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The Crystal and Molecular Structure of a Bicyclo[3,3,1]nonane System: Structure of D,L-1,7-Dicarbomethoxy-3a,7-methano-3a*H*-decahydrocyclopentacyclooctene-2,10-dione

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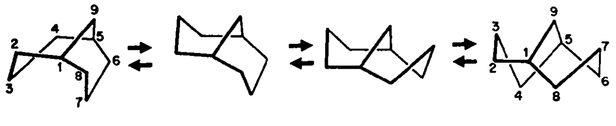
The crystal and molecular structure was determined from three-dimensional diffractometer data. The compound crystallizes in the monoclinic space group $P2_1/c$, with four molecules in a unit cell of dimensions $a=10{\cdot}907$ (3), $b=9{\cdot}520$ (7), $c=15{\cdot}638$ (13) Å, $\beta=111{\cdot}19$ (4)°. The crystal structure was solved by direct-method phasing and it was refined by the full-matrix least-squares method to a conventional R of 0·056 on 2390 independent reflections. The structure is disordered. The bicyclo[3,3,1]nonane system in the molecule assumes two conformations, the di-chair and the boat-chair forms. The occupancy factors are 0·7 and 0·3 respectively. Strain due to the close contact, 2·097 Å, between C(5) and C(9) and the *trans* fused perhydroindane system cause considerable flattening of the rings and distortions of the valency angles and bond lengths. The carbomethoxy group at C(1) and the methylene group at C(4) are in the *trans* configuration.

Introduction

The crystal structure of 1,7-dicarbomethoxy-3a,7-methano-3a*H*-decahydrocyclopentacyclooctene-2,10-dione (DCPCO) was undertaken to study the conformation of the bicyclo[3,3,1]nonane system and to determine the configurations at C(1) and at the junction of the *A* and *B* rings (see Fig. 1 for numbering scheme). The results were essential for establishing the stereochemical relationships in a one-step assemblage of 3a,7-methano-3a*H*-cyclopentacyclooctene systems (Danishefsky, Hatch, Sax, Abola & Pletcher, 1973). The crystal structure is of further interest in that it shows how the conformation of the bicyclo[3,3,1]nonane system is affected by the fusion of a cyclopentanone ring to one of its bicyclo rings.

It has been suggested that certain 9-keto derivatives [C(10) in DCPCO] of the bicyclononane system would exhibit an equilibrium distribution consisting of the boat–chair (1*b*) and di-twist-boat (1*d*) conformations, because of the removal of the flag-pole hydrogen and certain torsional interactions (Eliel, Allinger, Angyal & Morrison, 1966). Neither of these conformers was found in previous structure determinations of bicyclononane systems (Webb & Becker, 1967; Brown, Martin & Sim, 1965). Only (1*a*) was observed previously. However, two of the conformers, the di-chair (1*a*) and boat–chair (1*b*) forms, do occur in this crystal structure. The possible role of the *trans* fused perhydroindane in facilitating a distribution of conformations is considered.



(1*a*) (1*b*) (1*c*) (1*d*)

Experimental procedures

DCPCO was synthesized and given to us by Dr W.E. Hatch and Dr Danishefsky of the Chemistry Department in the University of Pittsburgh. Crystals were grown by slow evaporation from an ethanol solution.

The crystal selected for this analysis was a colorless flat plate with dimensions 0·8 × 0·6 × 0·1 mm. The space group was determined from oscillation and Weissenberg photographs. A tendency of the DCPCO to form twin crystals required a survey of several specimens before one suitable for intensity-data collection could be found. The unit-cell dimensions were determined from a least-squares (Picker, 1972) fit of 12 centered reflections using a Picker FACS-1 diffractometer system with graphite-monochromated Cu $K\alpha$ radiation and equipped with a NaI scintillation detector. The crystal was oriented so that the b axis coincided with the φ axis of the full-circle goniostat. Table 1 contains the crystal data.

