

angle of 21.1° . There is, however, no noticeable change in the interior angle C(3)–C(4)–C(5) which is $106.7(2)$ and $107.2(1)^\circ$ in the β - and γ -isomers, respectively. The changes in the ring angles are largest at atoms C(3) and C(6), suggesting that the ring strain is taken up at these atoms.

Equivalent bond lengths are approximately the same in the two structures, except for the three bonds C(2)–C(3), C(4)–C(9), and C(10)–C(11) where significant differences of 0.02 \AA are observed. The C–N bond lengths have a mean value of 1.471 \AA in both structures.

As shown in Fig. 3, intermolecular hydrogen bonds of the type O–H \cdots N link molecules which are related by the screw axis to form infinite chains along b , with all molecules of each chain having identical chirality. The geometry of these hydrogen bonds is as follows: O–H = 0.91 \AA , H \cdots N = 1.93 \AA , O \cdots N = 2.811 \AA , and O–H \cdots N = 162.1° . It is important to note that the two hydrogen bonds of each molecule are *cis* relative to the piperidine ring, while they are *trans* in the γ -isomer. It is possible, therefore, that the analgetic activity is

enhanced when the molecule can assume a geometry such that the hydrogen donor and the hydrogen acceptor of the same molecule are *cis* relative to the piperidine ring. This particular point will be examined further in the subsequent parts of this series.

Grateful acknowledgement is made to Drs A. F. Casey and K. McErlane of the University of Alberta for supplying the crystals, and to Mrs M. E. Pippy for assistance with the computations.

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The Crystal and Molecular Structure of a Non-Alternant Hydrocarbon: Heptafulvalene*

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Heptafulvalene, $C_{11}H_{12}$, crystallizes in $P2_1/c$ with $Z=2$, $a=9.688(4)$, $b=7.730(2)$, $c=6.971(2) \text{ \AA}$ and $\beta=98.03(2)^\circ$ [$\cos \beta = -0.1399(2)$]. 630 reflections were accessible using Ni filtered $Cu K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and each of these was measured using a computer-controlled, four-circle diffractometer; $d_{\min}=0.98 \text{ \AA}$. The crystal structure of heptafulvalene has been solved using the symbolic addition procedure. The molecule is approximately S shaped; largest deviations from the best molecular plane are 0.35 \AA . There is an alternation of almost single and almost double bonds in the seven-membered ring in fair agreement with the results of earlier π -electron molecular orbital calculations on a planar idealized molecule. It is shown that there is a strong correlation between bond length and bond torsion, the strain in the seven-membered ring being relieved almost exclusively in the longer bonds.

Introduction

Though the molecular structure of non-alternant hydrocarbons is of considerable importance for comparison with theoretical predictions, few precise structure determinations of unsubstituted molecules are available. For example, the determination of the mole-

cular structure of azulene has been hampered by disorder (Robertson, Shearer, Sim & Watson, 1962; Pawley, 1965), but a complex with trinitrobenzene (Hanson, 1965) and a dipropionic acid derivative (Ammon & Sundaralingam, 1966) have been analyzed. Other derivatives for which the structures have been described include dicyanoheptafulvene (Shimanouchi, Ashida, Sasada & Kakudo, 1966) and dimethylfulvene (Norman & Post, 1961).

The work described in the present paper was

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started in 1966, after predictions based on π -molecular orbital calculations were made for the bond lengths in a number of non-alternant hydrocarbons (Dewar & Gleicher, 1965). A preliminary account was presented in 1967 (Coppens & Thomas, 1967).

Experimental

A reasonably well-shaped wine-red crystal fragment of heptafulvalene was selected from material kindly supplied by W. E. Doering. It was mounted in a thin-walled glass capillary under dry nitrogen. The idealized shape of the selected crystal fragment was that of a regular triangular prism. The parallel, equilateral triangular faces measured approximately 0.3 mm on edge and the prism was approximately 0.1 mm thick. All five boundary crystal faces were indexed by placing each in reflecting position on a diffractometer so that the observed values of 2θ , χ and φ could be compared with the calculated values. The equilateral triangular faces were the (100) and the $(\bar{1}00)$ planes; the three rectangular faces were (01 $\bar{1}$) and approximately (3 $\bar{1}$ 4) and (35 $\bar{1}$).

