Bonding in Donor–Acceptor Complexes. III. The Relative Contributions of Electrostatic, Charge-Transfer, and Exchange Interactions in Aromatic–Halogen and Aromatic–TCNE Complexes[1a]

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Abstract: The relative contributions of electrostatic, charge-transfer, and exchange repulsion interactions are calculated for molecular complexes of both the bπ–aπ (aromatic-TCNE) and bπ–aσ (aromatic-halogen) type. The calculations are based on the perturbation formalism of Murrell, Randic, and Williams appropriate in the region of small overlap. All electrostatic contributions are approximated by the appropriate interactions of atomic multipoles and bond polarizabilities. The results indicate that all types of interactions are important in describing molecular complexes, and that, when all interactions are included, reasonable interaction energies are obtained. The results further predict the existence of two stable rotational isomers of the *p*-xylene complex and indicate the existence of important high-energy charge-transfer states in *p*-xylene complexes. Comparison of the measured and calculated quadrupole moments of small molecules indicates that π-orbital quadrupoles make a significant contribution to the quadrupole moments of π-type molecules.

I. Introduction

A considerable amount of effort has been devoted in the last 2 decades to constructing a satisfactory model describing the weak interactions responsible for the stabilization of weak electron donor–acceptor complexes.[2] In spite of this effort, many questions about these complexes remain unanswered. One of these questions is the extent to which classical electrostatic forces as opposed to "charge-transfer" forces contribute to the observed properties (stability constants, energies of formation, spectral properties, etc.) of these complexes. Briegleb first used an electrostatic model to rationalize the stability of certain aromatic π–π complexes in which the acceptor molecule possessed nitro group substituents.[3] Later, however, Mulliken proposed that the observed properties of these complexes could be rationalized by mixing charge-transfer excited states into the ground-state wave function of the complex.[4] This charge-transfer model was remarkably successful in explaining the striking spectral changes that occur with complex formation in many cases, and, in spite of Mulliken's original statement[4a] that charge-transfer interactions must be *in addition* to all classical electrostatic interactions, many of the properties of these complexes have been attributed exclusively to charge-transfer resonance.

In earlier papers of this series, Hanna has proposed that quadrupole-induced dipole interactions may make nonnegligible contributions to the energy of formation and induced dipole moments[5] as well as to the changes in the infrared spectra[6] of benzene–halogen complexes. Other authors have also discussed the importance of electrostatic interactions in weak donor–acceptor complexes.[7,8]

The purpose of this paper is to examine in considerable detail the binding of molecular complexes of both the bπ–aπ (aromatic–TCNE) and bπ–aσ (aromatic–halogen) types. Specifically the relative contributions of electrostatic, charge-transfer, and repulsion interactions will be evaluated at the same level of approximation, and the relative importance of these three interactions in determining the ground state properties will be discussed.

II. Theory

The perturbation theory of Murrell, Randic, and Williams[9] treating intermolecular forces in the region of small overlap is a particularly appropriate starting point for this calculation as it factors the complex stabilization energy into terms which can be identified with each of the interactions which we wish to examine.

The theory has been successfully applied to such problems as the nature of the hydrogen bond[10,11] and the structure of crystalline chlorine.[12]

The basis of the theory involves the expansion of the intermolecular energy as a double perturbation series in the intermolecular potential and the intermolecular overlap between unperturbed wave functions on the component molecules A and B. The possibility of electron exchange or transfer between A and B is taken into account.

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[1] (a) Supported in part by the National Science Foundation under NSF Grant GP-7070; (b) NSF and NDEA Predoctoral Fellow.

[2] The literature on this subject is voluminous. For reviews, see G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964; R. S. Mulliken and W. B. Person, "Molecular Complexes, A Lecture and Reprint Volume," John Wiley and Sons, Inc., New York, N. Y., in press.

[3] G. Briegleb, "Zwischenmolekular Krafte," Enke, Stuttgart, 1927.

[4] (a) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); (b) *J. Phys. Chem.*, **56**, 801 (1952).

[5] Paper I: M. W. Hanna, *J. Am. Chem. Soc.*, **90**, 285 (1968).

[6] Paper II: M. W. Hanna and D. E. Williams, *ibid.*, **90**, 5358 (1968).

[7] M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, 7, 97 (1966).

[8] M. Mantione and B. Pullman, *Compt. Rend.*, **262**, 1492 (1966).

[9] J. N. Murrell, M. Randic, and D. R. Williams, *Proc. Roy. Soc.* (London), **A284**, 566 (1965).

[10] F. B. vanDuijnveldt and J. N. Murrell, *J. Chem. Phys.*, **46**, 1759 (1967).

[11] F. B. vanDuijnveldt, *ibid.*, **49**, 1424 (1968).

[12] I. H. Hillier and S. A. Rice, *ibid.*, **46**, 3881 (1967).

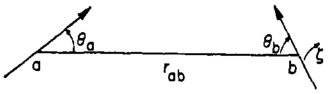

Figure 1. Configuration of an interacting pair of axially symmetric charge distributions.

The stabilization energy of the complex is then presented as a series of terms

$$U = U^{10} + U^{20} + U^{12} + U^{22} + \cdots \qquad (1)$$

where the first suffix refers to the order of the potential and the second to the order of the overlap. These terms are called, respectively, the Coulomb energy, the induction and dispersion energies, the exchange repulsion, and the charge-transfer energy. The exact evaluation of each of these terms requires exact wave functions for A and B. Since such wave functions are not available for large molecules, we have approximated each term to the same degree of accuracy. The approximations follow a classical treatment where possible.

A. Coulomb Energy. The term U^{10} in the Murrell treatment represents the interaction between the ground-state wave functions of the separated molecules and is called the Coulomb energy. If the molecules are separated by rather large distances, the Coulomb energy is well represented by the first terms of the interaction of two multipole expansions[13]

$$U_{\mathrm{C}} = U_{q_{\mathrm{A}}q_{\mathrm{B}}} + U_{q_{\mathrm{A}}\mu_{\mathrm{B}}} + U_{\mu_{\mathrm{A}}q_{\mathrm{B}}} + U_{q_{\mathrm{A}}\theta_{\mathrm{B}}} + \ldots \qquad (2)$$

where the q's are the changes, μ's the dipoles, and θ's the quadrupole moments of molecules A and B, respectively. In the complexes considered here, however, the dimensions of the component molecules are of the same order as the intermolecular distance. In these cases, it is well known that expansion 2 converges very slowly (or not at all). In an effort to circumvent this difficulty, Coulomb interactions are often approximated as the interactions between point charges placed at the atomic centers in the molecules.[14] This latter approximation has been applied to hydrogen-bonding studies[14] and to the calculation of base-base interactions in nucleic acids.[15,16] We will present evidence (section IV) in the form of a comparison of calculated and measured molecular quadrupole moments, which indicates that the point-charge model is not an adequate description of the charge distribution of a large conjugated molecule. In place of a point-charge model, we propose the more complete expansion

$$U_{\mathrm{C}} = \sum_{a=1}^{N_{\mathrm{A}}} \sum_{b=1}^{N_{\mathrm{B}}} (U_{q_aq_b} + U_{q_a\mu_b} + U_{u_aq_b} + U_{q_a\theta_b} + \ldots + U_{\theta_a\theta_b}) \qquad (3)$$

q_a, μ_a, and θ_a are now *point* multipoles on the atomic center a of molecule A, and N_{A} and N_{B} are the number of atomic centers on molecules A and B.

