Uebersfeld[28] produced the green $PH_2\cdot^+$ radical by adding an acidified solution of phenazine to a solution of dihydrophenazine in a reaction that is probably mechanistically similar to the one proposed here. Unfortunately they gave no kinetic data. If the complex were a N—H···N bonded complex, for instance, hydrogen bonding could stabilize it until it split by homolytic cleavage to give two neutral PH· radicals. These neutral radicals would then be rapidly protonated by the high concentration of free protons in the medium.

In Figure 7, the computer-simulated curve or 1.27×10^{-5} M phenazine solutions matches the experimental curve for $t > 750$ μsec but not for $t < 750$ μsec. The mismatch at $t < 750$ μsec has been shown to be partially due to the presence of another shorter lived species absorbing at 445 mμ. The PH^+ triplet is known to absorb in this region and has a lifetime consistent with the mismatch of the curves. The addition of 10^{-2} M dibromomethane to the reaction mixture caused the experimental curve to show none of the rounding associated with the unquenched data and to match more closely the simulated curve, as shown in Figure 7. The remaining mismatch between the curves has been ascribed to the initial assumptions that half of the phenazine present initially is in each of the reactive forms [(PH_2) and (PH^+)]. This would cause an error in the absolute magnitude of the second-order rate constants which would not be greater than a factor of 4 or 5.

Rate constants for eq 13 and 17 may be estimated in the manner used previously. Again assuming $\epsilon = 200\ M^{-1}\ cm^{-1}$ for the $n \rightarrow \pi^*$ transition buried under the π,π^* band, $k_{13} \geq 10^9\ sec^{-1}$ and $k_{17} \geq 10^8\ sec^{-1}$. The computer model was changed to include the possible effect of eq 17 on the growth rate of $PH_2\cdot^+$. It was found that pseudo-first-order rate constants larger than $10^7\ sec^{-1}$ had no effect on the over-all rate of reaction when $k_{18} = 9.5 \times 10^8\ M^{-1}\ sec^{-1}$ and $k_{19} = 6.0 \times 10^4\ sec^{-1}$.

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Intramolecular Perturbation Effects in Diamine–Iodine Charge–Transfer Complexes[1]

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Contribution from the Photochemistry and Spectroscopy Laboratory,
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Abstract: A method has been developed for determining the association constants (K_1 and K_2) of the 1:1 and 2:1 iodine complexes of diamines in nonpolar solution. The method was checked with triethylamine which, as expected, gave $K_2 = 0$ within experimental error and a value of K_1 which is in good agreement with values obtained by the Benesi-Hildebrand procedure. With all the polyfunctional amines studied $K_1 > K_2$, or in the limit, $K_1 \simeq K_2$. Compounds of the type $(CH_3)_2N(CH_2)_nN(CH_3)_2$ gave little indication of interaction between the nitrogen atoms, and the trend in K_1 values can be interpreted in terms of steric effects. With $n = 6$, $K_1 \simeq K_2$. The cage amines quinuclidine (ABCO) and triethylenediamine (DABCO) emerge as the strongest donors reported to date, with K_1 values of 3.3×10^5 and 6.8×10^4 l./mol, respectively, at 23°, and $K_1/K_2 \simeq 30$ for DABCO. Only the comparison of these compounds furnishes clear-cut spectral and thermodynamic evidence of interaction between the donor sites. By contrast, hexamethylenetetramine behaves like a simple trialkylamine with a diminished number of alkyl groups. For this tetramine, $K_1/K_2 \simeq 5$. The spectral features of the amines and their iodine complexes and the nature of the perturbation effects are discussed.

Of the known n–σ types of charge-transfer complexes, those involving iodine and amines as acceptor and donors, respectively, have been most extensively studied. In these complexes the intermolecular bond is localized, and the N–I–I moiety is linear.[2] For ammonia and monofunctional amines, the complexes are strong with formation constants in the range 10^2–10^4 l./mol (20°) and enthalpies between −5 and −12 kcal/mol.[3] They are also quite polar (*e.g.*, the dipole moment of the triethylamine–iodine complex is *ca.* 5.5 D[4]), which is the indicative of substantial charge transfer in the ground state. In the interpretation of spectral and thermodynamic data, it is generally assumed that only 1:1 complexes are formed, and these properties pertain to adducts of this stoichiometry. There is some evidence that, under certain conditions, complexes

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[1] This research was supported by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contracts No. AF 19(628)-3836 and F 19628-67-C-0118.

[2] O. Strømme, *Acta Chem. Scand.*, **13**, 268 (1959).

[3] H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

[4] P. Boule, *J. Am. Chem. Soc.*, **90**, 517 (1968).

