

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1967, by the American Chemical Society

VOLUME 89, NUMBER 22

OCTOBER 25, 1967

## Physical and Inorganic Chemistry

### Molecular Calculations and Complexes. Self-Consistent Molecular Orbital Approach to the First and Second Charge-Transfer Transitions of Tetracyanoethylene-Aromatic Hydrocarbon Interactions<sup>1a</sup>

Arthur R. Lepley<sup>1b</sup> and Clifton C. Thompson, Jr.<sup>1c</sup>

Contribution from the Department of Chemistry, Marshall University, Huntington, West Virginia. Received April 13, 1967

**Abstract:** From molecular orbital calculations of varying degrees of sophistication the highest and penultimate occupied orbital energies for a series of aromatic hydrocarbons are compared with the first and second charge-transfer transitions of molecular complexes formed by these electron donors with tetracyanoethylene. Hückel molecular orbital (HMO) calculations, with and without overlap, and self-consistent molecular orbital (SCMO) calculations of the Pariser, Parr, and Pople type have been carried out with and without modifications for electron correlation and allowance for variable bond lengths. Effects of solvent and state changes on spectral shifts are small, whereas very significant differences in relative molecular energy levels are obtained with the various methods of calculation. While either the first or second charge-transfer bands can be treated separately with limited success by the different HMO modifications, all transitions give a high degree of correlation with the SCMO methods.

Molecular orbital interpretations of charge-transfer spectra,<sup>2-5</sup> for the molecular complexes formed between  $\pi$ -electron systems, have appreciably extended early theories of such spectral transitions. Mulliken's<sup>6</sup> charge-transfer treatment was readily simplified in resonance notations and applied to iodine<sup>7</sup> and chloranil<sup>8</sup> complexes *via* a linear relationship between donor ionization potential,  $IP_D$ , and acceptor electron affinity,  $EA_A$

(1) (a) Presented in part before the Division of Physical Chemistry, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract R156. (b) Department of Chemistry, Marshall University. (c) Department of Chemistry and Physics, Middle Tennessee State University, Murfreesboro, Tenn.

(2) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

(3) M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962).

(4) A. R. Lepley, *ibid.*, **84**, 3577 (1962).

(5) M. J. S. Dewar and C. C. Thompson, Jr., *Tetrahedron Suppl.*, No. 7, 97 (1966).

(6) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952).

(7) H. McConnel, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(8) N. Smith, Doctoral Dissertation, University of Chicago, 1954.

$$\Delta E_{ct} = IP_D - EA_A + C \quad (1)$$

where  $\Delta E_{ct}$  is the energy of the charge-transfer transition,  $C$  is a collective constant for solvation, A-D polarization and nonbonding contributions. Most recently direct calculations on the whole complex have been attempted.<sup>9,10</sup>

A simple perturbation treatment of the molecular orbital form which considers only ground-state interaction<sup>2-5</sup> replaces eq 1 with

$$\Delta E_{ct} = B_j - (\alpha + x_i\beta) \quad (2)$$

where  $B_j$  is the lowest unoccupied acceptor orbital,  $\alpha$  and  $\beta$  are, respectively, the Coulomb and resonance integrals for  $sp^2$ -hybridized carbon, and  $x_i$  is the donor highest occupied orbital energy level coefficient. The  $x_i$  from Hückel molecular orbital, HMO, approxima-

(9) R. L. Flurry, Jr., *J. Phys. Chem.*, **69**, 1927 (1965); and private communications.

(10) S. Iwata, J. Tanaka, and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

Table I. Observed Charge-Transfer Bands and Calculated Donor Orbital Energies of Molecular Complexes with Tetracyanoethylene

