References

Boer, F. P. & Turley, J. W. (1969). *J. Amer. Chem. Soc.* **91**, 1371–1375.

Chieh, P. C., Subramanian, E. & Trotter, J. (1970). *J. Chem. Soc.* (*A*), p. 179–184.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Denne, W. A. & Small, R. W. H. (1971). *Acta Cryst.* B**27**, 1094–1098.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

IUPAC (1970). *J. Org. Chem.* **35**, 2849–2867.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Kenyon, G. L. & Rowley, G. L. (1971). *J. Amer. Chem. Soc.* **93**, 5552–5560.

Klement, U. (1969). *Acta Cryst.* B**25**, 2460–2465.

Long, R. E. (1965). Thesis, Univ. of California, Los Angeles.

Rademacher, P., Stølevik, R. & Lüttke, W. (1968). *Angew. Chem.* **80**, 842.

St. Clair, D., Zalkin, A. & Templeton, D. H. (1971). *Inorg. Chem.* **10**, 2587–2591.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–2187.

Acta Cryst. (1973). B**29**, 54

The Structure of a Ring-*D*-Bridged Steroid†

By George I. Birnbaum

Division of Biological Sciences, National Research Council, Ottawa, Canada

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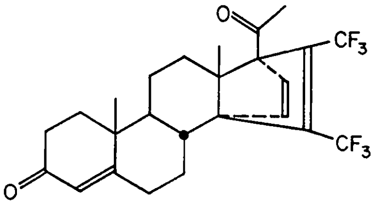
14α,17α-Etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione, $C_{25}H_{26}O_2F_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z=4$) with cell dimensions $a=20\cdot523\pm0\cdot003$, $b=14\cdot224\pm0\cdot003$, $c=7\cdot833\pm0\cdot003$ Å. Crystal densities are $D_m=1\cdot36$ and $D_x=1\cdot37$ g cm^{-3}. Intensity data were collected at room temperature with an automatic four-circle diffractometer. The structure was solved by direct methods and refined by the least-squares procedure to a final value of $R=0\cdot061$ for 2369 observed reflexions. The conformation of ring *A* is intermediate between a half-chair and a sofa. Rings *B* and *C*, which are *trans* fused, are chair shaped. The geometry of the bicyclic system consisting of rings *D* and *D** is very similar to that of norbornadiene.

Introduction

In the course of their chemical and pharmacological studies of steroids with bridged *D*-rings, Solo and his colleagues observed that, in compounds containing two double bonds in the bicyclic system, the hydrogen atoms attached to C(18) are unusually deshielded, as shown by a shift of 0·30 ppm in the n.m.r. spectrum (Solo, Eng & Singh, 1972). In the hope that the precise knowledge of the geometry of the bicyclic system and its vicinity would yield some explanation of this phenomenon an X-ray analysis of 14α,17α-etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione (I) was undertaken.



Experimental

Crystal data

14α,17α-etheno-15,16-di(trifluoromethyl)-4,15-pregnadiene-3,20-dione, $C_{25}H_{26}O_2F_6$; F. W. 472·47; orthorhombic:

$a=20\cdot523\pm0\cdot003$ Å $Z=4$
$b=14\cdot224\pm0\cdot003$ $D_x=1\cdot37$ g cm^{-3}
$c=\ 7\cdot833\pm0\cdot003$ $D_m=1\cdot36$ (flotation)
$V=2286\cdot6$ Å^3 $\mu=10\cdot5$ cm^{-1} (Cu *Kα*)
$F(000)=984$.

Absent reflexions: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group: $P2_12_12_1$.

The material was obtained by a Diels–Alder addition of hexafluoro-2-butyne to 3β-acetoxy-20-keto-5,14,16-pregnatriene, followed by a hydrolysis of the acetate group and an oxidation of the resulting alcohol (Solo & Singh, 1967). The product was crystallized from t-butyl propionate to give colourless prisms (elongated parallel to **c**) with a diamond-shaped base. One of the crystals was cut to a size of 0·3 × 0·4 × 0·6 mm and mounted with **c** parallel to φ on a card-controlled Picker four-circle diffractometer equipped with a Cu

