

## The Crystal and Molecular Structure of a Di-*t*-butylsesquifulvalene–Dimethyl Acetylenedicarboxylate Addition Product

BY WALTER HENSLEE\* AND RAYMOND E. DAVIS†

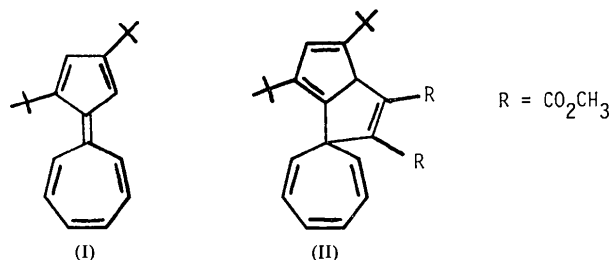
Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

(Received 29 March 1974; accepted 3 January 1975)

Crystals of  $C_{30}H_{32}O_4$  are triclinic,  $P\bar{1}$ , with  $a=9.787(1)$ ,  $b=14.669(1)$ ,  $c=9.117(1)$  Å,  $\alpha=109.40(1)^\circ$ ,  $\beta=109.01(1)^\circ$ ,  $\gamma=87.54(1)^\circ$ ,  $V=1164$  Å<sup>3</sup>,  $Z=2$ ,  $M=408.52$ ,  $D_x=1.166$  g cm<sup>-3</sup>,  $D_{exp}=1.16$  g cm<sup>-3</sup>. 4868 independent intensity measurements were made by continuous scans on a Syntex  $P2_1$  autodiffractometer. The structure was refined by anisotropic full-matrix least-squares methods to a final conventional  $R$  of 0.068 and a weighted  $R$  of 0.036. The molecule is a [4+2] cycloaddition product. Steric interactions between the seven-membered ring, the bridgehead *t*-butyl group and the adjacent methoxy-carbonyl group exert a dramatic effect on the overall geometry of the molecule. The seven-membered ring shows marked alternation in bond length and adopts a boat conformation. The question of non-planarity (torsion about the single bonds) in structures containing a heptafulvene moiety is discussed. X-ray data for a wide variety of structures containing C=C bonds and opposing CCC angles are tabulated and an approximately linear relationship between the exocyclic C=C bond length and opposite CCC bond angle is shown for structures with a heptafulvene entity present. Tropone and tropolone type structures, as well as molecules containing a fulvene fragment, are discussed.

### Introduction

Non-alternant hydrocarbons and their cycloaddition products have been areas of recent interest with respect to reaction mechanisms and intermediates (see, e.g., Prinzbach, 1971). The molecular structures of these species are also of considerable importance for their comparison with predictions based on  $\pi$ -molecular orbital calculations (Dewar & Gleicher, 1965; Thomas & Coppens, 1972; Nishi, Sasada, Ashida & Kakudo, 1966). However, few X-ray determinations of such structures have been reported. A [12+2] cycloaddition has been proposed for the tetracyanoethylene (TCNE) adduct of di-*t*-butylsesquifulvalene (I) and a [6+2] addition (II) has been suggested for the dimethyl acetylenedicarboxylate (MAD) adduct (Prinzbach & Knöfel, 1969; Prinzbach, 1971). Following the X-ray determination of the TCNE adduct (Davis, 1973), the present structural analysis of the MAD adduct of di-*t*-butylsesquifulvalene was undertaken.



\* Present address: Central Laboratories, Dow Chemical Co., Freeport, Texas 77541, U.S.A.

† Author to whom correspondence should be addressed.

### Experimental

Pale yellow crystals of an MAD adduct of di-*t*-butylsesquifulvalene were kindly supplied by Professor Horst Prinzbach, Freiburg. Space-group determination and data collection were carried out at ambient room temperature ( $\sim 23^\circ\text{C}$ ) with the software package of a Syntex  $P2_1$  autodiffractometer and monochromatized Mo  $K\alpha$  radiation ( $\lambda_1=0.70926$ ,  $\lambda_2=0.71354$  Å). A crystal, obtained from heptane recrystallization, with dimensions approximately  $0.2 \times 0.3 \times 0.6$  mm was mounted with the long dimension parallel to the  $\varphi$  axis. Based on  $\omega$  and  $\theta$ ,  $2\theta$  scans and examination with a polarizing microscope, this crystal appeared to be of suitable quality for single-crystal intensity measurements.

The observed density of  $1.16$  g cm<sup>-3</sup> (floatation in aqueous zinc chloride solution) agrees with the calculated density for  $Z=2$  to within the limits of experimental error. Cell constants were determined by a least-squares refinement of 42 independent  $2\theta$  measurements on a General Electric XRD-5 diffractometer with Cu  $K\alpha_1$  ( $1.54050$  Å) and Cu  $K\alpha_2$  ( $1.54433$  Å) well resolved. The resulting lattice parameters are  $a=9.787(1)$ ,  $b=14.669(1)$ ,  $c=9.117(1)$  Å,  $\alpha=109.40(1)$ ,  $\beta=109.01(1)$ ,  $\gamma=87.54(1)^\circ$ .

4868 independent reflections, to  $2\theta$  max =  $53^\circ$ , were measured on the autodiffractometer *via* continuous scans ( $2\theta$   $K\alpha_1$ - $0.8^\circ$  to  $2\theta$   $K\alpha_2$ + $1.0^\circ$ ) at speeds ranging from  $3^\circ$  to  $15^\circ$  min<sup>-1</sup>. Backgrounds were determined by counting at each extreme of the scan for a period equal to  $\frac{1}{2}$  the scan time.

On the basis of four standard reflections, monitored every 96 reflections throughout data collection,

it was concluded that the crystal had suffered neither misalignment nor radiation damage during the 118 h of data collection. An analysis of the standard reflections was carried out according to the following scheme: The intensity,  $y_i$ , of each standard,  $j$ , was plotted *versus* X-ray exposure hours,  $x_i$ , and the best straight line (defined by  $y = p_j + q_j x$ ) through these points was extrapolated to zero exposure time, yielding an  $I_{o_j}$  value for this standard. Each point in this plot was divided by the  $I_o$  value, giving a set of normalized  $y_i$  values for this standard,  $j$ . This procedure was followed for each of the four different standard reflections. A weighted [ $w_j = 1/\sigma^2(I_{o_j})$ ] average of the four normalized values was computed for each value of exposure hours. This weighted average was plotted *versus* exposure hours. The best linear correction factor (defined by  $K = 1 + sx$ ) was determined through these averaged points. The entire process was repeated for the four standards, each fitted to a quadratic curve defined by  $y = p_j + q_j x + r_j x^2$ . The normalized values, weighted as before, were averaged, plotted *versus* exposure hours, and the best quadratic correction factor (defined by  $K = 1 + sx + tx^2$ ) was determined through these points. Since the value of  $t$  in the quadratic workup was  $5(10) \times 10^{-7}$  the linear correction factor  $K = 1 + (4.1 \times 10^{-5})x$  was applied, resulting in a maximum correction factor of 1.005.

The intensity values were reduced by application of this decay correction and the Lorentz and polarization

corrections including monochromator effects. Since the absorption coefficient was quite low ( $\mu = 0.83 \text{ cm}^{-1}$ ) no correction for absorption was applied. Standard deviations in intensities based on counting statistics (Evans, 1961) were used to determine  $\sigma(|F_o|)$ .

