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The Crystal Structure of 2,3,6,7,7,8-Hexamethyl-1,5-diphenyl-tetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one

BY CAROL G. BIEFELD AND HARRY A. EICK

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, *U.S.A.*

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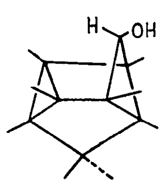
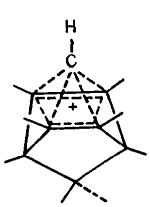
The structure of 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one ($C_{26}H_{28}O$) has been determined from room-temperature X-ray diffractometer data. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a=9{\cdot}155$ (3), $b=14{\cdot}635$ (9), $c=15{\cdot}425$ (4) Å, $\beta=100{\cdot}7$ (2)°; $Z=4$. The structure was solved by direct methods and refined by full-matrix least-squares techniques to a final R value of 0·062. The cyclobutane ring is non-planar with a dihedral angle of 133 (1)° and contains two exceptionally long C–C bonds of 1·608 (8) and 1·602 (10) Å which reflect the internal strain of the cage system. The molecule, disregarding the phenyl rings, exhibits near mirror symmetry.

Introduction

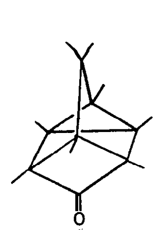
Recently Stohrer & Hoffmann (1972) predicted the existence of a novel intermediate, $(CH)_5^+$, in the carbonium ion rearrangements of the tricyclo[2,1,0,$0^{2,5}$]-pentane system. Soon thereafter many reports appeared (Masamune, Sakai, Ona & Jones, 1972; Goldstein & Kline, 1973; Hogeveen & Kwant, 1973; and Lustgarten, 1972) concerning $(CH)_5^+$-type carbonium ions as intermediates in other carbonium ion rearrangements. In one case, Hart & Kuzuya (1972) reported, on the basis of spectroscopic data and various labelling experiments, that alcohol (I) ionizes in fluorosulfonic acid to the pyramidal cation (II), a $(CH)_5^+$-type carbonium ion.



(I)



(II)



(III)

Since the geometry of the tetracyclic system was unknown, a structural analysis of (I) or the closely related compound (III) could provide additional evidence to support the existence of $(CH)_5^+$-type ions if the molecular parameters obtained were consistent with those expected for rearrangement to the ion. In addition data would be provided on how the molecular parameters are affected by the strain present in this system. For these reasons the investigation of the crystal structure of (III) – 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one – was undertaken.

Experimental

A sample of 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,$0^{2,8}$,$0^{3,6}$]octan-4-one (HDTO) was supplied by Professor H. Hart. Recrystallization (Hart & Love, 1971) from petroleum spirit produced clear, colorless crystals in the form of flat plates. Preliminary measurements of the lattice parameters and space-group determination were made by precession camera techniques with Zr-filtered Mo $K\alpha$ radiation. All subsequent measurements were made *via* a computer-controlled, four-circle, Picker goniometer with Mo $K\alpha$ radiation, graphite monochromator, and at a temperature of 23 (2)°. The crystal used was roughly a rectangular prism (0·144 × 0·182 × 0·328 mm) mounted with the long dimension [100] parallel to the φ axis of the goniometer. Cell constants were obtained from least-squares refinement of 12 reflections which had been hand-centered on the goniometer. The density was determined by flotation in aqueous potassium iodide.

$C_{26}H_{28}O$, $M=356{\cdot}51$;
$a=9{\cdot}155$ (3), $b=14{\cdot}635$ (9), $c=15{\cdot}425$ (4) Å;
$\beta=100{\cdot}7$ (2)°.
Systematic absences: $h0l$, $l=2n+1$; $0k0$, $k=2n+1$.
Space group: $P2_1/c$, (No. 14).
$Z=4$; $F(000)=768$; $V=2030{\cdot}7$ Å^3;
$\mu=0{\cdot}75$ cm^{-1} (Mo $K\alpha$);
$D_{exp}=1{\cdot}155$ (2), $D_{calc}=1{\cdot}166$ g cm^{-3};
λ(Mo $K\alpha_1$, graphite monochromator)$=0{\cdot}7093$ Å.