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target tube and a scintillation counter. The cell dimensions were measured at room temperature, using a small take-off angle, a narrow slit, and both Cu $K\alpha_1$ ($\lambda = 1{\cdot}5405$ Å) and Cu $K\alpha_2$ ($\lambda = 1{\cdot}5443$ Å) peaks. Monochromatization was achieved by using a nickel filter and a pulse-height analyser. The moving-crystal, moving-counter method ($\theta/2\theta$ scan) was used to measure the intensity data (2° scans for $2\theta \leq 100°$, 3° for $100° < 2\theta \leq 130°$) and background counts were recorded for 20 sec at the beginning and end of each scan. When the count rate exceeded 20,000 cps the current was reduced and, if necessary, brass attenuators were used. A standard reflexion (12,0,0) was monitored at intervals of approximately $1\frac{1}{2}$ hr. Its intensity decreased by 15% after one-half of the data had been measured and the crystal was replaced by another one of the same dimensions, and mounted in the same manner. The second crystal showed no signs of deterioration. Additional reflexions with $130° < 2\theta \leq 155°$ were measured by transferring the crystal to a manually operated G. E. XRD-5 diffractometer. Except for using a 4° scan the operating conditions remained unchanged. A net count of 90 was observed to produce noticeable deflexions above background, and this count or 5% of the background, whichever was higher, was accepted as threshold intensity below which reflexions were considered unobserved. Of the 2766 reflexions with $2\theta \leq 155°$ 2370 (85%) had intensities above threshold values. They were indexed with respect to a right-handed set of axes. Absorption corrections were considered unnecessary and were not applied.

Structure determination

The structure was solved by direct methods developed for non-centrosymmetric space groups (Karle & Hauptman, 1956). The initial approach involved the application of the $\sum_2$ equation followed by tangent refinement (Karle, 1970). This approach was unsuccessful although numerous starting sets were chosen. In these attempts different reflexions were used to define the origin and the enantiomorph. Symbolic phases were assigned to many others, usually two or three in each starting set. The 30–50 phases thus derived were subjected to tangent refinement, and nine E maps were calculated from the relatively more consistent sets of phases. In all cases the E maps contained only one strong peak. The method which finally led to a solution was based on suggestions of Germain & Woolfson (1968). Three three-dimensional reflexions were included in the starting set and the phases $\pm\pi/4$ and $\pm 3\pi/4$ were successively assigned to them. Tangent refinement was carried out for each of the 64 possible phase combinations and the number of reflexions included was gradually increased from 66 with $E \geq 2{\cdot}0$ to 267 with $E \geq 1{\cdot}55$. In 63 runs the final value of R(Karle) $= \sum(|E_o| - |E_c|/\sum|E_o|)$ ranged from 0·29 to 0·38; in one run, however, it was substantially lower, *viz.* 0·22. The phases from this run were further refined by extending the number of reflexions to 396 with $E \geq 1{\cdot}4$, which resulted in a reduction of R (Karle) to 0·19. During that stage the phases of the three general reflexions in the starting set were also allowed to refine. The initial and refined phases of the starting set are shown in Table 1. An E map calculated with these refined phases revealed the positions of all 33 non-hydrogen atoms.

Table 1. *Initial and refined phases of the starting set*

h	k	l	E	φ	
6	0	7	2·8	90°	define origin
19	0	2	2·7	0	
6	5	0	2·5	0	
17	1	0	2·2	90	defines enantiomorph
1	11	4	2·8	135 → 160°	
19	5	1	2·6	45 → 99	
4	3	7	2·6	135 → 122	

The atomic scattering factors for C, O and F were those given by Doyle & Turner (1968) and those for bonded H were taken from Stewart, Davidson & Simpson (1965). Both the oxygen and the fluorine curve were corrected for anomalous dispersion with $\Delta f' = 0{\cdot}0$ and $\Delta f'' = 0{\cdot}1$ (*International Tables for X-ray Crystallography*, 1962). The substance under investigation having been derived from a naturally occurring steroid, the known absolute configuration of this class of compounds was assumed. After five cycles of least-squares refinement, using the block-diagonal approximation and isotropic temperature parameters, the value of R had decreased to 0·14. Throughout the refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized and a factor of 0·8 was applied to all shifts. A low-angle difference Fourier map was calculated after five more cycles of refinement in which anisotropic temperature parameters had been used. This map yielded the positions of 17 hydrogen atoms on peaks ranging from 0·25 to 0·40 e.Å^{-3}. The remaining nine hydrogen atoms were placed in calculated positions (recalculated after each cycle) and the contributions of all 26 atoms were included in subsequent structure factor calculations. The isotropic temperature parameters assigned to them were based on those of the carbon atoms to which they are attached as well as their peak heights in the difference map. The weighting scheme used in the later stages of the refinement was $w = w_1 \, . \, w_2$ where