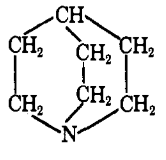
containing more than one molecule of donor or acceptor can exist.[5-7]

To our knowledge, there has been no systematic investigation of complexation involving multifunctional donors or acceptors. Multifunctionality poses several significant problems, such as the nature and extent of the interaction between active sites in the ground state of the donor or acceptor, and how complexation at one site influences the reactivity of the uncomplexed sites. In this paper we report the results of a study of the complexes of iodine with a series of symmetrical diamines (I–IV) and with hexamethylenetetramine (V) which, by virtue of their relatively high stability and spectral characteristics, are good models for examining these interaction effects (Chart I).

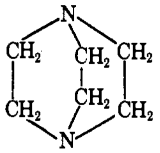
Chart I

$(CH_3)_2N(CH_2)_nN(CH_3)_2$

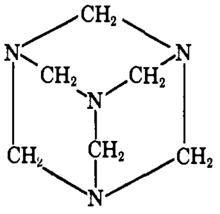
I



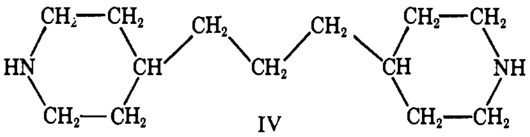
II



III



V



IV

Multiple charge-transfer equilibria pose difficult experimental problems.[8] The Benesi–Hildebrand procedure[9] is not suitable for the study of such systems, since it may provide linear plots even if stable higher complexes are formed.[10] Analogous limitations apply to the Job continuous variations method[11] which can indicate erroneous complex stoichiometries.[8,12] We have developed a method of approach which is particularly suited for iodine complexes and is, in principle, applicable to other systems as well. This report is confined to the presentation of the experimental results and to the examination, in a qualitative fashion, of the nature of the perturbation effects. The theoretical implications and quantitative correlations will be explored in a forthcoming paper.

Experimental Section

Materials. The solvents used were Spectroquality *n*-heptane and methylcyclohexane (Matheson Coleman and Bell). They were redistilled over sodium wire and stored in nitrogen-filled vessels. The solvent purity was checked by ultraviolet transmission measurements and by glpc. The liquid diamines (K & K Chemical Co.) and triethylamine (Matheson Coleman and Bell) were purified by distillation under reduced pressure over potassium hydroxide or anhydrous barium oxide. The middle fractions, which were stored under nitrogen, had the following boiling points and densities (g/cm^3 at 25°): N,N,N′,N′-tetramethylmethanediamine, 83–84° (760 mm), 0.646; N,N,N′,N′-tetramethyl-1,2-ethanediamine, 41–42° (38 mm), 0.768; N,N,N′,N′-tetramethyl-1,3-propanediamine, 36–37° (12 mm), 0.766; N,N,N′,N′-tetramethyl-1,4-butanediamine, 52–53° (10 mm), 0.788; N,N,N′,N′-tetramethyl-1,6-hexanediamine, 50–51° (0.5 mm), 0.793; triethylamine, 90° (760 mm), 0.727.

A highly purified sample of triethylenediamine (1,4-diazabicyclo[2.2.2]octane, DABCO), obtained from the Houdry Process Co., was used without further treatment. 1,3-Di-4-piperidylpropane (Reilly Tar and Chemical Co.) was also used without further purification. To ensure the absence of water with this diamine, its dilute solution in methylcyclohexane was kept over sodium wire. Quinuclidine (1-azabicyclo[2.2.2]octane, ABCO) was prepared from its hydrochloride (Aldrich Chemical Co.) by pouring a concentrated aqueous solution of the amine salt into a very concentrated solution of potassium hydroxide. The solid amine was filtered and dissolved in *n*-pentane, and the solution was dried over sodium wire. After removal of the solvent under vacuum, the amine was sublimed through a U tube coated with a sodium mirror. The colorless, flaky ABCO had mp 161.5–162° (sealed tube) (lit.[13] mp 156°). Hexamethylenetetramine (Matheson Coleman and Bell) was sublimed before use.

Preparation of Solid Complexes. A. DABCO. Iodine (91.4 mg, 0.360 mmol) in 25 ml of *n*-heptane was added to a solution of DABCO (41.3 mg, 0.368 mmol) in 25 ml of *n*-heptane. A red solid precipitated immediately and was washed with solvent and dried (mp 190–195° dec). Elemental analyses[14] indicated 82.10% of iodine and 4.68% of nitrogen, corresponding to an I_2:DABCO ratio of 1.93. The same 2:1 complex was obtained when 0.738 mmol of iodine was mixed, in solution, with 0.362 mmol of DABCO. In this case the solid contained 81.98% of iodine and 4.48% of nitrogen which yields the ratio I_2:DABCO = 2.02.

