

Charge Density Study on Bullvalene ($C_{10}H_{10}$) *

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Z. Naturforsch. **48a**, 55–57 (1993); received December 31, 1991

Low-temperature single-crystal neutron and X-ray diffraction data were collected for bullvalene (Figure 1). X–N Fourier and multipole static deformation electron density maps were calculated and compared. Atomic mean-square-displacement parameters were analysed in the framework of the rigid-body motion model and the residual amplitudes ($U_{\text{obs}} - U_{\text{TLS}}$) were graphically interpreted. The preliminary results presented here reveal either a bias in the X-ray anisotropic displacement parameters (ADPs) due to improper modelling of the electron density or unresolved errors in the neutron data.

Key words: Dynamic deformation density (DDD); Static deformation density (SDD); Multipole refinement; Anisotropic displacement parameter (ADP); Root-mean-square displacement surface (RMSDS); Rigid-body motion (RBM).

X-ray Data

Bullvalene, tricyclo-[3.3.2.0^{2,8}]-deca-2,5,8-triene, $M_r = 130.2$, P_{2_1}/n , $Z = 4$, $a = 6.106(2)$, $b = 20.584(13)$, $c = 6.122(5)$ Å, $\beta = 116.00(2)^\circ$, $V = 691.6$ Å³, (MoK α) = 0.71068 Å, $\mu = 0.76$ cm⁻¹, $T = 110(1)$ K, $((\sin \Theta)/\lambda)_{\text{max}} = 1.05$ Å⁻¹. From 9740 measured reflections 6479 were unique, $R = 0.0155$ for internal merging. The results of the neutron diffraction measurement have been published [1].

Multipole Refinement

In addition to the conventional treatment of the observations, multipole refinement (MOLLY [2]) was carried out on the X-ray data ($R = 0.0342$, $R_w = 0.0229$ for 4480 reflections with $F > 3\sigma(F)$ and $w = 1/\sigma(F)$). Adopting approximate C_{3v} molecular symmetry, four types of chemically different carbon atoms were considered, for which the valence density was described up to the hexadecapolar level of the expansion.

Further restraints dictated by the local site symmetries of each atom were introduced to decrease the number of variables to be refined. The positional and thermal parameters of the hydrogen atoms were fixed at the values obtained from the neutron measurement, and the charge asphericity was represented by a bond directed dipole. The two ethylenic hydrogen atoms were assumed to be chemically equivalent and their density parameters constrained to be equal. Radial screening parameters (α) for both the Hartree-Fock and Slater-type orbitals were also included in the refinement.

Deformation Densities

DDD maps were generated by X–N Fourier synthesis, where only the low-order data $((\sin \Theta)/\lambda)_{\text{max}} =$

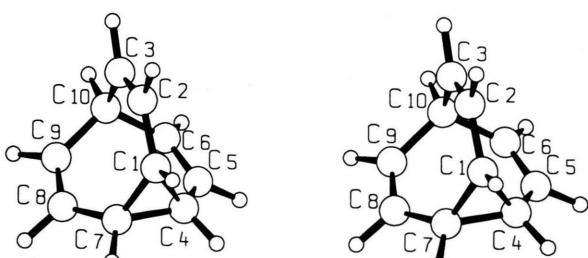


Fig. 1. Stereo drawing of the bullvalene molecule (SCHAKAL 88) [6].

* Presented at the Sagamore X Conference on Charge, Spin and Momentum Densities, Konstanz, Fed. Rep. of Germany, September 1–7, 1991.