Preliminary precession X-ray photographs established that heptafulvalene is monoclinic, belonging to space group $P2_1/c$ as uniquely determined by the systematic extinctions, $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$. Approximate unit-cell dimensions were refined by least-squares analysis using observed diffractometer data for twenty left/right centered and top/bottom balanced reflections to yield: $a=9.688 \pm 0.004$, $b=7.730 \pm 0.002$, $c=6.971 \pm 0.002$ Å, and $\beta=98.03 \pm 0.02^\circ$ ($\cos \beta = -0.1399 \pm 0.0002$). Hence the unit-cell volume is $V=516.93$ Å³ and the calculated density is $D_x=1.158$ g.cm⁻³ assuming $Z=2$. The assumption of two molecules per unit cell is proved correct by the structure determination.

Using Ni filtered Cu $K\alpha$ radiation, $\lambda=1.5418$ Å, all accessible unique reflections plus one set of equivalent reflections were measured by means of a computer-controlled, four-circle diffractometer; $d_{\min}=0.98$ Å. No reflections beyond this limit were observable. A step scan in the θ - 2θ mode was performed for each reflection. Of the total of 630 unique reflections collected, 54 were systematically absent, 407 were of

measurable intensity and 169 were below the 3σ threshold limit of observability.

Data processing

The raw step-scan data for each reflection were smoothed using a procedure described by Whittaker & Robinson (1944). After integration and background correction for each peak, Lorentz, polarization and absorption corrections (Coppens, Leiserowitz & Rabinovich, 1965) were applied.

A standard error for use in weighting the least-squares refinement was calculated for each reflection as follows:

$$\sigma_{(I-B)}^2 = \left[I + \left(\frac{n_I}{n_B} \right)^2 B \right] + (0.03)^2 \left[I - \left(\frac{n_I}{n_B} \right) B \right]^2 + (0.03)^2 (I_{\text{corr}} - I)^2$$

where I is the total integrated intensity in the peak, B is the total integrated intensity in the background, n_I is the number of steps in the peak, n_B is the number of steps in the background and I_{corr} is the intensity in the peak corrected for absorption. The first term in this expression is the counting statistical error in the background corrected peak intensity; *viz.*, $[I - (n_I/n_B)B]$. The second term is an estimate proportional to the magnitude of the background corrected peak intensity and the third term is an estimate proportional to the magnitude of the absorption correction.

When the unique reflections and their equivalents were averaged, a value of 2.97% was obtained for a weighted discrepancy index between the two sets, calculated as follows:

$$R_w = \frac{\sum w|F - \langle F \rangle|}{\sum w|F|}$$

where $w=1/\sigma^2$, $\langle F \rangle$ is the weighted average over the two symmetry-equivalent reflections measured, F is the observed structure factor from each individual data set and the summation extends over all reflections common to both data sets.

A Wilson scale-temperature plot determined a value of 4.65 Å² for the overall isotropic temperature factor

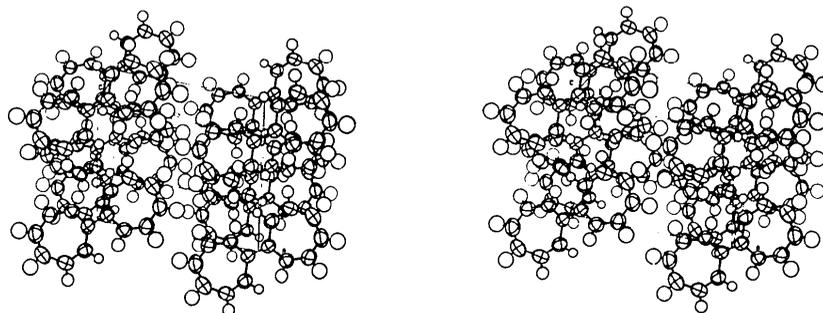


Fig. 1. Molecular packing.

B. The value of the scale factor did not undergo major changes during subsequent refinement calculations.

Structure determination and refinement

The crystal structure of heptafulvalene was solved by the direct determination of the phases using the symbolic addition procedure. The multipass computer program *SORTE*, written by Bednowitz (1967), for centrosymmetric crystals was used.

The heptafulvalene data contained 182 reflections with $|E| \geq 1$; 86 of these had $|E| \geq 1.5$. From a list of the Σ_2 interactions for all $|E| \geq 1.0$, three linearly independent, origin-determining reflections were chosen such that simultaneously the number of the Σ_2 interactions and magnitudes of the E -factors were large. The reflections $51\bar{3}$, $12\bar{1}$ and $16\bar{2}$ were arbitrarily assigned plus phases. From these three starting reflections a total of 36 additional reflections could be assigned symbolic phases, using the Σ_2 interactions and the symbols plus, minus, A , and B . The 36 symbolic phases were used as input data for the first pass with *SORTE*. During the first pass, 53 new phases were determined within 98% probability of being correct and A and B were found to be plus and minus, respectively. A second pass with *SORTE*, still considering only $|E|'s \geq 1.0$, produced 68 new phases within 98% probability of being correct and a final pass produced all remaining phases except three.

