References

BEKAROGLU, Ö., SARISABAN, S., KORAY, A. R. & ZIEGLER, M. (1977). *Z. Naturforsch. Teil B*, **32**, 387–392.

ENDRES, H., GENC, N. & NÖTHE, D. (1983). *Acta Cryst.* C**39**, 701–703.

ENDRES, H. & JANNACK, T. (1980). *Acta Cryst.* B**36**, 2136–2138.

ENDRES, H. & SCHENDZIELORZ, M. (1983). *Acta Cryst.* C**39**, 1528–1530.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

PEARSE, G. A. JR & PFLAUM, R. T. (1959). *J. Am. Chem. Soc.* **81**, 6505–6508.

SHELDRICK, G. M. (1981). *SHELXTL. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.

TSCHUGAEFF, L. & SURENJANZ, J. (1907). *Chem. Ber.* **40**, 181–185.

UNGNADE, H. E., KISSINGER, L. W., NARATH, Q. & BARHAM, D. C. (1963). *J. Org. Chem.* **28**, 134–136.

WENGER, P. E., MONNIER, D. & KAPÉTANIDIS, I. (1957). *Helv. Chim. Acta*, **40**, 1456–1468.

Acta Cryst. (1984). C**40**, 456–464

Structures of Various Adducts Between 2,5-Dimethyl-1,4-benzoquinone or 2-Methyl-1,4-naphthoquinone and 1,1′-Bicycloalkenyls*

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Abstract. (1) $C_{18}H_{22}O_2$, $M_r = 270{\cdot}37$, $P2_1/c$, $a = 8{\cdot}491\ (4)$, $b = 20{\cdot}029\ (10)$, $c = 8{\cdot}650\ (4)$ Å, $\beta = 96{\cdot}48\ (2)°$, $U = 1461{\cdot}67$ Å^3, $Z = 4$, $D_x = 1{\cdot}228$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}43$ cm^{-1}, $F(000) = 584$, $R = 0{\cdot}062$ for 1985 reflections. (2) $C_{20}H_{26}O_2$, $M_r = 298{\cdot}43$, $P2_1/c$, $a = 18{\cdot}509\ (9)$, $b = 9{\cdot}250\ (5)$, $c = 21{\cdot}229\ (10)$ Å, $\beta = 112{\cdot}56\ (3)°$, $U = 3356{\cdot}44$ Å^3, $Z = 8$, $D_x = 1{\cdot}181$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}40$ cm^{-1}, $F(000) = 1296$, $R = 0{\cdot}079$ for 3118 reflections. (3) $C_{19}H_{24}O_2$, $M_r = 284{\cdot}40$, $Pna2_1$, $a = 9{\cdot}080\ (5)$, $b = 15{\cdot}706\ (8)$, $c = 10{\cdot}994\ (6)$ Å, $U = 1567{\cdot}86$ Å^3, $Z = 4$, $D_x = 1{\cdot}205$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}20$ cm^{-1}, $F(000) = 616$, $R = 0{\cdot}038$ for 1345 reflections. (4) $C_{22}H_{24}O_2$, $M_r = 320{\cdot}43$, $P2_12_12_1$, $a = 34{\cdot}069\ (15)$, $b = 7{\cdot}039\ (4)$, $c = 7{\cdot}093\ (4)$ Å, $U = 1700{\cdot}98$ Å^3, $Z = 4$, $D_x = 1{\cdot}251$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}34$ cm^{-1}, $F(000) = 688$, $R = 0{\cdot}064$ for 1631 reflections. (5) $C_{21}H_{28}O_2$, $M_r = 312{\cdot}45$, $P2_12_12_1$, $a = 20{\cdot}091\ (10)$, $b = 9{\cdot}187\ (5)$, $c = 9{\cdot}331\ (5)$ Å, $U = 1722{\cdot}28$ Å^3, $Z = 4$, $D_x = 1{\cdot}205$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}41$ cm^{-1}, $F(000) = 680$, $R = 0{\cdot}070$ for 1230 reflections. (6) $C_{24}H_{28}O_2$, $M_r = 348{\cdot}49$, $P2_1$, $a = 19{\cdot}254\ (1)$, $b = 9{\cdot}841\ (5)$, $c = 9{\cdot}985\ (5)$ Å, $\beta = 93{\cdot}74\ (3)°$, $U = 1891{\cdot}83$ Å^3, $Z = 4$, $D_x = 1{\cdot}223$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 5{\cdot}13$ cm^{-1}, $F(000) = 752$, $R = 0{\cdot}057$ for 3145 reflections. (7) $C_{22}H_{30}O_2$, $M_r = 326{\cdot}48$, $P2_1/n$, $a = 18{\cdot}389\ (9)$, $b = 15{\cdot}398\ (8)$, $c = 6{\cdot}370\ (3)$ Å, $\beta = 90{\cdot}22\ (2)°$, $U = 1803{\cdot}67$ Å^{-3}, $Z = 4$, $D_x = 1{\cdot}202$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}40$ cm^{-1}, $F(000) = 712$, $R = 0{\cdot}061$ for 2191 reflections. (8) $C_{25}H_{30}O_2$, $M_r = 362{\cdot}51$, $P2_1/c$, $a = 16{\cdot}965\ (9)$, $b = 10{\cdot}122\ (5)$, $c = 12{\cdot}739\ (6)$ Å, $\beta = 111{\cdot}74\ (2)°$, $U = 2031{\cdot}94$ Å^3, $Z = 4$, $D_x = 1{\cdot}185$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}39$ cm^{-1}, $F(000) = 784$, $R = 0{\cdot}081$ for 1718 reflections. (9) $C_{22}H_{30}O_2$, $M_r = 326{\cdot}48$, $P\bar{1}$, $a = 15{\cdot}338\ (8)$, $b = 9{\cdot}268\ (5)$, $c = 7{\cdot}036$ Å, $\alpha = 80{\cdot}08\ (3)$, $\beta = 103{\cdot}41\ (3)$, $\gamma = 102{\cdot}70\ (3)°$, $U = 941{\cdot}33$ Å^3, $Z = 2$, $D_x = 1{\cdot}152$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}38$ cm^{-1}, $F(000) = 354$, $R = 0{\cdot}064$ for 2560 reflections. (10) $C_{22}H_{30}O_2$, $M_r = 326{\cdot}48$, $C2/c$, $a = 12{\cdot}513\ (6)$, $b = 14{\cdot}103\ (7)$, $c = 21{\cdot}044\ (11)$ Å, $\beta = 106{\cdot}03\ (3)°$, $U = 3569{\cdot}25$ Å^3, $Z = 8$, $D_x = 1{\cdot}215$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}41$ cm^{-1}, $F(000) = 1424$, $R = 0{\cdot}054$ for 2326 reflections. Crystal structures of eight adducts of 2,5-dimethyl-1,4-benzoquinone or 2-methyl-1,4-naphthoquinone and 1,1′-bicycloalkenyls containing rings of various sizes ranging from five- to seven-

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* (1) 6b,9-Dimethyl-1,2,3,4,5,6,6a,6b,10a,10b-decahydrobenz[*e*]indacene-7,10-dione.

(2) 8b,11-Dimethyl-1,2,3,4,5,6,7,8,8a,8b,12a,12b-dodecahydro-9,12-triphenylenedione.

(3) 7b,10-Dimethyl-2,3,4,5,6,7,7a,7b,11a,11b-decahydro-1*H*-cyclopenta[*l*]phenanthrene-8,11-dione.

(4) 7b-Methyl-2,3,4,5,6,7,7a,7b,13a,13b-decahydro-1*H*-benzo[*b*]cyclopenta[*l*]phenanthrene-8,13-dione.

(5) 4b,7-Dimethyl-2,3,4,4a,4b,8a,8b,9,10,11,12,13-decahydro-1*H*-cyclohepta[*l*]phenanthrene-5,8-dione.