Three-dimensional single-crystal intensity data in one quadrant (hkl, $hk\bar{l}$) to the limit $2\theta=45°$ were collected by the ω-scan technique with a scan range of 0·8°, scan rate of $\frac{1}{2}°$ min^{-1}, and a $K\alpha_1$–$K\alpha_2$ dispersion factor of 0·692. The counting system employed a scintillation detector with pulse-height discrimination. Individual background measurements were made at the endpoints of the scan range for 10 s each. Neither filters nor attenuators were used. The standard deviation from the average intensities of two periodically monitored reflections was 3·0%, which indicated that the crystal had not suffered appreciable radiation damage during the eight days of data collection. 3010 reflections were collected, exclusive of standards.

The data were corrected for background and considered for use in the refinement by the criterion $I>3\sigma(I)$, where $I=P-B$ and $\sigma^2(I)=P+CB+[D(I)]^2$. In these equations $P=10(I_c)+5$, (I_c=integrated peak counts), $B=C[10(I_{B1}+I_{B2}+1)]$, (I_{B1} and I_{B2} are integrated background counts) [factors of 10 arise because

Table 1. *Fractional coordinates* (× 10⁴) *of the nonhydrogen atoms*

E.s.d.'s × 10⁴ are given in parentheses.

	x	*y*	*z*
C(1)	5559 (7)	1693 (4)	3060 (4)
C(2)	5763 (7)	1936 (4)	4056 (4)
C(3)	6952 (7)	1254 (5)	4475 (4)
C(4)	6504 (7)	399 (6)	3915 (4)
C(5)	6733 (6)	922 (4)	3097 (4)
C(6)	8034 (7)	1412 (4)	3783 (4)
C(7)	8016 (7)	2415 (4)	3555 (4)
C(8)	6333 (7)	2571 (4)	3425 (4)
C(9)	5708 (7)	3516 (4)	3209 (4)
C(10)	8594 (7)	2599 (5)	2690 (4)
C(11)	8850 (7)	3004 (5)	4322 (4)
C(12)	4422 (8)	2140 (5)	4496 (4)
C(13)	7443 (8)	1200 (5)	5454 (4)
C(14)	9532 (7)	913 (5)	3994 (4)
C(15)	6985 (7)	459 (5)	2778 (5)
C(16)	6489 (7)	822 (5)	1448 (5)
C(17)	6761 (8)	401 (6)	692 (5)
C(18)	7589 (9)	−396 (7)	769 (6)
C(19)	8090 (8)	−762 (5)	1574 (7)
C(20)	7811 (7)	−356 (5)	2337 (5)
C(21)	4071 (7)	1602 (5)	2498 (4)
C(22)	3467 (8)	2242 (5)	1875 (4)
C(23)	2061 (9)	2122 (6)	1354 (5)
C(24)	1242 (8)	1350 (7)	1464 (6)
C(25)	1817 (8)	707 (6)	2080 (6)
C(26)	3231 (8)	829 (5)	2606 (4)
O(1)	6313 (6)	−385 (3)	4091 (3)

