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Orbital Electronegativities in Molecules and Ionic Character in Molecular Complexes

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The orbital electronegativities in the nine aromatic hydrocarbons were estimated on the basis of the ionization potentials and the appearance potentials of the doubly-charged ions. Then, by applying the principle of electronegativity equalization to molecular complexes, the orbital electronegativities in typical electron acceptors were evaluated. The ionic character in single and crystal complexes were discussed in terms of the electronegativities of the component molecules. Consideration of neither the ionization potential of the donor molecule, the electron affinity of the acceptor molecule, nor the orbital electronegativities appeared to be enough to define the ionic character in a complex.

The formation of molecular complexes by aromatic compounds has been interpreted in terms of weak covalent interaction between the π-electrons of the donor and acceptor.[1] The donor is a molecule with a relatively low ionization potential and the acceptor is a molecule with a relatively high electron affinity. The transfer of a negative charge from the donor to the acceptor takes place by the interaction. As the orbital electronegativity, defined as the derivative of the energy with respect to the charge, has been known to be a measure of the power of atoms and groups to attract an electron,[2,3] the extension of this concept to molecules might be useful in systematizing the experimental data and in gaining an understanding of the ionic character in molecular complexes.

The molecular electronegativity introduced by Becker and Wentworth is constant for aromatic hydrocarbons, 4.07 ± 0.05 eV,[4] and so is apparently different from the quantities considered in this paper.

Orbital Electronegativities in Molecules

We assume that the form:

$$\varepsilon(\rho) = a\rho + b\rho^2 \qquad (1)$$

is a good approximation of the true equation for representing the energies of molecules in various states of ionization. ε represents the total energy of all the electrons in a molecule, taking the energy of the neutral molecule to be zero. ρ is the charge on the molecule at a particular state of ionization. The differentiation of Eq. (1) with respect to ρ gives the electronegativity:

$$\chi(\rho) = a + 2b\rho \qquad (2)$$

Specifically for the neutral molecule:

$$\chi(0) = a \qquad (3)$$

As the compounds under consideration are neutral, closed-shell entities, the ε *vs.* ρ curve has a discontinuity in the slope at $\rho=0$. The electronegativity evaluated with $\varepsilon(1)$ and $\varepsilon(2)$ is for the highest occupied orbital and is different from that evaluated with $\varepsilon^*(-1)$ and $\varepsilon^*(-2)$. The latter is the electronegativity of the lowest vacant orbital. (Hereafter the quantities involving the lowest vacant orbital are indicated by asterisks.) Becker and Wentworth have defined their molecular electronegativity by an average of the ionization potential, $\varepsilon(1)$, and the electron affinity, $-\varepsilon^*(-1)$. Thus, theirs is not the property of a single orbital but concerns both the highest occupied and the lowest vacant orbitals.

The ionic character in donor-acceptor complexes may be defined by the following equation, which is based on the principle of electronegativity equalization or on the concept of bond electronegativity:[3]

$$\rho = \frac{a_A^* - a_D}{2(b_D + b_A^*)} \qquad (4)$$

where the subscripts D and A refer to the donor and the acceptor respectively. This approximation may not be poor provided that the ionic character is low. Equation (4) corresponds to the condition for minimizing the energy of the complex by charge transfer:

1) G. Briegleb and J. Czekalla, *Angew. Chem.*, **72** 401 (1960).
2) R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).
3) J. Hinze, M. A. Whitehead and H. H. Jaffé, *ibid.*, **85**, 148 (1963).
4) R. S. Becker and W. E. Wentworth, *ibid.*, **85**, 2210 (1963).

$$\varepsilon_C(\rho) = a_D\rho + b_D\rho^2 - a_A^*\rho + b_A^*\rho^2 \quad (5)$$

By eliminating ρ from Eq. (5) using Eq. (4), we obtain the contribution of the charge transfer to the binding energy:

$$\varepsilon_C = -\frac{(a_A^* - a_D)^2}{4(b_D + b_A^*)} \quad (6)$$

Thus, the stabilization energy may be anticipated to be nearly proportional to the square of the difference in orbital electronegativity.

Once the parameters, a and b, for a typical donor (or acceptor) molecule are known, those in the acceptor (or donor) molecule may be estimated on the basis of the magnitude of the ionic character or the charge transfer, ρ, in the complex. Of course, the value of $\varepsilon^*(-1)$ for the acceptor (or $\varepsilon(1)$ for the donor) must be available, but generally it can be easily measured or estimated.