Table 1. *Crystal data*

$C_{16}H_{20}O_6$ M.W. 308·35
Monoclinic, space group $P2_1/c$ from systematic absences:
$h0l$ absent for l odd; $0k0$ absent for k odd.

$a = 10{\cdot}907$ (13) Å
$b = 9{\cdot}520$ (7)
$c = 15{\cdot}638$ (13)
$\beta = 111{\cdot}19$ (4)°
} 24°C
$V = 1514{\cdot}6$ Å^3
$Z = 4$
$d_x = 1{\cdot}352$ g cm^{-3}
$\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å
$\mu(\text{Cu } K\alpha) = 8{\cdot}7$ cm^{-1}
$F(000) = 656$

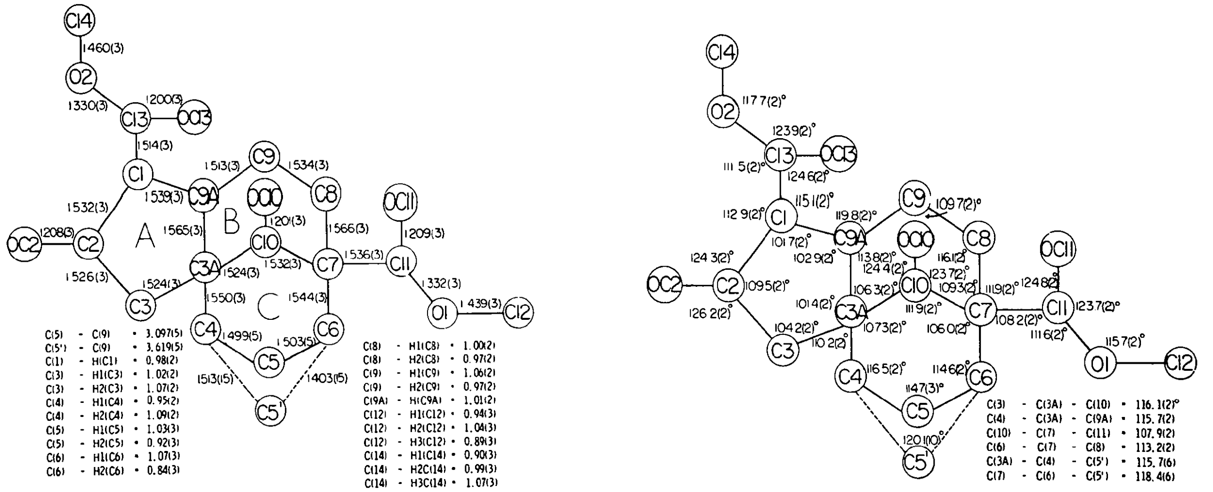
The integrated intensity measurements were made by scanning reflections in the θ:2θ mode at a rate of 1° min^{-1} over a 2θ range of 2°. The background was counted for 20 s at each of the scan limits. Three reflections were chosen as standards, and these were monitored after the measurement of every 50 reflections. A reduction in the intensity of the standards exceeding 3% was used as a criterion for automatic realignment of the crystal.

A total of 2502 independent reflections with sin $\theta \geq 0{\cdot}896$ were measured. Of these 298 had a net intensity, I, less than $3\sigma(I)$ where $\sigma(I)$ is given by $A[N + k^2(N_{B1}+N_{B2})]^{1/2}$ and I is given by $A[N-k(N_{B1}+N_{B2})]$. In these expressions N is the total number of counts accumulated during the scan; N_{B1} and N_{B2} are the background counts at either end of the scan range; k is the ratio of the total scan time to the total background time; and A is the attenuator factor. In this group of 298 reflections, 112 which had $I \leq 0$ were dropped from the data set (Shiono, 1971*a*) leaving a total of 2390 independent reflections with 186 classified as unobserved. The intensities were corrected for Lorentz and polarization effects but not for absorption. The reduction to structure amplitudes was performed during the data collection using the Picker (1972) DOS Software System.

