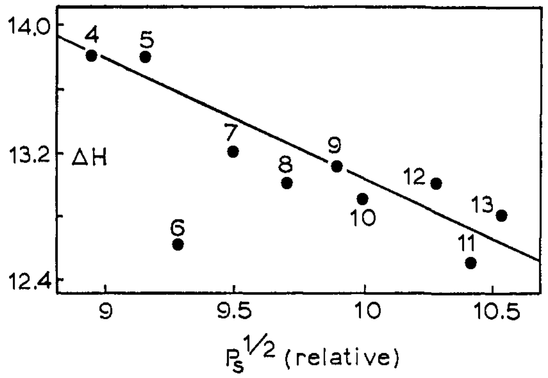

Figure 8. Reaction of pyridine with methyl iodide (ref 32). $\Delta H^{\ddagger}$ *vs.* the square root of the internal pressure of the solvent.

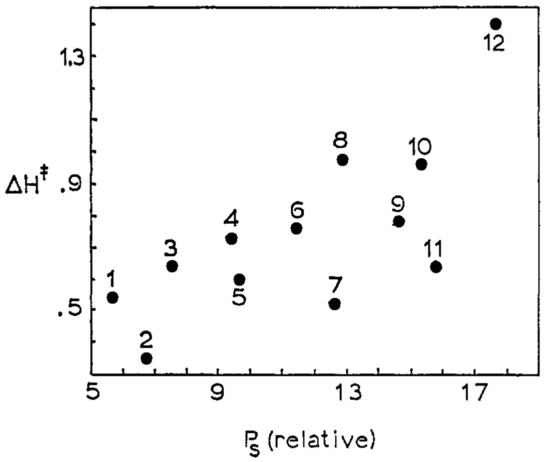

Figure 9. Reaction of methyl acrylate with cyclopentadiene (ref 33). $\Delta H^{\ddagger}$ *vs.* the square root of the internal pressure of the solvent.

worthy to point out that the internal pressure–log k plots in Figures 4 to 7 are far better correlations than those in which log k is correlated with the dielectric constant of the medium. Apparently the rates of certain polar reactions correlate well with the dielectric properties of the medium only if the latter is a mixture of different solvents.[21,25] The applicability of eq 2 and 6 to reactions in mixed solvents cannot be tested, however, without measuring the fundamental quantity ($\delta P/\delta T$) for the different solvent mixtures. A check of several other polar reactions randomly selected from the literature showed that nearly all of the systems checked conformed to the foregoing considerations, and as we already explained deviations of the experimental points from the theoretical curves are understandable. Some of these reactions are the following: decomposition of benzoyl azide,[26] reaction of aniline with phenacyl bromide,[27] decomposition of *t*-butoxy radicals,[28] decomposition of nitrogen pentoxide,[29] racemization of the dimethyl ester of 2,2′-dimethoxy-6-6′-dicarboxydiphenyl,[30] decomposition of phenylazotriphenylmethane,[31] benzoylation of *m*-nitroaniline,[32] reaction of cyclopentadiene with methyl methacrylate and with methyl *trans*-crotonate.[33]

Acknowledgments. This work was supported by the National Science Foundation, the American Chemical Society Petroleum Research Fund, and the Research Corporation. We gratefully acknowledge this support.

---

(25) E. Tomila, *Acta Chem. Scand.*, 13, 622 (1959).

(26) M. S. Newman, S. H. Lee, and A. B. Garret, *J. Am. Chem. Soc.*, 69, 113 (1947).

(27) H. E. Cox, *J. Chem. Soc.*, 119, 142 (1921).

(28) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963).

(29) H. Eyring and F. Daniels, *ibid.*, **52**, 1473 (1930).

(30) B. M. Graybill and J. E. Leffler, *J. Phys. Chem.*, **63**, 1461 (1959).

(31) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, 76, 1425 (1954).

(32) N. J. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936).

(33) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

Charge-Transfer Intensities of Iodine Complexes with N-Heterocyclics[1a]

V. G. Krishna[1b] and Benoy B. Bhowmik

Contribution from the Department of Biophysics, Michigan State University, East Lansing, Michigan. *Received October 7, 1967*

Abstract: The oscillator strengths of charge-transfer bands in the molecular complexes of iodine with six pyridines and four quinolines are shown to increase with the heats of formation in agreement with Mulliken's previous prediction. An empirical method of obtaining dissociation energies of iodine complexes is described.

Our present knowledge of the relationships between the stability of the charge-transfer (CT) complexes and their transition probability is in an unsatisfactory state, even though such knowledge is of central importance in the CT theory for the following reason.[2,3] The usage of the term CT complex implies that the

---

[1] (a) Supported in part by Grant GM-1422 from National Institutes of Health. Part of the work by V. G. K. was done during 1964–1965 at the Institute of Molecular Biophysics, Florida State University, Tallahassee, Fla., and supported by Division of Biology and Medicine of the U. S. Atomic Energy Commission. (b) Department of Chemistry, University of Arizona, Tucson, Ariz. 85721.