Aromatic Hydrocarbons. There are, at present, very few compounds for which both $\varepsilon(1)$ and $\varepsilon(2)$ or $\varepsilon^*(-1)$ and $\varepsilon^*(-2)$ are known. For several aromatic hydrocarbons the ionization potentials, $\varepsilon(1)$, and the appearance potentials of doubly-charged ions, $\varepsilon(2)$, have been measured by Wacks and Dibeler.[5,6] The electronegativities of the highest occupied orbitals can be evaluated by means of Eq. (1). The results are presented in Table 1 with the values of $\varepsilon(1)$ and $\varepsilon(2)$. The appearance potentials of doubly-charged ions have been reported to have an estimated probable error of ± 0.5 eV; therefore, the estimation of a_D and b_D cannot be very accurate. It must be noted that the electronegativity, a_D, is more variable than the ionization potential. Moreover, the changes in these two quantities are not quite parallel. The values of the b_D parameters are scattered in the range from 3 to 4 eV, and no correlation with the ionization potential is noted.

Table 1. Ionization potentials $\varepsilon(1)$, appearance potentials of doubly charged ions $\varepsilon(2)$ and electronegativities of the highest occupied orbitals in some aromatic hydrocarbons

Hydrocarbon	$\varepsilon(1)$ (eV)	$\varepsilon(2)$ (eV)	a_D (eV)	b_D (eV)
Benzene	9.38	26.4	5.56	3.82
Naphthalene	8.26	22.7	5.17	3.09
Anthracene	7.55	21.1	4.55	3.00
Phenanthrene	8.03	23.1	4.51	3.52
Pyrene	7.72	24.00	3.44	4.28
Tetracene	6.95	22.14	2.83	4.12
Tetraphene	7.53	22.03	4.04	3.49
Chrysene	8.01	23.35	4.35	3.67
Triphenylene	8.19	24.10	4.33	3.86

5) M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, **31**, 1557 (1959).

6) M. E. Wacks, *ibid.*, **41**, 1661 (1964).

Acceptors. Electron affinities have been estimated for a number of acceptors by Briegleb.[7] Recent measurements of the affinity of *p*-benzoquinone by the magnetron technique have suggested that Briegleb's value is too low, probably by 0.8 eV.[8] We assume that this difference can be used in estimating the acceptors now under consideration.

If the wave function of the ground state of a single 1 : 1 complex is approximated by:

$$a\psi_0(D, A) + b\psi_1(D^+\text{-}A^-) \quad (7)$$

where $\psi_0(D, A)$ is the wave function for a no-bond structure and $\psi_1(D^+\text{-}A^-)$ is that for a dative structure formed by the transfer of one electron from the donor (D) to the acceptor (A) molecule, while the ionic character is given by b^2. Briegleb *et al.* have measured the dipole moments of the three naphthalene complexes in solution and estimated the coefficients, a and b, in Eq. (7).[9] The parameters, a_A^* and b_A^*, may then be calculated using Eq. (4), with the values of $b^2(=\rho)$ and the electron affinities, $-\varepsilon_A^*(-1)$, estimated separately. The results are summarized in Table 2. Contrary to the case of the electron donors, the electronegativity, a_A^*, is relatively constant in these three acceptors. The change in the electron affinity arises mostly from the change in the b_A^* parameter.

Table 2. Electron affinities of acceptors $-\varepsilon_A^*(-1)$, ionic character ρ estimated for the naphthalene complexes and electronegativities of the lowest vacant orbitals of acceptors

Acceptor	$-\varepsilon_A^*(-1)$ (eV)	ρ	a_A^* (eV)	b_A^* (eV)
s-Trinitrobenzene	1.5	0.028	5.57	4.07
p-Chloranil	2.2	0.041	5.71	3.51
TCNE	2.6	0.063	5.99	3.39

Ionic Character in Donor-Acceptor Complexes

Single Complexes. With the parameters listed in Tables 1 and 2, the ionic character in the tetracyanoethylene (TCNE) complexes can be estimated by means of Eq. (4), they are presented in Table 3. The values for the complexes of large hydrocarbons seem to be too high. For example, Kuroda *et al.* have reported that the dipole moment of the pyrene

7) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

8) A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **62**, 3072 (1966).

