An Approach to the Synthesis of Dodecahedrane: The *X*-Ray Crystal Structures of Six Intermediate Compounds

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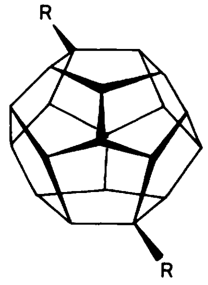
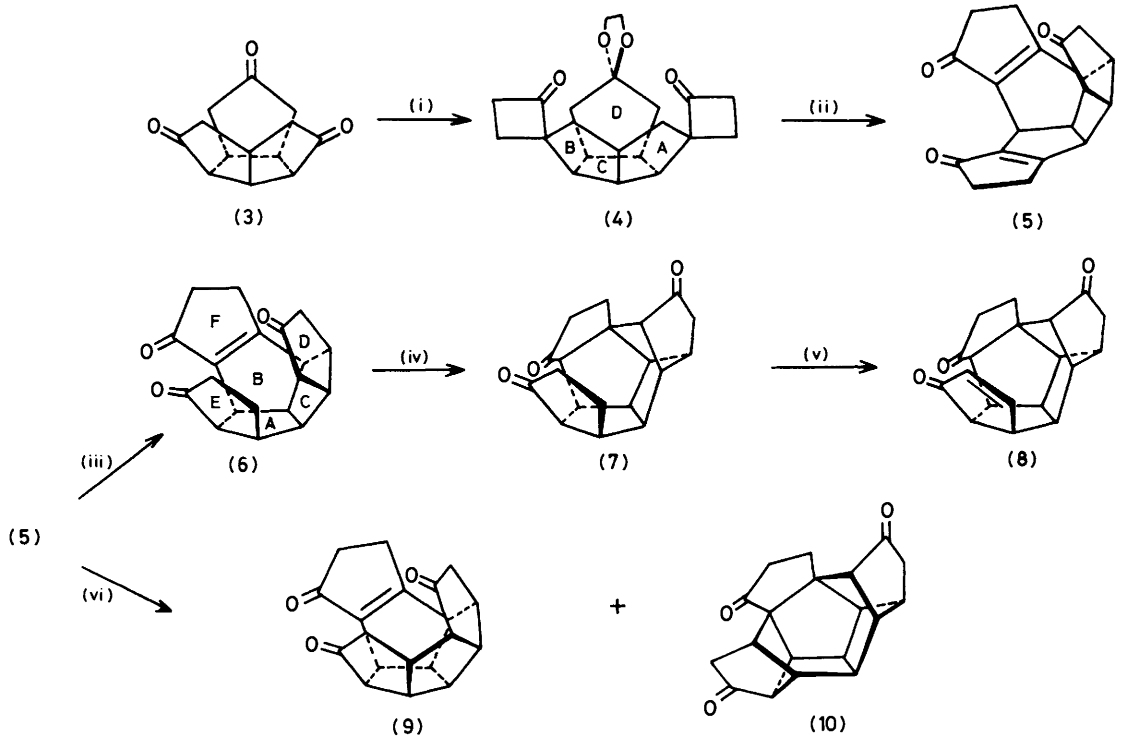
The *X*-ray crystal structures ($0.03 < R < 0.06$) of six compounds isolated during an approach to the synthesis of dodecahedrane are described. The highly substituted C_{13}-tetraquinane (4) and the C_{19}-hexaquinanetrione (6) are twisted out of mirror symmetry to minimise steric interactions. The bridged C_{19}-hexaquinanetriones (7) and (8) and the C_{19}-heptaquinanetrione (9) show signs of strain in the molecular skeleton and the doubly bridged C_{19}-hexaquinanetrione (10) is even more distorted showing both bond stretching and bond compression.

The development of a synthesis of pentagonal dodecahedrane (1) has attracted considerable attention [1] over the last 20 years and recently Paquette's group have published the preparation [2] of the parent compound (1) and the *X*-ray crystal structure [3] of the 1,16-dimethyl derivative, (2). We have been pursuing a different synthetic approach to dodecahedrane suggested by the three-fold rotational symmetry of the target molecule. In the course of this work it has been necessary to determine the structures of six compounds, (4) and (6)—(10), by *X*-ray crystallography and these are described here because of the interesting conformations forced on two of the molecules, (4) and (6), by steric factors and because of the considerable strain evident in the molecular skeletons of the other four. The synthetic route which produced these molecules has been briefly reported [4] and is summarised in the Scheme. The resulting heptacyclic C_{19}-polyquinane (9) has suitable functionality for conversion into dodecahedrane.[4]

The structures to be described have been analysed in terms



(1) R = H
(2) R = Me



Scheme. (i) (a) $(HOCH_2)_2$–H^+, (b) phenylsulphonium cyclopropylide–MeCN, (c) SiO_2; (ii) (a) H_2O_2–^-OH–MeOH, (b) aqueous Me_2CO–H^+, (c) P_2O_5–$MeSO_3H$–40 °C; (iii) Pd-C–H_2; (iv) Na_2CO_3–aqueous MeOH; (v) (a) PhSeCl–EtOAc, (b) H_2O_2–pyridine–CH_2Cl_2; (vi) MeOH–NaOH–100 °C, sealed tube. Ring labels A—F in (6) as in Figure 2

Table 1. Parameters defining the conformation of the five-membered rings in (3), (4), and (6)—(10). Δ (°), the phase angle of pseudo-rotation;[6] ω_0 (°), the amplitude of puckering; β, the bond[a] about which there is maximum torsion or, for the envelope conformation, the atom at the ' flap '

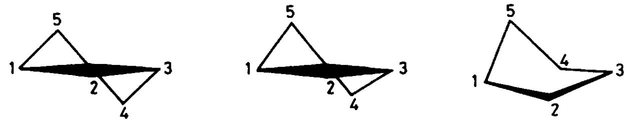
	Ring								
	A			B			D		
Compd.	Δ	ω_0	β	Δ	ω_0	β	Δ	ω_0	β
(3)	9	15	*C(6)*-C(13)	4	26	C(5)-*C(6)*	17	35	C(16)
(4)	12	44	C(7)-*C(8)*	4	33	C(4)-C(12)	1	20	C(12)-C(15)
(6)	7	30	C(8)-*C(14)*	11	3	*C(12)*-C(13)	0	38	C(15)-C(16)
(7)	1	28	C(6)-C(13)	7	36	C(4)-*C(12)*	9	57	*C(15)*-C(16)
(8)	14	32	C(6)	14	36	C(12)	11	57	*C(15)*-C(16)
(9)	5	14		9	15		10	15	
	10	13	*C(7)*-C(8)	6	16	C(12)-*C(13)*	7	15	C(12)-*C(15)*
(10)	11	59	C(6)-*C(7)*	18	42	C(13)	10	58	C(12)-*C(15)*

