served while the lower energy component is lost. If the a_{2u} orbital is heavily involved in the latter transitions, this result would be expected when the half-filled a_{2u} orbital is filled in the postulated $\pi-\pi'$ bond of the dimer. We assign the near-infrared band of the dimer to an internal charge transfer from the $\pi-\pi'$ bonding orbital to its antibonding counterpart. We thus predict that this band will be polarized perpendicular to the porphyrin planes in contrast to all the other porphyrin transitions which are restricted to the plane. This excitation may also cause photodissociation of the dimer, but the rapidity of the dimerization may make this prediction hard to detect experimentally. These predictions are unique to the $\pi-\pi'$ bonded dimer and could serve to distinguish this structure from alternatives such as a single bond between meso carbons.

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Electron Population Analysis of Accurate Diffraction Data. III. Application of One- and Two-Center Formalisms to Tetracyanoethylene Oxide[1]

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Abstract: One- and two-center variable-coefficient scattering factor formalisms have been used to obtain a least-squares fit to accurate experimental diffraction data for tetracyanoethylene oxide. In some cases, calculations were carried out using both self-consistent-field isolated atom and standard molecular exponent Slater-type minimal basis sets. In general, refinements of selected one-center products of the first-order density matrix give net atomic charges in agreement with INDO results except for the cyano groups which appear neutral. When the two-center density pieces are included, the average charge of the cyano group is −0.10 (5) electron. A π to σ electron transfer at the cyano atoms relative to the INDO result is indicated by an analysis of the one-center density matrix refinement. This and similar previously observed charge migrations for certain atoms in α-oxalic acid dihydrate and cyanuric acid are interpreted in terms of a simulation of π density in the bonding region by appropriately thermally averaged σ orbitals. The absence of such migration in a refinement which explicitly includes two-center π-bond density pieces indicates this shift to be an artifact of the one-center approximation.

In principle, the diffraction of X-rays by crystals is capable of providing detailed information concerning the time-averaged electron distribution. However, it has been shown by us and others that the spherical atom scattering factor formalism which is used in the conventional X-ray experiment introduces a bias into the least-squares refinement procedure which results in systematic errors in the derived parameters. While these errors are of minimal consequence as far as routine crystal structure analysis is concerned, they tend to almost completely obscure bond density features in, for example, Fourier difference maps. The standard X-ray diffraction approach is therefore inadequate for obtaining accurate charge densities.

Recently, considerable success has been achieved in resolving charge density features in several molecular crystals by using neutron diffraction experiments to obtain thermal and positional parameters which are unbiased by any assumed form of the scattering factor, since neutron form factors are constant functions of the magnitude of the scattering vector.[3-6] While the difference maps phased with these parameters have proved quite useful in qualitative discussions, it has become clear that more quantitative results are needed to facilitate a more convenient comparison with theoretical calculations.

The approach used here attempts to span an experimental charge distribution by a minimal basis set of atomic wave functions with variable coefficients. The density is a sum of the contribution from each molecular orbital.

$$\rho = \sum_i^{\text{occ}} \psi_i^* \psi_i$$

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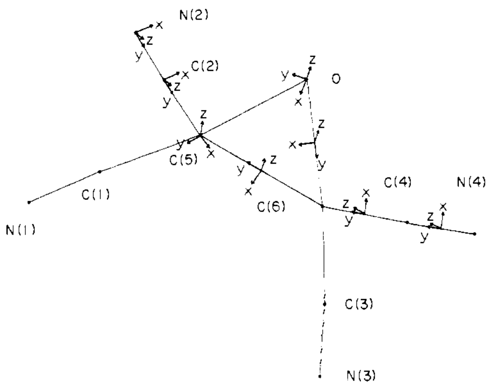

Figure 1. Atomic numbering and coordinate systems for density matrix refinements. Axis systems for chemically equivalent atoms and bonds are obtained by appropriate reflections through the molecular mirror planes.

The molecular orbitals are represented as linear combinations of atomic basis functions according to

$$\psi_i = \sum_u C_{ui}\phi_u$$

Thus

$$\rho = \sum_i^{\text{occ}}\sum_u\sum_v C_{ui}{}^*C_{vi}\phi_u\phi_v = \sum_{u,v} P_{uv}\phi_u\phi_v$$

The Fourier transforms for the orbital products $\phi_u\phi_v$ have been obtained by Stewart.[7] The variable density matrix coefficients P_u are then fit by least-square techniques to the observed X-ray structure amplitudes utilizing positional and thermal parameters derived from a neutron diffraction experiment. The availability of accurate neutron parameters is important since early experience with this formalism indicated very high correlations between thermal parameters and orbital product coefficients when the former were not fixed by the independent experiment.[8,9]

