solvent, however, and appreciable interactions of n-hexane with the base and with the acceptors are unlikely. This last point will be examined in more detail in later papers.

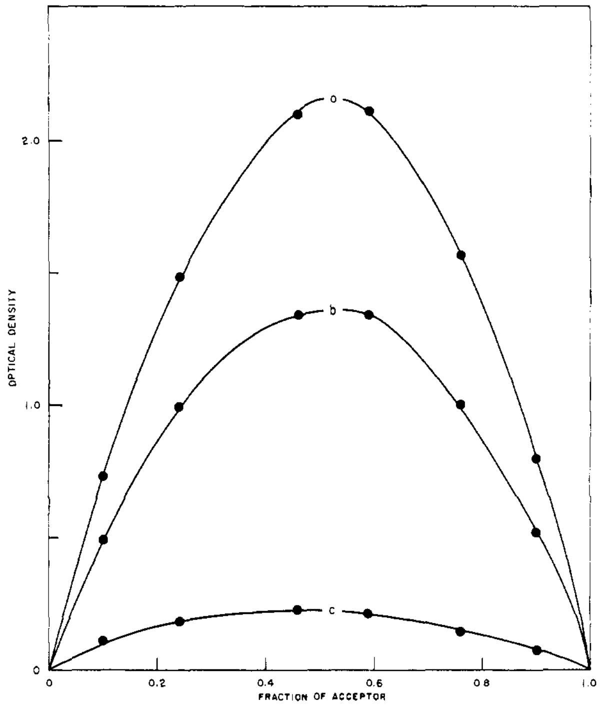

Figure 9. Continuous variation plots for TMAE with a, nitrobenzene at 500 mμ, A + D = 0.4 M; b, pyrazine at 425 mμ, A + D = 0.4 M; c, pyridine at 425 mμ, A + D = 1.00 M. Readings for b and c were in excess of the TMAE absorption.

There is possible evidence that the small positive K values for chloronitrobenzene and phenazine are larger than those for the other acceptors, although the low solubility of phenazine and the associated small absorbances produce an increased data scatter. In terms of this scatter though, none of the equilibrium constants, including the negative, differ significantly from zero. For systems where absorption maxima were absent, the decrease of absorbance on dilution again demonstrates effectively zero K values. Figures 5 and 6 show decreases from 1.32 to 0.27 at 475 mμ for pyrene, and from 1.05 to 0.23 at 460 mμ for anthracene, for a dilution of 2.2. The pyrazine system absorption at 450 mμ decreases from 0.73 to 0.18 when the solution is doubled. The pyridine and perylene systems were not studied accurately, although these too decreased rapidly on dilution.

Hence, it appears that the intensities of the charge-transfer bands arise mainly from contact-pair interactions as described by Mulliken.[28] The continuous variation diagrams of Figure 9 are parabolic and have maxima at equimolar positions, indicating that these absorptions, and hence by implication the others, result from predominantly 1 : 1 interactions.

Complexes of nitrobenzene are characterized by small association constants,[29] whereas complexes of aromatic hydrocarbon and azahydrocarbon acceptors have not been studied. On the other hand, increasingly stable complexes of an acceptor with a series of donors generally occur with decreasing wavelength of

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(23) C. Heller, personal communication, 1966.

(24) (a) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19B**, 5 (1964); (b) W. H. Urry and J. Sheeto, *Photochem. Photobiol.*, **4**, 1067 (1965).

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(28) R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1964).

(29) N. B. Jurinski and P. A. D. De Maine, *J. Am. Chem. Soc.*, **86**, 3217 (1964).

the charge-transfer band, and thus with decreasing donor ionization potential. That the TMAE interactions here and with the perhalobenzenes[30] are characterized by only small K must be ascribed to the bulk of the molecule, and this is discussed in greater detail below.

