only 2–5% isomer conversion resulted. Poassium ferrioxalate actinometry was employed.[82] Tubes containing solutions of potassium ferrioxalate (0.006 F) in 0.1 N sulfuric acid were irradiated prior to, during, and at the end of each experiment. The production of ferrous ion was determined by measuring the optical density of its complex with 1,10-phenanthroline. The extinction coefficient of the complex at 5100 Å., (1.132 ± 0.003) × 10⁴ 1. mole⁻¹ cm.⁻¹, was determined by the recommended procedure[82] using a standardized solution of ferrous sulfate. The quantum yield for ferrous ion production at 3660 Å. was taken as 1.21.[82,85]

Excitation Energies.—A detailed study of .phosphorescence spectra from sensitizers used in this work will be published shortly.[89] The values of triplet excitation energies (used) refer to 0–0 band maxima in phosphorescence spectra of sensitizer solutions in glasses consisting of methylcyclohexane and isopentane (5:1 by volume) at 77°K. The emission spectra of biacetyl and benzil were also measured at room temperature in various solvents. The phosphoroscopes used in such experiments have been described.[66,90] In some cases phosphorescence could not be detected and the excitation energies refer to 0–0 bands in $S_0 \rightarrow T_1$

absorption spectra measured in ethyl iodide, carbon disulfide, oʳ in the presence of high pressures of oxygen. Such values were taken from the literature.[49,91–94]

The triplet-state energy of duroquinone was estimated by assuming it to be identical with the excitation energies of 2,3-dimethyl-1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone.[95]

The phosphorescence spectra of 4-acetylbiphenyl and 2-acetylfluorene were recorded and excitation energies of 67.5 and 64.1 kcal./mole were indicated for these two compounds, respectively. These values were not used because the presence of emitting impurities was suspected. In view of the stilbene stationary states established in the presence of these sensitizers and the fact that the 0–0 band of the phosphorescence spectrum of 4-benzoylbiphenyl is reported to be at 60.6 kcal./mole,[96] we tentatively assumed that the 0–0 phosphorescence bands for 4-acetylbiphenyl and 2-acetylfluorene are close to 60.6 kcal./mole.[97]

The 0–0 band of the phosphorescence spectrum of benzanthrone was estimated to lie at about 46.0 kcal./mole.[98]

(85) The higher value (1.7) reported by Lee and Seliger[86] is probably in error. The ferrioxalate actinometer has been checked against uranyl oxalate actinometry[82,87] and against benzophenone–benzhydrol actinometry[68] and in all cases the values of Hatchard and Parker appear to be correct.

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Charge-Transfer Complexes in Solution. I. Spectrophotometric Studies of Aromatic Hydrocarbon–Aromatic Nitro Compounds Dissolved in Carbon Tetrachloride

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Here there is reported an ultraviolet absorption spectral study of the charge-transfer complexes formed between certain methylbenzenes and selected aromatic nitro compounds in carbon tetrachloride at 20 and 45°. Toluene, *m*-xylene, mesitylene, durene, pentamethylbenzene, and hexamethylbenzene were the donors used. Acceptors were nitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrobenzene, and *sym*-trinitrotoluene. The new computer method[2] designed to eliminate ambiguities from the literature was used to process all experimental information. For a given donor, the absorptivity of the complex (a_C) increases as the strength of the acceptor is increased by increasing the number of nitro groups. This fact is predicted by the charge-transfer theory. The relative order of a_C for each donor is nitrobenzene, *m*-dinitrobenzene, *p*-dinitrobenzene, *sym*-trinitrotoluene, and *sym*-trinitrobenzene. This contrasts with the well-known contradictions of Mulliken's charge-transfer hypotheses reported for complexes of a given acceptor with donors of increasing strength. Formation constants, computed with the assumption that only a 1:1 complex is formed, vary with the wave length, and the absorptivities of the complexes vary with the temperature. These facts are explained by the simultaneous formation of isomeric 1:1 and higher order complexes. Average formation constants for each of the twenty-two systems studied at 20 and 45° are given.

Introduction

It has been well established that aromatic nitro compounds are capable of forming complexes of the charge-transfer type as described by Mulliken[3–5] and more recently by Dewar and Lepley.[6] Bier[7] has investigated *sym*-trinitrobenzene complexed with aromatic amines and hydrocarbons in chloroform. Foster and co-workers[8–10] have studied a number of

nitro systems. From these works it has been determined[8] that steric effects play an important role in complex formation. Further, it has been shown that an increase in the number of nitro groups in the acceptor molecule produces an increase in the degree of association as shown by the magnitude of association constants with a number of amines.[10] Thompson and de Maine[2] have studied the effect of solvent on the *sym*-trinitrobenzene–naphthalene system. A change of solvent was found to be able to vary the magnitude of the association constants, K, by a factor of at least five. Also, the solvent has been shown to change the absorptivity of the complex.