In this paper, we report the application of this method to tetracyanoethylene oxide (TCEO). This strained three-member ring molecule is of considerable interest due to the apparent breakdown of the concept of directed valence. Accurate X-ray and neutron diffraction data for the compound have been reported elsewhere,[10] and recently a detailed discussion of X-ray minus neutron (X − N) difference density maps for a number of chemically interesting parts of the molecule has been published.[5]

Refinement of Coefficients of the First-Order Density Matrix. The large number of parameters needed to fully describe the various orbital products centered on each atom can be substantially reduced if restrictions are applied according to chemical reasoning. It might be expected that as more coefficients are included in the refinement, the agreement between calculated and experimental charge densities will progressively improve. A convenient comparison can be made by contrasting the X − N maps with those calculated by subtracting a spherical atom from the density obtained from the population refinement. The latter are referred to here as population asphericity maps. In general, two levels of approximation are distinguished according to the types of orbital product coefficients which are varied in the least-squares fit. The one-center refinement constrains P_{uv} to be zero unless ϕ_u and ϕ_v are centered on the same atom. This restriction is removed for two-center refinements, but P_{uv} is assumed to be zero if ϕ_u and ϕ_v are on atoms not joined by a chemical bond.

In all calculations, the core electrons are frozen at the self-consistent-field Hartree–Fock density. In order to evaluate the effect of different basis functions, the valence density is fit by Gaussian expansions of isolated atom Hartree–Fock (HF) wave functions[11] and by Gaussian expansions of Slater-type (STO) functions[12] with standard molecular exponents.[13] The crystal was constrained to remain neutral during each refinement.

In Figure 1, we present the coordinate systems and numbering convention for TCEO. Note that coordinates are chosen so that chemically similar orbital product coefficients will appear with the same subscripts and thus are directly comparable. Since TCEO crystallizes with one molecule per asymmetric unit,[10] chemically equivalent parts of the molecule (in the gas phase) are crystallographically independent. Tables I and II give results for restricted one-center refinements with atomic HF and STO basis functions. The ethylene oxide ring valence electrons are assumed to exhibit no asymmetry with respect to the plane defined by the average position of the nuclei of these atoms while the exocyclic atoms are constrained by imposing perpendicular mirror planes which have their lines of intersection along the y axes which are along the bond directions. The effect of these restrictions on the derived orbital product coefficients is small as can be seen from a comparison with refinements in the absence of constraints except at the cyano nitrogens (Table III).

In the present study, every refinement with STO basis functions gave better agreement between observed and calculated structure amplitudes than is the case for atomic HF orbitals.[14] For this reason, we limit our discussion of two-center refinements to the use of STO-type orbitals with the same restrictions as those adopted in Table II for the one-center case. These results appear in Table IV.

Discussion

The –C–C≡N Atoms. The results in Tables I and II show that the cyano groups tend to be almost neutral in the one-center refinements but that the partition of density between C and N is strongly dependent on the choice of atomic basis functions. With the exception of C(3) and N(3), the STO functions give no significant dipole for the cyano group, but the atomic HF basis set produces a large charge separation with the carbon atom being the more negative. Compared to carbon STO functions, the atomic HF basis orbitals are considerably more diffuse and span more of the density in the cyano

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Table I. One-Center Population Coefficients of Hartree–Fock Orbital Products[a]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)	N(2)	N(3)	N(4)	O
p_xp_x	0.42 (5)	0.76 (6)	0.65 (5)	0.80 (6)	1.20 (6)	1.30 (6)	1.05 (6)	1.10 (7)	0.80 (5)	0.81 (8)	1.87 (6)
p_xp_y	0	0	0	0	−0.33 (9)	−0.06 (9)	0	0	0	0	0
p_yp_y	2.27 (10)	1.85 (10)	2.16 (9)	1.96 (11)	0.67 (5)	0.98 (5)	1.79 (10)	1.81 (10)	1.57 (9)	1.70 (11)	1.09 (5)
p_zp_z	0.65 (5)	0.61 (6)	0.74 (5)	0.47 (6)	1.15 (7)	0.69 (6)	0.61 (6)	0.56 (7)	0.84 (6)	0.98 (7)	1.58 (5)
sp_x	0	0	0	0	−0.01 (6)	−0.07 (7)	0	0	0	0	−0.04 (5)
sp_y	−0.22 (10)	−0.09 (10)	−0.16 (9)	0.06 (11)	−0.19 (6)	−0.12 (6)	−0.26 (10)	−0.02 (9)	−0.02 (8)	0.00 (10)	0
Total atomic population, e	6.34	6.22	6.55	6.23	6.02	5.97	6.70	6.72	6.45	6.74	8.04
Net charge	−0.34	−0.22	−0.55	−0.23	−0.02	+0.03	+0.30	+0.28	+0.55	+0.26	−0.04
					R_2[b] 0.088 → 0.051						

[a] Numbers in parentheses are estimated standard deviations. Parameters not refined if no standard deviation is indicated. The C, N, and O $2s^2$ populations are fixed at 1.00, 1.25, and1, 50 e, respectively. [b] $R_2 = \{\Sigma w|F_o - k|F_c||^2/\Sigma wF_o^2\}^{1/2}$.