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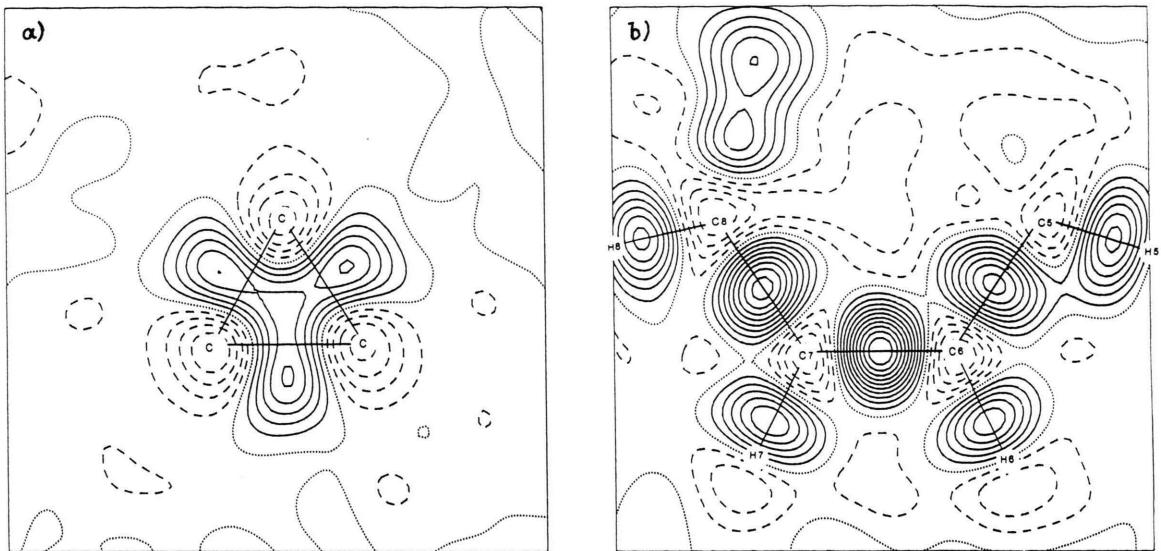


Fig. 2. X-N Fourier maps in the plane of the cyclopropane ring (a) and the ethylene wing (b). Contour intervals: $0.05 \text{ e}\text{\AA}^{-3}$.

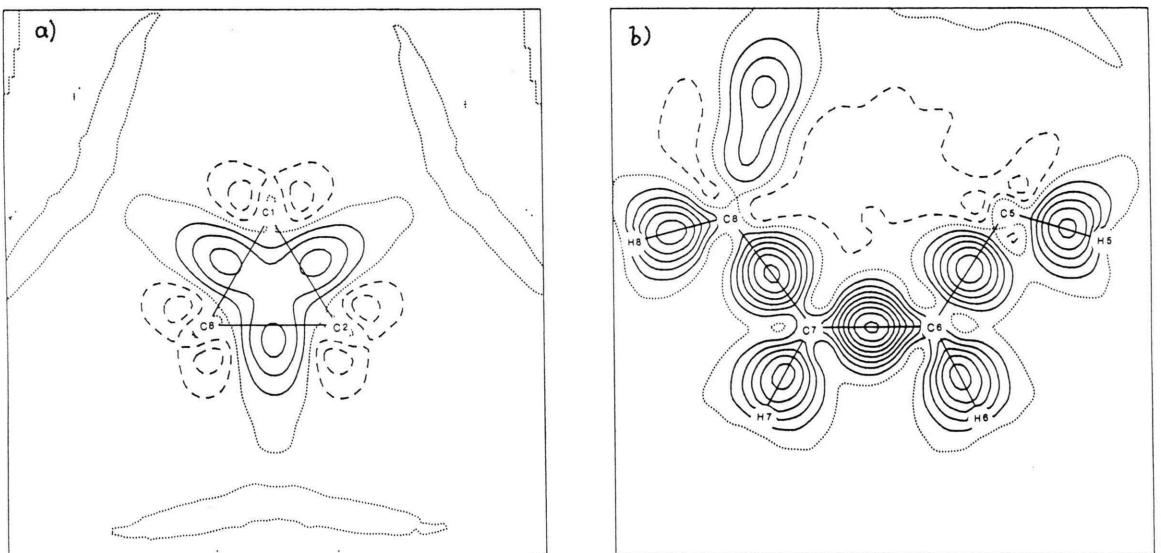


Fig. 3. Static deformation density in the plane of the cyclopropane ring (a) and the ethylene wing (b). Contour intervals: $0.1 \text{ e}\text{\AA}^{-3}$.