No.	Compound	Band	$\lambda$ , m $\mu$	$\Delta E_{ct}$ , ev	Calculated orbital energies					
					HMO <sup>a</sup>	HMOO <sup>b</sup>	PPP1 <sup>c</sup>	SPO1 <sup>c</sup>	PPP2 <sup>c</sup>	SPO2 <sup>c</sup>
1	Benzene	1	383-390 <sup>d-g</sup>	3.237-3.178	1.000	0.800	0.000	0.000	0.000	0.000
2	Acenaphthylene	1	502-515 <sup>d,e</sup>	2.470-2.407	0.637	0.549	0.920	0.784	0.672	0.598
3	Azulene	1	735-740 <sup>d,e</sup>	1.686-1.674	0.477	0.426	1.562	1.511	1.518	1.467
4	3,4-Benzopyrene	1	820-825 <sup>d,e</sup>	1.511-1.502	0.371	0.340	1.835	1.725	1.609	1.402
5	Perylene	1	894-920 <sup>d,e,g,h</sup>	1.387-1.347	0.347	0.319	1.862	1.749	1.641	1.426
6	Picene	1	590-595 <sup>d,e</sup>	2.101-2.083	0.501	0.445	1.403	1.306	1.202	1.012
7	<i>m</i> -Terphenyl	1	500-510 <sup>e,f</sup>	2.480-2.432	0.662	0.568	0.914	0.861	0.836	0.769
8	Triphenylene	1	555-570 <sup>d,e,g</sup>	2.253-2.176	0.684	0.584	0.952	0.918	0.888	0.828
9	Anthracene	1	740 <sup>g</sup>	1.674	0.414	0.375	0.576	1.490	1.387	1.204
		2	465 <sup>g</sup>	2.667	1.000	0.800	0.314	0.386	0.407	0.459
10	1,2-Benzanthracene	1	699-700 <sup>d,g</sup>	1.773-1.771	0.452	0.406	1.494	1.405	1.315	1.151
		2	541-555 <sup>g</sup>	2.291-2.234	0.715	0.607	0.828	0.802	0.768	0.713
11	Biphenyl	1	500-505 <sup>e-g</sup>	2.480-2.453	0.704	0.599	0.682	0.628	0.721	0.659
		2	389-393 <sup>e,g</sup>	3.185-3.156	1.000	0.800	0.020	0.019	0.016	0.015
12	Chrysene	1	629-630 <sup>d,e,g</sup>	1.970-1.968	0.520	0.460	1.347	1.266	1.170	1.003
		2	532-545 <sup>e,g</sup>	2.332-2.275	0.792	0.661	0.742	0.752	0.738	0.707
13	Naphthalene	1	550-561 <sup>d-i</sup>	2.254-2.210	0.618	0.535	0.980	0.908	0.826	0.672
		2	427-432 <sup>e-i</sup>	2.902-2.870	1.000	0.800	0.201	0.248	0.262	0.291
14	Phenanthrene	1	540 <sup>d,e,h</sup>	2.295	0.605	0.526	1.076	1.000	0.923	0.783
		2	527-530 <sup>g,h</sup>	2.352-2.338	0.769	0.645	0.702	0.696	0.678	0.644
15	Pyrene	1	715-730 <sup>d-h</sup>	1.734-1.697	0.445	0.400	1.603	1.503	1.404	1.236
		2	488-500 <sup>e-h</sup>	2.540-2.480	0.879	0.721	0.584	0.632	0.634	0.657
16	<i>p</i> -Terphenyl	1	564-568 <sup>e,f</sup>	2.198-2.182	0.593	0.516	1.110	1.044	1.014	0.930
		2	386 <sup>e</sup>	3.213	1.000	0.800	0.056	0.064	0.058	0.054

<sup>a</sup> Hückel method, orbital coefficients in  $\beta$  units from: C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Mathematical Institute, Oxford, England, and the Centre de Chimie Theorique de France, Paris, France, 1955; C. A. Coulson and A. Streitwieser, Jr., "Dictionary of  $\pi$ -Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965. <sup>b</sup> Hückel method with overlap, orbital energies in  $\gamma$  units calculated from eq 7; cf. ref 25 and footnote a. <sup>c</sup> Pariser-Parr-Pople and split-p-orbital methods, orbital energies in ev, calculated using the general methods described in ref 15, 19, and 20. <sup>d</sup> Reference 3. <sup>e</sup> Reference 5. <sup>f</sup> R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). <sup>g</sup> G. Briegleb, J. Czekalla, and G. Reuss, *Z. Physik. Chem. (Frankfurt)*, **30**, 316 (1961). <sup>h</sup> H. Kuroda, M. Kobayesh, and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962). <sup>i</sup> A. R. Lepley, *J. Am. Chem. Soc.*, **86**, 2545 (1964).

tions gave a linear correlation comparable to that obtained with eq 1.<sup>7,8,11</sup> Briegleb<sup>12</sup> has suggested that the inclusion of overlap in the ground-state HMO evaluation of donors might significantly improve the correlation of calculated and observed charge-transfer energies in eq 2.

