Comparison of Theoretical, Absolute Interaction Energies with Heats of Complexation in Carbon Tetrachloride

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Abstract ☐ The absolute interaction energies for the methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride are calculated by using net atomic charges and bond polarizabilities. The theoretical results are then compared to the experimentally determined heats of complexation in carbon tetrachloride. The trend of increasing complex strength with methyl substitution within each series is qualitatively predicted by this method, but the theoretical increase per methyl group is less than the experimental solution value by a factor of two to three. The overall correlation between the complex strength and the absolute interaction energy is poor. These results indicate that the contribution of the nonpolar solvent carbon tetrachloride to the overall complex strength is significant and perhaps greater than the absolute interaction energy of the substrate and ligand.

Keyphrases ☐ Interaction energies—methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride, net atomic charges and bond polarizabilities, compared to experimental heats of complexation in carbon tetrachloride ☐ Complexation, heats—absolute interaction energies for methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride (net atomic charges and bond polarizabilities) compared to experimental heats of complexation in carbon tetrachloride ☐ Carbon tetrachloride—contribution to complex strength, methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride, net atomic charge and bond polarizability theoretical results compared with experimental heats of complexation ☐ Solvents—contribution of carbon tetrachloride to the overall complex strength of methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride

Complexation has been extensively discussed in the pharmaceutical literature. It is known, for example, that complexation can affect the solubility (1), dissolution (2), chemical reactivity (3–6), and membrane transport (7) properties of drugs. While extensive experimental studies have led to empirical correlations between the structure and the equilibrium constant of interacting molecules (8, 9), detailed molecular calculations of the forces (and energies) involved have not been reported. It is difficult to perform accurate calculations on molecules as large as those of pharmaceutical interest (10, 11). However, recent theoretical developments show considerable promise in this direction (12).

In this report the method of monopoles-bond polarizabilities (12), in which a molecule is considered as a collection of monopoles (net atomic charges) and a collection of bonds (bond polarizabilities), is discussed and used to calculate the structures and absolute interaction energies for the methylbenzene complexes with fluoranil, chloranil, and tetrachlorophthalic anhydride. These results are then compared

with the experimentally determined heats of complexation in solution. In subsequent reports the effect of solvent on the energetics of complexation and the correlation between predicted structure and chemical reactivity will be discussed.

THEORETICAL

In the usual development of intermolecular force theory, two approximations are introduced (10, 11). The first is a truncation of the perturbation expansion to second order, leading to the electrostatic (first order) and polarization and dispersion (second order) terms. The second approximation is the development of the interaction terms in a multipole expansion, usually truncated after the first nonvanishing term (the dipole–dipole term for neutral molecules). Of these two approximations, the second seems to be the least reliable when the intermolecular distance is of the same order of magnitude as the dimensions of the interacting molecules (12). The method of monopoles-bond polarizabilities makes the following more reasonable approximations (12, 13):

1. For the first-order (electrostatic) term, the ground-state charge distribution is divided up into a set of monopoles located at the nuclei of the respective atoms. The electrostatic energy is then calculated by Eq. 1:

$$E_{el} = \sum_{1} \sum_{2} \frac{q\nu_1 q\nu_2}{r(\nu_1\nu_2)} \qquad \text{(Eq. 1)}$$

where $q\nu_1$ and $q\nu_2$ are the net atomic charges on nuclei ν_1 and ν_2 of molecules 1 and 2, respectively; $r(\nu_1\nu_2)$ is the ν_1, ν_2 distance; and the summations are over all nuclei in molecules 1 and 2.

2. For the second-order dispersion energy term, the transition charge density (14) is represented by a set of transition dipoles located at the center of the bonds. The dispersion energy is then a summation over all bonds and all excited states of each molecule. This latter summation, requiring a knowledge of the excited states of each molecule, is difficult to perform so a further approximation is to replace the bond transition dipole summations with the experimentally known bond polarizability tensors (15). To introduce the bond polarizability into the theoretical expression, two additional approximations are required: (a) each excitation must be localized over a single bond, and (b) a mean excitation energy must be used.