B. N,N,N′,N′-Tetramethylmethanediamine. To a stirred solution of iodine (1.89 mmol) in 500 ml of methylcyclohexane at 50°, a solution of N,N,N′,N′-tetramethylmethanediamine (0.81 mmol) in 30 ml of the same solvent was slowly added. On cooling and standing overnight, a dark material settled out. Spectral examination of the supernatant solution revealed that 0.21 mmol of iodine had not reacted. Thus the molar ratio of iodine consumed to diamine added was 2.07. The complex was collected by dissolution in dichloromethane and evaporation of the solvent. Analysis revealed 83.30% of iodine and 4.60% of nitrogen, corresponding to I_2:diamine = 2.01.

Procedure for the Determination of Formation Constants. In essence, the method calls for the accurate determination of the concentration of free iodine in solutions containing varying amounts of donor. This was accomplished by spectral measurements in the visible absorption region of iodine, using a Beckman DK-1 recording spectrophotometer. A matched pair of quartz cells (10-cm path length) was employed. The sample cell was attached to a 100-ml flask in which solutions of the components could be rapidly mixed. Temperature control to ±1° was achieved by means of the Beckman temperature-regulated cell holder (catalog no. 92527), which was modified to accommodate the sample cell. To improve the accuracy of the spectral measurements, the transmission scale was used for solutions with optical densities <0.4. Complications arising from the presence of moisture were minimized by warming all cells, flasks, and pipets and flushing them with dry nitrogen immediately before use.

The complex solutions were prepared directly in the flask attached to the sample cell by adding the liquid amine or very concentrated amine solutions to the solution of iodine, whose initial concentration never exceeded 1×10^{-4} *M*. Successive additions of amine

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(5) C. D. Schmulbach and D. M. Hart, *J. Am. Chem. Soc.*, **86**, 2347 (1964).

(6) D. W. Larsen and A. L. Allred, *ibid.*, **87**, 1219 (1965).

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(8) G. Briegleb, "Elektronen Donator-Acceptor Komplexe," Springer Verlag, Berlin, 1961, Chapter 12.

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(10) G. D. Johnson and R. E. Bowen, *ibid.*, **87**, 1655 (1965).

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(14) The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and the Galbraith Laboratories, Inc., Knoxville, Tenn.

Table I. Spectral Characteristics of the Amine–Iodine Complexes and Ionization Potentials of the Amines

Amine	Ionization potential, eV	Charge-transfer band[a] λ_{max}, mμ	$\epsilon_{max} \times 10^{-4}$,[d] l./mol cm	f[e]	Shifted I_2 band[a] λ_{max}, mμ	$\epsilon_{max} \times 10^{-3}$,[d] l./mol cm
Triethylamine	7.50 ± 0.02[b]	278	2.5	0.88	412	1.82
Tetramethyl-1,2-ethanediamine (I, $n = 2$)	7.60 ± 0.05[c]	270	2.1	0.85	410	1.80
Tetramethyl-1,6-hexanediamine (I, $n = 6$)		271	2.3	0.73	412	1.80
ABCO (II)	7.72 ± 0.05[c]	272	2.8	0.86	400	2.02
DABCO (III)	7.2 ± 0.1[c]	310	1.0	0.32	395	. . .[f]
Hexamethylenetetramine (V)		268	2.3	0.73	410	1.83

[a] In *n*-heptane or methylcyclohexane. In these solvents, the free iodine band has λ_{max} 520 mμ, and the complex spectra are identical. [b] K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957). [c] A. M. Halpern, J. L. Roebber, and K. Weiss, *ibid.*, **49**, 1348 (1968). These are photoionization values, and the large uncertainty arises from very low ionization cross sections near the ionization threshold. [d] For the 1:1 complexes. [e] Oscillator strength. [f] Shoulder; overlapped by the charge-transfer band.

