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An X-ray Determination of the Conformation of 1,6-Dimethyl-8,8-dicyanoheptafulvene

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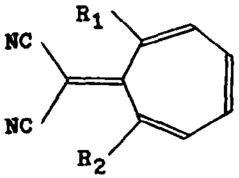
It has been already reported that 8,8-dicyanoheptafulvene (I) has a planar structure (1). Recently many halogen derivatives of (I) have been prepared and the positions of substituents have been determined by means of the dipole moment measurements (2). However, in the 1,6-disubstituted derivatives (II a-c) the observed moments were always lower than the calculated ones by 1.2-2.5D. This suggests some conformational changes of the molecules owing to the strong intramolecular interaction between the dicyanomethylene group and the substituents (3). The present work was undertaken in order to reveal the conformation of (II a) and from our general interests to the aromaticity of the non-benzenoid aromatic compounds.



I $R_1=R_2=H$
II a, $R_1=R_2=CH_3$
b, $R_1=Br$, $R_2=CH_3$
c, $R_1=Br$, $R_2=Ph$

Crystals of this compound (II a) are monoclinic, with four molecules in an unit cell of the dimensions a=8.84, b=13.33, c=9.21Å and β=103.9°; the space group is $P2_1/c$. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs using CuKα radiation and measured visually against a standard scale. The crystal structure was determined by the symbolic addition procedure and refined by the least-squares method. After three cycles of refinement the R factor was reduced to 0.14.

The molecule projected down the a axis is shown in Fig.; the seven-membered ring takes a boat form as those in cycloheptatriene (4,5) and dibenzo[b,f]tropone (6). The anomalies of the dipole moments mentioned above can be reasonably interpreted on the basis of the present molecular geometry, and the feature of UV spectra is also compatible with it. Therefore, it may be concluded that the steric form of the molecule in the crystal is similar to that in solution. There are no abnormal short contacts between the molecules in the crystal.

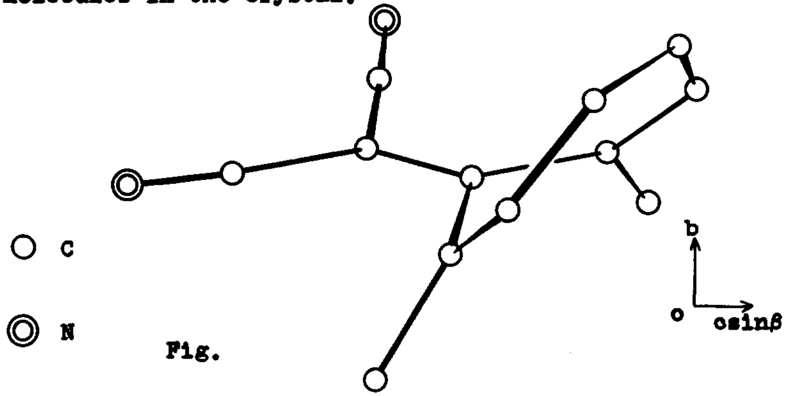


Fig.

Further refinements are in progress, and a detailed account of this work will be presented in the near future.

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