probable for CF_3 than for CH_3, contrary to our observations.

The probability of cage combination of CH_3 with CF_3 seems to be closer to that found for CH_3 combination than for CF_3 combination. This would be expected if the rate of radical rotation is the determining factor.

It has been suggested by a referee that the different efficiency of the cage combination of CH_3 and CF_3 radicals may be attributed to different a values; *i.e.*, their initial separation, following the photodissociation, is larger for CF_3 than for CH_3. It is not obvious, though, why the trend should be in this direction. He also pointed out that a may be an increasing function of temperature. This would lead to a slight curvature in the plots of $1/p$ *vs.* $T^{1/2}/\eta$ making the lines concave. Hence, this suggestion provides an alternative explanation for some low values of intercepts. However, had the temperature been effective in modifying a, a curvature should be observed in individual lines, such as shown in Figure 1 of this paper or Figure 3 of the preceding paper. This is not the case; however, an attempt will be made to extend these studies to a much wider temperature range.

Finally, following the reasons given in part I, we plotted log $P(CH_3)$ *vs.* $1/T$. The results are shown in Figure 3. Again, the resulting lines are parallel to each other; the *formal* activation energies, $E_c - E_d$, are constant within experimental uncertainties, *viz.*, -1.7 ± 0.2 kcal/mole. We feel, therefore, that the constancy of $E_c - E_d$ has some deeper significance which needs further studies. Similar plots for the mixed combination, $CH_3 + CF_3$, give $E_c - E_d = -2.1$ kcal/mole, *i.e.*, a value in between those found for CF_3 and for CH_3 radicals. However, let us stress again that $E_c - E_d$ does not represent conventional activation energies.

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Bonding in Donor–Acceptor Complexes. I. Electrostatic Contributions to the Ground-State Properties of Benzene–Halogen Complexes[1a]

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Abstract: The contribution to the energy of formation and the dipole moment of benzene–halogen complexes from the benzene quadrupole–halogen-induced dipole interaction has been evaluated. The results show that this interaction makes an important contribution to these experimental quantities and that it should not be neglected in discussions of the ground state of donor–acceptor complexes. For the benzene–iodine monochloride complex, the quadrupole–dipole interaction was calculated, and it also makes a nonnegligible contribution to the energy of formation. This work suggests that the relative importance of electrostatic and charge-transfer interactions in the ground state of these complexes needs further investigation.

The interactions between "electronegative" and "electropositive" molecules to form donor–acceptor complexes have been an important subject for theoretical and experimental investigation. Much of the work in this field has been summarized in two recent books[2] and numerous reviews.[3–7] The properties of these complexes can be divided into two classes depending on whether they are determined only by the structure of the ground state of the complex or whether they depend on both the ground- and excited-state structures. Properties of the complex such as its geometry, formation constant, enthalpy of formation, dipole moment or change in dipole moment, enhanced intensities and frequency shifts in the infrared spectra, and magnetic properties fall in the first class. The electronic spectrum of the complex falls into the second class.

The charge-transfer model, originally proposed by Mulliken,[8] has been used almost exclusively to rationalize these properties. This model is so well known that only the pertinent points will be summarized here. In the wave function for the ground state of the complex

$$\Psi_N = a\Psi_0 + b\Psi_1 \tag{1}$$

the "no-bond" wave function Ψ_0 contains all "classical" intermolecular interactions between donor and acceptor

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(1) (a) Supported in part by Grant GM-09187-04 from the National Institutes of Health, Public Health Service, and by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-216-65; (b) Alfred P. Sloan Fellow.

(2) (a) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 964.

(3) L. J. Andrews, *Chem. Rev.* **54**, 713 (1954).

(4) S. P. McGlynn, *ibid.*, **58**, 1113 (1958).

(5) J. N. Murrell, *Quart Rev.* (London), **15**, 191 (1961).

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

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and makes the dominant contribution. A small admixture of the "dative-bond" wave function Ψ_1 into the ground state gives this state some charge-transfer character. That is, there is a partial "transfer" of an electron from donor to acceptor in the complex, and the magnitude of this "charge transfer" is measured by the dative coefficient *b*. The following points summarize how the above experimental data on complexes are rationalized by this mode.[4,8]

(1) The additional stabilization of the complex over and above the usual London dispersion forces is attributed to "resonance" interactions between the two limiting structures. This stabilization is formally similar to the case where the Heitler–London wave function for the hydrogen molecule is improved by adding ionic terms.