(6) 15a-Methyl-2,3,4,5,6,7,8,9,9a,9b,15a,15b-dodecahydro-1*H*-benzo[*b*]cyclohepta[*l*]phenanthrene-10,15-dione.

(7) 2,4a-Dimethyl-4a,4b,5,6,7,8,9,10,11,12,13,14,14a,14b-tetradecahydrodicyclohepta[*a,c*]naphthalene-1,4-dione.

(8) 10b-Methyl-1,2,3,4,5,6,7,8,9,10,10a,10b,16a,16b-tetradecahydrodicyclohept[*a,c*]anthracene-11,16-dione.

(9) 1-Hydroxy-3,20-dimethylpentacyclo[$10.8.0.0^{5,20}.0^{6,12}.0^{13,19}$]-icosa-2,18-dien-4-one.

(10) 1,4-Dimethylhexacyclo[$10.8.0.0^{2,11}.0^{4,19}.0^{5,11}.0^{12,18}$]icosane-3,20-dione.

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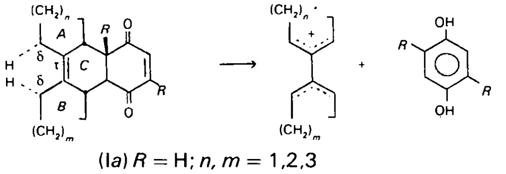
membered, and two irradiated products were solved by X-ray diffraction methods at room temperature. The conformations of the various rings are compared and related to the photochemical reactivity of one of the adducts. The photochemical reactions involve an H-abstraction in the solid state and in benzene or ethyl acetate solutions and a competing $2\pi + 2\pi$ cycloaddition to a cage cyclobutane derivative in ethyl acetate solution.

Introduction. The fragmentation behaviour of diones (I*a*) under electron impact was investigated by Deutsch & Mandelbaum (1969, 1971) and Karpati, Rave, Deutsch & Mandelbaum (1973).



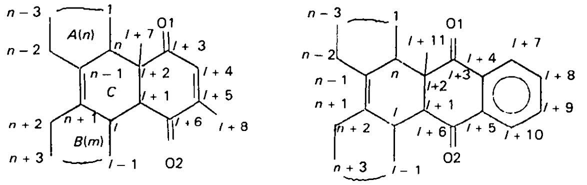
(I*a*) $R = H$; $n, m = 1,2,3$
(I*b*) $R = CH_3$
(I)

The most abundant ion appeared at m/z 160 corresponding to a retro-Diels–Alder fragmentation accompanied by the migration of two H atoms (RDH-2H). A deuterium labelling study showed that the origins of these two H atoms were at positions δ. A similar behaviour was observed for analogous diones differing in the size of rings *A* and *B*. The corresponding ions were of highest abundance when both rings were five-membered (m/z 132) or one was five- and the other six-membered (m/z 146). Lower abundance was observed for the analogue with seven-membered rings *A* and *B* (m/z 188). Similar behaviour was observed in the methyl-substituted diones (I*b*), where a high degree of stereo specificity could be established. In (I*b*) a regular RDA fragmentation competes with the RDA-2H process.

The crystalline dione (7) (see II) (*A* and *B* are seven-membered rings) undergoes an interesting rearrangement on irradiation resulting in a keto-alcohol. It is clear that this rearrangement involves migration of a H atom from a position δ to a carbonyl group. This rearrangement takes place also on irradiation of benzene or ethyl acetate solutions of (7). In the latter a competing $2\pi + 2\pi$ cycloaddition gives rise also to a cage cyclobutane derivative.

The obvious relationship between the electron-impact behaviour and the photochemical rearrangement in the solid and liquid states prompted the need for detailed crystal structures.

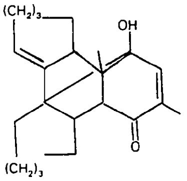
The following eight adducts shown in (II) (with atomic notations) and the two irradiated products were crystallized and used for detailed crystal structure determination. The crystal and molecular structures are presented while other details including photochemical rearrangement and electron-impact experiments will be published elsewhere (Mandelbaum, Kaftory & Weisz, 1984).



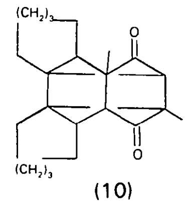
(1) $n = m = 5$ membered rings.
(2) $n = m = 6$
(3) $n = 6; m = 5$
(5) $n = 6; m = 7$
(7) $n = m = 7$

(4) $n = 6; m = 5$
(6) $n = 6; m = 7$
(8) $n = m = 7$

$l = n + m$



(9)



(10)

(II)

Table 1. *Crystallographic and experimental details for* (1)–(10)

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Crystal shape	Needle	Needle	Prism	Needle	Prism	Needle	Needle	Prism	Needle	Prism
Crystal size (mm)	0·2×0·2×0·3	0·2×0·2×0·3	0·3×0·3×0·3	0·2×0·2×0·3	0·2×0·2×0·2	0·3×0·3×0·4	0·3×0·4×0·6	0·2×0·2×0·2	0·3×0·3×0·5	0·3×0·3×0·3
$\Delta\omega$(°)	1·2	1·2	1·07;0·17(*a*)	1·0;0·06(*a*)	1·2	1·0;0·12(*a*)	1·2	1·4	1·4	1·2
Scan time (s)	24·0	24·0	(*a*)	(*a*)	30·0	(*a*)	24·0	28·0	28·0	24·0
Background time (s) (*b*)	24·0	20·0	20·0	20·0	30·0	20·0	20·0	20·0	20·0	20·0
θ_{max} (°)	25·0	23·0	63·0	63·0	22·0	63·0	24·0	23·0	25·0	24·0
Reflections measured	2575	4676	1494	1651	1245	3406	2829	2492	3320	2929
Significant $[F_o > 1{\cdot}5\sigma(F_o)]$	1985	3118	1345(*c*)	1631(*c*)	1230(*c*)	3145	2191	1718	2560	2326
Weighting coefficients (*k*;*g*) (*d*)	1·1161	1·4569	1·0000	0·5408	(*e*)	1·0000	1·1803	1·2890	1·9529	1·0013
	0·0032	0·0009	0·0096	0·0115	(*e*)	0·0365	0·0036	0·0029	0·0009	0·0066
$(\Delta/\sigma)_{max}$	0·9	0·8	0·6	0·6	0·5	1·2	1·2	1·3	1·3	0·1
$(\Delta\rho)_{max}$	0·2	0·25	0·15	0·3	0·2	0·2	0·2	0·25	0·4	0·2
$(\Delta\rho)_{min}$	−0·2	−0·3	−0·25	−0·2	−0·3	−0·2	−0·4	−0·2	−0·25	−0·2
R_w	0·070	0·071	0·042	0·077	0·070	0·063	0·070	0·081	0·067	0·068
R	0·062	0·079	0·038	0·064	0·070	0·057	0·061	0·081	0·064	0·054

Notes: (*a*) $\Delta\omega = a + b\,\mathrm{tg}\theta$ and scan time according to $\Delta\omega$ and scan speed; (*b*) total background counting time; (*c*) $F_o > 0{\cdot}0$; (*d*) $w = k/[\sigma^2(F_o) + gF_o^2]$; (*e*) unit weight.

Experimental. Crystallographic data, details of intensity measurements and structure refinement are given in Table 1. Densities not measured. Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo *K*α or Cu *K*α radiation. Lattice parameters calculated using 25 reflections for each compound. Three standard reflections (for each compound) monitored: variations in intensities *ca* 5%. Absorption and extinction corrections not applied. Structures solved either by *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) or by *MULTAN*80 (Main *et al.*, 1980), and refined by full-matrix least squares (based on *F*) (Sheldrick, 1976) with anisotropic thermal parameters for C and O atoms, isotropic for H. All H positions (see *Structural commentary*) located from difference Fourier maps. Scattering factors for C and O from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965).