$$\begin{aligned} w_1 &= 1 && \text{for } |F_o| \leq 9 \\ &= \frac{9}{|F_o|} && \text{for } |F_o| > 9; \\ w_2 &= 1{\cdot}67 \sin^2\theta && \text{for } \sin^2\theta \leq 0{\cdot}4 \\ &= 1 && \text{for } \sin^2\theta > 0{\cdot}4\,. \end{aligned}$$

This weighting scheme was fairly successful in eliminating the dependence of $w\Delta F^2$ on $|F_o|$ and $\sin^2\theta$. Only the strongest reflexion, 020 ($|F_o| = 185{\cdot}9$, $F_c = 219{\cdot}1$), was noticeably affected by extinction and was therefore excluded from the subsequent refinement.

The refinement converged after the 13th cycle with the average coordinate shift equalling $0{\cdot}1\sigma$ and the largest one $0{\cdot}3\sigma$. The agreement index $R=(\sum|\Delta F|/\sum|F_o|)$ for 2369 observed reflexions was 0·061 and the weighted index $R'=(\sum w\Delta F^2/\sum wF_o^2)^{1/2}$ was 0·075. For the full set of 2765 reflexions $R=0{\cdot}072$. The final difference Fourier map showed two small peaks, 0·26 and 0·36 e Å^{-3}, near the strongly vibrating atoms O(2) and F(5), respectively, but was otherwise featureless. The final coordinates and temperature parameters are shown in Tables 2 and 3. The estimated standard deviations (shown in parentheses and referring always to the last digits) were derived from the inverses of the least-squares matrices. Observed and calculated structure factors are shown in Table 4.

The structure was subjected to a rigid-body analysis in terms of translation (**T**), libration (**L**) and screw motion (**S**) tensors (Schomaker & Trueblood, 1968). When the whole molecule was assumed to vibrate as a rigid body the value of $\sigma(U_{\text{calc}})=[\sum(\Delta U^{ij})^2/(n-s)]^{1/2}$ was 0·0108 Å^2, six times higher than the average value of $\sigma(U^{ij}_{\text{obs}})$. Exclusion of the CF_3 groups and the side chain attached to C(17) from the assumed rigid body led to $\sigma(U_{\text{calc}})=0{\cdot}0043$ Å^2. Although in the latter case the assumption of a rigid body was marginally valid, the corrections in bond lengths did not exceed σ and were therefore not applied.

Table 3. *Final parameters of hydrogen atoms*

	x	y	z	B
H(11)	0·572	0·068	0·387	6·0 Å^2
H(12)†	0·592	−0·029	0·481	6·5
H(21)	0·658	0·002	0·221	7·5
H(22)†	0·701	−0·004	0·410	7·5
H(41)	0·708	0·258	0·455	5·0
H(61)	0·676	0·218	0·843	5·5
H(62)	0·679	0·305	0·724	5·5
H(71)	0·586	0·316	0·928	5·0
H(72)	0·555	0·302	0·715	5·0
H(81)	0·570	0·143	0·945	4·5
H(91)	0·521	0·159	0·596	4·5
H(111)	0·521	−0·007	0·800	5·0
H(112)	0·503	−0·005	0·600	5·0
H(121)	0·411	−0·009	0·778	6·0
H(122)	0·409	0·101	0·689	6·5
H(151*)	0·455	0·305	0·715	5·0
H(161*)†	0·326	0·273	0·791	5·0
H(181)†	0·439	0·065	1·200	6·5
H(182)	0·429	−0·030	1·060	6·5
H(183)†	0·502	0·032	1·088	6·5
H(191)†	0·645	0·051	0·876	6·5
H(192)†	0·631	−0·040	0·755	7·5
H(193)	0·693	0·023	0·728	7·5
H(211)	0·237	0·068	0·919	7·5
H(212)†	0·282	0·088	0·784	7·5
H(213)†	0·237	0·166	0·881	7·5

† Calculated positions.