Table II. One-Center Population Coefficients of Slater Orbital Products

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)	N(2)	N(3)	N(4)	O
p_xp_x	0.50 (3)	0.75 (4)	0.73 (3)	0.85 (4)	1.16 (4)	1.24 (4)	1.20 (4)	1.18 (5)	1.03 (4)	0.99 (5)	1.87 (4)
p_xp_y	0	0	0	0	−0.13 (6)	−0.05 (6)	0	0	0	0	0
p_yp_y	1.78 (6)	1.47 (6)	1.71 (6)	1.54 (6)	0.66 (3)	0.87 (3)	1.71 (6)	1.73 (7)	1.52 (6)	1.6 5(7)	1.18 (4)
p_zp_z	0.68 (3)	0.71 (4)	0.74 (3)	0.55 (4)	1.09 (4)	0.80 (4)	0.87 (4)	0.85 (4)	1.09 (4)	1.16 (5)	1.64 (4)
sp_x	0	0	0	0	0.01 (4)	0.01 (4)	0	0	0	0	−0.07 (3)
sp_y	−0.14 (6)	−0.07 (6)	−0.07 (5)	−0.10 (6)	−0.09 (4)	−0.04 (4)	−0.17 (6)	−0.00 (6)	−0.02 (5)	+0.05 (5)	0
Total atomic population, e	5.96	5.93	6.18	5.94	5.91	5.91	7.03	7.01	6.89	7.05	8.19
Net charge	+0.04	+0.07	−0.18	+0.06	+0.09	+0.09	−0.03	−0.01	+0.11	−0.05	−0.19
					R_2 0.081 → 0.038						

Table III. One-Center Population Coefficients of an Expanded Set of Slater Orbital Products

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)	N(2)	N(3)	N(4)	O
p_xp_x	0.49 (3)	0.76 (4)	0.72 (3)	0.86 (3)	1.17 (4)	1.24 (3)	1.18 (4)	1.13 (4)	1.07 (3)	0.98 (5)	1.84 (3)
p_xp_y	−0.04 (5)	0.01 (5)	−0.09 (5)	0.11 (6)	−0.13 (6)	−0.14 (6)	0	0	0	0	−0.12 (6)
p_xp_z	0.22 (6)	−0.06 (5)	0.08 (5)	−0.09 (6)	−0.18 (5)	−0.07 (6)	0	0	0	0	0.06 (5)
p_yp_y	1.86 (6)	1.55 (6)	1.76 (6)	1.55 (6)	0.70 (3)	0.84 (4)	1.65 (6)	1.72 (6)	1.48 (5)	1.61 (7)	1.18 (3)
p_yp_z	0.09 (5)	0.40 (5)	0.04 (5)	0.29 (6)	−0.18 (6)	0.01 (6)	0	0	0	0	−0.22 (6)
p_zp_z	0.64 (3)	0.69 (4)	0.69 (3)	0.53 (4)	1.05 (4)	0.82 (4)	0.91 (4)	0.88 (4)	1.11 (4)	1.21 (5)	1.65 (3)
sp_x	0.11 (3)	0.11 (3)	0.04 (3)	0.12 (3)	−0.02 (4)	0.02 (3)	0	0	0	0	−0.11 (3)
sp_y	−0.17 (6)	−0.16 (6)	−0.10 (5)	−0.13 (6)	−0.15 (4)	−0.05 (4)	−0.20 (6)	−0.02 (5)	−0.02 (5)	+0.04 (6)	0.04 (3)
sp_z	−0.00 (3)	−0.03 (3)	0.17 (3)	0.05 (3)	0.03 (4)	−0.08 (4)	0	0	0	0	−0.18 (3)
Total atomic population, e	5.99	6.00	6.17	5.94	5.92	5.90	6.99	6.98	6.91	7.05	8.17
Net charge	+0.01	+0.00	−0.17	+0.06	+0.08	+0.10	+0.01	+0.02	+0.09	−0.05	−0.17
					R_2 0.081 → 0.034						

Table IV. Two-Center Refinement of Population Coefficients of STO Orbital Products[a]

