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Structure of *cis-cisoid-cis-* and *cis-transoid-cis-*Tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione and *cis-cisoid-cis-* and *trans-cisoid-trans-*Tricyclo[9.3.0.0^{3,7}]tetradecane-2,9-dione

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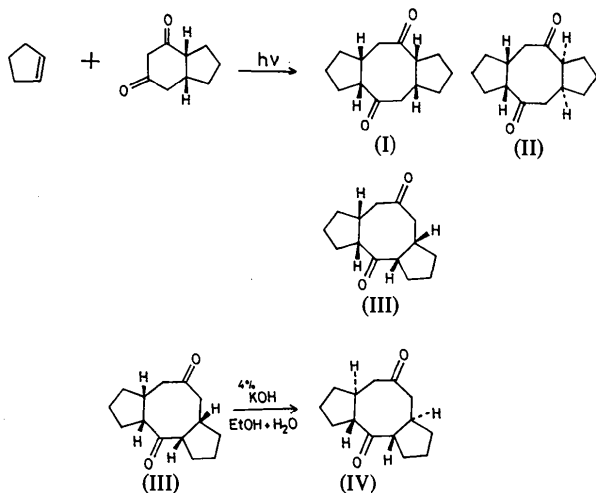
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Abstract. C₁₄H₂₀O₂, $M_r = 220.3$, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $F(000) = 480$ or 240 , $T = 295\text{--}299$ (1) K. *cis-cisoid-cis*-Tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione (m.p. 477.2–477.7 K) (I): monoclinic, $C2/c$, $a = 11.994$ (2), $b = 5.451$ (1), $c = 18.306$ (2) \AA , $\beta = 91.49$ (2) $^\circ$, $V = 1196.4$ (3) \AA^3 , $Z = 4$, $D_m = 1.21$ (2), $D_x = 1.22 \text{ Mg m}^{-3}$, $\mu = 0.07 \text{ mm}^{-1}$, $R = 0.040$ for 745 observed unique reflections. *cis-transoid-cis*-Tricyclo[9.3.0.0^{4,8}]tetradecane-2,9-dione (m.p. 415.2–416.2 K) (II): monoclinic, $P2_1/n$, $a = 11.761$ (3), $b = 9.208$ (1), $c = 5.594$ (1) \AA , $\beta = 98.02$ (2) $^\circ$, $V = 599.9$ (2) \AA^3 , $Z = 2$, $D_m = 1.19$ (2), $D_x = 1.22 \text{ Mg m}^{-3}$, $\mu = 0.07 \text{ mm}^{-1}$, $R = 0.048$ for 603 reflections. *cis-cisoid-cis*-Tricyclo[9.3.0.0^{3,7}]tetradecane-2,9-dione (m.p. 369.2–370.2 K) (III): monoclinic, $P2_1/n$, $a = 12.316$ (2), $b = 17.833$ (3), $c = 5.390$ (1) \AA , $\beta = 90.06$ (2) $^\circ$, $V = 1183.8$ (4) \AA^3 , $Z = 4$, $D_m = 1.23$ (2), $D_x = 1.24 \text{ Mg m}^{-3}$, $\mu = 0.08 \text{ mm}^{-1}$, $R = 0.052$ for 1293 reflections. *trans-cisoid-trans*-Tricyclo[9.3.0.0^{3,7}]tetradecane-2,9-dione (m.p. 393.2–394.2 K) (IV): monoclinic, $P2_1/c$, $a = 11.625$ (3), $b = 5.306$ (1), $c = 21.108$ (3) \AA , $\beta = 104.18$ (1) $^\circ$, $V = 1262.3$ (4) \AA^3 , $Z = 4$, $D_m = 1.14$ (3), $D_x = 1.16 \text{ Mg m}^{-3}$, $\mu = 0.07 \text{ mm}^{-1}$, $R = 0.038$ for 601 reflections. The 5-8-5 compounds (I), (II) and (III) synthesized by a photochemical reaction have ring junctions all *cis*. (I) and (II) are geometrical isomers having different relative configuration of two ring junctions, *cisoid* and *transoid*. In an alkaline solution (III) was changed to the geometrical isomer (IV). The central eight-membered rings in

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(I), (II), (III) and (IV) take twist-boat, chair, boat-chair and chair-chair forms, respectively.