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The formation of a 1:1 complex has long been postulated to explain certain spectral data with varying degrees of success. Benesi and Hildebrand[11] first suggested a method of calculating the association constant, K, and the molar absorptivity, a_C, of a complex for the system: $A + D \overset{K}{\rightleftharpoons} C$. The Scott[12a] and the Ketelaar[12b] equations are two more recent treatments. Recently de Maine and Seawright[13] have developed an iterative method of analysis of spectroscopic data which was employed in this study and which is discussed more fully below.

The validity of a spectral analysis performed in any of these procedures has often been questioned. Variations in the value of K have shown (at times) a dependence upon wave length contrary to what is predicted. Scott[12a] has attributed variations to the neglect of activity coefficients. Ketelaar, et al.,[12b] have tried to correct for absorption due to an undercutting band of the free acceptor to obtain constant results. Corkill, et al.,[14] have used a competitive system of donors to study the decrease in intensity of a well known band of one complex by the competing equilibrium for the common acceptor by the second donor. de Maine and Seawright's method[13] has adequately allowed for all corrections of this nature and thus any variations noticed cannot be attributed to absorption by some of the uncomplexed species.

A further consideration is the possibility that more than one type of complex is formed, thus invalidating the assumption of 1:1 interaction producing a single product. Higher order interactions forming 2:1 and other complexes have been considered likely due to the excess of one reagent normally required as an experimental limitation imposed by a mathematical approximation in most analyses. Using carefully selected systems Landauer and McConnell,[15] Foster, et al.,[16] and Hayman[17] have studied this possibility and have found, respectively, evidence for a 2:1 complex, no evidence for a 2:1 complex, and support for a nonspectroscopic method indicating higher order complexes. Jurinski[18] has shown that an exact solution for the formation constants (K_1 and K_2) and the molar absorptivities (a_{C_1} and a_{C_2}) for 1:1 and 2:1 simultaneous complexes may be determined assuming Beer's law is valid for all species. It is seen in this treatment that the association "constant" determined assuming only 1:1 complex formation is not a true constant and thus could be expected to vary with wave length.

Orgel and Mulliken[19] have postulated that isomeric and contact charge-transfer complexes may play an important role but that their presence should lead to a wave length independent value of K. Several workers have reported variations in the calculated association constant with wave length.[2,20] Zingaro, et al.,[21] have found spectral evidence for 2:1 complex formation for some very highly associated systems and have noted anomalous deviations in the formation constant for some of their other systems. Thompson and de Maine[2] have found a variation in formation constant for the naphthalene–sym-trinitrobenzene complex in n-heptane at wave lengths greater than 370 mμ at 20°. In agreement with Orgel and Mulliken these authors have concluded that the variation may not be explained by postulation of any "isomeric" or "contact" 1:1 interaction and thus must be due to formation of a 2:1 or higher order complexes.

The present work will discuss a series of methylbenzenes complexed with a series of nitrobenzenes and sym-trinitrotoluene. The formation constants and the absorptivities of the complexes have been determined at 20.0 and 45.0° assuming a simple 1:1 donor–acceptor interaction to occur.

Experimental

A. Materials.—Fisher Spectrograde carbon tetrachloride was used as solvent for all solutions. Fisher certified grade nitrobenzene (NB), b.p. 212°, was used as supplied. Eastman reagent grade chemicals were: m-dinitrobenzene (m-DNB), m.p. 88–89°; p-dinitrobenzene (p-DNB), m.p. 169.5–171.0°; sym-trinitrobenzene (s-TNB), m.p. 119.5–121.0°; durene (DUR), m.p. 77–80°; pentamethylbenzene (PMB), m.p. 49–52°; hexamethylbenzene (HMB), m.p. 162–163°. sym-Trinitrotoluene (s-TNT), m.p. 78.5–79.5°, was obtained from K and K Laboratories. Eastman Spectrograde mesitylene (MES) and Matheson Spectrograde toluene (TOL) and m-xylene (m-Xy) were used. All solids were recrystallized from alcohol and Spectrograde liquids were used as supplied without further purification. Anhydrous nitrogen of dew point less than −40° was obtained from Matheson Co., Joliet, Ill.

