1·344 (4) and 1·349 (4) Å (substituted), 1·331 (4) and 1·351 (5) Å (unsubstituted) in the two independent molecules compared to 1·329 (7) Å (substituted) and 1·317 (8) Å (unsubstituted) in the present molecule.

Other bond lengths and bond angles in the present compound are comparable to those observed in the systems referenced above. The most significant intermolecular contact in the present molecule is a possible hydrogen bond O(1)···H(71) ($\frac{1}{2}-x$, $-\frac{1}{2}-y$, $\frac{1}{2}-z$) of length 2·49 (7) Å [C(1)—O(1)···H(71) = 115 (1)°; C(7)—H(71)···O(1) = 135 (5)°]. All other O···H contacts are >2·70 (6) Å in length. A view of the crystal packing is given in Fig. 2.

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Structure of All-*trans*-3,4-didehydroretinal (Retinal$_2$)

BY CHARLES J. SIMMONS*

Chemistry Department, University of Puerto Rico, Rio Piedras, Puerto Rico 00931, *USA*

AND ALFRED E. ASATO AND ROBERT S. H. LIU

Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822, *USA*

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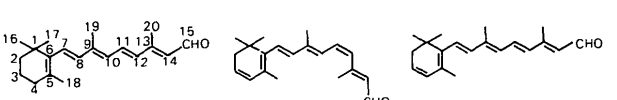
Abstract. $C_{20}H_{26}O$, $M_r = 282·4$, monoclinic, $P2_1/c$, $a = 15·054$ (8), $b = 8·105$ (3), $c = 18·417$ (10) Å, $\beta = 127·01$ (3)°, $V = 1794$ (1) Å^3, $Z = 4$, $D_x = 1·046$ Mg m^{-3}, λ(Cu $K\bar{\alpha}$) = 1·5418 Å, $\mu = 0·44$ mm^{-1}, $F(000) = 616$, $T = 302$ K. Final $R = 0·052$ for 2115 unique significant reflections. Except for the chemical and structural differences between the rings, all-*trans*-3,4-didehydroretinal (or retinal$_2$) and all-*trans*-retinal are nearly isomorphous. It is found that the distance between the center of the ring and the aldehydic carbon is 12·3 Å for both all-*trans*-retinal$_2$ and retinal. This distance exceeds the longitudinal restriction of the binding zone of bovine opsin, which explains why the *in vitro* pigment yields for both are too low to measure.

Introduction. Several studies have recently explored the relationship between the structural properties of retinal isomers (1) and homologues and their *in vitro* rates of pigment formation with bovine opsin (Matsumoto & Yoshizawa, 1978; Daemen, 1978; Matsumoto, Liu, Simmons & Seff, 1980; Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984; Liu & Asato, 1984). On the basis of these results, a longitudinal restriction of the binding cavity of opsin was postulated: low recombination rates occur when the distance between the center of the trimethylcyclohexenyl ring and the reacting aldehydic C(15) atom (see Fig. 1) is above or below a particular optimum range, *ca* 10·1–10·9 Å (Matsumoto *et al.*, 1980; Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984). What is surprising, however, is the lack of information about retinal$_2$ isomers and homologues, even though the 11-*cis* isomer, (2), is the only other visual chromophore (besides 11-*cis*-retinal) known in naturally occurring systems to form a pigment known as porphyropsin (Wald, 1953; Bridges, 1972).



(1) All-*trans*-retinal (2) 11-*cis*-Retinal$_2$ (3) All-*trans*-retinal$_2$

* To whom correspondence should be addressed.

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One reason for the lack of experimental results for retinal$_2$ systems is because the isomers are less stable and relatively unavailable. In fact, only seven out of the 16 possible geometric isomers have thus far been prepared – six (all-*trans*, 9-*cis*, 11-*cis*, 13-*cis*, 9,13-di*cis*, and 11,13-di*cis*) by Isler and coworkers (Schwieter, Saucy, Montavan, Planta, Rüegg & Isler, 1962), and one, the sterically hindered 7-*cis* isomer, by Liu and coworkers (Liu, Asato & Denny, 1977). Preliminary results indicate that the 7-*cis*, 9-*cis*, and 9,13-di*cis*, as well as the naturally occurring 11-*cis* isomer, are capable of pigment formation when incubated with bovine opsin (Matsumoto, Asato & Liu, 1979; Azuma, Azuma & Kito, 1973; Matsumoto & Liu, 1980, unpublished results).