An E map based on the 179 determined phases showed all carbon atoms of the heptafulvalene structure as the most prominent peaks. As expected from the crystal data, the molecular center coincides with a crystallographic center of symmetry.

The heptafulvalene structure was refined by least squares using the full matrix of the normal equations. $R' = \sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ is the weight for each observation F_o and $\sigma(F_o)$ is the standard error described in the previous section. Atomic scattering factors used were those for hydrogen and valence-state carbon atoms as listed in *International Tables for X-ray Crystallography* (1962).

During the refinement of the heptafulvalene structure, special consideration was given to the 169 reflections which had an intensity less than 3σ . Each of these reflections was included in the refinement only if the value of the calculated structure amplitude was greater than three times the experimental standard deviation. In this way these reflections contributed to the determination of the refined model parameters, but only so long as their contribution was necessary to shift the parameters towards values which predicted these reflections to be below the 3σ threshold value. In the final least-squares cycles described below, none of these reflections was calculated to be larger than the respective threshold value.

The isotropic refinement of the carbon atoms only converged after four cycles with $R = \sum |F_o - kF_c| / \sum |F_o| = 12.6\%$ and $R_w = [\sum w(F_o - kF_c)^2]^{1/2} / (\sum wF_o^2)^{1/2} =$

13.2%. The single scale factor, atomic position parameters and individual temperature factors were varied. A difference Fourier synthesis at this stage revealed all the hydrogen atoms, together with indications of anisotropic thermal motions for the carbon atoms. The hydrogen atoms were included in the model and isotropic refinement continued varying the atomic position parameters for all atoms, the individual temperature factors for the carbons only, the scale factor and an overall isotropic temperature factor. In this way an approximately correct magnitude for the isotropic temperature factor for the hydrogen atoms was found to be 6.8 \AA^2 . Convergence was achieved after two cycles with $R = 8.1$ and $R_w = 7.7\%$. A final isotropic cycle varied only the individual temperature factors for the hydrogen atoms. These converged to reasonable values with $R = 7.9$ and $R_w = 7.6\%$.

The anisotropic refinement proceeded in a straightforward manner. The position parameters for all atoms, the scale factor, and the anisotropic temperature parameters for the carbon atoms were varied and convergence was achieved after two cycles with $R = 4.8$ and $R_w = 4.4\%$. When the individual isotropic temperature factors for the hydrogen atoms were also allowed to vary, convergence was achieved after one cycle with $R = 4.5$ and $R_w = 4.1\%$. The resulting values for the isotropic temperature factors of the hydrogen atoms reflected their positions in the molecule regarded as a rigid body. That is, the temperature factors were larger for hydrogen atoms near the ends of the molecule than for those near the center.

The final least-squares cycle included an isotropic extinction parameter (Zachariassen, 1967) and R and R_w were reduced to 4.1 and 3.8% respectively. Extinction was not severe: for only 58 reflections was the extinction correction factor $y < 0.99$ and for only four of these was $y < 0.9$, the lowest value being 0.78. The equivalent mosaic spread parameter η was found to be 15.04 seconds and the equivalent spherical-domain radius r had the value $6 \times 10^{-5} \text{ cm}$.

Tables 1, 2 and 3 respectively list the final atomic position parameters, β_{1j} coefficients for the carbon atoms and B coefficients for the hydrogen atoms

Table 1. *Final atomic position parameters*

$10^4 \sigma$ and $10^3 \sigma$ is given in parentheses for carbon and hydrogen atoms respectively.