B. Solutions.—All solutions were prepared at room temperature using CCl₄ as solvent, and concentrations were corrected to the temperature of measurement. No special precautions were made to exclude water vapor and oxygen from the samples during preparation, but solvents were purged with dry nitrogen immediately before use and dispensed from automatic burets operated under an atmosphere of dry nitrogen. Individual samples were prepared by using aliquots of a single bulk for the two-component systems. For the mixed, three-component systems solutions were prepared using two identical acceptor bulks and the pure liquid donor or a single donor bulk for the solid donors. For each system studied eighteen samples, whose donor concentrations varied over a twentyfold range, were measured at 20.0 and 45.0° at 50 Å. intervals between 300 and 400 mμ. Six freshly prepared duplicate samples provided a check on the accuracy of the spectral measurements.

C. Spectral Measurements.—Measurements in the ultraviolet and visible regions were made with a Bausch and Lomb Spectronic 505 double beam spectrophotometer and with two Beckman DU spectrophotometers fitted with standard temperature control accessories and with photomultiplier tubes. Four matched 1-cm. quartz cells with glass stoppers were used for all measurements. Pure CCl₄ was used as reference liquid in all cases. Absorbance measurements made with the Beckman spectrophotometers were easily reproduced to within 2% even after several hours. Data collected with the Spectronic 505 were not used in the calculations.

D. Method of Data Analysis.—All data have been processed using the system of programs developed by de Maine and Seawright.[13] Concentrations of all solutions were calculated in moles/l. at 20.0 and 45.0° using quantities measured at room temperature. Volume additivity of all components was assumed for all systems.

Absorptivities of all individual components were determined at the wave lengths of interest by fitting the spectral data for the

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Table I

Association Constants at 20° for the Hexamethylbenzene and sym-Trinitrobenzene Complexes, Calculated with the Assumption that Only One 1:1 Complex Is Formed[a]

λ, mμ	Hexamethylbenzene +					sym-Trinitrobenzene +				
	NB	m-DNB	p-DNB[b]	s-TNT	s-TNB	PMB	DUR	MES	m-Xy	TOL
300							3.48 (0.19)	1.02 (0.01)		
305							1.01 (0.26)	0.72 (0.01)		
310						3.52 (0.10)	0.78 (0.18)	0.69 (0.02)		
315						3.40 (0.09)	1.14 (0.19)	0.71 (0.02)		
320		1.02 (0.29)		1.85 (0.26)		3.05 (0.09)	1.50 (0.32)	0.77 (0.02)		
325	1.46 (0.67)	0.82 (0.21)	2.24 (2.46)	1.53 (0.36)	4.75 (0.13)	3.21 (0.09)	1.86 (0.95)	0.80 (0.02)		
330	1.02 (0.29)	0.77 (0.23)	1.48 (1.30)	1.63 (0.33)	4.46 (0.18)	3.17 (0.98)	1.83 (0.51)	0.83 (0.02)		0.27 (0.01)
335	0.96 (0.30)	0.84 (0.20)	1.24 (1.12)	1.70 (0.30)	4.44 (0.18)	3.14 (1.34)	1.86 (1.89)	0.86 (0.02)		0.23 (0.01)
340	0.72 (0.25)	0.78 (0.25)	0.94 (0.93)	1.32 (0.31)	4.33 (0.19)	2.97 (1.42)	1.86 (1.21)	0.87 (0.02)		
345	0.97 (0.27)	0.82 (0.23)	0.96 (0.93)	1.39 (0.28)	4.41 (0.18)	2.94 (0.99)	1.84 (0.36)	0.77 (0.02)	0.69 (0.02)	
350	0.95 (0.29)	0.71 (0.23)	0.77 (0.78)	1.42 (0.31)	4.42 (0.17)	2.91 (0.12)	1.90 (0.06)	0.78 (0.02)	0.51 (0.01)	
355	0.87 (0.31)	0.79 (0.21)	0.79 (0.92)	1.22 (0.27)	4.55 (0.16)	2.97 (0.04)	1.87 (0.01)	0.79 (0.02)	0.43 (0.01)	
360	0.85 (0.31)	0.85 (0.18)	0.75 (0.77)	1.48 (0.31)	4.58 (0.15)	3.07 (0.08)	1.98 (0.06)	0.71 (0.02)	0.43 (0.01)	0.38 (0.02)
365	1.24 (0.34)	0.71 (0.18)	0.72 (0.84)	1.47 (0.27)	4.67 (0.15)	3.13 (0.10)	2.01 (0.07)	0.75 (0.02)	0.42 (0.01)	0.45 (0.03)
370	1.36 (0.34)	0.74 (0.16)	0.64 (0.67)	1.55 (0.23)	4.78 (0.14)	3.14 (0.10)	1.98 (0.07)	0.55 (0.01)	0.36 (0.01)	0.67 (0.04)
375	1.56 (0.35)	0.69 (0.14)	0.58 (0.73)	1.70 (0.33)	4.91 (0.14)	3.14 (0.09)	2.01 (0.07)	0.52 (0.01)	0.33 (0.01)	0.70 (0.04)
380		0.72 (0.25)	0.61 (0.83)	1.82 (0.26)	4.89 (0.13)	3.16 (0.09)	2.09 (0.07)	0.46 (0.01)	0.32 (0.01)	1.06 (0.05)
385		0.84 (0.20)	0.60 (0.64)	1.66 (0.18)	4.92 (0.12)	3.19 (0.09)	1.99 (0.06)	0.39 (0.01)	0.28 (0.01)	1.62 (0.07)
390		0.92 (0.10)	0.62 (0.77)	1.75 (0.22)	5.13 (0.12)	3.32 (0.09)	2.13 (0.06)		0.36 (0.01)	1.38 (0.06)
395		0.74 (0.08)		1.96 (0.04)	5.15 (0.12)	3.44 (0.08)	2.05 (0.05)		0.14 (0.02)	
400		0.91 (0.02)		2.17 (0.04)	5.28 (0.11)	3.62 (0.08)	2.27 (0.05)			
410					5.43 (0.11)					
420					5.36 (0.11)					
430					5.50 (0.11)					
440					5.72 (0.12)					
450					5.71 (0.12)					