were made with an accurately calibrated micrometer buret (RGI, Inc., Vineland, N. J.) and, with the exception of hexamethylenetetramine, the total volume added was always less than 0.2 ml. The total (complexed and free) amine concentrations were in the range 1–30 × 10^{-5} *M*. Again with the exception of the cage amines, higher iodine and amine concentrations could not be employed owing to the extremely low solubility of the complexes.[15] Although its complex is quite soluble, the tetramine is not very soluble in *n*-heptane and methylcyclohexane. With this donor it was necessary to prepare a nearly saturated solution by warming the amine with solvent and, since sizable volumes of this solution were employed, to apply dilution corrections to the spectral data. In all cases, the amine addition had to be made slowly and with vigorous agitation to prevent turbidity and to achieve proper equilibration. The spectra were recorded immediately after the addition of the amine; successive additions and spectral measurements were continued until most of the iodine was consumed, or until the system became turbid. It was found that turbidity at a level undetectable by eye is readily revealed by an increase in optical density throughout the visible region and by the fact that the curves no longer pass through the isosbestic point of the overlapping free and complexed iodine absorptions. The value of the molar extinction coefficient of iodine at 520 mμ (absorption maximum in *n*-heptane and methylcyclohexane) was determined as 920 ± 10 l./mol cm from Beer's law plots. This agrees well with the reported value of 918 in *n*-heptane.[16] Uncertainties in the values of the formation constants were estimated from the maximum and minimum values of the slope and intercept of α *vs.* β plots (*cf.* Results).

Results

The spectral features of the diamine–iodine complexes are illustrated in Figure 1, which shows the absorption spectra of various ratios of tetramethyl-1,6-hexanediamine and iodine in methylcyclohexane solution. The point to be noted is that there is no detectable change in the position of the shifted iodine band at 416 mμ even though the solutions contain varying proportions of 1:1 and 2:1 iodine–diamine complexes (*vide infra*). Similarly, it was found that the charge-transfer maximum remains constant at 271 mμ. Pertinent spectral data for some complexes and the ionization potentials of the amines are given in Table I. Although the energy of the charge-transfer transition varies in the expected manner with the ionization potential of the donor, the values of these parameters for DABCO do not correlate well with those for the simple amine–iodine complexes.[17] Thus the ionization potential of DABCO estimated from its charge-transfer maximum with the aid of the ionization potential *vs.* charge-transfer energy curve is too low. The shifted iodine band bears no simple relationship to the donor ionization potentials, and its extinction coefficient at the wavelength of maximum absorption remains essentially constant.

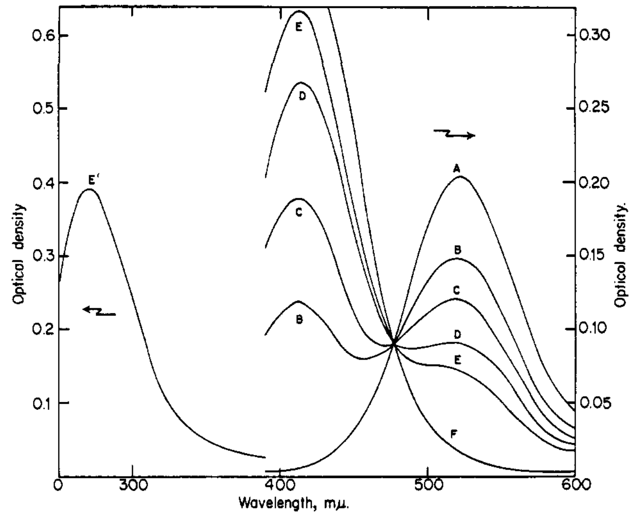

Figure 1. Spectra of solutions of iodine (2.21 × 10^{-5} *M*) and N,N,N′,N′-tetramethyl-1,6-hexanediamine in methylcyclohexane. The diamine concentrations (*M*) are A, 0; B, 2.30 × 10^{-5}; C, 4.6 × 10^{-5}; D, 9.20 × 10^{-5}; E and E′, 14.7 × 10^{-5}; F, 8.9 × 10^{-3}. Curve E′ was measured in a 1-cm cell, and all others were measured in a 10-cm cell.

In contrast with ABCO, the diamines of structure I, and the simple alkylamines, which have strong absorption bands below 2000 Å, DABCO in solution shows a well-defined absorption maximum at 2280 Å with ϵ_{max} 2.2 × 10^3 and an oscillator strength of ~0.1. This band is substantially enhanced by complexation with iodine, as can be seen by inspection of Figure 2. In view of the magnitude of the formation constants (*vide infra*), almost all of the iodine is complexed under the conditions employed (large excess of donor). The maximum concentration of complexed donor is therefore equal to the initial iodine concentration, and the difference spectrum (curve D) indicates ϵ_{max} >3 × 10^4. This increase in extinction coefficient is not accompanied by a detectable change in the position of the absorption maximum of DABCO.

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(15) Dichloromethane was found to be an excellent solvent for the diamine complexes, but spectral measurements revealed that I_3^- ions are rapidly generated in such solutions.

