Deformation electron density in the organic paramagnetic $C_{13}H_{17}N_2O_2$

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(Submitted 17 May 1979)
Pis'ma Zh. Eksp. Teor. Fiz. **30**, No. 2, 107–110 (20 July 1979)

A different map is obtained from single-crystal x-ray diffraction data and the electron distribution in free atoms, making it possible to form an opinion about the location of the valence electrons in the stable nitroxyl radical $C_{13}H_{17}N_2O_2$.

PACS numbers: 61.65. + d, 61.10.Fr

Stable nitroxyl radicals—a new class of organic paramagnetics—are attracting interest by virtue of their distinctinve physical and chemical properties.[1,2] The nonlinear optical characteristics of the $C_{13}H_{17}N_2O_2$ crystal have recently been discovered and examined.[3] The structure-sensitive properties of these compounds are determined by the electron structure of the radicals and by the character of the exchange interactions, which depend on the relative arrangement of the paramagnetic centers in the crystal. The goal of this work is to establish experimentally the distribution of the deformation electron density in the $C_{13}H_{17}N_2O_2$ single crystal. By the deformation density we mean the difference $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \Sigma\rho_i(\mathbf{r} - \mathbf{r}_i)$, where $\rho(\mathbf{r})$ is the electron density distribution in the crystal, $\Sigma\rho_i(\mathbf{r} - \mathbf{r}_i)$ is the sum of the spherically symmetrical densities of the free (noninteracting) atoms of the structure. In the determination of the deformation density in crystals the most complicated procedure is that of excluding the effect of the anisotropy of the thermal vibrations of the atoms on $\delta\rho(\mathbf{r})$. There are two ways to overcome this obstacle: 1) combined analysis of x-ray and neutron experiments, 2) a parallel investigation of the total and high-angle x-ray diffraction data.[4] We have pursued the second of these approaches.

The integral intensities of the diffraction reflections were measured on a spherical sample with $\mathbf{r} = 0.181$ (4) mm (Mo radiation, graphite monochromator) to $(\sin\theta)\lambda^{-1} \leqslant 1.00$ Å^{-1} in the DAR-UMB automatic diffractometer. After discarding the defective reflections and reflections with $|F_{hkl}|_{\exp} < 3\sigma_{|F|}$, a set of 1220 experimental $|F_{hkl}|$ was formed, 404 reflections of which with $(\sin\theta)\lambda^{-1} > 0.57$ $^{-1}$ constituted the high-angle data file. If the x-ray scattering by the internal $1s^2$ electrons C, N, and

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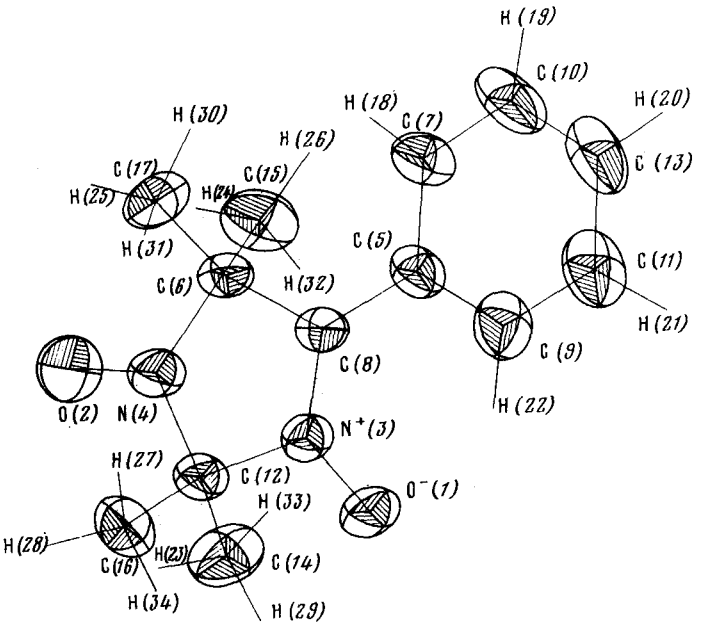

FIG. 1. Structure of the stable $C_{13}H_{17}N_2O_2$ nitroxyl radical.

O atoms amounts to 33.3, 28.6 and 25.0% of the total at the zero angle, then the corresponding fraction at the angle $(\sin\theta)^{-1} = 0.55$ Å^{-1} increases to 98.3, 95.5 and 84.3%. This fact makes it possible, by using the high-angle data, to obtain by the least-squares method the coordinates and parameters of the anisotropic thermal motion of atoms that are practically free of the influence of the asymmetry of the valence electron distribution. The crystallographic characteristics of the compound $C_{13}H_{17}N_2O_2$ are: $a = 7.584$ (8), $b = 9.500$ (13), $c = 18.127$ (94) Å, $\gamma = 76.15(10)°$, symmetry group *Bb*.