If retinal isomers are to be used as meaningful 'probes' to better understand protein–substrate interactions, then accurate molecular structures of a series of them are needed. The crystal structures of several retinal isomers have been determined, *viz* all-*trans*-retinal (Hamanaka, Mitsui, Ashida & Kakudo, 1972), 11-*cis*-retinal (Gilardi, Karle & Karle, 1972; Drikos, Rüppel, Dietrich & Sperling, 1981), 13-*cis*-retinal (Simmons, Liu, Denny & Seff, 1981), methyl 7,9-di*cis*-retinoate (the retinal is an oil; Matsumoto *et al.*, 1980), 9-*cis*-retinal (Simmons & Liu, 1985, unpublished results), and 19,19,19-trifluoro-9-*cis*-retinal (Simmons & Liu, 1985, unpublished results), but, prior to this study, no structure of a retinal$_2$ isomer had been determined.

The introduction of the 7-*cis* geometry to the retinal$_2$ series by photochemical methods (Liu *et al.*, 1977; Ramamurthy & Liu, 1973) now provides a pathway for synthesizing the seven remaining isomers containing the hindered geometry. Thus, it is opportune to carry out detailed conformational analyses on retinal$_2$ isomers in solutions (Nakayama, Bopp & Liu, 1984) as well as in solids. The present study on all-*trans*-retinal$_2$ (3) represents our initial effort to determine the crystal structures of isomers in this series.

Experimental. All-*trans*-retinal$_2$ was prepared according to standard procedures (Schwieter *et al.*, 1962). The compound was purified by flash chromatography on a silica-gel column and then recrystallized from *n*-hexane. Its spectroscopic properties (UV and ^{1}H NMR) were identical to those published.

Irregularly shaped orange-colored crystal, 0·62 × 0·28 × 0·28 mm, selected for X-ray diffraction study. Syntex $P\bar{1}$ four-circle computer-controlled diffractometer with graphite-monochromatized Cu $K\alpha$ radiation ($K\alpha_1 = 1{\cdot}5406$; $K\alpha_2 = 1{\cdot}5444$ Å) used for measurement of all diffraction intensities. Unit-cell constants and their standard deviations determined by least-squares treatment of angular coordinates of 15 reflections with 2θ values up to 57°. To avoid possible photodecomposition of the crystal, all intensities were measured in a darkened room. θ–2θ scan mode, constant scan speed (ω) in 2θ of 2° min^{-1}. Background time to scan time 0·5, scan range varied from −0·8 to 0·8° (2θ) about $K\alpha_1$–$K\alpha_2$ angles. Intensities of three check reflections, measured after every 100 reflections, showed a slight decrease of *ca* 4% during course of data collection, for which an appropriate linear decay correction was subsequently applied to the intensity data. Standard deviations assigned according to formula $\sigma(I) = \{[CT + (t_c/t_b)^2(B_1 + B_2)]\omega^2 + (pI)^2\}^{1/2}$, where CT is the total integrated count, t_c/t_b is the ratio of the total scan time to total background time, B_1 and B_2 are the background counts, $I = \omega[CT - (t_c/t_b)(B_1 + B_2)]$, and p (0·02) is a factor used to downweight intense reflections. Of 2482 unique reflections measured ($3 < 2\theta < 116°$, h 0→16, k 0→8, l −20→16), 2115 had intensities such that $I > 2\sigma(I)$. Intensities corrected for Lorentz and polarization effects, but not for absorption.

Table 1. *Fractional atomic coordinates* (×10^4, ×10^3 *for* H) *and isotropic thermal parameters with e.s.d.'s in parentheses*

The equivalent isotropic temperature factors, B_{eq}, have been calculated by $B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \cdots + \beta_{23}bc\cos\alpha)$; $\sigma(B_{eq}) = [\frac{8}{9}a^4\sigma^2(\beta_{11}) + \cdots + \frac{8}{9}b^2c^2\cos^2\alpha\sigma^2(\beta_{23})]^{1/2}$. This expression differs from that obtained from the usual propagation-of-error expression by a factor of $1/\sqrt{2}$ (Schomaker & Marsh, 1983).