Structure determination and refinement

Structure-factor amplitudes were placed on an absolute scale and normalized by means of a Wilson plot (Shiono, 1971*b*). Different scale factors were applied to sets of reflections as a function of sin θ, in order to renormalize the $|F|$'s so that the average value of E^2 would equal unity for each set separately. The signs of 450 reflections with $|E| \geq 1{\cdot}5$ were determined by use of the computer program *MULTAN* (Germain, Main & Woolfson, 1971). An E map (Karle, Hauptman, Karle & Wing, 1958) revealed the 22 nonhydrogen atomic positions in the molecule.

The positional and thermal parameters of these atoms were refined by the full-matrix least-squares method, using the program *ORFLS-PX* of Busing, Martin & Levy (1962) as modified by Shiono (1971*a*). The function minimized was $w\,(|F_o| - k|F_c|)^2$ where k is a single scale factor and w is a weighting factor. The weighting scheme employed was $w = 1/\sigma^2(F)$ where $\sigma^2(F) = \{(\sigma(I)/2\text{Lp}F)^2 + (0{\cdot}03I)^2\}$ and Lp are the Lorentz and polarization factors. The unobserved reflections were assigned $w = 0$. The hydrogen atoms were located in a difference Fourier synthesis computed when the



C(5) - C(9)	•	3.097(5)
C(5') - C(9)	•	3.619(5)
C(1) - H(C1)	•	0.98(2)
C(3) - H1(C3)	•	1.02(2)
C(3) - H2(C3)	•	1.07(2)
C(4) - H1(C4)	•	0.95(2)
C(4) - H2(C4)	•	1.09(2)
C(5) - H1(C5)	•	1.03(3)
C(5) - H2(C5)	•	0.92(3)
C(6) - H1(C6)	•	1.07(3)
C(6) - H2(C6)	•	0.84(3)

C(8) - H1(C8)	•	1.00(2)
C(8) - H2(C8)	•	0.97(2)
C(9) - H1(C9)	•	1.06(2)
C(9) - H2(C9)	•	0.97(2)
C(9A) - H(C9A)	•	1.01(2)
C(12) - H1(C12)	•	0.94(3)
C(12) - H2(C12)	•	1.04(3)
C(12) - H3(C12)	•	0.89(3)
C(14) - H1(C14)	•	0.90(3)
C(14) - H2C(14)	•	0.99(3)
C(14) - H3C(14)	•	1.07(3)

C(3) - C(3A) - C(10)	•	116.1(2)°
C(4) - C(3A) - C(9A)	•	115.7(2)
C(10) - C(7) - C(11)	•	107.9(2)
C(6) - C(7) - C(8)	•	113.2(2)
C(3A) - C(4) - C(5')	•	115.7(6)
C(7) - C(6) - C(5')	•	118.4(6)

Fig. 1. Schematic drawing of the molecule showing the interatomic distances and valency angles along with the numbering system used to identify the atoms.

conventional R was 0·10. The positional parameters of these atoms were varied in additional cycles of refinement. The anisotropic thermal parameters of the carbon atoms to which the hydrogens are bonded were assigned to these atoms and they were not varied. Refinement converged at an $R=0·068$ and a difference

Table 2. *Observed and calculated structure factors*

The columns within each group in order from left to right are: the running index l, $10|F_o|$, $10|F_c|$. Asterisks indicate unobserved reflections and crosses indicate reflections omitted from refinement due to possible extinction effects.

