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CNDO/2 Difference Electron Density Contours in Saturated Three-membered Rings

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Theoretical difference electron density contours in the NCC, CCC, and OCC ring planes of ethyleneimine quinone, *cis*-1,2,3-tricyanocyclopropane and tetracyanoethylene oxide molecules, respectively, were calculated by the CNDO/2 molecular orbital method. They are qualitatively in good agreement with the experimental contours, and have reproduced the most characteristic features of the observed electron distributions in the bent bonds in the three-membered rings. The theoretical difference contours in the three-membered ring planes of aziridine, cyclopropane and oxirane molecules have shown essentially the same bonding electron distributions as the corresponding contours in the more complex molecules mentioned above.

The saturated CCC, NCC, and OCC three-membered rings are typical examples of highly strained structures. Coulson and Moffitt[1] have shown the bent bond nature in cyclopropane by a valence bond treatment of the molecule. Several diffraction studies of electron distributions have also revealed the bent bonds in these three-membered rings: the CCC rings in 2,5-dimethyl-7,7-dicyanonorcaradiene[2] and in *cis*-1,2,3-tricyanocyclopropane,[3] the OCC ring in tetracyanoethylene oxide,[4] and the NCC ring in ethyleneimine quinone.[5]

Although various kinds of molecular orbital calculations have recently been reported on these three-membered ring systems,[6] the results are not given in a form suitable for comparison with diffraction observations. In the present work, therefore, appropriate difference electron density contours were calculated by the semi-empirical CNDO/2 molecular orbital method,[7] and compared with the experimental contours.[3–5]

Theoretical Model

Let us first summarize the definition of the X-ray difference electron density. It is usually defined as:

$$\overline{\Delta\rho_{\mathrm{o}}}(\boldsymbol{r}) = \bar{\rho}_{\mathrm{cryst}}(\boldsymbol{r}) - \sum_{j}^{\mathrm{atoms}} \bar{\rho}_{j}(\boldsymbol{r}), \tag{1}$$

where $\bar{\rho}_{\mathrm{cryst}}$ is the observed electron density in the crystal; the second term is the calculated electron density of the "free atoms model", in which the atoms (or the ions) in the unit cell of the crystal are assumed to be free atoms (or free ions) with spherical electron distributions ρ_j, and be placed at the same positions as they occupy in the crystal. The bars on the ρ's indicate the time-average over thermal vibration.

In practice, however, $\overline{\Delta\rho_{\mathrm{o}}}$ is obtained by Fourier summation of the differences between the observed and calculated structure factors, F_{o}—F_{c}, over lattice planes:

$$\overline{\Delta\rho_{\mathrm{o}}}(\boldsymbol{r}) = (1/V)\sum_{h}\sum_{k}\sum_{l}[F_{\mathrm{o}}(hkl) - F_{\mathrm{c}}(hkl)] \times \exp\left[-2\pi i \boldsymbol{S}_{hkl}\cdot\boldsymbol{r}\right], \tag{2}$$

where V is the unit cell volume of the crystal, and $\boldsymbol{S}_{hkl}$ is the scattering vector of a plane, hkl. F_{c} is the Fourier transform of the second term in Eq. (1); it can be calculated by:

$$F_{\mathrm{c}}(hkl) = \sum_{j}^{\mathrm{atoms}} f_{j} T_{j} \exp 2\pi i \boldsymbol{S}_{hkl}\cdot\boldsymbol{r}_{j}, \tag{3}$$

where f_j is the theoretical free atom scattering factor of the j-th atom in the unit cell, whereas the nuclear position $\boldsymbol{r}_j$ and the thermal vibration factor T_j can be obtained from crystal structure analysis. The X-ray difference density defined by Eqs. (1)—(3) is called the difference Fourier synthesis or the D-synthesis.