	x	y	z	B_{eq},B_{iso}(Å^2)
C(1)	8165 (2)	10867 (3)	2723 (1)	4·7 (1)
C(2)	7925 (3)	10157 (4)	1847 (2)	6·5 (1)
C(3)	8673 (2)	8758 (3)	2019 (2)	6·1 (1)
C(4)	9041 (2)	7773 (3)	2704 (2)	5·8 (1)
C(5)	8816 (2)	8036 (3)	3369 (1)	4·9 (1)
C(6)	8378 (2)	9484 (3)	3371 (1)	4·5 (1)
C(7)	8170 (2)	9867 (3)	4037 (2)	5·1 (1)
C(8)	7566 (2)	8988 (3)	4196 (2)	5·2 (1)
C(9)	7343 (2)	9351 (3)	4847 (1)	5·0 (1)
C(10)	6588 (2)	8414 (3)	4832 (2)	5·4 (1)
C(11)	6270 (2)	8546 (3)	5424 (2)	5·2 (1)
C(12)	5490 (2)	7606 (3)	5354 (2)	5·2 (1)
C(13)	5186 (2)	7605 (3)	5967 (1)	4·9 (1)
C(14)	4399 (2)	6544 (3)	5809 (2)	5·7 (1)
C(15)	4001 (3)	6361 (4)	6347 (2)	7·5 (1)
C(16)	7140 (3)	11894 (4)	2423 (3)	7·6 (1)
C(17)	9188 (3)	11983 (4)	3197 (2)	7·1 (1)
C(18)	9162 (3)	6657 (4)	4037 (2)	6·9 (1)
C(19)	7966 (3)	10722 (4)	5511 (2)	6·1 (1)
C(20)	5779 (3)	8766 (5)	6750 (2)	6·6 (1)
O(21)	3270 (2)	5403 (3)	6161 (2)	10·6 (1)
H(2*A*)	706 (3)	968 (4)	142 (2)	10 (1)
H(2*B*)	801 (2)	1113 (4)	152 (2)	9 (1)
H(3)	882 (2)	851 (3)	158 (2)	7 (1)
H(4)	942 (2)	680 (3)	274 (2)	8 (1)
H(7)	849 (2)	1088 (3)	436 (2)	6 (1)
H(8)	721 (2)	800 (3)	384 (1)	6 (1)
H(10)	621 (2)	758 (3)	435 (2)	7 (1)
H(11)	669 (2)	935 (3)	591 (2)	6 (1)
H(12)	510 (2)	682 (3)	488 (2)	6 (1)
H(14)	400 (2)	585 (3)	527 (2)	6 (1)
H(15)	440 (2)	708 (4)	692 (2)	9 (1)
H(16*A*)	693 (2)	1269 (3)	190 (2)	9 (1)
H(16*B*)	740 (3)	1244 (4)	295 (3)	16 (2)
H(16*C*)	651 (2)	1109 (3)	219 (2)	10 (1)
H(17*A*)	926 (2)	1249 (3)	376 (2)	8 (1)
H(17*B*)	912 (2)	1299 (4)	284 (2)	9 (1)
H(17*C*)	987 (3)	1124 (4)	336 (2)	11 (1)
H(18*A*)	992 (3)	629 (4)	430 (2)	9 (1)
H(18*B*)	922 (3)	698 (4)	461 (2)	11 (1)
H(18*C*)	868 (3)	574 (5)	373 (2)	12 (1)
H(19*A*)	783 (3)	1080 (4)	598 (2)	12 (1)
H(19*B*)	868 (3)	1071 (5)	581 (2)	12 (1)
H(19*C*)	774 (3)	1167 (4)	522 (2)	9 (1)
H(20*A*)	553 (2)	871 (3)	710 (2)	8 (1)
H(20*B*)	665 (3)	848 (4)	715 (2)	11 (1)
H(20*C*)	571 (2)	989 (4)	658 (2)	10 (1)

