The molecules are packed in very different ways in the three crystals in spite of the very similar overall shape of the molecules. This can be seen by a comparison of Figs. 4 to 8. No close relation is found between the packing of the molecules in the racemate crystal, HJBR-1, and the packing in the corresponding chiral crystal HJBR-1*a*, as was the case in the structures reported by Cheng, Koo, Mellor, Nyburg & Young (1970). It seems likely that the packing of the HJBR-2 molecules is more favourable than the others. There are no short intermolecular distances in this structure, although the unit cell of HJBR-2 is the smallest one.

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The Crystal Structure of the *trans* Isomer of β-Ionylidenecrotonic Acid. II. Determination of Subsequent Data and Revaluation of Previous Results

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Following a previous paper on $C_{17}H_{24}O_2$, 9,10-*trans*-β-ionylidene-γ-crotonic acid, or conventionally *trans*-(2′,6′,6′-trimethylcyclohex-1′-enyl)-3-methylhexa-1,3,5-triene-6-carbooxylic acid, all crystal structure data have been determined with an automatic single-crystal diffractometer (Cu $K\alpha$ radiation) at room temperature. Space group $P\bar{1}$, $Z=2$. Cell constants: $a=10{\cdot}391$, $b=13{\cdot}481$, $c=7{\cdot}546$ Å, $\alpha=108{\cdot}12$, $\beta=127{\cdot}81$, $\gamma=68{\cdot}01°$. A least-squares anisotropic block-diagonal refinement was started from the previously published positional parameters of the carbon and oxygen atoms. Moreover all hydrogen atoms were refined, with individual isotropic B values. Final $R=0{\cdot}07$. The results allow a better comparison with those obtained more recently for the *cis* analogue and with details of other vitamin A and carotenoid related substances. The torsion angle between the ring-ethene system and the plane of the first three adjacent chain-carbon atoms is 10·4° from *s-trans*. Some possible physical interpretations of the very large anisotropic U_{ij} values of some ring atoms are discussed, in view of the significance of geometrical data in this and other related structures.

Introduction

This redetermination of the molecular and crystal structure and production of additional data of 9,10-*trans*-β-ionylidene-γ-crotonic acid, reported formerly in a paper by Eichhorn and MacGillavry (1959) has been undertaken in order to update the results. Comparison with the *cis* analogue (Eichhorn, 1957; Koch & MacGillavry, 1963; Koch, 1972) and with other vitamin A related (Stam & MacGillavry, 1963; Paul-Roy, Schenk & MacGillavry, 1969; Schenk,1969) and carotenoid related (Sly, 1964; Sterling, 1964; Bart & MacGillavry, 1968; Braun, Hornstra & Leenhouts, 1971) substances need an improved basis, in view of recent quantum, mechanical calculations (Pullman, Langlet & Berthod, 1969; Langlet, Pullman & Berthod, 1970) and semi-empirical calculations/nuclear magnetic resonance measurements (Honig, Hudson, Sykes & Karplus, 1971). Various experimental data on these compounds are also compared in the review articles by Hubbard & Wald (1968) and Schwieter, Englert, Rigassi & Vetter (1969).

The numbering of the carbon and oxygen atoms, used in this paper is given in Fig. 1 and that of the hydrogen atoms in Fig. 4.

Experimental

From a small single crystal (obtained from a 96% alcohol solution; m.p. 158 °C; dimensions 0·3 × 0·2 × 0·1 mm) lattice and three-dimensional intensity data were collected at room temperature.* The cell constants were calculated from 83 observations, calibrated with powder lines of Al (a_0=4·0491 Å). The least-squares results are

a=10·931 (2) Å	α=108·12 (2)°
b=13·481 (3)	β=127·81 (1)
c= 7·546 (1)	γ= 68·01 (2)

V_c=769·53 Å^3

E.s.d.'s in the last decimal places are given in parentheses.

* The crystals appeared to crack at liquid air temperature (Eichhorn, 1956).