(a) One-Center Coefficients

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	N(1)	N(2)	N(3)	N(4)	O
p_xp_x	1.20 (8)	1.27 (9)	1.35 (8)	1.77 (8)	1.25 (14)	1.44 (13)	0.79 (5)	0.79 (6)	0.83 (5)	0.67 (6)	1.83 (10)
p_yp_y	2.78 (14)	2.33 (13)	2.28 (13)	2.50 (14)	0.92 (9)	1.16 (9)	1.10 (8)	1.31 (8)	1.18 (8)	0.85 (10)	0.80 (9)
p_zp_z	1.47 (8)	1.37 (8)	1.21 (8)	1.48 (9)	1.91 (13)	1.94 (13)	0.58 (5)	0.72 (5)	0.83 (5)	0.87 (6)	1.77 (4)
sp_x	0	0	0	0	−1.14 (32)	−0.63 (33)	0	0	0	0	−0.06 (13)
sp_y	0	0	0	0	0	0	−1.12 (12)	−0.61 (11)	−0.55 (11)	−1.06 (13)	−0.22 (2)
Total atomic population, e	8.45	7.97	7.84	8.75	7.08	7.54	5.72	6.07	6.09	5.64	7.90

(b) Two-Center Coefficients for Cyano Bonds

	N(1)–C(1)	electrons	N(2)–C(2)	electrons	N(3)–C(3)	electrons	N(3)–C(4)	electrons
p_ys	−6.35 (66)	−2.61	−4.56 (66)	−1.88	−4.29 (65)	−1.76	−7.05 (73)	−2.93
p_xp_x	1.69 (23)	0.50	1.81 (27)	0.53	0.76 (23)	0.22	1.19 (27)	0.35
p_yp_y	−3.01 (60)	0.92	−1.39 (57)	0.43	−1.90 (60)	0.59	−4.06 (65)	1.30
p_zp_z	1.61 (23)	0.47	0.95 (23)	0.28	1.26 (22)	0.37	1.02 (27)	0.30
Total bond population, e		−0.72		−0.64		−0.58		−0.98

(c) Two-Center Coefficients for Exocyclic Carbon-Carbon Bonds[b]

	C(1)–C(5)	electrons	C(2)–C(5)	electrons	C(3)–C(6)	electrons	C(4)–C(6)	electrons
p_yp_y	1.70 (52)	−0.56	1.84 (54)	−0.60	1.50 (50)	−0.51	2.35 (55)	−0.76
Total bond population, e		−0.56		−0.60		−0.51		−0.76

(d) Two-Center Coefficients for Ethylene Oxide Ring Bonds

	O–C(5)	electrons	O–C(6)	electrons	C(6)–C(5)	electrons
p_xs	19.6 (34)		11.2 (35)		−13.3 (36)	
p_ys	−1.1 (25)	−0.27	−1.6 (27)	−0.40		
sp_x	9.4 (27)		4.3 (27)			
p_xp_x	5.2 (20)	0.70	2.7 (19)	0.37	5.3 (12)	0.95
p_xp_y	15.5 (20)		8.2 (19)		−5.9 (21)	
p_yp_x	0.7 (26)		−1.2 (26)		0.3 (16)	
p_yp_y	2.3 (23)	−0.72	3.1 (25)	−0.89	0.24 (70)	−0.08
p_zp_z	−1.8 (11)	−0.25	−1.9 (10)	−0.26	−4.89 (64)	−0.87
Total bond population, e		−0.54		−1.18		0.0

R_2 0.082 → 0.026

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[a] The C, N, and O one-center $2s^2$ populations are fixed at 1.00, 1.25, and 1.50, respectively. The two-center 2s2 scoefficients are set at zero. [b] In all the bonds the y axis is directed along the bond direction.

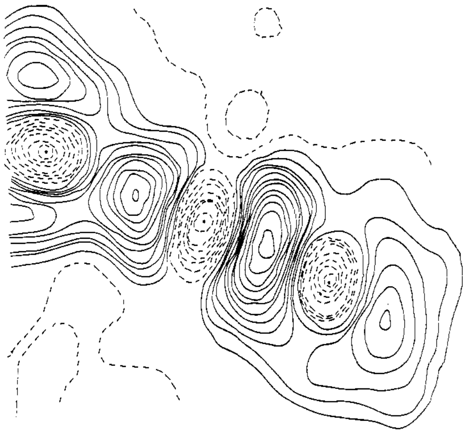

Figure 2. The difference function of ρ_{X-N} calculated in the plane of C(5)–C(1)–N(1). The scale is the same as in Figure 5. Atoms are indicated by dots with N(1) in the lower right hand corner. Negative and zero contours are broken. The contours are at 0.05-e/Å^3 increments.

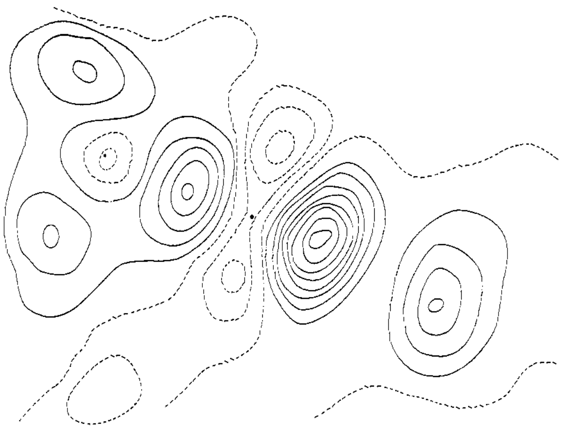

Figure 3. One-center population asphericity map in the plane of C(5)–C(1)–N(1). The refinement is described in Table II. The scale is the same as in Figure 2.