It is important to point out that each term in (3) does not correspond to the similar term in (2). Each term in (3) is actually an approximation to all higher order terms in (2), *i.e.*, $\Sigma\Sigma_{\mathrm{AB}}U_{q_aq_b}$ is an approximation to U_{C} itself, and $\Sigma\Sigma_{\mathrm{AB}}U_{\theta_a\theta_b}$ is an approximation to quadrupole–quadrupole and higher terms. For this reason, it is felt that termination of (3) at the quadrupole–quadrupole term will lead to very small errors in U_{C}.

In this work, bond dipoles are decomposed into point charges located at atomic centers so that only terms in point charge and point quadrupole are included in (3). If the point distributions are represented as the multipoles of interacting pairs of axially symmetrical charge distributions as in Figure 1, then the various terms in (3) are given by[13]

$$\sum_{\mathrm{A,B}}\sum U_{q_aq_b} = \sum_{\mathrm{A,B}}\sum \frac{q_aq_b}{r_{ab}} \qquad (4)$$

$$\sum_{\mathrm{A,B}}\sum U_{q_a\theta_b} = \sum_{\mathrm{A,B}}\sum \frac{q_a\theta_b}{2r_{ab}^{\ 3}}(3\cos^2\theta_b - 1) \qquad (5)$$

$$\sum_{\mathrm{A,B}}\sum U_{\theta_a\ b} = \sum_{\mathrm{A,B}}\sum \frac{3\theta_a\theta_b}{4r_{ab}^{\ 5}}(1 - 5\cos^2\theta_a - 5\cos^2\theta_b + 17\cos^2\theta_a\cos^2\theta_b + 2\sin^2\theta_a\sin^2\theta_b\cos^2\zeta + 16\sin\theta_a\sin\theta_b\cos\theta_a\cos\theta_b\cos\zeta) \qquad (6)$$

B. Induction Energy. The term U^{20} in the perturbation expression 1 contains two types of contributions. The first arises from the interaction of locally excited states of one molecule with the ground state of the second (and *vice versa*) and is called the induction energy. Neglecting hyperpolarizabilities, this can be represented by[13]

$$U_{\mathrm{I}} = -\frac{1}{2}\mathbf{F}_{\mathrm{A}}\cdot\boldsymbol{\alpha}_{\mathrm{B}}\cdot\mathbf{F}_{\mathrm{A}} - \frac{1}{2}\mathbf{F}_{\mathrm{B}}\cdot\boldsymbol{\alpha}_{\mathrm{A}}\cdot\mathbf{F}_{\mathrm{B}} \qquad (7)$$

where $\mathbf{F}_{\mathrm{A}}$ is the electric field due to molecule A evaluated at molecule B and $\boldsymbol{\alpha}_{\mathrm{B}}$ is the polarizability tensor of molecule B.

In keeping with the earlier assumption that the molecular charge distributions can be best represented by point charges and quadrupoles, we introduce

$$\mathbf{F}_{\mathrm{A}} = \sum_{a=1}^{N_{\mathrm{A}}}\mathbf{f}_a = \sum_{a=1}^{N_{\mathrm{A}}}(\mathbf{f}_{a,q} + \mathbf{f}_{a,\theta}) \qquad (8)$$

where $\mathbf{f}_{a,q}$ and $\mathbf{f}_{a,\theta}$ are the fields due to a point charge and a point quadrupole on atomic center a. Further, it is assumed that a better approximation to the induction energy results if the molecular polarizability is decomposed into a sum of bond contributions located at the midpoint of each of the bonds as suggested by Pullman[15] and by Rein, Claverie, and Pollack.[17] In this way, eq 7 expands to

$$U_{\mathrm{I}} = -\sum_{i=1}^{N_{\mathrm{A}}}\sum_{j=1}^{N_{\mathrm{A}}}\sum_{\beta=1}^{M_{\mathrm{B}}}\frac{1}{2}\mathbf{f}_i\boldsymbol{\alpha}_\beta\mathbf{f}_j - \sum_{k=1}^{N_{\mathrm{B}}}\sum_{l=1}^{N_{\mathrm{B}}}\sum_{\alpha=1}^{M_{\mathrm{A}}}\frac{1}{2}\mathbf{f}_k\boldsymbol{\alpha}_\alpha\mathbf{f}_l \qquad (9)$$

where M_{A} and M_{B} are the number of bonds in molecules A and B and where f_i is the sum of the fields due to a point charge and point quadrupole at atomic center i of molecule A evaluated at bond β of molecule B.

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[13] A. D. Buckingham, *Quart. Rev.* (London), **13**, 183 (1959).

[14] B. Pullman, P. Claverie, and J. Caillet, *Proc. Natl. Acad. Sci. U. S.*, **55**, 904 (1966).

[15] P. Claverie, B. Pullman, and J. Caillet, *J. Theor. Biol.*, **12**, 419 (1966).

[16] R. Rein, P. Claverie, and M. Pollack, *Int. J. Quant. Chem.*, **2**, 1296 (1968).

[17] J. O. Hirschfelder, C. E. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, and references therein.

If the field is represented by its components as shown in Figure 2, then the appropriate field contributions due to each point charge and point quadrupole are

$$f_r = \frac{q}{r^2} + \frac{3\theta}{2r^4}(3\cos^2\theta - 1)$$

$$f_s = \frac{3\theta}{2r^4}\sin\theta\cos\theta \qquad (10)$$

$$f_t = 0$$

In this work, the method of evaluating (9) involves the computation of the field components at each bond (10) and transformation of these into the coordinate system in which the polarizability is diagonal and represented by its components $\alpha_{\|}$ and $\alpha_{\perp}$, parallel and perpendicular to the bond.

C. Dispersion Energy. The second contribution to U^{20} is the interaction of locally excited states on both molecules. In the case that we can imagine isotropic oscillators located at point molecules, the dispersion energy is given by the Drude model

$$U_{\mathrm{D}} = -\frac{3I_{\mathrm{A}}I_{\mathrm{B}}\alpha_{\mathrm{A}}\alpha_{\mathrm{B}}}{2(I_{\mathrm{A}} + I_{\mathrm{B}})R_{\mathrm{AB}}{}^6} \qquad (11)$$

where the I's are often approximated by the ionization potentials of the component molecules.[17]

Again we have the situation that a single point model (point charge or point oscillator) is not adequate for close molecular complexes as are studied in this paper. However, as a first approximation, each molecule may be thought of as a group of point oscillators centered at the midpoint of bonds and having average bond polarizabilities $\alpha = {}^1/_3(\alpha_{\|} + 2\alpha_{\perp})$. In this approximation, (11) becomes

$$U_{\mathrm{D}} = -\frac{3I_{\mathrm{A}}I_{\mathrm{B}}}{2(I_{\mathrm{A}} + I_{\mathrm{B}})}\sum_{\alpha=1}^{M_{\mathrm{A}}}\sum_{\beta=1}^{M_{\mathrm{B}}}\frac{\alpha_\alpha\alpha_\beta}{r_{\alpha\beta}{}^6} \qquad (12)$$

In reality the ionization potentials should be the appropriate ionization potentials for each pair of bonds and should be *inside* the sum. Since these constants would have no relationship to measured ionization potentials, the simpler form (12) is retained.

D. Charge-Transfer Energy. The charge-transfer energy U^{22} of a complex[18] can be thought of as arising from the interaction of the charge distribution produced on one molecule (the acceptor) by the transfer of one electron to it, with the charge distribution produced on the other molecule (the donor) by the loss of one electron—all weighted by the likelihood of this happening.