### Structure determination and refinement

The structure was solved by the symbolic addition method (Karle & Karle, 1966, and references therein) using 387 reflections in terms of three symbols. The  $E$  map corresponding to the non-trivial case with the least number of indeterminates (22) allowed location of 28 of 30 nonhydrogen atoms. The remaining two carbon atoms were found with the aid of a subsequent difference density map.

Refinement on structure amplitudes was carried out with Ibers's modification of the Busing, Martin & Levy (1963) full-matrix least-squares program *ORFLS*. Relative weights,  $w(hkl) \propto 1/\sigma^2(|F(hkl)|)$ , were used for the 2009 reflections with  $I_{\text{net}} > 2\sigma(I)$ ; the remaining reflections were excluded from the refinement.

A scale factor, an extinction parameter (Zachariasen, 1968), 30 anisotropic non-hydrogen atoms and 32 isotropic hydrogen atoms were varied during refinement. The value of the extinction coefficient was  $2.0(6) \times 10^{-7}$ . The ratio of largest parameter shift in the final cycle to parameter standard deviation was 0.55 for nonhydrogen coordinates, 2.5 for nonhydrogen  $\beta$  values,

Table 1. Final positional ( $\times 10^4$ ) and thermal parameters ( $\times 10^4$ ) of the nonhydrogen atoms with estimated standard deviations in parentheses

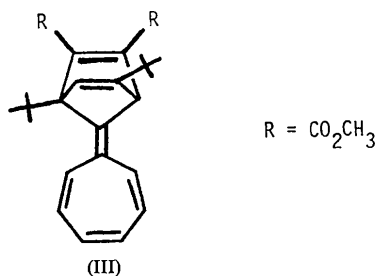
The temperature factor expression was  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	5878 (4)	7514 (3)	-461 (5)	97 (7)	74 (4)	142 (10)	3 (4)	45 (7)	39 (5)
C(2)	6878 (5)	8150 (3)	-335 (5)	127 (8)	93 (4)	190 (12)	10 (5)	83 (9)	73 (6)
C(3)	8140 (5)	8585 (4)	1076 (6)	130 (9)	89 (5)	221 (13)	-11 (6)	84 (9)	46 (7)
C(4)	8839 (5)	8182 (4)	2205 (6)	101 (9)	107 (6)	176 (13)	-7 (6)	32 (9)	32 (7)
C(5)	8485 (5)	7246 (4)	2214 (5)	109 (8)	86 (5)	197 (11)	18 (5)	50 (8)	55 (6)
C(6)	7172 (4)	6782 (3)	1612 (5)	91 (7)	78 (4)	179 (10)	16 (4)	38 (7)	64 (5)
C(7)	5810 (4)	7167 (3)	856 (4)	76 (6)	54 (3)	117 (9)	0 (4)	33 (6)	28 (4)
C(8)	4562 (4)	7182 (2)	1144 (4)	83 (6)	32 (3)	106 (8)	0 (3)	20 (6)	21 (4)
C(9)	3856 (4)	6889 (3)	2254 (4)	84 (6)	39 (3)	118 (8)	2 (3)	29 (6)	25 (4)
C(10)	2476 (4)	6352 (3)	863 (5)	101 (6)	41 (3)	135 (8)	-7 (3)	38 (6)	33 (4)
C(11)	2087 (4)	6752 (3)	-289 (4)	80 (6)	46 (3)	124 (9)	0 (4)	29 (6)	28 (4)
C(12)	3195 (4)	7612 (4)	315 (5)	104 (6)	52 (3)	126 (8)	3 (3)	47 (6)	54 (4)
C(13)	2996 (4)	8329 (3)	1854 (5)	90 (7)	41 (3)	148 (9)	4 (3)	35 (6)	35 (4)
C(14)	3381 (4)	7927 (3)	3023 (4)	92 (7)	42 (3)	119 (9)	2 (4)	31 (6)	20 (4)
C(15)	3165 (4)	8346 (3)	4666 (5)	100 (7)	48 (3)	161 (10)	7 (4)	17 (8)	29 (5)
C(16)	3979 (6)	9528 (5)	7311 (8)	206 (14)	133 (7)	201 (15)	10 (9)	48 (12)	-66 (8)
C(17)	2406 (4)	9277 (3)	1885 (5)	124 (8)	49 (4)	198 (12)	-7 (4)	48 (8)	33 (6)
C(18)	1497 (8)	10662 (5)	3410 (9)	358 (21)	55 (5)	461 (29)	63 (8)	225 (22)	63 (10)
C(19)	820 (4)	6511 (3)	-1861 (4)	90 (6)	56 (3)	115 (9)	10 (4)	28 (6)	24 (4)
C(20)	38 (5)	7424 (4)	-1938 (7)	126 (10)	89 (6)	231 (15)	15 (6)	-43 (11)	31 (7)
C(21)	1390 (6)	6154 (4)	-3309 (6)	185 (12)	116 (7)	132 (12)	2 (8)	38 (10)	13 (7)
C(22)	-222 (6)	5736 (4)	-1974 (7)	158 (10)	106 (6)	192 (14)	-57 (6)	-14 (10)	42 (7)
C(23)	4641 (4)	6318 (3)	3394 (4)	107 (7)	49 (3)	115 (8)	10 (4)	23 (6)	42 (4)
C(24)	4946 (6)	5335 (3)	2345 (6)	186 (10)	47 (4)	178 (11)	28 (5)	74 (9)	50 (5)
C(25)	3667 (5)	6123 (4)	4292 (6)	178 (10)	80 (5)	182 (12)	27 (6)	88 (9)	80 (7)
C(26)	6039 (5)	6871 (4)	4700 (6)	120 (8)	79 (5)	132 (10)	14 (5)	21 (7)	47 (6)
O(1)	2125 (3)	8134 (2)	4935 (3)	164 (6)	88 (3)	203 (8)	-2 (3)	92 (6)	39 (4)
O(2)	4228 (3)	8986 (2)	5746 (3)	135 (5)	81 (3)	178 (7)	-4 (3)	42 (5)	-11 (3)
O(3)	2070 (3)	9715 (2)	3245 (4)	225 (7)	46 (2)	282 (9)	35 (3)	129 (6)	48 (4)
O(4)	2257 (3)	9616 (2)	823 (4)	293 (8)	67 (3)	274 (9)	40 (3)	114 (7)	90 (4)

2.9 for the  $y$  coordinate of H(12) ( $\leq 1.0$  for all other hydrogen coordinates) and 3.0 for hydrogen  $B$  values. A final difference map revealed no regions of residual electron density greater than  $0.24 \text{ e } \text{\AA}^{-3}$ . The atomic scattering factors used were those of Stewart, Davidson & Simpson (1965) for hydrogen and those of Cromer & Waber (1965) for carbon and oxygen. Final agreement indices for the 2009 reflections used in refinement were  $R_1=0.068$  and  $R_2=0.036$ . The values including all 4868 reflections were  $R_1=0.185$  and  $R_2=0.047$ .\*

### Discussion

Crystal structure analysis has confirmed the predicted [12+2] addition product for TCNE (Davis, 1973) but the present study establishes an unexpected [4+2] addition (III) for MAD.