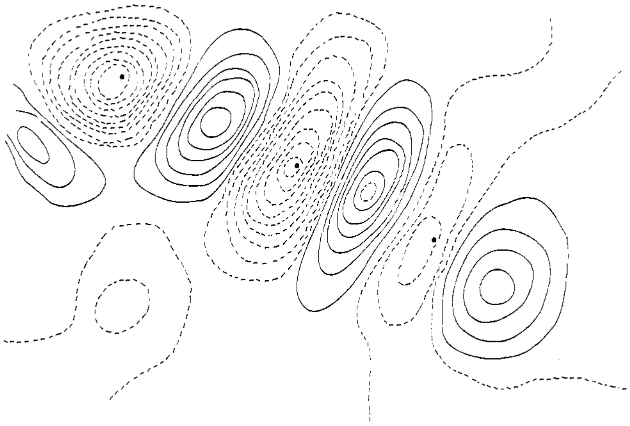

Figure 4. Two-center population asphericity map in the plane of C(5)–C(1)–N(1). The refinement is described in Table IV.

bonding region. The effects of these differences in the two basis sets are particularly pronounced for the cyano group due to the very short bond length and large concentration of electron density in the bonding area. It is worthwhile to note that a slightly larger exponent for the cyano carbon (or smaller exponent for the nitrogen) produces a polarity for CN more in accord with most, but not all,[15] theoretical treatments. However, a qualitative analysis of the X – N map for TCEO indicates that the aspherical charge distribution in all four C–N bonds is polarized toward the carbon atom,[5] and we could equally well construe the population refinements to be a quantitative substantiation of this interpretation.

The origin of the larger net charges for C(3) and N(3) is unclear, however; it apparently is not due to any systematic error in the neutron parameters since an extended L-shell refinement[14,16] with spherical shell scattering factors is independent of the neutron experiment and gives net charges of −0.15 (2) and +0.15 (2), respectively. An intermolecular effect is also unlikely since packing forces in the neighborhood of the cyano groups are not very different.[10] We note that there is a large correlation coefficient −0.68 between the two p_yp_y one-center products (the *g* axes of the exocyclic atoms are along the bond directions). The net charges on N(3) and C(3) are also highly correlated, and their sum is much better determined than their difference.

When the X – N map in Figure 2 is compared with the population asphericity maps for the plane of C(5)–C(1)–N(1) in the one-center and two-center approximations (Figures 3 and 4), it is clear that a better fit to the experimental charge distribution is obtained when the two-center density pieces which explicitly account for density in bonding regions are included. However, attempts to determine atomic populations from the orbital product coefficients introduce a certain arbitrariness concerning how the density associated with two-center terms should be partitioned. A simple Mulliken population analysis[17] which divides the overlap density equally between the adjoining atoms gives an unrealistically large charge separation. Alternatively, an evaluation of the gross charge in the cyano group as a whole involves only a decision as to the division of charge in the p_yp_y two-center term between the exocyclic and endocyclic carbons. This bond is expected to have almost no dipole. A refinement identical with that described in Table IV except for the inclusion of p_ys terms for each exocyclic carbon–carbon bond showed no reduction in the agreement factor which indicates that the C–C bond density is quite symmetric with respect to the midpoint of the bond. Thus, no significant error was introduced by dividing the density equally between the two carbon atoms. The cyano groups then have negative charges of −0.05, −0.09, −0.11, and −0.15. This is in qualitative agreement with the usual chemical characterization of the cyano group as strongly electron withdrawing and with ESCA results.

An interesting result which emerged from one-center refinements of α-oxalic acid dihydrate and cyanuric acid[14] was an apparent π → σ electron transfer relative to the INDO calculation for the carbon atom in oxalic acid and for all ring atoms in cyanuric acid. The one-center refinements for TCEO show a similar substantial transfer of π electrons into σ orbitals for both the exo-

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cyclic carbon and nitrogen atoms relative to the theoretical INDO results (Table V). The effect is especially pronounced in the case of the cyano carbon atom. Of special interest in this regard is the shape of the negative region associated with the cyano carbon atom in the one-center population asphericity map. The regions of greatest negative density appear as lobes symmetrically disposed around the carbon atom nuclear position in contrast to a minimum at the nuclear position in the X − N map. In the four C≡N bonds, the extension is similar for all directions perpendicular to the carbon–nitrogen atom internuclear axis up to the −0.10-e/Å^3 contour level. This implies that density has been transferred out of the p_xp_x as well as the p_zp_z one-center products. (Note that the *x* and *z* axes on the exocyclic atoms are perpendicular to the bond directions.)