Removal of some of the additional assumptions and restrictions of the HMO method in this application might be achieved by the use of self-consistent molecular orbital calculations of the type described by Pariser and Parr<sup>13</sup> and Pople<sup>14</sup> together with modifications for electron correlation.<sup>15</sup> Any improvement in the relationship between calculated energy levels and measured values should include both the first and higher charge-transfer transitions. Since no quantitative correlation of the second charge-transfer bands has been found, we have considered the inclusion of both first and higher energy charge-transfer bands and their relationship to orbital energies from HMO and self-consistent molecular orbital calculations.

## Methods of Calculation

**Hückel Molecular Orbital (HMO) and HMO with Overlap (HMOO).** The standard methods<sup>16</sup> for these approximations have been employed. In the HMOO

(11) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(12) G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964).

(13) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(14) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(15) A. L. H. Chung, M. J. S. Dewar, and N. L. Sabelli, "Molecular Orbitals in Chemistry, Physics and Biology," Academic Press Inc., New York, N. Y., 1964, pp 395-404.

(16) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

method the usual value of the overlap integral,  $S = 0.25$ , is assumed to apply to nearest neighbor terms.

**Pariser-Parr-Pople (PPP1) Method.** The standard<sup>13,14</sup> semiempirical SCF approach has been used to calculate donor orbital energies. In the current work, the two-center electron repulsion integrals ( $ii$ ,  $jj$ ) were evaluated in the computer program from molecular geometries by the uniformly charged sphere approximation, the one-center repulsion integrals ( $ii$ ,  $ii$ ) were estimated by previously described empirical methods,<sup>13,17</sup> and the one-electron resonance integrals,  $\beta_{ij}$ , were estimated by the method of Dewar and Schmeising.<sup>18</sup>

**Split p-Orbital (SPO1) Method.** The SPO modification of the SCF treatment has been introduced in an effort to allow for vertical electron correlation. It has been pointed out,<sup>15</sup> however, that the original SPO method results in an "over correction" for electron correlation. Therefore, we have used an approximation which is two-thirds normal PPP and one-third extreme SPO. Complete details of the computational procedure and input parameters have been described elsewhere.<sup>19</sup>

**Variations in Bond Length.** It is well known that bond lengths in aromatic hydrocarbons generally differ somewhat from the "aromatic" C-C bond length (1.397 Å). Because of the linear relationship between bond length and bond order,<sup>20</sup> it is a simple matter to make both the PPP and SPO treatments self-consistent with respect to variations in the distances between bonded carbon atoms. During each iteration of the

(17) R. G. Parr and L. C. Snyder, *J. Chem. Phys.*, **34**, 1661 (1961).

(18) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

(19) M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

(20) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 685 (1965).

SCF calculations bond orders,  $p_{ij}$ , are recalculated. On the basis of the new values of  $p_{ij}$  we computed corresponding bond lengths,  $r_{ij}$ , for adjacent atoms and subsequently the appropriate resonance and repulsion integrals using the new bond lengths. In the following discussion the variable bond-length modifications as applied to the Pariser-Parr-Pople and SPO methods are referred to as the PPP2 and SPO2 treatments, respectively.

## Results and Discussion

Polycyclic aromatic hydrocarbons, both alternant and nonalternant, comprise the largest single group of donors on which molecular orbital calculations can be carried out without corrections for hybridization, variation in effective nuclear charge, or significant changes in the initial homonuclear bond lengths. Similarly tetracyanoethylene (TCNE) is the most practical acceptor for multiple transitions, since the majority of the literature reports of second or higher charge-transfer bands have been with this reagent.

Table I gives the range of wavelengths which have been reported for the maxima,  $\lambda_{\max}$ , of lowest and higher energy charge-transfer bands in a series of aromatic hydrocarbon donors with TCNE. In order to obtain a broad range of wavelengths, it was necessary to include data on all reported complexes. Thus the range includes measurements made in carbon tetrachloride, chloroform, methylene chloride, and in the solid state. We have tried to avoid selectivity in establishing the wavelength range; all reported values are included except in those limited cases where assignments were obviously not the same in the literature. In the latter case, we have used the range most frequently reported.

The molecular energy levels of each donor which correspond to the lowest and higher energy charge-transfer bands have been listed in Table I for the six molecular orbital treatments.