(2) For complexes in which neither the donor nor acceptor has a dipole moment, the dipole moment of the complex is due to, and is a measure of, the dative-bond contribution. The complexes of benzene and symmetrically substituted benzenes with the homonuclear halogens provide examples of donor–acceptor pairs possessing such dipole moments. In complexes where either the donor or the acceptor has a dipole moment, there is often a change in the dipole moment on complexing. This change in dipole moment is also attributed to the dative-bond contribution. The benzene–iodine monochloride complex would be an example of such a case. The dipole moment of iodine monochloride is 0.65 D in the gas phase,[9] but its moment in complexing media has not yet been determined.

(3) The intensity enhancements of the halogen stretching frequencies are attributed to a change in dative coefficient upon vibration.[10,11]

(4) In the earliest papers[8] plausible predictions of geometry of complexes were made by assuming that the interaction between Ψ_0 and Ψ_1 would be a maximum when the overlap between the highest energy filled π orbital of the donor and the lowest energy unfilled orbital of the acceptor was a maximum. However, it was recognized that other donor and acceptor orbitals might also be important, and in later papers the need to recognize their importance in explaining the observed geometries of stable solid-state complexes was discussed.[12] For benzene–halogen complexes, in particular, the axial symmetry observed in the alternating chains of benzene–halogen–benzene–halogen... molecules in the solid, if appropriate for 1:1 complexes in solution, would indicate that the lower energy filled MO in benzene acts as the donor orbital. Such a modification of the original theory is necessary because, for axial geometry, the overlap integral of the highest filled π orbital of benzene with the lowest energy unfilled halogen orbital is zero. This modification brings added complications into the interpretation of the charge-transfer spectra of the benzene–halogen complexes.[12]

In Mulliken's original paper[8] it was pointed out that the contribution to the energy made by the no-bond structure represented by the wave function Ψ_0 was to include all "classical" intermolecular forces. Since in many donor–acceptor complexes neither the donor nor acceptor possesses a dipole moment, it was assumed that the only such intermolecular contribution of importance was the induced dipole–induced dipole interaction (dispersion interaction). This interaction has been estimated for benzene–halogen complexes[8,13] and is in the range of 0.5–1.5 kcal. In solution, however, dispersion interactions tend to cancel one another because the interactions between isolated donor and acceptor molecules with *solvent* are of the same order of magnitude as the interaction of donor and acceptor with each other. Most estimated values of the dispersion contribution to the stabilization energy of the complex are, consequently, subject to considerable uncertainty.

To the author's knowledge, no one has studied the possible importance of other electrostatic interactions in the benzene–halogen complexes.[14] Specifically, aromatic and halogen molecules have quadrupole moments and, in addition, the halogen molecules are quite polarizable. Thus, the quadrupole–induced dipole interaction (or quadrupole–dipole interaction if either or both partners has a dipole moment) may make a substantial contribution to the ground-state properties of these complexes. It is the purpose of this paper to investigate this possibility.

Theory

A. Introduction. Electrostatic interactions will be discussed within the formalism developed by Murrell and coworkers.[15] In this formalism a perturbation technique is used which allows the energy to be separated into several contributions: coulomb, induction, dispersion, exchange, and charge-transfer energies. The coulomb interaction is a direct multipole–multipole interaction. In benzene–halogen complexes, the lowest order coulomb interactions would be quadrupole–quadrupole except in the benzene–iodine monochloride complex where the lowest order would be quadrupole–dipole. The induction energy is composed of multipole–induced multipole interactions. For benzene–halogen complexes the quadrupole–induced dipole interaction is the lowest order such term, and it is the contribution from this term that will be the principal subject of this paper. The exchange energy comes about as a result of the Pauli principle in cases where the overlap between filled orbitals becomes important. The coulomb energy may be either attractive or repulsive, the induction and dispersion energies are always attractive, and in this formalism the exchange energy is always repulsive.

Direct calculations of the integrals involved in Murrell's theory would be quite difficult because of the complexity of the molecules involved and the unavailability of good molecular wave functions. It is possible, however, to estimate the magnitude of the appropriate contributions using a phenomenological theory that utilizes experimentally determined properties of the

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[9] C. H. Townes, *Phys. Rev.*, **70**, 665 (1946); C. H. Townes, A. N. Holden, and F. R. Merritt, *ibid.*, **73**, 1334 (1948).

[10] E. Fergusen, *J. Chim. Phys.*, **61**, 257 (1964).

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[12] R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1964).

[13] K. Fukui, A. Imamura, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, **35**, 33 (1962).

[14] Briegleb has evaluated electrostatic contributions in complexes with very polar acceptors such as trinitrobenzene; see ref 1, p 167 ff.

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

isolated molecules and simple models of the electron distribution in donor and acceptor molecules.

