

06.2-8 ELECTRON DENSITY DISTRIBUTION IN CAGE LIKE COMPOUNDS : DIRECTIONAL PREFERENCES OF ELECTROPHILIC AND NUCLEOPHILIC ATTACK. By Vedavati G. Puranik, S.S. Tavale and T.N. Guru Row, Physical and Structural Chemistry Unit, National Chemical Laboratory, Pune 411008, India.

Organic "cages" present themselves as highly distorted and yet compact structures. These compounds therefore are viable for external electrophilic and nucleophilic attack. But the distorted electron density distributions on the surface of the molecules hamper the directional preferences.

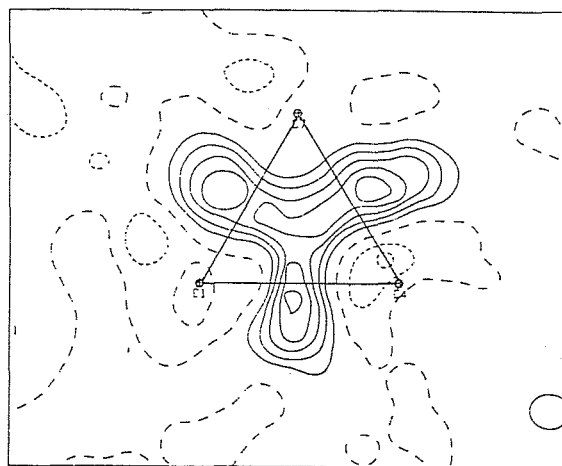
The compound heptacyclo [8.5.0.1^{2,9}.0^{3,8}.0^{6,12}.0^{5,14}.0^{11,15}] hexadecane-4,7-dione is such an example and high precision X-ray diffraction data has been collected using CAD-4F-11M diffractometer ($\omega/2\theta$ scan, $\sin\theta/\lambda$ upto 0.95, 1376 unique reflections). Crystals are orthorhombic F2dd, $a = 6.576(1)$, $b = 14.700(2)$, $c = 22.787(2)$ Å, $Z = 8$. Structure was solved by direct methods to $R = 0.027$ and $R_w = 0.025$. The molecule utilizes the crystallographic two fold axis, thus reducing the number of parameters to be refined in order to obtain a meaningful X-X $\mu.o.$ deformation map. Another data set collected at $T = 180$ K does not show any significant improvement of the quality of data. X-X $\mu.o.$ maps calculated based on room temperature data will be presented. The possible directional preferences inferred from these maps will be discussed.

06.2-10 X-N CHARGE DENSITY STUDIES ON BULLVALENE AT 110K. By P. Luger, J. Buschmann and Th. Richter, Institut für Kristallographie, Freie Universität Berlin, West Germany; R.K. McMullan, Chemistry Department, Brookhaven National Laboratory, Upton, N.Y., USA; J.R. Ruble, P. Matias and G.A. Jeffrey, Department of Crystallography, University of Pittsburgh, USA.

Bullvalene, $C_{10}H_{10}$, attracted much attention, when first proposed theoretically (Doering, W.E. von, Roth, W.R. (1963), Tetrahedron 19, 715-737) and synthesized thereafter (Schröder, G. (1963). Angew. Chem., Int. Ed. Engl. 2, 481-482). Its property to form more than 1,2 million identical isomers by Cope rearrangement is unique in organic chemistry. Room temperature X-ray analyses (Johnson, S.M., McKechnie, J.S.; Lin, B.T.-S., Paul, I.C. (1968) J. Am. Chem. Soc. 89, 7123 and Amit, A., Huber, R., Hoppe, W. (1968). Acta Cryst. B24, 865-869) provided no evidence of the valence isomerism, occurring in bullvalene, in the solid state. The molecular geometry derived from both X-ray analyses showed significant distortions from the expected C_{2v} symmetry. Our recent neutron diffraction refinement of bullvalene, however, based on a 110K measurement revealed only minor deviations from this symmetry (Luger, P., Buschmann, J., McMullan, R.K., Ruble, J.R., Matias, P., Jeffrey, G.A. (1986). J. Am. Chem. Soc. 108, 7825-7827).

Here we present a charge density study of bullvalene based on the above mentioned neutron data set taken at the High Flux Beam Reactor of the Brookhaven National Laboratory, wavelength 1.0504(2)Å, 3077 reflections with $\sin\theta/\lambda < 0.78\text{Å}^{-1}$ and on an X-ray data set taken at 110 K with $M\alpha$ radiation, 8600 reflections with $\sin\theta/\lambda < 1.05\text{Å}^{-1}$.

In the plane of the cyclopropane ring the difference density maxima lie clearly outside the three membered ring (Fig. 1), consistent with the description of so called "banana bonds". The non-spherical density distributions along the ethylenic bonds are indicative of their π character.



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06.2-9 ELECTRON DEFORMATION DENSITY DISTRIBUTION IN NONAQUANEODYMIUM TRIS(TRIFLUOROMETHANESULPHONATE).

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The deformation density in the title compound has been determined at 295 K from a combination of X-ray and neutron diffraction data. Evidence for trigonally deformed distribution of 4f electrons around neodymium is observed in the final X-N map. The electron density and electron deficient regions along metal-water oxygen vector are found in the map. The differing geometries of the trigonal and tetrahedral water molecules in the complex studied are reflected in differences in the electron density distributions along the lines joining the metal ion to the water oxygen atoms. The electron density migration in the metal-equatorial water oxygen bonding and in the lone-pair regions can also be observed.