Mulliken[4] has derived an approximate expression for the charge-transfer energy.

$$U_{\mathrm{CT}} = \sum_{m,n}\sum\frac{-|H_{mn}|^2}{(E_n - E_m)} \qquad (13)$$

The sum is over all charge-transfer matrix elements between the filled levels of one molecule and the unfilled levels of the other (and *vice versa*).

Following Mulliken,[19] H_{mn} is assumed to be proportional to the overlap (S_{mn}) between the orbitals m and n, and $(E_n - E_m)$ is identified with the spectroscopic charge-transfer excitation energy $h\nu$. With these approximations, (13) becomes

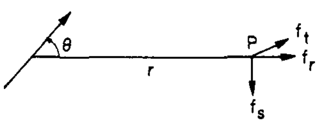

Figure 2. The components of the field at a point P due to an axially symmetric charge distribution.

$$U_{\mathrm{CT}} = \sum_{m,n}\sum\frac{-|kS_{mn}|^2}{h\nu_{mn}} \qquad (14)$$

Accurate evaluations of k are extremely difficult[20,21] and this quantity is normally estimated from either complex dipole moments or from the extinction coefficients of the charge-transfer band. The experimental determinations of both of these quantities are uncertain and consequently considerable uncertainty is introduced into values of k. We have chosen to estimate k's by other means while making certain that these estimates give dipole moments that bracket possible experimental values. Now, the charge-transfer energy as approximated by eq 14 is dependent on two variables, k and the overlap S ($h\nu$ being experimentally determined). In these calculations we use both SCF and Slater-type atomic orbitals. Since SCF orbitals give much larger overlaps, k's for SCF bases will be smaller than those for Slater bases. Thus, an estimate of k = 6.66 eV from Aono's work[20] gives a reasonable lower limit for the charge-transfer part of the dipole moment of aromatic–halogen complexes (and hence a lower limit foı the charge-transfer contribution to the stabilization energy) when a basis set of Slater orbitals on the aromatic and SCF atomic orbitals on the halogens is used. With an all-SCF basis and k = 6.66 eV, or equivalently with the above-mentioned basis and k = 11.5 eV, upper limits are obtained.

For aromatic–TCNE complexes, k = 34.5 eV was estimated from the π–π off-diagonal element of the approximate Fock matrix of ethylene[22] using the relation $H_{ij} = kS_{ij}$. In these complexes the basis set consists of Slater-type orbitals on both molecules. The difference in basis sets is apparently the reason for the large differences in values of k.

E. Exchange Repulsion Energy. The exchange energy U^{12} is a purely quantum mechanical phenomenon which arises from the repulsions of electrons of the same spin in overlapping charge distributions. In the formulation of Murrell, Randic, and Williams,[9] the contribution is zero for electrons of opposite spin. In this way the term is quite different from the "exchange energy" of valence-bond treatments of molecules and should not be confused with it.

It has been found[9] that a good approximation to the exchange repulsion of two atomic orbitals each containing one electron is given by

$$U_{\mathrm{ER}} = cS_{\mathrm{AB}}{}^2/r_{\mathrm{AB}} \qquad (15)$$

Since the repulsion is between electrons of the same spin only, repulsion between two orbitals *each* containing two electrons is twice that of (15). Williams[23a]

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[18] The suggestion of Murrell, Randic, and Williams[9] is followed that another term in E^{22}, the so-called exchange polarization, is small, and this term is neglected.

[19] R. S. Mulliken, *Rec. Trav. Chim.*, **75**, 845 (1956).

[20] S. Aono, *Progr. Theor. Phys.* (Kyoto), **22**, 313 (1959).

[21] M. Mantione and B. Pullman, *Compt. Rend.*, **D262**, 1942 (1966).

[22] W. E. Palke and W. N. Lipscomb, *J. Am. Chem. Soc.*, 88, 2384 (1966).

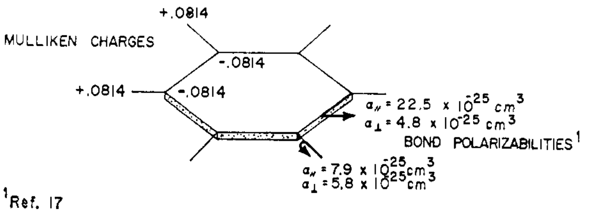

Figure 3. Charge distribution and bond polarizabilities of benzene. Charges in fraction of electronic charge.

has found that for three helium atoms the exchange energy is pairwise additive to within 1%. For three carbon atoms, at distances of 3.5 Å or greater, deviations from pairwise additivity are less than 3%.[23b] Thus for the interaction of two large molecules, the exchange should be given by a pairwise sum over atomic orbitals

$$U_{\mathrm{ER}} = \sum_i \sum_j c_{ij} S_{ij}^2 / r_{ij} \tag{16}$$

where the sums over i and j are over all atomic orbitals on molecules A and B, respectively, where $c_{ij} = c$ or $c_{ij} = 2c$ depending on the number of electrons in the two orbitals.

The *a priori* calculation of c is extremely difficult,[9] but c can be easily evaluated if it is assumed that the gas-phase equilibrium intermolecular distance is the same as that which we have assumed in these calculations. At the equilibrium intermolecular distance, the intermolecular potential must be a minimum and the correct value of c must be the one that makes the slope of the total energy *vs.* R_{AB} zero at that point. In fact, evaluation of c in this manner makes the total energy almost insensitive to the charge-transfer or exchange repulsion contributions taken by themselves, since both the charge-transfer and the exchange vary in roughly the same way (S^2) with intermolecular overlap and any increases in k will be compensated by an increase in c (see section V.A).

F. Dipole Moment Contributions. In the case that the component molecules have no permanent dipole moments, there are two contributions to the dipole moment of a molecular complex: one coming from the dipoles induced in both donor and acceptor by the charge distribution of the other, and one due to actual "charge transfer"[24] in the ground state. Therefore, we can write

$$\mu = \mu_{\mathrm{CT}} + \mu_{\mathrm{Ind}} \tag{17}$$

Using the same arguments as were used to develop induction energy, we arrive at the analog of eq 9.[25]

$$\boldsymbol{\mu}_{\mathrm{Ind}} = \sum_{i=1}^{N_{\mathrm{A}}} \sum_{\beta=1}^{M_{\mathrm{B}}} \mathbf{f}_i \boldsymbol{\alpha}_\beta + \sum_{k=1}^{N_{\mathrm{B}}} \sum_{\alpha=1}^{M_{\mathrm{A}}} \mathbf{f}_k \boldsymbol{\alpha}_\alpha \tag{18}$$

The charge-transfer contribution is evaluated in the following way. The ground-state wave function of the complex can be written to include several possible

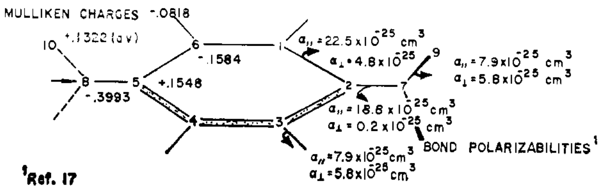

Figure 4. Charge distribution and bond polarizabilities of *p*-xylene; charges in fraction of electronic charge.