Introduction. One of the authors (MU) aims to synthesize a linearly fused 5-8-5 ring system (Umehara, Hishida, Okumoto, Ohba, Ito & Saito, 1987). The title compounds were obtained by the photocycloaddition of bicyclo[4.3.0]nonane-2,4-dione to cyclopentene, and separated by column chromatography. The *cis* junction of 5-8 ring compounds is changed to *trans* in an acidic or alkaline solution (Umehara, Hishida, Fujieda, Ogura & Takayanagi, 1978; Begley, Mellor & Pattenden, 1983). By the use of this reaction, (III) could be isomerized to (IV).



An X-ray crystal structure determination of these compounds was undertaken to reveal the ring junctions and conformations of the eight-membered rings.

Experimental. D_m measured by flotation in aqueous solution of potassium iodide. Rigaku AFC-5 four-circle diffractometer, Mo $K\alpha$ radiation monochromatized with graphite plate. Unit-cell parameters refined by least squares for 20–24 reflections ($20 < 2\theta < 30^\circ$). No absorption correction. Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Non-H atoms refined with anisotropic thermal parameters. All H atoms located in difference synthesis and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ was minimized. $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); Universal Crystallographic Computation Program System *UNICSIII* (Sakurai & Kobayashi, 1979), FACOM M-380R computer of this university. Final atomic parameters are listed in Table 1, and bond lengths and angles in Table 2. Experimental details are as follows. (I): Colorless prismatic crystals from an acetone solution, $0.2 \times 0.2 \times 0.55$ mm. Laue

Table 1. Positional parameters ($\times 10^4$) and equivalent isotropic temperature factors (Hamilton, 1959)

	x	y	z	$B_{eq}(\text{\AA}^2 \times 10)$
(I)				
O	-1450 (1)	-2638 (3)	2266 (1)	43
C(1)	-1125 (2)	1410 (3)	1835 (1)	28
C(2)	-1193 (1)	-526 (3)	2416 (1)	29
C(3)	-958 (2)	188 (4)	3203 (1)	32
C(4)	-90 (2)	2190 (3)	3352 (1)	28
C(5)	-11 (2)	2858 (5)	4175 (1)	46
C(6)	1211 (2)	2639 (5)	4413 (1)	47
C(7)	1665 (2)	741 (4)	3898 (1)	41
(II)				
O	1723 (2)	-799 (2)	2719 (3)	53
C(1)	1163 (2)	-1250 (3)	-1463 (5)	40
C(2)	1322 (2)	-319 (3)	763 (4)	36
C(3)	956 (2)	1248 (3)	526 (5)	40
C(4)	116 (2)	1722 (3)	2218 (5)	38
C(5)	56 (3)	3357 (4)	2469 (10)	88
C(6)	-1143 (3)	3728 (4)	2859 (6)	64
C(7)	1841 (3)	-2657 (4)	-1268 (7)	78
(III)				
O(1)	4062 (2)	2486 (1)	2601 (3)	44
O(2)	1222 (2)	2475 (1)	1972 (4)	49
C(1)	3668 (2)	1722 (2)	6109 (5)	33
C(2)	3861 (2)	2463 (2)	4824 (5)	31
C(3)	3797 (2)	3164 (2)	6363 (5)	32
C(4)	4263 (3)	3875 (2)	5268 (6)	48
C(5)	3802 (3)	4495 (2)	6779 (8)	75
C(6)	2775 (3)	4213 (2)	7947 (6)	55
C(7)	2631 (2)	3389 (2)	7156 (5)	36
C(8)	1802 (2)	3321 (2)	5047 (6)	44
C(9)	1512 (2)	2550 (2)	4101 (5)	36
C(10)	1530 (2)	1884 (2)	5836 (5)	39
C(11)	2541 (2)	1378 (2)	5566 (5)	36
C(12)	2685 (2)	1006 (2)	3048 (6)	45
C(13)	3846 (3)	721 (2)	3021 (6)	50
C(14)	4428 (3)	1098 (2)	5209 (6)	50
(IV)				
O(1)	8069 (3)	2887 (6)	6671 (2)	64
O(2)	4911 (3)	251 (9)	6396 (2)	112
C(1)	8054 (4)	-1058 (8)	6142 (2)	42
C(2)	8115 (3)	614 (8)	6725 (2)	38
C(3)	8166 (3)	-588 (8)	7377 (2)	36
C(4)	8971 (4)	825 (11)	7960 (2)	63
C(5)	8436 (4)	324 (12)	8536 (2)	81
C(6)	7319 (4)	-1216 (9)	8289 (2)	58
C(7)	6961 (4)	-683 (9)	7555 (2)	41
C(8)	6076 (4)	-2554 (10)	7156 (2)	56
C(9)	5555 (4)	-1584 (10)	6483 (2)	62
C(10)	5896 (4)	-2764 (11)	5901 (2)	64
C(11)	6811 (4)	-1232 (9)	5666 (2)	50
C(12)	7080 (5)	-2246 (11)	5041 (2)	78
C(13)	8275 (6)	-1202 (15)	5028 (2)	118
C(14)	8838 (4)	-179 (11)	5695 (2)	69