A theoretical difference electron density can be defined in analogy with Eq. (1) as follows:

$$\Delta\rho_{\mathrm{c}}(\boldsymbol{r}) = \rho_{\mathrm{mol}}(\boldsymbol{r}) - \sum_{j}^{\mathrm{atoms}} \rho_{j}(\boldsymbol{r}), \tag{4}$$

where ρ_{mol} is the theoretical electron density of a free molecule; the second term represents again the "free atoms model", the summation extending over the atoms which constitute the molecule. The theoretical difference density of Eq. (4) was originally introduced by Roux and coworkers.[8] For a molecule in a closed shell electron configuration, the molecular electron density can be expressed as:

$$\rho_{\mathrm{mol}}(\boldsymbol{r}) = 2\sum_{i}^{\mathrm{occ}} \psi_{i}^{2}(\boldsymbol{r}), \tag{5}$$

where ψ_i is the i-th molecular orbital, and the summation is taken over the molecular orbitals occupied with pairs of electrons.

In the CNDO/2 approximation,[7] molecular orbitals are obtained as linear combinations, with coefficients $\boldsymbol{C}_{\mathrm{o}}$, of the orthogonalized atomic orbitals of the valence shells. Therefore, deformation of the 1s core electrons by molecule formation is ignored in the present model. Eq. (5) can be evaluated in a straightforward way by transforming the coefficients $\boldsymbol{C}_{\mathrm{o}}$ to the coefficients $\boldsymbol{C}_{\mathrm{s}}$ for the Slater type atomic orbitals by the Löwdin transformation $\boldsymbol{C}_{\mathrm{s}} = \boldsymbol{S}^{-1/2}\,\boldsymbol{C}_{\mathrm{o}}$.[9] The electron density of a spherical free atom, ρ_j in Eq. (4), can be represented by a single valence s atomic orbital $\chi_{\mathrm{s},j}$:

$$\rho_{j}(\boldsymbol{r}) = N_{j}\chi_{\mathrm{s},j}^{2}(\boldsymbol{r}), \tag{6}$$

where N_j is the number of the valence electrons of the j-th neutral free atom; N_j is 1, 4, 5, and 6 for H, C, N, and O atoms, respectively. Eq. (6) is consistent with the CNDO/2 scheme in which the 2s and 2p atomic orbitals of an atom are given the same Slater exponent; in this case, spherically averaged density distribution of a 2p electron is identical with the density distribution of a 2s electron. The theoretical difference density defined by Eqs. (4)—(6) may be called the "molecule—free atoms" density.

It is evident from the definitions that both the experimental and theoretical difference densities represent the deviations of the densities in a crystal or in a molecule from those of the "free atoms model". Although both densities represent approximately the same physical quantity, the following two factors distinguish between the two. (a) The effect of thermal vibration (the thermal smearing of the electron density) is not taken into account in $\Delta\rho_c$, whereas $\overline{\Delta\rho_o}$ is inevitably influenced by thermal vibration. The effect will be examined in future studies. (b) The effect of the crystal field (the intermolecular interaction) is ignored in the calculation of ρ_{mol}. The effect is considered to be generally small compared with that of chemical bonding, but strong interactions such as hydrogen bonding may not be ignored.

Results and Discussion

The theoretical difference electron density contours in the NCC, CCC, and OCC ring planes of ethyleneimine quinone, *cis*-1,2,3-tricyanocyclopropane and tetracyanoethylene oxide molecules, respectively, were calculated by Eqs. (4)—(6), and compared with the experimental contours.[3-5] The molecular geometries found in the crystal[3-5] were used for the CNDO/2 calculations.

Ethyleneimine Quinone. The electron density in ethyleneimine quinone, 2,5-di(1-aziridinyl)-*p*-benzoquinone, $C_6H_2O_2(NC_2H_4)_2$, was studied by X-ray at 110 K.[5] The two aziridinyl groups are equivalent in the crystal because the molecule lies on an inversion center.

The CNDO/2 calculations[7] were performed for the whole molecule with 72 valence electrons. The "molecule–free atoms" map in the NCC ring plane (Fig. 1) may be compared with the X-ray contours (Fig. 2).