In what follows, it is found that a very significant interaction in the benzene–halogen complexes is the benzene quadrupole–halogen-induced dipole interaction. For the iodine monochloride complex, the benzene quadrupole–halogen dipole contribution also has appreciable magnitude. It should be emphasized that the coulomb and induction contributions that are here being neglected (quadrupole–quadrupole, halogen quadrupole–benzene-induced dipole, etc.) can only *increase* the magnitude of the electrostatic contributions to the energy of formation and the dipole moments of these complexes.

B. Quadrupole Potential of Benzene. The electrostatic potential of a benzene ring will be considered to be made up of two contributions: a π-electron contribution and a σ-bond framework contribution. The general procedure used in the calculations that follow is to write the potential as a multipole expansion. Any electric field vectors necessary for the calculation of induced dipole moments may then be obtained by differentiation of the potential with respect to the appropriate coordinates.

The simplest model for the π-electron wave function can be written as an antisymmetrized product of one-electron molecular orbitals. Thus

$$\chi = \mathcal{A}\omega_1(1)\bar{\omega}_1(2)\omega_2(3)\bar{\omega}_2(4)\omega_3(5)\bar{\omega}_3(6)$$

where $\mathcal{A}$ is the antisymmetrization operator and where a bar indicates β spin. Since the electronic multipole moment operators are one-electron operators, the expectation value of these operators will be specified completely by the first-order density matrix for the system. For the π electrons in benzene, using a simple LCAO function with neglect of overlap, the first-order density matrix (more commonly called the bond-order matrix) has diagonal elements equal to unity. These diagonal elements have the physical significance that they represent the probability of finding an electron in a particular 2p π orbital in the benzene ring. Thus, at this level of approximation, the π-electron distribution of benzene can be thought of as a superposition of six atomic distributions, each of which has a single π electron localized in a 2p π orbital. The electrostatic potential for such a π-electron distribution can be estimated as follows.

Consider the electrostatic potential at a point $\underset{\sim}{R}$ due to an electron in a 2p$_Z$ orbital located at the origin. There is also a unit positive charge at the origin. This situation and the necessary coordinates are shown in Figure 1.

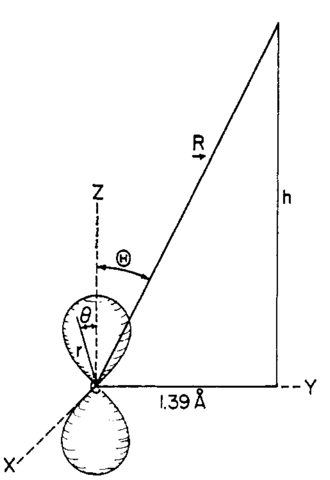

Figure 1. Quantities used in the calculation of the electrostatic potential at a point $\underset{\sim}{R}$ due to an electron in a 2p$_Z$ orbital and a unit positive charge at the origin.

The potential at point $\underset{\sim}{R}$ outside the region containing the charges can be represented by an expansion in spherical harmonics[16]

$$\Phi(\underset{\sim}{R}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{+l}\frac{4\pi}{2l+1}q_{lm}\frac{Y_{lm}(\Theta,\Phi)}{R^{l+1}} \tag{2}$$

where the coefficients q_{lm} are given by

$$q_{lm} = \iiint Y^*_{lm}(\theta,\phi)r^l\rho(r,\theta,\phi)r^2 \sin\theta \, dr \, d\theta \, d\phi \tag{3}$$

and where $\rho(r,\theta,\phi)$ is the charge distribution. For an electron in a 2p$_Z$ Slater orbital

$$-\rho = \frac{(2\alpha)^5}{32\pi}r^2e^{-2\alpha r}\cos^2\theta \tag{4}$$

The quantity $\cos^2\theta$ can be written as a linear combination of spherical harmonics, however

$$\cos^2\theta = aY_{00}(\theta,\phi) + bY_{20}(\theta,\phi) \tag{5}$$

where a and b are constants, and, because of the orthonormality properties of the spherical harmonics, only the monopole and quadrupole coefficients in eq 3 are nonvanishing. The monopole contribution of the electron is exactly cancelled by the contribution of the positive charge at the origin and, therefore, the π-electron contribution to the electrostatic potential is rigorously a quadrupole potential. Evaluating the coefficient q_{20}, one obtains

$$-q_{20} = \frac{6}{(2\alpha)^2}\sqrt{\frac{5}{\pi}} \tag{6}$$

and the potential at the point $\underset{\sim}{R}$ is then

$$\Phi(\mathrm{R}) = -\frac{6}{(2\alpha)^2}\frac{3(\cos^2\Theta) - 1}{R^3} \tag{7}$$

To calculate the induction energy for a polarizable molecule brought into this electrostatic potential, it is necessary to have the value of the Z component of the electric field. To obtain this, one evaluates

$$E_Z = -\frac{\partial\Phi}{\partial Z} = -\frac{18}{(2\alpha)^2}\left\{\frac{\cos\Theta}{R^4}[5(\cos^2\Theta) - 3]\right\} \tag{8}$$

The magnitude of this electric field as a function of distance along the hexagonal axis of benzene is shown in Figure 2. In this calculation the orbital exponent 2α was taken as 3.25.