[a] Association constants are in moles/l. units. Maximum permitted errors are given in parentheses. [b] DEV = 5.0%.

separate system to the equation: $a_X = {}_0a_X + {}_1a[X]$, where a_X is the molar absorptivity of X, ${}_0a_X$ and ${}_1a$ are empirical constants for a first-order dependence of a_X upon the molar concentration of X, [X].

The mixed systems may be represented by the 1:1 reaction, $n_1A + n_2D \overset{K}{\rightleftharpoons} C$. Following the method of de Maine and Seawright[22] for the special case $n_1 = n_2 = 1$

$$C_C = (KC_A + KC_D + 1 - [K^2(C_A - C_D)^2 + 2KC_A + 2KC_D + 1]^{1/2})/2K \quad (1)$$

$$A_C = a_C C_C = A_M - a_A(C_A - C_C) - a_D(C_D - C_C) \quad (2)$$

$$\frac{C_A C_D}{A_C} = \frac{1}{Ka_C} + \frac{(C_A + C_D - C_C)}{a_C} \quad (3)$$

where A_M is the measured absorbance and A_C is that of the complex. C, defined by its subscript, represents the initial concentrations of the reactants (donor and acceptor) and the equilibrium concentration of the complex. The absorptivities of each reactant at each temperature and wave length were calculated from data for CCl_4 solutions of each separate reactant as described above. The above equations were solved by an iterative method with spectral data collected at each wave length and temperature.

In the computer method certain error factors are incorporated to define the limits of reliability of the data. Thus the lower limit of reliability for the absorbance (WL1) was preselected at 0.060 and the upper limit (WU1) at 1.400 for all mixed systems. Since the treatment of spectral data sometimes involves a small difference in two large numbers, with a resulting uncertainty in the result, another factor, WAC1, was employed such that if $(A_C/A_M) <$ WAC1 the data are automatically rejected. Here A_C is the calculated absorbance of the complex. WAC1 for the mixed systems was chosen as 0.25. In fitting the data points to a straight line in the final iteration a 2% error zone was allowed (DEVF1 = DEVF2 = 0.02). This ensures the automatic rejection of any datum point whose associated individual error is more than ±2% of the correct value as determined by the final iteration cycle. Errors quoted for the association constants in Table I are "maximum permitted errors" as defined in ref. 13 and are critically dependent upon the magnitude of DEVF1 and DEVF2 (see the system p-DNB–HMB).

(22) See p. 124 of ref. 13.

Results

The individual components used were measured in CCl_4 solution over the range of concentrations used and the wave lengths employed in the subsequent study of the mixed systems. It was found that for the donors studied the constant ${}_1a$ was effectively zero within a 1% error limit (DEVF = 0.01). For the nitro acceptors it was seen that the slopes ${}_1a$ were significant and hence could not be discarded in solving eq. 2.

The absorbances of all systems were measured using pure CCl_4 as a reference liquid. The data were processed in the manner just described. The resultant values of K and a_C were determined along with their associated maximum permitted errors over the wave length range from 300 to 450 mμ.[23] Values of K for the association of hexamethylbenzene with the various acceptors and of sym-trinitrobenzene with the various donors used are given in Table I for these systems at 20.0° as a typical example of variations in the association constant with wave length. Table II lists the association constants for the systems studied at 20 and 45°. These values have been determined by averaging over the range of wave lengths studied regardless of the variation. It is seen from the observed values of K that acceptor strength increases as the number of nitro groups is increased.