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(17) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

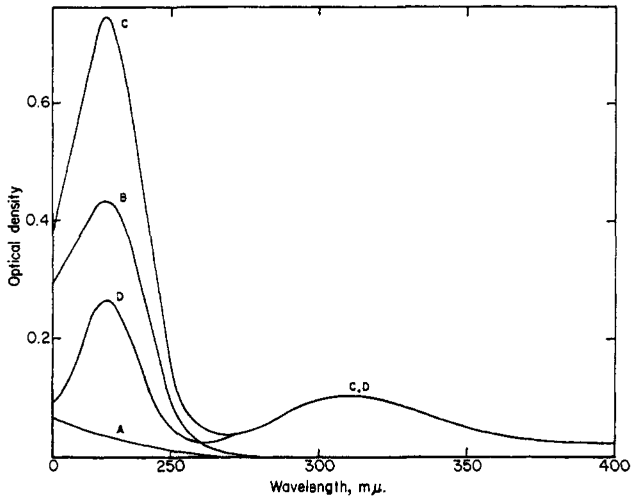

Figure 2. Enhancement of the DABCO transition by complexation with iodine. The solvent is methylcyclohexane and the path length 1 cm: curve A, 1.0×10^{-5} M I_2; curve B, 1.9×10^{-4} M DABCO; curve C, 1.0×10^{-5} M I_2 and 1.9×10^{-4} M DABCO; curve D, solution of curve C against 1.9×10^{-4} M DABCO as reference.

At this point it seems pertinent to present proof that stable 2:1 iodine–diamine complexes exist. Mixing DABCO and iodine in methylcyclohexane solution, either in equimolar quantities or in the ratio 1:2, produces a red, insoluble solid which elemental analysis shows to contain iodine and DABCO in the ratio 2:1. Similarly, tetramethylmethanediamine (I, $n = 1$) furnishes a solid 2:1 complex.

The method of determining the formation constants of the 1:1 and 2:1 iodine–diamine complexes is based on the following development. Let D and A represent the donor and acceptor (iodine), respectively. The two equilibria may then be formulated as

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{DA} \qquad K_1 = C_1/(C_A C_D) \tag{1}$$

$$\mathrm{DA} + \mathrm{A} \rightleftharpoons \mathrm{A_2D} \qquad K_2 = C_2/(C_1 C_A) \tag{2}$$

The concentrations are designated by the symbol C, with C_1 and C_2 representing the 1:1 complex (DA) and 2:1 complex (A_2D), respectively. The initial concentrations are $C_D{}^0 = C_D + C_1 + C_2$ for the donor and $C_A{}^0 = C_A + C_1 + 2C_2$ for the acceptor, and the change in acceptor concentration due to complex formation is $\Delta C_A = C_A{}^0 - C_A$. Incorporating these expressions into eq 1 and 2 furnishes the relation

$$\frac{\Delta C_A}{C_D{}^0} = \frac{K_1 C_A + 2K_1K_2C_A{}^2}{1 + K_1C_A + K_1K_2C_A{}^2} \tag{3}$$

Note that eq 3 contains only the measurable parameters $C_D{}^0$, C_A, and ΔC_A; $C_D{}^0$ is known from the preparation of the solution, and the other concentrations are available from the measurement of the optical density of A at its maximum. Since the complexed iodine band near 400 mμ tails to longer wavelengths, a correction for absorption due to the complex is applied. Thus $\Delta C_A = (D^0 - D)/(\epsilon_{I_2} - \epsilon_{I_2}{}^*)l$, where D^0 and D are the initial and equilibrium optical densities, respectively, of free iodine at 520 mμ, ϵ_{I_2} and $\epsilon_{I_2}{}^*$ are the corresponding extinction coefficients, and l is the path length in centimeters. The extinction coefficient $\epsilon_{I_2}{}^*$ is determined by converting all the iodine into complexed form with a large excess of amine (*cf.* Figure 1, curve F).[18]

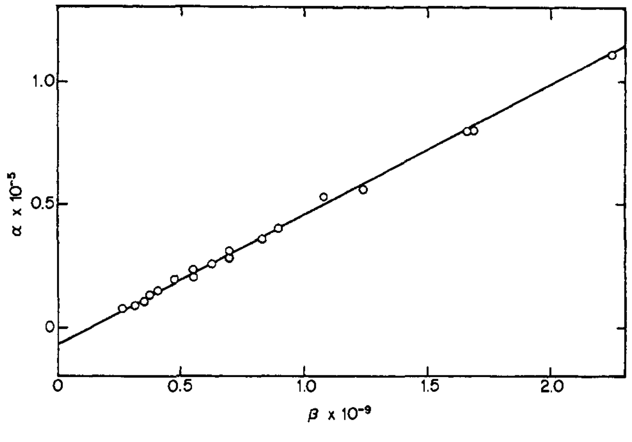

Figure 3. Plot of eq 4 for the N,N,N′,N′-tetramethyl-1,6-hexanediamine–iodine complex in methylcyclohexane at 25°.