Space group $P2_1/c$ assigned unambiguously on basis of systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$. A 21-atom fragment from the structure of all-*trans*-retinal (Hamanaka *et al.*, 1972) was used as input to *MULTAN* (Germain, Main & Woolfson, 1971). An overall isotropic thermal parameter, $B_{iso} = 5{\cdot}3$ Å^2, was calculated from the Debye curve, and normalized structure-factor amplitudes for the 300 reflections with $|E| > 1{\cdot}57$ were used to generate a three-dimensional E function. This function, phased as indicated by the solution with the largest-combined-figure-of-merit, 2·10, revealed the positions of all 21 non-H atoms; all H atoms found from subsequent Fourier difference syntheses. Full-matrix least-squares refinements (Gantzel, Sparks & Trueblood, 1976) with anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for all H atoms led to $R = 0{\cdot}052$, $wR = 0{\cdot}062$, and $S = 3{\cdot}67$. $w = [\sigma(F_o)]^{-2}$, 294 parameters refined. Function minimized $\sum w(|F_o| - |F_c|)$. Atomic scattering factors used (*International Tables for X-ray Crystallography*, 1974*a*) corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974*b*). Largest shift in a non-H parameter in final cycle of least-squares refinement 48% of its corresponding e.s.d., and for an H parameter, 81%. Final Fourier difference map featureless; largest residual peaks $< 0{\cdot}15$ e Å^{-3}, located at chemically implausible positions. There was no indication of any conformational disorder in the ring.

Table 2. *Bond lengths* (Å), *bond angles* (°), *and selected torsion angles* (°) *involving non*-H *atoms with e.s.d.'s in parentheses*

C(1)–C(2)	1·537 (4)	C(7)–C(8)	1·319 (4)
C(1)–C(6)	1·524 (3)	C(8)–C(9)	1·457 (4)
C(1)–C(16)	1·534 (5)	C(9)–C(10)	1·353 (4)
C(1)–C(17)	1·528 (5)	C(9)–C(19)	1·493 (4)
C(2)–C(3)	1·491 (4)	C(10)–C(11)	1·434 (4)
C(3)–C(4)	1·302 (4)	C(11)–C(12)	1·339 (4)
C(4)–C(5)	1·469 (4)	C(12)–C(13)	1·451 (4)
C(5)–C(6)	1·347 (3)	C(13)–C(14)	1·346 (4)
C(5)–C(18)	1·505 (4)	C(13)–C(20)	1·487 (4)
C(6)–C(7)	1·470 (4)	C(14)–C(15)	1·441 (5)
		C(15)–O(21)	1·215 (5)
C(2)–C(1)–C(6)	110·6 (2)	C(5)–C(6)–C(7)	122·5 (2)
C(2)–C(1)–C(16)	106·0 (3)	C(6)–C(7)–C(8)	126·3 (2)
C(2)–C(1)–C(17)	109·9 (3)	C(7)–C(8)–C(9)	127·2 (2)
C(6)–C(1)–C(16)	111·9 (2)	C(8)–C(9)–C(10)	118·5 (2)
C(6)–C(1)–C(17)	108·9 (2)	C(8)–C(9)–C(19)	118·8 (3)
C(16)–C(1)–C(17)	109·5 (2)	C(10)–C(9)–C(19)	122·7 (3)
C(1)–C(2)–C(3)	113·0 (3)	C(9)–C(10)–C(11)	127·1 (3)
C(2)–C(3)–C(4)	119·9 (3)	C(10)–C(11)–C(12)	124·0 (3)
C(3)–C(4)–C(5)	122·8 (3)	C(11)–C(12)–C(13)	126·5 (3)
C(4)–C(5)–C(6)	119·2 (2)	C(12)–C(13)–C(14)	118·7 (2)
C(4)–C(5)–C(18)	115·7 (2)	C(12)–C(13)–C(20)	117·9 (3)
C(6)–C(5)–C(18)	125·0 (3)	C(14)–C(13)–C(20)	123·4 (3)
C(1)–C(6)–C(5)	120·7 (2)	C(13)–C(14)–C(15)	126·4 (3)
C(1)–C(6)–C(7)	116·6 (2)	C(14)–C(15)–O(21)	123·5 (3)
C(1)–C(2)–C(3)–C(4)	32·0*	C(5)–C(6)–C(7)–C(8)	−55·6
C(1)–C(6)–C(5)–C(4)	−2·8	C(6)–C(7)–C(8)–C(9)	−179·5
C(1)–C(6)–C(5)–C(18)	173·7	C(7)–C(6)–C(1)–C(16)	−37·9
C(1)–C(6)–C(7)–C(8)	129·4	C(7)–C(6)–C(1)–C(17)	83·3
C(2)–C(1)–C(6)–C(5)	29·1	C(7)–C(6)–C(5)–C(18)	−1·0
C(2)–C(1)–C(6)–C(7)	−155·8	C(7)–C(8)–C(9)–C(10)	171·7
C(2)–C(3)–C(4)–C(5)	−4·4	C(7)–C(8)–C(9)–C(19)	−9·2
C(3)–C(2)–C(1)–C(6)	−42·1	C(8)–C(9)–C(10)–C(11)	178·5
C(3)–C(2)–C(1)–C(16)	−163·6	C(9)–C(10)–C(11)–C(12)	177·9
C(3)–C(2)–C(1)–C(17)	78·2	C(10)–C(11)–C(12)–C(13)	175·5
C(3)–C(4)–C(5)–C(6)	−11·6	C(11)–C(10)–C(9)–C(19)	−0·6
C(3)–C(4)–C(5)–C(18)	171·6	C(11)–C(12)–C(13)–C(14)	−178·3
C(4)–C(5)–C(6)–C(7)	−177·5	C(11)–C(12)–C(13)–C(20)	0·7
C(5)–C(6)–C(1)–C(16)	147·0	C(12)–C(13)–C(14)–C(15)	179·4
C(5)–C(6)–C(1)–C(17)	−91·8	C(13)–C(14)–C(15)–O(21)	178·4
		C(15)–C(14)–C(13)–C(20)	0·5