The position of the charge-transfer absorptions leaves no doubt as to the exceptionally strong donor properties of TMAE in this respect. Thus for the common acceptor nitrobenzene, the absorption maximum is displaced by 0.48 ev to low energy compared with N,N,N′,N′-tetramethyl-*p*-phenylenediamine.[31] Absorptions for complexes of the latter are themselves displaced[32] about 0.60 ev to lower energies than those for dimethylaniline, for which a photoionization potential of 7.35 ev has been reported.[33] Direct application of eq 2 provides an estimate of 6.27 ev for the ionization potential for TMAE, whereas the difference in polarographic oxidation potentials[14] indicates a value of 5.91 ev. These values may be compared with the reported[34] appearance of the parent ion in the mass spectrum of the base at an ionization voltage of 6.5 ev. Absorption maxima were similarly observed from interactions of some of the acceptors with donor II, but were displaced about 20 mμ to longer wavelengths. These small effects, which show slightly superior donor properties for II compared with I, are no larger than the changes in amine ionization potentials produced by alkyl substitution.[3]

Where definite absorption maxima are seen, their location should reflect the relative electron affinities of the acceptor molecules. For the weaker acceptors, the charge-transfer band merges with the TMAE absorption suggesting mixing of the dative and of the electronically excited donor–acceptor states. All that can be compared in this case is the size of the absorption tails, and conclusions as to acceptor strengths are open to dispute. For identical donor and acceptor concentrations, the tail of the perylene–TMAE absorption is bigger than that of the anthracene, which in turn is bigger than that of the pyrene. The hydrocarbon electron affinities are possibly in this order. Replacement of an aromatic C–H group for nitrogen displaces the absorption maximum to lower energies, and thus produces a stronger acceptor. Thus replacement of one C–H group of anthracene produces a maximum at 462 mμ for acridine, whereas a replacement of two moves it to 554 mμ for phenazine. Similarly the absorption tail for pyrazine is considerably larger than that for pyridine. A very small shift of the TMAE (0.91 M) absorption edge to longer wavelengths in the presence of benzene (1.00 M) is probably just a neutral hexane to hexane-benzene solvent shift, for this occurs for N,N-dimethylaniline and N,N,N′,N′-tetramethylphenylenediamine in cyclohexane.[30] As in the case of hydrocarbons, previous studies of the complexing abilities of the azahydrocarbons have been confined to their donor properties. The only spectral evidence for acceptor properties has been a tentative identification of an absorption of pyridine with the superoxide ion O_2^- as a charge-transfer band.[35]

The effect of temperature on the spectra of this and related systems will be discussed in later papers.[1]

Structure of Tetrakis(dimethylamino)ethylene. Kuwata and Geske[14] have used the Hückel molecular orbital approximation (HMO) to interpret the electron spin resonance spectrum, esr, of the TMAE monocation. They find qualitative agreement with experiment over a considerable range of parameter values. Where the nitrogen Coulomb integral is given by $\alpha_N = \alpha_C + h\beta_{CC}$ and the CN resonance integral is given by $\beta_{CN} = k_{CC}$, they considered $0 \leq h \leq 1$ and $0.7 \leq k \leq 1$. Zweig, *et al.*,[16] obtained a close correlation between polarographic oxidation potentials and HMO calculations for a number of dimethylamino-substituted benzenes using $h = 1$ and $k = 0.8$. Godfrey and Murrell[36] have considered the steric effects of substitution adjacent to the amino group in N,N-dimethylaniline and *p*-nitro-N,N-dimethylaniline. Their study shows considerable steric reduction in the interaction between the lone-pair nitrogen electrons and the π electrons of the ring even in the case of a single methyl group substituted adjacent to the dimethylamino group. In the case of TMAE, this steric effect should be greater and hence the k values of Kuwata and Geske may be too large. In Figure 10, the HMO orbitals for TMAE and aniline-like systems are compared.[37]

In the configuration of minimum steric interaction between the methyl groups on adjacent nitrogens (the CNC planes perpendicular to the NNC=CNN plane), $k = 0$. Values of $k \sim 1$ correspond to near coplanarity of the CNC and the NNC=CNN which is equivalent to large steric interactions. Designating those orbitals where energy decreases on increasing k as rotating and those whose energy increases as antirotating relative to the configuration of minimum steric interaction, in the TMAE ground state, two rotating (A_1 and B_1) and one antirotating orbital (A_1^*) are doubly occupied. On an HMO basis the contributions of A_1 and A_1^* are equal and opposite in sign independent of the choice of parameter values. Thus the net effect is dominated by the doubly occupied B_1 orbital which is opposed by the steric interactions between the methyl groups. With the particular choice of parameters illustrated there are two doubly occupied rotating orbitals (B_1 and B_1^*) in the aniline-like ground state. The $B_1^\dagger$ orbital can be made either antirotating or rotating as h is increased or decreased from zero. Since the B_1 and B_1^* orbitals of the aniline-like system are considerably less rotating than the B_1 orbital of TMAE, TMAE might be expected to have a greater tendency toward the coplanar configuration. The interaction between adjacent dimethylamino groups is sterically similar to that between the methyl and dimethylamino groups in a 2-methyl-N,N-dimethylaniline where a significant deviation from planarity is deduced from the observed decrease in intensity of the intramolecular charge-transfer band,[36] whereas the *cis*-oriented di-

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(30) P. R. Hammond, *J. Chem. Soc.*, in press.