0.7 \AA^{-1}) were included in the summation, and the neutron ADPs were scaled by an overall isotropic mean-square-displacement parameter fitted to the X-ray data. The maps presented in Fig. 2 are symmetry-averaged sections in the plane of the three-membered ring and the ethylenic wing. In Fig. 3 the correspond-

ing static deformation densities (SDDs), as calculated from the refined multipole populations, can be seen. Both types of maps clearly reveal the bent bond in the cyclopropane ring. Sections perpendicular to and through the center of different types of C-C bonds show their typical characteristics (Figure 4).

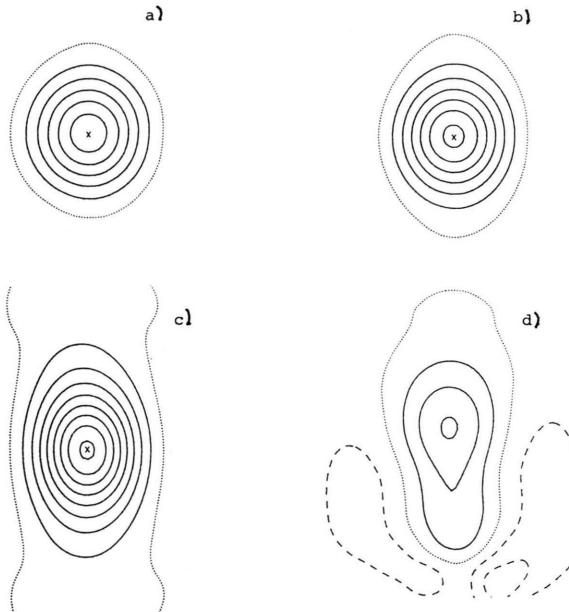


Fig. 4. Static deformation density in the sections perpendicular to and through the center of different C-C bonds: (a) single, (b) exocyclic single with π -character, (c) double, (d) bent bond in the ring. Contour intervals: 0.1 eÅ^{-3} .

The exocyclic bond appears to have partial π -character, supporting the concept of the conjugation observed for cyclopropyl derivatives [3].

Thermal-Motion Analysis

ADPs for both observations were tested against the rigid body motion (RBM) model (THMA11) [4]. In both cases good fits were achieved. The difference between the X-ray and neutron data can mainly be described by the translation component. In Fig. 5 the residual ADPs ($\Delta U = U_{\text{OBS}} - U_{\text{TLS}}$) are visualized with the computer-graphics program PEANUT [5] which displays the root mean square displacement surfaces (RMSDSs) represented by the ΔU tensors.

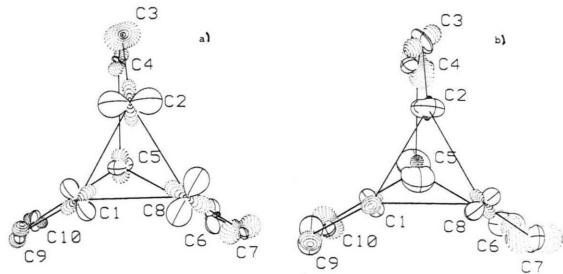


Fig. 5. Residual root-mean-square displacement surfaces ($\langle \Delta u^2(n) \rangle^{1/2} = (n' \Delta Un)^{1/2}$) [7], (a) ADPs from X-ray multipole refinement, (b) neutron data.

Figure 5 a, based on the X-ray data, shows systematic features in the cyclopropane ring. At each C atom the positive/negative residuals are parallel/perpendicular to the opposite bond formed by the other two carbons. Although this residual "motion" could be accounted for by an internal libration around the three-fold axis of the molecule, its physical significance is not supported by the neutron data (Figure 5 b).

Concluding Remarks

Our results can be interpreted in two different ways: (1) The molecule is nearly rigid as suggested by the neutron data, and the systematic trend revealed by the X-ray ADPs is due to inadequacy in the density model, i.e. charge asphericities are absorbed in the thermal parameters. (2) The residual RMSDSs, calculated from the X-ray ADPs, represent an internal contribution to the molecular motion, and the neutron data are biased by unresolved systematic errors. Regardless which argument applies here, an important point emerges: a procedure to extract the SDD from X-ray diffraction data should include the analysis of the thermal motion to test for the physical significance of the obtained displacement parameters. Further refinements on both data sets and studies on the internal motion of the bullvalene molecule are being undertaken, and the final results will be published elsewhere.

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