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The TCNE-Benzene Complex: A CNDO Approach*

D. B. CHESNUT and PAUL E. S. WORMER**
Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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CNDO/2 calculations on the TCNE-benzene complex are reported. A stable complex is found which exhibits a relatively large stabilization energy (0.2 a.u.) at a short interplanar separation (1.75 Å); the binding apparently arises solely through charge transfer. Mulliken population analyses were performed by reinterpreting the CNDO orbitals as Löwdin orbitals. Sample calculations on small organic molecules and first row diatomics indicate the procedure to be satisfactory. It is shown that generally only overlap populations that are summed over the orbitals of the atoms in question reflect the symmetry of the molecule.

Die Ergebnisse von CNDO/2-Rechnungen an Tetracyanaoäthylen-Benzol-Komplexen werden mitgeteilt. Es wird ein stabiler Komplex gefunden, der eine relativ große Stabilisierungsenergie (0,2 A.E.) bei geringem Abstand (1,75 Å) der Molekülebenen besitzt; die Bindung entsteht anscheinend nur durch Ladungsübertragung. Eine Populationsanalyse nach Mulliken wurde mit Hilfe der Interpretation der CNDO-Orbitale als Löwdin-Orbitale durchgeführt. Berechnungen an Beispielen wie kleinen organischen Molekülen und zweiatomigen Molekülen aus Elementen der ersten Reihe zeigen, daß die Methode befriedigende Ergebnisse liefert. Es wird gezeigt, daß im allgemeinen nur die Überlappungs-Populationen, die über die Orbitale der betrachteten Atome summiert werden, die Symmetrie des Moleküls widerspiegeln.

Calculs CNDO/2 sur le complexe TCNE-benzène. Un complexe stable apparaît pour une séparation interplan courte (1,75 Å) avec une énergie de stabilisation relativement forte (0,2 u.a); la liaison provient apparemment du seul transfert de charge. Une analyse de population de Mulliken a été effectuée en réinterprétant les orbitales CNDO comme orbitales de Löwdin. Des calculs échantillonés sur de petites molécules organiques et des molécules diatomiques de la première ligne montrent que le procédé s'avère satisfaisant. On montre qu'en général, seules les populations de recouvrement sommées sur les orbitales des atomes en question reflètent la symétrie de la molécule.

Introduction

π-π molecular complexes pose an interesting study in bonding. The question of the prime effect in stabilizing such systems is not yet clear due mainly to the difficulty in adequately treating such large systems. For some time it was generally felt that charge transfer stabilization was mainly responsible for bonding, but spectroscopic measurements on some TCNE (tetracyanoethylene) complexes do not seem to support this idea [1]. Studies employing a π-only extended Hückel approach [2] have given indications of reproducing relative molecular geometries at chosen experimental interplanar intermolecular separations but in general fail to predict absolute binding. The advent of approximate self-consistent field

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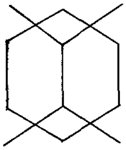
** Present address: Department of Theoretical Chemistry, University of Nijmegen, The Netherlands.

treatments introduced by Pople and coworkers [3] allows a more readily justifiable treatment of large systems and avoids many of the pitfalls of one-electron methods. For example, several recent calculations [4, 5] using this method on hydrogen bonded systems have yielded reasonable results. In the present paper we present CNDO/2 calculations of the TCNE-benzene complex for a restricted region of relative intermolecular geometry.

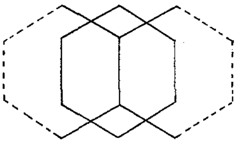
A basic purpose for initiating such a calculation is the elucidation of those factors which dictate the observed relative intermolecular geometry characteristic of the majority of both charge transfer and charge resonance complexes. Unfortunately, the current calculations do not reveal any particular simplifying feature; on the contrary, the issue is clouded a bit by our results which indicate small and negative intermolecular overlap populations and a high degree of charge transfer. It is worthwhile to discuss these results in light of the general problems above. Too, since no previous CNDO calculations on systems of this kind have been performed the present calculations may be taken as a model study of the CNDO approach to a π-bonded bimolecular system.