Fourier synthesis at this point showed a large peak of about 1·53 e Å^{-3} near the position of C(5). Analysis of the geometry around the peak indicated that a model with C(5) disordered was plausible. Occupancy factors assigned to this carbon atom were 0·3 for C(5′) and 0·7 for C(5). The refinement of this disordered model converged to $R=0·056$ for 2390 independent reflections and to $R=0·052$ for 2204 observed reflections. (In the final cycles of the refinement, seven reflections which were seriously affected by extinction were assigned zero weight but were still listed as observed reflections. These reflections are marked with a cross in Table 2, which lists the structure factors.) Inspection of the final difference Fourier synthesis showed no scattering density ≥ 0·25 e Å^{-3}. The atomic scattering factors used for carbon and oxygen are those of Cromer & Waber (1965) while those of Stewart, Davidson & Simpson (1965) were used for hydrogen. Computer calculations were made on the PDP-10 in the Computer Center of the University of Pittsburgh and on the IBM 1130 in the Crystallography Dept. of the University of Pittsburgh. Illustrations were prepared using the computer plotting program *ORTEP* (Johnson, 1965). The final positional and thermal parameters along with their estimated standard deviations are presented in Table 3.

Table 3. *Atomic parameters, their estimated standard deviations, and root-mean-square displacements about principal axes of vibration*

(*a*) Nonhydrogen atoms. Thermal parameters are in the form $\exp[-(h^2\beta_{11}+\ldots 2kl\beta_{23})]$. All values are × 10⁴.

	Fractional coordinates			Thermal parameters						Root-mean-square displacements (Å)		
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$D1$	$D2$	$D3$
O(1)	1688 (2)	−334 (2)	−908 (1)	133 (2)	93 (2)	33 (1)	−38 (2)	10 (1)	0 (1)	1794	1915	2978
O(2)	6670 (1)	4221 (2)	2902 (1)	68 (2)	153 (2)	44 (1)	−20 (2)	2 (1)	11 (1)	1727	2273	2878
O(C2)	3318 (2)	5295 (2)	2781 (1)	117 (2)	153 (2)	41 (1)	−15 (2)	30 (1)	−33 (1)	1717	2444	2901
O(C10)	645 (2)	2158 (2)	−58 (1)	83 (2)	199 (3)	52 (1)	−64 (2)	33 (1)	−36 (1)	1661	2140	3349
O(C11)	608 (2)	1082 (2)	−2085 (1)	101 (2)	121 (2)	34 (1)	−6 (2)	−3 (1)	−7 (1)	1687	2371	2747
O(C13)	5392 (2)	2631 (2)	3222 (1)	117 (2)	130 (2)	42 (1)	−7 (2)	16 (1)	23 (1)	1854	2402	2824
C(1)	4459 (2)	4129 (2)	1904 (1)	71 (2)	83 (2)	26 (1)	−12 (2)	11 (1)	−2 (1)	1659	1841	2126
C(2)	3259 (2)	4652 (2)	2101 (1)	88 (2)	93 (2)	32 (1)	−10 (2)	20 (1)	−3 (1)	1831	1984	2227
C(3)	2006 (2)	4236 (2)	1312 (1)	75 (2)	128 (3)	37 (1)	−5 (2)	20 (1)	−15 (1)	1858	1971	2517
C(3A)	2489 (2)	3737 (2)	563 (1)	64 (2)	90 (2)	27 (1)	−6 (2)	14 (1)	−3 (1)	1689	1834	2058
C(4)	2567 (2)	4989 (2)	−49 (1)	104 (2)	83 (2)	35 (1)	−4 (2)	13 (1)	3 (1)	1897	1972	2482
C(5)	2917 (4)	4643 (5)	−868 (3)	95 (4)	94 (4)	34 (2)	−16 (4)	13 (2)	15 (2)	1650	2025	2563
C(5′)	2136 (16)	4683 (13)	−1065 (8)	284 (25)	102 (13)	27 (6)	44 (19)	34 (12)	17 (7)	1518	2177	4001
C(6)	2287 (3)	3329 (2)	−1367 (1)	155 (3)	112 (3)	26 (1)	−22 (2)	27 (1)	3 (1)	1602	2195	2951
C(7)	2310 (2)	2070 (2)	−739 (1)	78 (2)	90 (2)	25 (1)	−13 (2)	14 (1)	−3 (1)	1630	1895	2189
C(8)	3731 (2)	1529 (2)	−182 (1)	77 (2)	117 (3)	35 (1)	−2 (2)	17 (1)	−13 (1)	1814	8022	2420
C(9)	4601 (2)	2508 (2)	573 (1)	66 (2)	102 (3)	33 (1)	−3 (2)	14 (1)	−6 (1)	1812	1957	2198
C(9A)	3834 (2)	3041 (2)	1142 (1)	64 (2)	79 (2)	26 (1)	−12 (2)	11 (1)	−1 (1)	1635	1774	2052
C(10)	1672 (2)	2593 (2)	−71 (1)	72 (2)	97 (2)	27 (1)	−9 (2)	11 (1)	0 (1)	1680	1945	2188
C(11)	1433 (2)	907 (2)	−1331 (1)	86 (2)	100 (3)	30 (1)	−10 (2)	19 (1)	−6 (1)	1755	2039	2247
C(12)	950 (3)	−1503 (3)	−1425 (2)	153 (3)	109 (3)	52 (1)	−54 (3)	16 (2)	−12 (2)	1798	2470	3212
C(13)	5535 (2)	3564 (2)	2750 (1)	82 (2)	98 (3)	27 (1)	−6 (2)	16 (1)	−8 (1)	1657	2091	2173
C(14)	7824 (3)	3717 (3)	3656 (2)	90 (3)	198 (4)	55 (1)	4 (3)	−6 (2)	11 (2)	1861	2928	3115