[2] (a) S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958); (b) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

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

stability of the complex is mainly due to the mixture of ionic CT states with the otherwise neutral ground state of the donor–acceptor pair. Further, in the CT theories it has usually been assumed that the same pair of orbitals is involved in the bonding and the transition. However, at least in some complexes, the possibility of bonding partly or solely due to (a) the overlap of orbitals other than those involved in the observed CT transition and (b) interactions other than those of CT type cannot be ruled out. In such cases the bonding and the transition are perhaps best treated by different theories, instead of using the currently prevalent oversimplified models.[4]

If the bonding in a series of complexes is mainly due to CT interaction, it should be possible to relate, as was first done by Mulliken,[5] the transition probability to the stability (or enthalpy of formation, ΔH), unless different sets of orbitals are involved in the two phenomena. Mulliken predicted that the oscillator strengths, f, of CT transitions should vary directly with $-\Delta H$ in a series of related complexes.

Most previous experimental work has been concerned with the "weak complexes" with relatively low probabilities for CT transition.[3] Further, many of these investigations, unfortunately, compare the formation constants, K, with molar extinction coefficients, ϵ, instead of the more meaningful quantities, ΔH and f. Experiments on weak complexes disagree with Mulliken's prediction.

Modifications to Mulliken's theory have been suggested to account for the observed discrepancy in such cases. The first modification involves the contribution from the nonbonded contact pairs to the CT intensity.[6] The second takes into account the possibility of interaction between the locally excited states of the donor and the CT states as a source of CT intensity.[7,8] It is interesting to see that the recent theories of excimers analogously invoke the interaction of CT and exciton states.[9]

For strong complexes with high oscillator strengths, the contribution to the CT band through the above mechanisms should be negligible and Mulliken's prediction should hold, unless the above-mentioned premises of the CT theory are wrong. This investigation was undertaken with the contention that the previous results on strong complexes are not conclusive. For example, exceptions to Mulliken's prediction can be found in an investigation ($\epsilon_{\max}$ and ΔH reported) on CT complexes of I_2 with primary and tertiary amines.[10] There seems to be only one report that agrees with Mulliken's prediction, but the authors compared their investigation on only two CT complexes with three others from previous work.[11]

This article reports investigations on two series of CT complexes with emphasis on intensity–stability relationships. The first series, complexes of I_2 with pyridines, offers an attractive possibility for an experimental study of Mulliken's theory. These complexes are known to be of 1:1 composition with relatively high formation constants.[12,13] The oscillator strengths of these complexes have not been determined previously except for the pyridine–iodine complex.[13,14] The present study shows that the CT transitions in these series have oscillator strengths close to 1.0. The second series, I_2 complexes with quinolines, is also an example of strong complexes. The results and conclusions from I_2 complexes with pyridines are corroborated by the quinolines–I_2 series.

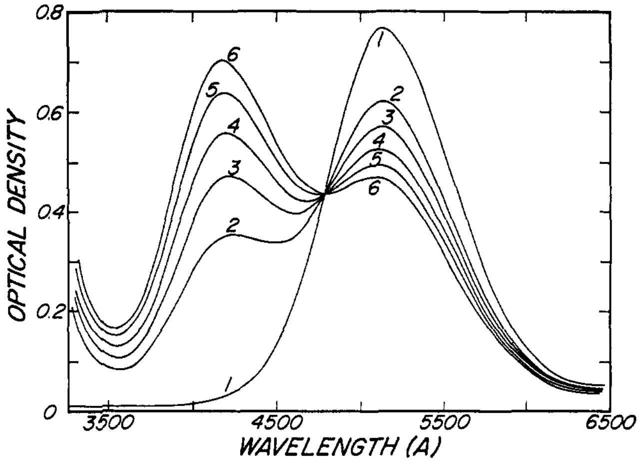

Figure 1. Perturbation of the visible ($B \leftarrow X$) bands of iodine by quinoline. The spectra were recorded in heptane at 25° with 1-cm cells. Concentration of iodine: 8.22×10^{-4} M. Concentration of quinoline (M): (1) 0.0, (2) 2.704×10^{-3}, (3) 4.056×10^{-3}, (4) 5.408×10^{-3}, (5) 6.76×10^{-3}, and (6) 8.112×10^{-3}.