The geometry of the molecule is shown by the stereoscopic drawing in Fig. 1. The final positional parameters and anisotropic temperature factors for non-hydrogen atoms are given in Table 1, with reference to the numbering scheme in Fig. 2. Final positional and isotropic thermal parameters for hydrogen atoms are shown in Table 2. Bond lengths and bond angles appear in Figs. 2 and 3, respectively. Bond lengths involving hydrogen atoms range from 0.84 to 1.13 Å with a mean value of 0.97 Å. Selected torsion angles

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30862 (24 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

are shown in Table 3. Fig. 4 depicts the crystal packing; no intermolecular distances less than the sum of the van der Waals radii occur. Polar components of different molecules face each other across inversion centers at corners, faces or the center of the unit cell. The same may be said of the non-polar parts of the molecule.

A striking structural feature is the severe steric hindrance between the seven-membered ring, the bridgehead t-butyl group and the adjacent methoxycarbonyl group. Short intramolecular non-bonded con-

Table 2. Final positional ( $\times 10^3$ ) and isotropic thermal parameters for hydrogen atoms with estimated standard deviations in parentheses

	$x$	$y$	$z$	$B$
H(1)	503 (3)	721 (2)	-158 (4)	4.4 (11)
H(2)	670 (3)	829 (2)	-128 (4)	3.9 (12)
H(3)	852 (4)	916 (2)	110 (4)	6.0 (14)
H(4)	971 (3)	842 (2)	295 (4)	4.0 (12)
H(5)	931 (4)	689 (2)	274 (4)	6.1 (12)
H(6)	709 (3)	615 (2)	178 (4)	4.9 (12)
H(10)	201 (3)	584 (2)	94 (3)	2.6 (10)
H(12)	330 (3)	789 (2)	-37 (3)	2.4 (9)*
H(16A)	481 (5)	978 (4)	789 (6)	11.3 (19)
H(16B)	309 (6)	906 (4)	730 (7)	15.6 (18)
H(16C)	335 (6)	997 (4)	696 (6)	12.5 (24)
H(18A)	238 (5)	1111 (3)	362 (6)	11.7 (23)
H(18B)	126 (6)	1083 (4)	432 (6)	12.6 (22)
H(18C)	85 (6)	1066 (4)	252 (6)	13.8 (26)
H(20A)	64 (5)	791 (3)	-178 (5)	9.4 (22)
H(20B)	-39 (6)	754 (4)	-101 (6)	14.3 (24)
H(20C)	-80 (4)	717 (3)	-297 (4)	6.7 (15)
H(21A)	60 (4)	598 (2)	-431 (4)	5.3 (14)
H(21B)	183 (4)	547 (3)	-344 (5)	8.8 (17)
H(21C)	194 (4)	661 (3)	-329 (5)	7.8 (21)
H(22A)	34 (4)	509 (3)	-204 (5)	9.7 (18)
H(22B)	-109 (4)	559 (2)	-308 (4)	5.5 (12)
H(22C)	-63 (5)	594 (3)	-115 (5)	8.7 (19)
H(24A)	401 (4)	486 (3)	173 (5)	7.0 (14)
H(24B)	557 (4)	500 (3)	292 (4)	5.5 (14)
H(24C)	534 (4)	534 (2)	150 (4)	5.2 (12)
H(25A)	410 (3)	568 (2)	495 (4)	4.6 (12)
H(25B)	260 (4)	588 (3)	349 (5)	7.5 (15)
H(25C)	354 (3)	663 (2)	508 (4)	4.1 (13)
H(26A)	582 (3)	747 (2)	537 (4)	4.2 (14)
H(26B)	673 (4)	697 (2)	421 (4)	5.9 (13)
H(26C)	655 (4)	648 (2)	544 (4)	5.4 (12)

\* Thermal parameter was fixed in final stage of refinement due to erratic behavior.

Table 3. Selected torsion angles

The convention followed in defining torsion angles is that used in *Molecular Structures and Dimensions* (1972) [suggested by Klyne & Prelog (1960)].

C(1) [C(2), C(3)] C(4)	28.1°	C(8) [C(9), C(23)] C(24)	-62.0°
C(1) [C(7), C(6)] C(5)	51.9	C(8) [C(9), C(23)] C(25)	-179.0
C(1) [C(7), C(8)] C(9)	176.9	C(8) [C(9), C(23)] C(26)	61.0
C(1) [C(7), C(8)] C(12)	-5.2	C(9) [C(14), C(13)] C(12)	-0.5
C(2) [C(1), C(7)] C(6)	-53.1	C(13) [C(14), C(15)] O(1)	93.2
C(2) [C(1), C(7)] C(8)	130.4	C(13) [C(14), C(15)] O(2)	-85.0
C(2) [C(3), C(4)] C(5)	1.0	C(13) [C(17), O(3)] C(18)	179.2
C(3) [C(2), C(1)] C(7)	3.8	C(14) [C(13), C(17)] O(3)	-8.9
C(3) [C(4), C(5)] C(6)	-30.4	C(14) [C(13), C(17)] O(4)	170.6
C(4) [C(5), C(6)] C(7)	-1.8	C(14) [C(15), O(2)] C(16)	171.7
C(5) [C(6), C(7)] C(8)	-132.1	C(15) [C(14), C(13)] C(17)	6.0
C(6) [C(7), C(8)] C(9)	1.1	C(16) [O(2), C(15)] O(1)	-6.6
C(6) [C(7), C(8)] C(12)	179.0	C(18) [O(3), C(17)] O(4)	-0.2

tacts are  $H(12)\cdots H(1)=2.33$ ,  $H(6)\cdots H(24C)=2.02$ ,  $H(6)\cdots H(26B)=2.28$  Å.

One effect of this steric hindrance can be seen in the significant lengthening of the bridge bonds,  $C(8)-C(9)$  (1.57 Å) and  $C(9)-C(14)$  (1.57 Å), compared with the other  $Csp^2-Csp^3$  bonds in this molecule (1.54, 1.53, 1.51, 1.53, 1.50 Å), and to the accepted literature value [1.53 (1) Å, *International Tables for X-ray Crystallography*, 1962]. These  $Csp^2-Csp^3$  bridge bonds are as long as or longer than the  $Csp^3-Csp^3$  bridge bonds re-

ported for structures containing a bicyclo[2,2,1]heptadiene (or heptene) moiety (Declercq, Germain & Henke, 1973; Dahl & Wei, 1963, and references therein). In all of the above structures, differing greatly in the environment surrounding the bridge, the angle in the 1-bridge [ $C(12)-C(8)-C(9)$ ] varies only from  $93^\circ$  to  $95^\circ$  and the non-bonded distance across the bridge [ $C(9)\cdots C(12)$ ] varies only from 2.25 to 2.30 Å (2.26 Å in the present molecule).

