All-Valence-Electron Calculations on Molecular π Complexes

Sir:

This preliminary paper outlines the results of several calculations on aromatic hydrocarbon–tetracyanoethylene (TCNE) molecular complexes in which we employ a perturbational molecular orbital approach, and in which we consider all valence electrons. We have studied in detail two aspects of the intermolecular association: the relative orientations of the donor and acceptor molecules, and the relative magnitudes of π-electronic and σ-electronic interactions. The results have implications concerning the nature of molecular complexes.

The theoretical model is similar to that described in our earlier papers where we discussed reactivity in the Diels–Alder reaction,[1] and the theoretical approach is similar to that described in several other papers.[2–12] Molecular orbitals for the two interacting molecules are obtained by separate calculations. A molecular geometry is chosen for the interacting state, and the energy difference between separated molecules and interacting molecules is calculated to second order by perturbation theory. Since we wished to consider the interactions of the σ orbitals of donor and acceptor molecules, we used the all-valence-electron SCF procedure of Pople and Segal[13] (CNDO/2) to obtain wave functions. For the perturbed state the two molecules were assigned to parallel planes; the arbitrarily chosen interplanar distance was 3.20 Å. The energy difference between separated and interacting molecules was calculated from eq 1; this equation is a well-known result of the application of perturbation theory to this type of problem.[1,9–12] The two interacting molecules M and N have eigenvectors $a_{m,i}$ and

$$\Delta E = 2\left[\sum_{m}^{\text{occ}}\sum_{n}^{\text{vac}} - \sum_{m}^{\text{vac}}\sum_{n}^{\text{occ}}\right]\left[\sum_{ij} a_{m,i}b_{n,j}P_{mi,nj}\right]^2 \Big/ (E_m - E_n) \qquad (1)$$

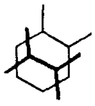
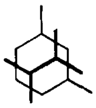
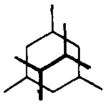
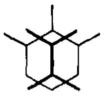
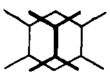
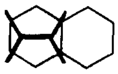
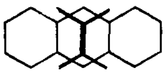
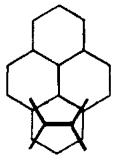
$b_{n,j}$, respectively. The sum subscripted ij is over pairs of atoms i and j through which M interacts with N. $P_{mi,nj}$ is the interaction integral and was calculated from the Wolfsberg–Helmholz approximate formula[14] (eq 2), where α's are valence-state ionization potentials and S is the Slater overlap integral. This procedure is quite empirical, being tantamount to an

$$P_{mi,nj} = (\alpha_{mi} + \alpha_{nj})S_{mi,nj} \qquad (2)$$

assumption of a one-electron undefined perturbation Hamiltonian. With these assumptions and those inherent in the CNDO/2 method, there was no necessity to introduce arbitrary scaling factors to obtain good agreement of calculated and experimental results.

The computer program (IBM 7040) which carries out the perturbation energy calculation rotates or translates the TCNE moiety with respect to the hydrocarbon molecule, and so we were able to obtain the most stable orientation at the chosen interplanar distance. The calculated perturbation energies, some experimentally determined heats of formation, and the most stable geometries are given in Table I for a few selected complexes.

Table I. Aromatic Hydrocarbon–TCNE Complexes. Perturbation Energies and Heats of Formation (kcal/mole)

 3.54 (3.35)[a]	 7.90 (8.0)[b]	 5.30	 7.57 (7.4)[b]
 7.71 (9.2)[b]	 7.71	 9.88 (10.1)[b]	
 4.15 (4.06)[a]	 4.87	 4.47 (4.1)[c]	

[a] CCl$_4$ solution: G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem.* (Frankfurt), **30**, 334 (1961). [b] Gas phase; M. Kroll, *J. Am. Chem. Soc.*, **90**, 1097 (1968). [c] CCl$_4$ solution: H. Kuroda, T. Amano, I. Ikemoto, and H. Akamatu, *ibid.*, **89**, 6056 (1967).

There are several interesting aspects of our results which are not tabulated, and we will briefly state three of the important points.

1. π–π interactions are calculated to be only a small fraction of the total stabilization energy. The π–π contribution for benzene–TCNE is only 1.8% of the total perturbation energy, for pyrene–TCNE 1.6%, and for durene–TCNE 1.2%. In the methylated compounds, interactions involving the 1s orbitals of hydrogen atoms contribute on the order of 60% to the perturbation energy.