In addition to the intensity–stability relations, a method of obtaining approximate dissociation energies, D, of I_2 complexes is described. The dissociation energies are perhaps a more direct measure of the stability than $-\Delta H$ even though the two quantities are related.[15]

Procedures and Results

Fischer certified I_2 was resublimed under reduced pressure. All pyridines and quinolines were supplied by Aldrich Chemical Co. and were fractionally distilled just before use. Matheson Coleman and Bell Spectroquality heptane was used as solvent without further purification.

Absorption spectra were recorded on a Cary Model 15 spectrophotometer with fused silica cells of 1.0- and 0.1-cm optical paths. The latter cells were used to investigate the CT bands.

Formation Constants. Figure 1 shows the visible absorption band of iodine and the bathochromic shift due to complexation with quinoline. The shapes of the visible bands of the other CT complexes (not shown) are similar. The formation constants were obtained from this shifted band.

---

[4] This was pointed out by R. S. Mulliken (*J. Chim. Phys.*, **61**, 20 (1963)) himself, who also suggested that the term donor–acceptor complexes is preferable to decribe these complexes.

[5] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[6] L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

[7] J. N. Murrell, *ibid.*, **81**, 5037 (1959).

[8] M. Chowdhury and L. Goodman, *ibid.*, **86**, 2777 (1964).

[9] See, for example, M. T. Vala, Jr., I. H. Hillier, S. A. Rice, and J. Jortner, *J. Chem. Phys.*, **44**, 23 (1966).

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

[11] H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

[12] J. Nag-Chaudhuri and S. Basu, *Trans. Faraday Soc.*, **55**, 898 (1959).

[13] C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954).

[14] H. D. Bist and W. B. Person, *J. Phys. Chem.*, **71**, 2750 (1967).

[15] W. B. Person, *J. Am. Chem Soc.*, **84**, 536 (1962).

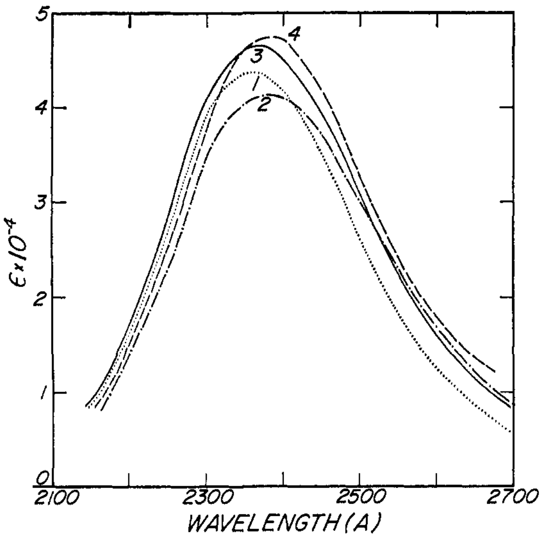

Figure 2. Charge-transfer bands of iodine complexes with pyridine (1), 2-picoline (2), 3-picoline (3), and 4-picoline (4).

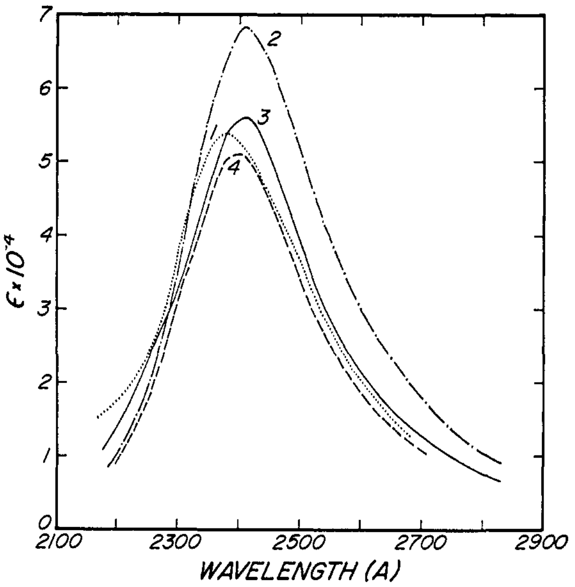

Figure 3. Charge-transfer bands of iodine complexes with quinoline (1), isoquinoline (2), 6-methylquinoline (3), and 6-chloroquinoline (4).

Method 1. For a 1:1 complex Lang[16,17] has shown that ϵ_p, the molar extinction coefficient of the perturbed iodine band, and K can be obtained by an iterative procedure from

$$\frac{C_D C_A}{\text{OD}} = \frac{1}{\epsilon_p}\left(C_D + C_A - \frac{D}{\epsilon_p}\right) + \frac{1}{\epsilon_p K} \qquad (1)$$

where C's are initial concentrations and OD is the optical density at a given wavelength. Table I lists the values obtained from eq 1. The perturbed I_2 bands overlap significantly with free I_2 bands only in the complexes of 2- and 3-chloropyridine. For these two complexes the data given in Table I were obtained by replacing ϵ_p in eq 1 with $\epsilon_p - \epsilon_D$, where ϵ_D is the molar extinction coefficient of the donor.