Discussion. Final positional parameters for (1)–(10) are given in Tables 2–11 respectively.* Molecular stereoviews for representative molecules (1,2,3,5,7,9,10) are shown in Figs. 1–7 respectively.

Structural commentary

(1) The five-membered rings have different conformations; one adopts the envelope the other the half-chair conformation. The first has a pseudo mirror plane passing through atom C(9) and the midpoint of C(6)–C(7), the second has a pseudo twofold axis

Table 2. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (1), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	*y*	*z*	U_{eq}(Å^2)
O(1)	5958 (3)	2363 (1)	2531 (3)	61 (1)
O(2)	7991 (3)	188 (1)	5584 (3)	59 (1)
C(1)	2569 (3)	1823 (2)	1976 (3)	47 (2)
C(2)	1975 (3)	1755 (2)	250 (4)	50 (2)
C(3)	3409 (4)	1528 (2)	−516 (3)	46 (2)
C(4)	4398 (3)	1138 (1)	729 (3)	34 (1)
C(5)	3763 (3)	1242 (1)	2272 (3)	36 (1)
C(6)	5708 (3)	798 (1)	614 (3)	34 (1)
C(7)	6645 (3)	751 (1)	−770 (3)	45 (1)
C(8)	8243 (4)	450 (2)	−117 (3)	52 (2)
C(9)	8375 (3)	602 (2)	1635 (3)	49 (2)
C(10)	6676 (3)	474 (2)	1995 (3)	35 (2)
C(11)	6137 (3)	661 (1)	3601 (3)	33 (1)
C(12)	5128 (3)	1314 (1)	3591 (3)	33 (1)
C(13)	6255 (3)	1894 (1)	3400 (3)	40 (1)
C(14)	7789 (4)	1874 (2)	4400 (4)	48 (2)
C(15)	8431 (3)	1324 (2)	5075 (3)	44 (1)
C(16)	7553 (3)	683 (1)	4839 (3)	39 (1)
C(17)	4469 (3)	1390 (1)	5166 (3)	44 (1)
C(18)	10000 (4)	1299 (2)	6062 (4)	70 (2)

Table 3. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (2), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	*y*	*z*	U_{eq}(Å^2)
Molecule *A*				
O(1)	3665 (2)	845 (4)	8005 (2)	74 (2)
O(2)	1020 (2)	−576 (4)	8185 (2)	67 (2)
C(1)	1676 (3)	1273 (5)	6987 (2)	51 (3)
C(2)	1190 (3)	2114 (6)	6339 (2)	62 (3)
C(3)	550 (3)	2990 (6)	6431 (2)	58 (3)
C(4)	889 (2)	3978 (5)	7064 (2)	50 (3)
C(5)	1332 (2)	3121 (4)	7695 (2)	37 (2)
C(6)	2006 (2)	2303 (4)	7608 (2)	41 (2)
C(7)	1182 (2)	3070 (5)	8258 (2)	40 (2)
C(8)	584 (3)	4058 (6)	8378 (2)	65 (3)
C(9)	132 (3)	3353 (6)	8764 (3)	73 (3)
C(10)	686 (3)	2689 (6)	9415 (2)	71 (3)
C(11)	1181 (3)	1539 (6)	9272 (2)	64 (3)
C(12)	1653 (2)	2150 (5)	8871 (2)	44 (2)
C(13)	2137 (2)	1003 (5)	8692 (2)	37 (2)
C(14)	2596 (2)	1663 (4)	8288 (2)	38 (2)
C(15)	3089 (3)	529 (5)	8127 (2)	47 (3)
C(16)	2854 (3)	−996 (5)	8095 (2)	54 (3)
C(17)	2210 (3)	−1435 (5)	8176 (2)	49 (3)
C(18)	1713 (3)	−332 (5)	8335 (2)	47 (3)
C(19)	3139 (2)	2892 (5)	8698 (2)	49 (3)
C(20)	1928 (3)	−2961 (6)	8081 (3)	92 (4)
Molecule *B*				
O(1)	6328 (3)	762 (4)	7242 (2)	104 (3)
O(2)	6524 (2)	−651 (4)	9669 (2)	67 (2)
C(1)	7703 (3)	1161 (5)	8909 (2)	61 (3)
C(2)	8474 (3)	1970 (7)	9260 (3)	84 (4)
C(3)	8470 (3)	2864 (7)	9861 (3)	79 (4)
C(4)	7764 (3)	3884 (5)	9642 (2)	63 (3)
C(5)	7011 (2)	3053 (5)	9312 (2)	44 (3)
C(6)	7008 (2)	2220 (5)	8691 (2)	48 (3)
C(7)	6423 (3)	3031 (5)	9521 (2)	46 (2)
C(8)	6354 (3)	4071 (5)	10055 (2)	66 (3)
C(9)	5996 (3)	3457 (6)	10519 (2)	70 (3)
C(10)	5231 (3)	2695 (6)	10135 (2)	73 (3)
C(11)	5364 (3)	1512 (5)	9697 (2)	63 (3)
C(12)	5700 (2)	2099 (5)	9191 (2)	45 (3)
C(13)	5809 (2)	952 (5)	8730 (2)	39 (2)
C(14)	6185 (2)	1584 (5)	8252 (2)	44 (2)
C(15)	6275 (3)	433 (5)	7779 (2)	56 (3)
C(16)	6319 (3)	−1093 (5)	7978 (2)	54 (3)
C(17)	6323 (3)	−1508 (5)	8574 (2)	51 (3)
C(18)	6247 (2)	−407 (5)	9060 (2)	46 (3)
C(19)	5668 (3)	2800 (6)	7815 (2)	64 (3)
C(20)	6434 (4)	−3063 (6)	8811 (3)	97 (4)

Table 4. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (3), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	*y*	*z*	U_{eq}(Å^2)
O(1)	9204 (2)	2338 (1)	3032 (3)	63 (1)
O(2)	10616 (2)	−262 (1)	5714	60 (1)
C(1)	8775 (3)	1775 (2)	6037 (3)	49 (1)
C(2)	7946 (3)	2095 (2)	7158 (3)	58 (1)
C(3)	7189 (3)	136 (2)	7821 (3)	56 (1)
C(4)	6147 (3)	896 (2)	6963 (3)	50 (1)
C(5)	6935 (2)	596 (1)	5828 (3)	39 (1)
C(6)	7710 (2)	1318 (1)	5154 (3)	38 (1)
C(7)	7004 (2)	−212 (1)	5484 (3)	41 (1)
C(8)	6348 (3)	−984 (2)	6099 (3)	55 (1)
C(9)	6870 (4)	−1749 (2)	5350 (4)	69 (1)
C(10)	8287 (3)	−1438 (2)	4724 (4)	57 (1)
C(11)	7878 (2)	−517 (1)	4400 (3)	40 (1)
C(12)	9055 (2)	115 (1)	4009 (3)	35 (1)
C(13)	8366 (2)	1022 (1)	3907 (3)	37 (1)
C(14)	9536 (2)	1664 (1)	3506 (3)	43 (1)
C(15)	11096 (2)	1477 (2)	3758 (3)	47 (1)
C(16)	11535 (2)	808 (1)	4413 (3)	43 (1)
C(17)	10409 (2)	169 (1)	4813 (3)	40 (1)
C(18)	7120 (2)	1024 (2)	2955 (3)	45 (1)
C(19)	13090 (3)	677 (2)	4832 (4)	64 (1)

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* List of structure factors, thermal parameters and H-atom parameters, and tables of bond lengths and angles for all compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38989 (181 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

passing through atom C(4) and the midpoint of C(1)–C(2).

(2) The unit cell contains two independent molecules in the asymmetric unit. The six-membered rings adopt the chair conformation; however, one is slightly flattened at the double-bond bridge.