Correlation of the energy,  $\Delta E_{ct}$ , for the series of charge-transfer transitions and the simple HMO energy level coefficients is given in Figure 1. It is immediately apparent that the higher energy charge-transfer transitions appreciably increase the scatter over that considering only the highest occupied orbitals. Least-squares determination of the values for eq 2 gave  $\beta = -2.52$  eV and  $B_j - \alpha = -0.23$  as compared to  $-3.06$  and  $-0.34$ , respectively, from extensive studies of the first band alone.<sup>3</sup> The correlation is still evident with second-band inclusion, but a great deal of scatter and a certain nonlinearity are obvious from Figure 1. The nonlinearity may be due either to the lack of consideration of nonbonding states in eq 2 as previously suggested<sup>6,11,21</sup> for the resonance treatment or to the over-simplification imposed by the HMO method. In the latter regard, it should be noted that disparities have been observed in other applications of the HMO theory when several energy levels are involved.<sup>13</sup>

The curvature in Figure 1 may be accounted for by adding nonbonding terms to eq 1<sup>11</sup>

$$\Delta E_{ct} = IP - EA + C' + \frac{C_2}{IP - EA + C'} \quad (3)$$

where  $C_2$  is a new constant from the sum of the squares

(21) For a discussion of this point, see R. S. Mulliken and W. G. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

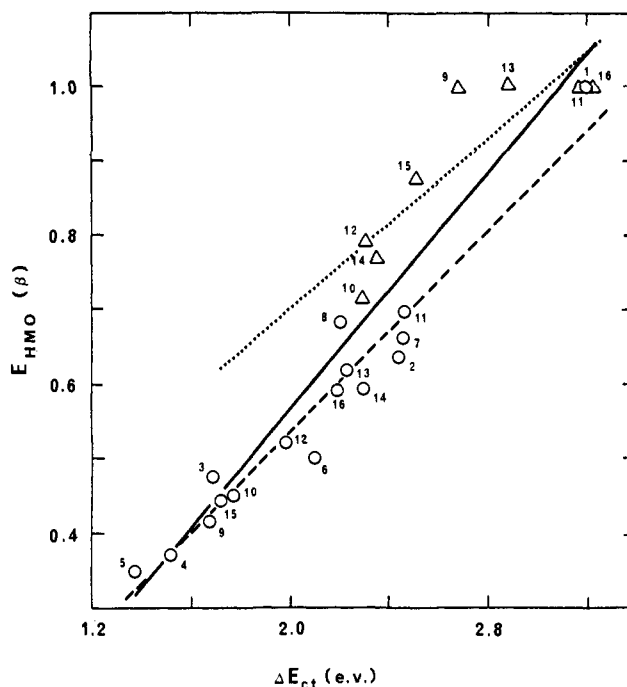


Figure 1. Correlation of the highest and penultimate occupied HMO coefficients in  $\beta$  units with the respective charge-transfer energies of the first (O) and second ( $\Delta$ ) band maxima in eV for the TCNE molecular complexes with aromatic hydrocarbons. Least-squares lines are given for the first (dashed), second (dotted), and both first and second (solid) charge-transfer bands with the calculated orbital energies. Compound numbering follows that given in Table I.

of the resonance integrals perturbed in a weak complex. Since more than one donor level participates in the complex, interaction as indicated by the multiple  $\Delta E_{ct}$  values,  $C'$  evidently is somewhat more complicated than normally assumed. Conversion of eq 3 to terms of molecular orbital energy levels gives

$$\Delta E_{ct} = B_j - \alpha - x_i\beta + \frac{C_2}{B_j - \alpha - x_i\beta} \quad (4)$$

where  $B_j$  as usual contains all other indeterminate energy terms. If only a single acceptor is considered,  $B_j - \alpha$  is a constant  $C_1'$  and the simplification, eq 5, is<sup>22</sup>

$$\Delta E_{ct} = C_1' - x_i\beta + \frac{C_2}{C_1' - x_i\beta} \quad (5)$$

A similar consideration of the excited state is obtained directly from eq 2 by an approximate term  $\gamma_i$ <sup>23</sup>

$$\gamma_i = x_i - \left( \frac{n-1}{n} \right) \omega \quad (6)$$

where  $n$  is the number of  $\pi$  electrons in the donor molecule and  $\omega = 1.4$ .<sup>13</sup> The excited state is included in eq 6 through the charge-density ratio in which one electron has been removed.<sup>24</sup>

(22)  $C_1'$  is directly converted into the  $C_1$  of ref 11 by  $C_1' = -C_1 - \alpha + k$ , where  $k$  is a scaling factor from the relationship between HMO coefficients and ionization potentials.