	Ring								
	D			E			F		
Compd.	Δ	ω_0	β	Δ	ω_0	β	Δ	ω_0	β
(3)	2	33	C(15)-C(16)						
(4)	2	43	C(17)-C(19)						
(6)	13	35	C(15)	6	23	*C(7)*-C(11)	2	11	C(1)-C(2)
(7)	13	57	C(16)	2	31	C(9)-C(10)	3	37	C(3)-C(4)
(8)	15	57	C(16)	10	14	*C(7)*-C(8)	7	35	*C(3)*-C(4)
(9)	0	26	C(17)-C(19)	15	29	C(10)	3	9	C(1)-C(2)
	2	25		13	31		3	6	
(10)	17	54	C(16)	6	55	*C(8)*-C(9)	6	35	*C(2)*-C(3)

	Ring								
	G[b]			H[c]			J[d]		
Compd.	Δ	ω_0	β	Δ	ω_0	β	Δ	ω_0	β
(3)									
(4)									
(6)									
(7)	1	66	C(15)-C(16)						
(8)	1	65	C(15)-C(16)						
(9)				5	9	*C(8)*-C(14)			
				6	11				
(10)	9	66	C(15)-*C(16)*				10	67	C(7)-*C(8)*

[a] For conformations intermediate between the half-chair and envelope forms the atom which more nearly approximates to the ' flap ' of an envelope is in italics. [b] Ring C(4)-C(12)-C(15)-C(16)-C(18). [c] Ring C(9)-C(8)-C(14)-C(16)-C(18). [d] Ring C(5)-C(6)-C(7)-C(8)-C(9).

of the conformations of their composite five-membered rings (Table 1). The conformation of a cyclopentane ring can be described[5,6] by two parameters, ω_0 and Δ, and a specification of the bond or atom about which ring torsion is at a maximum. The two parameters can be calculated from the five torsion angles around the ring. The amplitude of puckering, ω_0, represents the distortion of the ring from planarity ($\omega_0 = 0°$) but the phase angle, Δ, needs rather more explanation. For a given value of ω_0, cyclopentane can exist in a continuum of possible conformations of equal energy among which the half chair (11) and envelope (13) are readily recognised because of their symmetry. The relationship between all these conformations is shown in Figure 1. In the half chair (11), if the two atoms C(4) and C(5) are displaced in the same general direction with respect to the plane of the other three atoms C(1)—C(3), and no bond lengths are allowed to change, then the ring passes through a continuum of conformations until C(4) comes into the C(1)—C(3) plane at which point the envelope conformation (13) is formed. The phase angle represents the position of a conformation along the path between the half chair (Δ = 0°) and the envelope (Δ = 18°) for a given value of ω_0. The conformation of (12) represents an intermediate position (Δ *ca.* 9°). Since the molecular skeleton shown in Figure 2 is common to five of the structures described, albeit with extra bridging bonds in some cases, the indicated labelling of atoms and rings has been adopted and the labelling of molecule (4) (Scheme) is consistent with this where comparable.



(11) Δ = 0°; C(4)—C(5)

(12) Δ *ca.* 9°; C(4)—C(5)

(13) Δ = 18°; C(5)

Figure 1. For a given amplitude of puckering (ω_0) the conformation of a cyclopentane ring can be described by a phase angle Δ (0° ⩽ Δ ⩽ 18°) and the location of the bond [or atom for the envelope (13)] about which there is maximum torsion

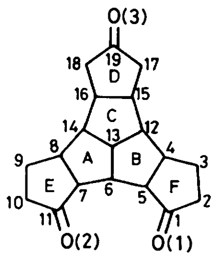


Figure 2. The crystallographic numbering scheme and the ring labelling system for (6)—(10). (6) C(4)–C(5) is a double bond; (7) extra bond from C(4) to C(18); (8) as (7) but C(9)–C(10) is a double bond; (9) extra bond from C(9) to C(18) and C(4)–C(5) is a double bond; and (10) as (7) but an extra bond from C(5) to C(9)

Molecule (4) was synthesized from the triketone (3) whose *X*-ray structure [7] had already shown the molecule to be twisted out of mirror symmetry. It was therefore interesting to see how the spiro fusion of two cyclobutanone rings and an ethylene-acetal group would affect this conformation and to see how the cyclobutanone carbonyl groups would arrange themselves with respect to the molecular cavity formed by the fused rings A—D. The conformation of this molecule is shown in Figure 3. The molecule is twisted out of mirror symmetry and both carbonyl groups point into the molecular cavity. The twist reduces the steric interactions between the two carbonyl groups and hydrogen atoms on C(17) and C(18), which would have been severe in the mirror-symmetric conformation. Two further effects maximise the separation of these moieties. Firstly, the cyclobutanone rings are buckled about their diagonals so bending the carbonyl groups away from the hydrogens, the C(1)—C(4) ring being buckled by twice as much as the C(8)—C(11) ring (27 and 14°, respectively) and secondly, the main twists (Table 1) in rings A and B occur on bonds to the spiro junction so that the spiro atoms (and the spiro groups) are bent away from the molecular cavity. The shortest contacts from O(1) and O(2) are to the hydrogen atoms H(172) [2.68(3) Å] and H(182) [2.24(3) Å], respectively. The twisting in the fused ring system originates in ring C which adopts a half-chair conformation with the main twist about the C(12)–C(15) bond so that C(15) is moved towards the molecular cavity. Ring D completes the twist with a half-chair conformation about the C(17)–C(19) bond so that C(17) lies in the cavity. The triketone (3) twists in a different way with the main twists in rings C and D lying along the C(15)–C(16) bond, ring C having an envelope flap at C(16), which is bent out of the molecular cavity and the amplitude of puckering in this ring being rather larger (35°) than in (4) (20°). In the triketone, ring A is considerably flatter because the bond fusing it to ring C is diametrically opposite to the envelope flap of the latter ring.

The low accuracy of the bond lengths and angles for (4) (Tables 2 and 3) means that few comments can be made reliably except to note that the bond at the fusion of rings A and B appears to be rather long (1.58 Å) while the bonds fusing C with A and B appear unexceptional (1.53—1.54 Å). The triketone's longest bond [1.558(3) Å] also occurs at the fusion of rings A and B and the only bicyclo[3.3.0]octane measured [9] shows a similar stretching of the bridgehead bond [1.559(6) Å]. In ring D the fusion bond C(15)–C(16) and its two neighbours appear long (1.56—1.58 Å) while those to the acetal carbon C(19), which carries two oxygen substituents, are shorter (1.51—1.52 Å).