(3) The five-membered ring adopts an envelope conformation with C(10) out of the plane. The six-membered ring adopts an almost perfect chair conformation.

(4) This compound is analogous to compound (3). The conformations of the five- and six-membered rings are identical to those found in (3).

Table 5. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (4), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	453 (1)	4319 (5)	2128 (4)	71 (1)
O(2)	1356 (1)	4364 (4)	8135 (4)	59 (1)
C(1)	1421 (1)	5795 (5)	3217 (6)	48 (2)
C(2)	1790 (1)	6450 (6)	2189 (6)	60 (2)
C(3)	2149 (1)	5376 (6)	2883 (8)	66 (2)
C(4)	2096 (1)	3247 (6)	2670 (8)	66 (2)
C(5)	1727 (1)	2597 (5)	3653 (5)	46 (1)
C(6)	1359 (1)	3624 (5)	2961 (5)	45 (2)
C(7)	1721 (1)	1356 (5)	5053 (5)	46 (2)
C(8)	2066 (1)	386 (5)	5989 (7)	59 (2)
C(9)	1895 (1)	−798 (7)	7621 (7)	70 (2)
C(10)	1503 (1)	177 (6)	8085 (6)	55 (2)
C(11)	1357 (1)	768 (5)	6124 (5)	43 (1)
C(12)	1028 (1)	2255 (5)	5944 (4)	38 (1)
C(13)	974 (1)	2789 (5)	3812 (5)	42 (2)
C(14)	639 (1)	4218 (5)	3592 (5)	49 (1)
C(15)	547 (1)	5545 (5)	5185 (6)	46 (1)
C(16)	765 (1)	5480 (5)	6845 (5)	45 (2)
C(17)	1086 (1)	4045 (5)	7067 (5)	41 (1)
C(18)	248 (1)	6887 (6)	4976 (7)	60 (2)
C(19)	168 (1)	8117 (6)	6427 (9)	71 (2)
C(20)	382 (1)	8062 (6)	8083 (8)	69 (2)
C(21)	684 (1)	6754 (6)	8304 (6)	56 (2)
C(22)	865 (1)	995 (6)	2674 (6)	56 (2)

Table 6. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (5), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	141 (2)	5356 (6)	12256 (7)	75 (4)
O(2)	2173 (3)	3859 (6)	9016 (6)	57 (3)
C(1)	565 (3)	5735 (8)	8512 (7)	43 (4)
C(2)	300 (3)	6517 (9)	7183 (8)	56 (4)
C(3)	829 (4)	7383 (9)	6442 (8)	56 (4)
C(4)	1165 (3)	8443 (8)	7491 (7)	47 (4)
C(5)	1440 (3)	7617 (7)	8777 (7)	40 (4)
C(6)	893 (3)	6803 (8)	9557 (8)	40 (4)
C(7)	2094 (3)	7544 (7)	9124 (7)	39 (4)
C(8)	2622 (3)	8382 (9)	8339 (7)	50 (4)
C(9)	3129 (4)	9195 (9)	9302 (10)	68 (5)
C(10)	3732 (4)	8360 (11)	9725 (8)	61 (5)
C(11)	3593 (4)	7085 (11)	10748 (9)	62 (5)
C(12)	3041 (3)	6031 (8)	10295 (8)	50 (4)
C(13)	2335 (3)	6678 (7)	10415 (7)	38 (4)
C(14)	1823 (3)	5520 (7)	10902 (7)	36 (4)
C(15)	1122 (3)	6205 (7)	11033 (7)	36 (4)
C(16)	634 (4)	5062 (8)	11587 (9)	52 (4)
C(17)	760 (4)	3523 (8)	11190 (9)	56 (5)
C(18)	1286 (4)	3059 (8)	10443 (8)	47 (4)
C(19)	1812 (3)	4136 (7)	9991 (7)	36 (4)
C(20)	1126 (3)	7460 (8)	12148 (8)	51 (4)
C(21)	1389 (4)	1539 (9)	9994 (10)	67 (5)

Table 7. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (6), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
Molecule *A*				
O(1)	2762 (1)	−132 (4)	−182 (3)	69 (1)
O(2)	5035 (1)	2870	−582 (2)	52 (1)
C(1)	3238 (2)	3388 (4)	397 (3)	45 (1)
C(2)	2954 (2)	4683 (4)	1028 (3)	53 (2)
C(3)	3481 (2)	5308 (4)	2038 (4)	56 (2)
C(4)	3743 (2)	4278 (4)	3085 (3)	55 (2)
C(5)	4050 (1)	3043 (3)	2428 (3)	37 (1)
C(6)	3503 (1)	2372 (3)	1479 (3)	37 (1)
C(7)	4717 (1)	2646 (3)	2612 (3)	38 (1)
C(8)	5235 (2)	3329 (4)	3580 (4)	56 (2)
C(9)	5681 (2)	2403 (5)	4515 (4)	63 (2)
C(10)	6350 (2)	1902 (5)	3948 (4)	63 (2)
C(11)	6244 (2)	907 (5)	2766 (5)	72 (2)
C(12)	5764 (2)	1425 (4)	1628 (4)	57 (1)
C(13)	4982 (1)	1399 (3)	1901 (3)	40 (1)
C(14)	4521 (1)	1054 (3)	639 (3)	36 (1)
C(15)	3747 (1)	954 (3)	981 (3)	36 (1)
C(16)	3298 (2)	504 (3)	−267 (3)	42 (1)
C(17)	3523 (1)	906 (3)	−1608 (3)	41 (1)
C(18)	4140 (1)	1629 (3)	−1759 (3)	39 (1)
C(19)	4607 (1)	1945 (3)	−537 (3)	37 (1)
C(20)	3096 (2)	587 (4)	−2773 (3)	49 (1)
C(21)	3289 (2)	1001 (4)	−4029 (3)	54 (2)
C(22)	3900 (2)	1706 (4)	−4147 (4)	58 (2)
C(23)	4321 (2)	2044 (4)	−3008 (3)	51 (2)
C(24)	3651 (2)	−91 (4)	2071 (4)	53 (2)
Molecule *B*				
O(1)	7857 (1)	3564 (3)	4527 (3)	64 (1)
O(2)	10082 (1)	504 (3)	5611 (2)	52 (1)
C(1)	8294 (1)	−41 (3)	4117 (3).	48 (1)
C(2)	8016 (2)	−1335 (4)	3396 (4)	56 (2)
C(3)	8545 (2)	−1970 (4)	2537 (4)	57 (2)
C(4)	8823 (2)	−951 (4)	1579 (3)	55 (2)
C(5)	9126 (1)	285 (3)	2317 (3)	40 (1)
C(6)	8574 (1)	974 (3)	3097 (3)	38 (1)
C(7)	9790 (1)	688 (3)	2306 (3)	37 (1)
C(8)	10322 (2)	5 (4)	1470 (3)	53 (2)
C(9)	10769 (2)	977 (5)	677 (4)	65 (2)
C(10)	11435 (2)	1470 (4)	1439 (4)	60 (2)
C(11)	11328 (2)	2423 (4)	2588 (4)	61 (1)
C(12)	10837 (2)	1885 (4)	3614 (3)	53 (1)
C(13)	10055 (1)	1923 (3)	3098 (3)	40 (1)
C(14)	9584 (1)	2305 (3)	4210 (3)	34 (1)
C(15)	8813 (1)	2395 (3)	3650 (3)	38 (1)
C(16)	8362 (1)	2850 (3)	4768 (3)	42 (1)
C(17)	8559 (1)	2450 (3)	6189 (3)	42 (1)
C(18)	9170 (2)	1719 (3)	6505 (3)	40 (1)
C(19)	9652 (1)	1391 (3)	5449 (3)	38 (1)
C(20)	8122 (2)	2758 (4)	7197 (4)	54 (1)
C(21)	8291 (2)	2367 (4)	8505 (4)	61 (2)
C(22)	8880 (2)	1636 (4)	8806 (3)	60 (2)
C(23)	9330 (2)	1309 (4)	7822 (3)	49 (1)
C(24)	8736 (2)	3430 (4)	2497 (3)	47 (1)

(5) The six-membered ring adopts the chair conformation; the seven-membered ring adopts a slightly twisted chair conformation.