(31) M. E. Peover, *Trans. Faraday Soc.*, **60**, 479 (1964).

(32) R. Foster, *Tetrahedron*, 10, 96 (1960).

(33) F. I. Vilesov, *Zh. Fiz. Khim.*, **35**, 2010 (1961); *Chem. Abstr.*, **56**, 3014*c* (1962).

(34) Communication from N. Wiberg and J. W. Buchler, quoted in ref 14.

(35) W. Slough, *Chem. Commun.*, 184 (1965).

(36) M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.* (London), **A278**, 71 (1964).

(37) Based on the relative ionization potentials of ethylene and trimethylamine where the nitrogen is expected to be inductively similar to that of the dimethylamino group bonded to carbon; $h = 0$ is qualitatively of the correct magnitude.

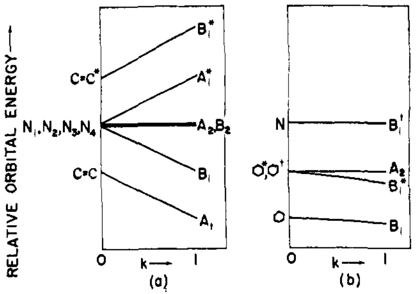

Figure 10. HMO orbital energies for TMAE, a, and N,N-dimethylaniline, b. Orbitals are properly scaled at $k = 0$ and $k = 1$ for $h = 0$. In b only orbitals occupied in the ground state are shown.

methylamino groups are sterically similar to the more pronounced 2-*t*-butyl-N,N-dimethylaniline. On this basis it would appear that the steric interaction in TMAE may well be dominant, giving rise to an equilibrium configuration where the CNC planes are essentially perpendicular to the NNC=CNN plane ($k \sim 0$). This is in accord with nuclear magnetic resonance measurements, nmr, that show that in the neutral TMAE molecule the methyl groups are all equivalent.[24a,38]

In the $k = 0$ configuration, the nitrogen lone-pair electrons occupy equivalent localized orbitals. Thus excitation of these electrons or their removal by ionization would result in a number of degenerate configurations whose degeneracy would be removed as a consequence of distortion of the nuclear frame. In the case of ionization, the nature of the distortion can be inferred from the HMO picture (Figure 10). The removal of an electron from the antirotating A_1* orbital would increase the net number of electrons in rotating orbitals tending to distort the molecule away from the $k = 0$ configuration and would delocalize the lone-pair electrons in qualitative accord with the esr observations of the monocation.[14] The removal of the second electron to the dication would be expected to further delocalize the electrons and to further distort the molecule toward the coplanar configuration. This is in accord with the splitting of the nmr proton signal observed for the dication.[21] Further for $k \sim 1$, the B_1 orbital is C=C antibonding while the A_1 orbital is C=C bonding. Both orbitals are N–C–N bonding. Thus the dication would be expected to have a high double-bond character associated with these groups as suggested by infrared evidence.[39] As a consequence of the decreased double-bond character of the C=C, steric interaction may be reduced compared to the neutral TMAE molecule.