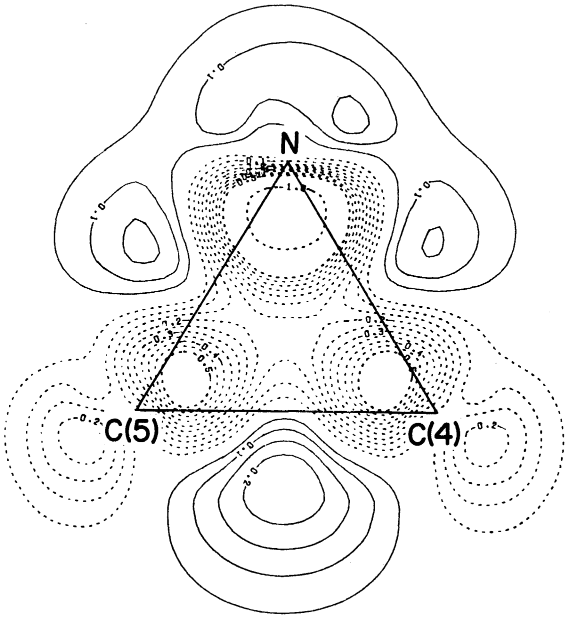


Fig. 1. Theoretical difference electron density contours, the "molecule—free atoms" map, in the NCC ring plane of ethyleneimine quinone.
Negative contours are dotted and zero contours are omitted. The contours are at intervals of 0.05 above −0.5, and 0.5 below −0.5 e.Å^{-3}.

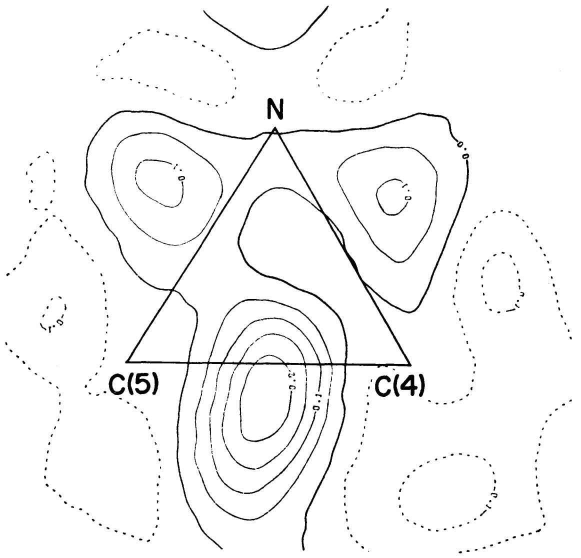


Fig. 2. X-Ray difference Fourier map in the NCC ring plane of ethyleneimine quinone.[5]
Negative contours are dotted. The contours are at intervals of 0.05 e.Å^{-3}.

The two maps are qualitatively in good agreement in the internuclear regions where both the theoretical and experimental densities are less influenced by systematic errors (see below). Both maps clearly illustrate characteristic features of the bent bond; bonding electron peaks of about 0.1 and 0.2 e.Å^{-3} are observed in the N–C and C–C bonds respectively, but displaced outside of the NCC triangle. The broad peak at the back of the nitrogen atom in the theoretical map is a tail-off of the nitrogen lone pair electrons.

The sharp depressions near the nuclear positions in the theoretical map are absent in the X-ray map. The following systematic errors in $\overline{\Delta\rho_o}$ and $\Delta\rho_c$ may account for the discrepancies: (a) The atomic parameters (the nuclear positions $\boldsymbol{r}_j$ and the thermal parameters T_j) determined by the X-ray structure analysis may be systematically in error. In fact, they were so determined as to give the best fit between the observed and calculated structure factors, that is, to minimize $\overline{\Delta\rho_o}$ in Eq. (2). Therefore, any aspherical features of electron distributions around the nuclear positions which could be fitted by the expression Eq. (3) were absorbed into apparent changes of atomic parameters, especially into those of anisotropic thermal parameters. In this respect, determination of the atomic parameters by neutron diffraction is preferable.[10] (b) Thermal vibration which will considerably smear out the sharp depressions is not taken into account in the present theoretical model. (c) The CNDO/2 electron density near the nuclear position may be a poor approximation to the true density.

cis-1,2,3-Tricyanocyclopropane. The electron density in *cis*-1,2,3-tricyanocyclopropane, $(CHCN)_3$, was studied by Hartman and Hirshfeld[3] by X-ray at room temperature. The molecule lies on a three-fold symmetry axis through the center of the ring in the crystal. Bonding electron peaks of 0.05 e.Å^{-3} have been observed in the C–C bonds, 0.32 Å outside of the CCC triangle.[3]