Table 3 (*cont.*)

(*b*) Hydrogen atoms.* Fractional coordinates × 10³.

	x	y	z
H(C1)	484	492	169
H1(C3)	135	505	112
H2(C3)	155	340	155
H1(C4)	311	570	33
H2(C4)	158	543	−26
H1(C5)	264	548	−131
H2(C5)	381	453	−67
H1(C6)	126	355	−171
H2(C6)	248	312	−183
H1(C8)	357	65	11
H2(C8)	411	137	−65
H1(C9)	543	195	101
H2(C9)	489	330	30
H(C9A)	360	218	143
H1(C12)	119	−233	−108
H2(C12)	103	−154	−207
H3(C12)	9	−136	−159
H1(C14)	752	353	411
H2(C14)	857	439	382
H3(C14)	808	267	353

* The two hydrogen atoms bonded to the disordered carbon (C5′) are not included.

Results and discussion

The interatomic distances and valency angles with their e.s.d.'s are summarized in Fig. 1. Data on least-squares planes through various groups of atoms appear in Table 4. Torsion angles are listed in Table 5.

Two conformational isomers of DCPCO were observed in the crystal structure corresponding to the di-chair and the boat–chair forms of the cyclohexanones with relative abundances of 70% and 30% respectively. The major conformer is similar to those reported by Brown, Martin & Sim (1965) and by Webb & Becker (1967), but the boat–chair form has not been observed previously. Fig. 2 shows the two conformers of the bicyclononane system observed in DCPCO and Fig. 3 is a stereoscopic view of DCPCO indicating the 50% probability ellipsoids. The crucial configurational relationships to be noted are the *trans* fused perhydroindane system, the *trans* relationship of the carbomethoxy at C(1), and the C(4) methylene group attached to C(3*A*).

Strong steric interactions between C(5) and C(9) and constraints introduced by the *trans* fusion of rings *A* and *B* have a marked influence on the structural details of the bicyclononane ring system. There is clearly a flattening of the *B, C* ring system as evidenced by the increased separation between C(5) and C(9) which is expected to be 2·10 Å for the ideal twin-chair bicyclononane. The nonbonding distances between the observed positions for C(5) and C(9) in the twin-chair and the boat–chair forms are 3·097 and 3·619 Å, respectively. The former distance is comparable with

Table 4. *Least-squares planes and atomic displacements*

Coefficients ($\times 10^4$) are given for $Ax+By+Cz=D$, referred to the crystallographic axes (x, y and z in Å). The atomic displacements (d) $\times 10^3$ are in Å; atoms included in the plane are designated in bold-face type. The standard deviation in the plane, $\sigma(\times 10^3)$, is given by $(\sum_m d_m^2/m-3)^{1/2}$ where m is the number of atoms included in the plane.