An equally dramatic effect of this steric hindrance

Table 4. Comparison of compounds with seven-membered rings

	Exocyclic C=C	Opposite CCC	Average of other ring angles	Reference
<b>Heptafulvenes</b>				
1. MAD adduct of di- <i>t</i> -butylsesquifulvalene	1.329 (5) Å	112.6 (3)°	126.2°	This work
2. Perchloroheptafulvalene	1.332 (5)	112.3 (2)	122.8	Ishimori <i>et al.</i> (1971)
3. <i>syn</i> -2,3;6,7;2',3';6',7'-Tetrabenzoheptafulvalene	1.342 (2)av.	113.2 (1)av.	123.2	Dichmann <i>et al.</i> (1974)
4. <i>trans</i> -2,3;6,7;2',3';6',7'-Tetrabenzoheptafulvalene	1.348 (4)	115.1 (2)	123.6	Dichmann <i>et al.</i> (1974)
5. 1,6-Dimethyl-8,8-dicyanoheptafulvene	1.361 (7)	115.2 (4)	125.8	Shimanouchi <i>et al.</i> (1974a)
6. 1-Isopropyl-8,8-dicyanoheptafulvene	1.367 (8)	117.8 (5)	126.7	Shimanouchi <i>et al.</i> (1974b)
7. Heptafulvalene	1.379 (5)	117.6 (3)	128.5	Thomas & Coppens (1972)
8. 1,2,3,4-Tetrachlorobenzo[ <i>g</i> ]sesquifulvalene	1.40 (5)	122 (1)	129	Nishi <i>et al.</i> (1966)
9. 8,8-Dicyanoheptafulvene	1.422 (13)	125.1 (7)	129.1	Shimanouchi <i>et al.</i> (1966)
<b>Fulvenes</b>				
10. Dimethylfulvene	1.343 (11)	106.2 (6)	108.4	Norman & Post (1961)
11. 1,2,3-Tribromo-6-( <i>o</i> -methoxyphenyl)fulvene	1.36 (3)	105.6	109	Kato <i>et al.</i> (1965)
12. 2-Formyl-6-dimethylaminopentafulvene	1.389	105.7	108.6	Ammon & Plastas (1971)
13. 1,2,3,4-Tetrachlorobenzo[ <i>g</i> ]sesquifulvalene	1.40 (5)	104 (1)	109	Nishi <i>et al.</i> (1966)
14. Perchlorofulvalene	1.49	106	108	Wheatley (1961)
<b>Tropones and tropolones</b>				
15. 2,7-Diphenyl-4,5-benzotropone	1.216 (5)	124.3 (3)	129.2	Ibata <i>et al.</i> (1973)
16. Tropolonyl <i>p</i> -chlorobenzoate	1.225 (5)	120.3 (4)	129.9	Schaefer & Reed (1971)
17. 2,7-Dimethyl-4,5-benzotropone	1.227 (5)	124.4 (3)	128.9	Ibata <i>et al.</i> (1973)
18. 2-Chlorotropone	1.230 (15)	120.9 (15)	129.8	Watkin & Hamor (1971)
19. 5-Chloro-2,3-benzotropone	1.23 (1)	124 (1)	129	Ibata <i>et al.</i> (1972)
20. 5,7-Dibromo-2,3-benzotropone	1.23 (1)	122 (1)	130	Ibata <i>et al.</i> (1972)
21. 3-Azidotropone	1.234 (9)	123	130	Cruickshank <i>et al.</i> (1972)
22. 4,5-Benzotropone	1.244	126.9	128.7	Hata <i>et al.</i> (1969)
23. 4-Isopropyltropolone	1.261 (5)	122.8 (4)	129.5	Derry & Hamor (1972)
24. Tropolone	1.261 (3)	124.2 (2)	129.2	Shimanouchi & Sasada (1973)
25. Sodium tropolonate	1.284 (5)	125.0 (4)	130.0	Shiono (1961); Sasada & Nitta (1956)

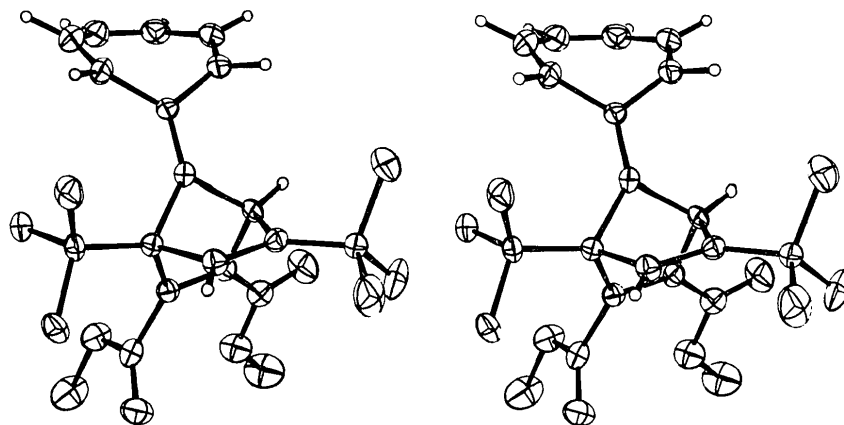


Fig. 1. Stereoscopic drawing of the molecule with 25% probability ellipsoids for nonhydrogen atoms. Hydrogen atoms are shown as spheres of radius 0.11 Å; methyl hydrogens have been omitted. Note the planarity of each ethylenic system in the seven-membered ring and the rotation of one methoxycarbonyl group away from the adjacent *t*-butyl group.

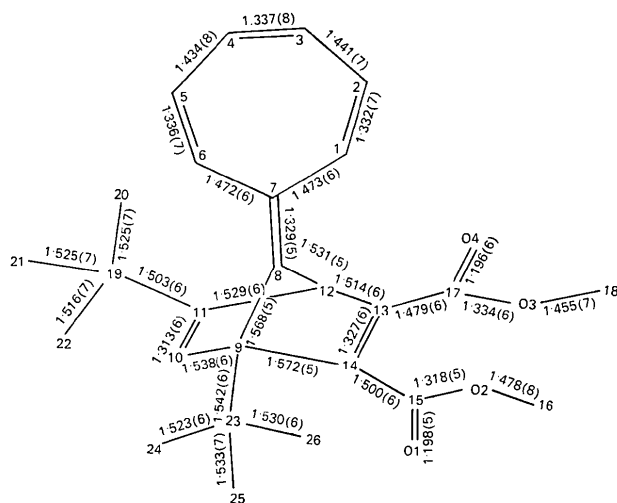


Fig. 2. Bond lengths between nonhydrogen atoms.