Table V. σ and π Charges Obtained in Aspherical One-Center Refinement With STO Basis Set[a]

Atom	Method	s[b]	σ	π
C(1)	Exp	1.12	1.82	1.05
	INDO	1.12	0.91	1.89
C(2)	Exp	1.12	1.51	1.37
	INDO	1.12	0.91	1.89
C(3)	Exp	1.12	1.72	1.32
	INDO	1.12	0.91	1.89
C(4)	Exp	1.12	1.51	1.31
	INDO	1.12	0.91	1.89
N(1)	Exp	1.71	1.50	1.79
	INDO	1.71	1.24	2.18
N(2)	Exp	1.71	1.58	1.71
	INDO	1.71	1.24	2.18
N(3)	Exp	1.71	1.33	1.88
	INDO	1.71	1.24	2.18
N(4)	Exp	1.71	1.46	1.89
	INDO	1.71	1.24	2.18
Av exocyclic C	Exp	1.12	1.64	1.26
	INDO	1.12	0.91	1.89
Av N	Exp	1.71	1.47	1.82
	INDO	1.71	1.24	2.18

[a] These results refer to the refinement described in Table II. [b] The experimental populations of the 2s orbitals have been adjusted to the theoretical values. Compensating changes have been made in the spherical average of the coefficients of the $p\pi^2$ and $p\sigma^2$ orbital products.

The differences between the one-center population asphericity maps and the function ρ_{X-N} suggest that the one-center fit is not accurately reproducing the experimental charge distribution normal to the cyano group internuclear axis in the neighborhood of the carbon nucleus. The two-center model for TCEO gives a better fit to the experimental diffraction data than does the one-center model as evidenced by a lower *R* factor and by population asphericity maps which are in closer agreement with the X − N maps. It is therefore of interest to use the results of the two-center refinement in order to further investigate the origin of the apparent $\pi \rightarrow \sigma$ electron transfer at the cyano carbon atom. Extraction of relative π- and σ-electron populations when two-center terms are included is subject to the same ambiguities discussed above for the gross atomic charges. Therefore, we choose to deal with the cyano group as a whole and equally partition the p_yp_y two-center term between the exocyclic and endocyclic carbon atoms. (Note that for the two center products the *y* axes are always parallel to the bonds.)

Table VI indicates that while the one-center refinement shows a substantial $\pi \rightarrow \sigma$ electron transfer relative to the INDO result, the two-center refinement gives a σ to π ratio much closer to the theoretical value. The choice of which two-center density pieces are varied in the least-squares fit seems to have some effect on this ratio. Thus, when no p_ys coefficients are varied for the cyano bonds, the σ to π ratio for the four cyano groups ranges from 0.53 to 0.63 with an average value of 0.57 in close agreement with the INDO result. It appears that the $\pi \rightarrow \sigma$ migration observed in the one-center calculation for TCEO is due to the neglect of multicenter terms in the scattering factor formalism.

Table VI. Cyano Group σ and π Charges for One and Two-Center STO Refinements[a]

Group	Method	$p\sigma$[b]	$p\pi$	$p\sigma/p\pi$
CN(1)	One-center refinement	3.32	2.84	1.17
	Two-center refinement	1.72	4.62	0.37
	INDO	2.15	4.07	0.53
CN(2)	One-center refinement	3.09	3.08	1.00
	Two-center refinement	1.70	4.57	0.37
	INDO	2.15	4.07	0.53
CN(3)	One-center refinement	3.05	3.20	0.95
	Two-center refinement	1.85	4.42	0.42
	INDO	2.15	4.07	0.53
CN(4)	One-center refinement	2.97	3.20	0.93
	Two-center refinement	1.15	5.05	0.23
	INDO	2.15	4.07	0.53
Av	One-center refinement	3.11	3.03	1.02
	Two-center refinement	1.61	4.66	0.35
	INDO	2.15	4.07	0.53

[a] The density in the exocyclic carbon–carbon bond is divided equally between carbons. [b] The experimental populations of the 2s orbitals have been adjusted to the theoretical values. Compensating changes have been made in the spherical average of the coefficients of the $p\pi^2$ and $p\sigma^2$ orbital products.