Table 2. *Anisotropic thermal parameters*

The temperature factor expression used was
$$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)],$$
where $B_{ij}=4\beta_{ij}/a_i^*a_j^*$. E.s.d.'s are given in parentheses.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2·7 (3)	3·5 (3)	3·5 (3)	0·0 (3)	0·5 (3)	−0·0 (3)
C(2)	3·1 (3)	4·3 (4)	4·1 (3)	0·5 (3)	1·3 (3)	0·6 (3)
C(3)	3·7 (3)	5·0 (4)	3·6 (3)	0·2 (3)	1·0 (3)	0·5 (3)
C(4)	2·7 (3)	4·7 (4)	5·9 (4)	1·1 (3)	1·2 (3)	1·3 (4)
C(5)	2·6 (3)	3·8 (3)	3·8 (3)	−0·1 (3)	0·9 (3)	0·1 (3)
C(6)	3·2 (3)	4·6 (4)	4·4 (4)	0·4 (3)	0·9 (3)	0·4 (3)
C(7)	3·7 (4)	4·2 (4)	4·3 (3)	−0·2 (3)	0·9 (3)	0·3 (3)
C(8)	3·3 (3)	3·8 (4)	3·9 (3)	0·7 (3)	0·9 (3)	0·5 (3)
C(9)	4·8 (4)	4·1 (4)	6·1 (4)	0·0 (3)	1·2 (3)	0·0 (3)
C(10)	4·7 (4)	5·9 (4)	4·4 (3)	−0·7 (3)	2·0 (3)	0·1 (3)
C(11)	4·0 (4)	6·5 (4)	5·0 (4)	−0·9 (3)	0·5 (3)	−0·9 (3)
C(12)	4·7 (4)	6·1 (4)	5·8 (4)	0·5 (3)	3·0 (3)	0·0 (3)
C(13)	5·9 (4)	7·9 (5)	4·6 (4)	0·5 (4)	1·0 (3)	1·3 (4)
C(14)	2·8 (3)	7·0 (4)	5·9 (4)	1·3 (3)	0·3 (3)	0·2 (3)
C(15)	2·2 (3)	4·0 (4)	5·1 (4)	−0·8 (3)	0·9 (3)	−0·3 (3)
C(16)	3·6 (4)	5·6 (4)	4·4 (4)	−0·6 (3)	1·3 (3)	−0·8 (4)
C(17)	4·4 (4)	7·1 (5)	6·1 (5)	−0·7 (4)	2·4 (4)	−1·4 (4)
C(18)	4·8 (5)	8·0 (6)	6·8 (4)	−1·4 (5)	2·8 (4)	−2·3 (5)
C(19)	3·5 (4)	5·9 (5)	8·7 (5)	−0·1 (4)	2·3 (4)	−2·5 (5)
C(20)	2·3 (3)	4·4 (4)	7·5 (5)	−0·2 (3)	1·4 (3)	−0·9 (3)
C(21)	2·6 (3)	4·0 (4)	3·8 (3)	0·2 (3)	0·9 (3)	−0·3 (3)
C(22)	3·7 (4)	5·9 (4)	4·5 (4)	0·3 (3)	0·0 (3)	0·3 (3)
C(23)	4·8 (5)	6·8 (5)	6·4 (5)	1·3 (4)	0·0 (4)	−0·3 (4)
C(24)	2·9 (4)	8·4 (6)	7·7 (5)	1·1 (4)	0·8 (4)	−1·0 (5)
C(25)	3·5 (4)	6·9 (5)	7·5 (5)	−0·6 (4)	1·0 (4)	−1·1 (4)
C(26)	2·9 (4)	5·4 (4)	6·0 (4)	0·3 (3)	1·3 (3)	−0·3 (3)
O(1)	7·1 (3)	4·5 (3)	7·9 (3)	0·3 (3)	2·9 (3)	2·0 (2)

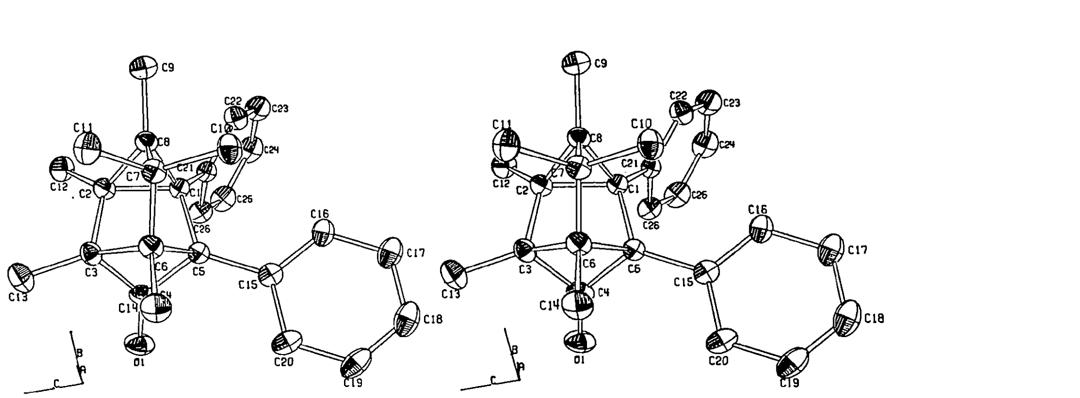


Fig. 1. Stereoscopic view of 2,3,6,7,7,8-hexamethyl-1,5-diphenyltetracyclo[3,3,0,0^{2,8},0^{3,6}]octan-4-one.

of truncation in the data-collection program], C is the ratio of total peak count time to total background count time, and D is a 2% instrumental drift factor. An absorption correction was considered unnecessary in view of the small μ. The data were corrected for Lorentz and polarization effects by A. Zalkin's program *INCOR*, which was altered to include a perpendicular monochromator correction. After Friedel pairs and equivalent reflections had been averaged, 2675 independent reflections remained, of which 1577 had intensities $> 3\sigma(I)$.