Method 2. The formation constants were also obtained from the decrease of the I_2 absorption at 5200 Å and higher wavelengths (Figure 1) by a procedure described before.[13,18] Values of formation constants from the two methods agree closely (Table I). Table I also lists the positions and the extinction coefficients of the shifted iodine bands.

Table I. Visible Bands of Iodine and the Formation Constants

Donor	K, l./mole at 25° Method 1	Method 2	Perturbed ($B \leftarrow N$) I_2 Band[a] λ_{max}, Å	ϵ_{max}[b]	f_{BN}[c]
Pyridine[d]	160.5	159.5	4220	1305	0.025
2-Picoline	225.0	225.2	4210	1390	0.026
3-Picoline	296.0	298.0	4180	1555	0.029
4-Picoline	368.0	357.5	4170	1480	0.028
2-Chloropyridine	5.0	4.9	4480	1285	0.023
3-Chloropyridine	23.9	22.1	4350	1285	0.025
Quinoline	114.6	117.5	4230	1700	0.032
Isoquinoline	294.0	281.0	4180	1540	0.030
6-Methylquinoline	175.0	185.0	4210	1615	0.031
6-Chloroquinoline	66.7	...	4300	1250	0.023

[a] The data for free iodine ($B \leftarrow X$) bands is λ_{max} 5200 Å, ϵ_{max} 912, and f = 0.013. [b] From Method 1. [c] From eq 2. [d] Previously reported values for the K of pyridine–iodine complex are: 185 at 25°,[12,13] 45 at 28°,[11] 107 ± 25 at 26° (A. G. Maki and E. K. Plyler, *J. Phys. Chem.*, **66,** 766 (1962)), 101 at 25° (A. I. Popov and R. H. Rygg, *J. Am. Chem. Soc.*, **79**, 4622 (1957)), and 140 at 25°.[13] ΔH values do not show this wide variation.

ΔH and ΔS. These quantities were obtained from the formation constants at three different temperatures (35, 25, 17°) by the usual method.[19] The measurements at 35 and 17° were made by preheating and precooling the cells with the solutions in a constant-temperature bath. A sharp isosbestic point was used to check the constancy of the temperature. ΔH and ΔS are listed in Table II.

Table II.[a] Thermodynamic and Spectroscopic Data

Donor	From method 1 $-\Delta F°$, kcal	$-\Delta H°$, kcal	$-\Delta S°$, eu	Dissociation energy, D	Charge-transfer band λ_{max}, Å	$\epsilon_{max} \times 10^{-4}$	f[b]
Pyridine	3.03	7.47	14.90	7.65	2360	4.32	1.01
2-Picoline	3.23	7.95	15.80	8.45	2390	4.14	1.08
3-Picoline	3.40	8.33	16.51	8.69	2380	4.66	1.10
4-Picoline	3.52	8.93	18.20	8.90	2390	4.77	1.15
2-Chloropyridine	0.96	3.08	7.10	3.26	2300	3.88	0.85
3-Chloropyridine	1.89	5.32	11.50	5.20	2330	3.76	0.84
Quinoline	2.82	7.22	14.75	7.31	2380	5.32	1.11
Isoquinoline	3.39	8.33	16.59	8.63	2405	6.82	1.31
6-Methylquinoline	3.08	7.76	15.70	7.89	2410	5.61	1.16
6-Chloroquinoline	2.50	6.41	13.10	6.40	2400	5.18	1.01

[a] No comparison of the data between the pyridine–iodine and quinoline–iodine series is attempted; each series is treated separately. [b] From eq 2.

CT Absorption. CT bands in both these series were found around 2500 Å. The donors and the acceptor also absorb in this region. The following procedure

---

(16) R. P. Lang, *J. Am. Chem. Soc.*, **84,** 1185 (1962).

(17) See also T. Kubota, *ibid.*, **87,** 458 (1965).

(18) V. G. Krishna and M. Chowdhury, *J. Phys. Chem.*, **67,** 1067 (1963).

(19) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 104.

was used to compensate for the absorption of the donor and acceptor. Two cells were placed in the sample compartment, one containing donor–I_2 complex and the other pure solvent. The reference compartment contained equilibrium concentrations of iodine and the donor in two different cells. Thus the absorption due to free iodine and donor is automatically subtracted in recording the spectra. The vibrational structure of the donor appears in the spectra if the donor absorption is not completely compensated; "troughs" appear in the CT absorption if the donor is in excess in the reference compartment. This fact was used to judge the reliability of the results. Figures 2 and 3 show the CT bands of some of the complexes studied here.