Table 1. *Positional and thermal parameters*

(*a*) Fractional positional parameters (×10^4) and individual parameters U_{ij}(×10^3).
Temperature factor=exp $[-2\pi^2\{h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*(2U_{12})+klb^*c^*(2U_{23})+lhc^*a^*(2U_{31})\}]$.
The e.s.d.'s are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1)	7494 (6)	1995 (5)	7834 (9)	56 (3)	79 (4)	54 (3)	−48 (5)	23 (5)	56 (5)
C(2)	8674 (8)	1332 (7)	7024 (12)	59 (4)	148 (7)	84 (4)	−38 (8)	38 (9)	82 (7)
C(3)	7908 (9)	1369 (8)	4650 (12)	75 (4)	168 (8)	81 (5)	−37 (9)	33 (10)	103 (8)
C(4)	6380 (8)	904 (5)	3173 (10)	86 (4)	81 (4)	65 (4)	−12 (6)	6 (6)	102 (7)
C(5)	5284 (7)	1260 (4)	4049 (8)	66 (3)	48 (3)	47 (3)	−21 (5)	13 (4)	60 (5)
C(6)	5750 (6)	1770 (4)	6146 (8)	48 (3)	49 (3)	46 (3)	−14 (4)	19 (4)	46 (5)
C(7)	4538 (6)	2119 (4)	6725 (8)	51 (3)	59 (3)	52 (3)	−29 (5)	18 (5)	49 (5)
C(8)	4532 (6)	2764 (4)	8490 (9)	52 (3)	66 (3)	54 (3)	−35 (5)	12 (5)	52 (5)
C(9)	3233 (6)	3034 (4)	8859 (9)	54 (3)	53 (3)	59 (3)	−12 (4)	23 (5)	64 (5)
C(10)	3480 (7)	3626 (4)	10827 (9)	58 (3)	63 (3)	60 (3)	−14 (5)	14 (5)	64 (5)
C(11)	2384 (6)	3917 (4)	11541 (9)	59 (3)	56 (3)	63 (3)	−5 (5)	16 (5)	77 (5)
C(12)	2721 (7)	4456 (4)	13545 (9)	67 (3)	63 (3)	67 (3)	−22 (5)	6 (6)	81 (6)
C(13)	1569 (7)	4694 (4)	14214 (9)	62 (3)	68 (4)	61 (3)	−21 (5)	19 (5)	73 (5)
C(14)	3591 (8)	985 (5)	2314 (10)	83 (4)	82 (4)	57 (3)	−76 (7)	−17 (6)	55 (6)
C(15)	7351 (9)	3209 (6)	8086 (11)	86 (4)	102 (5)	77 (4)	−106 (8)	17 (7)	57 (7)
C(16)	8385 (7)	1642 (6)	10153 (10)	49 (3)	113 (5)	58 (3)	−30 (6)	58 (7)	31 (5)
C(17)	1711 (7)	2589 (5)	7148 (10)	59 (3)	89 (4)	77 (4)	−45 (6)	−6 (6)	88 (6)
O(1)	297 (5)	4361 (4)	13058 (7)	78 (3)	106 (3)	71 (2)	−81 (5)	−41 (5)	98 (4)
O(2)	2005 (5)	5278 (3)	16152 (7)	79 (3)	90 (3)	64 (2)	−62 (4)	−32 (4)	89 (4)

(*b*) Fractional position parameters (×10^3) and individual Debye–Waller parameters with e.s.d.'s in parentheses for hydrogen atoms. (See Fig. 4).