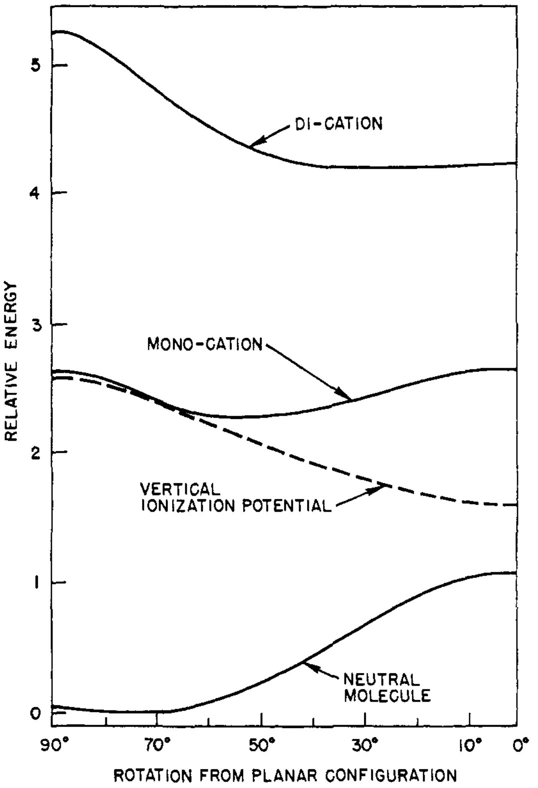

Figure 11. Representative ground-state potentials for the neutral TMAE molecule and its ions.[42]

Relative to the long wavelength electronic transition in TMAE, the excitation of an electron from the A_1* to the B_1* orbital would not affect the net number of electrons in rotating orbitals. Thus away from $k = 0$, little difference would be expected between the configuration of the ground state and that of the first excited state. In the neighborhood of the $k = 0$ configuration, the near-degeneracy of A_1*, A_2, B_2, and B_1 would suggest that there would be a distortion of nuclear frame in the excited state. This degeneracy would be effectively split by an unsymmetrical distortion which would remove the A_2, B_2 degeneracy. Thus the large observed Stokes shift between the absorption and fluorescence[39] is further evidence suggesting the near $k = 0$ configuration for the ground state.[40]

A distortion away from the $k = 0$ configuration increases the net electronic binding energy of the ion. This could account for a low isothermal ionization potential, and would in fact predict that the vertical ionization potential as estimated by a mass spectral appearance potential should be larger than the isothermal ionization potential as inferred from polarographic measurement. A further reduction in isothermal ionization potential would be predicted for the monocation going to the dication in agreement with the ease with which the dication is obtained in solution.[14]

Interpretation of the donor strength is less straightforward. Measurements on charge-transfer absorption maxima provide information relevant to donor vertical ionization potentials.[13,41] As the interactions are most likely contact, the TMAE structure will be little changed from that of the isolated molecule. The spectra indicate powerful, vertical, donor properties, and, although the estimate of ionization potential so obtained is certainly inexact, it is well below the 7.82 ev reported for trimethylamine. Another difficulty with the $k \sim 0$ configuration occurs in accounting for

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[38] The nmr spectrum of TMAE (0.2 *M*) in *n*-heptane with tetramethylsilane internal standard showed a single sharp line, whose chemical shift and peak height, compared with the silane, did not alter in the temperature range from 80° down to −60°, the limit of the experimental conditions.

[39] H. E. Winberg, J. R. Downing, and D. D. Coffman, *J. Am. Chem. Soc.*, 87, 2054 (1965).

[40] It should be noted that infrared and Raman evidence[39] precludes an unsymmetrical distortion in the ground state of the TMAE molecule.

[41] R. S. Mulliken, *J. Phys. Chem.*, 56, 801 (1952).

the relatively high intensity of the long-wavelength electronic transition of the neutral molecule.[20] Both of these results suggest a configuration where the C–N–C planes have an appreciable projection onto the $N_2C{=}CN_2$ plane. This is readily explained by considering the contra-behavior of the electronic energy and the steric interaction as the C–N–C planes are rotated relative to the $N_2C{=}CN_2$ plane. Our proposal for the relative energetics for ground states of the neutral molecule and its ions is illustrated graphically in Figure 11.[42]

Near the $k \sim 1$ and $k \sim 0$ configurations (angles $\sim$0 and $\sim$90° in Figure 11), the electronic binding energy and the steric interaction have opposite extremes; hence the net energy will be dominated by the relative curvature of the two energy components as a function of angle. An energy minimum near these configurations will have barriers to distortion through them which are small compared to $|\beta|$. Taking the energy of the $A_1{}^*$ orbital as a measure of the vertical ionization potential, for $\beta = -3$ ev the estimates cited above would predict that the minimum for the neutral molecule is in the neighborhood of 50°. Smaller values of $|\beta|$ would predict larger angles of rotation. For angles of this magnitude the observed intensity of the long-wavelength transition is not unreasonable.