The oscillator strengths (Table II) were obtained from the approximate formula[20]

$$f = (4.319 \times 10^{-9})\epsilon_{\max}\nu_{1/2} \qquad (2)$$

where $\nu_{1/2}$ is the band width for half-intensity in cm^{-1}. Measurements of ϵ at the two edges of the CT transition are not reliable in these complexes. Thus the more accurate method[21] of determining f will not be an improvement over the use of eq 2.

Discussion

In accordance with the experimental evidence N-heterocyclics will be considered as donors of nonbonded (n) electrons.[2b,3,18]

The three electronic states of a complex necessary to understand the spectra reported here are the ground or normal state (N), the locally excited state of I_2 corresponding to the absorption at 5200 Å in free iodine (B), and the CT excited state (E). In the valence-bond theory for CT interactions developed by Mulliken,[5] these states are given by

$$\begin{aligned} N &= a(\ldots n^2)(\ldots \pi_g{}^4) + b(\ldots n)(\ldots \pi_g{}^4\sigma_u) \\ B &= (\ldots n^2)(\ldots \pi_g{}^3\sigma_u) \qquad (3) \\ E &= a^*(\ldots n)(\ldots \pi_g{}^4\sigma_u) - b^*(\ldots n^2)(\ldots \pi_g{}^4) \end{aligned}$$

The first of the parentheses in the above expressions represents the donor orbitals and the second the iodine orbitals. A serious inadequacy of the above N and E functions is that only one excited configuration is allowed to interact with the no-bond structure.

$B \leftarrow N$ Absorption. The 5200-Å visible absorption of iodine ($B \leftarrow X$) is identified as mainly due to the $^3\pi_{ou}{}^+ \leftarrow {}^1\Sigma_g{}^+$, $\sigma_u \leftarrow \pi_g$ transition.[22] The corresponding transition occurs at a lower wavelength in the CT complexes of I_2. In the N-heterocyclics this absorption appears around 4000–4500 Å with increased oscillator strength. This new absorption is identified as a transition from the ground state of the complex to an almost locally excited B state of the I_2.

The above functions show that the energy of the B state is not affected by complexation, while that of the N state is lowered. The transition dipole moment for this band in the complex, $\mathbf{M}_{BN}$, is equal to

$$\mathbf{M}_{BN} = a\mathbf{M}_{BX} + be\langle n|\mathbf{r}|\pi_g\rangle \qquad (4)$$

where $\mathbf{M}_{BX}$ is the transition moment for the uncomplexed I_2.

The second term vanishes for a configuration of the complex in which the nitrogen and both iodine atoms are linear[23] (C_{2v} symmetry for pyridine–I_2 complex).[24,25] Since $a < 1$, complexation should decrease the transition probability of the 5200-Å band if it were not for the interaction of B with N and E. The enhanced absorption will then be due to borrowing from the $E \leftarrow N$ CT transition and possibly from the dipole moment of the N state.[26] Since $E \leftarrow N$ is expected to be polarized along the N–I–I axis and the $B \leftarrow X$ transition is polarized along the same axis,[27] this mechanism is allowed.

It should be noted that any lowering of the energy of the B state due to this interaction will be counteracted at least partly by the interaction of the B and N states. The matrix elements $\langle B|\mathcal{H}'|E\rangle$ and $\langle B|\mathcal{H}'|N\rangle$ can be expected to have comparable values in these complexes due to a relatively large coefficient, b. Further the energy separations are almost equal. Thus the energy of the B state can be expected not to change drastically after complexation.[28]

The shift of the onset (corresponding to 0,0 band) of the 5200-Å transition should be due to the lowering of the ground state and changes in the energy of B. In addition, the Franck–Condon restriction on the B state determines the shift of the absorption maximum. Even in complexes with low stabilization energies the shift of the maximum is relatively large. This led Mulliken to point out the importance of the Franck–Condon restriction.[29]

While investigating the $B \leftarrow N$ bands, an empirical relation was found between $-\Delta H$ of the complex and the shift of the absorption maximum. Both $B \leftarrow X$ and $B \leftarrow N$ bands are bell-shaped curves (Figure 1). Let the points ν_1 of $B \leftarrow X$ and ν_2 of $B \leftarrow N$ be defined as the "corresponding points" if $\epsilon_{B\leftarrow X}^{\max}/\epsilon_1 = \epsilon_{B\leftarrow N}^{\max}/\epsilon_2$. The energy differences of the "corresponding points" on the red side of the maxima are then found to converge to a value almost equal to ΔH. It will presently be shown that these values are very likely the dissociation energies, D, of the complexes. Table II compares ΔH determined from the equilibrium constants with D's obtained by this method.

---

(20) H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).

(21) W. Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957, p 581.

(22) G. Herzberg, "Molecular Spectra and Structure I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton, N. J., 1950.