Determination and refinement of the structure

The corrected intensity data were processed through the program *FAME* (Dewar & Stone, 1969). The 272 largest $|E|$'s were then put into the program *MULTAN* (Germain, Main & Woolfson, 1971) which chose the three reflections needed for origin specification plus two other starting reflections and determined four sets of phases for the input reflections. The solution associated with the highest absolute figure of merit, ABS FOM, proved to be the correct one, since the corresponding E map revealed the positions of all 27 non-hydrogen atoms.

Three cycles of least-squares refinement of positional and isotropic temperature parameters yielded an R value of 0·132. A difference Fourier map calculated at this point contained peaks which corresponded to all 28 hydrogen atoms, the largest peak height being 0·63 e $Å^{-3}$. Positional and anisotropic thermal parameters were refined for C and O atoms. For H atoms positional parameters were refined with isotropic thermal parameters fixed at 7 $Å^2$. Refinement of the hydrogen atom positions proved unsuccessful; thus, further refinement of these parameters was effected by recalculating hydrogen atom positions after refinement of the carbon and oxygen atom parameters. The phenyl

Table 3. *Fractional coordinates* ($\times 10^3$) *and isotropic temperature factors for the hydrogen atoms*

	x	y	z	B
H(9A)	638	401	365	7·0 $Å^2$
H(9B)	456	353	333	7·0
H(9C)	570	372	252	7·0
H(10A)	973	266	310	7·0
H(10B)	868	234	204	7·0
H(10C)	824	332	258	7·0
H(11A)	1006	289	443	7·0
H(11B)	844	288	494	7·0
H(11C)	856	370	406	7·0
H(12A)	385	150	461	7·0
H(12B)	364	260	408	7·0
H(12C)	490	247	513	7·0
H(13A)	837	72	563	7·0
H(13B)	651	98	577	7·0
H(13C)	780	190	566	7·0
H(14A)	934	18	409	7·0
H(14B)	1013	100	344	7·0
H(14C)	1020	120	460	7·0
H(16)	591	139	140	7·0
H(17)	639	67	10	7·0
H(18)	780	−71	23	7·0
H(19)	867	−133	163	7·0
H(20)	819	−63	293	7·0
H(22)	406	279	180	7·0
H(23)	164	259	91	7·0
H(24)	23	126	110	7·0
H(25)	128	16	215	7·0
H(26)	365	37	305	7·0

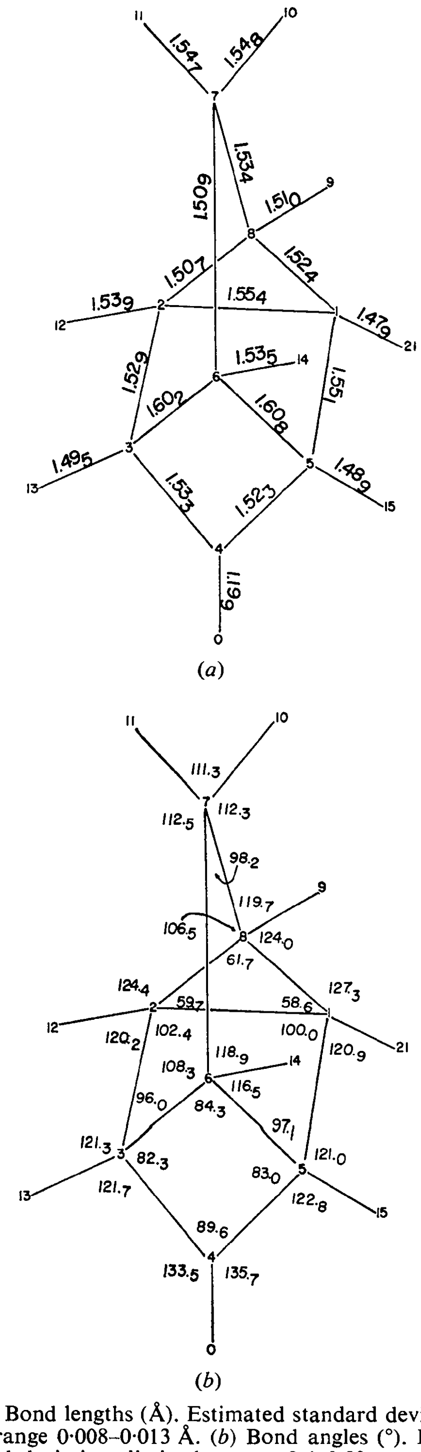


Fig. 2. (*a*) Bond lengths (Å). Estimated standard deviations lie in the range 0·008–0·013 Å. (*b*) Bond angles (°). Estimated standard deviations lie in the range 0·4–0·8°.