It is possible that using a single Slater orbital will not give a very good estimate of the electrostatic potential since it is known that a Slater orbital does not describe the outer region of the wave function too well. To investigate this possibility, we have also computed the potential and E_Z along the hexagonal axis using the SCF atomic orbitals of Roothaan and Clementi.[17]

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(16) J. D. Jackson, "Classical Electrodynamics," John Wiley and Sons, Inc., New York, N. Y., 1962, p 99.

(17) C. C. J. Roothaan and E. Clementi, *Phys. Rev.*, 127, 1618 (1962).

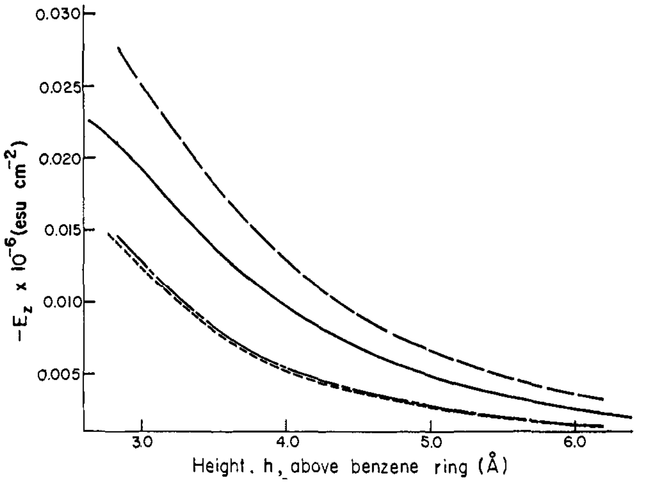

Figure 2. Various contributions to the electric field strength along the hexagonal axis of benzene from a single C–H fragment: ———, the π-electron contribution from a Slater atomic orbital; — — — —, π-electron contribution from an SCF atomic orbital; — — —, σ-bond dipole contribution (model 1); - - - -, σ-bond dipole contribution (model 2).

The results of this calculation are also shown in Figure 2 where it can be seen that the SCF atomic orbitals increase the magnitude of the quadrupole field by about 30%.

The contribution of the σ bonds to the electrostatic potential can arise from σ-bond dipole and σ-bond quadrupole moments. The σ-bond dipole contribution can be easily estimated, but the quadrupole contribution is much more difficult to evaluate. Buckingham[18] and Krishnaji[19] have discussed the possibility of evaluating bond quadrupole moments, but the experimental data on molecular quadrupole moments is currently so meager that it is impossible to establish any reliable set of bond quadrupole moments. The σ-bond quadrupole contribution to the electrostatic potential will, therefore, be neglected when σ-bond dipoles are present.

The σ-bond dipole moment contribution to the electrostatic potential can be calculated using two different models. One model locates the full C–H bond moment in the center of the C–H bond. In the second model, the dipole moment is divided into appropriate charges localized at the carbon and hydrogen atoms. The calculation of the potential is then straightforward and the only question that remains is the value of C–H bond moment to be used. There has been considerable discussion about the magnitude of this bond moment,[20] but a value (determined from ir intensity measurements) of $\mu_{CH} = 0.65$ D with the hydrogen positive seems to be on firm ground at present.[21] Such a dipole moment corresponds to an electronic charge of $+0.125$ on the hydrogen and -0.125 on the carbon. Such charges are in agreement with recent SCF net atomic charges for ethylene reported by Newton, Boer, and Lipscomb (± 0.140)[22] but are considerably larger than the corresponding values reported for benzene (± 0.04).[22] Since we desire to calculate a lower limit for electrostatic contributions, we will adopt electronic charges of 0.08 on each atom. This corresponds to an average of the SCF values for ethylene and benzene and would give rise to a value of $\mu_{CH} = 0.42$ D. The results of calculations of E_Z as a function of distance along the hexagonal axis of benzene using the two models discussed above are also shown in Figure 2. It can be seen that the electric field contributions from the two models are practically indistinguishable. It should be noted that the contribution to E_Z from the C–H bond dipoles is about two-thirds as large as the contribution from the π electrons and that the two contributions supplement each other.