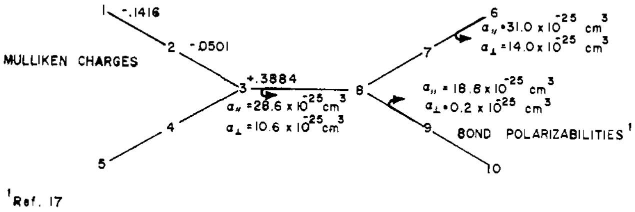

Figure 5. Charge distribution and bond polarizabilities of tetracyanoethylene (TCNE); charges in fraction of electronic charge.

"charge-transfer" states

$$\psi = a\psi_{\mathrm{DA}} + b\psi^*_{im} + c\psi^*_{jn} + \ldots \tag{19}$$

where the ψ^*_{im}'s represent transfer of an electron from a filled (i,j) orbital on one molecule to an unfilled (m,n) orbital on the other molecule, and where a, b, and c, etc., are suitably normalized. Then the charge-transfer contribution to the dipole moment is[24]

$$\mu_{\mathrm{CT}} = \mu_1(b^2 + abS_{im} + c^2 + acS_{jn} + \ldots) \tag{20}$$

where μ_1 is the dipole moment of the pure dative form of the complex (usually taken as er_{AB}). The ratio of coefficients is given by

$$b/a = (H_{im} - S_{im}W_i)/(W_m - W_i) \tag{21}$$

Using the same approximations that were used to simplify the charge-transfer energy contribution, this becomes

$$b/a = kS_{im}/h\nu_{im} \tag{22}$$

III. Molecular Wave Functions

In order to evaluate the terms of the Murrell perturbation theory mentioned above, it is necessary to have the electron distribution of the component molecules of the complexes. This is obtained in the form of their molecular orbitals. The orbitals of the diatomic halogens are symmetrical and overlap determined if it is assumed that the matrix elements between overlapping s and p orbitals are negligible.

It was felt that the molecular orbitals of the π-type systems, benzene, p-xylene, and TCNE, could be best represented in the framework of the nonempirical method of Lipscomb, *et al.*[26] This is a single iteration SCF method including all electrons in which the kinetic energy part of the Fock matrix elements is calculated exactly and the potential part of the off-diagonal elements is taken as

$$U_{ij} = K_{ij}S_{ij}(U_{ii} + U_{jj})/2 \tag{23}$$

where K_{ij} is a constant close to 1.0 which can be obtained from the Lipscomb papers,[26] S_{ij} is the overlap

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(23) (a) D. R. Williams, L. J. Schaad, and J. N. Murrell, *J. Chem. Phys.*, **47**, 4916 (1967); (b) D. R. Williams, *ibid.*, in press.

(24) G. Briegleb, "Electronen-Donator-Acceptor Komplexe," Springer-Verlag, Gottingen, 1961, and references therein.

(25) For both types of complexes discussed in this paper, the z axis is taken perpendicular to the aromatic plane. The x and y components of the dipole moment will average zero in both the charge-transfer and induced contributions because of the assumed symmetry of the complex.

(26) M. D. Newton, F. B. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353 (1966).

Table I. Benzene (Lipscomb-Type[a]) π-Molecular Orbitals

π-Molecular orbitals	Coefficients						Energy, eV
	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	
$a_{2u}(2)$	0.3253	0.3253	0.3253	0.3253	0.3253	0.3253	−15.627
$e_{1g}(2)$	−0.2640	−0.5279	−0.2640	0.2640	0.5279	0.2640	−8.334
$e_{1g}(2)$	−0.4572	0.00	0.4572	0.4572	0.00	−0.4572	−8.334
$e_{2u}(0)$	0.5831	0.00	−0.5831	0.5831	0.00	−0.5831	7.091
$e_{2u}(0)$	0.3366	−0.6733	0.3366	0.3366	−0.6733	0.3366	7.091
$b_{2g}(0)$	0.5444	−0.5444	0.5444	−0.5444	0.5444	−0.5444	18.296

[a] Calculated by the method of ref 26.

Table II. p-Xylene (Lipscomb-Type[a]) π Orbitals

π-Molecular orbitals	Coefficients[b]										Energy, eV
	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8	χ_9[c]	χ_{10}[c]	
$\omega_1(2)$	0.2009	0.2718	0.2053	0.2009	0.2718	0.2053	0.2888	0.2888	−0.1556	0.1556	−17.959
$\omega_2(2)$	−0.0672	−0.2208	−0.0822	0.0672	0.2208	0.0822	−0.3788	0.3788	0.2274	0.2274	−16.519
$\omega_2(2)$	−0.2825	−0.1504	−0.2716	−0.2825	−0.1504	−0.2716	0.2798	0.2798	−0.2341	0.2341	−12.478
$\omega_4(2)$	−0.4742	−0.0381	0.4368	0.4742	0.0381	−0.4368	−0.0173	0.0173	−0.0240	−0.0240	−8.333
$\omega_5(2)$	0.2342	0.4600	0.3061	−0.2342	−0.4600	−0.3061	−0.1151	0.1151	0.2210	0.2210	−5.834
$\omega_6(0)$	0.2541	0.3725	−0.6262	0.2541	0.3725	−0.6262	0.1849	0.1849	0.2353	−0.2353	6.990
$\omega_7(0)$	−0.6079	0.4774	0.1510	−0.6079	0.4774	0.1510	0.1246	0.1246	0.2296	0.2296	7.176
$\omega_8(0)$	−0.3608	0.2467	−0.3304	0.3608	−0.2467	0.3304	0.6162	−0.6162	0.5226	0.5226	14.389
$\omega_9(0)$	0.0721	−0.3467	0.1704	0.0721	−0.3467	0.1704	0.8062	0.8062	0.5565	0.5565	18.911
$\omega_{10}(0)$	0.4013	−0.5270	0.4188	−0.4013	0.5270	−0.4118	0.5698	−0.5698	0.3501	0.3501	22.157

[a] Calculated by the method of ref 26. [b] Numbering as in Figure 4. [c] Coefficient of upper hydrogen; lower hydrogen has $\chi' = -\chi$.

Table III. Tetracyanoethylene (TCNE) π Orbitals[a]

π-Molecular orbitals	Coefficients[b]										Energy eV
	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6	χ_7	χ_8	χ_9	χ_{10}	
$1b_{3u}(2)$	0.1695	0.2723	0.3207	0.2723	0.1695	0.1695	0.2723	0.3207	0.2723	0.1695	−17.401
$1b_{1g}(2)$	−0.2691	−0.3108	−0.1574	−0.3108	−0.2691	0.2691	0.3108	0.1574	0.3108	0.2691	−14.340
$1a_u(2)$	0.3118	0.3079	0.00	−0.3079	−0.3118	0.3118	0.3079	0.00	−0.3079	−0.3118	−13.151
$1b_{2g}(2)$	0.3239	0.2993	0.00	−0.2993	−0.3239	−0.3239	−0.2993	0.00	0.2993	0.3239	−12.642
$2b_{3u}(2)$	−0.3437	0.0885	0.4474	−0.0885	−0.3437	−0.3437	−0.0885	0.4474	0.0885	−0.3437	−6.892
$2b_{1g}(0)$	−0.3806	0.1953	0.4842	0.1953	−0.3806	0.3806	−0.1953	−0.4842	−0.1953	0.3806	1.965
$2a_u(0)$	0.4240	−0.4321	0.00	0.4321	−0.4240	0.4240	−0.4321	0.00	0.4321	−0.4240	9.796
$2b_{2g}(0)$	0.4153	−0.4480	0.00	0.4480	−0.4153	−0.4153	0.4480	0.00	−0.4480	0.4153	10.821
$3b_{3u}(0)$	−0.3617	0.4613	−0.3569	0.4613	−0.3617	−0.3617	0.4613	−0.3569	0.4613	0.3617	14.669
$3b_{1g}(0)$	0.2467	−0.4123	0.7361	−0.4123	0.2467	−0.2467	0.4123	−0.7361	0.4123	−0.2467	23.733

[a] Calculated by the method of ref 26. [b] Numbering as in Figure 5.

between atomic orbitals i and j, and U_{ii} is the diagonal matrix element taken from exact SCF calculations[22] of small molecules. Mulliken charges can be easily obtained from the molecular orbitals calculated by this method to give a readily applicable electron distribution. The π molecular orbitals of benzene, p-xylene, and TCNE are given in Tables I–III. The Mulliken charge distributions and the bond polarizabilities are shown in Figures 3–5. Differences with the calculation of Newton, Boer, and Lipscomb[26] are, as far as we can discern, due to slightly different choices of diagonal U_{ii} elements.