Choice of Model

The dominant structural fragment seen in most π-π molecular complexes consists of a bonds-over-bonds arrangement shown below,

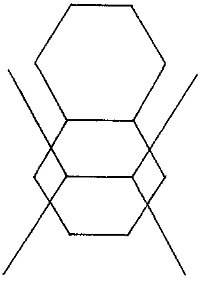


a



b

where the benzenoid moiety projects onto an ethylene-like fragment arising either from a real ethylene group (case a, as, for example, the central portion of TCNE itself) or from a fused benzenoid system (case b). Examples of such structures can be seen in Chesnut and Moseley's paper [2] and from the review paper of Prout and Wright [6]. We wished to carry out calculations on a system that exhibits such a characteristic projected structure and at the same time was small enough to minimize computer time. The available program is limited to 80 orbitals which severely restricts our selection. The TCNE-benzene system represents a 70-orbital problem and, although its structure is not known, one would expect a behavior similar to the general class of materials. Indeed, the TCNE-naphthalene crystal structure is known [7], exhibiting the projection



An interesting aspect of the TCNE-naphthalene structure is that as the TCNE and naphthalene molecules stack alternately with planes parallel to one another the TCNE molecules project onto one ring of the naphthalene below and the opposite ring of the naphthalene above.

Since we are interested in general trends we have concentrated on the above type of projected structure in the TCNE-benzene calculations. We have performed a few calculations on other geometries and, as discussed later, find that a rotated form of the complex exhibits greater binding according to the computational method we have employed. Aside from questioning the general integrity of the calculational approach, this raises the well-known problem of comparing calculations on an isolated molecular system (a gas-phase calculation) with experimental structural data obtained from studies of crystals.

Calculations and Method of Population Analysis

The calculations were performed on the IBM 360/75 computer at the Triangle Universities Computer Center, Research Triangle Park, North Carolina, using a modified version of the semiempirical self-consistent field CNINDO program supplied by the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Indiana. The semiempirical parameters used were the CNDO/2 parameters given by Pople *et al.* [3]. The internal geometries of TCNE and benzene were held fixed throughout the calculations. For TCNE, 120° angles plus the distances reported in Bekoe and Trueblood's crystal structure investigation [8] were used; for benzene, standard hexagonal symmetry was assumed with C–C and C–H distances of 1.40 Å and 1.08 Å, respectively. The molecular planes were always maintained parallel to each other.

Two modifications to the basic program were made. In its original form CNINDO showed diverging SCF cycles for TCNE and TCNE-benzene. To circumvent this difficulty the program was modified so that in the $(n+1)^{\text{th}}$ iterative SCF cycle the entered density matrix (charge and bond-order matrix), $\boldsymbol{P}^{(n)}$, used was taken to be

$$\boldsymbol{P}^{(n)} = \boldsymbol{P}^{(n-1)} + \delta(\boldsymbol{P}^{(n)'} - \boldsymbol{P}^{(n-1)}),$$

where $\boldsymbol{P}^{(n-1)}$ is the density matrix entering the n^{th} cycle, $\boldsymbol{P}^{(n)'}$ is the density matrix *exiting* the n^{th} cycle, and δ is a damping factor. A value of 0.7 for δ was found to yield optimum convergence for TCNE (convergence in 14 cycles) and proved satisfactory for the TCNE-benzene complex and another large cyanocarbon, TCNQ (tetracyanoquinodimethane). An average calculation on the TCNE-benzene complex took about 12.5 minutes.

The second modification involved the addition of a subroutine to perform a Mulliken population analysis [9] in terms of a transformed basis. One of the main points of interest of this work was the question of whether or not one can detect intermolecular bonding in the complex. One such measure has been simply to use the non-diagonal elements of the charge and bond-order matrix, the bond orders [10]. We are interested in the total measure of bonding between any two atoms and would thus want to sum individual bond orders of the various atomlocalized orbitals. This procedure, however, fails in general for an arbitrary choice of local atomic coordinate systems (to which the localized AO's are attached); physically equivalent (symmetry related) bonds can have different total summed bond orders (See Appendix). A simple example is to note that the π-bond order between a pair of P_z-π orbitals in an aromatic system is changed in sign by inverting one of the local z-axes. The fact that the use of simple bond orders is justified in π-electron calculations depends upon the standard choice of parallel local axes normal to the π-plane.