(6) This compound is analogous to (5). There are two independent molecules in the asymmetric unit. The six- and seven-membered rings adopt the same conformations as in (5).

(7) Both seven-membered rings adopt the same chair conformation.

(8) This compound is analogous to (7). The conformations of both seven-membered rings are identical to those found in (7).

(9) The cycloheptene moiety is disordered. The disorder can be attributed to a flip of atoms C(3) and C(4) around the bond. The occupation factors are 0·75 and 0·25. (The latter were refined isotropically and no

bonded H atoms were introduced in the refinement procedures.) The cycloheptene appears in two conformations due to the disorder: the main conformation is a chair, the minor is a boat. The unit-cell packing consists of molecules held by H bonding along the short *c* axis. The H bonding is between the keto O(2) atom and the alcohol OH group [O(1)$\cdots$O(2) 2·788, O(2)$\cdots$HO(1) 1·845 Å, O(1)–HO(1)$\cdots$O(2) 171·1°].

(10) The compound consists of a planar four-membered ring, two five-membered rings in envelope conformations with either C(15) or C(16) as flap, two six-membered rings in boat conformations and two seven-membered rings, both in twist-chair conformations.

Conformations of the various rings

The geometrical data obtained from the ten structures enable a comparison of torsion angles (*i.e.* the conformation) in the various rings. The ten compounds contain five-, six- and seven-membered rings. A comparison between torsion angles is given in Tables 12–15. In these tables it should be noted that (*a*) rings *A* and *B* in (1)–(8) are compared with the appropriate

Table 8. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (7), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	4758 (1)	1321 (2)	6214 (4)	61 (1)
O(2)	3334 (1)	−417 (2)	611 (4)	67 (1)
C(1)	4520 (2)	3056 (2)	3832 (5)	47 (2)
C(2)	4284 (2)	4003 (2)	4044 (5)	53 (2)
C(3)	4069 (2)	4272 (2)	6235 (5)	54 (2)
C(4)	3399 (2)	3824 (2)	7088 (5)	50 (2)
C(5)	3463 (2)	2832 (2)	7225 (4)	40 (1)
C(6)	3324 (1)	2361 (2)	5191 (4)	31 (1)
C(7)	3890 (1)	2424 (2)	3459 (4)	35 (1)
C(8)	2764 (1)	1824 (2)	4816 (4)	33 (1)
C(9)	2187 (2)	1590 (2)	6391 (4)	42 (1)
C(10)	1433 (2)	1967 (3)	5904 (5)	57 (2)
C(11)	986 (2)	1435 (3)	4378 (5)	58 (2)
C(12)	1319 (2)	1316 (2)	2220 (5)	47 (2)
C(13)	2053 (2)	856 (2)	2179 (4)	40 (2)
C(14)	2706 (1)	1443 (2)	2612 (4)	34 (1)
C(15)	3445 (2)	1040 (2)	1868 (4)	36 (1)
C(16)	4107 (2)	1465 (2)	2954 (4)	37 (1)
C(17)	4291 (2)	1020 (2)	5056 (4)	42 (2)
C(18)	3928 (2)	208 (2)	5617 (5)	53 (2)
C(19)	3571 (2)	−281 (2)	4234 (5)	48 (2)
C(20)	3447 (2)	68 (2)	2102 (5)	43 (2)
C(21)	4776 (2)	1377 (2)	1541 (5)	50 (2)
C(22)	3324 (2)	−1186 (2)	4672 (7)	79 (2)

Table 9. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (8), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	9763 (2)	6606 (4)	108 (4)	71 (3)
O(2)	8310 (3)	2288 (4)	272 (4)	80 (3)
C(1)	7980 (4)	8030 (5)	−594 (6)	67 (4)
C(2)	7241 (4)	9036 (6)	−954 (6)	81 (4)
C(3)	6813 (4)	9233 (6)	−132 (7)	88 (5)
C(4)	6413 (4)	8045 (6)	180 (6)	73 (4)
C(5)	6993 (4)	6845 (5)	621 (5)	55 (3)
C(6)	7140 (3)	6036 (5)	−272 (4)	40 (3)
C(7)	7668 (3)	6591 (5)	−898 (5)	50 (3)
C(8)	6810 (3)	4811 (5)	−602 (5)	44 (3)
C(9)	6252 (4)	4068 (6)	−139 (5)	60 (3)
C(10)	5353 (4)	3826 (6)	−987 (7)	79 (4)
C(11)	5280 (4)	2656 (7)	−1771 (7)	83 (5)
C(12)	5796 (4)	2740 (7)	−2510 (6)	82 (4)
C(13)	6767 (4)	2740 (6)	−1853 (5)	66 (4)
C(14)	7120 (3)	4135 (5)	−1447 (5)	48 (3)
C(15)	8108 (3)	4162 (5)	−918 (5)	49 (3)
C(16)	8406 (3)	5623 (5)	−902 (5)	48 (3)
C(17)	9185 (3)	5937 (5)	152 (5)	51 (3)
C(18)	9179 (3)	5447 (5)	1234 (5)	47 (3)
C(19)	8774 (3)	4270 (5)	1274 (5)	47 (3)
C(20)	8393 (3)	3475 (6)	213 (6)	56 (4)
C(21)	9614 (3)	6122 (6)	2260 (6)	59 (4)
C(22)	9597 (4)	5612 (9)	3241 (6)	77 (5)
C(23)	9182 (5)	4448 (9)	3271 (7)	92 (6)
C(24)	8789 (4)	3759 (6)	2297 (7)	66 (4)
C(25)	8609 (4)	5850 (6)	−1950 (5)	74 (4)

Table 10. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (9), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	3634 (2)	6359 (3)	7617 (3)	48 (1)
O(2)	3651 (2)	4292 (3)	15184 (4)	61 (1)
C(1)	3334 (3)	9373 (4)	8594 (6)	57 (2)
C(2)	2787 (3)	10603 (4)	7810 (7)	66 (2)
C(3)	2077 (4)	10298 (5)	6027 (9)	67 (3)
C(4)	1266 (4)	9086 (5)	6408 (9)	65 (3)
C(5)	1473 (3)	7510 (5)	6820 (7)	64 (2)
C(6)	2086 (2)	7027 (4)	8281 (5)	42 (2)
C(7)	2830 (2)	7961 (4)	9655 (5)	43 (2)
C(8)	2203 (2)	5421 (4)	8923 (5)	38 (2)
C(9)	1723 (3)	4295 (4)	7501 (5)	47 (2)
C(10)	695 (3)	3761 (5)	7350 (7)	63 (2)
C(11)	427 (3)	2482 (5)	8922 (9)	74 (3)
C(12)	643 (3)	2894 (5)	11008 (8)	72 (3)
C(13)	1649 (3)	3448 (4)	11831 (6)	54 (2)
C(14)	2014 (2)	5059 (4)	11067 (5)	42 (2)
C(15)	2944 (2)	5782 (4)	12335 (5)	42 (2)
C(16)	3443 (2)	6816 (4)	10779 (5)	39 (2)
C(17)	3275 (2)	5669 (4)	9312 (5)	36 (2)
C(18)	3667 (2)	4308 (4)	10191 (5)	39 (2)
C(19)	3781 (2)	3773 (4)	12106 (5)	41 (2)
C(20)	3485 (2)	4600 (4)	13382 (5)	43 (2)
C(21)	4432 (3)	7473 (4)	11582 (6)	52 (2)
C(22)	4169 (3)	2403 (5)	13017 (6)	57 (2)
C(31)	165 (7)	1010 (12)	705 (16)	54 (30)*
C(41)	148 (7)	911 (11)	552 (15)	143 (30)*

* U_{iso} values.