* The signs of the torsion angles follow the convention adopted by the IUPAC–IUB Commission on Biochemical Nomenclature (1970) and are appropriate for the enantiomer shown in Fig. 1. The e.s.d.'s are *ca* 0·5°.

Discussion. The final positional coordinates are given in Table 1, while bond lengths, bond angles, and torsion angles are given in Table 2.*

The crystal and molecular structure of 3,4-didehydroretinal (synonymously 'vitamin A_2 aldehyde' or 'retinal$_2$') is shown in Figs. 1 and 2. The molecule consists of a trimethylcyclohexadienyl ring connected to an all-*trans*-polyene side chain which terminates in an aldehydic group. The C(5)–C(6)–C(7)–C(8) torsion angle, ψ_{5678}, which is characteristic of the attachment of the ring to the chain, is −55·6 (5)°, and falls within the spread of values observed for other 6-*s*-*cis* conformers of retinal compounds (see Table 3).

Aside from the presence of two ring double bonds in all-*trans*-retinal$_2$ (ATR$_2$), C(3)–C(4) and C(5)–C(6), and only one in all-*trans*-retinal (ATR), C(5)–C(6), they are nearly isomorphous.† Because the $|\psi_{5678}|$ torsion angle is *ca* 5σ less in ATR$_2$ than in ATR (which, incidentally, may result more from the slight differences in crystal-packing forces than from the chemical differences between the rings), the C(18)–H(18*B*)···H(8) intramolecular contact distance is shorter, 2·59 (5) *vs* 2·68 (5) Å; as a result, the steric repulsion is greater and the C(6)–C(7)–C(8) angle is *ca* 8σ larger, 126·3 (2) *vs* 124·3°. Also, the π character of the C(6)–C(7) bond should increase with a smaller ψ_{5678} torsion angle; accordingly, the corresponding bond distances are 1·470 (4) and 1·482 (5) Å. All torsion angles in the polyene chains agree to within 4·5°, and other than the marginally different C(15)–O(21) bonds and C(7)–C(8)–C(9) angles, 1·215 (5) *vs* 1·200 (5) Å and 127·2 (2) *vs* 126·3 (4)° in ATR$_2$ and ATR, respectively, the polyene chains are almost structurally identical.

As expected, there are some structural differences between the rings. There is no evidence of conformational disorder in the ring in ATR$_2$, but there is some evidence of this effect in ATR, as indicated by the

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42459 (130 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Compare the unit-cell parameters of ATR$_2$ corresponding to the space group $P2_1/n$ with those of ATR ($P2_1/n$; Hamanaka *et al.*, 1972): $a = 15{\cdot}232$ (5), $b = 8{\cdot}105$ (3), $c = 15{\cdot}054$ (8) Å, $\beta = 105{\cdot}10$ (4)° *vs* $a = 15{\cdot}270$ (4), $b = 8{\cdot}264$ (2), $c = 14{\cdot}942$ (3) Å, $\beta = 104{\cdot}73$ (2)° respectively.