A way of avoiding this problem is to use the sum of Mulliken orbital overlap populations. We show in the Appendix that these summed populations reflect the symmetry of the molecules. The CNDO orbitals, however, are orthogonal in the zero-differential-overlap approximation so that there are no non-vanishing overlap populations. We choose, however, to consider the CNDO orbital as Löwdin orbitals [11], that is, semi-localized orbitals which resemble localized atomic orbitals as closely as possible [12] and yet are mutually orthogonal. Thus, the CNDO orbital set $\{\phi_n\}$ is taken to be related to a localized, non-orthogonal set $\{\phi'_n\}$ by the transformation.

$$\phi' = \phi S^{1/2},$$

where S is the overlap matrix in the basis $\{\phi'_n\}$ and was constructed from the overlap integrals of the Slater orbitals used in the CNDO program. Expressing our CNDO wave functions in the $\{\phi'_n\}$ basis then allows one to perform a

Table 1. *Comparison of bond overlap populations*

Umbracketed values: Present work; bracketed values: Ref. [14], part A and Ref. [15], part B

Molecule	Bond	σ	π	Total
A Li_2	—	0.872 (0.962)	0.0 (0.0)	0.872 (0.962)
N_2	—	0.431 (0.220)	0.880 (0.880)	1.311 (1.100)
F_2	—	0.256 (0.297)	−0.017 (−0.001)	0.239 (0.296)
LiF	—	0.155 (0.190)	0.322 (0.208)	0.477 (0.398)
LiH	—	0.757 (0.691)	0.0 (0.0)	0.757 (0.691)
B benzene	C–C	0.876 (0.82)	0.240 (0.240)	1.116 (1.06)
	C–H	—	—	0.768 (0.78)
ethylene	C=C	0.916 (0.791)	0.428 (0.420)	1.344 (1.211)
	C–H	—	—	0.778 (0.812)
ethane	C–C	—	—	0.856 (0.710)
	C–H	—	—	0.766 (0.785)
acetylene	C–C	0.390 (0.544)	0.920 (0.918)	1.310 (1.462)
	C–H	—	—	0.810 (0.800)
cis-butadiene	C=C	0.910 (0.77)	0.412 (0.39)	1.322 (1.16)
	C–C	0.832 (0.81)	0.050 (0.09)	0.882 (0.92)
	C–H	—	—	0.764, 0.780, 0.798 (0.78)
HCN	C≡N	0.390 (0.544)	0.920 (0.918)	1.310 (1.462)
	C–H	—	—	0.810 (0.800)
TCNE	C=C	0.818	0.376	1.194
	C–C	0.844	0.052	0.896
	C≡N	0.824[a]	0.448[b]	1.272

[a] Includes the equivalent of one (in plane) π-bond.

[b] The "pure" π-bond.

Mulliken population analysis in terms of net atomic charges and total bond overlap populations and this is the procedure we have followed. Recently, Brown and Roby [13] have shown that this interpretation of zero-differential-overlap theories can be justified from first principles.

To test this procedure we calculated total bond orders for a series of first row diatomics and small organic molecules and compared our results with literature values. The agreement is quite adequate; the comparisons for some representative systems are shown in Table 1, where the present results are compared with the calculations of Fraga and Ransil [14] for the diatomics and with the calculations of Lipscomb and coworkers [15] for the polyatomics. We used the same diatomic distances as Fraga and Ransil; for the organic systems we employed values from the "Tables of Interatomic Distance and Configurations in Molecules and Ions" (The Chemical Society, London, 1965) which differ very slightly in a few instances with the values of Newton, Boer, and Lipscomb.

Results and Discussion

Although no experimental gas phase data are available for the stabilization energy, the dipole moment and the intermolecular of the TCNE-benzene complex, one can get a rough idea of the order of magnitude of these quantities by comparison with similar complexes. In Table 2 some illustrative experimental data for complexes in which TCNE acts as the acceptor are presented.

To date no calculations, except those of Chesnut and Moseley [2] on the TCNE-anthracene complex, have been performed that vary the interplanar distance. Lippert, Hanna, and Trotter [18] take the fixed interplanar distance 3.50 Å and calculate by means of Morrell's perturbation theory [16] a dipole moment of 0.54 D and a stabilization energy of -6.21 kcal/mole. Their method is especially devised for charge transfer complexes and they use some parameters that are determined for the case under consideration. Herndon and Feuer [20] take a fixed distance as well (3.20 Å). They apply a perturbational method using as first-order functions for the separate molecules CNDO/2 functions and find a -3.54 kcal/mole stabilization energy. Mantione [21] calculated Van der Waals – London interactions in TCNE complexes with *p*-xylene, *o*-xylene, mesitylene and durene. His results agree remarkably well with the experimental results. Again the distance was fixed (3.30 Å).