The TCNE calculation is of special interest and is probably the best calculation of the molecule available. Because this calculation includes all electrons, it is felt that the representation of the electron distribution in this paper is considerably better than that given by Hückel calculations.[27,28] A further discussion of the accuracy of the wave functions is given in section V.E.

IV. Electron Distributions and π Quadrupoles

Buckingham[29] has recently pointed out the importance of π-molecular orbital contributions to the quadrupole moment of ethylene. Hanna[5] has shown that the electric field above a benzene ring is in agreement with experiments if the following two assumptions were made: (1) there is a contribution to that field arising from point charges (here Mulliken charges); and (2) there is an additional contribution arising from the π-type atomic orbitals.

It is not difficult to show that the π contribution given in that paper is equivalent to a contribution by point quadrupoles due to each π atomic orbital having magnitudes of

$$\theta_i = -3M_i/\xi_i^2 \qquad (24)$$

where M_i is the number of electrons in atomic orbital i which has a Slater exponent ξ_i. Thus the electron distribution appears best represented as point charges plus point π quadrupoles.

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(27) B. R. Penfold and W. N. Lipscomb, *Acta Cryst.*, **14**, 589 (1961).

(28) J. Halper, W. D. Closson, and H. B. Gray, *Theor. Chim. Acta*, **4**, 174 (1966).

(29) A. D. Buckingham, R. L. Disch, and D. A. Dunmer, *J. Am. Chem. Soc.*, **90**, 3104 (1968).

That this approximation is, in fact, general to π systems is shown by comparing quadrupole moments calculated in this way with measured quadrupole moments. The agreement, as shown in Table IV, is striking. We have not included moments measured by microwave broadening since these are invariably much too small. It was this interesting result which led to the introduction of eq 3 as an improvement in the calculation of intermolecular forces.

Table IV. Approximate Quadrupole Moments of Linear Molecules[a]

	Point charge only	Including π quadrupoles	Exptl second virial data
Acetylene	+4.1	+7.4	5.0[b]
Benzene	−5.0	−14.1	15.6[c]
Ethylene	−1.7	−4.7	3.85[b]

Ethylene is not a spherically symmetric molecule and so cannot be represented by a single quadrupole moment. The calculated principle values for the quadrupole tensor are

	θ_{xx}	θ_{yy} (plane)	θ_{zz} (bond)
Point charges	−0.62	−1.67	+1.03
Including point quadrupoles	+2.15	−4.72	+2.56

Buckingham, Disch, and Dunmer[d] has estimated that $\theta_{zz} = +2.0 \pm 0.15$ by induced birefringence.

[a] All values in buckinghams (1 buckingham = 10^{-26} esu cm^2) [b] T. H. Spurling and E. A. Mason, *J. Chem. Phys.*, **46,** 322 (1967). [c] A. G. DeRocco, T. H. Spurling, and T. S. Storvich, *ibid.*, **46,** 559 (1967). [d] Reference 29.

While the electron distribution of the large π-type molecules must be represented in this rather complicated manner, it is felt that the halogen molecules are small enough to be represented simply by their quadrupole moments. Unfortunately, the quadrupole moments of Br_2 and I_2 have not been measured. Since the quadrupole moment varies as r^2, it was hoped that the quadrupole moment might be reasonably linear with the square of the bond length in these molecules. The approximation was tested for the hydrogen halides and was found to be roughly true. In this way, the quadrupoles of F_2 and Cl_2 were extrapolated to $\theta_{Br_2} = 9 \times 10^{-26}$ esu cm^2 and $\theta_{I_2} = 13 \times 10^{-26}$ esu cm^2. Other parameters used for calculations with the halogens are shown in Table V.

Table V. Ionization Potentials, Molecular Polarizabilities, and Quadrupole Moments of Halogens (X_2)

	Chlorine	Bromine	Iodine
Polarizability,[a] cm^3	66.0×10^{-25}	99.5×10^{-25}	175×10^{-25}
Quadrupole moment,[d] esu cm^2	6.1×10^{-26}	9×10^{-26}	13×10^{-26}
Ionization potential,[b] eV	11.5	10.6	9.4
Internuclear distance,[c] Å	2.00	2.28	2.66

[a] M. W. Hanna, *J. Am. Chem. Soc.*, **90,** 285 (1968). [b] V. I. Vedeneyev, *et al.*, "Bond Energies, Ionization Potentials and Electron Affinities," St. Martin's Press, New York, N. Y., 1966. [c] H. H. Landolt, "Zahlenwert und Funtionen," Vol. 1, Springer-Verlag, Göttingen, 1950. [d] Quadrupole moments for bromine and iodine were evaluated by extrapolation from literature values for fluorine and chlorine; see section IV.

V. Results and Discussion

A. Binding Energies. Computations of each of the contributions to the complex binding energy by the procedures outlined above were carried out, and the results for aromatic–halogen and aromatic–TCNE complexes are listed in Tables VI and VII, respectively. Overlap-dependent terms for iodine complexes could not be completed since no good wave functions are available for atomic iodine. For the aromatic–halogen complexes, the axial geometry and intermolecular distances found by Hassel and Strømme[30] for benzene–Cl_2 and benzene–Br_2 were assumed to be appropriate. In the TCNE complexes, the donor and acceptor were assumed to lie in parallel planes with the centers of the molecules lying directly above one another. The TCNE molecule was rotated to find the potential energy minimum. The interplanar distance in these complexes was taken to be the same as in crystalline TCNE–naphthalene.[31]

The principal conclusion that can be drawn from the results in Tables VI and VII is that *all contributions to the total stabilization energy of molecular complexes have to be taken into account before any accurate description of them can be made.* When all the contributions are considered, the complex stabilization energy compares favorably with the few available experimental results in the gas phase.

Within this context, it is useful to point out a few details concerning complex stability that came out of these calculations. Previously it seemed unlikely that electrostatic interactions involving multipoles higher than dipoles would be important. All of the component molecules treated in this paper have no dipole moment, yet the electrostatic interactions are several kilocalories mole^{-1} in magnitude. A second point is that a large part of this electrostatic energy comes from the interaction of the π-electron quadrupoles on one partner with the charge distribution of the other. The significance of this is that π-electron quadrupole effects cannot be neglected in discussions of the interactions of aromatic systems.