Table 2. Bond lengths (Å) for (4) with e.s.d.s in parentheses

O(1)–C(1)	1.21(1)
O(2)–C(11)	1.19(1)
O(3)–C(19)	1.43(1)
O(3)–C(20)	1.43(2)
O(4)–C(19)	1.45(1)
O(4)–C(21)	1.40(1)
C(1)–C(2)	1.53(1)
C(1)–C(4)	1.50(1)
C(2)–C(3)	1.58(2)
C(3)–C(4)	1.57(1)
C(4)–C(5)	1.54(1)
C(4)–C(12)	1.55(1)
C(5)–C(6)	1.54(1)
C(6)–C(7)	1.56(1)
C(6)–C(13)	1.57(2)
C(7)–C(8)	1.52(1)
C(8)–C(9)	1.57(1)
C(8)–C(11)	1.54(1)
C(8)–C(14)	1.55(1)
C(9)–C(10)	1.54(2)
C(10)–C(11)	1.51(1)
C(12)–C(13)	1.53(1)
C(12)–C(15)	1.54(1)
C(13)–C(14)	1.54(1)
C(14)–C(16)	1.53(1)
C(15)–C(16)	1.58(1)
C(15)–C(17)	1.56(1)
C(16)–C(18)	1.57(1)
C(17)–C(19)	1.51(1)
C(18)–C(19)	1.52(1)
C(20)–C(21)	1.51(2)

Table 3. Bond angles (°) for (4) with e.s.d.s in parentheses

C(19)–O(3)–C(20)	108.7(9)	O(2)–C(11)–C(10)	131.4(11)
C(19)–O(4)–C(21)	107.2(9)	C(8)–C(11)–C(10)	92.9(8)
O(1)–C(1)–C(2)	131.3(10)	C(4)–C(12)–C(13)	105.2(8)
O(1)–C(1)–C(4)	133.9(11)	C(4)–C(12)–C(15)	118.5(8)
C(2)–C(1)–C(4)	93.4(9)	C(13)–C(12)–C(15)	106.3(8)
C(1)–C(2)–C(3)	85.0(9)	C(6)–C(13)–C(12)	105.3(8)
C(2)–C(3)–C(4)	89.0(8)	C(6)–C(13)–C(14)	107.1(8)
C(1)–C(4)–C(3)	86.4(8)	C(12)–C(13)–C(14)	110.0(9)
C(1)–C(4)–C(5)	120.3(9)	C(8)–C(14)–C(13)	102.1(9)
C(1)–C(4)–C(12)	116.6(9)	C(8)–C(14)–C(16)	122.0(9)
C(3)–C(4)–C(5)	118.0(9)	C(13)–C(14)–C(16)	105.9(8)
C(3)–C(4)–C(12)	109.4(8)	C(12)–C(15)–C(16)	105.8(8)
C(5)–C(4)–C(12)	105.4(8)	C(12)–C(15)–C(17)	122.1(9)
C(4)–C(5)–C(6)	105.9(9)	C(16)–C(15)–C(17)	104.3(8)
C(5)–C(6)–C(7)	117.1(9)	C(14)–C(16)–C(15)	108.3(8)
C(5)–C(6)–C(13)	107.7(9)	C(14)–C(16)–C(18)	118.8(9)
C(7)–C(6)–C(13)	105.3(9)	C(15)–C(16)–C(18)	105.9(8)
C(6)–C(7)–C(8)	101.7(8)	C(15)–C(17)–C(19)	101.6(9)
C(7)–C(8)–C(9)	114.2(9)	C(16)–C(18)–C(19)	103.6(8)
C(7)–C(8)–C(11)	119.3(9)	O(3)–C(19)–O(4)	105.1(9)
C(7)–C(8)–C(14)	105.0(8)	O(3)–C(19)–C(17)	114.5(10)
C(9)–C(8)–C(11)	86.3(8)	O(3)–C(19)–C(18)	111.8(9)
C(9)–C(8)–C(14)	111.1(8)	O(4)–C(19)–C(17)	108.7(9)
C(11)–C(8)–C(14)	120.1(9)	O(4)–C(19)–C(18)	110.5(11)
C(8)–C(9)–C(10)	90.8(8)	C(17)–C(19)–C(18)	106.2(9)
C(9)–C(10)–C(11)	88.4(8)	O(3)–C(20)–C(21)	103.1(9)
O(2)–C(11)–C(8)	135.4(10)	O(4)–C(21)–C(20)	102.1(11)

The structures of the four compounds (6)—(9) are closely related (Scheme) and their bond lengths and bond angles are presented together in Tables 4 and 5 for comparison. Three of

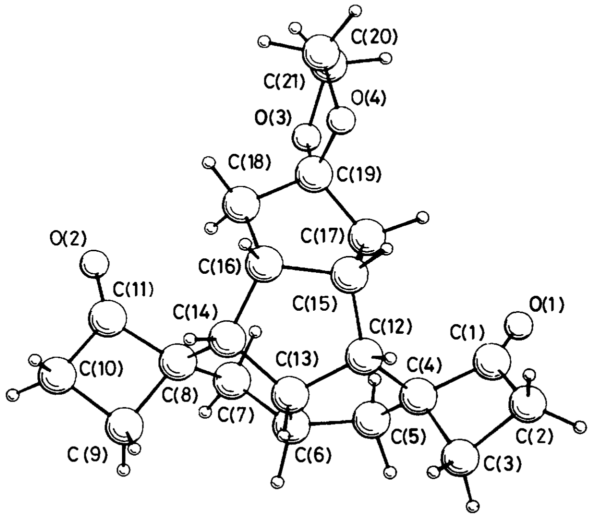


Figure 3. View of (4) drawn with the molecular graphics program SNOOPI [8]

the compounds (7)—(9) are more strained than the other one (6) because they possess one extra C–C bond which bridges the fused network of six five-membered rings. This bond forces some rigidity on these systems while the conformation of (6) is determined primarily by steric factors as for (3) and (4). Thus, yet again, the conformation of (6) (Figure 4) does not retain the mirror symmetry suggested by its structural formula. The C(15)–C(16) bond which fuses rings C and D is the site of the twisting in both rings and in this it resembles the triketone (3) rather than (4), although the conformations of rings C and D do not correspond exactly, with ring C being a half chair not an envelope, and *vice versa* for ring D. Ring D is twisted towards ring F rather than ring E because the former intrudes less into the molecular cavity since it is fused to the molecular skeleton by a double bond. Thus, C(17), C(18), and C(19) in ring D are all within van der Waals distance of C(4) in ring F while the only contact to the E ring is by H(182) on C(11). Rings B and F, which are fused by the double bond, are considerably flattened (ω_0 3 and 11°). The two olefinic carbons deviate in the same sense from the planes of their three respective surrounding atoms [C(4) 0.06, C(5) 0.09 Å], showing that ring F is bent slightly away from the molecular cavity about the olefinic bond. Reduction of the double bond by catalytic hydrogenation [4] could not be effected and this must be due to excessive steric crowding between the D and F rings in the product formed by addition of hydrogen from the outside surface of the molecule. Addition of hydrogen to the inside face of the double bond is presumably inhibited by the inaccessibility of this face to the catalytic surface.