group $2/m$, systematic absences hkl with $h + k$ odd and $h0l$ with h or l odd (space group Cc or $C2/c$). Intensities measured up to $2\theta_{\max} = 55^\circ$ ($h0 \rightarrow 14$, $k - 7 \rightarrow 0$, $l - 23 \rightarrow 23$), 1430 reflections measured, 783 observed [$|F_o| > 3\sigma(|F_o|)$], 745 unique ($R_{\text{int}} = 0.010$). Mean ratio of $|F_o|$ of five standard reflections, $0.996 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.007$. Tentatively, assuming space group Cc , the structure was solved ($R = 0.033$, $wR = 0.038$). The C–C bond lengths showed unusually large variation from 1.412 (6) to 1.613 (5) Å, and the atomic coordinates suggested that there was an intramolecular twofold axis parallel to **b**. Accordingly, the space group was determined to be $C2/c$. Final $R = 0.040$, $wR = 0.048$, $S = 1.91$, $(\Delta/\sigma)_{\max} = 0.32$, $-0.2 < \Delta\rho < 0.2 e \text{\AA}^{-3}$. (II): Colorless hexagonal prismatic crystals from an ether–hexane solution,

Table 2. Bond lengths (Å), bond angles (°) and transannular H...H distances (Å)

(I)			
O(1)–C(2)	1.221 (2)	O(1)–C(2)–C(1)	121.4 (2)
C(1)–C(2)	1.502 (2)	O(1)–C(2)–C(3)	119.8 (2)
C(2)–C(3)	1.512 (3)	C(1)–C(2)–C(3)	118.8 (1)
C(3)–C(4)	1.528 (3)	C(2)–C(3)–C(4)	117.6 (2)
C(4)–C(5)	1.550 (3)	C(3)–C(4)–C(5)	111.4 (2)
C(5)–C(6)	1.523 (3)	C(4)–C(5)–C(6)	107.1 (2)
C(6)–C(7)	1.511 (3)	C(5)–C(6)–C(7)	103.6 (2)
C(1)–C(4')	1.564 (3)	C(2)–C(1)–C(4')	114.5 (2)
C(1)–C(7')	1.519 (2)	C(2)–C(1)–C(7')	115.3 (2)
H(C1)...H(C4)	2.33 (1)	C(4')–C(1)–C(7')	104.5 (1)
H(C4)...H(C4')	2.21 (6)	C(3)–C(4)–C(1')	113.6 (2)
		C(5)–C(4)–C(1')	104.1 (1)
		C(6)–C(7)–C(1')	103.6 (2)
(II)			
O–C(2)	1.213 (3)	C(2)–C(1)–C(7)	115.1 (2)
C(1)–C(2)	1.502 (4)	O–C(2)–C(1)	121.9 (2)
C(1)–C(7)	1.517 (5)	O–C(2)–C(3)	119.9 (2)
C(2)–C(3)	1.506 (4)	C(1)–C(2)–C(3)	118.2 (2)
C(3)–C(4)	1.524 (4)	C(2)–C(3)–C(4)	114.9 (2)
C(4)–C(5)	1.515 (5)	C(3)–C(4)–C(5)	112.6 (2)
C(5)–C(6)	1.496 (5)	C(4)–C(5)–C(6)	107.3 (3)
C(1)–C(4')	1.566 (3)	C(2)–C(1)–C(4')	112.7 (2)
C(6)–C(7')	1.495 (5)	C(7)–C(1)–C(4')	104.9 (2)
H(C1)...H(C3)I	2.31 (3)	C(3)–C(4)–C(1')	115.7 (2)
		C(5)–C(4)–C(1')	104.2 (2)
		C(5)–C(6)–C(7')	102.3 (3)
		C(1)–C(7)–C(6')	102.3 (3)
(III)			
O(1)–C(2)	1.224 (3)	C(2)–C(1)–C(11)	113.7 (2)