Alternatively, in cases where the shifted iodine band is clearly separated and not overlapped by the charge-transfer absorption, ΔC_A may be obtained from optical density measurements at the maximum of this band.

If we let $\phi = \Delta C_A/C_D{}^0$ and define two new variables $\alpha = (1 - \phi)/[C_A(2 - \phi)]$ and $\beta = \phi/[C_A{}^2(2 - \phi)]$, eq 3 assumes the simple form

$$\alpha = (\beta/K_1) - K_2 \tag{4}$$

and values of K_1 and K_2 may be obtained from the slope and intercept, respectively, of plots of α against β. The plot for the tetramethyl-1,6-hexanediamine–iodine system is shown in Figure 3.

The data for amines I–IV are summarized in Table II. A statistical correction for equivalent sites has been applied to the values of the formation constants. The table portrays both the usefulness and limitations of the method. K_1 can be determined within reasonable error limits, but K_2 values are inherently less reliable. In a number of cases only the upper limits of K_2 could be estimated. This limitation of the method arises in part from the instability of the amine–iodine systems in nonpolar solvents with respect to precipitation. The solutions invariably become turbid after some time, and consequently the spectral measurements are made during a metastable interval which is often quite short. While the ultimate sources of error in the present method and in the Benesi–Hildebrand method are the same,[19] the former has the advantage that K_1 can be determined directly from the slope of the plot without recourse to the intercept. The reliability of the present method was checked with triethylamine, for which Table II lists K_1 as 4.9×10^3 l./mol in methylcyclohexane at 25°. The literature value[20] is 4.7×10^3 l./mol in n-heptane at 25°. Benesi–Hildebrand measurements in methylcyclohexane at 28° gave $k_1 = 3.5 \times 10^3$ l./mol which, corrected for the temperature difference,[20] corresponds to 4.3×10^3 l./mol at 25°. We consider the agreement between these numbers to be satisfactory. Since triethylamine is a monofunctional donor, $K_2 = 0$ is expected and, within the experimental limita-

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[18] This relationship is derived with the tacit assumption that $\epsilon_{I_2}{}^*$, which is the extinction coefficient per mole of complexed iodine, is the same for iodine found in the 1:1 complex and 2:1 complex. This approximation is considered acceptable since, with $\epsilon_{I_2}{}^* \approx 0.07\epsilon_{I_2}$ in all cases, the correction is small.

[19] *Cf.* ref 8, and P. R. Hammond, *J. Chem. Soc.*, 479 (1964).

[20] S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

Table II. Formation Constants in Methylcyclohexane for Amine–Iodine Complexes from Equation 4

Amine	Formula	$K_1 \times 10^{-4}$, l./mol	$K_2 \times 10^{-4}$, l./mol	Temp, °C
Triethylamine		0.49 ± 0.02	$<0.01^a$	25
Tetramethylmethanediamine	I, $n = 1$	0.060 ± 0.003	$<0.05^a$	27
Tetramethyl-1,2-ethanediamine	I, $n = 2$	0.55 ± 0.03	$<0.6^a$	27
Tetramethyl-1,3-propanediamine	I, $n = 3$	0.85 ± 0.04	$<0.2^a$	27
Tetramethyl-1,4-butanediamine	I, $n = 4$	1.0 ± 0.3	*b*	25
Tetramethyl-1,6-hexanediamine	I, $n = 6$	0.95 ± 0.03	1.2 ± 0.3	25
1,3-Di-4-piperidylpropane	IV	2.3 ± 0.3	1.2 ± 0.6	25
ABCO	II	33 ± 4	$<0.06^a$	23
DABCO	III	6.8 ± 0.3	0.2 ± 0.1	23
		4.6 ± 0.2^c	0.2 ± 0.1^c	26
Hexamethylenetetramine	V	0.24 ± 0.01	0.047 ± 0.013	26

[a] This is the upper limit of K_2; by physical necessity, the lower limit is 0. [b] K_2 could not be estimated due to exceptional instability. [c] In *n*-heptane.

tions of the method, is found. The largest negative intercept which can be obtained from the α *vs.* β plot provides an upper limit of 100 for K_2, which corresponds to $K_1/K_2 > 50$. ABCO, the other monofunctional amine listed in Table II, has $K_2 < 600$, but $K_1/K_2 > 550$.