In (6) only the C(6)–C(13) bond which fuses rings A and B is particularly long (1.564 Å), as observed for (3) and (4). A notable feature of this molecule is the asymmetry of the C–C–C bond angles at an atom which fuses just two rings. Thus, at C(12) in (6) the two endocyclic angles are quite compressed (102.9 and 104.9°) while the exocyclic angle is very wide (118.3°). In contrast, the three angles at C(13) which are all endocyclic are very similar (106.9—108.4°). A result of this is that the very small torsion angle about the C(12)–C(13) bond in ring B (3°) is not forced on to this bond in ring C (12°) and so this latter ring can adopt a half-chair conform-

Table 4. Bond lengths (Å) for (6)—(9) with e.s.d.s in parentheses

Bond	(6)	(7)	(8)	(9) molecule 1	(9) molecule 101
O(1)–C(1)	1.217(3)	1.209(4)	1.216(5)	1.223(6)	1.231(6)
O(2)–C(11)	1.210(3)	1.197(4)	1.208(6)	1.215(6)	1.201(6)
O(3)–C(19)	1.215(3)	1.205(4)	1.214(5)	1.212(6)	1.215(6)
C(1)–C(2)	1.509(4)	1.502(5)	1.501(6)	1.525(7)	1.528(8)
C(1)–C(5)	1.474(4)	1.523(4)	1.514(6)	1.472(7)	1.463(7)
C(2)–C(3)	1.531(4)	1.521(5)	1.525(7)	1.546(8)	1.530(8)
C(3)–C(4)	1.504(4)	1.542(4)	1.545(5)	1.505(7)	1.484(7)
C(4)–C(5)	1.326(4)	1.533(4)	1.543(5)	1.339(7)	1.350(7)
C(4)–C(12)	1.506(4)	1.562(4)	1.555(5)	1.482(7)	1.487(7)
C(4)–C(18)		1.564(4)	1.556(6)		
C(5)–C(6)	1.499(4)	1.541(4)	1.565(5)	1.521(7)	1.515(7)
C(6)–C(7)	1.546(4)	1.544(5)	1.539(6)	1.568(7)	1.563(7)
C(6)–C(13)	1.564(4)	1.550(5)	1.540(6)	1.565(8)	1.562(7)
C(7)–C(8)	1.537(4)	1.526(5)	1.526(6)	1.537(7)	1.544(7)
C(7)–C(11)	1.510(4)	1.523(5)	1.499(6)	1.504(7)	1.530(7)
C(8)–C(9)	1.544(4)	1.539(5)	1.510(6)	1.543(7)	1.549(7)
C(8)–C(14)	1.535(4)	1.540(5)	1.542(6)	1.539(8)	1.550(7)
C(9)–C(10)	1.525(4)	1.509(6)	1.337(8)	1.531(8)	1.538(7)
C(9)–C(18)				1.582(7)	1.574(7)
C(10)–C(11)	1.509(4)	1.499(7)	1.467(8)	1.500(8)	1.501(8)
C(12)–C(13)	1.549(4)	1.534(5)	1.542(5)	1.556(8)	1.568(7)
C(12)–C(15)	1.544(4)	1.537(5)	1.538(6)	1.557(8)	1.554(7)
C(13)–C(14)	1.532(4)	1.556(5)	1.536(6)	1.533(7)	1.532(7)
C(14)–C(16)	1.546(4)	1.527(5)	1.535(6)	1.530(8)	1.538(7)
C(15)–C(16)	1.536(4)	1.552(4)	1.539(6)	1.571(7)	1.570(7)
C(15)–C(17)	1.518(4)	1.518(5)	1.528(6)	1.533(8)	1.541(8)
C(16)–C(18)	1.543(4)	1.568(4)	1.558(5)	1.536(7)	1.537(7)
C(17)–C(19)	1.507(4)	1.526(5)	1.518(6)	1.509(8)	1.498(7)
C(18)–C(19)	1.504(4)	1.508(5)	1.513(6)	1.524(8)	1.518(7)

Table 5. Bond angles (°) for (6)—(9) with e.s.d.s in parentheses

Bond angle	(6)	(7)	(8)	(9) molecule 1	(9) molecule 101
O(1)-C(1)-C(2)	125.7(3)	125.6(3)	124.5(4)	125.4(5)	125.7(5)
O(1)-C(1)-C(5)	127.7(3)	125.0(3)	125.4(4)	128.2(5)	128.2(5)
C(2)-C(1)-C(5)	106.5(3)	109.4(3)	110.2(4)	106.3(4)	106.1(5)
C(1)-C(2)-C(3)	106.1(2)	105.1(3)	104.5(4)	106.5(4)	106.4(4)
C(2)-C(3)-C(4)	103.0(2)	104.5(3)	104.9(4)	102.3(4)	103.5(4)
C(3)-C(4)-C(5)	113.3(2)	103.6(2)	103.9(3)	114.1(5)	113.4(5)
C(3)-C(4)-C(12)	132.9(3)	117.5(2)	116.2(3)	132.9(5)	133.7(5)
C(3)-C(4)-C(18)		114.5(3)	115.5(3)		
C(5)-C(4)-C(12)	113.4(2)	105.1(2)	105.4(3)	113.0(4)	112.9(4)
C(5)-C(4)-C(18)		116.7(3)	115.6(3)		
C(12)-C(4)-C(18)		99.7(2)	100.3(3)		
C(1)-C(5)-C(4)	110.1(2)	104.2(3)	104.8(3)	110.1(4)	110.3(5)
C(1)-C(5)-C(6)	135.8(3)	112.6(3)	112.7(4)	136.7(5)	136.4(5)
C(4)-C(5)-C(6)	113.6(2)	108.7(2)	108.2(3)	112.9(4)	113.1(4)
C(5)-C(6)-C(7)	119.4(2)	117.3(3)	116.2(4)	118.8(4)	118.9(4)
C(5)-C(6)-C(13)	102.2(2)	102.9(3)	103.0(3)	101.6(4)	101.6(4)
C(7)-C(6)-C(13)	105.5(2)	104.9(3)	104.6(3)	105.7(4)	106.5(4)
C(6)-C(7)-C(8)	108.0(2)	108.4(3)	106.2(3)	108.4(4)	107.1(4)
C(6)-C(7)-C(11)	120.1(2)	119.7(3)	115.1(4)	119.7(4)	120.0(4)
C(8)-C(7)-C(11)	105.6(2)	104.9(3)	106.0(4)	105.3(4)	104.6(4)
C(7)-C(8)-C(9)	106.8(2)	107.2(3)	103.2(4)	107.6(4)	108.3(4)
C(7)-C(8)-C(14)	105.4(2)	106.7(3)	107.0(3)	107.1(4)	108.6(4)
C(9)-C(8)-C(14)	119.0(3)	119.2(3)	119.8(4)	108.5(5)	108.6(4)
C(8)-C(9)-C(10)	106.9(2)	105.0(4)	111.9(5)	105.3(5)	104.6(4)
C(8)-C(9)-C(18)				106.6(4)	106.2(4)
C(10)-C(9)-C(18)				115.9(4)	116.7(4)
C(9)-C(10)-C(11)	107.4(2)	104.9(3)	110.6(5)	104.8(4)	105.3(4)
O(2)-C(11)-C(7)	127.3(3)	124.8(5)	126.6(6)	126.5(5)	125.4(5)
O(2)-C(11)-C(10)	124.5(3)	126.3(5)	126.8(5)	124.5(5)	126.5(5)
C(7)-C(11)-C(10)	108.1(2)	108.9(3)	106.6(5)	109.0(4)	108.1(4)
C(4)-C(12)-C(13)	102.3(2)	100.8(2)	101.4(3)	103.2(4)	102.4(4)
C(4)-C(12)-C(15)	118.3(2)	103.8(2)	103.3(3)	114.6(4)	115.8(4)
C(13)-C(12)-C(15)	104.9(3)	104.7(3)	104.2(3)	107.0(4)	107.1(4)
C(6)-C(13)-C(12)	108.4(2)	110.2(3)	109.7(3)	107.2(4)	107.5(4)
C(6)-C(13)-C(14)	106.9(2)	105.1(3)	105.3(3)	108.4(4)	109.1(4)
C(12)-C(13)-C(14)	107.2(3)	103.6(3)	102.9(3)	108.5(5)	108.2(4)
C(8)-C(14)-C(13)	105.7(3)	107.3(3)	106.9(3)	108.7(5)	107.1(4)
C(8)-C(14)-C(16)	122.0(3)	122.0(3)	121.2(4)	108.0(4)	107.4(4)
C(13)-C(14)-C(16)	106.0(2)	102.2(3)	103.8(3)	108.1(4)	107.9(4)
C(12)-C(15)-C(16)	104.4(2)	93.6(2)	94.1(3)	106.2(4)	106.1(4)
C(12)-C(15)-C(17)	117.2(3)	114.6(3)	114.8(4)	115.3(5)	115.9(4)
C(16)-C(15)-C(17)	105.6(3)	104.9(3)	104.5(3)	105.7(4)	105.8(4)
C(14)-C(16)-C(15)	103.4(3)	102.0(3)	101.5(3)	108.1(4)	108.4(4)
C(14)-C(16)-C(18)	121.8(2)	119.0(3)	117.2(3)	108.7(4)	108.5(4)
C(15)-C(16)-C(18)	103.2(2)	93.0(2)	93.5(3)	108.2(4)	107.8(4)
C(15)-C(17)-C(19)	103.6(2)	101.7(3)	101.4(3)	105.6(5)	105.6(4)
C(4)-C(18)-C(16)		103.3(2)	103.3(3)		
C(4)-C(18)-C(19)		104.1(3)	102.9(3)		
C(9)-C(18)-C(16)				107.4(4)	108.1(4)
C(9)-C(18)-C(19)				114.9(4)	114.8(4)
C(16)-C(18)-C(19)	105.9(2)	100.4(3)	100.6(3)	104.9(4)	105.1(4)
O(3)-C(19)-C(17)	124.6(3)	126.3(3)	126.5(4)	125.0(5)	125.6(5)
O(3)-C(19)-C(18)	125.8(3)	127.5(3)	126.8(4)	125.8(5)	124.7(5)
C(17)-C(19)-C(18)	109.5(2)	106.3(3)	106.7(4)	109.2(4)	109.6(4)