9) G. Briegleb, "Elektron-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, Göttingen, Heidelberg (1961), p. 22.

complex is 2.0 debye.[10] By adopting Eq. (7), an ionic character about a half of the present estimation is obtained. This disagreement is rather serious. It has also been pointed out that Eq. (7) is too simple to represent the true wave function of the donor-acceptor complex.[10,11] The

TABLE 3. IONIC CHARACTERS AND STABILIZATION ENERGIES ESTIMATED FOR THE TETRACYANOETHYLENE COMPLEXES

Hydrocarbon	ρ by Eq. (4)	$-\varepsilon_C$ (eV) by Eq. (6)
Benzene	0.030	0.006
Naphthalene	(0.063)	0.026
Anthracene	0.113	0.081
Phenanthrene	0.107	0.079
Pyrene	0.166	0.212
Tetracene	0.210	0.332
Tetraphene	0.142	0.149
Chrysene	0.116	0.095
Triphenylene	0.114	0.095

significance of higher-energy charge-transfer configurations, including back charge-transfer configurations, has been emphasized. Therefore, the a_A^* and b_A^* parameters should be accepted only with some reservations. The disagreement in the pyrene complex may be regarded as an indication that the contributions from back charge-transfer configurations, D^--A^+, involving higher-energy orbitals, to the ground state of the pyrene complex are more appreciable than those to the ground state of the naphtalene complex. Table 3 includes the stabilization energies calculated by Eq. (6). These energies differ from the resonance energies given by the quantum mechanical treatment. Nevertheless, the calculated energies are mostly in the right order of magnitude, suggesting that the classical charge-transfer stabilization may be of some importance in the formation of molecular complexes.

Crystal Complexes. McConnell *et al.* have elaborated a Hartree-Fock molecular-field approximation to the energy of a 1 : 1 crystal complex and have proposed the following equation:[12]

$$E(\rho) = N(\varepsilon_0\rho - \varepsilon_1\rho^2) \tag{8}$$

Here $N\varepsilon_0$ is the energy required to charge the lattice so that there is a unit positive charge on each donor molecule and a unit negative charge on each acceptor molecule, while $-N\varepsilon_1\rho^2$ indicates the total attractive energy in the lattice. ε_0 is related to the ionization potential of the donor, $\varepsilon_D(1)$, and the electron affinity of the acceptor, $-\varepsilon_A^*(-1)$, by:

$$\varepsilon_0 = \frac{1}{2}[\varepsilon_D(1) + \varepsilon_A^*(-1)] \tag{9}$$

Assuming that ρ has to be in the range of 0 to 1, the energy is found by Eq. (8) to be at its minimum at $\rho=0$ when $\varepsilon_1<\varepsilon_0$ and at $\rho=1$ when $\varepsilon_1>\varepsilon_0$. Accordingly, they have concluded that 1 : 1 crystal complexes must divide quite sharply into two classes, namely, $\rho=0$ and 1.

Using the present approach, however, we reach conclusions very different from these. Within the framework of the electronegativity equalization, the energy of a crystal complex consisting of $N/2$ molecules of the donor and $N/2$ molecules of the acceptor is simply Eq. (5) multiplied by $N/2$, namely:

$$E(\rho) = \frac{N}{2}[(a_D - a_A^*)\rho + (b_D + b_A^*)\rho^2] \tag{10}$$

As $(a_D - a_A^*)$ is small in the complexes to which this approximation is good, the second term dominates in this equation. Therefore, the general features of the E *vs.* ρ curve given by Eq. (10) bear no resemblance to those suggested by McConnell *et al.* In Fig. 1 the energy of the naphthalene-TCNE complex is plotted against the charge using the parameters listed in Tables 1 and 2. The curve given by Eq. (8) is also illustrated for the sake of comparison.

If the ionic character in a crystal complex is high, the electrostatic ion-ion interaction becomes of major importance, just like the energy required to charge the lattice. Then:

$$E(\rho) = \frac{N}{2}[(a_D - a_A^*)\rho + (b_D + b_A^*)\rho^2 - 2\varepsilon_i\rho^2] \tag{11}$$

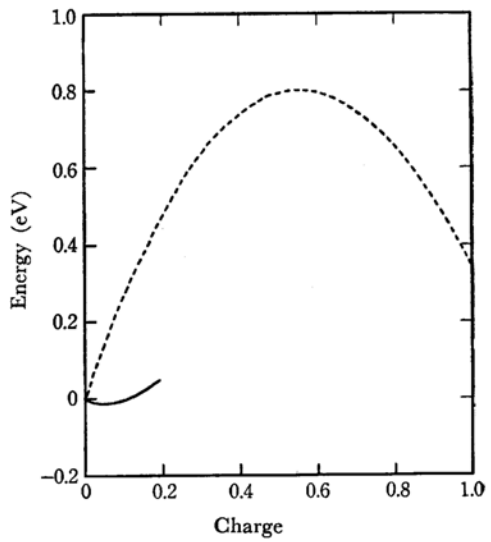

Fig. 1. Energy *vs.* charge as given by Eq. (10) (——) and by Eq. (8) (- - -) for naphthalene-TCNE complex.

