

SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1973). B29, 1358

The cause of non-planarity in the heptafulvalene molecule. By P. T. CHENG and S. C. NYBURG, *Lash Miller Chemical Laboratories, University of Toronto, Toronto M5S 1A1, Canada*

(Received 28 October 1972; accepted 5 February 1973)

The cause of non-planarity in the heptafulvalene molecule is shown to be more probably due to conflict of two pairs of hydrogen atoms within the molecule than the need to relieve bond angle strain within the rings.

Thomas & Coppens (1972) have reported on the crystal structure of heptafulvalene (I). The molecule is found to be significantly non-planar having an *S*-shape when viewed in the C(2) to C(7) direction. Although, as noted by Thomas & Coppens, the molecule of dicyanoheptafulvene (II) is essentially planar (Shimanouchi, Ashida, Sasada & Kakudo, 1966) they claim that because of an 'appreciable distortion of the bond angles' the molecule is strained and that 'the strain is relieved by appreciable distortions, some carbons being displaced by as much as 0.35 Å from the best plane through the molecule. . .'

(or other) atoms of the bifunctional *R* groups. Examples of known crystal structure are dibiphenylene-ethylene (III) (Nyburg, 1954) 10,10'-bianthronylidene (IV) (Harnik & Schmidt, 1954) and 9,9'-bixanthylidene (V) (Mills & Nyburg, 1963). In each case conflict at the starred hydrogen atoms causes the molecule to have a doubly-bent conformation (German: *doppelte Wannenförmig*). The distance between these hydrogen atoms in (III) is not accurately known but in (IV) and (V) it is about 2.9 Å. These structure analyses show how resistant to twisting is the central ethylenic system which remains essentially planar in all three molecules. Clearly heptafulvalene is a molecule of this type. However a sufficiently bulky group at one of each pair of conflicting position can cause the molecule to twist as evidenced in the crystal structure of the 1,1'-bis(isopropoxycarbonyl) derivative of (III) (Bailey & Hull, 1971).

Thomas & Coppens do not comment on these H...H distances which can be calculated from their listed atomic coordinates as only 2.13 Å. The molecule adopts the expected *doppelte Wannenförmig* because of this conflict. Given the positions of these hydrogen atoms the geometry of the molecule immediately follows. We first note, Fig. 1, that C(1), C(2), C(3) and H(2) are coplanar, the deviations from the best plane being only 0.004, -0.015, 0.004, and

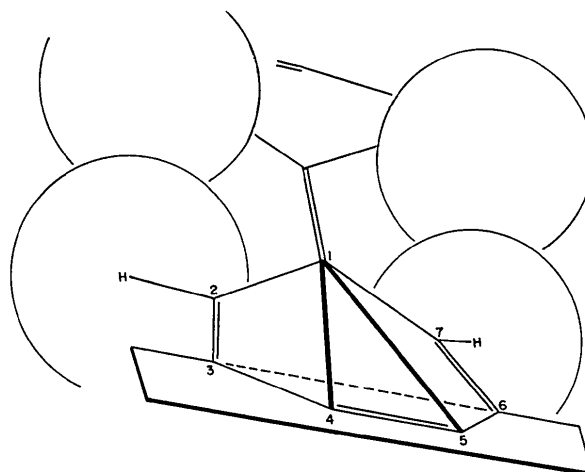
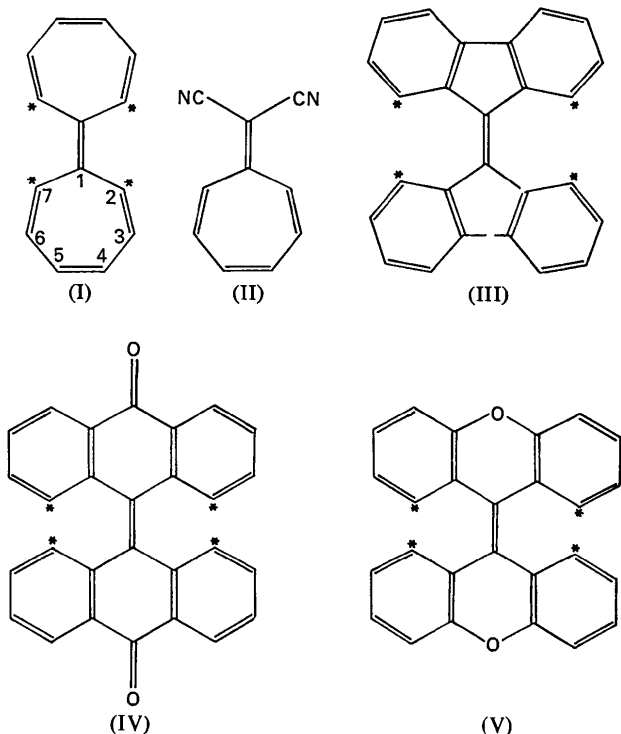


Fig. 1. Local planes in the heptafulvalene molecule.