	x	y	z	B	Bonding atom; conformation
H(1)	381 (7)	470 (5)	1474 (10)	4·1 (1·4)	C(12)
H(2)	126 (6)	375 (4)	1048 (9)	3·5 (1·2)	C(11)
H(3)	461 (8)	390 (5)	1185 (10)	4·3 (1·5)	C(10)
H(4)	554 (6)	312 (4)	965 (8)	2·7 (1·2)	C(8)
H(5)	352 (6)	180 (3)	568 (7)	1·4 (1·0)	C(7)
H(6)	656 (12)	13 (7)	278 (16)	11·1 (2·8)	C(4)
H(7)	555 (8)	114 (5)	157 (11)	4·9 (1·6)	C(4)
H(8)	875 (9)	92 (6)	413 (12)	7·3 (2·0)	C(3)
H(9)	748 (12)	231 (8)	458 (16)	10·6 (2·7)	C(3)
H(10)	987 (7)	159 (5)	821 (10)	5·2 (1·5)	C(2)
H(11)	878 (11)	36 (7)	693 (15)	9·0 (2·5)	C(2)
H(12)	346 (10)	67 (6)	77 (13)	7·9 (2·1)	C(14)
H(13)	349 (11)	50 (7)	279 (15)	9·1 (2·5)	*anti* conformation
H(14)	263 (10)	168 (6)	208 (13)	7·5 (2·1)	to C(5)=C(6)
H(15)	195 (10)	180 (7)	678 (14)	9·0 (2·3)	C(17)
H(16)	84 (7)	288 (4)	731 (9)	2·9 (1·3)	*anti* conformation
H(17)	127 (9)	278 (6)	577 (12)	7·4 (2·0)	to C(8)—C(9)
H(18)	841 (8)	337 (5)	918 (11)	5·0 (1·6)	C(15)
H(19)	678 (9)	342 (6)	651 (12)	6·5 (1·8)	*anti* conformation
H(20)	664 (7)	367 (4)	881 (9)	3·4 (1·3)	to C(1)—C(6)
H(21)	831 (9)	89 (6)	990 (12)	7·9 (2·0)	C(16)
H(22)	961 (9)	169 (6)	1109 (12)	7·0 (1·9)	*anti* conformation
H(23)	778 (8)	215 (5)	1086 (11)	5·8 (1·7)	to C(1)—C(6)
H(24)	117 (13)	541 (8)	1649 (17)	13·4 (3·3)	O(2); bridge

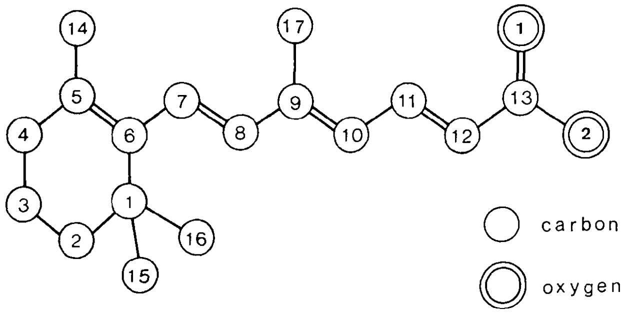


Fig. 1. Numbering of the carbon and oxygen atoms of *trans*-β-ionylidene-γ-crotonic acid (TBIC).

Space group: $P\bar{1}$, according to a statistical test on normalized structure factors; $Z=2$.

The intensity data were measured with a Nonius four-circle diffractometer through $\theta=4\cdot5$ to $68\cdot5°$ with $\theta/2\theta$ scan, using nickel-filtered Cu $K\alpha$ radiation and a scintillation counter (pulse-height discrimination with 44% resolution). The focal spot of the X-ray tube was 8 × 0·4 mm.

The crystal was mounted along the [001] axis, parallel to the largest dimension. During the measurements the intensities of the reference reflexions (530, $\overline{53}0$, 033) diminished by 20% of their initial values and all data were corrected for this effect. No corrections for absorption, extinction or countig losses were applied ($\mu=$ 5·4 cm^{-1}). Finally 1342 intensities out of about 2950 measured reflexions were used as independent significant data. The half limiting sphere contains 3516 possible reflexions, so 33·3% could be used, up to $d_{hkl}=$ 0·828 Å, as the corresponding value in direct space.