(23) In a less symmetric configuration, its contribution cannot be ignored. Thus in a configuration in which N–I and I–I bonds are perpendicular, or in the one tentatively suggested by Reid and Mulliken, this term can contribute as much as 0.1 to the oscillator strength of the $B \leftarrow N$ band. The observed enhancement of absorption is close to this value. The "linear" configuration is established in the crystalline state,[24] and there is no reason to believe that this may be radically altered in solution.

(24) O. Hassel and C. Rømming, *Acta Chem. Scand.*, 10, 796 (1956).

(25) O. Hassel, C. Rømming, and T. Tufte, *ibid.*, **15**, 967 (1961).

(26) L. Lohr, Jr., *J. Chem. Phys.*, **45**, 1362 (1962).

(27) O. Schnepp, J. L. Rosenberg, and M. Gouterman, *ibid.*, **43**, 2767 (1965).

(28) The following approximate calculations of the interaction energies illustrate this statement. The matrix elements $\langle B|\mathcal{H}|E\rangle$ can be estimated from f of $B \leftarrow N$. If all the observed enhancement of the absorption is from $E \leftarrow N$, then it can be accounted for by a value of 0.4 eV for the matrix element $\langle B|\mathcal{H}'|E\rangle$ for $a = 0.8$. From this the lowering of energy of B due to interaction with E is seen to be $\simeq$0.05 eV. Of the ionic and no-bond structures in (3) the ionic term would contribute predominantly to the interaction due to its delocalization over I_2. Thus $\langle B|\mathcal{H}'|E\rangle/\langle B|\mathcal{H}'|N\rangle = a^*/b \backsimeq 1.67$ (see Discussion). From this it follows that B would be raised by 0.015–0.02 eV due to the interaction with N. The net lowering of the energy of B due to complexation is around 0.03–0.035 eV.

(29) R. S. Mulliken, *Rec. Trav. Chim.*, 75, 845 (1956).

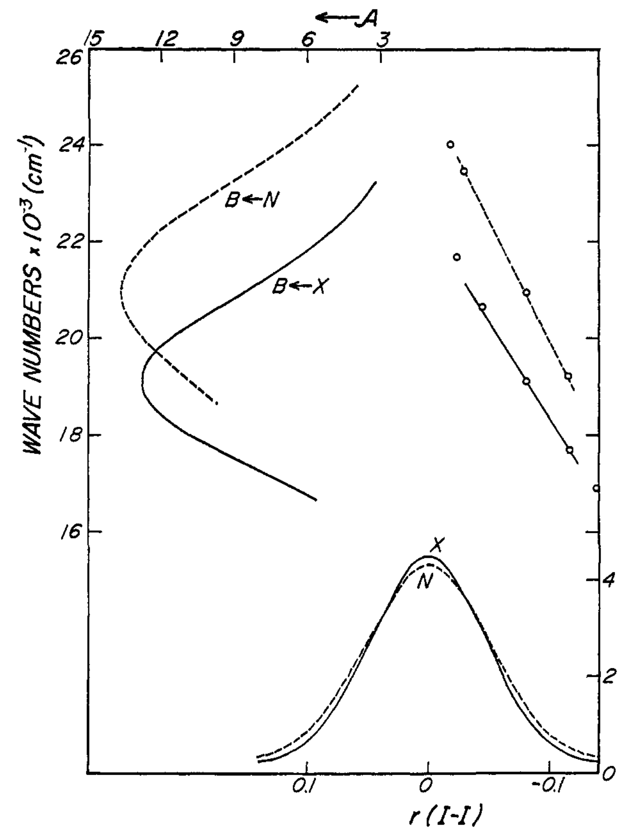

Figure 4. Potential energy curves (top right) of the B state in free iodine and iodine complexed with pyridine. Bell-shaped curves at the bottom designated as X and N represent the first vibrational functions of free iodine and iodine in pyridine–iodine complex. The potential curves are constructed from these and the observed spectra (see ref 30 and 31.) The two curves marked $B \leftarrow X$ and $B \leftarrow N$ are the 5200-Å band of iodine and its analog in the complex. The wave numbers of absorption are plotted on the vertical scale. A is related to the extinction coefficient by the equation $A = 10^{-7}\epsilon^{1/2}\nu^{1/2}$. The above figure shows only a segment of the potential energy curves for the B state, since they are constructed for a limited variation of the internuclear separation. r(I-I) represents the equilibrium internuclear distance of I_2 in both N and X states. The ground states of free and complexed iodine (X and N) are plotted at the same energy even though they differ by ΔH. In order to compensate for this $B \leftarrow N$ bands are red shifted in the above figure by $\Delta H = 2600\ \text{cm}^{-1}$.