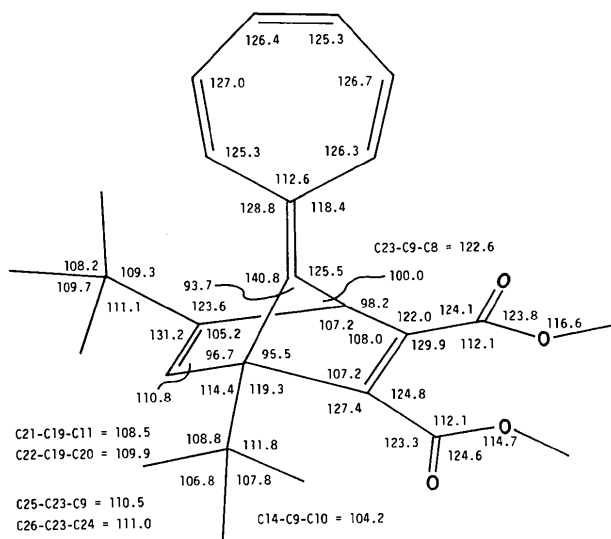


Fig. 3. Bond angles between nonhydrogen atoms. Estimated standard deviations range from 0.3 to 0.5°.

is apparent in the angles. The 'equivalent' bridge to seven-membered ring angles are: C(8)-C(7)-C(6) = 129° *vs.* C(8)-C(7)-C(1) = 118°; C(9)-C(8)-C(7) = 141° *vs.* C(12)-C(8)-C(7) = 126°. The *t*-butyl group is displaced away from the seven-membered ring [C(23)-C(9)-C(8) = 123°] and away from the adjacent methoxycarbonyl group [C(23)-C(9)-C(14) = 119°, compared with C(23)-C(9)-C(10) = 114°]. The differences in bridge system to ester distances and angles [C(14)-C(15) = 1.50 *vs.* C(13)-C(17) = 1.48 Å and C(15)-C(14)-C(9) = 127° *vs.* C(17)-C(13)-C(12) = 122°] and the unusually large twist of one ester group (torsion angle C(13) [C(14), C(15)] O(2) = -85.0°) can also be ascribed to this crowding.

A further consequence of the severe constraint of this *t*-butyl is seen by comparison of temperature factors between the two *t*-butyl groups. The isotropic temperature factors of the terminal carbons of the hindered *t*-butyl group (3.8, 4.6, 4.5 Å<sup>2</sup>) are much smaller than the corresponding values for the other *t*-butyl group (5.7, 5.1, 5.7 Å<sup>2</sup>). A similar contrast is seen in the average *B* values for the *t*-butyl hydrogens [5.5 Å<sup>2</sup> for H(24*A*)-H(26*C*) *vs.* 7.8 Å<sup>2</sup> for H(20*A*)-H(22*C*), excluding the exceptionally large value for H(20*B*)].

The seven-membered ring is quite non-planar, although each ethylenic system within it is planar to within 0.015 Å. The cause of non-planarity in heptafulvenes (methylenecycloheptatrienes) has been the subject of recent speculation (Thomas & Coppens, 1972; Cheng & Nyburg, 1973; Coppens, 1973; Dichmann, Nyburg, Pichard & Potworowski, 1974). Nyburg & co-workers maintain that the sole cause of nonplanarity in heptafulvalene is steric hindrance between the hydrogen atoms closest to the central double bond (at the α, α' carbons), analogous to several overcrowded structures. They further point out that 8,8-dicyanoheptafulvene, which does not suffer from these steric effects, is essentially planar. Any angle strain in heptafulvalene is attributed to a pinching of the CCC angle opposite the exocyclic C=C bond caused by H...H repulsions.

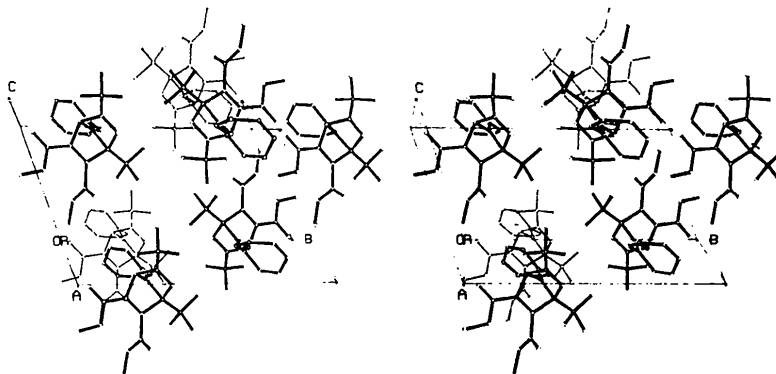


Fig. 4. Crystal packing within the unit-cell.

Coppens (1973) points out in reply that if heptafulvalene were planar the hydrogen atoms in question would be only 1.7 Å apart, which is roughly comparable to the analogous separation (1.8 Å) in experimentally planar diphenyl. On the other hand, if the molecules to which Cheng & Nyburg compare heptafulvalene were constrained to be planar, the hydrogens involved

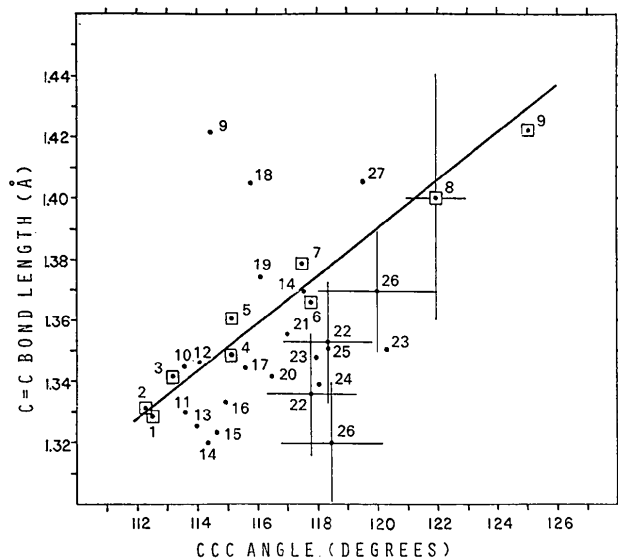


Fig. 5. Plot of C=C bond length *versus* the opposite CCC bond angle for a number of compounds: (1) MAD adduct of di-*t*-butylsesquifulvalene, this work; (2) perchloroheptafulvalene, Ishimori, West, Teo & Dahl (1971); (3) *syn*-2,3;6,7;2',3';6',7'-tetrabenzoheptafulvalene, Dichmann *et al.* (1974); (4) *trans*-2,3;6,7;2',3';6',7'-tetrabenzoheptafulvalene, Dichmann *et al.* (1974); (5) 1,6-dimethyl-8,8-dicyanoheptafulvene, Shimanouchi *et al.* (1974a); (6) 1-isopropyl-8,8-dicyanoheptafulvene, Shimanouchi *et al.* (1974b); (7) heptafulvalene, Thomas & Coppens (1972); (8) 1,2,3,4-tetrachlorobenzo[*g*]sesquifulvalene, Nishi *et al.* (1966); (9) 8,8-dicyanoheptafulvene, Shimanouchi *et al.* (1966); (10) *o*-chlorobenzylidene-malononitrile, Williams & Wright (1973); (11) 1,3,5,7-tetramethylcycloocta-*cis,cis,cis,cis*-1,3,5,7-tetraene, Avitabile, Granis & Petraccone (1969); (12) dimethylfulvene, Norman & Post (1961); (13) octamethylcyclooctatetraene, Bordner, Parker & Stanford (1972); (14) harunganin, Alden, Stout, Kraut & High (1964); (15) cyclooctatetraene carboxylic acid, Shoemaker, Kindler, Sly & Srivastava (1965); (16) calcium 2,4,6,8-cyclooctatetraene-1,2-dicarboxylate dihydrate, Wright, Seff & Shoemaker (1972); (17) tetracyanoethylene, Little, Pautler & Coppens (1971); (18) 7,7,8,8-tetracyanoquinodimethane-*N,N,N',N'*-tetramethyl-*p*-phenylenediamine complex, Hanson (1965); (19) tetracyanoquinodimethane, Long, Sparks & Trueblood (1965); (20) octaphenylcyclooctatetraene, Wheatley (1965); (21) *cis,cis*-1,2,3,4-tetraphenylbutadiene, Karle & Dragonette (1965); (22) vitamin A, Stam & MacGillavry (1963); (23) 15,15'-dehydro- $\beta$ -carotene, Sly (1964); (24) tetracyanoethylene, Trueblood (cited by Williams & Wallwork (1967); (25) tetracyanoethylene-naphthalene complex, Williams & Wallwork (1967); (26) 7,7-dihydro- $\beta$ -carotene, Sterling (1964); (27) 2-cyano-2-[3-cyano-4-diethylamino-1*H*-quinolyldiene-2]-*N,N*-diethylacetamide, Lerbscher & Trotter (1972). The best straight line for the heptafulvalene exocyclic C=C bond (enclosed points) is shown. Error limits are indicated for structures in which either  $\sigma(\text{bond length}) \geq 0.015$  Å or  $\sigma(\text{bond angle}) \geq 1.0^\circ$ .