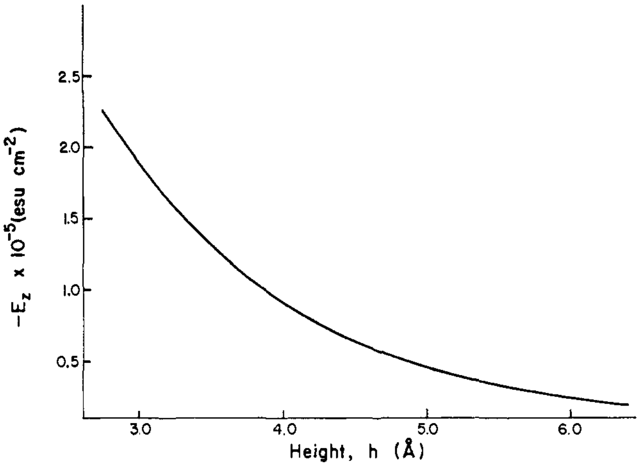

Figure 3. The total Z component of the electric field strength as a function of distance above the benzene ring.

The results shown in Figure 2 can be regarded as the contributions of a single C–H fragment with its π electron to the electrostatic potential. To obtain the total potential (or electric field component) along the hexagonal axis of the benzene molecule, the π-electron and the σ-bond dipole contributions must be summed and multiplied by 6. The total magnitude of E_Z along this axis is shown in Figure 3. In calculating the magnitude of E_Z shown in this figure, the π-electron contribution from a single Slater orbital rather than from a SCF orbital has been used. This was done so that the electrostatic contributions to the ground-state properties of donor–acceptor complexes calculated in the next section might represent lower limits.

The only way that these results can be compared with experiment is to compare the molecular quadrupole moment calculated from this model with experimental values. Values of the benzene quadrupole moment have been obtained from microwave line-broadening experiments ($\pm 3.6 \times 10^{-26}$ esu cm^2)[23] and more recently from second virial coefficient data ($\pm 15.7 \times 10^{-26}$ esu cm^2).[24] This latter value is probably more accurate than the value from microwave line-broadening measurements because the assumptions used in the microwave studies clearly do not apply to benzene and because a perusal of available data indicates that quadrupole moments determined from microwave line-broadening measurements are a factor of 3–10 times

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(24) A. G. DeRocco, T. H. Spurling, and T. S. Storvick, *ibid.*, **46**, 599 (1967).

lower than those determined by other methods. The molecular quadrupole moment of benzene calculated from the present model is -14.5×10^{-26} esu cm^2, which is in good agreement with the value obtained from virial coefficient data.

C. The Energy and Induced Dipole Moments of Benzene–Halogen Complexes. Consider the interaction of a polarizable or dipolar molecule with the quadrupole field of a benzene ring. The polarizability of a molecule is a tensor quantity and for a linear molecule is defined by the components of polarizability parallel and perpendicular to the bond. Unfortunately, the polarizability tensor has only been determined for chlorine for which the ratio $\alpha_{\perp}/\alpha_{\parallel}$ is 0.55. The scalar polarizability, determined from dielectric constant measurements, is related to the tensor components by the equation

$$\alpha_0 = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp}) \qquad (9)$$

and, if it is assumed that the ratio $\alpha_{\perp}/\alpha_{\parallel}$ remains constant throughout the series of halogens, the components of the polarizability tensor can be estimated from the scalar polarizabilities. The parallel component of polarizability for the halogens calculated in this way is given in Table I along with other pertinent data for the halogen complexes.

Table I. Experimental and Theoretical Quantities Used to Calculate Properties of Benzene–Halogen Complexes

Acceptor	$\alpha_{\parallel} \times 10^{25}$, cm^3	Z_1, Å	Z_2, Å	Z_M,[g] Å	$-E_1 \times 10^{-5}$, esu cm^{-2}	$-E_2 \times 10^{-5}$, esu cm^{-2}	$-E_M \times 10^{-5}$, esu cm^{-2}
Cl_2	66[a]	3.28[c]	5.27[c]	4.28	1.55	0.39	0.75
Br_2	99.5[b]	3.36[c]	5.64[c]	4.50	1.46	0.31	0.64
I_2	175[b]	3.47[d]	6.13[f]	4.80	1.35	0.22	0.53
ICl	136[b]	3.47[e]	4.77[f]	4.62	1.35	0.28	0.59

[a] Landolt–Bornstein, "Zahlenwerte und Functionen," Vol. I, Springer-Verlag, Berlin, 1951, p 510. [b] Calculated from scalar polarizabilities using assumptions discussed in text. [c] From crystal structure data: O. Hassel and K. Stromme, *Acta Chem. Scand.*, **12**, 1146 (1958); **13**, 1781 (1959). [d] Extrapolated from a plot of data on chlorine and bromine complexes *vs.* van der Waals radii. [e] Assumed identical with benzene–iodine complex. [f] Sum of Z_1 + normal halogen distance. [g] Distance to midpoint of halogen molecule.