Several general trends are apparent in the data of Table II. First, we note that in all cases $K_1 > K_2$ or, in the limit, $K_1 \approx K_2$. The latter condition applies to the hexanediamine (I, $n = 6$), whose active sites are evidently able to function independently of each other. Clearly, as expected, complexation at one end of the molecule can only decrease the reactivity of the other end. A second feature is that K_1 increases as the chain length is increased in the diamines I. In this series, the butanediamine (I, $n = 4$)–iodine system was found to be exceptionally unstable. The K_1 values for the tetramethylhexanediamine (I, $n = 6$) and triethylamine complexes are 9.5×10^3 and 4.9×10^3 l./mol, respectively, although one might expect them to be approximately equal. However, the data for a series of trialkylamine–iodine systems reveal that K_1 decreases as the alkyl group becomes longer.[3] From this point of view, trimethylamine is a better model for comparison, and indeed one finds $K_1 = 7.54 \times 10^3$ l./mol for this donor.[3] The secondary diamine, dipiperidylpropane (IV), is seen to be a stronger donor than compounds I. With nine carbon atoms between the donor sites, it seems surprising that $K_1 \approx 2K_2$. However, solutions containing diamine V and iodine were also observed to be particularly unstable, and we are inclined to believe that the two constants are in fact much closer in value than the quoted figures indicate.

The cage amines, ABCO and DABCO, are the strongest donors with respect to iodine which have been reported to date. The K_1 value for ABCO is *ca.* two orders of magnitude larger than that for triethylamine. Further, the enthalpy of association has been measured to be -13.9 kcal/mol for the ABCO complex; the value for the triethylamine complex is -12 kcal/mol.[3] The presence of a second nitrogen atom in DABCO causes K_1 for this donor to be smaller by a factor of *ca.* 5 than K_1 for ABCO. This result clearly shows that there is a substantial interaction between the lone electron pairs of the two nitrogen atoms. For DABCO $K_1/K_2 \approx 30$, which indicates that complexation at the second nitrogen atom is strongly suppressed.

Hexamethylenetetramine (V) requires some special comments. This donor has four tetrahedrally disposed nitrogen atoms and can, in principle, give rise to four complexes containing, respectively, one, two, three, and four molecules of iodine per molecule of amine. Extension of the treatment which furnished eq 4 to this situation leads to

$$\phi = \frac{K_1C_A + 2K_1K_2C_A^2 + 3K_1K_2K_3C_A^3 + 4K_1K_2K_3K_4C_A^4}{1 + K_1C_A + K_1K_2C_A^2 + K_1K_2K_3C_A^3 + K_1K_2K_3K_4C_A^4} \tag{5}$$

or

$$\phi + C_A(\phi - 1)K_1 + C_A^2(\phi - 2)K_1K_2 + C_A^3(\phi - 3)K_1K_2K_3 + C_A^4(\phi - 4)K_1K_2K_3K_4 = 0 \tag{6}$$

Since C_A and ϕ are experimental quantities, values of the four formation constants can be obtained by solution of a set of simultaneous equations (6) constructed with corresponding pairs of C_A and ϕ values. A simpler solution is possible if $K_4 \ll K_3 \ll K_2$. Under these circumstances, eq 5 reduces to eq 3 and we may evaluate K_1 and K_2 from eq 4. The above conditions appear to hold, for the plot of α *vs.* β for the compound V–iodine system is linear and provides the values $K_1 = 2.4 \times 10^3$ l./mol and $K_2 = 4.7 \times 10^2$ l./mol. Hexamethylenetetramine is thus seen to be a much weaker donor than the other two cage amines. The ratio $K_1/K_2 \approx 5$ reflects a smaller perturbation of the uncomplexed sites by the complexed site than is the case with DABCO.

Discussion

The results certainly reveal cases in which the donor sites interact, both in their free and complexed states. Consideration of the trends noted with the compounds studied strongly suggest that several factors are operative. To delineate these, let us first examine the spectral characteristics of the donors. A comparison of trimethylamine and tetramethyl-1,2-ethanediamine is revealing, since the latter can be approximately viewed as a bonded dimer of the former. Both compounds show strong absorption bands with maxima at 50,000 cm^{-1},[21] and, in line with this, their ionization potentials are close (7.8 eV for trimethylamine, 7.6 eV for the diamine). One would certainly expect sizable shifts in

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(21) A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, **49**, 1348 (1968).

these parameters if interactions between the nitrogen atoms in the diamine are important. This contrasts strongly with the situation for ABCO and DABCO. In this case there is a pronounced difference in the ionization potentials (*cf.* Table I), and, furthermore, the strong absorption bands of DABCO are substantially red shifted relative to those of ABCO. These bands have been assigned to n → p Rydberg transitions.[21] Again, DABCO can be considered to represent two ABCO units, and utilizing this concept in the framework of simple exciton theory has provided surprisingly good agreement between the observed and predicted spectral features. These results alone leave no doubt that the nitrogen chromophores interact in DABCO.