We believe the cause and the extent of non-planarity can be readily explained on other grounds. Heptafulvalene belongs to a family of molecules $R=C=C=R$ which are prevented from being planar by conflict between hydrogen

0.006 Å respectively (*i.e.* very slightly tetrahedral). As expected, C(1), C(6), C(7) and H(7) are similarly coplanar the deviations being even less: -0.001, -0.001, 0.004 and -0.002 Å. Thus we can say that the position of H(2) governs the position of C(3) and that H(7) governs the position of C(6). We then find, as expected, that the ethylenic system C(1), C(2), C(3) and C(4) is coplanar, the deviations being extremely small: 0.001, -0.002, 0.002 and -0.001 Å. Similarly for C(1), C(7), C(6) and C(5) the deviations are 0.000, -0.000, 0.001 and -0.001 Å. We find that these positions for C(4) and C(5) satisfy the requirement that C(3), C(4), C(5) and C(6) be coplanar, the deviations all being less than ± 0.001 Å. Fig. 1 shows how the planar parts of the molecule are related.

In a localized double bond system the C=C-C angle can be expected to be close to 122° (and hence C-C-C, 116°). Thus in a flat, seven-membered ring such as dicyanoheptafulvene these angles are presumably strained, and, if strained to equal extents, would be $122 + 7.4 = 129.4^\circ$ and $116 + 7.4 = 123.4^\circ$ respectively. These are close to the observed angles in dicyanoheptafulvene, the mean deviation being 0.9° . In heptafulvalene the C(1)-C(2)-C(7) angle is only 117.6° compared with 125.1° in dicyanoheptafulvene and, in this sense, is less strained. However this is achieved at the expense of making the remaining angles larger and is directly attributable to the conflicting hydrogen atoms. The repulsive force between them has a component exerted on

C(2), C(7) and on C(2'), C(7') which helps to close up the bond angles at C(1), C(1').

Perchloroheptafulvalene has also the *doppelte Wannenförmig* conformation (Ishimori, West, Teo & Dahl, 1971) and this clearly arises from an analogous cause, namely, conflict of the chlorine atoms at the 2 and 7 positions.

Thus we claim that any bond angle strain in a seven-membered heptafulvene ring is insufficient on its own to cause deviations from non-planarity. In other words if it were not for the H...H or similar conflicts in a heptafulvalene system we could reasonably expect the molecule to be flat.

References

- BAILEY, N. A. & HULL, S. E. (1971). *J. Chem. Soc. (D)*, pp. 960-961.
 HARNIK, E. & SCHMIDT, G. M. J. (1954). *J. Chem. Soc.* pp. 3295-3302.
 ISHIMORI, M., WEST, R., BOON KENG TEO & DAHL, L. F. (1971). *J. Amer. Chem. Soc.* **93**, 7107.
 MILLS, J. F. D. & NYBURG, S. C. (1963). *J. Chem. Soc.* pp. 308-321.
 NYBURG, S. C. (1954). *Acta Cryst.* **7**, 779-780.
 SHIMANOCHI, H., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1966). *Bull. Chem. Soc. Japan*, **39**, 2322-2331.
 THOMAS, R. & COPPENS, P. (1972). *Acta Cryst.* **B28**, 1800-1806.

Acta Cryst. (1973). **B29**, 1359

Heptafulvalene: ring strain or hydrogen repulsion? By PHILIP COPPENS, *Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214, U.S.A.*

(Received 4 December 1972; accepted 5 February 1973)

The cause of the non-planarity of the heptafulvalene molecule is discussed in terms of non-bonded H...H repulsions and strain in the seven-membered ring. It is concluded that steric hindrance in heptafulvalene is much less severe than in other 'overcrowded' compounds and that ring strain is a significant contributor to the deformation of the molecule.

Cheng & Nyburg (1973) have argued that the cause of the distortion from planarity of the heptafulvalene molecule is the steric crowding of the hydrogen atom *ortho* to the bridging bond in the molecule. The argument is based on a comparison of heptafulvalene with overcrowded molecules such as dibiphenylene-ethylene (III), 10,10'-bianthronylidene (IV) and 9,9'-bixanthylidene (V)* and it is stated that heptafulvalene belongs to the same general class of molecules.

To compare the molecules in terms of the degree of overcrowding and its effect on distortions from planarity, it is necessary to calculate the H...H distances that would exist in the planar conformation. For (III) this distance is given in the original publication (Nyburg, 1954) as 0.7 Å, while the C...C distance would be 2.5 Å. These distances correspond to strong repulsions which dictate a distortion of the molecule. The overcrowding is even more severe in (IV) and (V), where a planar geometry would lead to practical coincidence of the hydrogen nuclei, a clearly unacceptable

situation. A similar calculation for heptafulvalene, using bond lengths and angles from our original article (Thomas & Coppens, 1972), and assuming the CH bond of length 1.08 Å to be along the bisectrix of the adjacent C-C bonds, leads to $l(\text{H}\cdots\text{H}) = 1.7$ Å in the planar molecule. This is only 0.3 Å shorter than the sum of the recently revised van der Waals radii of the hydrogen atoms (Baur, 1972), and clearly contradicts Cheng & Nyburg's contention that heptafulvalene is as overcrowded as the molecules it is compared with. In fact the corresponding H...H distance in the experimentally planar diphenyl molecule can be derived from the geometry given by Robertson (1961) as about 1.8 Å. Thus, while some amount of H...H repulsion is not ruled out in heptafulvalene, the overcrowding in the planar molecule is much less severe than in compounds such as diphenylene-ethylene.

In a planar heptagon the average CCC angle would be 128.5° . In heptafulvalene the angle opposite the exocyclic double bond (117.5°) is much smaller than this value. As was noted by Bartell (1960) in an electron diffraction study of isobutylene, the CCC angles opposite C=C bonds are generally smaller than 120° . There is a good correlation

* The numbering of the molecules is as used by Cheng & Nyburg.