would be 0.7 Å or less apart. The comparison is therefore not valid. While acknowledging that steric effects cannot be ignored, Coppens explains the non-planarity of heptafulvalene primarily on the basis of relief of the angle strain caused by the small angle ( $117.6^\circ$ ) opposite the exocyclic double bond. Bartell (1960) noted in his study of isobutylene, that the CCC angle opposite the C=C bond is significantly less than  $120^\circ$ . In a planar heptagon however the average CCC angle would be  $128.5^\circ$ . Dicyanoheptafulvene is therefore planar because the angle opposite the exocyclic double bond is  $125.1^\circ$  and there is correspondingly little ring strain to be relieved.

Coppens also notes that there seems to be a good correlation between the C=C bond lengths and the opposite CCC bond angles. However when one plots C=C bond length *versus* bond angle for a variety of structures containing non-aromatic C=C bonds and considers the standard deviations involved, the good correlation is not apparent (Fig. 5). Nevertheless, when attention is restricted to the heptafulvenes, a quite linear relationship is seen, with the shorter exocyclic double bonds associated with the more acute CCC angle (enclosed points and straight line in Fig. 5).

The seven-membered rings in compounds 1-7 of Table 4 (those having the smallest exocyclic C=C distance) are significantly nonplanar, twisting about the single bonds in the ring (Coppens, 1973; Shimanouchi, Sasada, Kabuto & Kitahara, 1974a,b). Table 5 shows the degree of non-planarity for all nine molecules as reflected by the r.m.s. deviation from the best plane through the seven-membered ring and the  $\delta$  angles as defined by Shimanouchi *et al.* (1974a). Plots of the r.m.s. deviation,  $\delta_1$  and  $\delta_2$  *versus* CCC bond angle reveal linear, semiquantitative relationships [Fig. 6(a), (b), (c)]. The relationship between  $\delta_3$  and CCC angle in the range  $120$ – $125^\circ$  is not clear [Fig. 6(d)]. Data point 8 may be unreliable in this context, owing to a torsion of  $31^\circ$  about the exocyclic C=C bond. If

Table 5. Planarity of the seven-membered rings

Compounds are numbered with respect to Table 4;  $\sigma$  = r.m.s. deviation from the plane of the seven-membered ring. In cases where more than one seven-membered ring was present in a determination, all values are averages.



Compound	C=C	CCC	$\sigma$	$\delta_1$	$\delta_2$	$\delta_3$
1	1.329 Å	112.6°	0.236 Å	41.3°	23.6°	3.3°
2	1.332	112.3	0.311	49.4	36.3	2.5
3	1.342	113.2	0.286	55.8	28.2	4.7
4	1.348	115.1	0.279	52.6	29.0	2.9
5	1.361	115.2	0.225	45.3	20.1	4.0
6	1.367	117.8	0.199	37.3	19.5	5.6
7	1.379	117.6	0.146	24.7	15.7	6.7
8	1.40	122	0.070	13.8	5.8	9.8
9	1.422	125.1	0.009	2.6	1.8	2.7

that point were omitted, the curve might be taken to reach a maximum,  $\delta_3$  then decreasing with increasing angle to approach zero for the completely planar structure (CCC angle  $\approx 126^\circ$ ).

Steric considerations are not always the dominant factor in determining non-planarity, as can be seen by the fact that compound 3 in Table 4 has H...H non-bonded contacts of 2.4 Å compared to H...H non-bonded contacts of only 2.1 Å for heptafulvalene. The latter, however, is much more planar and has the larger CCC angle of the two compounds (Tables 4 and 5). Overcrowding in the title compound is relieved primarily by distortions elsewhere in the molecule (see above) and the heptafulvene assumes a conformation consistent with that summarized for other heptafulvenes in the distance-angle and nonplanarity plots.

The consistent relationships shown by these plots for molecules with *considerably different* steric interactions is difficult to reconcile with a model which attributes the distortions solely to steric hindrance. Clearly an interplay of several forces must be considered in these heptafulvene structures, with both steric interactions and relief of angle strain assuming some importance.

Similarly, in fulvene structures the CCC angle oppo-

site the exocyclic C=C bond is  $2^\circ$  to  $5^\circ$  less than the average of the remaining interior ring angles; however, there is little change in this angle with respect to changes in the length of the exocyclic C=C bond (see Table 4). In crowded fulvenes, for example perchlorofulvalene (Wheatley, 1961) and 1,2,3,4-tetrachlorobenzo[g]sesquifulvalene (Nishi *et al.*, 1966), the steric repulsions are accommodated by considerable torsion about and lengthening of the exocyclic C=C bond and the fulvene ring remains planar. It is interesting to note that in this latter example, which contains a heptafulvene as well as a fulvene moiety, the seven-membered ring remains much more planar than in heptafulvalene at the expense of torsion about the exocyclic C=C bond.

In tropone and tropolone structures, the CCC angle opposite the exocyclic C=O bond is significantly less (by  $2^\circ$  to  $9^\circ$ ) than the average of the other interior ring angles. In these structures, however, a strong correlation between C=O length and CCC angle is not observed (Table 4). The angle is always  $120^\circ$  or greater and the small amount of angle strain thus introduced is not sufficient to cause deviations from ring planarity of more than 0.1 Å. The conformation of the one reported nonplanar tropone structure, dibenzo[*b,f*]-