Figure 4 shows the potential energy curves for the B state in free and complexed iodine, the donor being pyridine. The curves are constructed from the absorption and the first vibrational eigenfunctions of the ground states (X and N) by an empirical method described by Bayliss.[30,31] The ground-state vibrational functions are obtained from the ir frequencies[32] of 213 cm^{-1} for the free iodine and 184 cm^{-1} for the complexed iodine and from the experimental internuclear distances[25] [r(I–I) = 2.67 and 2.83 Å in free iodine and 4-methylpyridine–iodine complex, respectively]. For a limited variation of internuclear distance this method of constructing the potential energy curves is probably accurate enough for the present purpose.

Figure 4 clearly shows that the potential energy curves of the excited iodine tend to converge to the same potential energy minimum. It was noted before that the electronic energy of the B state may be affected a little in the complex. Thus it is quite possible that the differences of the corresponding points converge to a value that depends on (i) the energy separation between the N and X states or D of the complex and (ii) changes in B due to complexation. (ii) is small compared to (i) and the values obtained by this extrapolation may then be determined by (i). Since the D's of strong complexes do not differ appreciably from the thermodynamic ΔH's,[15] the results of Table II can readily be justified.[33]

If the dissociation energies obtained by this method are reliable, it would be of considerable use in the investigation of weak complexes of iodine where the methods of obtaining ΔH may be unreliable.

CT Bands

Table II conclusively shows that the observed oscillator strengths (f's) of both pyridine–iodine and quinoline–iodine series increase with the stability of the complexes. Indeed a linear relation is found between the f's and the dissociation energies (or ΔH). Thus Mulliken's prediction is qualitatively confirmed in these series. Table II also indicates the importance of measuring ΔH (or D) and f since ϵ_{max} and K values of 2-picoline deviate from Mulliken's prediction.

From a knowledge of the coefficients a and b, theoretical transition dipole moments and hence the f's of the CT bands can be calculated, the expression for the former being[4]

$$\mathbf{M}_{EN} = eS(a^2 - b^2)(\mathbf{r}_{\text{n}} - \mathbf{r}_{\text{n}\sigma}) + eab(\mathbf{r}_{\text{n}} - \mathbf{r}_{\sigma}) \quad (5)$$

where $S = \int n\sigma_u dV$, $\mathbf{r}_{\text{n}}$ and $\mathbf{r}_\sigma$ are the average distances of an electron in n and σ_u orbitals, and $\mathbf{r}_{\text{n}\sigma}$ is the average distance of an electron occupying both n and σ^*_u orbitals. The coefficients a and b are related to the experimental ΔH only if all the lowering of the ground state is due to CT interaction. In such a case

$$(b/a)^2 = \Delta H/(W_1 - W_0) \quad (6)$$

where W_1 and W_0 are the energies of ionic and no-bond structures. However, in the 4-methylpyridine–iodine complex, the N–I distance is considerably shorter than the sum of van der Waals radii of these atoms. This leads to a large closed-shell repulsion between the donor and acceptor in these series of molecules. The measured stability of a complex is the difference between the charge-transfer binding and this repulsion. Person[34] estimated a value of 1.0 eV for the repulsion energy between the pyridine and iodine. Since the interactions in these complexes are localized between N and I atoms, it is not unreasonable to assume a relatively constant repulsion energy of 1.0 ± 0.25 eV between the non-*ortho*-substituted donors and iodine. The lowering of the ground state due to CT interaction, ΔE, will then be $(\Delta H_f + 1 \pm 0.25)$ eV and eq 6 becomes

$$(b/a)^2 = \Delta E/(W_1 - W_0) \quad (7)$$

If the values in the denominator can be reliably estimated, a quantitative comparison between b/a obtained from eq 7 and those that predict the observed trend in f would be illustrative. Figure 5 shows the

---

[30] N. S. Bayliss, *Proc. Roy. Soc.* (London), **158**, 551 (1937).

[31] See also E. U. Condon, *Phys. Rev.*, **32**, 858 (1928).

[32] E. K. Pyler and R. S. Mulliken, *J. Am. Chem. Soc.*, **81**, 823 (1959).

[33] It should be noted that this method of constructing potential curves is purely empirical.[28] Therefore the above treatment should not be judged as a proof that the values obtained from extrapolation are D.

[34] W. B. Person, *J. Chem. Phys.*, **38**, 109 (1963).

theoretical curves[35] of f's for different values of the overlap integral, $S = \int n\sigma_u dV$. The contribution from the first term in eq 5 is negligible for $b/a > 0.3$. The f's obtained from eq 5 are probably not radically affected for $b/a > 0.3$ even when other configurations are mixed in (3) since only the internuclear distances and not the detailed description of orbitals enter into the second term of eq 5. Agreement between the slopes of theoretical and experimental curves then may be reasonable.