Much of the discrepancy between the relative σ and π populations in the one- and two-center calculations may be due to the effectiveness of a p orbital with σ symmetry in simulating π electron density when this orbital is convoluted with a thermal function which has large amplitudes perpendicular to the bond axis. Under these conditions, the node on the internuclear axis characteristic of a static p_π function is no longer present. The large net charge accumulations at the cyano carbon and nitrogen atoms in the HF refinement are almost entirely due to the transfer of π electrons on nitrogen atom into the $p_y{}^2$ orbital product for the carbon atom. Since the carbon HF orbital is significantly more diffuse than the corresponding STO orbital, it will be directed deeper into the C–N bonding region and when thermally averaged will be especially capable of removing π electrons from nitrogen, although the $p_y{}^2$ population on nitrogen is also reduced. A similar explanation could account for the observed $\pi \rightarrow \sigma$ migration at the carbon atom in the one-center refinement of α-oxalic acid dihydrate.[14] The movement of electron density relative to the INDO result is out of the carbon $p_x{}^2$ into the carbon $p_z{}^2$ which is directed along the C–O(2) bond axis. The principal axis of molecular libration is directed almost perpendicular to this carbon–oxygen bond and will produce large thermal motion perpendicular to the plane of the molecule,[4] which is just the condition required for the activation of the above mechanism. Since π density in the carbon–

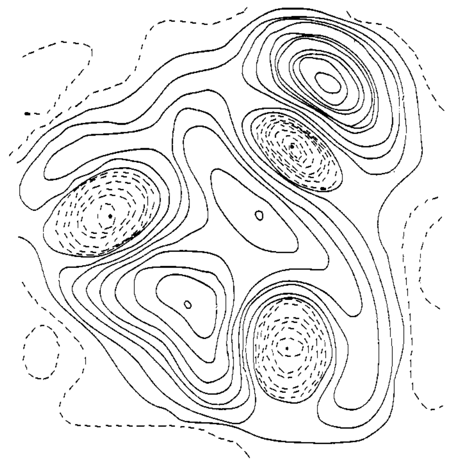
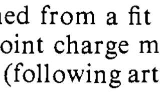


Figure 5. The difference function ρ_{X-N} calculated in the plane of the ethylene oxide ring. The oxygen atom is in the top right of the figure. The scale is the same as in Figure 2.

oxygen double bond would be better approximated by the more diffuse thermally averaged carbon p_y^2 one-center density piece, it is not surprising that the oxygen atoms in oxalic acid have σ to π ratios in better agreement with INDO results. The same type of charge migration has been observed for all ring atoms in a one-center refinement of cyanuric acid.[14] A rigid body analysis of the neutron diffraction data[6] shows that the root-mean-square amplitudes of vibration are twice as large perpendicular to the molecular plane as compared to other directions, thus causing the observed projection of π density into the π orbitals when the two-center orbital products are neglected.



The —C——C— Ring Atoms. The net atomic charges for atoms in the ethylene oxide ring as derived from STO one-center refinements (Tables II and III) are in fairly good agreement with INDO approximate self-consistent-field calculations which give values of +0.18 and −0.20 for the endocyclic carbon and oxygen, respectively. In addition, the results are in qualitative agreement with net atomic charges of 0.25 and −0.33 obtained from a fit of photoelectron spectra for TCEO to a point charge model for the potential at the atomic nuclei (following article).

In contrast to earlier results for α-oxalic acid dihydrate and cyanuric acid,[14] refinements using spherical valence shell scattering factors with variable occupancies give net atomic charges which, in some cases, are in marked disagreement with the aspherical one-center treatment. For example, the extended L-shell projection method with an STO atomic valence shell gives net charges of −0.06 (2) and −0.10 (2) for the endocyclic carbon atoms C(5) and C(6), respectively. One might argue that a least-squares procedure based on a spherical atom model would more readily place additional electron density on nearly spherical atoms such as C(5) and C(6) than on atomic centers where aspherical features were more pronounced. It is obvious that caution must be used in interpreting ELS refinement results for a molecule with large intramolecular differences in the acentric electron features around the constituent atom centers.

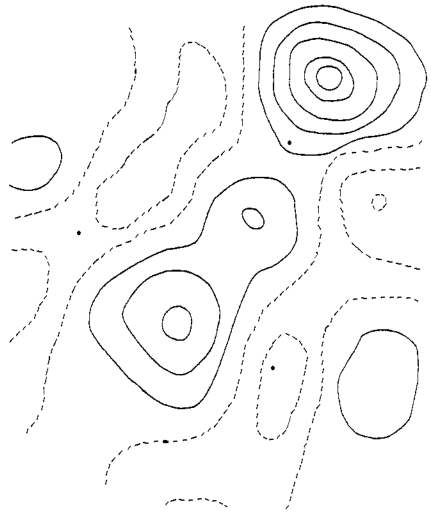


Figure 6. One-center population asphericity map in the plane of the ethylene oxide ring. The refinement is described in Table II. The scale is the same as in Figure 2.