O(2)–C(9)	1.209 (3)	C(2)–C(1)–C(14)	113.2 (2)
C(1)–C(2)	1.511 (5)	C(1)–C(1)–C(14)	101.6 (3)
C(1)–C(11)	1.545 (4)	O(1)–C(2)–C(1)	120.7 (3)
C(1)–C(14)	1.533 (5)	O(1)–C(2)–C(3)	121.5 (3)
C(2)–C(3)	1.502 (5)	C(1)–C(2)–C(3)	117.8 (3)
C(3)–C(4)	1.512 (5)	C(2)–C(3)–C(4)	117.5 (3)
C(3)–C(7)	1.552 (4)	C(2)–C(3)–C(7)	114.6 (2)
C(4)–C(5)	1.486 (5)	C(4)–C(3)–C(7)	104.0 (3)
C(5)–C(6)	1.500 (5)	C(3)–C(4)–C(5)	105.3 (3)
C(6)–C(7)	1.540 (5)	C(4)–C(5)–C(6)	107.7 (3)
C(7)–C(8)	1.532 (4)	C(5)–C(6)–C(7)	107.5 (3)
C(8)–C(9)	1.509 (5)	C(3)–C(7)–C(6)	102.5 (2)
C(9)–C(10)	1.512 (5)	C(3)–C(7)–C(8)	113.0 (2)
C(10)–C(11)	1.545 (4)	G(6)–C(7)–C(8)	110.9 (3)
C(11)–C(12)	1.521 (4)	C(7)–C(8)–C(9)	118.7 (3)
C(12)–C(13)	1.518 (5)	O(2)–C(9)–C(8)	119.4 (3)
C(13)–C(14)	1.535 (5)	O(2)–C(9)–C(10)	120.3 (3)
H(C1)...H(C3)	2.22 (3)	C(8)–C(9)–C(10)	120.2 (3)
H(C1)...H(C7)	2.83 (3)	C(9)–C(10)–C(11)	114.3 (2)
H(C1)...H(C10)I	2.22 (3)	C(1)–C(11)–C(10)	118.3 (3)
H(C7)...H(C10)I	2.22 (3)	C(1)–C(11)–C(12)	103.7 (2)
		C(10)–C(11)–C(12)	115.7 (2)
		C(11)–C(12)–C(13)	105.4 (2)
		C(12)–C(13)–C(14)	106.6 (3)
		C(1)–C(14)–C(13)	106.0 (3)
(IV)			
O(1)–C(2)	1.211 (5)	C(2)–C(1)–C(11)	114.6 (4)
O(2)–C(9)	1.214 (7)	C(2)–C(1)–C(14)	114.0 (4)
C(1)–C(2)	1.505 (6)	C(1)–C(1)–C(14)	102.7 (3)
C(1)–C(11)	1.547 (6)	O(1)–C(2)–C(1)	121.2 (4)
C(1)–C(14)	1.536 (7)	O(1)–C(2)–C(3)	119.9 (4)
C(2)–C(3)	1.505 (6)	C(1)–C(2)–C(3)	118.8 (4)
C(3)–C(4)	1.545 (6)	C(2)–C(3)–C(4)	113.8 (3)
C(3)–C(7)	1.537 (6)	C(2)–C(3)–C(7)	113.8 (3)
C(4)–C(5)	1.519 (7)	C(4)–C(3)–C(7)	103.4 (4)
C(5)–C(6)	1.515 (7)	C(3)–C(4)–C(5)	105.4 (4)
C(6)–C(7)	1.529 (6)	C(4)–C(5)–C(6)	107.7 (4)
C(7)–C(8)	1.526 (6)	C(5)–C(6)–C(7)	104.3 (4)
C(8)–C(9)	1.493 (6)	C(3)–C(7)–C(6)	102.4 (3)
C(9)–C(10)	1.516 (7)	C(3)–C(7)–C(8)	114.7 (4)
C(10)–C(11)	1.516 (7)	C(6)–C(7)–C(8)	114.7 (4)
C(11)–C(12)	1.526 (7)	C(7)–C(8)–C(9)	111.2 (4)
C(12)–C(13)	1.502 (9)	O(2)–C(9)–C(8)	120.8 (4)
C(13)–C(14)	1.501 (6)	O(2)–C(9)–C(10)	118.9 (4)
H(C1)...H(C3)	2.30 (3)	C(8)–C(9)–C(10)	120.2 (4)
H(C1)...H(C10)I	2.64 (4)	C(9)–C(10)–C(11)	112.8 (4)
H(C3)...H(C8)I	2.55 (4)	C(1)–C(11)–C(10)	116.0 (4)
H(C8)I...H(C10)I	2.38 (3)	C(1)–C(11)–C(12)	103.0 (4)
		C(10)–C(11)–C(12)	113.7 (4)
		C(11)–C(12)–C(13)	105.8 (4)
		C(12)–C(13)–C(14)	108.0 (5)
		C(1)–C(14)–C(13)	106.2 (4)