10) H. Kuroda, T. Amano, I. Ikemoto and H. Akamatu, *J. Am. Chem. Soc.*, **89**, 6056 (1967).
11) R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1963).
12) H. M. McConnell, B. M. Hoffman and R. M. Metzger, *Proc. Natl. Acad. Sci.*, **53**, 46 (1965).

where the ε_i has the same meaning as the ε_1 in Eq. (8). The amount of charge transfer in equilibrium is given by:

$$\rho = \frac{a_A^* - a_D}{2(b_D + b_A^* - 2\varepsilon_i)} \tag{12}$$

The condition $\varepsilon_i > [\varepsilon_D(1) + \varepsilon_A^*(-1)]/2$ leads to $\rho > 1/2$. As ε_i seems to be of the order of the magnitude of 2 eV,[13] among the donors and acceptors in Tables 1 and 2 the $\rho > 1/2$ condition is likely to be fulfilled when tetracene is combined with TCNE. Figure 2 presents the E *vs.* ρ curves given by Eqs. (8) and (11) with the parameters for this combination and with $\varepsilon_i = 2.5$ eV. If we employ Eq. (8), the assumption that $0 \leqq \rho \leqq 1$ is important. However, this does not seem very reasonable because each orbital may accommodate two electrons. It must be added that the presence of this particular complex is unlikely because of the chemical reaction between component compounds. Furthermore, as has been discussed in the preceding section, the ionic character defined by the parameters in Tables 1 and 2 may be too large and the $\rho > 1/2$ condition is not necessarily attained by the whole complex even if this complex could be prepared. Nevertheless, it should be emphasized that the presence of a number of crystal complexes in which $\varepsilon_i > [\varepsilon_D(1) + \varepsilon_A^*(-1)]/2$ is fulfilled has been indicated by the electronic and vibrational spectra.[14,15] The curves in Fig. 2 may be considered to present the general features of the ionic character in such complexes.

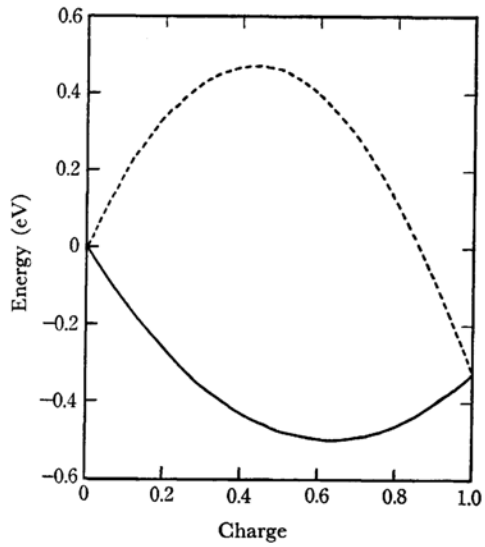

Fig. 2. Energy *vs.* charge as given by Eq. (11) (——) and by Eq. (8) (- - -) for tetracene-TCNE complex.

In conclusion, we wish to remark that consideration of neither the ionization potential of a donor, the electron affinity of an acceptor, nor the electronegativities represented by the a_D and a_A^* parameters is enough to define the ionic character in a complex. Let us therefore suppose the presence of some donors which have the same ionization potential as tetracene but which have a_D and b_D parameters different from those of the hydrocarbon, say, $a_D = 3.50$ and $b_D = 3.45$, and $a_D = 4.00$ and $b_D = 2.95$, respectively. Such donors may be considered to be more electronegative than tetracene; however, the ionic character in the TCNE complexes indicated by Eq. (12) may be anticipated to be higher than that in the tetracene complex, namely, 0.677 and 0.743 compared to 0.630.

13) Y. Matsunaga, This Bulletin, in press.

14) R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

15) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).