The molecule has 42 valence electrons. The "mole-

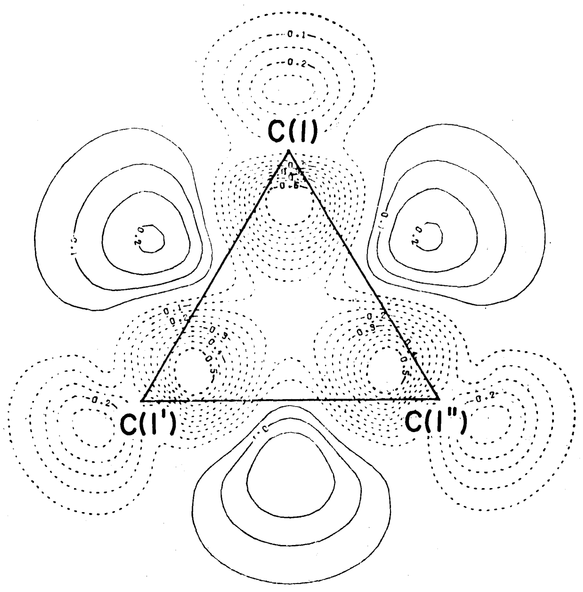


Fig. 3. The "molecule—free atoms" map in the CCC ring plane of *cis*-1,2,3-tricyanocyclopropane. The scale is the same as in Fig. 1.

cule—free atoms" map in the ring plane is shown in Fig. 3. The distribution of the bonding electrons is in qualitative agreement with the X-ray observations.[3] However, the theoretical peak heights of 0.15 e.Å^{-3} are three times higher than the experimental ones.

Tetracyanoethylene Oxide. The electron density in tetracyanoethylene oxide, $OC_2(CN)_4$, was studied by Matthews and Stucky[4] by a combined use of X-ray and neutron diffraction at room temperature. In this case, the electron density of the "free atoms model" in Eqs. (1)—(3) was calculated with the atomic parameters determined by neutron diffraction; a difference electron density map obtained with X-ray F_o and neutron F_c is called an X—N map.[10] The X—N map in the OCC ring plane of the molecule has revealed a bonding peak

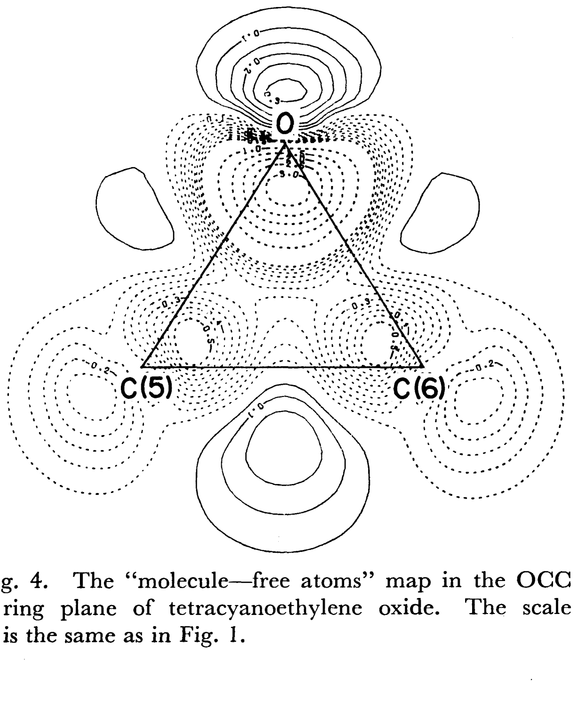
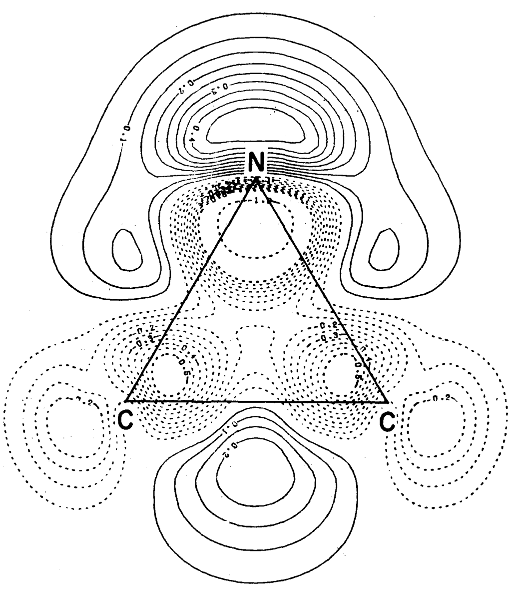
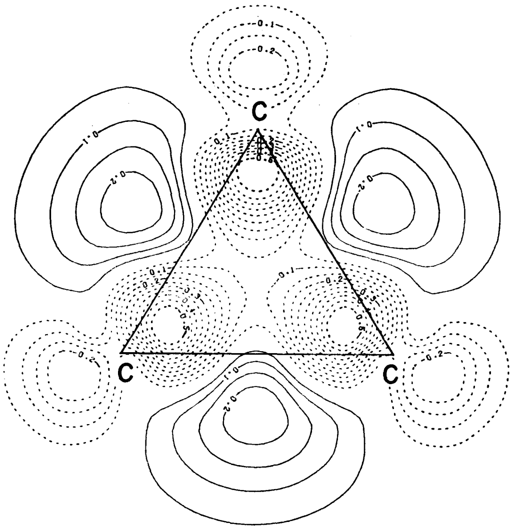