ation rather than being forced into the envelope with a flap diametrically opposite the C(12)-C(13) bond.

Under basic conditions molecule (5) undergoes an internal Michael reaction involving a carbanion at C(18) adding to the C(4)-C(5) double bond. A carbanion could also be formed at C(17) which, in (6), is almost the same distance from the site of attack [C(4)]. However, attack from C(18) may be favoured because, assuming no major conformational change on forming the carbanion, the angle of approach (Figure 5) to the double bond is better, the preferred direction [10] being at 109° to the C=C bond. The shortest non-bonding contact in the molecule is between H(182) [attached to C(18)] and the carbonyl carbon C(11) (2.47 Å, Figure 5). The carbonyl group appears to be very slightly pyramidalised about C(11) and towards this hydrogen, but without an accurate low-temperature measurement it is not possible to assess the significance of this observation.

Molecule (7) (Figure 6) differs from (6) in the formation of the bridging bond C(4)—C(18). This completes ring G [C(4)-C(12)-C(15)-C(16)-C(18)] which is highly puckered (ω_0 66°) as now are rings C and D [ω_0 57°, *ca.* 20° higher than in (6)]. The twists in rings C, D, and G all occur on the C(15)-C(16) bond with ring G adopting the half-chair conformation. The reduction in the C(4)-C(18) distance (3.17 to

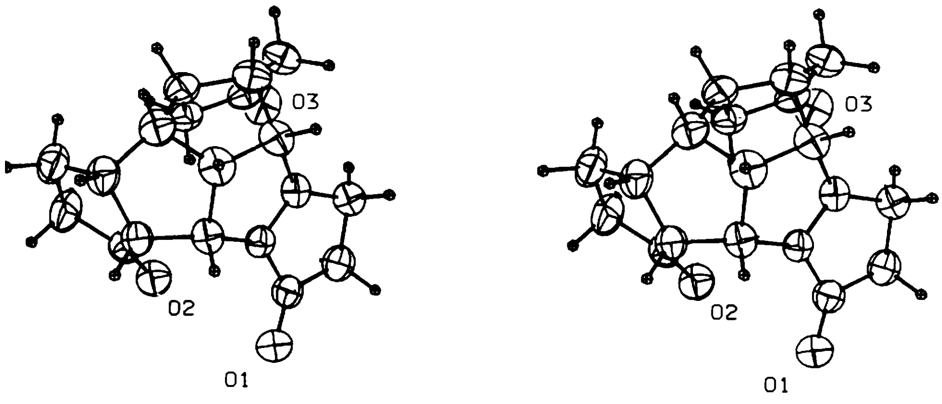


Figure 4. Stereoview [8] of (6) with thermal ellipsoids drawn at the 50% level

1.56 Å) on converting (6) into (7) forces ring D to change the location and orientation of its envelope flap. This is now at C(16) not C(15) and ' up ' so that this atom appears to protrude from the outer surface of the molecular skeleton rather than being ' down ' and so following the curve of the skeleton more closely. Atoms C(15) and C(16) are both apices of norbornane systems and show appropriately compressed apical angles (93—94°). Both these angles occur in ring G whose other three angles are also somewhat compressed (99.7—103.8°) and which, furthermore, contains the three longest bonds in the molecule (1.562—1.568 Å). There are also signs of bond stretching along the fusions of rings A and B, A and C, and C and D (1.552—1.556 Å). The necessary folding of the molecule compresses the exocyclic angle at C(12) from 118.3° in (6) to 103.8°, similar to the other two endocyclic angles at C(12). The two bonds to C(10) appear rather short, but the temperature factors of C(9), C(10), C(11), and O(2) are all about 50% larger than those for the equivalent atoms in ring F, suggesting that this shortening may be a result of thermal motion. This highly compact molecule contains ten pairs of non-bonded atoms, which are within the sum of their van der Waals radii of each other.