residual peaks in the final ΔF synthesis in the vicinity of C(2), C(16), and C(17), which correspond to alternative positions of the atoms in the other less predominate half-chair conformer (Hamanaka, *et al.*, 1972). Accordingly, the C(2)–C(3) bond distance in ATR_2, 1·491 (4) Å, is significantly longer than in ATR, 1·420 (5) Å. There are also some large differences between ring torsion angles, *viz* $\psi_{1234} = 32{\cdot}0$ *vs* 50·0°, $\psi_{2345} = -4{\cdot}4$ *vs* −30·8°, $\psi_{3456} = -11{\cdot}6$ *vs* 6·8°, $\psi_{34518} = 171{\cdot}6$ *vs* −172·3°, $\psi_{56116} = 147{\cdot}0$ *vs* 133·9°, and $\psi_{56117} = -91{\cdot}8$ *vs* −105·5° for the corresponding enantiomers of ATR_2 and ATR respectively.

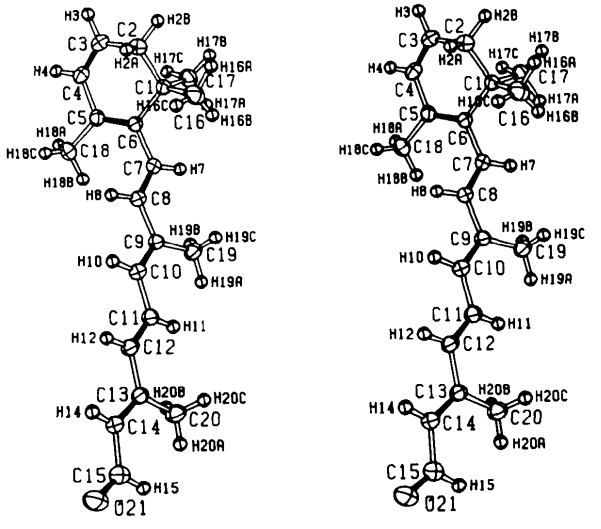

Fig. 1. Stereoview of all-*trans*-$retinal_2$ shown with 25% probability ellipsoids; all H-atom B_{iso}'s have been fixed at 3·0 Å^2. The distance between the center of the trimethylcyclohexadienyl ring and C(15) is 12·3 Å. Except for the presence of two ring double bonds in all-*trans*-$retinal_2$, C(3)–C(4) and C(5)–C(6), instead of only one in all-*trans*-retinal, C(5)–C(6), they are nearly isomorphous.

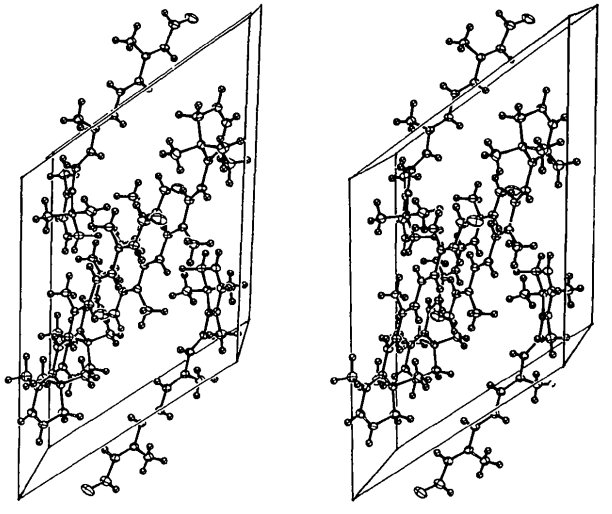

Fig. 2. Stereoview of the crystal structure of all-*trans*-$retinal_2$ using 15% probability ellipsoids; all H-atom B_{iso}'s have been fixed at 3·0 Å^2. The view is approximately into the +**b** direction, with −**a** extending along the right 53° from horizontal, and +**c** extending upwards in the plane of the page.

The distance between the center of the ring and C(15) is 12·3 Å for both ATR_2 and ATR, which is outside the apparent 10·1–10·9 Å binding zone of bovine opsin (Matsumoto *et al.*, 1980). Furthermore, this distance remains nearly invariant with respect to rotation about any single bond in the side chain. For example, rotation about the relatively flexible C(6)–C(7) single bond by ±30° from the $|\psi_{5678}|$ value (56°), changes the value by only *ca* 0·1 Å (Matsumoto *et al.*, 1980). Thus, it is not surprising that the *in vitro* pigment yields of ATR_2 and ATR with bovine opsin are too low to measure (Liu, Matsumoto, Kini, Asato, Denny, Kropf & DeGrip, 1984).