Table 2. *Final parameters (and their e.s.d.'s) of the non-hydrogen atoms*

All coordinates are × 10^4. The U_{ij} values (in Å^2) are × 10^3 and are defined by

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{13}hla^*c^*+2U_{12}hka^*b^*)\right]$$

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	6057 (2)	376 (3)	4581 (7)	66 (2)	72 (2)	85 (3)	−57 (4)	24 (4)	−17 (4)
C(2)	6677 (2)	356 (4)	3508 (8)	75 (2)	88 (3)	101 (3)	−59 (5)	48 (5)	−3 (4)
C(3)	6944 (2)	1321 (4)	3251 (6)	51 (1)	91 (3)	77 (2)	−9 (4)	8 (3)	3 (4)
C(4)	6863 (2)	1972 (3)	4657 (6)	50 (1)	78 (2)	82 (2)	−9 (4)	4 (3)	−11 (3)
C(5)	6517 (2)	1788 (3)	6081 (5)	44 (1)	68 (2)	73 (2)	−16 (3)	−9 (3)	−1 (3)
C(6)	6514 (2)	2464 (3)	7520 (6)	51 (2)	77 (2)	78 (2)	−19 (4)	−10 (3)	−29 (3)
C(7)	5818 (2)	2695 (2)	8117 (5)	56 (1)	55 (2)	72 (2)	−19 (3)	4 (3)	−20 (3)
C(8)	5458 (1)	1778 (2)	8564 (5)	45 (1)	52 (1)	58 (2)	−2 (3)	−12 (3)	0 (2)
C(9)	5432 (2)	1148 (2)	6965 (5)	48 (1)	47 (1)	63 (2)	−9 (3)	−6 (3)	5 (2)
C(10)	6131 (2)	886 (3)	6301 (5)	48 (1)	57 (2)	70 (2)	−15 (3)	−4 (3)	8 (3)
C(11)	4993 (2)	278 (2)	7174 (6)	62 (2)	49 (2)	85 (2)	−13 (3)	3 (4)	−4 (3)
C(12)	4301 (2)	543 (2)	7732 (6)	57 (2)	51 (2)	75 (2)	−15 (3)	0 (3)	−23 (3)
C(13)	4331 (2)	1072 (2)	9440 (5)	54 (1)	54 (2)	60 (2)	22 (3)	−5 (3)	−6 (3)
C(14)	4769 (2)	1970 (2)	9241 (4)	50 (1)	48 (1)	49 (1)	4 (3)	−12 (2)	3 (2)
C(15)	4642 (2)	2398 (2)	11028 (5)	59 (2)	53 (2)	57 (2)	0 (3)	−9 (3)	11 (3)
C(16)	4015 (2)	2255 (3)	11411 (5)	64 (2)	63 (2)	58 (2)	15 (3)	5 (3)	17 (3)
C(15*)	4332 (2)	2570 (2)	8067 (5)	57 (1)	50 (1)	63 (2)	12 (3)	−5 (3)	13 (3)
C(16*)	3713 (2)	2408 (3)	8475 (5)	55 (1)	61 (2)	66 (2)	5 (3)	−20 (3)	9 (3)
C(17)	3718 (2)	1696 (3)	9927 (5)	50 (1)	75 (2)	60 (2)	15 (3)	3 (3)	−4 (3)
C(18)	4534 (2)	395 (3)	10873 (6)	80 (2)	59 (2)	75 (2)	40 (4)	−16 (4)	2 (4)
C(19)	6497 (2)	250 (3)	7583 (7)	66 (2)	77 (2)	99 (3)	19 (5)	3 (4)	38 (4)
C(20)	3100 (2)	1132 (4)	10299 (7)	63 (2)	88 (3)	89 (3)	21 (5)	18 (4)	−15 (4)
C(21)	2605 (3)	1051 (5)	8945 (10)	73 (3)	112 (4)	124 (5)	−8 (7)	−19 (6)	−60 (5)
C(22)	5141 (2)	2888 (3)	12086 (5)	79 (2)	66 (2)	55 (2)	−9 (3)	−20 (3)	6 (3)
C(23)	3618 (2)	2638 (4)	12869 (6)	76 (2)	108 (3)	65 (2)	10 (5)	14 (4)	14 (5)
O(3)	7228 (2)	1535 (3)	1924 (5)	82 (2)	115 (2)	89 (2)	−26 (4)	46 (3)	−14 (4)
O(20)	3044 (3)	760 (5)	11671 (7)	111 (3)	165 (4)	116 (3)	106 (7)	22 (5)	−97 (6)
F(1)	5719 (1)	2482 (2)	11990 (4)	73 (1)	111 (2)	90 (2)	−45 (3)	−65 (3)	25 (3)
F(2)	5226 (2)	3785 (2)	11611 (4)	111 (2)	68 (1)	84 (2)	−19 (2)	−40 (3)	−28 (3)
F(3)	5004 (2)	2901 (3)	13757 (3)	108 (2)	117 (2)	58 (1)	−16 (3)	−29 (3)	1 (3)
F(4)	3836 (2)	3473 (3)	13432 (5)	117 (2)	110 (2)	93 (2)	−61 (4)	12 (3)	49 (4)
F(5)	3015 (2)	2791 (4)	12382 (5)	79 (1)	174 (3)	104 (2)	−47 (5)	25 (3)	58 (4)
F(6)	3625 (2)	2070 (3)	14218 (4)	157 (3)	146 (3)	67 (2)	33 (4)	44 (4)	−21 (5)