The assumption of localized excitations is reasonable for σ-electrons or π-electrons in a localized double bond but is questionable for delocalized π-electrons. This necessitates the use of an incremental π-electron polarizability (12, 13). The mean excitation energy is usually taken to be equal to the experimental ionization potential of the molecule. With these approximations, the dispersion energy is calculated using Eq. 2:

$$E_{disp} = -(I_1 \cdot I_2)/4(I_1 + I_2)\sum_{\mu_1}\sum_{\mu_2}$$

$$1/(r(\mu_1\mu_2))^6 \cdot \{6\alpha(\mu_1)^r\alpha(\mu_2)^r + \alpha(\mu_1)^r\delta(\mu_2)[3(\alpha(\mu_2)^l \cdot \hat{r}(\mu_1\mu_2))^2 + 1] +$$

$$\alpha(\mu_2)^r\delta(\mu_1)[3\widehat{\alpha}(\mu_1)^l \cdot \hat{r}(\mu_1\mu_2))^2 + 1] + \delta(\mu_1)\delta(\mu_2)[3(\alpha(\mu_1)^l \cdot \hat{r}(\mu_1\mu_2)) \cdot$$

$$(\widehat{\alpha}(\mu_2)^l \cdot \hat{r}(\mu_1\mu_2)) - (\widehat{\alpha}(\mu_1)^l \cdot \alpha(\mu_2)^l)]^2\} \qquad \text{(Eq. 2)}$$

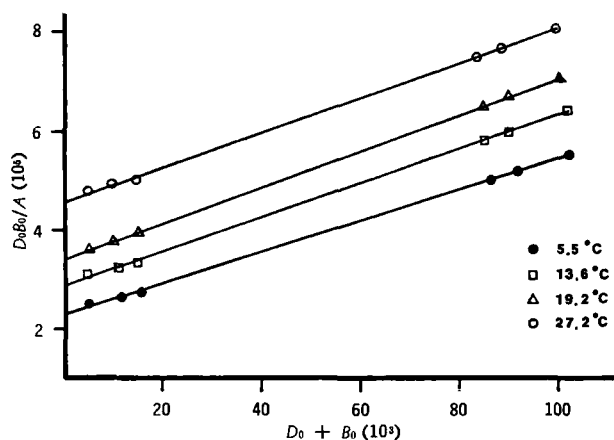where $\delta_\mu = \alpha_\mu^l - \alpha_\mu^r$; the subscripts 1 and 2 refer to molecules 1

Figure 1—*Plots of* D_0B_0/A *versus* $D_0 + B_0$ *for the chloranil–hexamethylbenzene complexes in carbon tetrachloride.*

and 2, respectively; μ refers to a particular bond; α^l and α^τ are the parallel and tangential polarizabilities, respectively; $\hat{\alpha}^l$ and $\hat{r}(\mu_1\mu_2)$ refer to the unit vectors in the direction of the bond and the intermolecular bond–bond distance, respectively; and the summation is over all bonds in molecules 1 and 2. If the bonds are considered isotropic, *i.e.*, $\alpha_\mu{}^l = \alpha_\mu{}^\tau = \alpha_\mu{}^m$, then $\delta_\mu = 0$ and Eq. 2 reduces to Eq. 3:

$$E_{\text{disp}} = -3/2 \frac{I_1 \cdot I_2}{I_1 + I_2} \sum_{\mu_1}\sum_{\mu_2} \frac{\alpha(\mu_1)^m \alpha(\mu_2)^m}{[(r(\mu_1\mu_2)]^6} \qquad (Eq.~3)$$

which is the London equation summed over bonds (16).

The polarization contribution to the second-order interaction energy is calculated using a set of monopoles to represent the ground-state charge distribution of molecule 2 (the same set as used for the electrostatic calculation, Eq. 1) and bond polarizabilities for the other (polarized) molecule, as in the dispersion energy. The resulting equation is:

$$E_{\text{pol}} = -(1/2)\sum_{\mu_1}[\alpha(\mu_1)^\tau \cdot (E(\mu_1) \cdot E(\mu_1)) + \delta(\mu_1) \cdot (E(\mu_1) \cdot \hat{\alpha}(\mu_1)^l)^2]$$
(1 by 2)
$$\qquad (Eq.~4)$$

where:

$$\bar{E}(\mu_1) = \sum_{\nu_2}[q\nu_2/(r(\nu_2\mu_1))^3]\bar{r}(\nu_2\mu_1)$$

$E(\mu_1)$ represents the electric field at bond μ_1 due to the changes on molecule 2, and $r(\nu_2\mu_1)$ is the distance vector from nucleus ν_2 to the middle of bond μ_1. The remaining terms are as defined for Eq. 2. Again in the case of isotopic bonds, $\delta_\mu = 0$ and Eq. 4 reduces to the classical expression (10). Interchanging the subscripts 1 and 2 in Eq. 4 gives the analogous equation for the polarization of molecule 2 by 1.