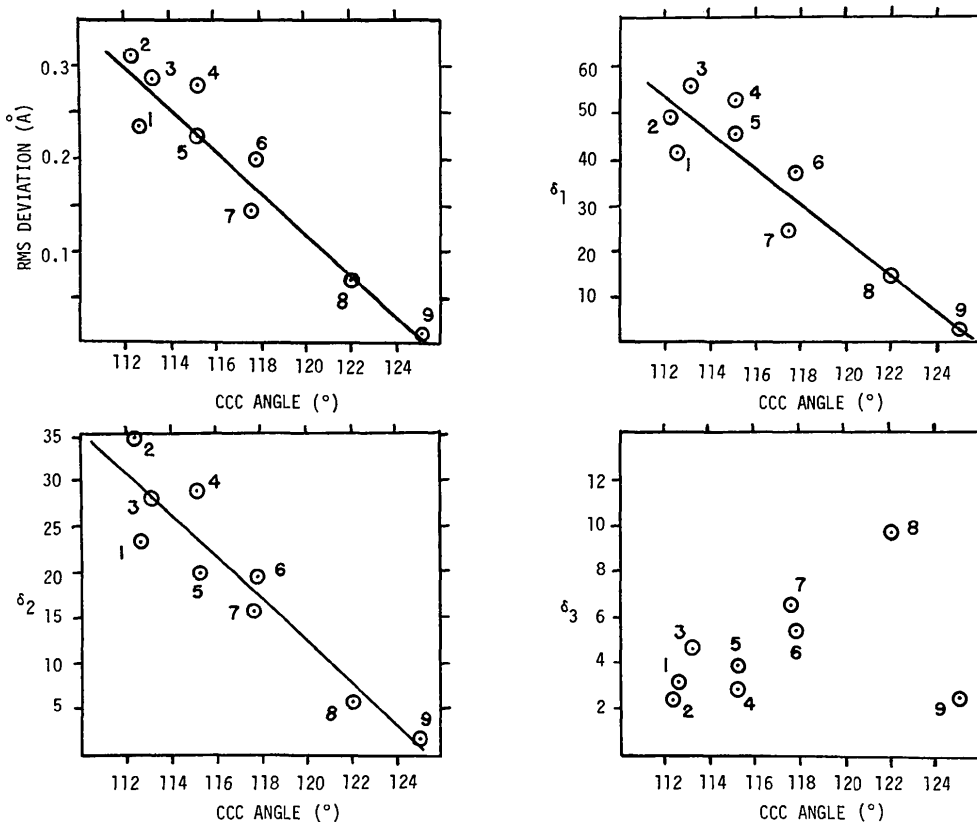


Fig. 6. Planarity of the seven-membered rings of heptafulvene compounds. Plots *versus* CCC angle (opposite exocyclic C=C bond) of (a) r.m.s. deviation (Å) of ring atoms from the plane of the seven-membered ring, (b)  $\delta_1$  ( $^\circ$ ) as defined in Table 5, (c)  $\delta_2$  ( $^\circ$ ) as defined in Table 5, (d)  $\delta_3$  ( $^\circ$ ) as defined in Table 5. Numbers beside data points are with respect to molecules named in Table 4.

tropone (Shimanouchi, Hata & Sasada, 1968) is understandable in terms of the dominance of steric effects in the absence of significant ring strain.

### Summary

The MAD adduct of di-t-butylsesquifulvalene is a [4+2] cycloaddition product. Steric interactions between the various parts of the molecule have a pronounced effect on the spatial arrangement, bond lengths and bond angles. For a wide variety of structures containing a bicyclo[2,2,1]heptadiene (or heptene) moiety (including the present one), the angle in the 1-bridge is  $\sim 94^\circ$  and the non-bonded distance across the 1-bridge is  $\sim 2.25 \text{ \AA}$ . In a wide variety of structures the CCC bond angle opposite a C=C bond is less than  $120^\circ$ , but no general distance-angle relationship is seen. In structures containing a heptafulvene entity there is a good correlation between exocyclic C=C bond length and the opposite CCC angle. The MAD adduct fits this correlation. The seven-membered rings of heptafulvenes which have a CCC angle (opposite the exocyclic C=C bond) much less than  $120^\circ$  are quite non-planar and the two compounds with CCC angles greater than  $120^\circ$  are nearly planar. In the nonplanar seven-membered rings, the distortion is observed as torsion about the C-C bonds in the ring. There is a semi-quantitative relationship between the r.m.s. deviation from the plane of the seven-membered ring and the CCC angle opposite the exocyclic C=C bond as well as between the front ( $\delta_1$ ) and back ( $\delta_2$ ) side distortion of the boat and this CCC angle. An understanding of conformations of distorted molecules must take into account the relative importance of ring strain and steric effects. In molecules containing a fulvene, tropone or tropolone moiety, the CCC bond angle opposite the exocyclic double bond is less than the average of the other ring angles and is often the smallest ring angle. In tropones and tropolones, the effects of ring strain are minimal and steric effects play the dominant role in determining ring conformation.

We wish to gratefully acknowledge the support of the Welch Foundation (Grant F-233); the Syntex P<sub>2</sub> autodiffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

### References

- ALDEN, R. A., STOUT, G. H., KRAUT, J. & HIGH, D. F. (1964). *Acta Cryst.* **17**, 109-121.
- AMMON, H. L. & PLASTAS, L. A. (1971). *Chem. Commun.* pp. 356-357.
- AVITABILE, G., GANIS, P. & PETRACCONE, V. (1969). *J. Phys. Chem.* **73**, 2378-2381.
- BARTELL, L. S. (1960). *J. Chem. Phys.* **32**, 824-826.
- BORDNER, J., PARKER, R. G. & STANFORD, R. H. (1972). *Acta Cryst.* **B28**, 1069-1075.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CHENG, P. T. & NYBURG, S. C. (1973). *Acta Cryst.* **B29**, 1358-1359.
- COPPENS, P. (1973). *Acta Cryst.* **B29**, 1359-1360.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.
- DAHL, L. F. & WEI, C. H. (1963). *Inorg. Chem.* **2**, 713-721.
- DAVIS, R. E. (1973). To be published.
- DECLERCO, J. P., GERMAIN, G. & HENKE, H. (1973). *Cryst. Struct. Commun.* **2**, 405-409.
- DERRY, J. E. & HAMOR, T. A. (1972). *J. Chem. Soc. Perkin II*, pp. 694-697.
- DEWAR, M. J. S. & GLEICHER, G. J. (1965). *J. Amer. Chem. Soc.* **87**, 685-692.
- DICHMANN, K. S., NYBURG, S. C., PICKARD, F. H. & POTWOROWSKI, J. A. (1974). *Acta Cryst.* **B30**, 27-36.
- EVANS, H. T. (1961). *Acta Cryst.* **14**, 689.
- HANSON, A. W. (1965). *Acta Cryst.* **19**, 610-613.
- HATA, T., SHIMANOUCI, H. & SASADA, Y. (1969). *Tetrahedron. Lett.* pp. 753-754.
- IBATA, K., HATA, T., SHIMANOUCI, H. & SASADA, Y. (1972). *Chem. Commun.* pp. 339-340.
- IBATA, K., SHIMANOUCI, H. & SASADA, Y. (1973). *Chem. Lett. Japan*, pp. 269-272.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 276. Birmingham: Kynoch Press.
- ISHIMORI, M., WEST, R., TEO, B. K. & DAHL, L. F. (1971). *J. Amer. Chem. Soc.* **93**, 7101-7102.
- KARLE, I. L. & DRAGONETTE, K. S. (1965). *Acta Cryst.* **19**, 500-503.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849-859.
- KATO, Y., SASADA, Y. & KAKUDO, M. (1965). *Bull. Chem. Soc. Japan*, **38**, 1761-1775.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521-523.
- LERBSCHER, J. A. & TROTTER, J. (1972). *J. Cryst. Mol. Struct.* **2**, 67-77.
- LITTLE, R. G., PAUTLER, D. & COPPENS, P. (1971). *Acta Cryst.* **B27**, 1493-1499.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932-939.
- Molecular Structures and Dimensions* (1972). Vol. A1, p. XV. Utrecht: Oosthoek.
- NISHI, Y., SASADA, Y., ASHIDA, T. & KAKUDO, M. (1966). *Bull. Chem. Soc. Japan*, **39**, 818-826.
- NORMAN, N. & POST, B. (1961). *Acta Cryst.* **14**, 503-507.
- PRINZBACH, H. (1971). *Pure Appl. Chem.* **28**, 281-329.
- PRINZBACH, H. & KNÖFEL, H. (1969). *Angew. Chem.* **81**, 900-901.
- SASADA, Y. & NITTA, I. (1956). *Acta Cryst.* **9**, 205-214.
- SCHAEFER, J. P. & REED, L. L. (1971). *J. Amer. Chem. Soc.* **93**, 3902-3904.
- SHIMANOUCI, H., ASHIDA, T., SASADA, Y., KAKUDO, M., MURATA, I. & KITAHARA, Y. (1966). *Bull. Chem. Soc. Japan*, **39**, 2322-2331.
- SHIMANOUCI, H., HATA, T. & SASADA, Y. (1968). *Tetrahedron Lett.* pp. 3573-3574.
- SHIMANOUCI, H. & SASADA, Y. (1973). *Acta Cryst.* **B29**, 81-90.
- SHIMANOUCI, H., SASADA, Y., KABUTO, C. & KITAHARA, Y. (1974a). *Acta Cryst.* **B30**, 1267-1273.
- SHIMANOUCI, H., SASADA, Y., KABUTO, C. & KITAHARA, Y. (1974b). *Acta Cryst.* **B30**, 1273-1277.
- SHIONO, R. (1961). *Acta Cryst.* **14**, 42-47.
- SHOEMAKER, D. P., KINDLER, H., SLY, W. G. & SRIVASTAVA, R. C. (1965). *J. Amer. Chem. Soc.* **87**, 482-487.
- SLY, W. G. (1964). *Acta Cryst.* **17**, 511-528.