(23) S. E. Ehrenson, *J. Phys. Chem.*, **66**, 706 (1962).

(24) Application of this equation to the ratio of HMO coefficients used in "improved" parent molecule excitation spectra relationship shows that

$$\delta_i/(\delta_j - \delta_i) = 0.5 - 0.125x_i$$

This direct relationship to  $x_i$  makes inherent the basic criticism to the HMO values themselves; cf. ref 12, eq 17.

**Table II.** Hückel and Self-Consistent Molecular Orbital Method Correlation Values for the First and Second Charge-Transfer Transitions of TCNE-Aromatic Hydrocarbon Complexes

Method of calcn	Eq	Transition								
		Slope	First $B_j^a$	$R^b$	Slope	Second $B_j^a$	$R^b$	Slope	Both $B_j^a$	$R^b$
HMO	2	2.93	-0.145	0.972	3.56	0.144	0.874	2.52	-0.231	0.944
HMOO	2 <sup>c</sup>	3.92	-0.040	0.975	5.29	0.225	0.872	3.45	-0.089	0.946
PPP1	8	-1.02	3.33	0.981	-0.834	2.66	0.979	-1.08	3.40	0.977
SPO1	8	-0.91	2.96	0.985	-0.799	2.58	0.992	-1.00	3.19	0.985
PPP2	8	-0.98	3.16	0.985	-0.820	2.64	0.989	-0.94	2.99	0.987
SPO2	8	-0.80	2.61	0.973	-0.756	2.46	0.987	-0.81	2.62	0.983

<sup>a</sup> Intercept of the form  $B_j - \alpha$  in  $\beta$  units for eq 2, and  $B_j$  in eV for eq 8. <sup>b</sup> Correlation coefficient. <sup>c</sup> Where  $\delta_i\gamma$  replaces  $x_i\beta$ .

A second method of accounting for the observed curvature in Figure 1 is to "improve" the calculations by inclusion of overlap. Wheland's relationship<sup>25</sup> between the HMO energy levels and those with overlap allows direct evaluation of the new coefficient  $\delta_i$

$$\delta_i = x_i / (1 + Sx_i) \quad (7)$$

where  $S$  is the overlap integral previously given for the HMOO method.

Equations 5-7 have a fundamental point in common; that is, they are all related by a simple mathematical transformation to  $x_i$ . Thus the curvature may change, and any or all of these equations could be legitimately employed; however, the spread in points will not be

method and shows a scatter of points similar to that in Figure 1. In both HMO and HMOO cases the least-squares fit for only the second charge-transfer transitions is appreciably poorer than the over-all results. The latter is strongly influenced by the rather good fit previously reported<sup>2-5</sup> for the first transition. Thus the second band correlation coefficient with  $x_i$  is slightly but not significantly better than that for  $\delta_i$ .

Combinations of any or all of the variants in eq 5-7 give basically the same conclusion with some minor gains and losses in the goodness of fit for both curvature and scatter. In order to achieve a significant improvement of the correlation it was necessary to consider more rigorous methods for calculation of the energy levels. A series of self-consistent molecular orbital methods as described in the preceding section has been used for this purpose. The highest occupied and penultimate orbital energies (Table I) from the four advanced methods used differ from the HMO and HMOO coefficients in two ways. First, the results are obtained directly in energy units (electron volts), rather than in terms of  $\beta$ . Secondly, the energy levels have been scaled by subtracting the calculated energy of the highest occupied orbital of benzene from each value, *i.e.*, PPP1, 0.5926; PPP2, 0.5803; SPO1, 0.4739; SPO2, 0.4612. A modification of eq 2 is necessary for the application of these values, *i.e.*

$$\Delta E_{ct} = B_j - A_i \quad (8)$$

where  $B_j$  and  $A_i$  are the energies of the unoccupied acceptor orbital and the occupied donor orbital, respectively, involved in the transition. Equation 8 is fundamentally comparable with the general equation for molecular excitation

$$\Delta E_{ij} = m_j - m_i$$

where the  $m$  terms are energy levels for occupied,  $i$ , and unoccupied orbitals,  $j$ , in a single molecule.