In addition to the preceding "attractive" terms, varying as R^{-n}, $n = 1, \ldots, 6$, it is experimentally known that as the distance between two molecules decreases a repulsive force predominates. The physical basis for this repulsion is the electron exchange that takes place when the overlap of the electron clouds of the two molecules becomes significant. A theoretical method applicable at these intermolecular distances (3–4 Å) was recently developed (17–19). In this double-perturbation method, the ground-state product wave function is antisymmetrized, with the result that the longrange terms previously discussed appear along with additional terms involving the overlap that decrease exponentially. While this theory justifies the calculation of the longrange terms by the usual methods in the region of interest, the accurate calculation of the shortrange terms is extremely difficult (20). For this reason, most methods utilize an empirical repulsive potential, varying exponentially or as approximately r^{-12}, to calculate the repulsive term. In this study the exponential repulsive potential developed by Kitaygorodsky (21) and modified by Huron and Claverie (22) is employed:

$$E_{\text{rep}} = 30,000 E(\nu_1) E(\nu_2) \exp[-11 \cdot r(\nu_1\nu_2)/\sqrt{4R(\nu_1) \cdot R(\nu_2)}] \quad (Eq.~5)$$

where $R(\nu)$ is the van der Waal radii of nucleus ν.

Detailed comparison of the method of monopoles-bond polarizabilities with other methods and with experimental results (12, 22–25) indicates that it is the most promising method available. For example, the molar volumes and vaporization energies of pyridine and benzonitrile and the solution energies of 11 small organic molecules were calculated and were in good agreement with experimental values (22, 26). Closely related methods were used to calculate the lattice energies and cell dimensions of benzene and triazine crystals and also were in good agreement with experimental values (27).

The theoretical method, as outlined here, gives no explicit recognition to the charge-transfer forces (28). While this force, arising from the resonance between the ground- and excited-state wave functions, may be important in strong complexes, for weak complexes such as those considered in this study, its contribution to the interaction energy appears to be significantly less than that due to the electrostatic, polarization, and dispersion forces (29–33).

EXPERIMENTAL

Materials—Carbon tetrachloride[1] was purified following the procedure of de Maine (34). Since no difference was observed in the spectrum of the donor, acceptor, or complex, it was used without further purification. Benzene[2] was distilled before use. Mesitylene[3], hexamethylbenzene[4], chloranil[5], and tetrachlorophthalic anhydride[4] were recrystallized to a constant melting point from a 7:3 mixture of ethanol and acetone before use.

Determination of Equilibrium Constant—Considering the simple complexation reaction $B + D \rightleftharpoons C$, where D = donor, B = acceptor, and C = complex, the following relationship is easily derived:

$$\frac{lD_0B_0}{A} = \frac{1}{\epsilon \cdot K} + \frac{B_0D_0}{\epsilon} - \frac{A}{\epsilon^2 l} \qquad (Eq.~6)$$

where A = absorbance; ϵ = molar absorptivity; l = path length; B_0 and D_0 = the initial amounts of acceptor and donor, respectively; and $K = [C]/([B][D])$. This relationship involves no assumptions other than Beer's law. If K is not very large, the last term in Eq. 6 can be neglected and Eq. 7 results:

$$\frac{lD_0B_0}{A} = \frac{1}{\epsilon \cdot K} + \frac{D_0 + B_0}{\epsilon} \qquad (Eq.~7)$$

This modified type of Scott equation becomes the Scott equation if $D_0 \gg B_0$ (35). Thus, a plot of D_0B_0/A *versus* $(D_0 + B_0)$ gives a straight line with slope $1/\epsilon$ and intercept $1/(\epsilon \cdot K)$. For the conditions of these experiments, $0.1 < K < 20$, $10 < [D]/[B] < 1000$, $[B] \simeq 10^{-3} M$, and $\epsilon \simeq 10^3$, it has been shown that the corrections to the linear approximation (Eq. 7) are negligible (36) and ensure a good separation of K and ϵ (37). If the spectra of the acceptor (B) and complex (C) overlap, Eq. 8 is appropriate:

$$\frac{lD_0B_0}{A - \epsilon_B B_0} = \frac{1}{K(\epsilon_C - \epsilon_B)} + \frac{D_0 + B_0}{\epsilon_C - \epsilon_A} \qquad (Eq.~8)$$

where ϵ_B and ϵ_C refer to the molar absorptivity of the acceptor and complex, respectively.