The current calculations represent an attempt at a somewhat more general approach in which the relative geometry is determined by the calculation. Even

Table 2. *Illustrative data for some* TCNE *complexes*

Donor	ΔE (kcal/mole)	μ (Debye)	R (Å)
benzene	-3.34[a]	—	—
durene	-10.1[b]	1.26[c]	—
naphthalene	-4.06[d]	1.28[e]	3.30[f]

[a] In CCl_4 (Ref. [16]).

[b] In gas phase (Ref. [17]).

[c] In CCl_4 (Ref. [16]).

[d] In CCl_4 (Ref. [16]).

[e] In CCl_4 (Ref. [15]).

[f] In solid state (Ref. [7]).

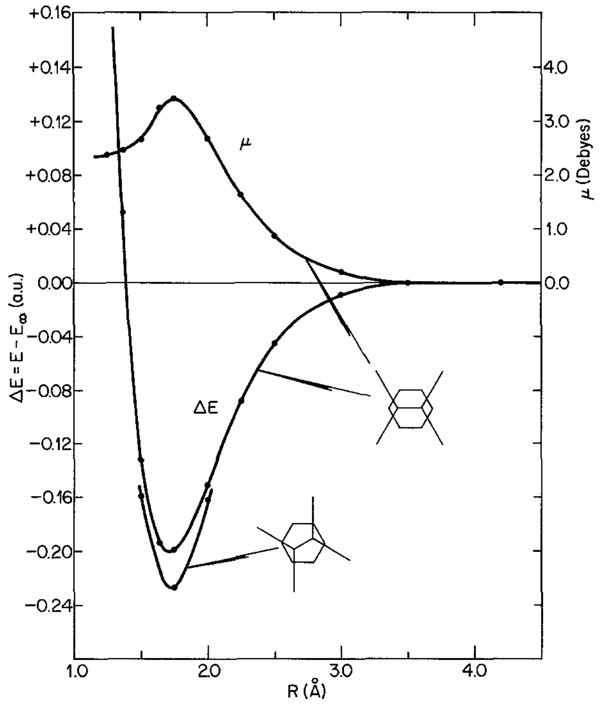


Fig. 1. $\Delta E = E - E_\infty$ (in a.u.) as a function of the interplanar separation, R (in Å), for the relative geometries studied. μ, the dipole moment (in Debyes) is also shown for the non-rotated structure. The structure projections are approximately to scale and illustrate the two relative geometries studied

so, finite computer time and funds necessitated a limitation on the possible geometries to be studied. Most of the calculations refer to that situation in which the two molecules are brought together directly on top of each other with the projected TCNE double bond direction colinear with the 1,4-carbon atoms on the benzene ring (the non-rotated form); a few points for the geometry in which the TCNE was rotated by 30° about the axis normal to its plane (the rotated forms) were also calculated. The non-rotated and 30° rotated geometries are shown in projection as part of Fig. 1. One must note that the optimum procedure in calculations of this kind would be to vary all distances to find the minimum energy; this would require very extensive calculations for the present case, calculations which we don't believe are warranted. Thus, in all our calculations the *internal* geometries of the component molecules are held fixed as the distance between them, R, was varied.

Fig. 1 shows the calculated energy versus the interplanar separation for both the rotated and non-rotated structures; in Table 3 the electronic and nuclear energy components are listed along with the total energy. While the non-rotated structure is the one for which most calculations were carried out, the rotated form (30°) at $R = 1.75$ Å actually exhibits a lower minimum ($E_{30°} < E_{15°} < E_{0°}$ at 1.75 Å). Relative to one's *a priori* prejudices, the energy curve shows too deep a minimum at too short an interplanar separation with an extremely steep variation

Table 3. *Relative energies (in a.u.) as a function of R*

E_N = nuclear repulsions, E_{el} = electronic energy = $E - E_N$, E = total energy = $E_N + E_{el}$