Recent estimates for $(W_1 - W_0)$ and S are around 2.5 eV and 0.3, respectively, for pyridine. This leads to b/a ratios between 0.6 and 0.7 for pyridines. In contradiction to the observed behavior, for $S = 0.3$, f should not vary with ΔH in this region!

The following alternative method seems to give a more acceptable result. The onset of the charge-transfer absorption corresponds to the energy difference between a point P on the potential curves of E where the transition probability vanishes, and the lowest point in the potential curve of N (ignoring the zero-point energy). P need not be the lowest point of the potential curve of E. If E is a repulsive state, $P \geqslant W_1$. Thus the upper limit of the denominator in eq 7 can be equated to the energy of the onset of the transition minus the dissociation energy of N. (If E is an attractive state, this may become the lower limit.) The determination of the energy of onset of CT transition or its variation from complex to complex cannot be done accurately, due to the shape of the bands. It is, however, certainly under 4 eV and probably around 3.5 eV. Due to the lack of alternative methods, the latter value was chosen for a calculation of b/a ratios from eq 7. The experimental f's of the pyridine–iodine series are plotted against the b/a ratios thus obtained in Figure 5.

The curves and experimental points in Figure 5 suggest values around 0.1–0.2 for the overlap integrals in these compounds. These are lower than the value of 0.3 recently suggested for pyridine–iodine complex.[34] In view of the above gross approximations, no definite statement can be made regarding S.

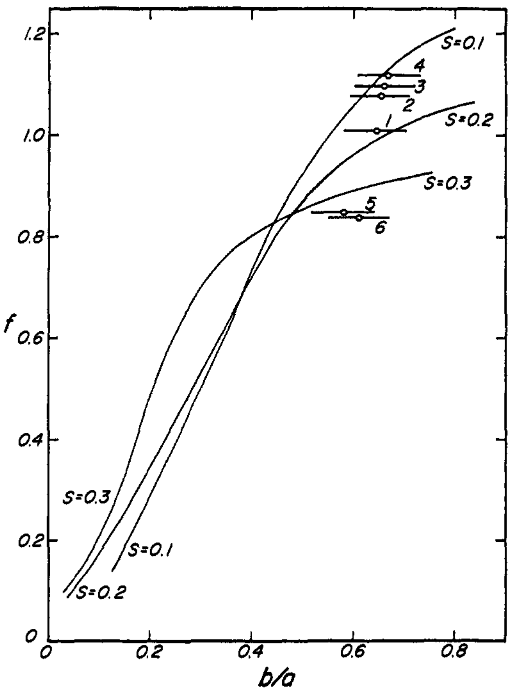

Figure 5. Theoretical curves (eq 5 and ref 33) for oscillator strengths. The points were determined by eq 7. The variation in b/a ratios is due to the use of 1 ± 0.25 eV for the repulsion energy between the donor and acceptor. Donors: (1) pyridine, (2) 2-picoline, (3) 3-picoline, (4) 4-picoline, (5) 2-chloropyridine, (6) 3-chloropyridine.

We conclude that these experiments agree with Mulliken's prediction qualitatively and that reliable quantitative treatment of the data is not possible at present.

---

[35] From eq 5 with $|\mathbf{r}_n - \mathbf{r}_\sigma| = 3.7$ Å and $|\mathbf{r}_n - \mathbf{r}_{n\sigma}| = 1.35$ Å. These values are based on the experimentally observed internuclear distances.[24]

The Microwave Spectrum, Structure, and Dipole Moment of Difluorophosphine[1]

Robert L. Kuczkowski

Contribution from the Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104. Received October 14, 1967

Abstract: The microwave spectra of PHF_2 and PDF_2 have been analyzed. Rotational constants are 24551.63, 8895.55, and 6854.02 Mc for PHF_2 and 21898.84, 8635.69, and 6778.49 Mc for PDF_2. The structural parameters of this pyramidal molecule are: d(PH) = 1.412 ± 0.006 Å; d(PF) = 1.582 ± 0.002 Å; $\angle$FPF = 99.0 ± 0.2°; $\angle$HPF = 96.3 ± 0.5°. The dipole moment was evaluated as $\mu = 1.32 \pm 0.01$ D.

Difluorophosphine, PHF_2, was recently characterized by Rudolph and Parry.[2] They concluded that its physical and chemical properties were consistent with an expected pyramidal structure. The detailed structural parameters, however, have not been determined and this microwave investigation was undertaken to obtain their values.

Experimental Section

The spectra were measured with conventional 80-kc square-wave Stark modulated spectrometers employing phase-sensitive de-

---

[1] This research was supported in part by a grant (GP 6814) from the National Science Foundation, Washington, D. C.

[2] (a) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, 4, 1339 (1965); R. W. Rudolph, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1966.