While higher order complexes (2:1, *etc.*) may exist, they are not expected to be important in the concentration ranges used in this study. Trotter and Yphantis (38) studied the hexamethylbenzene-tetracyanoethylene complex in methylene bromide by ultracentrifugation and determined that, at a 1 M concentration, approximately equivalent amounts of 1:1 and 2:1 complexes are present. Since $K = 21$ liters/mole and $\Delta H° = 7.75$ kcal/mole (39) for the 1:1 complex whereas $K \simeq 1.0$ liter/mole and $\Delta H° \simeq 2.0$ kcal/mole in this study (for the weaker complexes where higher concentrations are required for a good separation of K and ϵ), 2:1 complexation should be less significant in these systems. In addition, higher order complexes should be observed as a significant curvature in the plots according to Eq. 7 or 8 (40).

[1] Spectrophotometric grade, Aldrich Chemical Co.
[2] Spectrophotometric grade, Matheson, Coleman and Bell.
[3] Gold label, Aldrich Chemical Co.
[4] Purity of 99+%, Aldrich Chemical Co.
[5] Superior grade, Matheson, Coleman and Bell.

Table I—Summary of Experimental Results for the Hexamethylbenzene–Chloranil Complex

T	K, liters/mole	ϵ' (10^{-3}), liters/ (mole·cm)	$K\epsilon'$ (10^{-4}), liters[2]/ (mole[2]·cm)	ρ
27.20°	7.86 ± 0.22	2.82 ± 0.06	2.21 ± 0.02	1.000
19.24°	10.86 ± 0.40	2.72 ± 0.06	2.95 ± 0.05	1.000
13.60°	12.39 ± 0.64	2.84 ± 0.09	3.52 ± 0.10	1.000
5.52°	14.20 ± 0.29	3.11 ± 0.04	4.41 ± 0.05	1.000

Determination of Heats of Complexation—The heats of complexation were determined using the van't Hoff equation (Eq. 9):

$$\ln K = -\frac{\Delta H°}{R} \cdot \frac{1}{T} + \frac{\Delta S°}{R} \qquad \text{(Eq. 9)}$$

assuming that $\Delta H°$ is constant over the temperature range of interest (0–40° in this study). Because it is often difficult to separate K and ϵ, ϵ being nearly temperature independent (41), a plot of log $K \cdot \epsilon$ versus $1/T$ usually provides a more precise estimate of $\Delta H°$. The experimental procedure can be further facilitated by noting that incorporation of Beer's law into the equilibrium constant expression and taking the logarithm of both sides give the following

$$\log K \cdot \epsilon = \log A - \log(D_0 - C)(B_0 - C) \qquad \text{(Eq. 10)}$$

If K and $\Delta H°$ for the complex are small, the last term on the left-hand side of Eq. 10 does not change significantly with temperature and a plot of log A versus $1/T$ is equivalent to a plot of log $K \cdot \epsilon$ versus $1/T$. This considerably increases the precision of the determination of $\Delta H°$, since the absorbance data can be used directly and are independent of an accurate knowledge of concentrations[6]. Since ϵ usually decreases slightly over a temperature range of 0–40°, plots of log $K \cdot \epsilon$ or log A versus $1/T$ provide upper estimates of the heat of complexation.

Procedure—Spectrophotometric readings were taken on a spectrophotometer[7] equipped with thermal-jacketed cell holders. Samples were placed in glass-stoppered quartz cells and allowed to equilibrate in the cell compartment. The temperature in the compartment was monitored with two iron–constantan thermocouples. The blank in all cases was the initial stock solution of the acceptor.
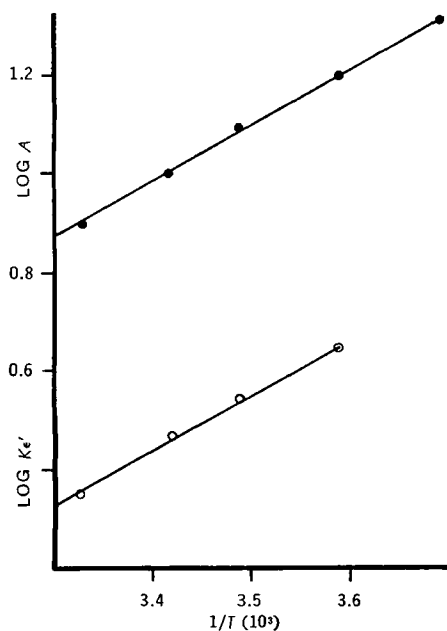
Figure 2—*Plots of log (absorbance) and log K versus $1/T$ for the chloranil–hexamethylbenzene complex.*