- STAM, C. H. & MACGILLAVRY, C. H. (1963). *Acta Cryst.* **16**, 62–68.  
 STERLING, C. (1964). *Acta Cryst.* **17**, 500–505.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 THOMAS, R. & COPPENS, P. (1972). *Acta Cryst.* **B28**, 1800–1806.  
 WATKIN, D. J. & HAMOR, T. A. (1971). *J. Chem. Soc. (B)*, pp. 2167–2170.  
 WHEATLEY, P. J. (1965). *J. Chem. Soc.* pp. 3136–3143.  
 WHEATLEY, P. J. (1961). *J. Chem. Soc.* pp. 4936–4938.  
 WILLIAMS, D. A. & WRIGHT, D. A. (1973). *J. Cryst. Mol. Struct.* **3**, 55–64.  
 WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* **22**, 899–906.  
 WRIGHT, D. A., SEFF, K. & SHOEMAKER, D. P. (1972). *J. Cryst. Mol. Struct.* **2**, 41–51.  
 ZACHARIASEN, D. H. (1968). *Acta Cryst.* **A24**, 212–216.

*Acta Cryst.* (1975). **B31**, 1519

## The Conformation of 3,20-Diethylenedioxy-9 $\beta$ ,11 $\beta$ -oxido-11 $\alpha$ -acetoxy-9,11-seco-11,19-cyclo-5 $\alpha$ ,14 $\beta$ ,17 $\alpha$ -pregnane

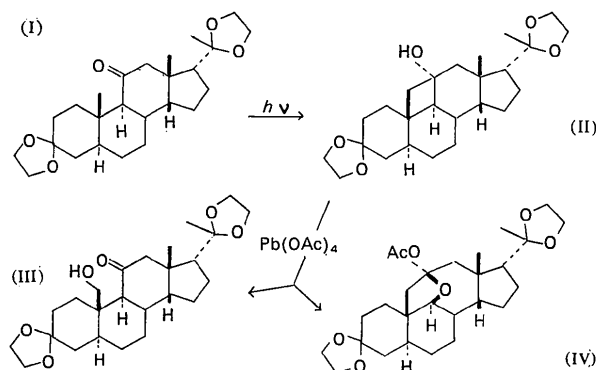
BY ISABELLA L. KARLE

*Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375, U.S.A.*

(Received 29 October 1974; accepted 22 January 1975)

The title compound,  $C_{27}H_{40}O_7$ , has been derived by photocyclization of a pregnane derivative and fragmentation with  $Pb(OAc)_4$ . It crystallizes in space group  $P2_12_12_1$  with  $a=13.833$  (7),  $b=25.375$  (20) and  $c=7.289$  (4) Å. The structure has been derived by using a combination of direct phase determination and a translation function. Introduction of an oxygen bridge between C(9) and C(11) and ring formation by the bonding of C(11) to C(19) have created strains in the molecule which are reflected in several CCC angles with values of  $118^\circ$  to  $122^\circ$  rather than near the more usual  $111^\circ$  in rings *A*, *B* and *C*. The seven-membered ring *C* has the boat conformation. Disorder in the two extreme five-membered rings limited the number of observable data. The final *R* is 11.4% for 1500 data.

The ultraviolet irradiation of various derivatives of pregnane can lead to a product in which cyclization has occurred between C(11) and the methyl group at C(19) to make a four-membered ring (see e.g. Gull, Saito, Wehrli & Jeger, 1974). Fragmentation of the new cyclo-product (II) by  $Pb(OAc)_4$  yields (IV) as the main product rather than the expected product (III). An X-ray diffraction analysis of the structure of (IV) confirmed the formula and stereo configuration.



The steroid nucleus undergoes a considerable conformational change with the ring closure between C(11) and C(19) and the introduction of an oxygen atom

between C(9) and C(11). Therefore, it was considered desirable to obtain detailed structural information for this region where considerable strain must be relieved by changes in bond angles as well as torsional angles.

### Experimental

Colorless crystals, somewhat opaque, in the form of elongated prisms were provided by Drs H. Wehrli and O. Jeger of the ETH, Zürich. The crystal data are: space group  $P2_12_12_1$ ;  $Z=4$ ;  $a=13.833$  (7),  $b=25.375$  (20),  $c=7.289$  (4) Å;  $V=2558.5$  Å<sup>3</sup>;  $C_{27}H_{40}O_7$ ; M.W. = 476.62;  $D_{calc}=1.237$  g cm<sup>-3</sup>; size 0.20 × 0.15 × 0.9 mm;  $\mu=7.31$  cm<sup>-1</sup>. Intensity data were collected with Cu radiation ( $\lambda=1.54178$  Å) on a four-circle automatic diffractometer with the  $\theta$ - $2\theta$  scan mode, a scan width of  $2.1^\circ$  and a scan rate of  $2^\circ$  min<sup>-1</sup>. The background was counted for 10 s at either end of the scan. Three reflections used as standards were monitored every hour and indicated a gradual deterioration of the crystal. The experimental  $I_{hkl}$  were scaled to compensate for the loss of scattering power up to a final factor of 1.09. Data were collected to a scattering angle of  $2\theta=120^\circ$  although the data with  $2\theta>90^\circ$  were very weak with only a few reflections of moderate size. For the least-squares refinement, only those data with  $2\theta<100^\circ$  were used.