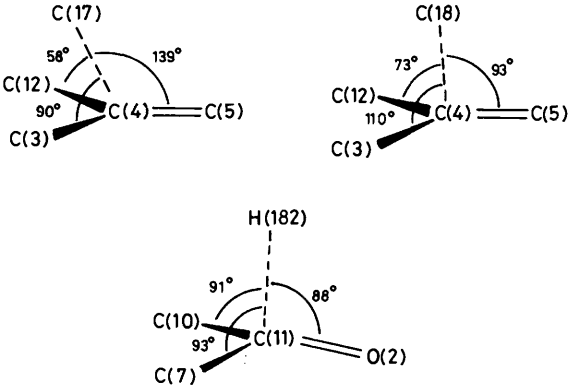


Figure 5. Angles of approach of certain atoms on to some sp^2 centres in (6)

Molecule (8) has the same connectivity as (7) except that C(9)–C(10) is a double bond, but this is not directly involved in the strained region of the molecule. Thus the conformations of rings C, D, and G are almost identical with those in (7). The double bond flattens ring E considerably (ω_0 14°) and the main twist in this ring occurs about the bond fusing it to ring A. Excluding the cyclopentene ring, there are only three significant differences in bond length between (7) and (8), thus in (8) the C(13)–C(14) and C(15)–C(16) bonds are shorter (by 0.022 and 0.013 Å) and the C(5)–C(6) bond is longer (by 0.024 Å). These changes move ring E, and C(9) in particular, closer to C(18). In (7) this was prevented by the steric interaction between H(91) and H(181), but this problem does not exist in (8) because C(9)–C(10) is now a double bond and H(91) has a different orientation.

The skeleton of molecule (9) (Figure 7) contains seven five-membered rings fused together in such a way as to form over half of the dodecahedrane structure. There are three tetra-fused rings A, C, and H, the latter being completed by the

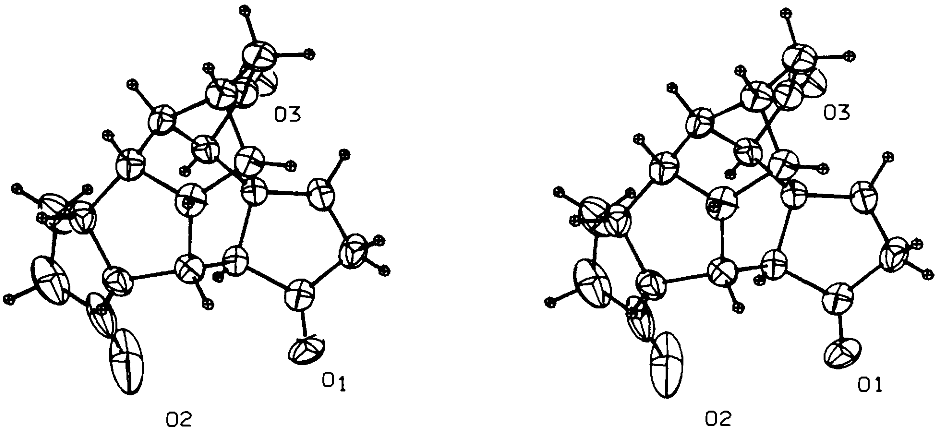


Figure 6. Stereoview [8] of (7)

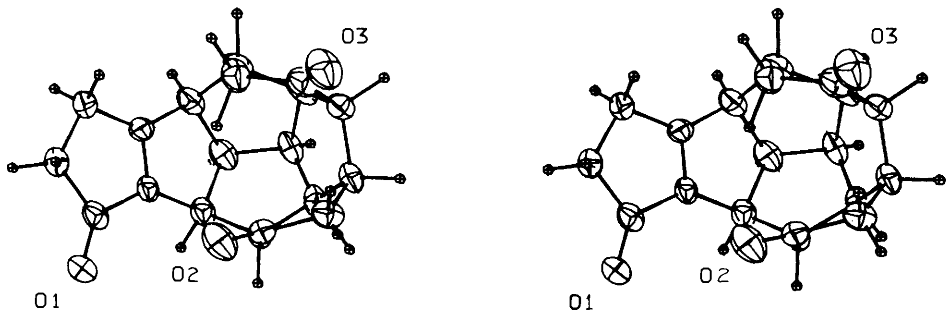


Figure 7. Stereoview [8] of (9)

C(9)–C(18) bond, which bridges the polyquinane system shown in Figure 2. There are two molecules of (9) per asymmetric unit and they have very similar conformations (Table 1), the largest difference being in ring A where the phase angles vary by 5°. The bond lengths and bond angles are in close agreement and only two bonds and two bond angles differ by more than two estimated standard deviations. Being fused to four other rings significantly flattens rings A, C, and H, which have puckering amplitudes in the range 10—15° while rings D and E, which are only fused to two rings, exhibit larger puckerings (25 and 30°). Rings B and F are also flattened because of the double bond fusing them together. The strain in the molecular skeleton shows in stretched bonds rather than in distorted bond angles. Thus of the nine bonds around the perimeter of the network formed by the fusion of rings A, C, and H (the tetra-fused rings) six bonds are longer than 1.55 Å and the longest, the bridging bond, is 1.578 Å* (Figure 8). All the bond angles within this system fall in the range * 106—109° and the three bonds to the central atom C(14) are of normal lengths (Figure 8). The strain in the closely related molecule (14) [11] is exhibited in the same general way though the three bonds to the ' central ' atom are slightly shorter [1.522(8) Å].

It is interesting to note in (9) that the olefinic carbon C(5) and the carbonyl carbon C(1) are slightly pyramidalised, deviating by 0.05 and 0.02 Å from the planes of their respective attached atoms towards the oxygen atom O(2), which is 2.97 Å from C(5) and 3.14 Å from C(1). This pyramidalisation may be caused by an sp^2 lone pair on O(2) ' nucleophilically ' attacking these unsaturated centres. The ' attacked ' carbonyl bond, C(1)–O(1), is significantly longer than the other two carbonyl bonds in the molecule, and the vector joining O(2) and C(1) makes a reasonable angle of approach [10] to the carbonyl group and lies near to the expected axis of an sp^2 lone pair on O(2) (Figure 9). The same lone pair may be implicated in the interaction with C(5).