Table II—Experimental Heats of Complexation

Complex	Method	$\Delta H°$, kcal/mole	ρ
Chloranil–hexamethylbenzene	log (Abs)	4.81 ± 0.26	0.999
	log ($K\epsilon$)	5.07 ± 1.29	0.997
Chloranil–mesitylene	log (Abs)	3.76 ± 0.11	0.999
	log (Abs)	3.84 ± 0.14	0.999
	log ($K\epsilon$)	3.97 ± 0.52	0.999
Chloranil–benzene	log (Abs)	2.36 ± 0.07	0.998
	log (Abs)	2.24 ± 0.12	0.996
	log ($K\epsilon$)	2.18 ± 0.62	0.996
Tetrachlorophthalic anhydride–benzene	log ($K\epsilon$)	4.19 ± 0.12	1.000

Table III—Thermodynamic Parameters at 20° for the Various Complexes

Complex	K_c, liters/mole	$\Delta H°$, kcal/mole	$T \Delta S°_c$, kcal/mole
Chloranil–hexamethylbenzene	10.04	−4.94	−3.57
Chloranil–mesitylene	2.12	−3.86	−3.42
Chloranil–benzene	0.39	−2.26	−2.81
Tetrachlorophthalic anhydride–benzene	6.87	−4.19	−3.07

The results were plotted according to Eq. 7 or 8 to determine the equilibrium constant and molar absorptivity and, according to Eq. 9 or 10, with appropriate density corrections, to determine the heat of complexation.

RESULTS

The systems studied experimentally are the chloranil complexes with benzene, mesitylene, and hexamethylbenzene and the tetrachlorophthalic anhydride complex with benzene in carbon tetrachloride. Figure 1 shows a typical plot of $D_0 B_0 / A$ versus $D_0 + B_0$ (Eq. 8) for the chloranil–hexamethylbenzene complex (each point in Fig. 1 represents the determination from a single sample). The plots are linear and Table I summarizes the results. In this and the following tables, $\epsilon' = \epsilon_C - \epsilon_B$ and ρ represents the correlation coefficient and the uncertainty to the 95% confidence limits. The equilibrium constants (K) and $K \cdot \epsilon'$ products are all significantly different, with the latter being more precise. Figure 2 shows a plot of log A (density corrected) and log $K \cdot \epsilon'$ as $1/T$. Both plots are linear, giving values of 4.81 ± 0.26 and 5.07 ± 1.29 kcal/mole, respectively, for the heat of complexation. Table II presents the heats of complexation for all complexes studied. As expected, the log A method provides the more precise measurement of $\Delta H°$.

Table III summarizes the thermodynamic parameters at 20° for the various complexes. The equilibrium constants (K) were determined from the $K \cdot \epsilon'$ product using an average ϵ' over the temperature range studied.

DISCUSSION

The experimental bond polarizabilities, ionization potentials, and van der Waals radii were taken from Refs. 15, 42, and 43, respectively. The net atomic charges were calculated[8] by the CNDO/2[9] method (44) for the independent molecules of fluoranil (I), chloranil (II), tetrachlorophthalic anhydride (III), benzene (IV), toluene (V), p-xylene (VI), mesitylene (VII), durene (VIII), pentamethylbenzene (IX), and hexamethylbenzene (X). The interaction energy is then calculated by summing the electrostatic, polarization, dispersion, and repulsive contributions (Eqs. 1, 4, 2, and 5, respectively).

Table IV—Contributions to Interaction Energy[a] for the Fluoranil Complexes

Fluoranil Complex	R^b	El[b]	Pol[b]	Disp[b]	Rep[b]	$E_{tot}{}^b$
Benzene	3.60	0.136	−0.364	−7.709	3.452	−4.394
Toluene	3.60	0.135	−0.376	−8.222	3.850	−4.613
p-Xylene	3.65	0.152	−0.361	−8.147	3.555	−4.802
Mesitylene	3.65	0.104	−0.406	−8.747	3.803	−5.241
Durene	3.65	0.189	−0.403	−9.142	4.036	−5.320
Pentamethylbenzene	3.65	0.196	−0.426	−9.593	4.310	−5.513
Hexamethylbenzene	3.70	0.218	−0.422	−9.473	3.947	−5.730

[a] In kilocalories per mole. [b] R = interplanar distance in Å, El = electrostatic energy, Pol = polarization energy, Disp = dispersion energy, Rep = repulsive energy, and E_{tot} = total interaction energy.