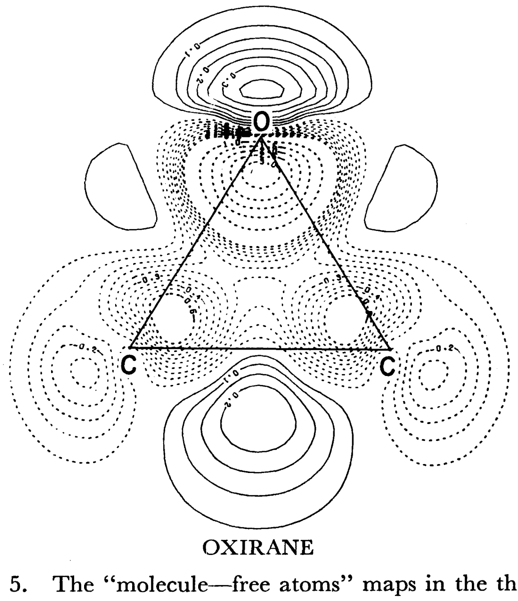
Fig. 4. The "molecule—free atoms" map in the OCC ring plane of tetracyanoethylene oxide. The scale is the same as in Fig. 1.



AZIRIDINE



CYCLOPROPANE



OXIRANE

Fig. 5. The "molecule—free atoms" maps in the three-membered ring planes of aziridine, cyclopropane and oxirane. The scale is the same as in Fig. 1.

of 0.45 e.Å^{-3} in the C–C bent bond region, but the bend in the C–O bonds has been obscured by the tail-off of the broad peak of 0.35 e.Å^{-3} at the center of the ring.[4]

The molecule has 50 valence electrons. The "molecule—free atoms" map in the ring plane is shown in Fig. 4. The positive peak in the C–C bent bond is much higher than those in the C–O bonds, qualitatively in agreement with the experimental observations. Quantitatively, however, the theoretical peak heights are about three times lower than the experimental ones. The experimentally observed electron build-up at the center of the ring is not reproduced in the theoretical map.

It should be noted that in this case of tetracyanoethylene oxide, in which the experimental difference density was obtained with the neutron atomic parameters, the sharp depressions near the nuclear positions in the theoretical map are in qualitative agreement with the experimental observations.[4]

Related Molecules. The "molecule—free atoms" maps in the ring planes of aziridine, $NH(CH_2)_2$, cyclopropane, $(CH_2)_3$ and oxirane, $O(CH_2)_2$ molecules were also calculated (Fig. 5). The molecular geometries used were taken from the literature.[11] The electron distributions in the bent bond regions are essentially the same as those obtained for ethyleneimine quinone, *cis*-1,2,3-tricyanocyclopropane and tetracyanoethylene oxide, respectively.

The numerical calculations were performed on the FACOM 230—75 computer of this Institute. The author wishes to thank Dr. Tsunetoshi Kobayashi of the University of Tokyo for his valuable advice in performing the CNDO/2 calculations.

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