Refinement

Starting from positional parameters according to Eichhorn & MacGillavry (1959) for carbon and oxygen atoms only and 1342 reflexions, a least-squares refinement using block-diagonal matrices throughout, various relaxation factors and atomic scattering factors given by Moore (1963), could be performed immediately. The Cruickshank weighting scheme was used according to the formula $w=3/(2+0\cdot1\ F_o+0\cdot000445\ F_o^2)$. After four isotropic cycles with individual Debye–Waller parameters B and four anisotropic cycles (with alternating use of subsets and full data sets) the discrepancy factor $R=\sum||F_o|-|F_c||/\sum|F_o|$ decreased from 0·18 to 0·12. At this stage calculated positions for the hydrogen atoms (C–H put to 1·08 Å and C–C–H = 109·5°, C=C–H = 118 or 119°) and positions derived from a difference synthesis were compared. The hydrogen atoms H(1)–H(5), H(7), H(10), H(12), H(14)–H(23) could be detected with electron densities varying from 0·32–0·54 e.Å^{-3} and H(13) with 0·26 e.Å^{-3}; H(8) was notably diffuse (0·21 e.Å^{-3}). Fig. 4 and the second part of Table 1 give the conformations in which the *gem*-methyl hydrogens were found [see also Fig. 7(*a*)]. By use of the formula $\sigma(\Delta\varrho)=(1/V_c)\{\sum(\Delta F)^2\}^{1/2}$ for ΔF based on the unit cell and all reflexions within the limiting sphere, a rounded-off value of $2\,\sigma(\Delta\varrho)=0\cdot20$ e.Å^{-3} was taken as a threshold value for probable significance. All calculated positions could be accepted for use at fixed points with estimated fixed B values in the next three refinement cycles (2 with data subsets).

The regions in the difference Fourier synthesis surrounding the axial hydrogen atoms of the cyclohexene ring H(6), H(9) and H(11) gave some uncertainty because of diffuseness and overlap with other faint maxima of about 0·3 e.Å^{-3}. Nevertheless, as all these hydrogen atoms could be found at nearly their calculated positions with densities of 0·32 to 0·37 e.Å^{-3}, they were also included in the refinement in the same way as above. The bridge-hydrogen atom H(24) was found in a very diffuse region; a calculated position was inserted. This difference Fourier synthesis also showed some faint maxima of about 0·27 e.Å^{-3} in the region of the chain (some of which could be interpreted as ghosts of chain atoms) and moreover at a small distance (0·4 Å)

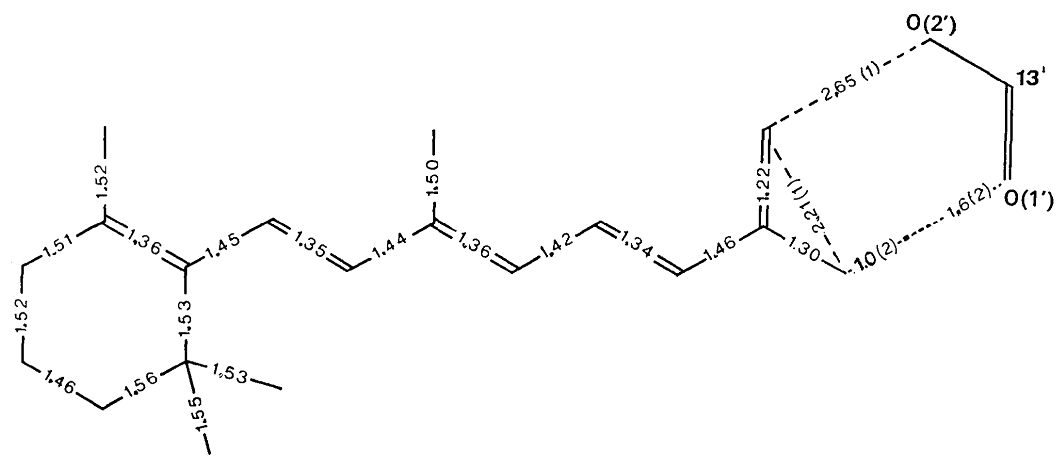


Fig. 2. Bond lengths between non-hydrogen atoms and O(2)–H(24). The e.s.d.'s are 0·01 Å (ranging from 0·007 to 0·012 Å), except for the bond O(2)–H(24) and the distance H(24)···O(1').

from C(15) a maximum of 0·47 e.Å^{-3} was observed. C(16) displayed some diffuse overlap with H(21) and H(23). A slight indication for some of the methyl hydrogen atoms to occupy alternative positions is probably present.