For a polarizable molecule in a *uniform* electric field, the energy and induced dipole are given by $W = {}^1/_2\alpha E^2$ and $\mu = \alpha E$. From Figure 3 it is clear that the electric field along the hexagonal axis of benzene is both nonuniform and nonlinear, and, therefore, some kind of averaging procedure which distributes the polarizability over the molecule must be used. Three possible procedures are readily apparent.

(1) Locate all of the polarizability at the midpoint of the halogen bond. In this case the formulas above can be used to calculate W and μ, and the electric field is taken at a value of Z corresponding to the midpoint of the bond.

(2) Divide the polarizability into two equal parts located at each atom. In this case the energy and dipole moments of the complex are

$$W = \frac{1}{2}\frac{(\alpha_{\parallel})}{2}(E_1^2 + E_2^2) \qquad (10)$$

$$\mu = \frac{\alpha_{\parallel}}{2}(E_1 + E_2) \qquad (11)$$

where E_1 and E_2 are the electric field strengths at the nearest and farthest halogen atoms, respectively.

(3) Divide the polarizability into more than two parts distributed in some way along the halogen–halogen bond. Energy and dipole moment formulas are then

$$W = \frac{1}{2}\frac{(\alpha)}{n}\sum_{i=1}^{n} E_i^2$$

$$\mu = \frac{\alpha}{n}\sum_{i=1}^{n} E_i$$

Since the polarizability is a macroscopic phenomenological property of the molecule as a whole, any of the above procedures will be an approximation. The first procedure is the simplest. The second is in accord with the well-known additivity property of atomic and group refractions. The third presents problems of deciding on a value of n and on the boundaries of the electronic distribution in the molecule. A consideration of the shape of the electric field *vs.* distance curved in Figure 3 shows that procedure 1 will tend to underestimate values of the electrostatic contributions to μ and W, while procedure 2 will tend to give high contributions.[25] In the next section results using both procedures will be given.

For an acceptor molecule with a permanent dipole moment such as iodine monochloride, the dipole–quadrupole contribution must be added to the induced dipole–quadrupole interaction when calculating the energy. This dipole–quadrupole interaction has been estimated by dividing the dipole moment of ICl into appropriate charges located on each of the atoms. The energy of interaction can then be calculated from a knowledge of the quadrupole potential at the two atoms. Thus

$$W(\text{dipole–quadrupole}) = q(\Phi_1 - \Phi_2) \qquad (12)$$

where q is the absolute value of the charge located on each atom and Φ_1 and Φ_2 are the electrostatic potentials at the near and far atoms, respectively. To calculate the additional induced dipole moment in ICl using procedure 2 above, one must assign appropriate polarizabilities to the iodine and chlorine atoms. This was accomplished by assuming

$$\frac{\alpha_{\parallel}(\text{I})}{\alpha_{\parallel}(\text{Cl})} = \frac{\alpha_0(\text{I}_2)}{\alpha_0(\text{Cl}_2)} \qquad (13)$$

where $\alpha_0(I_2)$ and $\alpha_0(Cl_2)$ are the scalar polarizabilities of molecular iodine and chlorine, respectively.

Results and Discussion

Using the procedures outlined above, the electrostatic contributions to the energies of formation and the induced dipole moments have been calculated for the benzene–halogen complexes. The results are summarized and compared with experimental data in Table II.

Two points are immediately clear from a consideration of Table II. First, the contributions of the

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(25) Procedure 3 could give contributions larger than procedure 2 if the regions beyond the two nuclei were considered.