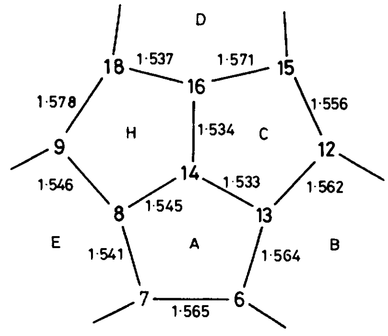


Figure 8. Lengths of bonds (Å) surrounding the A, C, and H rings in (9)

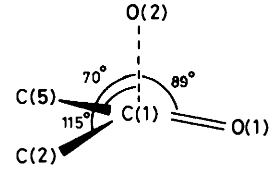
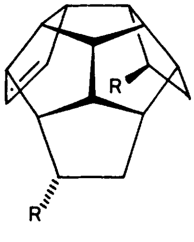


Figure 9. The geometry of the interaction of O(2) with the C(1)=O(1) carbonyl group in (9)



(14) R = CH_2CN

The final molecule (10) (Figure 10), an unexpected extra product from the diene (5) under basic conditions, has a remarkable cage structure. This is formed by two bonds, C(4)–C(18) and C(5)–C(9), which bridge the network of five fused cyclopentane rings A—E, so forming two very highly puckered rings G and J (ω_0 66 and 67°). The puckering caused by one of these bridging bonds, C(4)–C(18), has already been seen in structures (7) and (8), and the second bond repeats these effects in rings A, E, and J, so that only ring F, which has just one fusion, is unaffected (ω_0 35°). Bond lengths and bond angles for this molecule are given in Tables 6 and 7. The molecule contains two pairs of fused norbornane systems with apices at C(7), C(8), C(15), and C(16) and the apical angles are compressed as expected (93—94°). The remaining bond angles within the cyclopentane rings show considerable variation within the range 99—109°. Thus two of the angles at C(13), the fusion point of three rings, are 101.7° while the other one is 109.3°. This particular asymmetry was seen to a lesser degree in the singly bridged molecules (7) and (8) but not at all in (9) or in the unbridged system (6). The bond angles at the two tetra-substituted carbons C(4) and C(5) lie in the range 100—120° with the bridging bonds always making large angles (113—120°) with the bonds of ring F.

The strain imposed by this cage structure is clearly evident in the wide variation in the bond lengths (1.513—1.582 Å). Ignoring the oxygen atoms the molecule possesses almost mirror symmetry with respect to a plane passing through

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* Averaged values for both molecules.

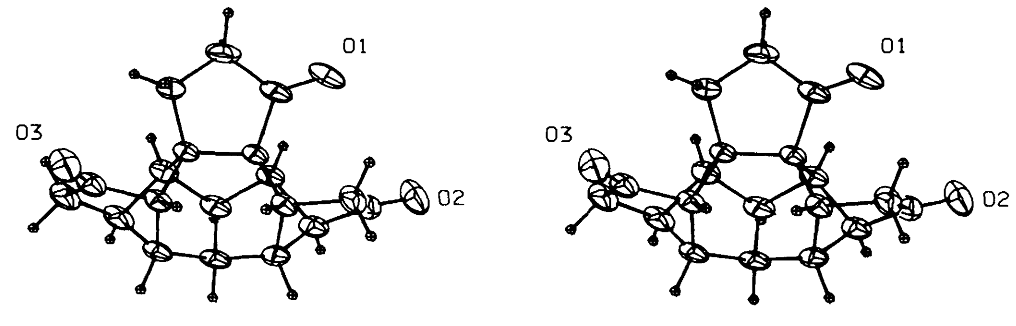

Figure 10. Stereoview [8] of (10)

C(2), C(13), and C(14), and this relationship holds for the bond lengths (Figure 11), the bond angles, and the conformations of all the rings, except D and E. From Figure 11 it is clear that there are three long bonds running almost parallel to the mirror plane so helping to stretch the cage round while the two bonds to C(13), which are more nearly perpendicular to the mirror plane, are strongly compressed (1.513 Å). This, on communication through two cyclopentane rings, allows C(9) and C(18) to take up reasonable positions to form bridging bonds, which do not make too large angles with the bonds of ring F. The bridging bonds are only slightly stretched (1.557 and 1.548 Å) but the bond which joins the two bridging bonds, C(4)-C(5), is longer (1.569 Å). This is necessary to minimise the steric interaction between the two hydrogen atoms from C(9) and C(18) which lie just 1.97 Å apart. The C(9)-H(91) and C(18)-H(181) bonds are almost coplanar, being related by the mirror plane through the molecular cage. Ring B adopts an envelope conformation with a flap at C(13) in accord with the mirror symmetry and rings A and C adopt very similar conformations with the maximum torsion angles about the C(6)-C(7) and C(12)-C(15) bonds, respectively.

This last molecule shares a slightly puzzling feature with molecules (3), (6), (7), and (8), namely that the C(15)-C(17) is consistently rather short, typically 1.518 Å. The conformation about this bond is very similar in all these cases, with the C(17)-C(19) bond being *gauche* to the C(12)-C(15) and C(15)-C(16) bonds. However, in ring E of compound (10) where there is a very similar arrangement of bonds in a similarly fused ring no equivalent bond shortening is observed and there is no significant difference in thermal parameters for corresponding atoms, suggesting that the bond shortening is not an artefact of thermal motion.

Experimental

The *X*-ray crystal structures of compounds (4) and (6)—(10) were determined as described below. Particular data for each structure are presented in Table 8 and tables of fractional atomic co-ordinates, anisotropic temperature factors, and structure factors are included in Supplementary Publication Sup. No. 23738 (103 pp.).*

Table 6. Bond lengths (Å) for (10) with e.s.d.s in parentheses

O(1)-C(1)	1.205(2)
O(2)-C(11)	1.212(2)
O(3)-C(19)	1.209(2)
C(1)-C(2)	1.500(3)
C(1)-C(5)	1.519(2)
C(2)-C(3)	1.512(2)
C(3)-C(4)	1.538(2)
C(4)-C(5)	1.569(2)
C(4)-C(12)	1.569(2)
C(4)-C(18)	1.557(2)
C(5)-C(6)	1.582(2)
C(5)-C(9)	1.548(2)
C(6)-C(7)	1.546(2)
C(6)-C(13)	1.512(2)
C(7)-C(8)	1.552(2)
C(7)-C(11)	1.495(2)
C(8)-C(9)	1.549(2)
C(8)-C(14)	1.540(2)
C(9)-C(10)	1.533(2)
C(10)-C(11)	1.510(3)
C(12)-C(13)	1.514(2)
C(12)-C(15)	1.536(2)
C(13)-C(14)	1.577(2)
C(14)-C(16)	1.543(2)
C(15)-C(16)	1.547(2)
C(15)-C(17)	1.517(2)
C(16)-C(18)	1.547(2)
C(17)-C(19)	1.511(2)
C(18)-C(19)	1.515(2)