Table 4. *Observed and calculated structure factors* (× 10)

An asterisk indicates an unobserved reflexion to which the estimated threshold value was assigned.

Description of the structure

A stereoscopic view of the molecule is shown in Fig. 1; bond lengths, bond angles and torsional angles can be seen in Fig. 2. The conformation of ring *A* could be described as being approximately intermediate between a half-chair and a sofa. The qualitative nature of such statements must be emphasized in view of some confusing nomenclature in recent publications dealing with *A*-rings in Δ^4-3-keto steroids. Duax, Eger, Pokrywiecki & Osawa (1971) seemed to equate a half-chair with a six-membered envelope in which C(2) was displaced from the least-squares plane through the other five atoms in the ring, yet the latter description corresponds to a sofa conformation. The calculated torsional angles for the two conformations of unsubstituted cyclohexene rings are shown in Fig. 3 (Bucourt & Hainaut, 1965). A comparison with the torsional angles in 2,2,6β-trichlorotestosterone (Duax, Osawa, Cooper & Norton, 1971) reveals that a description of its *A*-ring as a 'normal half-chair' was incorrect since it has three pairs of angles of equal magnitudes and opposite signs; it would have been better to describe it as a somewhat puckered sofa. Similarly, ring *A* in 4-chlorocortisone assumes an almost ideal sofa conformation and it is misleading to call it a chair (Duax, Cooper & Norton, 1971). Thus the conclusion that *A*-rings in Δ^4-3-keto steroids are normally in half-chair conformation (Duax, Eger, Pokrywiecki & Osawa, 1971) seems doubtful, particularly since it appears to be based on deviations of atoms from a least-squares plane. An evaluation of torsional angles is clearly preferable in ascertaining the conformation of a ring.