Table II. Calculated Values of the Quadrupole–Induced Dipole Contribution to the Energies and Dipole Moments of Benzene–Halogen Complexes Compared with Experimental Results

	Approximation 1		Approximation 2		Experimental			
Acceptor	μ, D	$-W$, kcal mole^{-1}	μ, D	$-W$, kcal mole^{-1}	K_x, mole fraction^{-1}	$-\Delta G_f$, kcal mole^{-1}	$-\Delta H_f$, kcal mole^{-1}	μ, D
Cl_2	0.50	0.27	0.64	0.61				
Br_2	0.64	0.29	0.88	0.80	1.04[e]	0.22	1.06[i]	
I_2	0.93	0.35	1.37	1.18	1.55[f]	0.26	1.3[f]	1.8[i]
					4.5 (K_c)[g]		2.0[g]	
ICl	0.80	0.34	1.29	1.14				
	0.65[a]	0.65[b]	0.65[a]	0.65	5.56[h]	1.01	2.84[h]	
	1.45[c]	0.99[d]	1.94[c]	1.79[d]				

[a] Contribution of the permanent dipole moment. [b] Quadrupole–dipole contribution to the energy. [c] Total predicted dipole moment of benzene–ICl. [d] Sum of quadrupole–dipole and quadrupole–induced dipole contributions. [e] R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **72**, 4677 (1950). [f] R. M. Keefer and L. J. Andrews, *ibid.*, **77**, 2164 (1955). [g] Vapor-phase values: F. T. Long and R. L. Strong, *ibid.*, **87**, 2345 (1965). [h] N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, **77**, 4202 (1955). [i] G. Kortum and H. Walz, *Z. Elektrochem.*, **57**, 73 (1953).

quadrupole–induced dipole (and quadrupole–dipole for ICl) are between 30 and 80% of the experimental quantities and, therefore, they should not be neglected in a discussion of the stability of the ground state of these complexes. Second, the quadrupole–induced dipole contributions increase as complex strength increases, again indicating that this interaction may play an important role in stabilizing the complex. It is of special interest to compare the difference in the free energies of formation[26] of the benzene–iodine and the benzene–iodine monochloride complexes with the calculated quadrupole–dipole contribution to the energy of the benzene–iodine monochloride complex. If the electrostatic contribution is quite important these two quantities should be about equal since the main difference in energy between the two complexes should be due to the presence of the dipole moment in ICl. The close agreement of these two quantities is probably fortuitous, but this result as well as those discussed above is at least suggestive that the importance of electrostatic contributions to the ground-state properties needs further investigation.

The results presented above suggest the possibility that while the charge-transfer model gives a correct explanation of the electronic spectrum of donor–acceptor complexes, its importance in determining ground-state properties of these complexes may have been overemphasized. Similar suggestions have recently been made by Hooper,[27] Dewar and Thompson,[28] and in a number of papers about complexes important in biology by Pullman and coworkers.[29]

The electrostatic model developed above has the added advantage that properties of complexes can be estimated from a fairly simple calculation using the properties of the isolated molecules in advance of experimental measurements. For example, the dipole moment of ICl at infinite dilution in benzene should be between 1.6 and 1.8 D. There is a possibility, however, that this electrostatic model would predict solvent–halogen complexes with similar stabilities to the benzene–halogen complexes, thus making the net electrostatic energy stabilization and induced dipole moment in solution quite small. To test this possibility, the interaction of an iodine molecule in an axial position to a cyclohexane ring was calculated. Using the same level of approximation as that used above, the quadrupole field of a cyclohexane ring would arise from the C–H bond dipoles in the σ-bond system. Using a C–H bond dipole of 0.4 D in the saturated system with the hydrogen positive and an iodine–cyclohexane distance of 3.47 Å, one calculates $W = 0.004$ kcal/mole and $\mu_{\text{ind}} = 0.08$ D for the cyclohexane–iodine complex. Thus, one would expect the calculated energy of formation and the induced dipole moment of the benzene–iodine complex in cyclohexane to be reduced only slightly from the values given in Table II.

Finally, some considerations about complex geometry should be mentioned. The quadrupole–induced dipole contribution to the energy and induced dipole moment of the benzene–halogen complex using the resting model are somewhat less than, but still the same order of magnitude as, the corresponding properties calculated for the axial model. The axial configuration maximizes the attractive contribution from the quadrupole–quadrupole interaction, however, while in the resting configuration, the quadrupole–quadrupole interaction is repulsive. Preliminary calculations indicate that this interaction may also make an appreciable contribution to the energy of formation of these complexes.[30] In any complete theory of complex stabilization repulsive forces must also be considered. Person has pointed out that repulsive forces are greater in the resting than in the axial models, however.[31] Thus, it is possible that for these weak complexes, geometry is determined as much by a minimization of repulsive forces as by a maximization of attractive forces. This phenomenon was found in a recent study of weak hydrogen bonds.[32]

It is clear that the results presented in the paper suggest that an important contribution is made to the ground-state properties of donor–acceptor complexes by van der Waals interactions. Among the questions that still need to be answered are the following. (1)

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(26) Strictly speaking, enthalpies of formation should be compared but the enthalpies of formation of weak molecular complexes in solution determined by the Benesi–Hildebrand method are subject to even more error than the equilibrium quotients. As an estimate of energy differences for such complexes, free energies are probably more significant than enthalpies; see ref 13.