R (Å)	$E_N - E_{N,\infty}$	$E_{el} - E_{el,\infty}$	$\Delta E = E - E_\infty$
1.25	271.401	−270.925	0.476
1.375	262.258	−262.206	0.052
1.50	253.567	−253.700	−0.133
1.64	244.349	−244.543	−0.194
1.75[a]	237.471	−237.670	−0.199
1.75[b]	237.417	−237.629	−0.212
1.75[c]	237.358	−237.586	−0.228
2.00	222.948	−223.099	−0.151
2.25	209.827	−209.915	−0.088
2.50	197.945	−197.990	−0.045
3.00	177.339	−177.348	−0.009
3.50	160.180	−160.181	−0.001

[a] 0° rotation. – [b] 15° rotation. – [c] 30° rotation.

of the energy at both small and large values or R. Whereas stabilization energies of the order of 2 to 5 kcal/mole might be expected, an energy minimum here is calculated to be approximately 125 kcal/mole. Whereas interplanar separations *in crystals* are from 3.2 to 3.5 Å, the minimum here occurs at approximately 1.75 Å. The energy curve at large R approaches an R^{-14} behavior with no hint of the London R^{-6} dispersion force behavior. The absence of the London forces in our results need not be surprising since it is generally held that these forces cannot be reproduced in a self-consistent field calculation without configuration interaction.

The large value of ΔE, the energy of stabilization, is somewhat characteristic of the CNDO method which tends to overemphasize binding. This property may well also explain why the minimum in ΔE occurs at too short a distance. To improve usefulness of these calculations a detailed study of what parameters or integrals led to this effect should be made and the necessary reparameterization be made. As alluded to above, the importance of configuration interaction must also be ascertained. The lowering of $\Delta E_{\min}$ that occurs in going to the rotated complex occurs through a lowering of the nuclear repulsion terms which overcome an *increase* in the electronic energy (see Table 3). It is clear that the detailed geometry may well be very sensitive to the specific input parameters in systems as large and complicated as the present one. Jesaitis and Streitwieser [22] point out that because the CNDO method uses *s*-orbitals to calculate the coulomb repulsion, the electron-electron repulsive energy may be underestimated in systems where the charge can be highly delocalized. This effect may be quite significant in the present case since transfer of charge from benzene to TCNE allows the transferred electron greater delocalization. Thus, the underestimation of coulomb repulsion would promote such charge transfer.

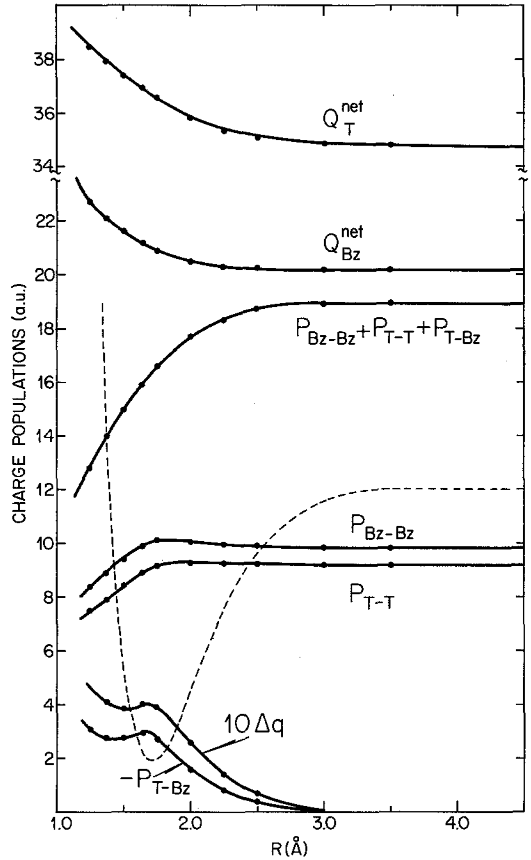
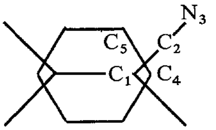


Fig. 2. Various summed overlap and net charge populations and the amount of charge transfer (all in a.u.) as a function of the interplanar separation R for the non-rotated structure. See text for definition of symbols

Also plotted in Fig. 1 is the dipole moment, μ, which was calculated directly in the CNDO approximation. Here again the value at the calculated equilibrium separation (about 3.5 debyes) is larger than the generally expected moments (of the order of 1 to 1.5 debyes). The large dipole moments is attributed to the large degree of charge transfer found in the calculations. The behavior of the dipole moment and also the charge populations shown in Fig. 2 as one approaches the equilibrium separation and proceeds to shorter distances indicates clearly the onset of the repulsive interactions which have clearly changed the behavior of the electrons in the complex. Although μ tends to drop ultimately, Δq, the amount of charge transfer, continues to increase as shorter distances are approached. Were we to take our interpolated results at, say, 3.25 Å, we obtain at ΔE of -3.3 kcal/mole and a dipole moment of about 0.1 Debye. Clearly one must be cautious in handling results obtained from a single geometry.