A third point which should be emphasized is that the charge-transfer and exchange repulsion terms involve the same overlap dependence. The difference is that repulsion involves overlap between filled shells while charge transfer involves overlap between filled and unfilled orbitals. Even so, both overlaps have roughly the same intermolecular distance dependence. This similarity has the important consequence (Table VI) that no matter what value of the charge-transfer constant k is chosen, any increase in the charge-transfer energy is offset by an increase in the exchange repulsion energy if c is evaluated as described in section II.E.

Following previous workers we have chosen to introduce two constants into the total energy expression (k in the charge-transfer equations and c in the exchange repulsion relations). One of these (k) is almost arbitrary, and the other is determined as giving a minimum in the potential energy surface. As far as the energy is concerned, however, another method might have been chosen. This method involves measuring the intermolecular distance dependence of

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(30) O. Hassel and K. Strømme, *Acta Chem. Scand.*, **12,** 1146 (1958); **13,** 178 (1959).

(31) R. M. Williams and S. C. Wallwork, *Acta Cryst.*, **22,** 899 (1967).

Table VI. Contributions to the Stabilization Energy of Some Aromatic–Halogen Complexes[a]

Molecular complex written as A–B	Benzene–Cl_2	Benzene–Br_2	Benzene–I_2[b]	p-Xylene–Cl_2
Distance between centers of mass, Å	4.28	4.50	4.80	4.28
Interaction between point charges (on A) and point quadrupole (on B)	−0.88	−1.07	−1.21	−0.91
Interaction between point quadrupoles	−2.38	−2.81	−3.05	−2.40
Total Coulomb energy	−3.26	−3.88	−4.26	−3.31
Induction energy	−0.34	−0.41	−0.50	−0.41
Dispersion energy	−0.92	−1.07	−1.16	−0.96
Charge-transfer energy				
k = 6.66 eV[c]	−0.53	−0.81		−0.36[d]
k = 11.5 eV[c]	−1.55	−2.39		−1.04[d]
Repulsion constant c, au				
k = 6.66 eV[c]	1.314	1.176		1.232
k = 11.5 eV[c]	1.891	1.793		1.655
Exchange repulsion energy				
k = 6.66 eV[c]	+1.90	+2.41		+1.88
k = 11.5 eV[c]	+2.74	+3.68		+2.49
Total calculated ΔE_f of complex				
k = 6.66 eV	−3.15	−4.07		−3.15
k = 11.5 eV	−3.33	−3.76		−3.21
Measured ΔE_f of complex				
Gas phase			−1.9 ± 0.1[g,h]	
Solution	−1.1[e]	−1.1[e]	−1.3[f]	

[a] Energies are in kcal/mole of complex. [b] None of the overlap dependent terms of the benzene–I_2 complex could be evaluated since good wave functions were not available for atomic iodine. We have included terms independent of overlap to show the trends of these terms in a series of halogen complexes. [c] k = 6.66 eV gives an estimate of the minimum contribution of charge transfer to the total energy of the complex. Hence, k = 6.66 eV also gives an estimate of the minimum exchange repulsion contribution. k = 11.5 eV gives estimates of the maximum contributions. k = 6.66 and k = 11.5 eV do *not* give estimates of the error bounds on the total energy. [d] See Table X. [e] Assuming $T\Delta S$ is equal to that for benzene–I_2. [f] Reference 24. [g] W. K. Duerkson and M. Tamres, *J. Am. Chem. Soc.*, **90**, 1379 (1968). [h] F. T. Lang and R. L. Strong, *ibid.*, **87**, 2345 (1965).

Table VII. Contributions to the Stabilization Energy of Some Rotational Isomers of Complexes of Tetracyanoethylene with Benzene and p-Xylene[a]

Molecular complex written as A–B.	Benzene[b]		p-Xylene[c]			
Rotation from most stable isomer[b,c]	0°	30°	0°	30°	60°	90°
Interplanar distance, Å	3.50	3.50	3.50	3.50	3.50	3.50
Interactions between point charges	−2.30	−2.30	−2.51	−2.51	−2.38	−2.27
Interactions between point charges (on A) and point quadrupoles (on B)	+0.85	+0.85	+0.96	+0.88	+0.84	+0.87
Interactions between point charges (on B) and point quadrupoles (on A)	−4.05	−4.05	−4.09	−4.09	−4.08	−4.07
Interactions between point quadrupoles	+1.49	+1.49	+1.51	+1.50	+1.50	+1.50
Total Coulomb energy	−4.01	−4.01	−4.13	−4.22	−4.12	−3.97
Induction energy	−1.05	−1.05	−1.14	−1.13	−1.11	−1.12
Dispersion energy	−3.59	−3.59	−3.62	−3.77	−3.78	−3.65
Charge-transfer stabilization energy	−1.80	−1.67	−2.50[d]	−2.98	−2.31	−2.24[d]
Repulsion constant c, au	3.943	3.943	3.685	3.685	3.685	3.685
Exchange repulsion energy	+4.24	+4.26	+5.12	+9.18	+8.97	+5.51
Total calculated ΔE_l of complex	−6.21	−6.06	−6.27	−2.92	−2.35	−5.47
Measured ΔE_f of complex						
Gas phase[e]			−7.36			
Solution[f]	−2.30		−3.37			

[a] Energies in kcal/mole of complex. [b] 0° such that TCNE C=C axis is directly above an HC···CH axis of benzene. [c] 0° such that TCNE C=C axis is perpendicular to $H_3CC\cdots CCH_3$ axis of p-xylene. [d] See Table IX. [e] M. Kroll, *J. Am. Chem. Soc.*, **90**, 1097 (1968). [f] Reference 24.

some intermolecular overlap (almost any overlap would do) and setting the total stabilization energy equal to

$$U = U_C + U_D + U_I + \kappa(S^2) \tag{25}$$

where κ is determined by the requirement that the potential energy surface be a minimum at the equilibrium distance. Essentially what this means is that the total stabilization *energies* as presented in this paper do not involve any undetermined constants. It is also interesting to speculate that the method outlined above could be an easier way to obtain estimates of the stability of molecular complexes in a routine way since the overlap need be no better than between, say, Hückel orbitals.

B. Rotational Isomers. A fourth point concerns complex geometry. From the calculations of the energy of the p-xylene-TCNE complex as a function of rotational angle of the TCNE about the p-xylene dyad axis (Table VII), it is evident that only the exchange repulsion interaction changes significantly upon rotation. This result provides additional evidence for the suggestion made earlier[5] that geometry may be determined as much by minimizing repulsion interactions as by maximizing attractive interactions. The charge-transfer contribution to the stabilization energy of a molecular complex is given by eq 14. The stabilization is proportional to the square of the overlap. It is interesting to notice (Table VII) that the charge-

Table VIII. Dipole Moments of Some Aromatic Charge-Transfer Complexes

Complex	Benzene–Cl_2	Benzene–Br_2	*p*-Xylene–Cl_2	Benzene–TCNE	*p*-Xylene–TCNE
Intermolecular Distance, Å	4.28	4.50	4.28	3.50	3.50
Overlap S_{01}	0.0478	0.0582	0.285[a]	0.0150	0.0144[a]
μ_{CT}(D)					
k = 6.66 eV[b]	+0.18[c]	+0.28	+0.09		
k = 34.5 eV				+0.43[b]	+0.63[b]
k = 11.5 eV[b]	+0.42	+0.82	+0.23		
μ_{Ind}(D)	+0.32	+0.42	+0.29	+0.11	+0.14
μ_{total}					
k = 6.66 eV[b]	+0.50	+0.70	+0.38		
k = 34.5 eV				+0.54	+0.77
k = 11.5 eV[b]	+0.74	+1.24	+0.52		