hydrogen atom positions were calculated from the equation $\mathbf{r}_H = \mathbf{r}_{C_B} + (1\cdot0/2\cdot8)(\mathbf{r}_{C_B} - \mathbf{r}_{C_A})$, where $\mathbf{r}_H$, $\mathbf{r}_{C_B}$, and $\mathbf{r}_{C_A}$ represent a hydrogen atom, the carbon atom to which it is bonded, and the carbon atom *para* to C_B, respectively (Anzenhofer & DeBoer, 1970). The methyl hydrogen atom positions were calculated from tetrahedral geometry and a carbon–hydrogen bond length of 1·10 Å. An additional six cycles of refinement with carbon and oxygen positional and anisotropic thermal parameters varied and hydrogen atom positional parameters recalculated after every two cycles served to complete the structure. The largest shift in the final cycle was less than 0·3 of an estimated standard deviation. A final difference Fourier map contained no features other than a randomly fluctuating background below 0·37 e $Å^{-3}$. Weights equal to $1/\sigma_F^2$ where $\sigma_F = \sigma(I)F/2I$ were used in the least-squares full-matrix calculations, which included only the reflections with intensities $> 3\sigma(I)$. Atomic scattering factors used for carbon and oxygen atoms were those of Cromer & Waber (1965) and those for hydrogen atoms were from *International Tables for X-ray Crystallography* (1962).

Calculations were effected on a Control Data 6500 computer. Programs used for structure-factor, least-squares, and Fourier calculations were provided by A. Zalkin. Various other data-processing programs of local origin were used.

Final atomic parameters are given in Tables 1, 2, and 3. The estimated standard deviations were calculated from the inverse matrix of the final least-squares cycle. The final R values, weighted and unweighted, respectively, are 0·062 and 0·082 for the 1577 observed reflections. Calculated and observed structure factor magnitudes are listed in Table 4.

Discussion of the structure

The structure of HDTO is illustrated in the stereoscopic drawing (Johnson, 1965) of Fig. 1, which shows the 20% equiprobability ellipsoids derived from the anisotropic thermal parameters. Bond distances and angles, shown in Fig. 2 and also in Tables 5 and 6, were calculated with the program *ORFFE* (Busing, Martin & Levy, 1964).

Table 4. *Observed and calculated structure factors*

H	L	FOBS	FCAL
[illegible]	[illegible]	[illegible]	[illegible]

Table 5. *Bond lengths*

E.s.d.'s are given in parentheses.

endo-Cage carbon–carbon bonds			
C(1)–C(2)	1·554 (9) Å	C(3)–C(6)	1·602 (10) Å
C(1)–C(5)	1·551 (9)	C(4)–C(5)	1·523 (10)
C(1)–C(8)	1·524 (9)	C(5)–C(6)	1·608 (8)
C(2)–C(3)	1·529 (9)	C(6)–C(7)	1·509 (9)
C(2)–C(8)	1·507 (9)	C(7)–C(8)	1·534 (9)
C(3)–C(4)	1·533 (10)		
exo-Cage carbon–carbon bonds			
C(1)–C(21)	1·479 (8)	C(6)–C(14)	1·535 (9)
C(2)–C(12)	1·539 (10)	C(7)–C(10)	1·548 (10)
C(3)–C(13)	1·495 (9)	C(7)–C(11)	1·547 (9)
C(5)–C(15)	1·489 (10)	C(8)–C(9)	1·510 (9)
Carbon–carbon distances within the phenyl rings			
C(15)–C(16)	1·383 (10)	C(21)–C(22)	1·380 (9)
C(16)–C(17)	1·382 (11)	C(22)–C(23)	1·396 (10)
C(17)–C(18)	1·385 (13)	C(23)–C(24)	1·384 (13)
C(18)–C(19)	1·352 (13)	C(24)–C(25)	1·371 (12)
C(19)–C(20)	1·385 (13)	C(25)–C(26)	1·406 (10)
C(20)–C(15)	1·406 (10)	C(26)–C(21)	1·395 (10)
		Mean C–C*	1·385 (15)
C=O bond			
C(4)–O(1)	1·199 (10)		

* E.s.d.'s for mean bond distances are calculated from the equation $\sigma = \{[\sum_{i=1}^{i=N}(x_i-\bar{x})^2]/(N-1)\}^{1/2}$, where x_i is the ith bond length and $\bar{x}$ is the mean of the N equivalent bond lengths.