The search for possible intermolecular bonding was one of the initial reasons for initiating this study and was the reason for performing the Mulliken population analyses. For $R \geqq 1.75$ Å *no* positive intermolecular overlap populations (OP's) are found; indeed, all values are in the range generally expected for non-bonded atoms.



At $R = 1.75$ Å the C_2–C_5 OP is -0.078, the largest magnitude observed, while the C_1–C_4 OP is -0.018. One might have expected this latter OP to be most indicative of bonding; perhaps the fact that it is the least negative of the significant OP's does hint at this fact. All of the atoms "near" each other exhibit similar negative OP's and this includes the hydrogen interactions (which would indeed normally be expected to show repulsive effects).

To indicate some general trends in the charge populations we have plotted certain sums for the non-rotated structure in Fig. 2. P_{T-T} and P_{Bz-Bz} represent the *sums* of OP's between atoms (all atoms) on TCNE and, separately, on benzene, respectively; P_{T-Bz} represents the summed OP's between all atoms on the two different molecules. Q_T^{net} and Q_{Bz}^{net} are the *net* Mulliken charges summed for the separate molecules and Δq represents the total charge transferred *from benzene to* TCNE; a value of $+1$ for Δq would represent the system $(\mathrm{TCNE})^{-1}$ $(\mathrm{benzene})^{+1}$. Δq is calculated by dividing P_{T-Bz} equally between the two molecules and represents the increase in the total Mulliken gross charge on TCNE.

The energy curve is indicated in the background for reference. There are several interesting aspects. The P_{T-T} and P_{Bz-Bz} sums hardly change (slight increase) as R decreases, indicating that the net intramolecular binding is not being much affected by those forces which are stabilizing the complex. The total OP $(P_{T-T} + P_{Bz-Bz} + P_{T-Bz})$ does show a uniform decrease throughout the range of decreasing R while both net charge sums increase. We interpret this to indicate that the stabilization arises essentially solely from charge transfer. Nearly all the individual atomic net charges increase, except for the hydrogen atoms which show a decrease.

Decreasing overlap populations are indicative of the increase of anti-bonding MO's in the total wave function. Such anti-bonding orbitals will tend to pile charge up on atoms as net charges at the expense of bond populations. This is apparently what is happening in our present calculation. The intermolecular OP's are being driven negative causing the net atomic charges to increase on *both* molecules. The distribution is such as to favor the more electron-accepting TCNE molecule giving rise to a finite Δq and dipole moment. The parallel nature of $-P_{T-Bz}$ and Δq would seem to indicate that it is basically only the intermolecular coupling which is anti-bonding (in the sense of negative OP's) and that the MO's of the whole complex are the MO's of the individual molecules weighted (polarized) toward the TCNE molecule. This fits in with the essentially constant behavior of P_{T-T} and P_{Bz-Bz} (down to $R = 1.75$ Å, at least) which indicates that molecular integrity is maintained for each molecular component. Although the calculated energy and equilibrium distance might indicate the formation of one "super molecule", the Mulliken population analysis shows clearly that this is not what is happening; rather, the two component molecules remain easily recognizable as such, down to the shortest distance calculated (1.25 Å).

Obviously a careful study of the dominant parameters in the CNDO approach should be made in order to make a proper evaluation of the method as applied to these systems. If London forces are indeed the significant factor perhaps more than a simple SCF approach will be necessary. However, if one is to accept both the present method of calculation and the premise that SCF wavefunctions are "reasonably good" one must conclude that charge transfer may yet prove to be a significant factor in the stability of molecular complexes.

Acknowledgement. We are indebted to Duke University and the Duke University Computational Center for partial support of our computer calculations and for technical assistance.