When we examine the charge-transfer absorption of the complexes of diamines I and of hexamethylenetetramine we encountered what appears to be an anomalous situation. All of these complexes show bands with maxima near 270 mμ, which are essentially unshifted relative to those of the monoamine complexes (278 mμ for triethylamine, 266 mμ for trimethylamine,[20] and 272 mμ for ABCO). Yet the K_1 values for these diamines indicate that the second center exerts an effect on the donor ability. A correlation is expected between the formation constant and the charge-transfer transition energy such that the former decreases as the latter increases.[22] Thus for compounds I and V we have little or no spectral perturbation coupled with changes in donor activity. These facts can be reconciled if we consider the magnitude of K_1 to be influenced by steric as well as electronic factors. The electronic factors invoked here are, of course, apart from those arising from the alkyl groups *per se*, *i.e.*, their inductive effect. We suppose that the electronic interaction between the donor sites requires them to assume rather specific orientations and that, on statistical grounds, the corresponding conformations of the freely rotating diamines I have a low probability. For these diamines we suggest that the steric influence of one dialkylamino group tends to block complexation at the other groups. In the case of tetramethylmethanediamine (I, $n = 1$), the smaller effective number of alkyl groups per nitrogen atom may contribute to the smallness of the K_1 value (*vide infra*). The steric interference becomes less as the groups move apart, and K_1 increases. Once a site is complexed, the resulting N–I_2 moiety experiences little perturbation and shows spectral features closely resembling those of the monoamine complexes. Values of $K_2 < K_1$ can be qualitatively accounted for by similar steric considerations.

We now turn our attention again to the cage amines and their complexes. Only for these systems is a detailed theoretical treatment considered worthwhile. For hexamethylenetetramine we note that K_1 is distinctly smaller than for the trialkylamines, yet examination of a molecular model indicates no steric interference to the approach of the first iodine molecule. The charge-transfer spectrum reveals no interaction between the nitrogen atoms, which is probably due to unfavorable orbital orientations. A rather crude interpretation of these features is possible in terms of the decreased number of alkyl groups per nitrogen atom in hexamethylenetetramine relative to the trialkylamines. K_1 values in the series methylamine, dimethylamine, and trimethylamine increase rapidly in the order given.[20] Now, the tetramine has 1.5 CH_2 groups per nitrogen atom, and, if these can be considered equivalent to methyl groups and all other effects are ignored, interpolation of the values for the methylamines provides $K_1 \sim 3000$ l./mol, which is to be compared with $K_1 = 2400$ l./mol found experimentally.

Only the comparison of DABCO and ABCO furnishes clear-cut spectral and thermodynamic evidence of electronic interaction between the donor sites. The charge-transfer band in DABCO is shifted *ca.* 0.5 eV to lower energy relative to ABCO. Thus, contrary to the general behavior of the monoamine–iodine complexes,[22] there is a *decrease* in the charge-transfer transition energy coupled with a *decrease* in K_1. Some discussion can be sustained regarding the nature of the interaction between the centers. The esr spectrum of the radical cation of DABCO[23] is pertinent, since it shows not only that the nitrogen atoms are equivalent, but also that there is substantial spin density on the methylene groups. Recent MO calculations on DABCO and ABCO using an extended Huckel-type theory predict a large interaction between the nitrogen lone pairs.[24] These calculations indicate that the coupling occurs predominantly through the two-carbon bridges rather than through space. The value of *ca.* 0.01 which we have estimated for the overlap integral between Slater-type sp^3-hybrid orbitals centered on the nitrogen atoms of DABCO in the ground state tends to confirm this result.[21] The calculations of Hoffman and coworkers[24] also predict the observed red shift of the absorption of DABCO relative to ABCO. Although the calculated orbital energies are obviously not realistic, the model provides an estimate of the difference in ionization potentials (0.41 eV) which is in good agreement with the experimental difference of 0.5 ± 0.1 eV. No meaningful speculations regarding the interaction between a complexed and an uncomplexed site in DABCO can be made at this time, and discussion of this system is deferred for a later paper.

Finally, we note that an enhancement of the donor transition by complexation has also been reported for the iodine complexes of quinoline and isoquinoline.[25] It was proposed that the donor transition borrows intensity from the charge-transfer band.

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(22) *Cf.* Figure 62 on p 135 of ref 8.

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