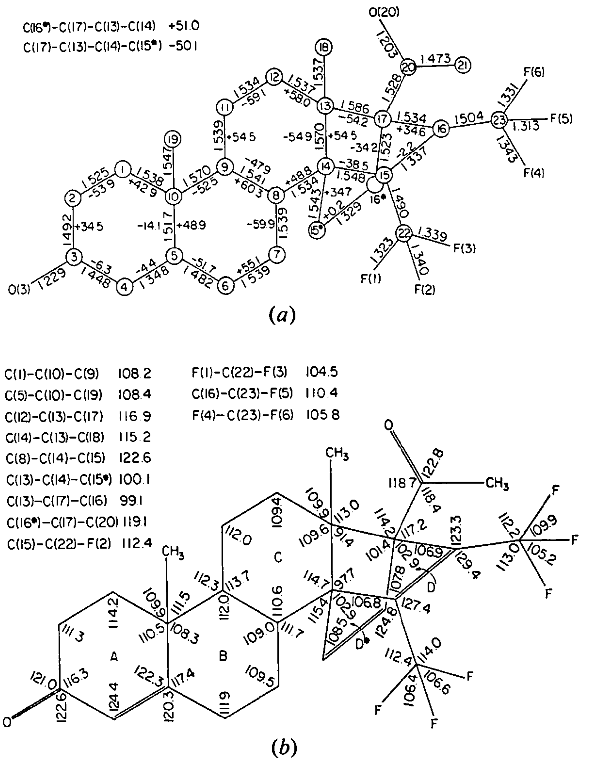


Fig. 2. (*a*) Bond lengths and torsional angles. The ranges of the e.s.d.'s are 0·005–0·007 Å and 0·3–0·6°, respectively. (*b*) Bond angles. The e.s.d.'s are 0·2–0·5°.

Rings *B* and *C* are chair shaped. A comparison of their torsional angles with recently calculated values for the 14α-androstane skeleton (Allinger & Wu, 1971) reveals some distortions attributable to the strain transmitted from adjacent rings. The presence of the trigonal atom C(5) causes a flattening of the *B*-ring which is reflected by decreased absolute values (6–8°) of torsional angles about the bonds C(5)–C(6) and C(5)–C(10). Consequently the angle at the junction with ring *C* is increased by 5°. That junction being *trans*, such increase would normally cause a comparable closing of the adjacent torsional angle C(14)–C(8)–C(9)–C(11). However, the strain transmitted from ring *D* acts in the opposite direction (Altona, Geise & Romers, 1968). The puckering of ring *D* is abnormally large [the distance of C(13) from the least-squares plane of the ring is 0·931 Å] and the effect of the large torsional angle C(17)–C(13)–C(14)–C(15), when transmitted across the *trans* *C*/*D* junction, is to make the adjacent angle in ring *C* 7° smaller than normal. Ordinarily, this would make the torsional angle at the junction with ring *B* larger, but, for reasons outlined above, that angle has an approximately normal value.

The geometry of the bicyclic system formed by rings *D* and *D** is of particular interest since most X-ray analyses of norbornadiene derivatives have not achieved the precision of this determination. Except for a small distortion (see below), which causes the C(13)–C(14)–C(15) angle to be smaller, chemically equivalent bond lengths and angles in the bicyclic

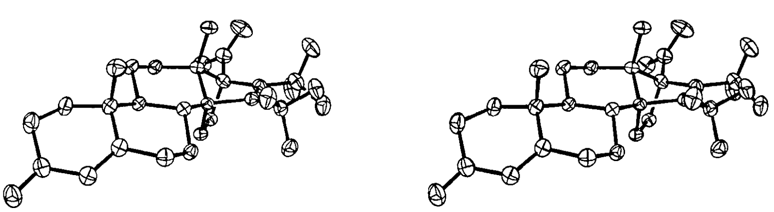


Fig. 1. Stereoscopic view of the structure; the ellipsoids include 20% probability.

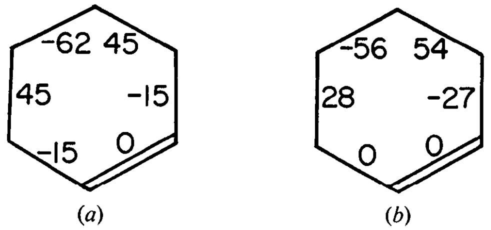


Fig. 3. Calculated torsional angles in cyclohexene: (*a*) half-chair, (*b*) sofa conformation.

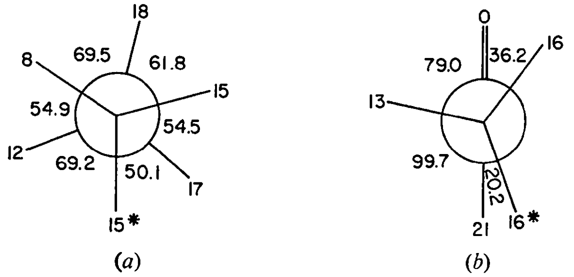
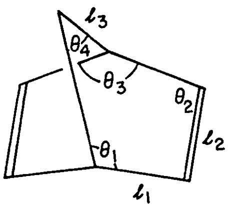