These considerations suggest that in the neutral TMAE molecule the C–N–C planes lie well out of the $N_2C{=}CN_2$ plane and have a small barrier to rotation through the perpendicular configuration. The nmr evidence cited above suggests that at all readily accessible temperatures this is an essentially free libration which may crudely be described as a "wobble" about the perpendicular configuration.

Relative to the charge-transfer interactions, the methyl groups lying above or below the $N_2C{=}CN_2$ plane severely inhibit the approach of the acceptor molecule, limiting the interaction to contact. Since the available electrons are associated largely with the nitrogen atoms, TMAE is essentially an n-type donor but differing from the types commonly encountered in that these electrons are distributed over the molecule in much the same sense as a π-type donor.

Anthracene–Methylbenzene Interactions. It is of interest to compare the interactions observed with TMAE and those reported by Wentworth and Chen[12] between methylbenzenes and polycyclic aromatic hydrocarbons. Considering the polycyclic aromatics as acceptors, they observed perturbations of the long-wavelength electronic transitions of the acceptors whose dependence on the concentration of donor suggested that they might be due to the presence of donor–acceptor complexes. Based on consideration of a single "no-bond" state and a single dative state, they established a correlation with the ionization potential of the donor and the electron affinity of the acceptor based on eq 2. Relative to this correlation it is noteworthy that the ionization potentials of the acceptors are in fact lower than those of the donors. Thus there is some arbitrariness in the assignment of donor and acceptor. A short extrapolation of their results would suggest that the anthracene–anthracene complex would be more stable than any of the observed examples. This contradicts a widely held opinion in the literature that aromatics do not form stable self π complexes in the ground state.[43,44] In this regard it should be noted that the experimental K values are sufficiently small as to be confounded by the conspiracy of errors mentioned with respect to our own K values. However, the consistent trend of Wentworth and Chen's K values with varying ionization potential requires further consideration.

As pointed out by Wentworth and Chen, the charge-transfer transition lies at considerably shorter wavelengths than the observed transition; thus there is at least one (probably more) neutral acceptor state between the ground state of the acceptor and the charge-transfer state. As a consequence, the system is not simply describable as the mutual perturbation of a single "no-bond" state and the dative state. Thus the rather good correlations observed must be to some extent fortuitous.

As an alternative explanation of the effect, intrusion of the methyl groups of the donor into the π cloud of the acceptor may be significant. On an HMO basis, the separation between the ground state of an acceptor and the first excited state is proportional to the electron affinity in the sense $\Delta E = 2(\alpha_c - E_a)$. Thus any perturbation of the acceptor which induced an interaction Δ between the ground state and the first excited state would in first order be expected to result in a stabilization $\Delta^2/2(\alpha_c - E_a)$. The resultant correlation between electron affinity and the induced stability would be the same as that observed by Wentworth and Chen.

A more convincing alternative perhaps is to ascribe the effect to a solvent shift of the acceptor absorption. It should be recognized that for the anthracene–*p*-xylene system, which is illustrated in ref 12, the observed shift in the spectrum of the complex relative to that of the uncomplexed anthracene is small compared to the anthracene solvent shift. If there were a charge-transfer interaction for this example, then a gradual building of an absorption on top of the "acceptor" absorption would be expected for increasing donor concentration. Their figure, and, in particular, the negative absorptivities they report, may reflect subtle differences in solvent shift associated with the inclusion of the methylbenzenes in the solvation complexes.

It is suggested that the observed correlations of ionization potential and electron affinity with the stability of the complex do not necessarily imply that the stabilization is a consequence of charge-transfer

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(42) The curves in Figure 11 are computed from the following considerations. (a) The electron energy is the sum of energies of the occupied one-electron HMO orbitals with $h = 0$ and $k = \cos\theta$ (θ is the angle of rotation). (b) The steric interaction is $3\cos^2\theta$ in units of $|\beta|$. (c) $\alpha = 2.6\beta$ in which case the energy is scaled in units of $|\beta|$. For $\beta \simeq -3$ ev, the chosen relationship between α and β fits the ionization potentials of ethylene and trimethylamine. For the constant in the steric potential, the value of 3 was chosen because this is near the minimum value that yields a minimum energy for the dication for $\theta > 0$. Decreasing the value of this constant shifts the location of the energy minima to smaller angles. A value near 2 would shift the minimum of the neutral molecule to a position near 50°. For the set of parameters as a whole, there is a considerable range of values that would give qualitatively similar results. Considering the very approximate nature of the HMO approach, exploration of parameter values has little meaning, particularly for the treatment of a single molecule.