The molar absorptivities for the complexes (a_C) at 20 and 45° were computed from the raw data and then were plotted as a function of wave length for each donor–acceptor pair. Typical plots are displayed in Fig. 1 and 2. In Table III is given for each complex the low energy wave length at which $a_C = 1000$. These values indicate the relative shift at each temperature of the charge-transfer band for different donors and acceptors. Values in Table IV illustrate the change

(23) For a more complete listing of these values than is presented here for the systems referred to see: Neil B. Jurinski, Ph.D. Dissertation, The University of Mississippi, 1963.

<div align="center">

Table II[a]

Average Values of Apparent Formation Constants at 20 and 45°

</div>

Donor	Temp.	NB	m-DNB	p-DNB	s-TNT	s-TNB
				Acceptor		
Toluene	20°	0.10 (0.08)	0.32 (0.29)	0.21 (0.15)	0.75 (0.47)	0.33 (0.05)
	45°	0.15 (0.17)	0.15 (0.10)	0.06 (0.02)	0.26 (0.22)	0.25 (0.04)
m-Xylene	20°	...	0.09 (0.08)	0.16 (0.02)	0.45 (0.07)	0.41 (0.11)
	45°	...	0.10 (0.01)	0.09 (0.02)	0.17 (0.05)	0.26 (0.10)
Mesitylene	20°	...	...	...	0.52 (0.02)	0.70 (0.14)
	45°	...	...	...	0.38 (0.02)	0.55 (0.06)
Durene	20°	...	...	0.41 (0.04)	0.68 (0.16)	1.91 (0.24)
	45°	...	...	0.64 (0.34)	0.58 (0.14)	1.21 (0.17)
PMB	20°	...	...	0.79 (0.30)	1.19 (0.09)	3.25 (0.25)
	45°	...	...	0.76 (0.43)	0.94 (0.11)	1.93 (0.25)
HMB	20°	1.09 (0.27)	0.80 (0.27)	0.82 (0.26)	1.61 (0.23)	4.92 (0.43)
	45°	1.82 (0.55)	0.68 (0.11)	0.99 (0.31)	1.17 (0.41)	3.07 (0.30)

[a] Standard deviations are listed in parentheses, the large standard deviations reflect the dependence of the formation constant on wave length; formation constants are in moles/l. units.

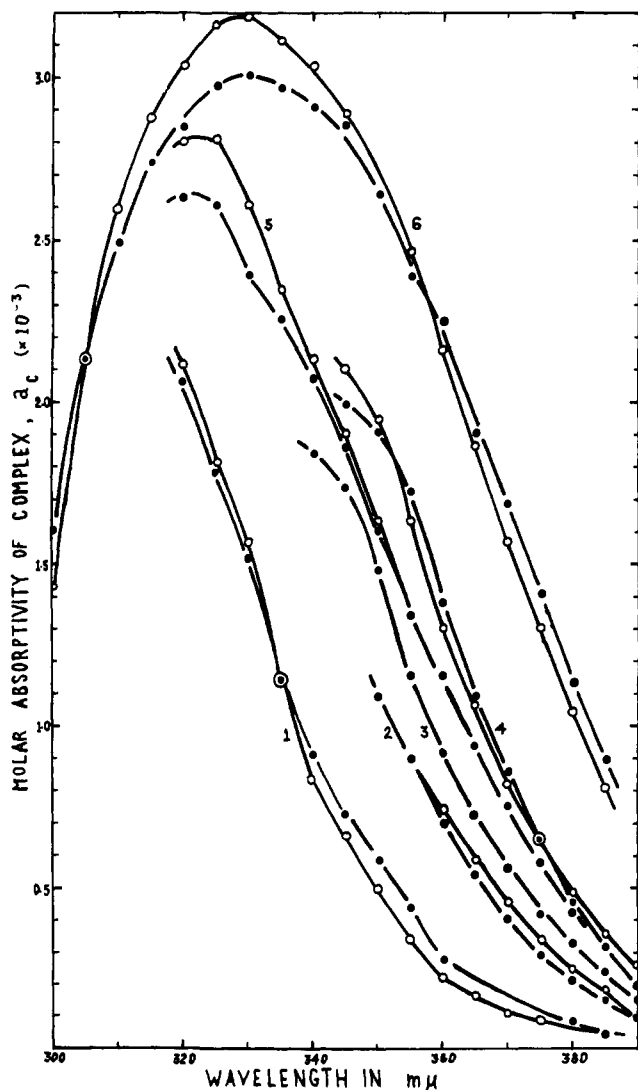in intensity of the charge-transfer band with change in donor or acceptor.

Fig. 1.—Absorption spectra for m-xylene and mesitylene complexes with nitro compounds at 20° (—●—) and 45° (—O—): 1, m-DNB; 2, s-TNT; 3, p-DNB; and 4, s-TNB for m-xylene systems; 5, s-TNT; and 6, s-TNB for mesitylene systems.