The structure of HDTO is closely related to that of the norbornyl system; however, owing to the strain induced by the cyclopropane and cyclobutane rings, the bond distances and angles do not closely resemble those usually found for norbornyl systems. [For a summary of bond distances and angles for these systems, see Altona & Sundaralingam (1972).] For example, the distances C(1)–C(8) of 1·524 (9) Å and C(2)–C(8) of 1·507 (9) Å are shorter than those found for comparable bonds in either unsubstituted gaseous norbornane, 1·54 (1) Å (Morino, Kuchitsu & Yokozeki, 1967), or substituted norbornane, 1·535 (4) Å (Fratini, Britts & Karle, 1967) and 1·53 (3) Å (MacDonald & Trotter, 1965), while the distances C(3)–C(6), 1·602 (10) Å, and C(5)–C(6), 1·608 (8) Å, are much longer. Such results are expected, however, because in this molecule these bonds comprise cyclopropane and cyclobutane rings, respectively. The bonds C(2)–C(8) and C(1)–C(8), which are in the cyclopropane ring, are expected to be shorter than the usual 1·537 (5) Å (Sutton, 1965) because of the phenomenon of bent bonds (Lukina, 1962). For example, the average C–C bond distance in the 3-membered ring in gaseous cyclopropane is 1·510 (2) Å (Bastiansen, Fritsch, & Hedberg, 1964), in cyclopropanecarboxamide 1·50 Å (Long, Maddox & Trueblood, 1969), in *cis*-1,2,3-tricyanocyclopropane, 1·518 (3) Å (Hartman & Hirshfeld, 1966), and in *exo-anti*-tricyclo[3,1,1,$0^{2,4}$]heptan-6-yl *p*-nitrobenzoate, henceforth *exo*[3,1,1,$0^{2,4}$], 1·50 (2) Å (Masamune, Vukov, Bennett & Purham, 1972). The structure of the latter compound is also related closely to HDTO, in that it is missing only the bridging carbon atom. In contrast to the C(1)–C(8) and C(2)–C(8) bond lengths, the C(1)–C(2) bond is longer than would be expected, 1·554 (9) Å, probably as a result of the considerable strain present in that region of the molecule. The exocyclic bond lengths and angles are expected to be shorter and larger, respectively, than the normal values, characteristic of bent bonding. The average exocyclic C–C bond length, 1·524 (9) Å, compares to 1·487 Å in bicyclopropane (Eraker & Rømming, 1967) and 1·478 (5) Å in a pentacyclic compound (Hwang, Donohue & Tsai, 1972). The average exocyclic angle is 123·4 (6)°, much greater than the predicted 116° (Lukina, 1962). This opening probably reflects one of the ways in which strain in the molecule is relieved.

The C–C bonds in cyclobutane rings are somewhat larger than expected and vary from 1·547 to 1·57 Å. [For a summary of dimensions of cyclobutane rings, see Adman & Margulis (1968).] This observation explains in part the long C(3)–C(6) and C(5)–C(6) bonds observed in HDTO, the two remaining bonds, C(3)–C(4), 1·533 (10) Å, and C(4)–C(5), 1·523 (10) Å, being shortened as a result of a change of hybridization on C(4). The presence of exceptionally long C(3)–C(6) and C(5)–C(6) bonds supports the observation (Hart & Kuzuya, 1973) that it is one of these that breaks when carbonium ions derived from this system rearrange. The average bond angle in the cyclobutane ring, 84·8 (5)°, compares to 87·8° in cyclobutane (Skancke, 1960), 84·8° in *exo*[3,1,1,$0^{2,4}$], and 88·0° in *trans*-bicyclo[4,2,0]octyl 1-3,5-dinitrobenzoate (Barnett & Davis, 1970). The dihedral angle in the cyclobutane ring is 133°, less than those found (145 to 160°) for other puckered cyclobutane rings, but not significantly different from that of 132° found for *exo*[3,1,1,$0^{2,4}$]. The bond lengths and angles of those exocyclic groups that involve atoms C(5) and C(6) approximate the expected values, while those that involve atom C(3) do not, and probably reflect an uneven distribution of strain in this part of the molecule.