2. Essentially free rotation of the two molecular partners is indicated by the calculations. In general, the barrier to rotation of the TCNE molecule with respect to the aromatic partner is found to be small: 0.06 kcal/mole in benzene–TCNE, 0.27 kcal/mole in pyrene–TCNE, and 5.68 kcal/mole in durene–TCNE. Also, the barrier is 6-fold in benzene–TCNE rather than 12-fold.

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3. The idea of isomeric donor–acceptor complexes[15] is supported by our results. Two energy minima are found in the energy surface for pyrene–TCNE, where the TCNE is situated over the center of each one of the two different kinds of rings, respectively. Isomeric complexes are also calculated for anthracene, naphthalene, durene, and *o*-xylene.

Space limitations allow only a short discussion of the first point. In theoretical discussions regarding the interactions between small unsaturated hydrocarbons, Coulson and Davies,[2] and Haugh and Hirschfelder[3] concluded that σ interactions outweigh π interactions. Several authors have implied that the σ electrons may be important in accounting for the stability of so-called π complexes.[16–21] A deficiency in perturbation theory has been invoked to account for the quantitative failure of the π-interaction theory.[7,20,22] The precise relative sizes of the π and σ interactions in molecular complexes are still a moot point. We know that the CNDO/2 method mixes σ and π levels,[23] and in our CNDO/2 calculations several highly energetic filled σ levels are found. However, it should be noted that the larger perturbation energy terms in our calculated results did not arise from near degeneracies of the interacting orbitals. We conclude that the role of the π-electron interactions in determining the stability of a molecular complex has certainly been overestimated in the past.

We will report the details of this work in a full paper. We are also carrying out calculations of a less empirical nature which we hope to present in the near future.

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Metastable Ion Characteristics. VIII. Characterization of Ion Decomposition Mechanisms by Metastable Ion Abundances

Sir:

From a submicrogram sample, the mass spectrometer can provide elemental composition data on a large number of ions produced by unimolecular decomposition of the sample molecules. Many of these ions retain the original arrangement of atoms in the molecule; in fact, Lederberg has proposed computer techniques for the complete elucidation of the structure of any acyclic compound using the *nonrearrangement* product ions of its mass spectrum.[1] Mechanistic studies[2,3] have made it possible to recognize many reactions involving rearrangements, but there is an obvious need for a general test to identify nonrearranged ions in the mass spectrum.[4]

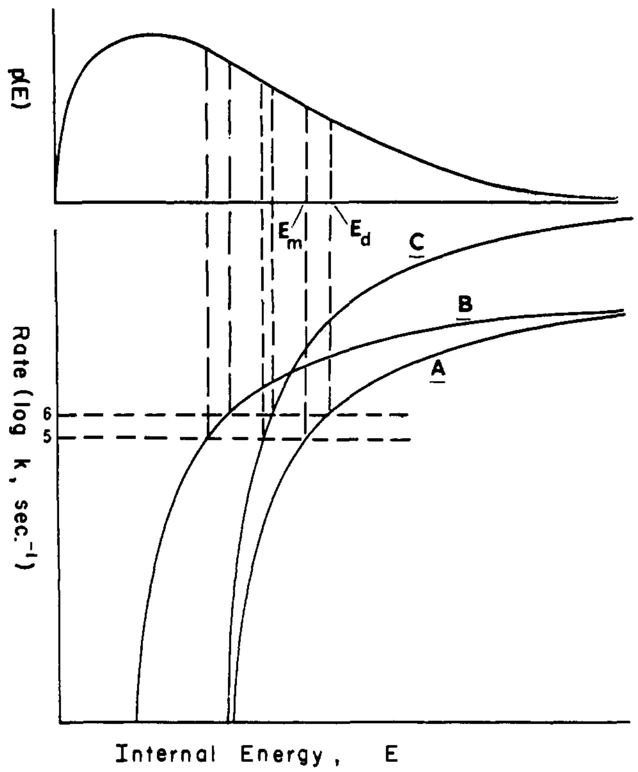

Figure 1. Lower curves: relation of the internal energy of the precursor ions to the corresponding rates of the hypothetical unimolecular reactions A, B, and C; upper curve: proportion of the precursor ions with a particular internal energy content *vs.* energy.

Chupka[5] has pointed out that reactions exhibiting low "frequency factors,"[6] a characteristic of rearrangement reactions, should show abundant metastable ions; surprisingly there apparently has been no attempt to date to utilize Chupka's conclusions in the interpretation of mass spectra.[2,3,8,9]

Referring to Figure 1, curve A describes the effect of the internal energy of the precursor ion (p) on its rate of decomposition. If instrument parameters are such

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