[a] The symmetry of *p*-xylene allows more than one important overlap; see Tables IX and X. [b] k = 6.66 eV gives an estimate of the minimum contribution of charge transfer to the dipole moment of the halogen complexes. k = 11.5 eV gives an estimate of the maximum contribution. For the TCNE complexes, k = 34.5 eV is found to give reasonable dipole moments. [c] Dipole from halogen to aromatic or TCNE to aromatic.

transfer stabilization energy is largest for the 30° isomer. Thus charge-transfer theory alone predicts an *increase* in stability for one of the orientations predicted by the total energy calculations to be the least stable. The calculated barrier to free rotation *in vacuo* of about 4 kcal mole^{-1} is not unreasonable since there are two rotational positions in which the nitrile groups of TCNE can get away from the methyl groups of *p*-xylene. Furthermore, it is doubtful that this result is in disagreement with the experimental result of Foster and Matheson[32] who found no rotational isomers in the hexamethylbenzene–TCNE complex, since there are no favorable rotational positions in the complex. Hence, the rotational barrier would be expected to be almost as low as that indicated here for benzene–TCNE (0.15 kcal).

C. Dipole Moments. The calculated values of the dipole moments of the aromatic–halogen and TCNE complexes are given in Table VIII. The upper and lower limits of the charge-transfer contribution were calculated using the two values of the charge-transfer constant (k) discussed in section II.D. These results indicate that the electrostatic interactions contribute between one-third and two-thirds of the total moment in the benzene–halogen complexes and about one-fourth of the total moment in the TCNE complexes. The result for the halogen complexes is similar to that found for electrostatic contributions to the infrared intensity enhancements and frequency shifts in these systems.[6] The conclusion must again be drawn that both contributions must be considered in these weakly complexing systems and that measured complex dipole moments should not be used to estimate the charge-transfer character of the ground state until the electrostatic effects have been subtracted. It should be pointed out that the electrostatic contributions in this work were calculated using model I of paper I[5] and, therefore, are probably lower limits to this effect. The upper limit for the charge-transfer part of the dipole moment probably overestimates its contribution.

The accuracy of these calculations can be seen by comparing the calculated dipole moments with available dipole moment measurements. Briegleb[24] lists dipole moments of the hexamethylbenzene–TCNE complex as 1.35 D and of durene–TCNE as 1.26 D, corrected for dissociation in CCl_4. Although these results may be an upper limit, they offer a reasonable comparison with the 0.77 and 0.54 D calculated for the *p*-xylene–TCNE and benzene–TCNE complexes.

For the halogen complexes, no experimental dipole moments are available, but a lower limit[24] of 0.6 D for benzene–I_2 and 0.9 D for *p*-xylene–I_2 has been obtained from uncorrected measurements in pure benzene and *p*-xylene. The calculated lower limits of benzene–Cl_2 and benzene–Br_2 as shown in Table VIII agree very well with these measured values. The same conclusions apply for the upper limits when compared to an equilibrium-constant-corrected dipole moment of 1.8 D[24] for benzene–I_2 in cyclohexane.

D. Multiple Charge-Transfer Bands. In this section we will discuss the presence of multiple charge-transfer bands, both high and low energy, and the common assumption[2] that the only important charge-transfer state is that involving the highest filled (and overlapping) orbital of the donor and the lowest unfilled orbital of the acceptor.

Of the complexes studied in this work, multiple bands in the visible and ultraviolet have been observed only for *p*-xylene–TCNE,[24] and Voigt[33] has attributed these two bands at 2.70 and 2.99 eV to charge-transfer bands arising from excitation from the two highest filled π orbitals of *p*-xylene (which are no longer degenerate) to the lowest unfilled orbital of TCNE. Our results (Table IX) show that for any one of the lowest energy configurations of the complex, one of the highest filled orbitals of *p*-xylene overlaps strongly with the lowest unfilled orbital of TCNE while the other overlaps negligibly. In the second low-energy configuration, the latter *p*-xylene orbital overlaps strongly and the former negligibly. We conclude that the doublet charge-transfer spectrum is due to two rotational isomers.[34]

We have also found large overlaps between orbitals that differ by as much as 10 eV (Tables IX and X) and would thus predict charge-transfer bands in the vacuum ultraviolet spectrum of the complexes of *p*-xylene with Cl_2, Br_2, I_2, and TCNE, although probably not at the

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(32) R. Foster and I. B. C. Matheson, *Spectrochim. Acta*, **A23**, 2037 (1967).

(33) E. M. Voigt, *J. Am. Chem. Soc.*, **86**, 3611 (1964); E. M. Voigt and C. Reid, *ibid.*, **86**, 3930 (1964).

(34) Simple orbital energy differences (Table IX) predict that the double peak should be split by 2.5 eV. This error must be attributed to an error in the *p*-xylene calculation which places the highest filled orbital more than 2 eV too high; see section V.E.

Table IX. Important Contributions to the Charge-Transfer Energy of the p-Xylene–TCNE Complex Showing the Two Most Stable Configurations

Mixing, a–b, p-xylene orbital–TCNE orbital	Orbital energy difference, $\epsilon_a - \epsilon_b$, eV	Spectroscopic energy difference, $h\nu_{CT}$, eV	Overlap,[a] S_{ab}		Charge-transfer[a,d] energy contribution, kcal/mole	
			0°	90°	0°	90°
ω_5–$2b_{1g}$	7.81	2.70[b]	0.00054	0.01267	0.0	−1.82
ω_4–$2b_{1g}$	10.32	2.99[b]	0.01440	0.00113	−2.17	0.0
ω_5–$2a_u$	15.64	10.53[c]	0.00095	0.01207	0.0	−0.42
ω_4–$2a_u$	18.15	10.82[c]	0.01102	0.00180	−0.33	0.0

[a] Angles as in Table VII. [b] Spectroscopic values from ref 33. [c] Assuming similar errors in ϵ_4 and ϵ_5. [d] Charge-transfer contribution is calculated from eq 14 where $h\nu_{CT}$ is the measured (or estimated) spectroscopic energy difference.

Table X. Contributions to the Charge-Transfer Energy of the p-Xylene–Cl_2 Complex. Investigation of Orbitals 18 eV above and below the Highest Filled Orbital of p-Xylene

p-Xylene orbital	Orbital energy, eV	Overlap with Cl_2 orbital			Transition energy, eV[b]	CT contribution, kcal[c]	
		$\pi^*3p_x(2)$	$\pi^*3p_y(2)$	$\sigma^*3p_z(0)$		k = 11.5 eV	k = 6.66 eV
π_1 17 (2)	−17.959			0.037612	9.731	−0.437	−0.149
π_2 19 (2)	−16.519			0.000000	8.228		
20 (2)	−15.786			0.005385	7.558	−0.012	−0.003
21 (2)	−15.125			0.000000	6.897		
22 (2)	−13.417			0.000000	5.189		
23 (2)	−13.037			0.002696	4.807	−0.005	−0.002
π_3 24 (2)	−12.478			0.000000	4.25[a]	−0.576	−0.196
25 (2)	−11.772			0.000000	3.544		
26 (2)	−11.592			0.000000	3.364		
27 (2)	−11.592			0.002111	3.364	−0.004	−0.001
π_4 28 (2)	−8.888			0.000000	0.110		
π_5 29 (2)	−5.834			0.000814	2.385		
π_6 30 (0)	6.990	0.000000	0.000170		≃16 est		
π_7 31 (0)	7.176	0.002845	0.000000		≃16 est	−0.001	−0.001
32 (0)	13.823	0.002952	0.000000		≃23 est		
33 (0)	14.253	0.008507	0.000000		≃23 est	−0.009	−0.003
					Total	−1.044	−0.355

[a] Assumed to be spectral transition; ref 24. [b] Calculated by assuming that charge-transfer band is due to the $\pi_3 \rightarrow \sigma^*$ transition, and that other transition energies are separated as the orbital energies. [c] Charge-transfer contribution is calculated from eq 14 when $h\nu_{CT}$ is the measured (or estimated) transition energy.

energies predicted in Tables IX and X. Furthermore Tables IX and X indicate that if two orbitals overlap strongly, even if separated by as much as 10 eV, they will make a nonnegligible contribution to the charge-transfer stabilization energy.