The structure of the $C_{13}H_{17}N_2O_2$ radical is shown in Fig. 1. In order to preserve the clarity of the figure the indicating surfaces of the thermal virbations of the H atoms are replaced by points. The five-membered heterocycle, sixmembered phenyl ring and the 2 atoms of the O radical lie in one plane. The CH_3 groups, joined to the C (6) and C (12) atoms, are arranged in pairs above and below this plane. Figure 2 shows the cross sections $\delta\rho(\mathbf{r})$ by the following planes: a) deviating the least from the O(1), O(2), N(3), N(4), C(5)—C(13) atoms; b) passing through the C(12), C(14), C(16) atoms; c) and d) containing the O(2)—N(4), O(1)—N(3) bonds and orthogonal to the plane of the radical. The positive deformation electron density is expressed by single-charged integers, with a unit corresponding to 0.1 of an electron per cubic Å. The C_6H_5 phenyl ring enters into the composition of the radical. It is known that it is a regular hexagon with one and one-half C—C bonds. Equal clusters $\delta\rho(\mathbf{r})$ should be located at the middles of its six bonds. The scatter in the locations and heights of these density concentrations serves as an objective criterion of the accuracy of the obtained distribution. In the five-membered heterocycle the largest cluster $\delta\rho(\mathbf{r})$ indicates the only

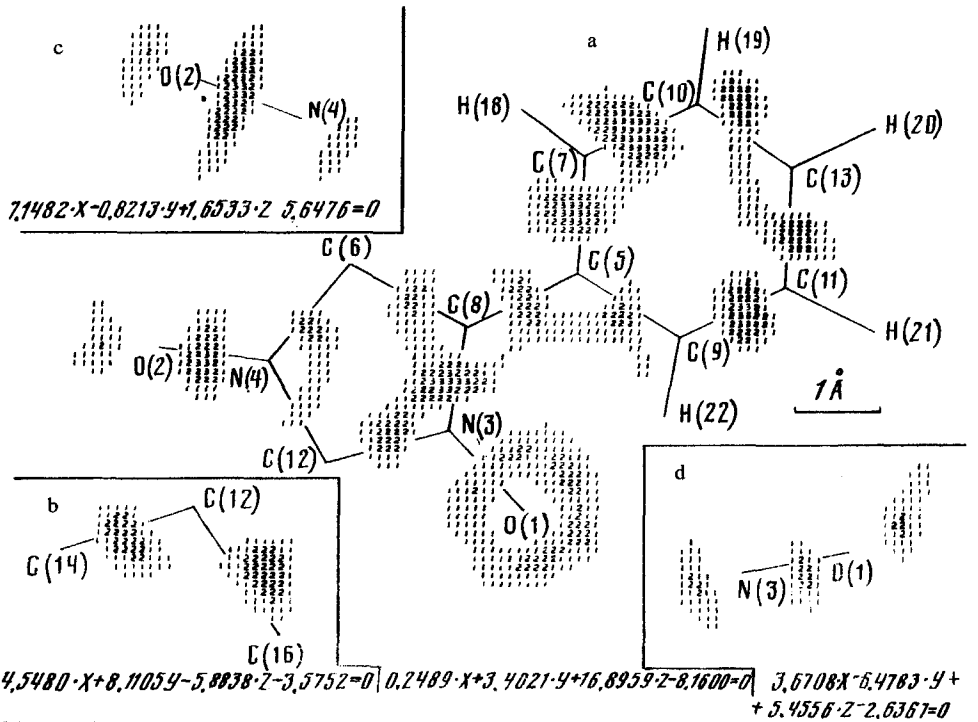

FIG. 2. Deformation electron density cross sections of $C_{13}H_{17}N_2O_2$ radical. Equations of planes are given in crystallographic coordinates.

double bond C(8) = N(3) in the cycle. The rest of the C—C and C—N bonds in this ring are single. The bonds with the C atoms of the methyl groups, which do not lie in the plane of the radical, are shown in Fig. 2(b).

Of greatest interest are the atomic groupings $>N^+(3)—O^-(1)$ and $>N(4)=O(2)$, each of which is shown by two cross sections in Fig. 2. An electron transfer from the nitrogen to the oxygen occurs in the first fragment, which leads to the thick $\delta\rho(\mathbf{r})$ halo near the O(1) atom. One of the density concentrations in this halo indicates the O(1)... H(22) bond, which closes the additional hexacycle O(1), N(3), C(8), C(9), H(22) and causes the planar configuration of the radical. The other density clusters in this halo can be attributed to the unshared electron pairs of the $O^-(1)$ ion. The accuracy of the obtained $\sigma\rho(\mathbf{r})$ map does not allow a more definite statement about the localization of these pairs. The deformation density picture is different in the vicinities of the paramagnetic fragment N(4)—O(2). The positive density $\delta\rho(\mathbf{r})$ at this bond is displaced somewhat from its center toward the electronegative oxygen. There is a well-defined electron cloud behind the O(2) atom, corresponding to a genuine electron pair. In accordance with existing concepts the unpaired electron, responsible for the paramagnetism, should occupy the π-orbital orthogonal to the plane of the radical and should be distributed between the O and N atoms. Figures 2(c) and 2(d) make it possible to compare the $\delta\rho(\mathbf{r})$ on the N(4)—O(2) and $N^+(3)—O^-(1)$ bonds in the orthogonal [Fig. 2 (a)] planes. The considerably greater thickness and extent of the density concentration on the N(4)—O(2) bond compared with the $N^+(3)$—

$O^-(1)$ indicates the localization region of the unpaired electron of the paramagnetic fragment N(4)—O(2). The N(4)—O(2) dumbbells, multiplied by the symmetry planes of the grazing b reflection, are aligned parallel to the b axis of crystal in a zigzag-shaped chain with a 38.1° angle between adjacent links and N(4)...N′(4), O(2)...O′(2) spacings of 5.304 and 4.991 Å, respectively. The shortest distance between adjacent chains is defined by the translation $a = 7.584$ Å.

The authors wish to thank B. K. Vaĭnshteĭn for his initiative in organizing the investigation, B. L. Volodarskiĭ, G. S. Belikkova, V. D. Shigorin for the synthesis, growing and description of the $C_{13}H_{17}N_2O_2$ single crystals, A. B. Tovbis for writing the program for computing the arbitrary cross sections ρ (**r**) and M. A. Poraĭ-Koshits for discussing the results.

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