Table 11. *Positional parameters* ($\times 10^4$) *and* U_{eq} *values* ($\times 10^3$) *for* (10), *with e.s.d's in parentheses*

$U_{eq} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U_{eq}(Å^2)
O(1)	2628 (2)	−2308 (1)	6849 (1)	52 (1)
O(2)	1526 (2)	−527 (2)	7838 (1)	55 (1)
C(1)	2189 (2)	−1310 (2)	5235 (1)	40 (1)
C(2)	2249 (3)	−845 (2)	4585 (2)	48 (2)
C(3)	3188 (3)	−152 (2)	4622 (2)	54 (2)
C(4)	3321 (3)	628 (2)	5142 (2)	45 (2)
C(5)	3690 (2)	246 (2)	5850 (1)	36 (1)
C(6)	2765 (2)	−37 (2)	6154 (1)	28 (1)
C(7)	1804 (2)	−628 (2)	5692 (1)	31 (1)
C(8)	2297 (2)	742 (2)	6562 (1)	28 (1)
C(9)	2748 (2)	1751 (2)	6612 (1)	34 (1)
C(10)	2080 (3)	2457 (2)	6098 (2)	41 (1)
C(11)	1158 (3)	2941 (2)	6328 (2)	47 (2)
C(12)	187 (3)	2318 (2)	6360 (2)	49 (2)
C(13)	477 (2)	1399 (2)	6751 (1)	39 (1)
C(14)	1015 (2)	663 (2)	6397 (1)	31 (1)
C(15)	873 (2)	−355 (2)	6626 (1)	34 (1)
C(16)	1317 (2)	−1130 (2)	6207 (1)	34 (1)
C(17)	2412 (2)	−1506 (2)	6661 (1)	36 (1)
C(18)	3175 (2)	−653 (2)	6795 (1)	30 (1)
C(19)	2731 (2)	112 (2)	7209 (1)	29 (1)
C(20)	1682 (2)	−299 (2)	7317 (1)	33 (1)
C(21)	439 (3)	−1892 (2)	5955 (2)	56 (2)
C(22)	3556 (2)	490 (2)	7820 (1)	38 (1)

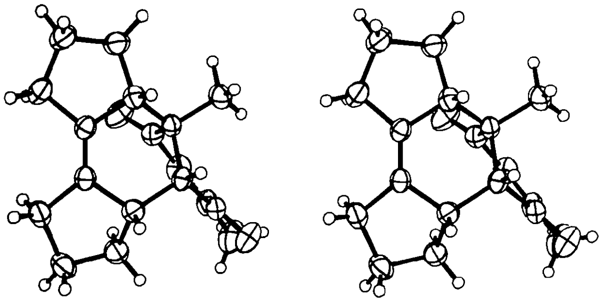


Fig. 1. Stereoscopic view of (1).

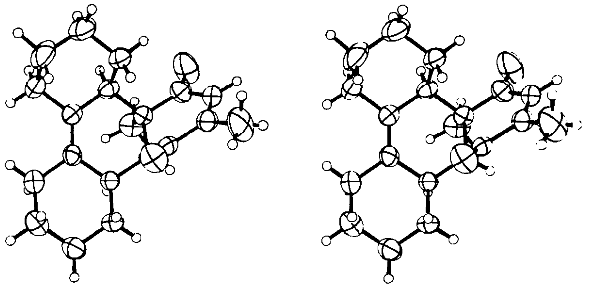


Fig. 2. Stereoscopic view of (2) (only one of the two independent molecules is shown).

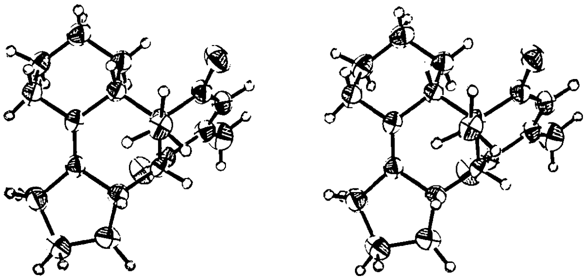


Fig. 3. Stereoscopic view of (3).

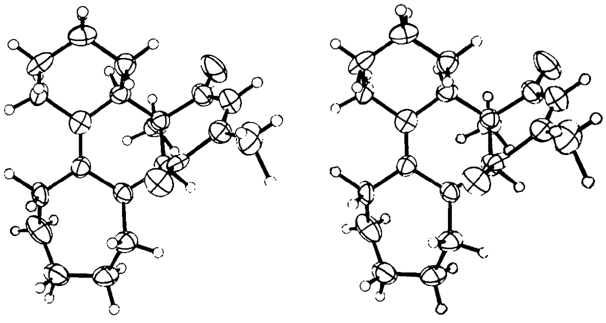


Fig. 4. Stereoscopic view of (5).

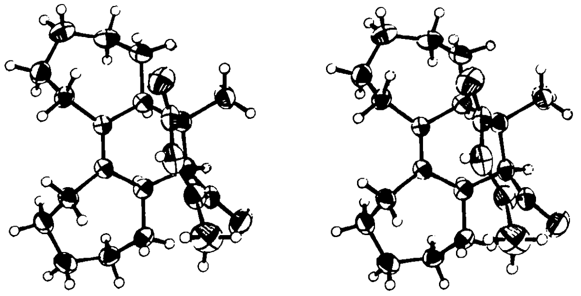
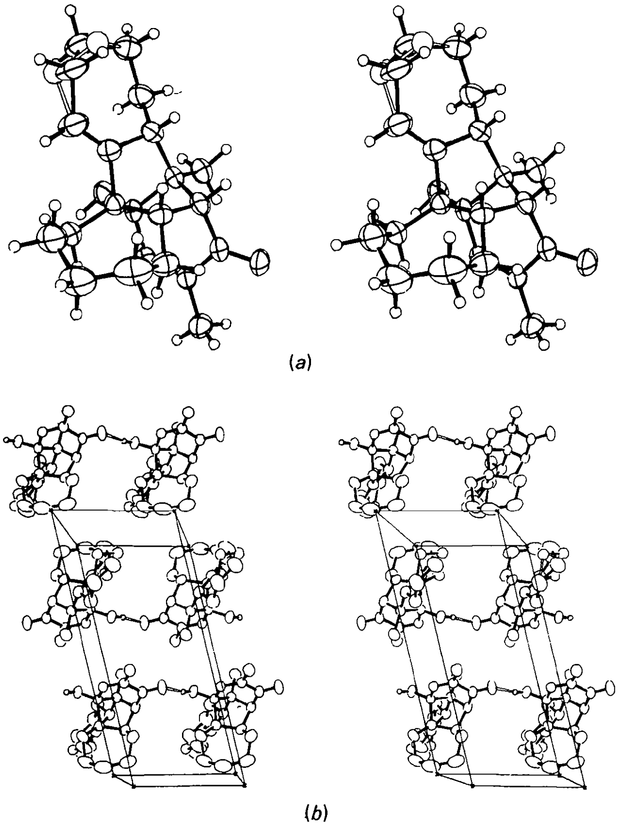


Fig. 5. Stereoscopic view of (7).



(a)

(b)

Fig. 6. (a) Stereoscopic view of (9). (b) Packing of molecules of the keto-alcohol (9) showing the hydrogen bonding.