(43) J. N. Murrell and J. Tanaka, *Mol. Phys.*, 7, 363 (1964).

(44) Note Added in Proof. See, however, E. A. Chandross, J. Ferguson, and E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966); and J. A. Katul and A. B. Zahlan, *ibid.*, 47, 1012 (1967).

interaction. For both alternatives above, arguments based on polarizability seem more appropriate.

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Magnetic Resonance Studies of Copper(II)–Triglycylglycine Complexes[1]

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Abstract: Cu(II)–triglycylglycine in solution (copper to peptide ratio 1:1; 5×10^{-3} *M*) has been studied in the pH range 2.5–11 by potentiometric titrations, electron paramagnetic resonance, and proton relaxation measurements. The complex formed at high pH has been investigated also in the form of a polycrystalline powder diluted with the corresponding diamagnetic Ni(II) salt. Relaxation data and epr results show that at low pH a complex is formed with the neutral peptide. This and the next complex formed at higher pH show no nitrogen hyperfine structure. The three complexes formed thereafter show nitrogen hyperfine structure due to two, three, and four nitrogens, respectively. The relative amounts of the different complexes have been estimated from epr spectra. Proton relaxation results are used to discuss the number of coordinating water molecules. Binding of at least one water molecule to the copper ion at the highest pH cannot be eliminated, in contrast to what is found in the crystal. However, a comparison between the high-pH complex in solution and in a powder yields the result that the nitrogen coordination is essentially the same.

The structure and properties of copper(II) complexes with amino acids and peptides have been extensively studied in recent years. For example, the electron paramagnetic resonance (epr) technique has been used in studies of copper complexes with glycylglycine[3] at different pH values and with some histidine-containing di-, tri-, and tetrapeptides at high pH.[4] Proton magnetic resonance has been applied by Sheinblatt[5] to the copper(II)–glycylglycine system with large excess of peptide over copper. Important information about the structure of the complexes in the solid state has been obtained from crystallographic studies, as discussed in a recent review.[6] The major aim of all these investigations has been to provide background knowledge for an understanding of the interaction of metals with proteins.

In this work we report studies on the copper complexes with triglycylglycine. This system has been studied earlier in potentiometric titrations[7,8] and with infrared spectroscopy.[8] We have followed the changes in the epr spectra and the proton relaxation rates as a function of pH in order to see what additional information about the number of complexes and their properties could be obtained.

In addition to the work on solutions we have also studied a crystalline powder of the complex at high pH. Its structure has been revealed by X-ray crystallography.[9a] The copper interacts only with four ligand atoms in a planar arrangement with no coordination in the fifth and sixth position. An interesting question concerns the extent to which structures determined in the crystalline state correspond to molecular species existing in solution. This is a particularly important problem to the protein chemist who is mainly interested in interactions occurring in aqueous solutions. Therefore, we have tried to compare results obtained from solutions and solid-state samples. For the problem at hand, it is important that the crystals of the Cu(II) and the corresponding diamagnetic Ni(II) complexes are isomorphous,[9b] so that dilute crystals of the Cu(II) complex can be made. This is a prerequisite for epr measurements on the solid compound.

Experimental Section

Materials. ^{63}Cu and ^{65}Cu were obtained from Oak Ridge National Laboratory. The monosodium salt of triglycylglycine was purchased from Fluka AG, Switzerland, and not further purified. All other reagents were analytical grade, and deionized water was used throughout.

Preparation of Crystals. Crystals of the Cu complex of triglycylglycine at high pH diluted with Ni were prepared in the following way. A solution (1 ml) containing 5×10^{-6} mole of $CuCl_2 \cdot 2H_2O$ and 5×10^{-4} mole of $NiCl_2 \cdot 6H_2O$ was warmed and mixed with 1 ml of 1 *M* NaOH. The mixture was stirred well; the precipitate was centrifuged off and washed three times with 5×10^{-3} *M* NaOH. The precipitate was added to 1 ml of a solution

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(8) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, **88**, 914 (1966).

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