	x/a	y/b	z/c
C(1)	0.0602 (3)	0.5086 (4)	0.5640 (4)
C(2)	0.1740 (4)	0.6173 (4)	0.5169 (5)
C(3)	0.3110 (4)	0.6105 (5)	0.5826 (5)
C(4)	0.3830 (4)	0.4935 (6)	0.7200 (6)
C(5)	0.3285 (4)	0.3979 (5)	0.8495 (6)
C(6)	0.1857 (4)	0.3913 (4)	0.8801 (5)
C(7)	0.0719 (4)	0.4385 (4)	0.7592 (5)
H(2)	0.148 (3)	0.704 (4)	0.419 (4)
H(3)	0.375 (3)	0.699 (4)	0.523 (4)
H(4)	0.487 (4)	0.498 (5)	0.721 (5)
H(5)	0.394 (3)	0.331 (4)	0.945 (4)
H(6)	0.166 (3)	0.347 (3)	1.004 (4)
H(7)	-0.016 (3)	0.428 (3)	0.803 (3)

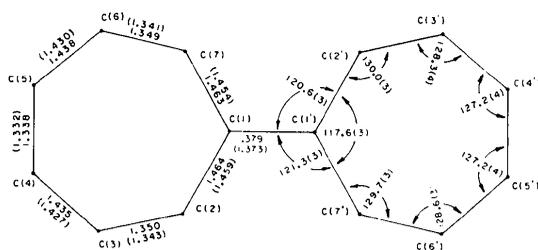


Fig. 2. Bond lengths and angles and numbering of atoms. The values in parentheses are before correction for apparent shortening due to thermal motion. Standard deviations in the bond lengths are estimated as 0.004–0.005 Å.

equal to one (see Ammon, Watts & Stewart (1970) for a discussion of this apparent contradiction). It may be noted that errors resulting from charge asymmetry around the carbon atoms (Coppens, 1967, 1971; Kay, Okaya & Cox, 1971) are expected to be smaller than these discrepancies, though allowing for these errors would tend to increase the length of the short bonds in the ring and thus reduce some of the discrepancies.

Ideally, a theoretical geometry should be obtained by minimizing the molecular energy with respect to the atomic coordinates (as realized by Dewar & Gleicher in their earlier article). Such a minimization now seems to be within reach, at least for zero differential overlap calculations (McIver & Komarnicki, 1971). The experimental results on heptafulvalene are presently being used to test such a procedure.

C–H bond lengths are in the usual range (Table 6). No unusual intermolecular H···H contacts were evident.

Table 6. C–H distances (Å)

C(2)–H(2)	0.96 (3)
C(3)–H(3)	1.05 (3)
C(4)–H(4)	1.01 (4)
C(5)–H(5)	1.00 (3)
C(6)–H(6)	0.98 (3)
C(7)–H(7)	0.95 (3)

Distortions from planarity

The existence of a planar seven-membered ring of carbon atoms would require an appreciable distortion of the bond angles. Nevertheless the ring in the molecule of dicyanoheptfulvalene was found to be planar, with all bond angles within 2.6° of 127.6° (Shimanouchi, Ashida, Sasada & Kakudo, 1966). In heptafulvalene, however, the strain is relieved by appreciable

distortions, some carbon atoms being displaced by as much as 0.35 Å from the best plane through the molecule (Table 7), while the C(2)–C(1)–C(7) angle is only 117.6 (3)° (Fig. 2). When seen sideways, the molecule has an *S*-shaped appearance, with the atoms C(4), C(5) and C(4'), C(5') being displaced most, and in opposite directions (Fig. 3). The straight part of the *S* is formed by the six central atoms which are almost coplanar (Table 7). Following Hirshfeld (1963) we define a bond-deformation parameter as the dihedral angle between the planes through the bond and each of its two adjacent bonds (Fig. 4). [For the C(1)–C(2) bond, we have chosen bonds *trans* to each other as the adjacent bonds.] When the deformation parameter is large there is an appreciable amount of torsion in the bond, and the overlap between the carbon π orbitals, and therefore the double-bond character, is decreased. The overlap integral is proportional to $\cos \theta$, and the restoring force for the deformation will be approximately proportional to its negative derivative, *i.e.* to $\sin \theta$. A plot of $\sin \theta$ (for which θ has been averaged over chemically equivalent bonds) against the bond length (Fig. 5) shows that the restoring force is larger for the shorter bonds and the torsion is therefore smaller. Thus, the mo-

Table 7. Distortions from planarity

(a) Deviations (Å) from planarity

	Best molecular plane (A)	Plane (B) through C(7)C(2)C(1)C(1')C(2')C(7')
C(1)	–0.126	0.04
C(2)	–0.350	–0.01
C(7)	–0.349	–0.01
C(3)	–0.178	0.465
C(6)	–0.178	0.464
C(4)	0.269	1.147
C(5)	0.271	1.148

Equations of planes

(A) $2.667x - 6.421y - 3.609z = 5.015$	} where x, y and z are coordinates expressed as fractions of the unit cell edges
(B) $4.488x - 6.333y - 2.783z = 4.558$	

(b) Dihedral bond angles (°)*

C(2)[C(1)C(1')]C(7')	8.1 (6)
C(1')[C(1)C(2)]C(7)	7.8 (6)
C(1')[C(1)C(2)]C(3)	24.4 (4)
C(1)[C(2)C(3)]C(4)	0.4 (6)
C(2)[C(3)C(4)]C(5)	19.7 (6)
C(3)[C(4)C(5)]C(6)	0.1 (6)

* Dihedral angles for chemically equivalent bonds have been averaged.