Appendix

In this appendix we will show that equivalent bonds in a molecule are not necessarily characterized by identical bond orders but that summed overlap populations do reflect the physical equivalence of symmetry-related bonds. The latter summed, or total, overlap populations are thus better suited to characterize chemical bonds within a molecule.

In most computer work the localized atomic orbitals (AO's) are determined by the local coordinate system whereas at other times one often employs equivalent AO's (characterized by the fact that symmetry operations induce essentially permutations of the equivalent AO's among themselves). We consider initially an arbitrary set of AO's.

The charge and bond order matrix, $\boldsymbol{P}$, for a single determinantal wave function constructed from orthonormal molecular orbitals is invariant under transformations of the subspace spanned by the occupied MO's. A symmetry operation g mixes only MO's of equal energy; thus, for a closed-shell system, symmetry operators transform only occupied MO's among themselves and therefore leave $\boldsymbol{P}$ invariant.

$$g\boldsymbol{P} \equiv \boldsymbol{P}' = \boldsymbol{P}\,. \tag{1}$$

To describe the symmetry operation g with respect to the AO's let $|\alpha i\rangle$ be the i^{th} AO on center α; then in general

$$g\,|\alpha i\rangle = \sum_{\beta j} |\beta j\rangle\, D(g)_{\beta j;\,\alpha i}\,. \tag{2}$$

Since g is a one-to-one mapping of the set of nuclei onto itself, we can write

$$D(g)_{\beta j;\,\alpha i} = \delta_{\beta\alpha'} D^{(\alpha)}(g)_{ji} \qquad g:\alpha \to \alpha' \tag{3}$$

in which α' is the g-image of α. If the atomic orbitals span representations of the full rotation group, then the matrix $\boldsymbol{D}^{(\alpha)}(g)$ will represent the rotation of the local axes on α' relative to the g-image of the α-coordinate system. We will assume that this is the case, and furthermore that the representation is orthogonal.

Consider next how the filled MO's $\{|s\rangle\}$ transform under g; let $|s\rangle$ be the MO

$$|s\rangle = \sum_{\alpha i} C_{\alpha i;\, s}\, |\alpha i\rangle .$$

Then

$$\begin{aligned} g\,|s\rangle &= \sum_{\alpha i} C_{\alpha i;\, s}\, g\, |\alpha i\rangle \\ &= \sum_{\alpha i}\sum_{\beta j} C_{\alpha i;\, s} D(g)_{\beta j;\, \alpha i}\, |\beta j\rangle \\ &= \sum_{\beta j} C'_{\beta i;\, s}\, |\beta j\rangle . \end{aligned} \tag{4}$$

Where the second and third lines of Eq. (4) define the quantity $C'_{\beta j;\, s}$. Thus, assuming for simplicity real coefficients,

$$\begin{aligned} P'_{\alpha i;\, \beta j} &= \sum_{s} C'_{\alpha i;\, s} C'_{\beta j;\, s} \\ &= \sum_{\gamma k}\sum_{\delta p}\sum_{s} D(g)_{\alpha i;\, \gamma k} D(g)_{\beta j;\, \delta p} C_{\gamma k;\, s} C_{\delta p;\, s} . \end{aligned} \tag{5}$$

Where, from the definition of the set $\{|s\rangle\}$, the sum over s implies a sum over the occupied MO's of the system.

The matrix representation $\boldsymbol{D}(g)$ of g is orthogonal, that is:

$$D(g)_{\alpha i;\, \gamma k} = D(g^{-1})_{\gamma k;\, \alpha i} . \tag{6}$$

Put $h = g^{-1}$ and define α'' by $h : \alpha \rightarrow \alpha''$.

$$D(g)_{\alpha i;\, \gamma k} = D(h)_{\gamma k;\, \alpha i} = \delta_{\gamma \alpha''} D^{(\alpha)}(h)_{ki} , \tag{7}$$

Eq. (1) indicates that $\boldsymbol{P} = g\boldsymbol{P} = \boldsymbol{P}'$, so

$$\begin{aligned} P_{\alpha i;\, \beta j} &= \sum_{\gamma k}\sum_{\delta p} \delta_{\gamma\alpha''} D^{(\alpha)}(h)_{ki} \delta_{\delta\beta''} D^{(\beta)}(h)_{pj} P_{\gamma k;\, \delta p} \\ &= \sum_{k,p} D^{(\alpha)}(h)_{ki} D^{(\beta)}(h)_{pj} P_{\alpha'' k;\, \beta'' p} . \end{aligned} \tag{8}$$