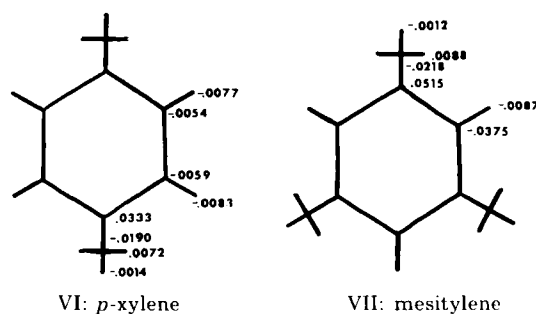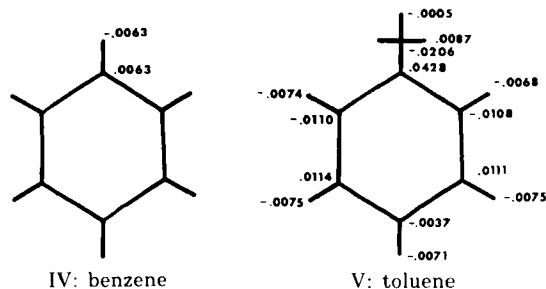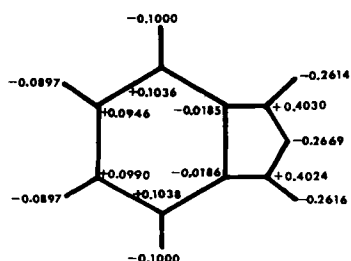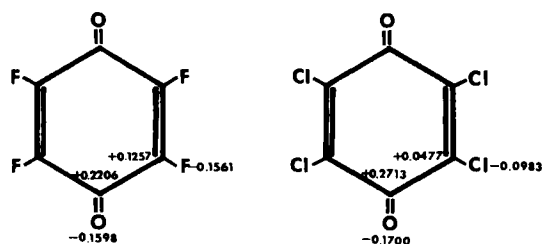**Table V**—Contributions to the Interaction Energy[a] for the Chloranil Complexes

Chloranil Complex	R^b	El[b]	Pol[b]	Disp[b]	Rep[b]	$E_{tot}{}^b$
Benzene	3.40	0.135	−0.356	−15.863	7.521	−8.563
Toluene	3.45	0.127	−0.345	−15.810	7.231	−8.796
p-Xylene	3.45	0.149	−0.357	−16.832	8.003	−9.037
Mesitylene	3.55	0.095	−0.345	−16.184	7.248	−9.186
Durene	3.60	0.145	−0.324	−15.904	6.769	−9.314
Pentamethylbenzene	3.60	0.163	−0.342	−16.855	7.546	−9.488
Hexamethylbenzene	3.65	0.193	−0.338	−16.777	7.175	−9.747

[a] In kilocalories per mole. [b] See Footnote b of Table IV.

When considering the methyl groups as fixed, the independent molecules have no internal degrees of freedom. The interaction energy is then a function of six variables, $E = E(\bar{R}, \bar{\theta})$, three translational $(\bar{R})$ and three rotational $(\bar{\theta})$. Since no general methods are available for locating a global minimum of a nonlinear function of six variables (45), a systematic search was employed. The procedure consisted of calculating the total energy at approximately 50 different combinations of $\bar{R}$ and $\bar{\theta}$ to obtain a preliminary potential energy map, and then the energy values were further refined at these minima[10]. For the methylbenzene complexes with chloranil and fluoranil, the structure with the lowest minima, highest binding energy is with the two six-membered rings directly above one another, as shown for the toluene–fluoranil complex (XI). For the benzene, mesitylene, and hexamethylbenzene complexes, a single potential energy minimum exists by symmetry. For the toluene, p-xylene, durene, and pentamethylbenzene, two separate potential energy minima are observed. In the case of the toluene–fluoranil complex, the structures would correspond to the methyl group, on toluene, lying between the oxygen and fluorine atoms (XI) or between two of the fluorine atoms of the fluoranil. The energy difference between the two minima is calculated to be less than 0.2 kcal/

mole for the fluoranil complexes and 0.5 kcal/mole for the chloranil complexes. This implies that with unsymmetrical donors, e.g., toluene, complex structural isomers may exist. The skewing of the two rings in these complexes results from a reduced repulsive interaction in this position. While there is a falloff in the dispersion energy, the dispersion interaction being at a maximum when the bonds are parallel, the falloff in the repulsive energy is somewhat larger. In the case of the benzene–fluoranil and chloranil complexes, the calculated total interaction energy of the parallel (i.e., all bonds being parallel) and skewed structures is less than 0.1 kcal/mole. An increasing preference for the skewed structure is observed with increasing methyl substitution on the donor due to the increased repulsion between the methyl groups and the oxygen or fluorines (chlorines) of the fluoranil (chloranil) molecule.