Fig. 3. Side view of the molecule showing the *S* shape.

Table 8. *Magnitudes ($\times 10^4$) and directions of principal components of molecular translation and vibration tensors \mathbf{T} and ω*

Magnitude ($\times 10^4$)	Direction cosines of principal tensor axes along inertial axes L , M and N defined in Table 10.		
	L	M	N
650 \AA^2	0.9912	0.0986	0.0928
575	0.1327	-0.7041	-0.6976
453	0.0008	-0.7037	0.7105
31.4($^\circ$) ²	-0.9237	0.1663	0.3451
8.8	-0.3688	-0.6299	-0.6835
7.4	-0.1037	0.7586	-0.6432

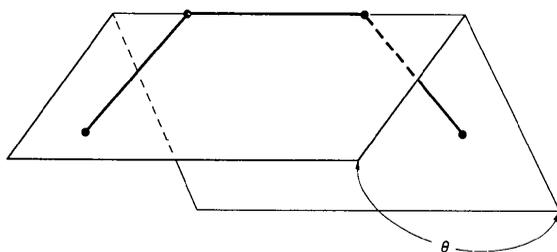


Fig. 4. Definition of a bond-distortion parameter.

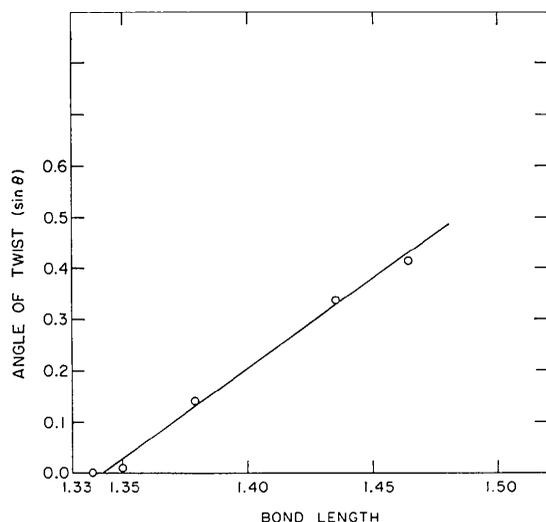


Fig. 5. Relation between the sine of the distortion angle and the C-C bond length.

molecular strain is relieved mainly in the bonds with less double-bond character.

Thermal motion

Since the molecule occupies a center of symmetry in the crystal, its three librational axes intersect and the center of libration is fixed. The rigid-body treatment then simplifies to the determination of the transla-

tional and librational tensors \mathbf{T} and ω . These were determined using a program written by Hirshfeld & Rabinovich (1966). Results are given in Tables 8, 9 and 10. The rigid-body fit is fairly good, even though internal vibrations are undoubtedly of importance in a molecule like heptafulvalene. The largest librations are about an axis approximately parallel to the length of the molecule. The largest translations are along this axis, but the anisotropy of the translational motion is much less pronounced than that of the librations.

Table 9. *Observed and calculated thermal vibration tensors U_{ij} ($\text{\AA}^2 \times 10^4$) referred to molecular axes of inertia L , M and N*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1) obs	595	459	598	14	71	18
calc	636	472	594	-23	27	11
C(2) obs	735	629	698	-76	-4	99
calc	688	642	680	-124	15	32
C(3) obs	717	910	778	-181	-19	17
calc	682	970	807	-170	-7	1
C(4) obs	670	1134	893	-5	-113	-97
calc	789	1089	888	22	-100	-70
C(5) obs	874	884	842	120	-241	-6
calc	852	876	841	103	-186	1
C(6) obs	900	691	622	-47	-85	52
calc	889	707	686	-14	-105	88
C(7) obs	687	632	669	-76	35	32
calc	741	582	606	-46	-1	52

Table 10. *Components of molecular inertial axes L , M , and N along dimensionless axes $\mathbf{a}_i = |\mathbf{a}^i| \mathbf{a}_i$*

	1	2	3	Direction
L	0.8970	-0.0523	0.5600	Along long axis of molecule
M	0.3916	0.5543	-0.6724	Parallel to C(4)-C(5)
N	0.2049	-0.8307	-0.4839	Perpendicular to best plane through atoms

We are grateful to Professor W. E. Doering who kindly supplied a sample containing some crystals suitable for X-ray analysis.