0.3 × 0.3 × 0.4 mm. Laue group $2/m$, systematic absences $h0l$ with $h+l$ odd and $0k0$ with k odd ($P2_1/n$). $2\theta_{\max} = 50^\circ$ ($h-14 \rightarrow 14$, $k-10 \rightarrow 0$, $l0 \rightarrow 6$), 1166 reflections measured, 668 observed, 603 unique ($R_{\text{int}} = 0.008$). Standard reflections, $1.000 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.009$. Since $Z = 2$, the molecule is required to possess a center of symmetry. Final $R = 0.048$, $wR = 0.052$, $S = 2.10$, $(\Delta/\sigma)_{\max} = 0.35$, $-0.2 < \Delta\rho < 0.2 \text{ e } \text{\AA}^{-3}$. (III): Colorless plate-like crystals from an ether–hexane solution, $0.3 \times 0.5 \times 0.6$ mm. Although β is very nearly a right angle, Laue group is $2/m$. Systematic absences $h0l$ with $h+l$ odd and $0k0$ with k odd ($P2_1/n$). $2\theta_{\max} = 50^\circ$ ($h0 \rightarrow 14$, $k0 \rightarrow 21$, $l-6 \rightarrow 6$), 2189 reflections measured, 1350 observed, 1293 unique ($R_{\text{int}} = 0.010$). Standard reflections, $0.988 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.004$. Final $R = 0.052$, $wR = 0.062$, $S = 2.48$, $(\Delta/\sigma)_{\max} = 0.45$, $-0.2 < \Delta\rho < 0.2 \text{ e } \text{\AA}^{-3}$. (IV): Colorless plate-like crystals from an ether–hexane solution, $0.4 \times 0.2 \times 0.1$ mm. Laue group $2/m$, systematic absences $h0l$ with l odd and $0k0$ with k odd ($P2_1/c$). $2\theta_{\max} = 40^\circ$ ($h-11 \rightarrow 11$, $k-5 \rightarrow 0$, $l0 \rightarrow 20$), 1207 reflections measured, 625 observed, 601 unique ($R_{\text{int}} = 0.007$). Standard reflections, $0.993 < \sum(|F_o|/|F_o|_{\text{initial}})/5 < 1.000$. Final $R = 0.038$, $wR = 0.036$, $S = 1.39$, $(\Delta/\sigma)_{\max} = 0.17$, $-0.2 < \Delta\rho < 0.1 \text{ e } \text{\AA}^{-3}$.*