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Table 3. C(5)–C(6)–C(7)–C(8) *torsion angles* (°) *for retinals and carotenoidal-type compounds with e.s.d.'s in parentheses*

Each compound in this table crystallizes in a centrosymmetric space group. Accordingly, each structure contains enantiomers with positive and negative torsion angles; only positive angles are given.

Compound	C(5)–C(6)–C(7)–C(8)	Reference
(*a*) 6-*s*-*cis* Conformers		
11-*cis*-Retinal (β *cis* form)	40·0 (1)	1
All-*trans*-retinoic acid (6-*s*-*cis* conformer)	41·2 (5)	2
11-*cis*-Retinal (α *cis* form)	41·4 (7)	3
15,15′-Dehydrocanthaxanthin	43 (7)	4
2-*cis*-4-Hydroxyretinoic acid γ-lactone	47·4 (7)	5
2,6-Di*cis*-4-hydroxyretinoic acid γ-lactone	48·3 (6)	6
Canthaxanthin	52 (18)	7
Methyl 7,9-di*cis*-retinoate	53 (3)	8
(*E*)-4-Methyl-5-[5-(2,6,6-trimethylcyclohexen-1-yl)-3-methyl-2(*E*),4(*E*)-pentadienylidene]-2(5*H*)-furanone	53*	9
All-*trans*-$retinal_2$	55·6 (5)	10
Methyl all-*trans* retinoate	57·9 (4)	11
All-*trans*-retinal	58·3 (6)	12
9-Ethyl analogue of retinoic acid	63·8 (6)	13
13-*cis*-Retinal (6-*s*-*cis* conformer)	65·4 (6)	14
19,19,19-Trifluoro-9-*cis*-retinal	67·9 (7)	15
9-*cis*-Retinal	76·0 (4)	15
(*b*) 6-*s*-*trans* Conformers		
All-*trans*-retinoic acid (6-*s*-*trans* conformer)	165·8 (3)	2
1,14 Bis(2,6,6-trimethylcyclohex-1-enyl-3,12-dimethyltetradeca-1,3,5,7,9,11,13-heptaene-6,9-dinitrile	166·4 (5)	16
3-(1,1,5-Trimethyl-5-cyclohexen-6-yl)propenoic acid	168·5 (3)	17
9,10-*trans*-β-Ionylidene-γ-crotonic acid	169·0 (7)	18
13-*cis*-Retinal (6-*s*-*trans* conformer)	174·9 (4)	14

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* The e.s.d. cannot be calculated from the information provided.

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Structures of Two Trichromophoric Anthraceno Cryptands

BY G. GUINAND AND P. MARSAU*

Laboratoire de Cristallographie et Physique Cristalline – UA 144, *Université de Bordeaux* I, *F*33405 *Talence CEDEX, France*

J. M. LEHN, F. KOTZYBA-HIBERT AND J. P. KONOPELSKI

Laboratoire de Chimie Organique Physique – UA 265, *Université Louis Pasteur*, 67070 *Strasbourg CEDEX, France*

AND J. P. DESVERGNE, F. FAGES, A. CASTELLAN AND H. BOUAS-LAURENT

Laboratoire de Chimie Organique, Photophysique et Photochimie Moléculaire – UA 348, *Université de Bordeaux* I, *F*33405 *Talence CEDEX, France*

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Abstract. 6,9,17,20-Tetraoxa-3,12-diaza[14.8^{3,12}](9,10)-anthracenophane (A_{22}), $C_{30}H_{40}N_2O_4$, and 7,10,19,-22-tetraoxa-4,13-diaza[16.8^{4,13}](9,10)anthracenophane (A_{33}), $C_{32}H_{44}N_2O_4$. A_{22} compound: $M_r = 492$, monoclinic, Pc, $a = 9{\cdot}816$ (4), $b = 14{\cdot}493$ (4), $c = 10{\cdot}523$ (5) Å, $\beta = 118{\cdot}26$ (3)°, $V = 1318{\cdot}6$ Å^3, $Z = 2$,

* Author to whom correspondence should be addressed.

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