

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.

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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.*

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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

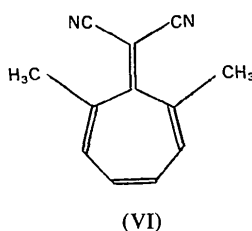
* The numbering of the molecules is as used by Cheng & Nyburg.

Table 1. C=C bond length and CCC angle in a number of compounds

| Compound | Bond length (Å) | Angle (°) | Reference |
|---------------------------------|-----------------|-----------|---------------------------------------------|
| Isobutylene | 1.331 (3) | 115.3 (1) | Bartell (1960) |
| Dimethylfulvene | 1.343 (11) | 114.0 (6) | Norman & Post (1961) |
| Tetracyanoethylene | 1.344 (3) | 115.6 (1) | Little, Pautler & Coppens (1971) |
| Tetracyanoquinodimethane (TCNQ) | 1.374 (3) | 116.1 (2) | Long, Sparks & Trueblood (1965) |
| Heptafulvalene | 1.379 (5) | 117.6 (3) | Thomas & Coppens (1972) |
| 8,8-Dicyanoheptafulvalene | 1.422 (13) | 125.1 (7) | Shimanouchi, Ashida, Sasada & Kakudo (1966) |

between the C=C bond length and the CCC angle. Some experimental data summarized in Table 1 show that heptafulvalene is no exception in this respect. Thus, the small value of the ring angle opposite the double bond is not a result of H...H repulsions in heptafulvalene as argued by Cheng & Nyburg (Bartell has explained the observed values successfully in terms of non-bonded 1-3 CC interactions). If the molecule were planar, the other six angles in the seven-membered ring would have an average value of 130.4°. The observed average of 128.5°, indicates that the distortion from planarity leads to a relief of the angle strain. In 8,8-dicyanoheptafulvalene (II) the exocyclic bond C=C bond is longer and the CCC angle correspondingly larger. As a result there is less ring strain and there is no necessity for a deviation from planarity.

That steric hindrance can cause a deviation from planarity is demonstrated by the geometry of 1,6-dimethyl-8,8-dicyanoheptafulvalene (VI) (Shimanouchi, Sasada, Kabuto & Kitahara, 1968). Obviously, the seven-membered fulvene ring is easily deformable because of its relative lack of aromaticity. Independent of its cause, the deformation will be a torsion of the single bonds, while the ethylene groupings will remain planar. In heptafulvalene the deformation leads to a slight increase of the non bonded H...H distances (from 1.7 to 2.1 Å) and a decrease of six of the seven ring angles from 130.4 to 128.5°. It seems fair to conclude that both ring strain and H...H repulsions are likely contributors to the marked distortion of heptafulvalene.



Only a detailed analysis of the molecular force field can give an accurate assessment of the relative importance of the two effects, but an estimate may be obtained from an approximate calculation. Using an angle bending force constant of 0.687 m dyne Å radian⁻² (Schachtschneider &

Snyder, 1963) and a reference angle of 120° (Jacob, Thompson & Bartell, 1966) we obtain a value of 6.5 kcal mole⁻¹ for the relief of the strain in both rings. If, on the other hand, the C=C-C angle in isobutylene (123.3°) is taken as a reference value, the strain relief is reduced to 4.2 kcal mole⁻¹. The choice between the two reference values is not obvious because the isobutylene angle may be distorted by intramolecular non-bonded repulsions (Bartell 1960). The corresponding number for relief of H...H repulsions depends on the potential function selected, but a choice of two rather different functions (De Boer, 1942; Bartell, 1960) leads to an estimate of 3-7.5 kcal mole⁻¹ (taking both short contacts into account. Note that C-C-H angle distortion in the planar molecule would reduce this number).

Summarizing, though H...H repulsions should not be ignored, steric hindrance in heptafulvalene is much less severe than in other 'overcrowded' compounds. It must be concluded that ring strain is a significant contributor to the deformation of the molecule.

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