Where the common acceptor TCNE is used,  $B_j$  is a constant. Application of eq 8 indicates that a plot of the experimental charge-transfer transitions *vs.* respective calculated donor orbital energies  $A_1$  and  $A_2$  should give a linear relationship with a slope of unity and an intercept at  $B_j$ . A considerable improvement in goodness of fit is evident from Figure 2 in which transition energies are plotted *vs.* donor orbital energies calculated by the PPP1 method. Linear least-squares results from the various methods are given in Table II for comparison with the requirements of eq 8. The relative slopes for first, second, and over-all least-squares fits in the figures come closer to one another using the self-consistent molecular orbital methods; for use in visual compari-

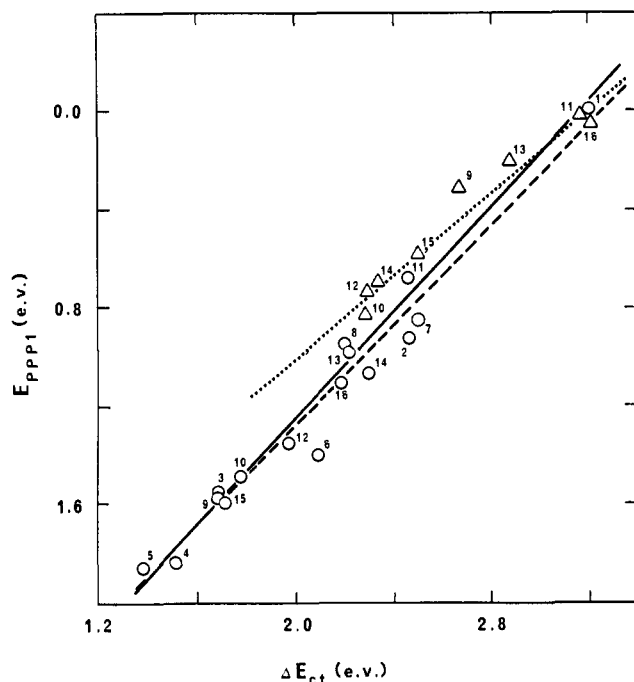


Figure 2. Correlation of the PPP1 energies in eV for the donor highest occupied and penultimate orbitals with the charge-transfer energies of the first (O) and second ( $\Delta$ ) band maxima in eV for the TCNE molecular complexes with aromatic hydrocarbons. Least-squares lines are given for the first (dashed), second (dotted), and both (solid) charge-transfer bands with the calculated respective orbital energies. Compound numbering follows that given in Table I.

affected. This is exemplified by the fact that the degree of correlation for all bands (Table II) with the inclusion of overlap is comparable with that for the simple HMO

(25) G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941).

sons, Figures 1 and 2 are scaled comparably for the calculated values.

In addition to the factors discussed thus far, at least three other considerations could influence the correlation of theoretical energies and experimental charge-transfer spectra for molecular complexes. These are (1) errors in the assignment of wavelengths for correlation, (2) the influence of changes in solvent on the position of the charge-transfer band, and (3) the perturbation of donor orbital energies on complexation with TCNE. While it is impossible to adequately correct for these factors from the limited information in the literature, a reasonable estimate of their combined effects would indicate a probable correction of not more than 0.1 eV. Obviously variations of this magnitude are relatively unimportant in view of the deviations shown in correlations between theoretical and experimental charge-transfer transition energies.

Thus the method of molecular calculation seems to have a major influence on whether or not correlation is

obtained. Correlation of the second charge-transfer bands for the TCNE complexes is poor with the Hückel molecular orbital method regardless of the inclusion of overlap in calculations or nonbonding terms in perturbation relationships. The use of highest occupied and penultimate orbital energies from self-consistent molecular orbital methods gives a reasonably good correlation with either first or second charge-transfer transitions.

Although a direct relationship considering only the energy of the donor orbital participating in the transition has been considered here, the variants discussed demonstrate the general means of applying this approach to other charge-transfer treatments.

**Acknowledgment.** The authors are indebted to Professors M. J. S. Dewar and G. J. Gleicher for the computer programs used in self-consistent molecular orbital calculations, and to the computer centers of the University of Texas and West Virginia University for CDC 1604 and IBM 7040 facilities, respectively.