The bond distances C(2)–C(3) of 1·529 (9) Å and C(1)–C(5) of 1·551 (9) Å do not differ significantly from those found in either norbornyl systems [1·539 (25) to 1·578 (18) Å] or in *exo*[3,1,1,$0^{2,4}$], 1·56 (2) and 1·59 (2) Å. The distances which involve the bridging carbon atom, C(7), are also comparable to those found in norbornyl systems. The bridging angle of 98·2 (5)° is slightly larger than those found in norbornyl derivatives, which range from 92 (1) to 96 (1)°. The values of the remaining *endo* angles in the cage of HDTO are less than the normal tetrahedral ones, an observation which is also consistent with that found in the norbornyl system.

The phenyl groups are planar, the deviations from the best plane through the carbon atoms of each ring range from 0·000 (8) to 0·004 (6) Å, while the greatest deviation of a hydrogen atom from the associated phenyl plane is 0·04 (1) Å. The average C–C distance and angle in the phenyl rings are 1·385 (15) Å and

Table 6. *Bond angles*

E.s.d.'s are given in parentheses.

C(2)—C(1)—C(5)	100·0 (5)°	C(4)—C(5)—C(15)	122·8 (6)°
C(2)—C(1)—C(8)	58·6 (4)	C(6)—C(5)—C(15)	123·3 (5)
C(2)—C(1)—C(21)	121·9 (6)	C(3)—C(6)—C(5)	84·3 (5)
C(5)—C(1)—C(8)	109·2 (5)	C(3)—C(6)—C(7)	108·3 (5)
C(5)—C(1)—C(21)	120·9 (5)	C(3)—C(6)—C(14)	115·4 (5)
C(8)—C(1)—C(21)	127·3 (5)	C(5)—C(6)—C(7)	107·8 (5)
C(1)—C(2)—C(3)	102·4 (5)	C(5)—C(6)—C(14)	116·8 (5)
C(1)—C(2)—C(8)	59·7 (4)	C(7)—C(6)—C(14)	118·9 (6)
C(1)—C(2)—C(12)	121·5 (5)	C(6)—C(7)—C(8)	98·2 (5)
C(3)—C(2)—C(8)	111·8 (6)	C(6)—C(7)—C(11)	112·5 (5)
C(3)—C(2)—C(12)	120·2 (6)	C(6)—C(7)—C(10)	112·3 (6)
C(8)—C(2)—C(12)	124·4 (6)	C(8)—C(7)—C(10)	110·9 (5)
C(2)—C(3)—C(4)	101·5 (5)	C(8)—C(7)—C(11)	111·0 (5)
C(2)—C(3)—C(6)	96·0 (5)	C(10)–C(7)—C(11)	111·3 (5)
C(2)—C(3)—C(13)	121·3 (6)	C(1)—C(8)—C(7)	108·0 (5)
C(4)—C(3)—C(6)	82·9 (5)	C(1)—C(8)—C(9)	124·0 (5)
C(4)—C(3)—C(13)	121·7 (6)	C(2)—C(8)—C(1)	61·7 (4)
C(6)—C(3)—C(13)	125·0 (6)	C(2)—C(8)—C(7)	106·5 (5)
C(3)—C(4)—C(5)	89·6 (5)	C(2)—C(8)—C(9)	123·0 (6)
C(3)—C(4)—O(1)	133·5 (6)	C(7)—C(8)—C(9)	119·7 (6)
C(5)—C(4)—O(1)	135·7 (7)	C(5)—C(15)–C(16)	122·4 (6)
C(1)—C(5)—C(4)	101·3 (5)	C(5)—C(15)–C(20)	119·8 (6)
C(1)—C(5)—C(6)	97·1 (5)	C(1)—C(21)–C(22)	123·6 (6)
C(1)—C(5)—C(15)	121·0 (5)	C(1)—C(21)–C(26)	118·1 (6)
C(4)—C(5)—C(6)	83·0 (5)		
Angles within the phenyl rings			
C(15)–C(16)–C(17)	122·0 (7)	C(21)–C(22)–C(23)	121·5 (7)
C(16)–C(17)–C(18)	119·0 (7)	C(22)–C(23)–C(24)	119·7 (7)
C(17)–C(18)–C(19)	120·0 (8)	C(23)–C(24)–C(25)	119·8 (7)
C(18)–C(19)–C(20)	121·7 (7)	C(24)–C(25)–C(26)	120·5 (8)
C(19)–C(20)–C(15)	119·4 (7)	C(25)–C(26)–C(21)	120·2 (6)
C(16)–C(15)–C(20)	117·8 (7)	C(22)–C(21)–C(26)	118·3 (6)
		Mean*	120·0 (13)

* E.s.d. was calculated from the formula in the footnote to Table 5, except that x_i is now the ith bond angle and $\bar{x}$ is the mean of the N equivalent bond angles.