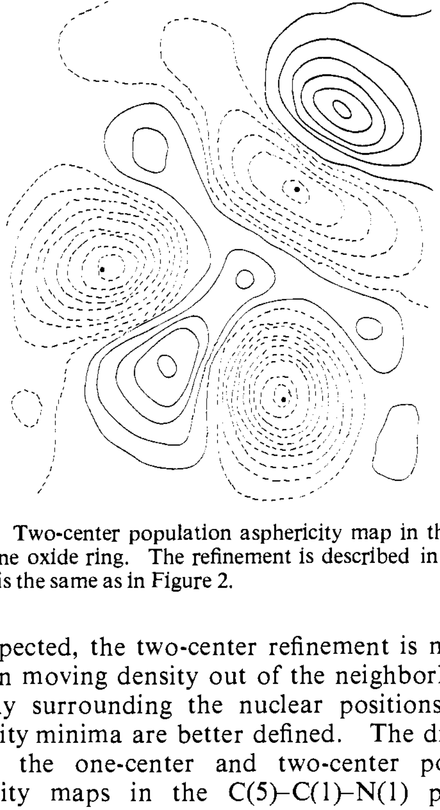


Figure 7. Two-center population asphericity map in the plane of the ethylene oxide ring. The refinement is described in Table IV. The scale is the same as in Figure 2.

As expected, the two-center refinement is more successful in moving density out of the neighborhood immediately surrounding the nuclear positions so that the density minima are better defined. The differences between the one-center and two-center population asphericity maps in the C(5)–C(1)–N(1) plane are smaller in the bonding and lone-pair regions than corresponding differences in the maps for the ring atoms in cyanuric acid (unpublished results) and for the plane of the ethylene oxide ring in TCEO (Figures 5–7). In the latter case, the one-center refinement generates only a small accumulation of charge density in the C–O bonds. The oxygen atom lone-pair feature is accurately reproduced relative to the two-center calculation; however, both population asphericity maps show this density to be less than in the X − N map. The "bent bonds" are clearly evident in the two-center map as is the concentration of density in the middle of the ring.

An examination of the one- and two-center orbital product coefficients in Table IV confirms that density is shifted by orbital products with zero overlap integrals in such a way as to describe lone-pair and "bent bond" features. Thus, all sp_y one-center products on nitrogen have negative coefficients as does the sp_z product on the oxygen. The positive x coordinate in the atomic axis system for an endocyclic carbon makes a small angle with respect to the C(5)–C(6) bond and the calculated coefficients for these density pieces correspond to density accumulations adjacent to the carbon–oxygen internuclear axis external to the ring. The p_zs and sp_z two-center terms between oxygen and the endocyclic carbons have positive coefficients which move charge from outside the ring near the C–O axes to regions inside the ring. A redistribution in the opposite direction is brought about by a positive coefficient for the p_zp_y two-center product. Note the substantial number of electrons placed in the C(5)–C(6) p_zp_z orbital product. This locates density adjacent to the endocyclic carbon–carbon bond axis both inside and outside the ring. The negative coefficient for p_xp_y shifts electron density across this axis and contributes to the accumulation of bonding density external to the ring.

The problem of statistical correlation between orbital product coefficients is often severe. For example, the physically unreasonable negative bond population obtained with the two-center formalism is attributable to strong correlations with one-center density pieces. Although the ultimate effect may be minimal in terms of obtaining population asphericity maps which agree closely with X − N maps, the coefficients of the individual orbital products are not well determined. The fewer the number of variables which can be used to obtain a satisfactory level of fit to the experimental density, the more meaningful will be the individual product coefficients. We find it advantageous in this regard to refer to molecular wave functions derived from INDO calculations to help decide which coefficients will be most significantly nonzero.[9] Often this represents just a substantiation of chemical intuition. Thus, when eight additional variable coefficients representing the p_xp_x and p_zp_z two-center terms for each exocyclic carbon–carbon bond were refined in addition to the coefficients listed in Table IV, no decrease in the R factor was observed and none of the populations were significantly nonzero. This agrees with simple valence bond concepts which classify the bond as almost entirely σ in character. A more detailed analysis of the correlation problem in the two-center population refinement is given in a following article.[9]

Conclusions

The main conclusions of this work are considered to be as follows. (1) Two-center population parameters give an adequate representation of the experimental electron density, but the parameters from the one-center refinement do not properly represent the aspherical features of the density maps. (2) There is a difference between net atomic charges obtained by ELS and aspherical treatments, which may be typical of molecules in which there is a variation in symmetry of the local environments around the atoms. Only the two-center treatment gives a chemically realistic description of the net charge in the cyano groups. (3) Thermal smearing of one-center orbitals directed along the bonds create a density distribution which is very similar to the density function of a $p\pi$–$p\pi$ two-center orbital product. The relative σ and π populations obtained from the one-center refinement are therefore ambiguous.

We consider the above analysis to be a first approximation to the treatment of aspherical scattering effects both theoretically and experimentally. Even though the full sphere of the X-ray data for this study had an internal discrepancy factor on F of 0.8%, it is clear that precision alone is not sufficient and that future studies for most compounds should concentrate on low-temperature analyses of 40°K or less in order to reduce low-energy anharmonic thermal effects and thermal diffuse scattering. Additional theoretical work is needed to formulate the aspherical scattering problem with the least number of uncorrelated parameters. Work in both of these areas is currently in progress in our laboratories.