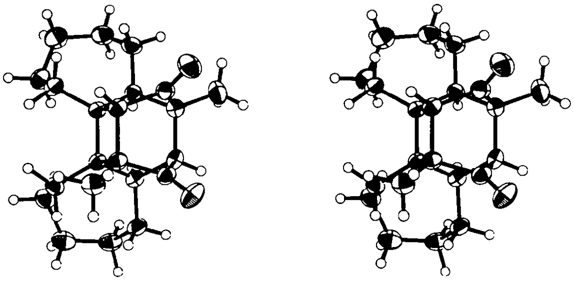


Fig. 7. Stereoscopic view of (10).

values in cycloalkanones (where these are available), otherwise the comparison is with the cycloalkane, (*b*) although compounds (9) and (10) contain only cycloalkanes, they are included in the tables with the appropriate title, (*c*) the order of assigning torsion angles is that *W*1 is defined as the torsion angle at the bond neighbouring the double bond (in the bicycloalkanones) and does not participate in the cyclohexene ring (*C*); the remaining ones are according to the notation in Tables 12–15. E.s.d.'s for torsion angles are 0·3–1·0°.

(*a*) *Five-membered rings* (*Table* 12). Cyclopentane is a puckered flexible ring characterized by 'pseudorotation'. The puckering rotates around the ring without an energy barrier, thus giving rise to an infinity of conformations which differ only in bond and torsion angles (Eliel, Allinger, Angyal & Morrison, 1965). However, Allinger, Tribble & Miller (1972) have calculated the difference in energy between the half-chair and envelope forms in cyclopentanone to be *ca* 13·4 kJ mol^{-1}. The most stable conformation is the half-chair (C_2) form and the less stable is the envelope (C_s) form. Altona, Geise & Romers (1968) have given torsion angles for the three main conformations found in fused cyclopentane in steroids (values for the envelope form are given in Table 12). Out of the six five-membered rings [four as rings *A* and *B* and two as cyclopentanone in compound (10)], only one was found to adopt the half-chair conformation with excellent agreement with the values obtained by electron diffraction for free cyclopentanone (Geise & Mijlhoff, 1971) with phase angle $P = -0{\cdot}3°$. Two other rings adopt the envelope conformation with phase angles within 0·5° of that of an envelope ($P = 18°$). The remaining three five-membered rings deviate from that conformation. Their phase angles are 2·7–6·3° from the ideal envelope conformation. [See also Fuchs (1978) and references cited therein.]

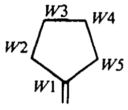
(*b*) *Six-membered rings* (*Table* 13). The chair conformation in cyclohexane is known to be *ca* 25·2 kJ mol^{-1} more stable than the boat form. In cyclohexanone the chair is in all likelihood not very different from that of cyclohexane but probably slightly flatter (Dillen & Geise, 1980). In the nine six-membered rings of *A* or *B* in compounds (2), (3), (4), (5) and (6) the chair conformation was found. Some flattening of this form was found in compound (2) where one of the cyclohexane rings was flattened at the neighbourhood of the double bond. The boat conformation was observed in the cage compound (10) where the rigidity of the molecule controls the conformations of these rings. In bicyclohexylidene (Sasvári & Low, 1965) the two cyclohexanes are related by a crystallographic inversion centre, both adopting the chair conformation. The *cis* fusion in compound (2) induces a pseudo mirror plane between the two cyclohexane rings without affecting the conformation of the individual rings.

(*c*) *Seven-membered rings* (*Table* 14). Cycloheptane has two types of conformation (boat and chair). Both of these conformations are flexible. Detailed calculations (Hendrickson, 1961) show that the chair form is more stable than the boat and a particular arrangement of the chair (twist chair) was considerably preferred over other alternatives. Allinger, Tribble & Miller (1972) have calculated the relative stability of cycloheptanone, using the most stable cycloheptane conformation (twist chair) with keto groups at various positions in the ring. They concluded that two out of four different positions of the keto groups have similar energy and might exist in a mixture at room temperature; the other two are less than 8 kJ mol^{-1} higher in energy. The boat forms are consistently 8·4–16·8 kJ mol^{-1} higher than the twist-chair conformations. Bocian & Strauss (1977) have found, from vibrational spectra, that cycloheptanone is a nonrigid pseudorotating molecule with a twist-chair average structure. The symmetric twist-chair and two other adjacent twist-chairs have practically the same energy.

For methylenecycloheptane four distinct twist-chair and four distinct chair conformers have to be considered. Bovill, Guy, Sim, White & Herz (1979) have calculated steric energies and equilibrium geometries for these eight forms and found that one of the twist-chair forms has the minimal energy (26·7 kJ mol^{-1}) while one of the chair conformations has the maximal energy (37·5 kJ mol^{-1}). The difference between the two is 10·8 kJ mol^{-1}. A comparison of the torsion angles in the various compounds containing seven-membered rings with the calculated values of the two equivalent conformations (3*a* and 3*e* in Bovill *et al.*, 1979) is given in Table 14. Out of seven comparable seven-membered rings, three adopted one of the four twisted-chair conformations (30·4 kJ mol^{-1}) and four adopted the most stable conformation among the chair forms (29·3 kJ mol^{-1}). The three cycloheptane rings (in 9 and 10) adopted the twist-chair conformation. The cycloheptene ring in (9) is found to be disordered with the main conformation as a chair and the minor as a boat.

(*d*) *Cyclohexene* (*Table* 15). The monoplanar conformation, also known as half-chair form, has long been recognized as the more stable conformation of cyclohexene. The boat form is the less stable conformation and its energy is *ca* 29·0 kJ mol^{-1} higher than that of the half-chair conformation. In six out of the eight compounds the cyclohexene was found to adopt a distorted half-chair conformation. The distortions are attributed to the transmitted strain due to the rings fused to the cyclohexene. A similar conformation was found in *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone and eight of its substituted derivatives (Scheffer & Dzakpasu, 1978, and references cited therein). This conformation is responsible for the photochemical rearrangement occurring in those compounds and involving also abstraction of an H atom in a β position

Table 12. *Comparison of torsion angles (°) in the five-membered rings*



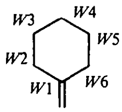
	Envelope* (C_s)	Half chair† (C_2)	(1)		(3)	(4)	(10) (cyclopentanone)	
*W*1	0	−11·1	−11·1	−5·1	0·4	0·5	−30·2	28·5
*W*2	27·4	29·0	29·5	−21·8	24·2	−23·6	−1·8	3·4
*W*3	−44·4	−37·2	−36·4	40·1	−38·8	37·0	32·2	−33·5
*W*4	44·4	29·0	28·9	−42·5	38·9	−37·0	−49·5	50·4
*W*5	−27·4	−11·1	−11·2	29·8	−24·7	22·9	50·1	−49·5
P‡	18	0	−0·3	24·3	18·4	17·5	52·3	50·5

* Altona, Geise & Romers (1968) (for fused five-membered ring in steroids).

† Geise & Mijlhoff (1971).

‡ The phase angle *P* (°) is defined according to tan $P = (W5 + W2 - W4 - W1)/3{\cdot}0777\,W3$.

Table 13. *Comparison of torsion angles (°) in the six-membered rings*

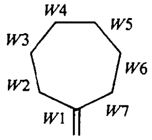


	Chair*	Boat†	(2*A*)		(2*B*)		(3)	(4)	(5)	(6)		(10) (cyclohexane; cyclohexanedione)	
*W*1	−54	−53	59·3	−42·2	−58·5	42·1	−55·5	56·4	−59·0	−59·4	−59·4	60·9	−65·3
*W*2	54	0	−56·2	52·6	55·6	−50·2	55·0	−55·1	55·7	56·5	55·7	1·9	−0·3
*W*3	−54	−52	53·5	−60·5	−54·2	57·1	−57·1	56·6	−54·3	−53·3	−52·9	−63·7	66·0
*W*4	54	52	−54·7	58·2	55·2	−58·1	58·5	−57·7	55·4	53·4	53·3	61·1	−63·2
*W*5	−54	0	56·6	−47·5	−56·9	51·8	−56·5	56·4	−56·5	−56·1	−56·2	1·5	−1·3
*W*6	54	53	−59·3	39·4	59·1	−42·2	55·5	−56·5	59·0	59·0	59·2	−63·9	67·5

* Buys (1969).