Discussion

Within the error limits of the data the association constants, K, agree with values determined previously for some of these systems.[2] The variation of the value

of K with wave length emphasizes the danger of limiting the analysis to data from a narrow range of wave lengths. An assumption that the absorptivity of the complex (a_C) is temperature independent near the maximum a_C value is not justified (Fig. 1 and 2).

<div align="center">

Table III[a]

</div>

Donor	NB	m-DNB	p-DNB	s-TNT	s-TNB
			Acceptor		
Toluene	315	327	350	342	350
m-Xylene	...	337	358	352	367
Mesitylene	...	...	...	364	383
Durene	...	...	376	373	402
PMB	...	...	378	400[c]	410[c]
HMB	330[b]	387	397[c]	406[c]	>420[c]

[a] The numbers in this table are the values for the wave length in mμ on the low energy band edge when the molar absorptivity of the complex is 1000. Temperature is 20°. [b] Maximum absorptivity is 350 at 330 mμ. [c] Extrapolated.

The temperature dependence of a_C at a fixed wave length and for a given complex (Fig. 1 and 2) can be interpreted in terms of "isomeric" or "orientational" 1:1 charge-transfer complexes in solution. Evidence for two or more isomeric 1:1 complexes in other systems have been reported.[2,24-27] The wave length variation in K for a given temperature (Table I) cannot be explained with the assumption that there are only 1:1 complexes.[2]

From the hexamethylbenzene–sym-trinitrobenzene data in Table I it is seen that a constant K value is obtained over a considerable region near the band maximum. For the system m-xylene–sym-trinitrobenzene a very noticeable variation occurs with no apparent region of constancy. In this case the position of the complex band maximum was obscured beneath high background absorption of the acceptor in the higher energy region. Orgel and Mulliken[19] have stated that at wave lengths of maximum absorption the absorptivities are less sensitive to orientational differences in the case of isomeric complexes. It seems unlikely that the observed variation in association constant is due to contact charge-transfer complex formation because this phenomenon should yield values of K which are wave length independent. The nitro compounds should be less likely to form

(24) P. A. D. de Maine, J. Chem. Phys., **26**, 1189 (1957).
(25) V. Ramakrishnan, J. Mol. Spectry, **11**, 255 (1963).
(26) V. Ramakrishnan and P. A. D. de Maine, J. Miss. Acad. Sci., **10**, 82 (1964).
(27) J. R. Gott and W. G. Maisch, J. Chem. Phys., **39**, 2229 (1963).

TABLE IV[a]

ABSORPTION SPECTRA DATA FOR THE INDICATED DONOR–ACCEPTOR COMPLEX AT 20°

Donor	NB	m-DNB	p-DNB	s-TNT	s-TNB
Toluene	<310 (>1580)	<320 (>1540)	<335 (>1840)	<330 (>1570)	<330 (>2340)
m-Xylene	...	<320 (>2060)	<340 (>1850)	<350 (>1100)	<345 (>2000)
Mesitylene	...	...	...	322 (2630)	330 (3000)
Durene	...	...	<330 (>1880)	337 (2260)	340 (2390)
PMB	...	...	353 (1400)	345 (2220)	370 (2440)
HMB	330 (350)	345 (2050)	378 (1360)	375 (2140)	385 (2500)

[a] 330 (3000) means the molar absorptivity for the mesitylene–s-TNB complex has a maximum value of 3000 at wave length 330 mμ. <310 (>1580) means the toluene–nitrobenzene complex has an absorption maximum greater than 1580 on the short wave length side of 310 mμ. Background absorption prevented the determination of λ_{max} and a_{max} in these cases.

contact charge-transfer complexes than the halogens because there is a smaller acceptor orbital in the former.[19]

The average association constants (Table II) indicate qualitatively that the relative complexing ability in the series of donors and acceptors increases with increased methylation of the donor or increased nitration of the acceptor. Data in Table III support this view with p-dinitrobenzene being the exception. However, the molar absorptivities (Table II) of the complexes follow the order noted previously for the methylbenzenes[28] in which the stronger donors exhibit less intense complex absorption. This is contrary to theoretical predictions, since a stronger complex implies greater overlap and hence greater absorption, In the present work it was noted that for a given donor molecule, the complex absorption was greater for stronger acceptors in agreement with the predicted order. Thus for the series of nitro compounds studied, sym-trinitrobenzene showed the strongest absorption with all donors used. An exception is p-dinitrobenzene which exhibits stronger absorption than expected. This has also been found true for ICl complexes.[28]

From the temperature study it was found that the complex bands were abnormally dependent on temperature. A normal vibrational broadening should enhance both sides of a band equally with no change at the band maximum. In several cases the band maximum decreased in intensity on going to a higher temperature. This has been found too in other solvents by Thompson and de Maine.[2] In other instances the sides of the complex bands were altered unevenly in a transition to the higher temperature, the greater enhancement being on the high energy side. Sometimes this effect was large enough to suggest a shift in the band maximum to higher energy with increase in temperature (see HMB–s-TNB system in Fig. 2).