Table 7. Bond angles (°) for (10) with e.s.d.s in parentheses

O(1)-C(1)-C(2)	125.4(2)	C(8)-C(9)-C(10)	102.1(1)
O(1)-C(1)-C(5)	126.1(2)	C(9)-C(10)-C(11)	102.0(1)
C(2)-C(1)-C(5)	108.3(1)	O(2)-C(11)-C(7)	126.7(2)
C(1)-C(2)-C(3)	104.8(1)	O(2)-C(11)-C(10)	127.2(2)
C(2)-C(3)-C(4)	104.8(1)	C(7)-C(11)-C(10)	106.1(1)
C(3)-C(4)-C(5)	105.8(1)	C(4)-C(12)-C(13)	100.8(1)
C(3)-C(4)-C(12)	116.2(1)	C(4)-C(12)-C(15)	104.6(1)
C(3)-C(4)-C(18)	114.6(1)	C(13)-C(12)-C(15)	102.7(1)
C(5)-C(4)-C(12)	106.1(1)	C(6)-C(13)-C(12)	109.3(1)
C(5)-C(4)-C(18)	113.7(1)	C(6)-C(13)-C(14)	101.8(1)
C(12)-C(4)-C(18)	100.5(1)	C(12)-C(13)-C(14)	101.6(1)
C(1)-C(5)-C(4)	104.9(1)	C(8)-C(14)-C(13)	103.6(1)
C(1)-C(5)-C(6)	109.2(1)	C(8)-C(14)-C(16)	121.3(1)
C(1)-C(5)-C(9)	120.2(1)	C(13)-C(14)-C(16)	103.5(1)
C(4)-C(5)-C(6)	107.1(1)	C(12)-C(15)-C(16)	93.8(1)
C(4)-C(5)-C(9)	114.0(1)	C(12)-C(15)-C(17)	114.0(1)
C(6)-C(5)-C(9)	100.8(1)	C(16)-C(15)-C(17)	105.4(1)
C(5)-C(6)-C(7)	104.0(1)	C(14)-C(16)-C(15)	103.3(1)
C(5)-C(6)-C(13)	99.8(1)	C(14)-C(16)-C(18)	114.3(1)
C(7)-C(6)-C(13)	102.9(1)	C(15)-C(16)-C(18)	93.7(1)
C(6)-C(7)-C(8)	93.3(1)	C(15)-C(17)-C(19)	101.7(1)
C(6)-C(7)-C(11)	110.3(1)	C(4)-C(18)-C(16)	99.9(1)
C(8)-C(7)-C(11)	105.3(1)	C(4)-C(18)-C(19)	106.3(1)
C(7)-C(8)-C(9)	93.7(1)	C(16)-C(18)-C(19)	102.8(1)
C(7)-C(8)-C(14)	103.2(1)	O(3)-C(19)-C(17)	126.9(2)
C(9)-C(8)-C(14)	115.5(1)	O(3)-C(19)-C(18)	126.3(2)
C(5)-C(9)-C(8)	99.2(1)	C(17)-C(19)-C(18)	106.8(1)
C(5)-C(9)-C(10)	112.1(1)		

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* For details of the Supplementary Publications Scheme, see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

Table 8. Crystal data for (4) and (6)—(10)

Compd.	Molecular formula	Cell parameters with e.s.d.s in parentheses: *a*, *b*, *c* (Å), α, β, γ (°)	Space group	*Z*	ρ [a]	$\theta_{\lim.}$ [b]	*N*(*I*) [c]	Weighting scheme coefficients [d]	Final *R*-value
(4)	$C_{21}H_{26}O_4$	8.139(2), 7.691(1), 13.842(7), 90, 95.61(4), 90	$P2_1$	2	1.32	25	864 [e]	1.07, −0.684	0.058
(6)	$C_{19}H_{20}O_3$	15.950(3), 13.246(5), 6.865(3), 90, 92.28(3), 90	$P2_1/n$	4	1.36	23	1 172	5.94, 7.66, 2.29	0.034
(7)	$C_{19}H_{20}O_3$	6.202(5), 15.827(4), 14.664(7), 90, 103.88(7), 90	$P2_1/n$	4	1.41	24	1 333	79.9, 108.4, 31.6	0.050
(8)	$C_{19}H_{18}O_3$	8.869(2), 15.085(7), 10.532(3), 90, 92.29(3), 90	$P2_1/n$	4	1.39	26	1 143	12.5, 16.9, 6.35	0.049
(9)	$C_{19}H_{18}O_3$	13.526(3), 13.164(5), 16.574(5), 90, 110.82(5), 90	$P2_1/a$	8	1.42	23	1 982	25.8, 32.1, 6.59, −0.411	0.056
(10)	$C_{19}H_{18}O_3$	8.183(5), 8.826(1), 11.748(9), 68.02(4), 66.59(4), 65.18(3)	$P\bar{1}$	2	1.43	26	2 311	2 430, 3 310, 929	0.045

[a] Calculated density. [b] Upper theta limit for reflection data. [c] Number of reflections used in the refinement, *i.e.* those with $I \geqslant 3\sigma(I)$. [d] Chebyshev weighting scheme.[12] [e] $I \geqslant 2\sigma(I)$.

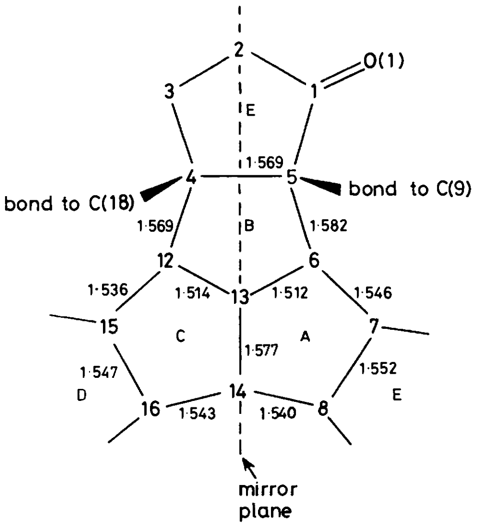

Figure 11. Diagram showing bond lengths (Å) in (10) near to the approximate mirror plane

Data Collection.—A single crystal, mounted on a glass fibre, was examined by Weissenberg photography and then transferred to the goniometer of an Enraf Nonius CAD4-F four-circle diffractometer. Accurate cell dimensions were determined from the refined setting angles of 25 reflections located by the ' search ' routine. Diffraction intensities were collected by ω/2θ scans out to the θ limit given in Table 8 and the space group determined from the systematic absences and Wilson statistics. The data were transferred to a VAX 11/750 computer, Lorentz and polarisation corrections applied, systematic absences rejected and equivalent reflections merged.

Structure Solution and Refinement.—The structures were solved by ' direct methods ' using MULTAN 80[13] and the atomic co-ordinates and isotropic temperature factors of the trial solution refined by the full-matrix least-squares method. The polar space group of (3) required that the sum of the shifts along the *y*-axis be constrained to zero. The refinement proceeded with anisotropic temperature factors using blocked-matrix least-squares. All hydrogen atoms were located from difference Fourier syntheses and refined, except for (4) where these atoms were placed geometrically and assigned an isotropic temperature factor of 0.05 and not refined. The weights for the final rounds of refinement were calculated from the Chebyshev series:[12] $w = [a_0t_0(x) + a_1t_1(x) + \ldots + a_nt_n(x)]^{-1}$ where $(x) = F_0/F_{\text{max.}}$ and the structures converged with *R*-values in the range 0.034—0.058. All calculations were performed with the CRYSTALS[14] package and the plots were drawn with the program SNOOPI.[8]

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