We conclude that $P_{\alpha i;\, \beta j}$ is in general not equal to $P_{\alpha'' i;\, \beta'' j}$ in which α'' and β'' denote atoms equivalent to, respectively, α and β. If we sum over i and j in order to obtain the total bond order, we will get different answer for the bond orders of the α-β and the α''-β'' bond; [unless, of course, $\boldsymbol{D}^{(\alpha)}(h)$ and $\boldsymbol{D}^{(\beta)}(h)$ are identity matrices, meaning that the local coordinate systems transform into one another under h].

We now prove the validity of the following relation between summed Mulliken overlap populations:

$$\sum_{i \text{ on } \alpha}\ \sum_{j \text{ on } \beta} P_{\alpha i;\, \beta j} S_{\alpha i;\, \beta j} = \sum_{i \text{ on } \alpha''}\ \sum_{i \text{ on } \beta''} P_{\alpha'' i;\, \beta'' j} S_{\alpha'' i;\, \beta'' j} . \tag{9}$$

First we transform $\boldsymbol{S}$ with h; since $\boldsymbol{S}$ is invariant under a unitary transformation:

$$\begin{aligned} S_{\beta j;\,\alpha i} = S''_{\beta j;\,\alpha i} &= \sum_{\gamma k}\sum_{\delta p} D(h)_{\gamma k;\,\beta j} D(h)_{\delta p;\,\alpha i} S_{\gamma k;\,\delta p} \\ &= \sum_{k,p} D^{(\beta)}(h)_{kj} D^{(\alpha)}(h)_{pi} S_{\beta'' k;\,\alpha'' p} \\ &= \sum_{k,p} D^{(\beta)}(h)^{-1}_{jk} D^{(\alpha)}(h)^{-1}_{ip} S_{\beta'' k;\,\alpha'' p}\,. \end{aligned} \tag{10}$$

Substituting the results (8) and (10) in the 1. h.s. of (9) and using the fact that $\boldsymbol{S}$ is symmetric we obtain:

$$\begin{aligned} \sum_{i,j} P_{\alpha i;\,\beta j} S_{\alpha i;\,\beta j} &= \sum_{i,j}\sum_{k,p}\sum_{q,r} D^{(\alpha)}(h)_{ki} D^{(\alpha)}(h)^{-1}_{ir} D^{(\beta)}(h)_{pj} D^{(\beta)}(h)^{-1}_{jq} P_{\alpha'' k;\,\beta'' p} S_{\alpha'' r;\,\beta'' q} \\ &= \sum_{k,p} P_{\alpha'' k;\,\beta'' p} S_{\alpha'' k;\,\beta'' p}\,. \end{aligned} \tag{11}$$

This result indicates that the overlap population between two atoms summed over the atomic orbitals of the atoms is identical for equivalent pairs of atoms.

If one is dealing with equivalent atomic orbitals, the matrix $\boldsymbol{D}^{(\alpha)}(g)$ takes a simple form. Suppose g transforms $|\alpha i\rangle$ into $E_{ii'}\,|\alpha' i'\rangle$, in which $E_{ii'} = \pm 1$ (if we use real AO's). $\boldsymbol{D}^{(\alpha)}(g)$ takes the form:

$$D^{(\alpha)}(g)_{ij} = \delta_{ji'} E_{ii'}\,. \tag{12}$$

Substituting this in (8):

$$P_{\alpha i;\,\beta j} = E_{ii'} E_{jj'} P_{\alpha' i';\,\beta' j'} \tag{13}$$

and in (10):

$$S_{\alpha i;\,\beta j} = E_{ii'} E_{jj'} S_{\alpha' i';\,\beta' j'}\,. \tag{14}$$

From this we see that symmetry related elements of $\boldsymbol{P}$ and $\boldsymbol{S}$ differ at most in sign; further the product equality

$$P_{\alpha i;\,\beta j} S_{\alpha i;\,\beta j} = P_{\alpha' i';\,\beta' j'} S_{\alpha' i';\,\beta' j'} \tag{15}$$

will hold.

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Dr. D. B. Chesnut
Department of Chemistry
Duke University
Durham, North Carolina 27700, USA