Band shapes for the complexes were broad and unsymmetrical when both sides of the band were observed. A possible underlying band on the low energy side of the complex band indicates the presence of more than one complex. The effects of temperature, already noted, support this possibility and indicate that the most stable species present absorbs at a slightly higher energy than any other complex present as the most stable form should be relatively more abundant at a higher temperature. Orgel[29] cites a similar result with chloranil and the halogens, where the isomeric complex absorbing at the shorter wave length was the more intense.

(28) L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc., 74, 4500 (1952).
(29) L. E. Orgel, J. Chem. Phys., 23, 1352 (1955).

As a large excess of donor was used in the present work, it is possible that there may be a 2:1 or higher order complex with more than one donor molecule, since "...the fact that one molecule is bound to another does not prevent a third from being attracted."[4]
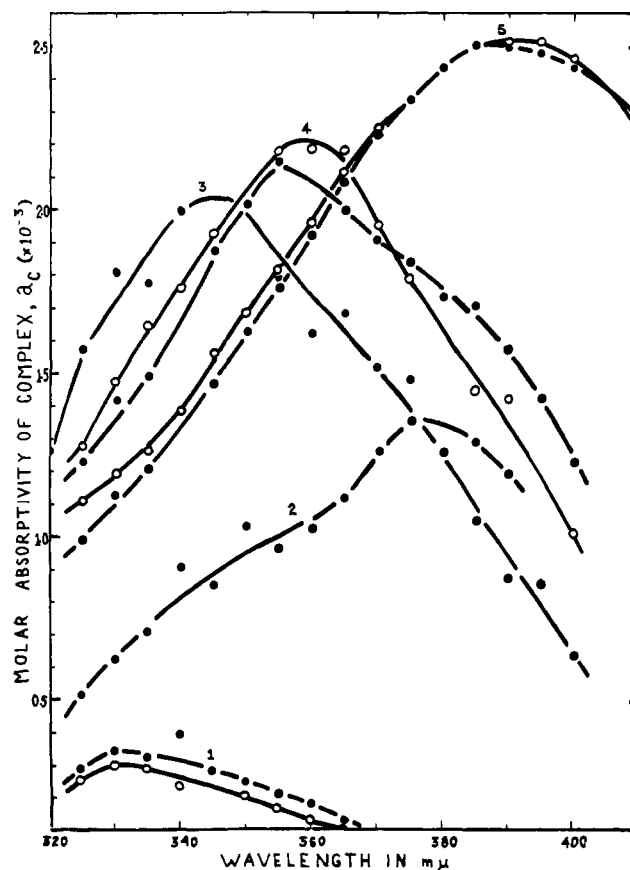

Fig. 2.—Absorption spectra for hexamethylbenzene–nitro compound complexes at 20° (—●—) and 45° (—O—): 1, NB; 2, p-DNB; 3, m-DNB; 4, s-TNT; 5, s-TNB.

Our data were processed to test this possibility,[18] but the results did not support a model of simultaneous 1:1 and 2:1 interactions. It is possible that the assumption that the complex obeys Beer's law is invalid. This could lead to the observed breakdown in the data analysis. Thus while there is ample evidence of the simultaneous formation of higher order and 1:1 complexes, either isomeric 1:1 complexes or higher order complexes, by themselves do not appear to explain the results.

An Empirical Model for Nonbonded H–H Repulsion Energies in Hydrocarbons

BY HOWARD E. SIMMONS AND JOHN K. WILLIAMS

A suggestion of Mulliken for estimating nonbonded H–H repulsion energies has been applied in cases of interest in organic chemistry. The energy expression, derived from LCAO theory, generates in effect a potential function which is only dependent on 1s–1s overlap integrals. This simple model has qualitative value in predicting rotation barriers, conformational enthalpies, and thermodynamic stabilities of hydrocarbons which are relatively free of angle strain. A scheme has been devised based on Dreiding models, an "Ångstrom ruler," and a plot of repulsion energy vs. distance that allows rapid estimation of LCAO repulsion energies and should be a useful adjunct to the use of molecular models.