Fig. 4. Newman projections (*a*) along the C(13)–C(14) bond, (*b*) along the C(17)–C(20) bond.

moiety of the molecule are equal within experimental error, indicating retention of the expected C_{2v} symmetry. One is therefore justified in calculating mean values of these parameters, and it is valuable to compare them with those obtained recently from an electron diffraction study of norbornadiene (Yokozeki & Kuchitsu, 1971). As can be seen (Table 5), there are no significant differences between the comparable results of the two experiments. The lengthening of the bonds forming the bridge reflects the angle strain present in the molecule. An extreme example of such bond stretching was recently encountered in a cyclobutane derivative (Birnbaum, 1972) where a C–C bond of 1·628 (2) Å was found. All C–F bond lengths, except the one involving the strongly vibrating F(5), agree with the value of 1·333 ± 0·005 Å given by Sutton (1965). The average angles, again excluding F(5), are 112·8 (2)° for C–C–F and 105·7 (2)° for F–C–F. Some nonbonded distances in and near the [2.2.1] bicyclic system are given in Table 6, while Table 7 shows least-squares planes and dihedral angles between them.

Table 5. *Geometries in two* [2.2.1]*bicycloheptadiene systems*



	X.R.*	E.D.†
l_1	1·537 (3) Å	1·535 ± 0·007 Å
l_2	1·333 (4)	1·343 ± 0·003
l_3	1·578 (4)	1·573 ± 0·014
θ_1	100·2 (2)°‡	
θ_2	107·5 (2)	
θ_3	102·9 (2)	
θ_4	91·4 (3)	94·1 ± 3·0°

* Averages from this structure analysis.

† Electron diffraction analysis of norbornadiene (Yokozeki & Kuchitsu, 1971).

‡ The angle C(13)–C(14)–C(15) was excluded from averaging; see text.

Table 6. *Selected nonbonded distances*

C(14)····C(17)	2·258 (5) Å
C(15)····C(15*)	2·418 (5)
C(16)····C(16*)	2·391 (6)
C(15*)···C(16)	2·736 (5)
C(15)····C(16*)	2·762 (5)
C(15)····H(181)	2·65
C(16)····H(181)	2·45
O(20)····H(181)	2·78

The distortion mentioned above is indicated by the torsional angle of −2·2° about the C(15)–C(16) double bond; consequently these two atoms are not coplanar with the four carbon atoms attached to them. This twisting of the double bond may be due to repulsion between the two $-CF_3$ substituents. The non-bonded distance between F(3) and F(4) is 2·545 (5) Å while the sum of the two van der Waals radii is 2·8 Å (Bondi, 1964). The distortion is very small, however, and is not expected to be responsible for the unusual n.m.r. spectrum. On the other hand, the orientation of the

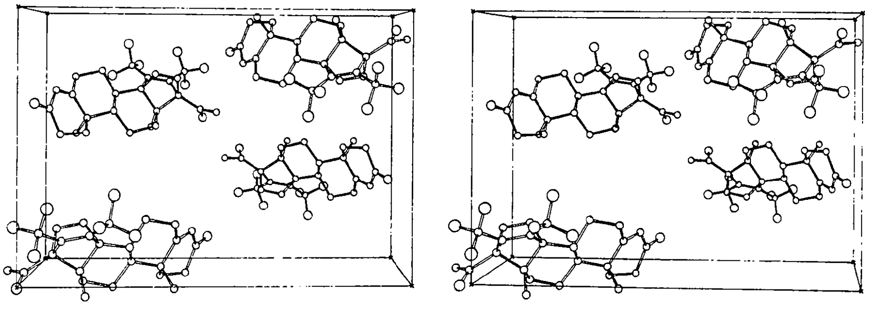


Fig. 5. Stereoscopic view along **z** of the contents of a unit cell. The directions of axes are **x** ← (from 0·25 to 1·25), **y** ↓ (0 to 1·0), and **z** up.

Table 7. *Least-squares planes and deviations of atoms from them*

The e.s.d.'s on *Δ* are 0·003–0·006 Å.