(27) H. O. Hooper, *J. Chem. Phys.*, 41, 599 (1964).

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

(29) See, for example, M. Mantione and B. Pullman, *Compt. Rend.*, 262, 1492 (1966).

(30) P. J. Trotter, Ph.D. Thesis, University of Colorado, 1967.

(31) W. Person, private communication.

(32) P. J. Berkeley and M. W. Hanna, *J. Chem. Phys.*, 41, 2530 (1964).

What role do electrostatic interactions have in determining changes in the infrared spectrum of donor–acceptor complexes? (2) Are electrostatic interactions as important in π–π-type complexes as they are in the benzene–halogen complexes? (3) Are electrostatic interactions important in determining the relative stability of a series of complexes using the same acceptor and different donors? (4) Are the logical consequences of the inclusion of electrostatic interactions borne out by experiment? For example, on the basis of electrostatic considerations, one predicts that a benzene–krypton complex should have about half the stability of the benzene–chlorine complex. (5) Can the repulsion contribution to the energy be reliably estimated? These questions will be discussed in forthcoming papers of this series.

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The Crystal and Molecular Structure of 14c-Hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione ($C_{30}H_{18}O_2$)[1]

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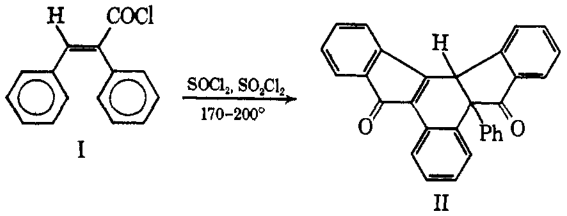
Abstract: α-Phenylcinnamoyl chloride (I) upon pyrolysis with thionyl chloride forms 14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione ($C_{30}H_{18}O_2$) (II). The chemical properties and ultraviolet and infrared spectra of II closely approximate those of indones. An X-ray structure analysis was performed in order to unequivocally establish the molecular structure. Data from a single crystal ($P2_1/a$, $a = 19.65 \pm 0.01$ A, $b = 10.55 \pm 0.01$ A, $c = 10.86 \pm 0.01$ A, $\beta = 111° 20' \pm 5'$, $Z = 4$) were collected using a four-circle diffractometer operating under control of a time-shared SDS 920 computer (Brookhaven Multiple Spectrometer Control System, MSCS). The structure was directly determined from the diffraction data using the symbolic addition method of phase determination. The complete molecule (II) was found from the E map based on the unique set of phases obtained. Least-squares and Fourier methods were used for refinement and hydrogen atom location. The molecule is acentric, with the racemic stereoisomers crystallizing in an ordered arrangement. The molecule consists of two planes intersecting along the Ph–C–CH bond.

New procedures for the formation of carbon-to-carbon bonds are of great interest and importance in organic chemistry. The present investigation is concerned with a novel one-step procedure which has been shown to result in the creation of four such bonds between two molecules of α-phenylcinnamic acid in such a way as to produce a system of six fused carbocyclic rings. The unusual chemistry of compounds containing this system and related systems will be the subject of subsequent reports. The present paper deals with the preparative procedure, with the chemical and spectroscopic evidence which permitted postulation of a preliminary structure for the first product of this type to be obtained, and particularly with the methods of X-ray crystallographic analysis which independently and finally provided a complete elucidation of the structure of the pentacyclic product.



I

II

The product in question is formed under relatively mild conditions, and we first encountered it inadvertently. During an attempt to prepare pure α-phenylcinnamoyl chloride (I) by reaction, over a steam bath, of the corresponding carboxylic acid with thionyl chloride in the presence of small amounts of sulfuryl chloride, the steam services to the laboratory were shut down. Since the reaction was already in progress, it was completed employing a Bunsen burner. After refluxing for 30 min in the presence of excess chlorinating reagent, the excess was removed by distillation. Toward the end of the distillation, the pot temperature rose to 160°, and a vigorous reaction ensued. Hydrogen chloride was evolved in large quantities, and the contents of the flask turned red and, upon cooling, formed a red glass. After two recrystallizations from glacial acetic acid, red-orange prismatic crystals melting at 253–255° were obtained. This phenomenon had never been encountered in our previous preparations of α-phenylcinnamoyl chloride using the same method

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(2) (a) Brookhaven National Laboratory; (b) Clarkson College of Technology; (c) Carnegie-Mellon University.

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