E. Critical Discussion. Using the theory of Murrell, Randic, and Williams[9] and wave functions of the Newton–Boer–Lipscomb[26] type, we have been able to obtain stabilization energies, dipole moments, and information concerning rotational isomers and multiple charge-transfer bands for three short series of complexes. Several disturbing things are apparent about the calculations, however, especially those involving p-xylene. First of all, it is expected from thermodynamic studies,[24,35] that the stability of these molecular complexes should increase with increased methylation of benzene. Tables VI and VII show no evidence for this. Secondly, dipole moments are also expected to increase with increased methylation,[24] and while the calculated dipole moments (Table VIII) of the TCNE complexes follow this trend, the calculated dipole moments of the Cl_2 complexes show a definite decrease in going from benzene to p-xylene as donor. Finally, while the doublet charge-transfer spectrum is separated by only 0.29 eV, these calculations predict a separation of 2.5 eV.[34]

We believe that these inaccuracies are due to errors in the molecular orbital calculations, particularly that of p-xylene, to the extent that overlaps are incorrectly calculated. We believe that the molecular orbitals and charge distribution obtained for TCNE are the most reasonable to date, especially more reasonable than that used by Mantione[36] for the calculation of electrostatic terms in TCNE–aromatic complexes. The same cannot be said for the charge distribution of p-xylene. But we do not believe that the particular errors in the charge distribution of the component molecules are the cause of incorrect trends for two reasons. First, the electrostatic terms for benzene–TCNE calculated in this work (Table VII) and those calculated by Mantione[36] with a grossly different charge distribution on TCNE[37] are almost identical. Secondly, the electrostatic terms calculated do increase in going from benzene to p-xylene complexes.

For these reasons we believe that the wave functions calculated for p-xylene are principally at fault. The Lipscomb-type calculation, which was performed on p-xylene and listed in part in Table III, splits the degenerate e_{1g} orbitals in benzene to −5.83 and −8.38 eV in p-xylene. Recent ionization potential studies[38]

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(35) M. Kroll, *J. Am. Chem. Soc.*, 90, 1097 (1968).

(36) M. Mantione, "Molecular Association in Biology," B. Pullman, Ed., Academic Press, New York, N. Y., 1968, p 411.

(37) M. Mantione, *Theor. Chim. Acta*, 11, 119 (1968).

for *p*-xylene indicate no ionization potential lower than about 8.2 eV.[39] This same study[38] also obtained a much lower a_{2u} ionization potential for benzene than that calculated by Newton, Boer, and Lipscomb,[26] and on that basis questioned the calculations. We must concur with the criticism and hence have, for instance, assumed the transition energy of the $\omega_5 \rightarrow 2b_{1g}$ transition in *p*-xylene–TCNE (Table IX) to be 2.70 eV (this effectively pulls orbital ω_5 down to -8.19 eV, within the region expected from ionization potential studies). The errors in the calculation, however, are rather serious and allow us to make no comments on the effects of increased methylation in molecular complexes.

Three very recent works have been brought to our attention dealing with the problem studied here.[36,37,40] Mantione has calculated the inductive contribution to the dipole moments[37] and the energy of formation[36] of a rather large number of TCNE–aromatic complexes. The form of the perturbation theory used by her does not contain a charge-transfer term and is probably equivalent to (25), although with a different form of the repulsion. Her method of evaluating electrostatic terms is much like ours except that she does not include π-quadrupole effects. In fact, comparable terms for benzene–TCNE in the Mantione work[37] are almost identical with those calculated here. Neglect of π quadrupoles, however, gives $\Delta E_f = -4.80$ kcal/mole for benzene–TCNE, as compared to the present $\Delta E_f = -6.27$ and measured $\Delta E_f = -7.36$. Neglect of π quadrupoles would seem important.

Le Févre, Radford, and Stiles[40] have attempted to evaluate the amount of charge transfer in the ground state of molecular complexes by attributing that part of the measured dipole moment not accounted for by the induced moment as being due to charge transfer, and hence a measure of the amount of charge transfer in the ground state. Their conclusion, that van der Waals forces rather than charge-transfer interactions seem primarily responsible for the ground-state dipole moment, is not in disagreement with our results. We do feel, however, that the present state of experimental complex dipole moments does not warrant use of this procedure as an accurate measure of amount of charge transfer.

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(38) A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc., B*, 22 (1968).

(39) The original paper of Newton, Lipscomb, and Boer[26] calculated an ionization potential for *p*-xylene of 6.98 eV, better than the present calculation but still subject to the same criticism. The difference in calculations is due to a different choice of diagonal U_{ii} matrix elements.

(40) R. J. W. Le Févre, D. V. Radford, and P. J. Stiles, *J. Chem. Soc., B*, 1297 (1968).

Theory of the Measurement of Weak Molecular Complexes. I. General Considerations

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Abstract: Some aspects of the measurement of formation constants and other constants for weak molecular complexes are considered from the standpoint of basic binding theory. The theoretical minimum errors in the formation constant k and the extinction coefficient ϵ are discussed as a function of the saturation fraction of the most dilute component, and it is shown in agreement with previous work that the most accurate values of either parameter are obtained when the saturation fraction lies *between* 0.2 and 0.8. Outside this region, the determined values become extremely uncertain, and in addition, insufficient data are available to adequately fit a given stoichiometric model. It is suggested that the criteria that the highest concentration of the excess component be not less than $0.1/k$ are insufficient to assign a given stoichiometric model to the data, but apply instead to the smallest range of saturation fraction required to show that a line of finite limiting slope and/or intercept exists. To develop criteria by which a given stoichiometric model can be considered in 1:1 correspondence with the phenomenological equation fitting the data, the principles of information theory are applied to the binding process. It is concluded that of the order of 75% of the saturation curve is required to show the correspondence between the equation of the model and the equation fitting the data. Also discussed are various plotting forms and the errors arising from various rearrangements of the basic binding equation.

The problem of the determination of formation constants and other constants for weak intermolecular complexes has received considerable attention during the past several years, and for good reason, since the proof of existence of such complexes depends largely on the obtention of unique values for the formation constant k and the extinction coefficient ϵ. The most critical discussion is that given by Person,[1] who points out what some authors seem to have missed: that the most accurate values of the formation constant are obtained when the concentration of the complex is approximately the same as the free concentration of the most dilute component. Although Person limited his discussion to a consideration of the errors arising when the concentrations fell below or above certain limits,

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(1) W. B. Person, *J. Am. Chem. Soc.*, **87**, 167 (1965).