The contributions to the total interaction energy of the fluoranil–methylbenzene complexes at the primary potential energy minimum are presented in Table IV. The interplanar distance $(R,$ in Å) increases with increasing methyl substitution on the donor due to the repulsive interaction. The electrostatic interaction energy is positive (repulsive), since the net atomic charges tend to be positive for the ring carbons and negative for the substituents in both donor and acceptor molecules (I–X). The polarization energy, due mainly to the polarization of the donor by the acceptor, in-

I: fluoranil

II: chloranil

III: tetrachlorophthalic anhydride

IV: benzene

V: toluene

VI: p-xylene

VII: mesitylene

[10] The reported results refer only to the lowest potential energy minimum. More complete information on the potential energy map can be obtained from the author on request.

Table VI—Contributions to the Interaction Energy[a] for the Tetrachlorophthalic Anhydride Complexes

Structure	Donor	R^b	El[b]	Pol[b]	Disp[b]	Rep[b]	$E_{tot}{}^b$
XII	Hexamethylbenzene	3.80	0.21	−0.45	−12.76	5.25	−7.75
XII	Benzene	3.50	0.14	−0.45	−12.49	5.79	−7.01
XIII	Hexamethylbenzene	3.80	0.20	−0.44	−12.79	6.59	−6.44
XIII	Benzene	3.60	0.13	−0.37	−10.72	4.65	−6.31
XIV	Hexamethylbenzene	3.80	0.16	−0.43	−11.30	4.16	−7.41
XIV	Benzene	3.40	0.10	−0.46	−12.24	6.07	−6.53
XV	Hexamethylbenzene	3.80	0.21	−0.45	−12.78	5.40	−7.62
XV	Benzene	3.50	0.14	−0.45	−12.57	5.82	−7.06

[a] In kilocalories per mole. [b] See Footnote b of Table IV.

creases with each additional methyl substitution and is a result of the accompanying increase in polarizability of the donor.

The most significant contributions to the total interaction energy are made by the dispersion and repulsive forces. Both forces significantly increase with each additional methyl substitution on the donor. The total (net) interaction energy, as well as the structure of these complexes, is thus essentially determined by the dispersion–repulsion balance. For example, in the case of the hexamethylbenzene complex, the dispersion and repulsive terms are actually lower than those of the pentamethylbenzene complex (Table IV). This is due to the larger equilibrium interatomic separation (3.70 versus 3.65 Å). At 3.65 Å, both the dispersion and repulsive contri-

VIII: durene

IX: pentamethylbenzene

X: hexamethylbenzene

XI

XII

XIII

XIV

XV

butions are larger in the hexamethylbenzene–fluoroanil complex.

Table V shows similar results for the chloranil–methylbenzene complexes. The trends observed are similar to those with fluoranil as the acceptor but with a large increase in the dispersion and repulsive forces. This is due to the larger polarizabilities and van der Waals radii of the chlorine atoms compared to the fluorine atoms.

Several structures (XII–XV) were considered for the benzene and hexamethylbenzene complexes with tetrachlorophthalic anhydride. As can be seen from the interaction energies in Table VI, the maximum interaction occurs in both cases with the donor approximately over the center of the acceptor. Displacement to either side of the acceptor significantly reduces the interaction energy due to a reduction in dispersion and/or increase in repulsive energies in those positions.

A comparison of the theoretical and experimental results for the benzene and hexamethylbenzene complexes with the various acceptors is presented in Table VII. It is apparent that while the trend of increasing complex strength with increasing methyl substitution on the donor is predicted for a given acceptor, the theoretical increase underestimates the experimental value by a factor of two to three. Furthermore, the absolute interaction energy provides a considerable overestimate of the experimental heat of complexation in solution, and the overall correlation between the heat of complexation and absolute interaction energy is poor.

These results suggest an important role for the nonpolar solvent carbon tetrachloride. Solute–solvent interaction would be expected to reduce the interaction energies while the solvent–solvent term would tend to increase the complex strength. The net effects of adding these terms to the absolute interaction energy must be to reduce the net interaction and to magnify the increase in complex strength per methyl group.