120·0 (13)° compared to the normal values of 1·394 (5) Å (Sutton, 1965) and 120°. The distances C(1)–C(21) and C(5)–C(15) of 1·479 (8) and 1·489 (10) Å also compare favorably with that expected, 1·505 (5) Å. Finally the angles involving the cage-phenyl carbon atoms are substantially larger than the expected tetrahedral angle; C(8)–C(1)–C(21) being particularly large at 127·3 (5)°, again probably due to a combination of steric strain and the observed opening of the exocyclic bonds of cyclopropane rings (Hartman & Hirshfeld, 1966).

The O(1)–C(4) distance is 1·199 (10) Å, similar to the normal value of 1·215 (5) Å (Sutton, 1965). The angles around C(4) might be expected to be 120° since it is an sp^2 carbon atom, but as it is also a member of the cyclobutane ring, one angle closes to 89·6 (5)°, and the other two angles open to an average of 134·6 (7)°. Chemically, one of the most significant features of the molecule is the distance of 2·145 (16) Å from C(4) to the midpoint of the C(1)–C(2) bond. The same distance is significantly longer, 2·23 Å, in *exo*[3,1,1,$0^{2,4}$]. This short contact facilitates the participation of the C(1)–C(2) bond in the ionization of (I) to (II), the $(CH)_5^+$-type carbonium ion.

The closest intermolecular (nonhydrogen atom) contact is 3·51 Å, which indicates that the molecular structure is composed of discrete molecules. Thus, packing would not seem to be the cause of the significantly long C(3)–C(6) and C(5)–C(6) bonds. The section of the structure containing these bonds is shielded from the neighboring molecules by methyl carbon atoms C(13) and C(14), by the bridging carbon atom C(7), and by a phenyl group. Therefore, the lengthening of the bonds must be due to internal steric strain. Further proof that packing is not an influence on these bonds is the almost perfect mirror plane exhibited by the molecule when the phenyl groups are neglected. The methyl carbon atoms on one side of the molecule and the phenyl rings on the other would surely create different packing environments.

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Refinement of the Crystal Structure of Caesium Triborate, $Cs_2O.3B_2O_3$

BY J. KROGH-MOE

Chemistry Department, University of Trondheim, Trondheim, Norway

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Caesium triborate, $Cs_2O.3B_2O_3$, crystallizes in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a=6{\cdot}213$ (1), $b=8{\cdot}521$ (1), $c=9{\cdot}170$ (1) Å and $Z=2$. The calculated density is $3{\cdot}357$ g cm^{-3}. The structure has previously been determined from film data in two projections (Krogh-Moe, 1960). A refinement with three-dimensional diffractometer data has now confirmed the early determination. The R index obtained in the refinement is 0·039. The borate anion of the structure forms a three-dimensional framework built up from triborate groups. The boron–oxygen bond lengths (standard deviation 0·009 Å) show a normal distribution in the framework. The caesium atoms are surrounded by oxygen atoms at distances upwards of 3·030 Å.

Introduction

The crystal structure of caesium triborate was determined by Krogh-Moe in 1960. Since this determination was based on film data in projections along two axes only, a complete three-dimensional refinement was considered desirable. A new data set was recorded with Mo $K\alpha$ radiation, on a Picker on-line single-crystal diffractometer. The crystal used for data collection was synthesized as previously described by Krogh-Moe (1960). It had an approximately prismatic shape, $0{\cdot}010 \times 0{\cdot}017 \times 0{\cdot}046$ cm, with edges corresponding to the a, b and c axes respectively, c being aligned with the goniometer axis.

Unit-cell dimensions and standard errors, $a=6{\cdot}213 \pm 0{\cdot}001$, $b=8{\cdot}521 \pm 0{\cdot}001$ and $c=9{\cdot}170 \pm 0{\cdot}002$ Å, were obtained by the method of least squares from angle data recorded at 22°C for 12 high-angle reflexions