Discussion. Molecular structures are shown in Fig. 1. (I) has a twofold axis and (II) has a center of symmetry. (IV) has approximate mirror symmetry passing through O(1), C(2), C(9) and O(2) atoms. The ring junctions in photochemical cycloaddition products (I), (II) and (III) are all *cis* as expected from the reaction mechanism. As there are two forms in the enolization of β -diketones, two kinds of structural isomers are obtained. Furthermore, *cisoid* and *transoid* connections between the *cis* ring junctions are possible, and hence four isomers are expected. One of them, the *transoid* isomer of (III), has not yet been isolated. The side views of the eight-membered rings are shown in Fig. 2. The conformations are (I) twist-boat, (II) chair, (III) boat-chair, and (IV) chair-chair forms. The variety of the conformations is the result of reduction in the puckering flexibility of the eight-membered ring by addition of the five-membered rings in different manners.

The molecular-mechanics calculation has been performed by the program *MM2* (Allinger, 1977). The molecular energies for the typical conformations are listed in Table 3. The stabilities of the observed forms in

* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom bond distances, angles and atomic positions for (I), (II), (III) and (IV) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44891 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(I) and (II) are well established. However, the other forms are suggested to be more stable for (III) and (IV). These molecules might take different conformations in solution. Further investigations are needed. The C—C bond length at ring fusions is longer by 0.04 Å on average than the other C—C bonds as observed in 5-8 ring compounds (Okumoto, Ohba, Saito, Ishii,