CONCLUSIONS

The results of absolute interaction energy calculations for the methylbenzene complexes with chloranil, fluoranil, and tetrachlorophthalic anhydride indicate that the dispersion force is the major attractive contributor to the total interaction energy and that the balancing of the dispersion and repulsive forces predomi-
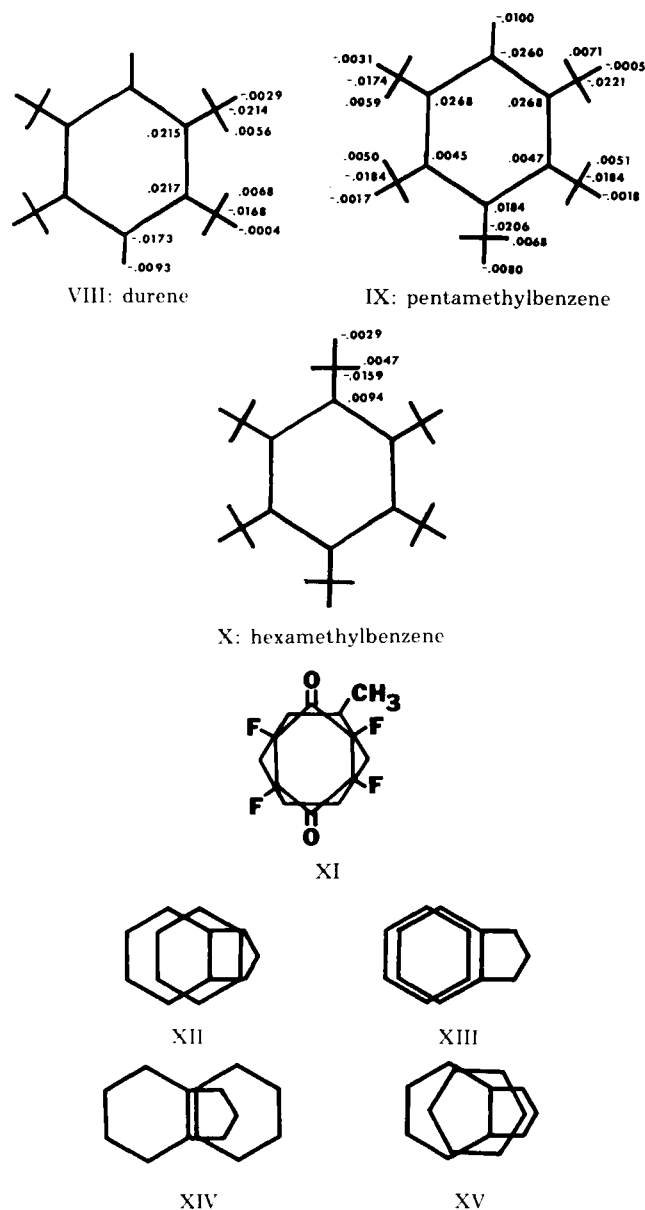
Table VII—Experimental and Theoretical (Gas Phase) Interaction Energies

Acceptor	Donor	Experimental $\Delta H°$, kcal/mole	Absolute Interaction Energy, kcal/mole
Fluoranil	Benzene	−2.0[a]	−4.39
Fluoranil	Hexamethyl-benzene	−5.4[a]	−5.73
Difference		3.4	1.34
Chloranil	Benzene	−2.26[b]	−8.56
Chloranil	Hexamethyl-benzene	−4.94[b]	−9.75
Difference		2.84	1.19
TCPA[c]	Benzene	−4.19[b]	−7.06
TCPA	Hexamethyl-benzene	−5.75[d]	−7.72
Difference		1.56	0.66

[a] R. Foster, C. Fife, and M. Foreman, Chem. Commun., **1967**, 913. [b] This work. [c] TCPA = tetrachlorophthalic anhydride. [d] J. Czekalla and K. Meyer, Z. Phys. Chem., **27**, 185(1961).

nantly determines the structures and net interaction energies.

While the correlation between the absolute interaction energy and experimental heat of complexation in carbon tetrachloride is poor, the trends within each complexing series are predicted. However, the theoretical increase in the interaction energy per methylene group underestimates the experimental increase by a factor of two to three.

Since the comparison is being made between absolute (gas phase) and solution interaction energies, the results suggest that the solvent effects must account for the additional increase in complex strength per methylene group as well as a lowering of the net interaction energies in solution.

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