† Bucourt (1977, and references cited therein).

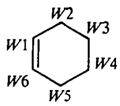
Table 14. *Comparison of torsion angles (°) in the seven-membered rings*



	Chair*	Twist chair*	(5)	(6*A*)	(6*B*)	(7)		(8)		(9) (heptene)	(9) (heptane)	(10) (heptane)	
*W*1	−67	−37	−33·9	−43·8	−43·8	71·5	−68·3	69·8	71·0	−11·6	20·5	44·7	−40·0
*W*2	84	83	86·0	88·0	88·7	−81·2	84·0	−78·1	81·3	60·4	−75·4	−89·7	88·7
*W*3	−65	−75	−71·6	−68·2	−69·1	59·8	−60·3	54·3	−60·4	−73·5	77·6	67·2	−71·5
*W*4	66	61	50·7	53·5	53·7	−64·9	60·5	−59·3	64·9	71·6	−60·8	−51·1	52·4
*W*5	−84	−75	−68·0	−75·2	−74·5	86·3	−83·2	85·0	−85·1	−74·3	68·6	72·8	−69·9
*W*6	66	83	89·5	86·6	86·9	−62·4	66·7	−66·2	63·4	72·1	−83·9	−86·8	88·3
*W*7	1	−37	−42·7	−31·9	−32·7	−7·0	0·7	−3·3	5·2	−44·4	49·2	35·0	−39·9

* Bovill *et al.* (1979).

Table 15. *Comparison of torsion angles (°) in cyclohexene rings*



	Half chair*	Boat*	(1)	(2*A*)	(2*B*)	(3)	(4)	(5)	(6*A*)	(6*B*)	(7)	(8)
*W*1	0	0	1·1	−2·0	3·8	1·1	1·0	−3·5	−2·9	−0·4	−8·1	7·3
*W*2	15	−39	34·5	−11·7	−11·0	9·5	−10·5	15·5	13·6	12·4	−51·7	−53·1
*W*3	−44	37	−58·6	42·0	−41·8	−39·5	39·7	−43·4	−42·2	−41·8	69·8	32·8
*W*4	61	0	52·3	−61·3	60·7	59·8	−59·7	61·6	63·0	61·8	−29·7	24·8
*W*5	−44	−37	−19·9	48·1	−46·6	−48·8	49·1	−48·7	−52·2	−50·1	−26·3	−68·9
*W*6	15	39	−8·5	−16·5	14·4	19·5	−21·3	20·3	22·3	19·5	49·6	53·2

* Bucourt (1977, and references cited therein).

to one of the carbonyl groups. In the present work no such behaviour was detected due to the absence of such an H atom. However, in compound (7) where *A* and *B* are seven-membered rings a similar rearrangement was detected. The cyclohexene is in a twisted-boat conformation in (7) and (8). This change in conformation compared with (1)–(6) is somewhat surprising since such a conformation of the cyclohexene ring is less stable; it is also noted that this conformation together with the seven-membered-ring conformation bring the two H atoms at the δ positions to a close proximity [1·98 (6) in (7) and 1·99 (9) Å in (8)]. These distances have been calculated from refined H positions; calculated positions revealed distances of 1·80 and 1·83 Å in (7) and (8) respectively. Moreover, model inspection shows that the conformations of the seven-membered rings are not altered by changing the conformation of the cyclohexene ring to the more stable half-chair form.

It is not clear whether the nature of the molecular structure of (7) is a result of molecular stability or packing effects. However, it seems that the unexpected conformation of the cyclohexene is responsible for the behaviour of (7) under irradiation. As a result of this conformation the non-bonded distance between one of the H atoms in a δ position and an O atom of a carbonyl group is short (2·727 Å) and an H abstraction takes place. In solution an H abstraction or a $2\pi + 2\pi$ cycloaddition may occur which indicates that the conformation found in the crystal also exists in solution.

Bond lengths and angles

Most bond lengths and angles need no comment; however, some features should be noticed.

As a result of the variation in the conformation of the central cyclohexene moiety in (7) and (8) the angles at the double bond are smaller than in (1)–(6). Those angles in (7)–(8) lie in the range 114·6 to 116·9° while in (1)–(6) those angles lie in the range 121·2 to 125·2°.

There are severe non-bonded interactions between H atoms at the position δ to the carbonyl groups (see I). The distances lie in the range 1·901 to 2·026 Å in compounds (2), (5)–(8). However, the non-bonded interactions do not exert significant distortions at the double bond. The outer torsion angles (τ in I) are 5·1° in (1) although no close contacts between H atoms are observed, and 4·1 to 11·9° in (2), (5)–(8).

The 'cage' in compound (10) consist of a planar four-membered ring, two five-membered rings and two six-membered rings showing the same pattern of conformations, bond distances and angles as found in similar compounds (Mehta, Singh, Srikrishna & Cameron, 1979; Golič & Leban, 1980; Schwarzenbach, 1968).

Conclusion

It is shown that in six out of the eight bicycloalkenyl adducts the molecular structures are controlled by the most stable conformations of the various ring systems. In two compounds, (7) and (8), the conformation of the central cyclohexene ring is the less stable one and is responsible for the photochemical rearrangement detected in (7).

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References

Allinger, N. L., Tribble, M. T. & Miller, M. A. (1972). *Tetrahedron*, **28**, 1173–1190.

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

Bocian, D. F. & Strauss, H. L. (1977). *J. Chem. Phys.* **67**, 1071–1081.

Bovill, M. J., Guy, M. H. P., Sim, G. A., White, D. N. J. & Herz, W. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 53–56.

Bucourt, R. (1977). *Top. Stereochem.* **8**, 159–225.

Buys, H. R. (1969). *Recl Trav. Chim. Pays-Bas*, **88**, 1003–1011.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Deutsch, J. & Mandelbaum, A. (1969). *J. Am. Chem. Soc.* **91**, 4809–4813.

Deutsch, J. & Mandelbaum, A. (1971). *J. Chem. Soc. B*, pp. 886–889.

Dillen, J. & Geise, H. J. (1980). *J. Mol. Struct.* **69**, 137–144.

Eliel, E. L., Allinger, N. L., Angyal, S. J. & Morrison, G. A. (1965). *Conformation Analysis*, pp. 38–40. New York: Interscience.

Fuchs, B. (1978). *Top. Stereochem.* **10**, 1–94.

Geise, H. J. & Mijlhoff, F. C. (1971). *Recl Trav. Chim. Pays-Bas*, **90**, 577–583.

Golič, L. & Leban, I. (1980). *Acta Cryst.* B**36**, 1520–1522.

Hendrickson, J. B. (1961). *J. Am. Chem. Soc.* **83**, 4537–4547.

Karpati, A., Rave, A., Deutsch, J. & Mandelbaum, A. (1973), *J. Am. Chem. Soc.* **95**, 4244–4248.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mandelbaum, A., Kaftory, M. & Weisz, A. (1984). To be published.

Mehta, G., Singh, V., Srikrishna, A. & Cameron, T. S. (1979). *Tetrahedron Lett.* pp. 4595–4598.

Sasvári, K. & Low, M. (1965). *Acta Cryst.* **19**, 840–848.

Scheffer, J. R. & Dzakpasu, A. (1978). *J. Am. Chem. Soc.* **100**, 2163–2173.

Schwarzenbach, D. (1968). *Acta Cryst.* B**24**, 238–246.

Sheldrick, G. M. (1976). *SHELX.* Program for crystal structure determination. Univ. of Cambridge, England.

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