No.	*A*	*B*	C	*D*	σ	*d*
1	9500	−727	−598	22931	51	**C(4)** 25, **C(6)** −26, **C(7)** 26, **C(3A)** −25, C(5) 489, C(10) −734, C(5′) −304
2	6067	7036	−5643	36100	87	**C(3A)** 43, **C(7)** −43, **C(8)** 44, **C(9A)** −44, C(9) 609, C(10) −704
3	3366	8307	−5351	31339	315	**C(1)** 175, **C(2)** −16, **C(3)** −146 **C(3A)** 264, **C(9A)** −277
4	4004	7923	−5739	31167	257	**C(1)** 236, **C(2)** −70, **C(3)** −223, **C(3A)** 284, **C(7)** 117, **C(8)** −170, **C(9A)** −173, C(10) −367

Planes	Dihedral angle (°)
1 and 4	79·47
2 and 3	17·68

Table 5. *Torsion angles*

The sign convention is that of Klyne & Prelog (1960). The torsion angles in the other enantiomorph are opposite in sign. φ in (*a*) and (*b*) is the torsion angle about the specified bond. The other two atoms required to define the angle are attached to the ends of the bond and are in the ring in question.

(*a*) Bicyclo[3,3,1]nonane nucleus

Ring *B*		Ring *C* (70% conformer)		Ring *C* (30% conformer)	
Bond	φ	Bond	φ	Bond	φ
C(3A)–C(9A)	61·6 (2)°	C(3A)–C(4)	−47·7 (3)°	C(3A)–C(4)	−13·5 (6)°
C(9A)–C(9)	−53·4 (2)	C(4)—C(5)	40·1 (4)	C(4)—C(5′)	−29·7 (13)
C(9)—C(8)	46·7 (2)	C(5)—C(6)	−43·8 (4)	C(5′)—C(6)	26·0 (13)
C(8)—C(7)	−48·5 (2)	C(6)—C(7)	54·7 (3)	C(6)—C(7)	19·7 (7)
C(7)—C(10)	56·9 (2)	C(7)—C(10)	−65·4 (2)	C(7)—C(10)	−65·4 (2)
C(10)–C(3A)	−62·7 (2)	C(10)–C(3A)	61·6 (2)	C(10)–C(3A)	61·6 (2)

(*b*) Ring *A*

C(1)—C(2)	−16·5 (2)
C(2)—C(3)	−11·5 (2)
C(3)—C(3A)	34·3 (2)
C(3A)–C(9A)	−45·5 (2)
C(9A)–C(1)	37·6 (2)

(*c*) At ring junction

C(1)–C(9A)–C(3A)–C(10)	−167·2 (1)
C(3)–C(3A)–C(9A)–C(9)	−176·6 (2)
C(1)–C(9A)–C(3A)–C(4)	73·8 (2)
C(3)–C(3A)–C(4)—C(5)	−174·9 (2)
C(3)–C(3A)–C(4)—C(5′)	−140·8 (6)

