06.2-8  ELECTRON DENSITY DISTRIBUTION IN
CAGE LIKE COMPOUNDS : DIRECTIONAL PREFERENCES
OF ELECTROPHILIC AND NUCLEOPHILIC ATTACK.


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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[3.5.0.1^7.9,3.8,6.1^2,5^3,1^4,0^1.15]
hexadecane-4,7-dione is such an example and high precision
X-ray data set taken at 110 K does not show any significant
distortions from the expected cubic symmetry.

The compound heptacyclo[3.5.0.1^7.9,3.8,6.1^2,5^3,1^4,0^1.15]
hexadecane-4,7-dione is such an example and high precision
X-ray diffraction data has been collected using CAD-4F-1M
diffraaetron (ω/2θ scan, sin θ/λ = 0.95, 1376 unique reflections). Crystals are orthorhombic P2_12_12, a = 6.376(1),
b = 14.702(2), c = 22.737(2) Å; Z = 8. Structure was solved
by direct methods to R = 0.027 and Rw = 0.025. The mole-
cule utilizes the crystallographic two fold axis, thus reducing
the number of parameters to be refined in order to obtain
a meaningful X-X Hirshfeld deformation map. Another data
set collected at T = 180 K does not show any significant
improvement of the quality of data. X-X Hirshfeld maps calcu-
lated based on room temperature data will be presented.
The possible directional preferences inferred from these maps
will be discussed.

06.2-9  ELECTRON DEFORMATION DENSITY
DISTRIBUTION IN NONAAQUANODYMUM
TRIS(TRIFLUOROMETHANSULPHONATE).

By A. Chatterjee, Department of Physics,
University of Rajshahi, Rajshahi, Bangladesh.

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.

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. McMullen, Chemistry Depart-
ment, 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_20H_10, attracted much attention, when
first proposed theoretically (Boering, W.E. von, Roth,
W.R. (1963), Tetrahedron 19, 715-737) and synthesized
thereafter (Schröder, E. (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,
865-869) provided no evidence of the valence iso-
merism, occurring in bullvalene, in the solid state. The molecu-
lar geometry derived from both X-ray analyses showed
significant distortions from the expected C_2 symmetry.

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, wavele~gth 1.0504(2)Å, 3077 reflections
with sin θ/λ<0.78Å and on an X-ray data set taken at
110 K with Mo Kα radiation, 8600 reflections with
sin θ/λ<1.05Å .

In the plane of the cyclopropane ring the difference
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 β character.

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