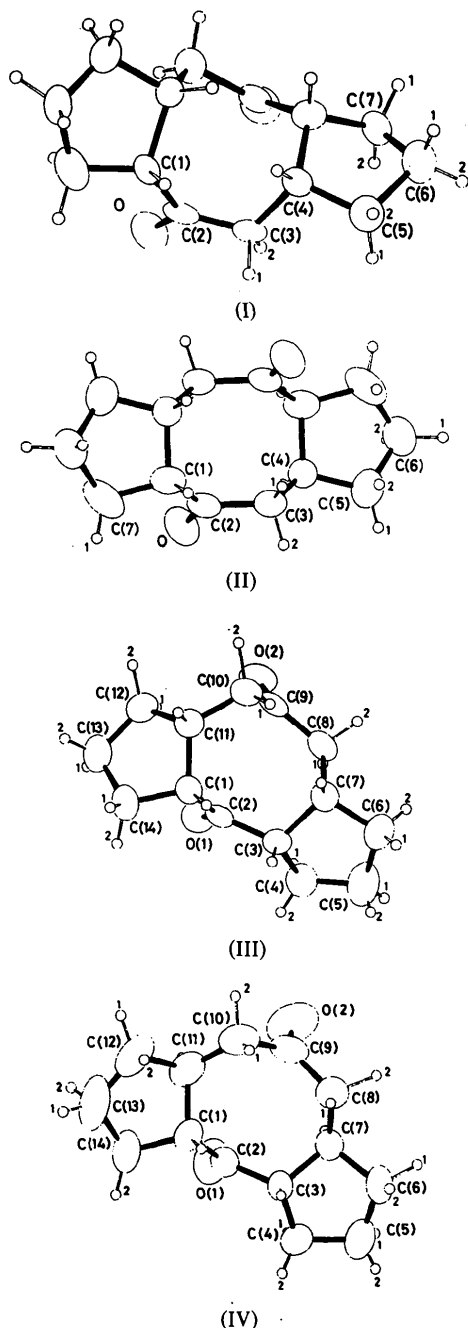


Fig. 1. ORTEP drawings (Johnson, 1965) of (I), (II), (III) and (IV) with 50% probability ellipsoids. H atoms are represented by circles of radius 0.08 Å.

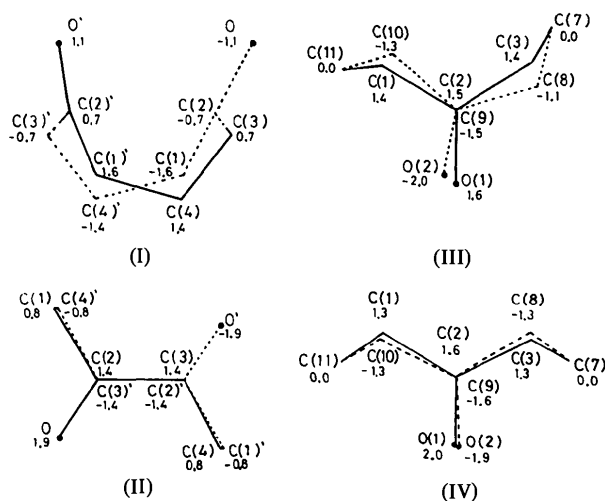


Fig. 2. Projections of the eight-membered rings in (I), (II), (III) and (IV) along the vectors: (I) midpoint of C(4) and C(1') to the midpoint of C(1) and C(4'); (II) midpoint of C(2) and C(3) to the midpoint of C(2') and C(3'), (III) and (IV) C(9) to C(2). The numerical values are the relative heights of the atoms (Å).

Table 3. Total energies (kJ mol^{-1}) calculated by MM2

Conformation of the central eight-membered ring	(I)	(II)	(III)	(IV)
Boat-chair	152.40	159.39	151.77 (obs.)	131.67
Twist boat-chair	—*	144.86	145.28	—
Chair-chair	160.94	153.07	170.07	143.65 (obs.)‡
Twist boat	139.84 (obs.)†	185.10	149.85	—
Twist chair	157.47	—	—	190.16
Chair	153.99	136.24 (obs.)	—	—

* No energy minimum around the starting conformation.

† Observed conformation in crystals.

‡ Top and bottom atoms of the observed chair-chair form of (IV) are C(7) and C(11). If they were C(3) and C(10), the molecular energy would reduce to $138.58 \text{ kJ mol}^{-1}$.

Umehara & Hishida, 1987). The cyclopentane rings take envelope conformations, out-of-plane atoms being (I) C(7), (II) C(6), (III) C(3) and C(11), and (IV) C(7) and C(11).