## The Molecular Structure of Perfluorodiazirine

J. L. Hencher and S. H. Bauer

*Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received April 3, 1967*

**Abstract:** The cyclic structure of  $F_2CN_2$  has been confirmed by an electron diffraction experiment on the vapor. Perfluorodiazirine has  $C_{2v}$  symmetry (planes of  $CF_2$  and  $CN_2$  are mutually perpendicular) with  $C-F = 1.315 \pm 0.004$  Å,  $C-N = 1.426 \pm 0.004$  Å,  $N=N = 1.293 \pm 0.009$  Å,  $\angle FCF = 111.84 \pm 0.52^\circ$ , and  $\angle NCN = 53.95 \pm 0.36^\circ$ . Comparison of the metrics of perfluorodiazirine with diazirine shows that  $C-N$  distance is shorter and the  $N=N$  distance is longer in the former than in the latter by about 0.06 Å. An analysis of the structures of related molecular species underscores the observation that the attachment of two or more fluorines to a carbon atom introduces a compacting of the structure in the immediate vicinity of the carbon atom.

Study of the structures and properties of triatom ring systems has proved to be an intriguing activity for experimental as well as theoretical chemists. Exclusive of postulated transient species, diazirine and perfluorodiazirine are the smallest molecules (five atoms) which incorporate such rings. Currently there is particular interest in their structural properties because they are precursors of carbenes. Perfluorodiazirine, a precursor of  $CF_2$ , was first prepared by Mitsch.<sup>1</sup> That this preparation produced a compound with a cyclic structure ( $C_{2v}$  symmetry), like that for diazirine, was deduced from a detailed analysis of its infrared and Raman spectra,<sup>2</sup> and the assignment of the fundamental frequencies was confirmed by an analysis of its ultraviolet spectrum.<sup>3</sup> Preparation of the noncyclic isomer (perfluorodiazomethane) has not yet been reported.

The present electron diffraction investigation of the vapor phase structure of perfluorodiazirine was undertaken to obtain interatomic distances and bond angles for comparison with the known geometry of diazirine.<sup>4</sup>

### Experimental Section

The gas chromatographically pure sample of  $CF_2N_2$  was obtained from Ronald A. Mitsch, Minnesota Mining and Manufacturing Co. The sample was kept in the vapor state at 0.5 atm in a 250-ml glass bulb, which was fitted with a pressure stopcock and a cold finger. The sample was frozen out and degassed before each pattern was taken. For the diffraction runs, the sample pressure was maintained at about 5 mm by immersing the bulb in a bath at  $-150^\circ$ . Sector diffraction patterns were obtained with the new electron diffraction apparatus, operated in the convergent mode.<sup>5,6</sup> Exposures were made on  $4 \times 5$  in. Kodak process plates. An  $r^3$  sector was used, and diffraction patterns were obtained for three regimes:  $q = 3-40$  Å<sup>-1</sup> (25 kv;  $L = 262.4$  mm);  $q = 6-75$  Å<sup>-1</sup> (75 kv;  $L = 262.4$  mm); and  $q = 12-143$  Å<sup>-1</sup> (75 kv;  $L = 129.4$  mm) ( $q = (40/\lambda) \sin \theta/2$ ). At each magnification four different gas diffraction exposures and one calibrating ZnO exposure were made.

The plates were microphotometered on a double-beam Jarrell-Ash microdensitometer, the stage of which was fitted with a rotating plateholder, driven at 600 rpm during the scan. A precision calibration plate (250- $\mu$  interval marks) was mounted on the second stage. Images of both plates were projected in split field onto a viewing screen, at the front of the instrument. The two plate stages were rigidly locked so that both images moved across the screen as the pattern was scanned. Motion of the calibration rulings was

(1) R. A. Mitsch, *J. Heterocyclic Chem.*, **3**, 245 (1966).

(2) C. W. Bjork, N. C. Craig, R. A. Mitsch, and J. Overend, *J. Am. Chem. Soc.*, **87**, 1186 (1965).

(3) J. D. Simmons, J. R. Bartky, and A. M. Bass, *J. Mol. Spectry.*, **17**, 48 (1965).

(4) L. Pierce and V. Dobyns, *J. Am. Chem. Soc.*, **84**, 2651 (1962).

(5) S. H. Bauer and K. Kimura, *J. Phys. Soc. Japan*, **17**, 300 (1962).

(6) S. H. Bauer, "Electron Diffraction Studies at High Temperatures," Nonr-401(41), Project NR092-504, ARPA Order No. 23-53, Dec 1967.