Plane I		Plane II		Plane III		Plane IV		Plane V		Plane VI	
	Δ		*Δ*		*Δ*		*Δ*		*Δ*		*Δ*
C(2)	−0·003 Å	C(3)	−0·037 Å	C(14)	0·005 Å	C(14)	0·000 Å	C(13)	0·000 Å	C(17)	0·001 Å
C(3)	0·007	C(4)	0·040	C(15)	−0·011	C(15*)	0·000	C(14)	0·000	C(20)	−0·006
O(3)	−0·002	C(5)	0·016	C(16)	0·014	C(16*)	−0·001	C(17)	0·000	O(20)	0·003
C(4)	−0·002	C(6)	−0·027	C(17)	−0·008	C(17)	0·000	C(12)†	1·263	C(21)	0·003
C(5)†	0·102	C(10)	0·001	C(22)†	−0·035	C(13)†	0·877	C(18)†	−1·246	C(16)†	−0·786
C(10)†	0·342	O(3)†	0·075	C(23)†	0·196					C(16*)†	−0·440
				C(13)†	−0·931						
$\chi^2=4·9$		$\chi^2=257$		$\chi^2=31·4$		$\chi^2=0·2$		$\chi^2=0$		$\chi^2=2·5$	

Dihedral angles: ∠III,IV 109·4°; ∠III,V 123·4°; ∠IV,V 127·2°; ∠III,VI 49·4°; ∠IV,VI 33·6°

Plane I $0·8707X-0·2982Y+0·3911Z=12·8521$ Å

Plane II $0·7909X-0·4434Y+0·4217Z=11·4753$

Plane III $0·2578X-0·8624Y+0·4357Z=3·2661$

Plane IV $0·0308X+0·7471Y+0·6640Z=7·2007$ Å

Plane V $0·2511X-0·0592Y+0·9662Z=9·2857$

Plane VI $0·4472X-0·8236Y-0·3488Z=-1·2874$

† Not included in the calculation of the plane.

acetyl group was suspected to cause deshielding of the C(18) hydrogen atoms. As can be seen in Fig. 4, the C=O bond is almost parallel to C(16*)–C(17) with the O atom in the *β* orientation, and it is also almost parallel to the C(13)–C(18) bond. There is no close contact between the O atom and either the angular methyl group or the $-CF_3$ substituent at C(16). The dihedral angle between the plane of the acetyl group (plane VI) and the plane of the *D*-ring (plane III) is 11° larger than that in the 14α,17α-ethano analogue (Solo, Singh, Shefter & Cooper, 1968). A detailed interpretation of the n.m.r. spectrum based on this structure analysis will be published elsewhere (Solo, Eng & Singh, 1972).

The packing of the molecules is shown in Fig. 5. All intermolecular distances are longer than the sums of the van der Waals radii.

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References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *IUCr World List of Crystallographic Computer Programs*. 2nd Ed. Appendix, p. 52.

Allinger, N. L. & Wu, F. (1971). *Tetrahedron*, **27**, 5093–5113.

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Birnbaum, G. I. (1972). *Acta Cryst.* B**28**, 1248–1254.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Duax, W. L., Cooper, A. & Norton, D. A. (1971). *Acta Cryst.* B**27**, 1–6.

Duax, W. L., Eger, C., Pokrywiecki, S. & Osawa, Y. (1971). *J. Med. Chem.* **14**, 295–300.

Duax, W. L., Osawa, Y., Cooper, A. & Norton, D. A. (1971). *Tetrahedron*, **27**, 331–335.

Germain, G. & Woolfson, M. M. (1968). *Acta Cryst.* B**24**, 91–96.

International Tables for X-ray Crystallography (1962). Vol. III, p. 214. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Karle, I. L. (1970). In *Crystallographic Computing*. Edited by F. R. Ahmed. Copenhagen: Munksgaard.

Karle, J. & Hauptman, H. (1956). *Acta Cryst.* **9**, 635–651.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Solo, A. J., Eng, S. & Singh, B. (1972). Submitted to *J. Pharm. Sci.*

Solo, A. J. & Singh, B. (1967). *J. Med. Chem.* **10**, 1048–1051.

Solo, A. J., Singh, B., Shefter, E. & Cooper, A. (1968). *Steroids*, **11**, 637–648.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement.* London: The Chemical Society.

Yokozeki, A. & Kuchitsu, K. (1971). *Bull. Chem. Soc. Japan*, **44**, 2356–2363.