Introduction

Intramolecular nonbonded repulsive interactions make important contributions to the general phenomenon of steric effects and so influence kinetic, thermodynamic, conformational, and spectral properties of organic molecules. These interactions are not fully understood theroetically, and their relationship to experimental observations has aroused much controversy. Notwithstanding this incomplete picture, organic chemists have found the concept of nonbonded repulsive interactions to be useful,[1] and several empirical and theoretical potential functions have been derived for their calculation.

The purpose of this paper is to consider a semi-empirical scheme, based on a suggestion of Mulliken,[2] for the estimation of nonbonded hydrogen–hydrogen repulsions in some selected hydrocarbons. At the outset it must be emphasized that no sound theoretical foundation can be offered for the resulting simple model of hydrocarbons. This treatment of these weak interactions may be useful to the chemist in the same spirit as many other modern empirical concepts.

A Semiempirical Model.—Recently Hoffmann[3] has shown that LCAO theory (using a basis set of 2s and 2p carbon and 1s hydrogen AO's) predicts a rotation barrier in ethane. When his treatment was adjusted to agree with the experimental barrier, subsequent calculations of the LCAO binding energy as a function of conformation showed that the gross geometry of several hydrocarbons was correctly predicted. This model, for example, correctly finds that the energy of the chair form of cyclohexane is lower than that of any boat form. It is not generally possible to relate a Hückel calculation (with its unspecified Hamiltonian) to the set of specific physical effects currently believed responsible for the determination of molecular geometry.[4] However, it has been suggested by Mulliken[2] that one of these effects, nonbonded H–H repulsions,

can be simulated by considering four electrons in two isolated carbon–hydrogen bonds and treating this system by either MO or VB theory. In this manner, Mulliken concluded that this repulsion energy was simply proportional to the square of the overlap integral of two 1s hydrogen distributions. Although this theory is too naive to represent the physical problem, it seems reasonable to us that nonbonded H–H repulsions will be reflected in a qualitative sense by the overlap integral.

Spectroscopic studies are not fully in agreement as to the magnitude of nonbonded H–H repulsions, particularly those of geminal hydrogens[5]; however the steric effect of hydrogen atoms has been used fruitfully to explain many observations in organic thermochemistry.[6,7] It is in this latter light that we will employ the term nonbonded H–H repulsion. Hendrickson[8] has studied the conformational energies of the C_5–C_7 cycloalkanes and concluded that their geometry is determined largely by the nonbonded H–H interactions. Attempts have also been made to treat nonbonded effects in hydrocarbons by considering principally carbon–hydrogen interactions.[9]

The Hoffmann[3] and Mulliken[2] views have a common origin, and we might expect that results obtained from the simple Mulliken theory will embody those from the lengthier solution of a secular equation. Our purpose is to explore the use of the Mulliken relation (1)[2]

$$E_{HH} = AIS^2/2(1 - S^2) \qquad (1)$$

where A is a constant, S is the overlap integral for two 1s hydrogen distributions, and I is the valence state ionization potential of hydrogen. In this way we seek to treat nonbonded H–H repulsions in a purely additive fashion. Since eq. 1 is to be used solely as a semiempirical relation, nonbonded attractions will not be taken explicitly into account although it is recognized that this is a serious simplification. Mulliken showed[2] that eq. 1 was able to reproduce remarkably well the van der Waals

(1) See articles by W. G. Dauben and K. S. Pitzer and by F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

(2) (a) R. S. Mulliken, J. Am. Chem. Soc., **72**, 4493 (1950); (b) R. S. Mulliken, Record Chem. Progr. (Kresge-Hooker Sci. Lib.), **13**, 67 (1952).

(3) R. Hoffmann, J. Chem. Phys., **39**, 1995 (1963).

(4) (a) K. S. Pitzer, Discussions Faraday Soc., **10**, 66, 124 (1951); (b) C. A. Coulson, "Valence," Oxford Press, London, 1952, pp. 314–317; (c) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954; (d) L. J. Oosterhoff, Discussions Faraday Soc., **10**, 79, 87 (1951); (e) K. S. Pitzer, J. Chem. Phys., **8**, 711 (1940).

(5) (a) T. Simanouti, ibid., **17**, 245, 734, 848 (1949); (b) D. F. Heath and J. N. Linnett, ibid., **18**, 147 (1950); (c) L. S. Bartell and K. Kuchitsu, ibid., **37**, 691 (1962).

(6) E. A. Mason and M. M. Kreevoy, J. Am. Chem. Soc., **77**, 5808 (1955).

(7) See the important series beginning J. Allinger and N. L. Allinger, Tetrahedron, **2**, 64 (1958), and later papers in J. Am. Chem. Soc.

(8) J. B. Hendrickson, ibid., **83**, 4537 (1961); ibid., **84**, 3355 (1962).

(9) A. I. Kitaygorodsky, Tetrahedron, **14**, 230 (1961).