(*d*) Extra-nuclear

O(C2)—C(2)—C(3)—C(3A)	168·4 (7)	O(C11)–C(11)–O(1)–C(12)	2·6 (3)
O(C2)—C(2)—C(1)—C(9A)	163·5 (2)	O(C13)–C(13)–C(1)–C(2)	56·9 (2)
O(C2)—C(2)—C(1)—C(13)	39·6 (3)	O(C13)–C(13)–C(1)–C(9A)	−59·2 (2)
O(C10)–C(10)–C(3A)–C(9A)	117·9 (2)	O(C13)–C(13)–O(2) C(14)	3·8 (3)
O(C10)–C(10)–C(3A)–C(4)	−117·7 (2)	C(1)—C(13)–O(2)–C(14)	−175·5 (2)
O(C10)–C(10)–C(3A)–C(3)	6·0 (3)	C(7)—C(11)–O(1)–C(12)	−177·6 (2)
O(C10)–C(10)–C(7)—C(6)	114·0 (2)	O(1)—C(11)–C(7)–C(6)	162·1 (2)
O(C10)–C(10)–C(7)—C(8)	−123·7 (2)	O(1)—C(11)–C(7)–C(8)	36·7 (2)
O(C10)–C(10)–C(7)—C(11)	−1·8 (3)	O(1)—C(11)–C(7)–C(10)	−83·7 (2)
O(C11)–C(11)–C(7)—C(6)	−18·1 (3)	O(2)—C(13)–C(1)–C(2)	−123·8 (2)
O(C11)–C(11)–C(7)—C(10)	96·1 (2)	O(2)—C(13)–C(1)–C(9A)	120·1 (2)
O(C11)–C(11)–C(7)—C(8)	−143·5 (2)		

the 3·11 Å separation reported for chlorobicyclo-[3,3,1]nonan-9-one (Webb & Becker, 1967). However, the fusion of rings *A* and *B* in DCPCO imposes a constraint on the bicyclonane system such that the extent of flattening in the *B* and *C* rings is no longer the same. Other bicyclo[3,3,1]nonane systems (*cf.* Webb & Becker, 1967) without this constraint show that C(5) and C(9) [corresponding to C(3) and C(7) in their structure] are equally displaced by ~0·50 Å from planes 2 and 1, respectively (the unstrained distance would be 0·73 Å). In DCPCO, however, there are significant differences in the deviations of these atoms from the least-squares planes. Distances of 0·49 and 0·61 Å for C(5) and C(9) from the planes of rings *C* and *B*, respectively, indicate a greater extent of flattening for ring *C* as compared with ring *B*. The deviation of C(5′) from plane 1 is −0·304 Å. The fusion of the five- and six-membered rings appears to reduce the energy difference between the di-chair and boat–chair forms.

A comparison of the interatomic distances and angles in this compound with those in 2-chlorobicyclo-[3,3,1]nonan-9-one (CBNO) (Webb & Becker, 1967) and in 1-*p*-bromobenzenesulphonyloxymethyl-5-methylbicyclo[3,3,1]nonan-9-ol (BCBO) (Brown, Martin & Sim, 1965) reveals similar distortions in the three structures. These distortions are very likely to relieve the strain within the molecule. For example, the angles around C(4), C(5), C(6) and C(8), C(9) and C(9A), which are involved in reducing the strains are necessarily larger than the tetrahedral angle and have an average value of 114·6° for DCPCO, 113·9° for CBNO and 114·0° for BSBO. The bridging angles C(4)–C(3A)–C(9A) and C(6)–C(7)–C(8) have an average of 114·1° in these structures. The interatomic distances between C(4)–C(5), C(5)–C(6) and C(9)–C(9A) of DCPCO are significantly short while those between C(7)–C(8) and C(3A)–C(9A) appear longer than normal. Similar trends from normal values are seen in the other bicyclononane systems [except for the values involving the disordered C(5) position]. The bonding properties of the quaternary carbons C(3A) and C(7) of DCPCO are comparable to that observed in BSBO. These bonding characteristics are also frequently encountered in crystal structures of steroids. Thus, the apparent long distances between C(7)–C(8) and C(3A)–C(9A) may be a general property that can be attributed to quaternary carbons.

A rigid-body motion analysis (Schomaker & Trueblood, 1968) has been applied to the perhydroindane system and the attached C(4) and C(6) methylene groups. The results of this analysis indicate that the perhydroindane system could be treated as a rigid body and bond-length corrections could be applied as suggested by Schomaker & Trueblood (1968). The thermal corrections to the interatomic distances range from $0{\cdot}67\sigma$ to $2{\cdot}3\sigma$ and average $1{\cdot}6\sigma$.