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Crystal and Molecular Structure of Racemic 2-*exo*-Norbornanol *p*-Toluenesulfonate: A Case of Enantiomeric Disorder

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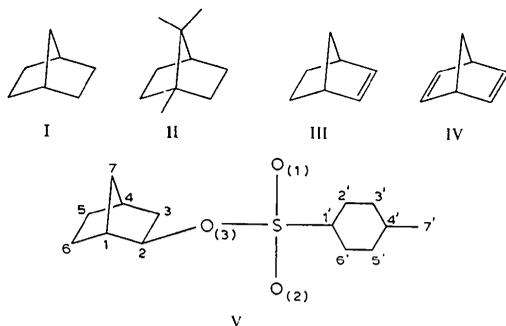
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The tosyl ester of racemic 2-*exo*-norbornanol (bicyclo[2.2.1]heptane-2-*exo*-ol *p*-toluenesulfonate), m.p. 54.5°, crystallizes in the triclinic system: $a = 6.181$, $b = 11.092$, $c = 11.060$ Å, $\alpha = 111.4$, $\beta = 103.6$, $\gamma = 94.8^\circ$, $Z = 2$. 2189 independent nonzero reflections were measured on a four-circle diffractometer (Cu $K\alpha$ radiation), utilizing the θ - 2θ scan mode. Statistical tests indicate the centric space group $P\bar{1}$. The structure was solved by the heavy-atom method. Full-matrix least-squares refinement reduced the R index to about 8%, and convergence seemed complete. However, a difference synthesis revealed partial disorder of carbon atoms C(1), C(3), C(4), and C(6) of the norbornane moiety. The disordered atoms form a second, enantiomeric cage, sharing the 'non-disordered' atoms C(2), C(5) and C(7) with the original molecule. The crystal packing about the cage atoms appears sufficiently loose to permit a statistical disruption of the regular arrangement of L and D molecules, approximately 24% of L being replaced by D and *vice versa*. Further refinement proceeded to a final R index of 4.1%. Atomic distances are (uncorrected for thermal libration): (C-C) average aromatic ring = $1.384(\pm 4)$, (C-C) average cage = $1.527(\pm 5)$, (S=O) average = $1.425(\pm 2)$, S-C(1') = $1.758(\pm 2)$, S-O(3) = $1.573(\pm 2)$, O(3)-C(2) = 1.473 Å.

Introduction

Accurate structural data of a series of carefully selected norbornanes might provide a basis for understanding various factors governing the ground-state energy and geometry of these moderately strained and moderately 'flexible' compounds (Altona & Sundaralingam, 1970).



A survey of the literature shows, surprisingly enough, that the exact geometry of the parent compound (I) and of simple derivatives cannot be regarded as settled. Recent electron-diffraction analyses of norbornane (Morino, Kuchitsu & Yokozeki, 1967; Chiang, Wilcox & Bauer, 1968; Dallinga & Toneman, 1968) and of 1,4-dichloronorbornane (Chiang *et al.*, 1968) yielded contradictory results for all carbon-carbon bond distances as well as for some valency angles. Two X-ray diffraction studies of (2,3-disubstituted) norbornanes have appeared (Fratini, Britts & Karle, 1967; Norment, 1965) and a preliminary report on a neutron-diffraction analysis of a highly hindered norbornanol compound is available (Johnson, 1967).

More is known of substituted camphanes (II) and camphors (Ferguson, Fritchie, Robertson & Sim, 1961; Brueckner, Hamor, Robertson & Sim, 1962; Cesur & Grant, 1965; Allen & Rogers, 1966; Wunderlich, 1967; Alden, Kraut & Traylor, 1968), of derivatives of norbornene (III) (MacDonald & Trotter, 1965*a,b*; Abrahamsson & Nilsson, 1966; Sato, Shiro & Koyama, 1968, 1969; Nilsson, 1968; Destro, Filippini, Gramaccioli & Simonetta, 1969) and of norbornadiene (IV)

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