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10-Fluoro-all-trans- α -retinal

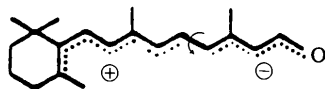
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Abstract. $C_{20}H_{27}FO$, $M_r = 302.41$, monoclinic, $P2_1/c$, $a = 6.105$ (5), $b = 21.673$ (22), $c = 13.925$ (7) Å, $\beta = 96.66$ (5)°, $V = 1830$ (2) Å³, $Z = 4$, $D_x = 1.10$, $D_m = 1.09$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.68$ cm⁻¹, $F(000) = 656$, $T = 298$ K, $R = 0.062$, $wR = 0.046$ for 1797 unique observed reflections. The principal distortions in the polyene portion of the molecule can be seen in the angles opposite the methyl groups (119.9 and 121.7°, a steric effect) and that opposite fluorine (131.9°, an inductive effect). The hexene ring is in the half-chair form, and its double bond is not in conjugation with the all-*trans* chain.

Introduction. It is well known that the only action of light in vision is to isomerize the retinal molecule from the 11-*cis* to the all-*trans* configuration (Hubbard & Kropf, 1958; Hamanaka, Mitsui, Ashida & Kakudo, 1972). The 11-*cis* isomer can be obtained by direct irradiation of the all-*trans* isomer in alcohol solvents (Hubbard & Wald, 1952–1953; Brown & Wald, 1956). The zwitterionic intermediate (Liu, Denny, Grodowski & Asato, 1979) leading to the formation of the 11-*cis* isomer twists about the C(11)–C(12) double bond. Any substituent which destabilizes the zwitterionic intermediate should suppress the yield of the 11-*cis* isomer.



The title compound was prepared to test this hypothesis, and its crystal structure was determined to learn accurate geometry for molecular-modelling calculations on this reaction.

Experimental. Yellow colored crystals. Approximate parallelepiped: 0.6 × 0.2 × 0.3 mm. D_m by flotation in aqueous NH_4Br . Data collected by a Syntex PI

automated diffractometer, graphite-monochromated $Mo K\alpha$ radiation. Cell constants from 15 reflections with $6.2 < 2\theta < 22.0^\circ$. No absorption correction. $2\theta_{max} = 50^\circ$ ($0 \leq h \leq 7$, $0 \leq k \leq 25$, $-16 \leq l \leq 16$). Three check reflections ($\bar{2}0\bar{2}$, $1\bar{5}0$, 014) measured after every 97 data points showed small fluctuations; corrections were made. 1797 of 3562 reflections with $I > 2\sigma(I)$ used in refinement. Lorentz–polarization correction applied. Non-H atoms were determined by *MULTAN80* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1976) for non-H atoms with isotropic thermal parameters converged to $R = 0.151$. After the final anisotropic refinement of the complete structure (isotropic for H atoms): $R = 0.062$, $wR = 0.046$, $S = 1.83$, max. $\Delta/\sigma = 0.08$; $\sum w(F_o - |F_c|)^2$ minimized, $w = \sigma^{-2}(F)$, $p = 0.02$ (Peterson & Levy, 1957). No significant features in the final ΔF synthesis with max. $\Delta\rho = 0.22$ e Å⁻³. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure of the title compound is presented in Fig. 1. The C(5)–C(6)–C(7)–C(8) torsion angle is +58.4° for the molecule shown in the figure. This torsion angle agrees with the theoretical angle (60°) based on the torsional potential calculated for the rotation of the cyclohexene ring about the C(6)–C(7) bond in the retinals (Honig, Warshel & Karplus, 1975). The double bond in the hexene ring is C(4)–C(5) (1.320 Å). The conjugated chain C(7)–O(21) has the all-*trans* configuration. The average single- and double-bond lengths in the conjugated chain are 1.437 and 1.320 Å respectively. The chain C(6)–O(21) is approximately planar (plane 1); C(10) shows the largest deviation (0.054 Å) from this least-squares plane. All atoms attached to this chain are also approximately in the same plane [largest deviation, F(22), 0.079 Å]. The measure of the in-plane bending in the polyene chain

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