The conformation of the *A* ring can be described by φm, the measure of puckering, and δ, the phase of the pseudorotation (Altona, Geise & Romers, 1968). The values found for DCPCO are $\varphi m=45{\cdot}5^\circ$ and $\delta=6{\cdot}76^\circ$. The magnitude for φm found is comparable to a suggested standard value of 46·7° (Altona *et al.*, 1968) which was found for the perhydroindane system in several steroid structures. The phase angle indicates the conformation of this ring can be described as being in the C_2 form (half chair). Although there is an additional rotational barrier in the cyclopentane ring due to the carbomethoxy group at C(1), compared with

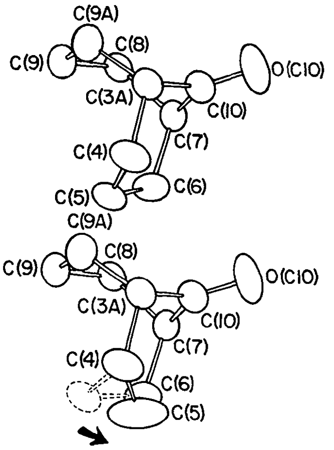


Fig. 2. The two conformations observed for the bicyclononane system. Top: chair–chair conformation; bottom: boat–chair conformation. The arrow indicates the change in position of C(5) in going from one conformer to the other.

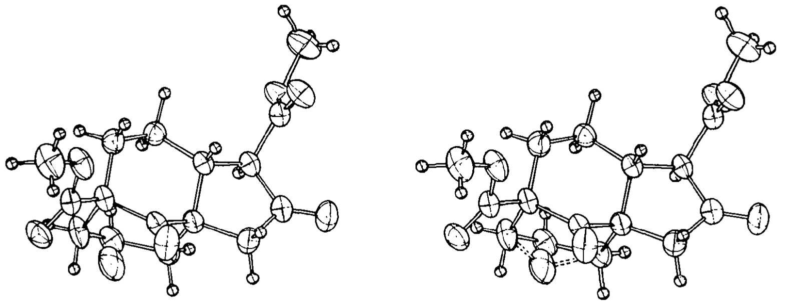


Fig. 3. Stereoscopic view of DCPCO showing both conformers. The atom in the low occupancy boat–chair conformer is shown as being bonded with dashed lines.

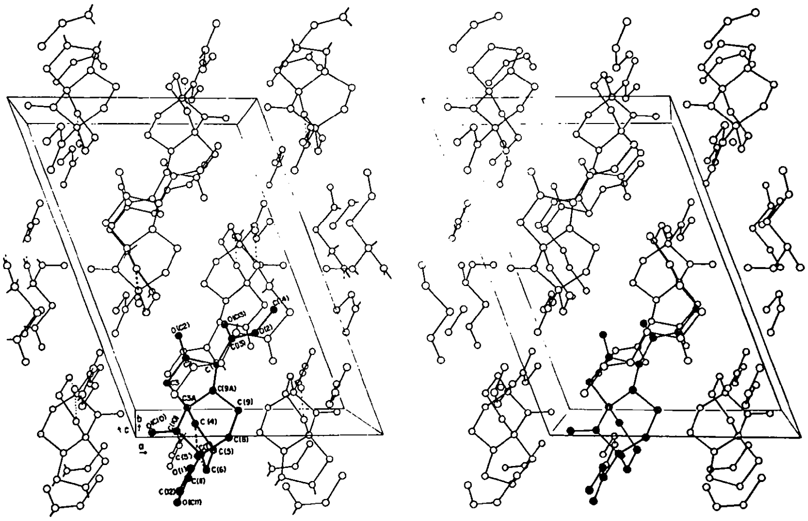


Fig. 4. Stereoscopic view down the *b* axis showing the molecular packing of DCPCO. The molecule represented by solid circles corresponds to the coordinates listed in Table 3. Bonds to the disordered C(5′) position are represented by dashed lines.

these steroids, the magnitude of φm does not vary significantly from the standard.

The molecular packing is illustrated in Fig. 4. The contacts between molecules correspond to normal van der Waals distances.

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