After the input of all hydrogen atoms the R value reduced to 0·08 in the three cycles mentioned above. At this stage a second difference synthesis was computed; from $\sum(\Delta F)^2_{1/2\mathrm{u.c.}}=259$ a level of acceptable significance of $2\sigma(\Delta\varrho)=0{\cdot}11$ e.Å^{-3} was derived. This one showed, at about the same places as in the first difference Fourier synthesis maxima of 0·14 to 0·21 e.Å^{-3} in the neighbourhoods of the ring part C(2)–C(3)–C(4) and of C(15) also. In the Fourier synthesis, at this stage of refinement, the peak densities of C(2) and C(3) were 4·0 e.Å^{-3} and of C(15) 4·5 e.Å^{-3}, being the lowest values; for C(6) a density of 6·6 e.Å^{-3} was found. Because of personal and other experience (Koch, 1972; Bart & MacGillavry, 1968) with these cyclohexene ring systems in similar substances these features were not at all unexpected. This matter will be referred to later on.

Another three refinement cycles, using 620 observational data up to $\sin\theta/\lambda=0{\cdot}4$ and keeping all parameters for the non-hydrogen atoms fixed [except for C(2) and C(3)] reduced R to 0·05. The shifts in the parameters for the positions of C(2) and C(3) were of the order of 0·001 Å and the e.s.d. 0·005 Å; the shifts for the H atoms ranged from 0·001 to 0·05 Å, and the e.s.d.'s from 0·003 to 0·06 Å, the higher values belonging to the axial ring-hydrogen atoms H(6), H(9) and H(11).

Another cycle followed using 1342 reflexions (R= 0·070) and refining all parameters, and there was a final cycle leaving out only the strongest reflexion $0\bar{3}1$. This first order reflexion of the plane of the molecule, has by far the largest intensity. It may be affected either by extinction or by counting loss, or by both. The last shifts of the position and thermal parameters were about one half to one third of the e.s.d.'s or even less [with only one exception for the B value of H(16)].

The final results of this refinement are given in the following specifications (exclusive of non-observed data):

$$R=0{\cdot}069;\ R_2=\{\sum(\omega\Delta^2/\sum F_0^2\}^{1/2}=0{\cdot}045$$

[$\sum(\omega\Delta^2=76$; 1341 reflexions, Δ values are based on the half unit cell] and in Table 1. Structure-factor tables can be obtained from the author on request.

Structure of the molecule

From Fig. 2 it can be seen that all intramolecular distances in the chain are normal within twice the calculated e.s.d.'s. The bond lengths between the atoms in the ring system are also comparatively normal except C(2)–C(3); this distance is frequently found to be too short (Bart & MacGillavry, 1968*b*, Table 16; Koch, 1972). The e.s.d.'s of the positional and thermal parameters of these atoms are significantly and consistently larger than for the other atoms (Table 1). The same holds to a less degree for C(4), C(14), C(15) and C(16) and also for O(1) and O(2). The vibrational ellipsoids in Table 4 show that these atoms have the largest values and that their directions of maximum vibration are concentrated toward the plane (001), in most cases approximately parallel to the b axis, the relation of which to the cyclohexene ring is shown in Fig. 6.

Sly (1964) interpreted the shortening of C(2)–C(3) as, at least in part, due to asymmetric vibrations of the atoms concerned,* but it is possible that the real explanation is conformational disorder. The most stable conformation for cyclohexene is the half-chair (Barton, 1970) and the activation energy for inversion is less than 7 kcal.mole^{-1} (Bucourt & Hainaut, 1967; Bushweller, 1967). Diffuse scattering on the Weissenberg

* Note that Table 6 in Sly's paper contains 'standard deviations' in a different meaning; the values quoted from Eichhorn & MacGillavry (1959) are in reality most probable errors per Å.

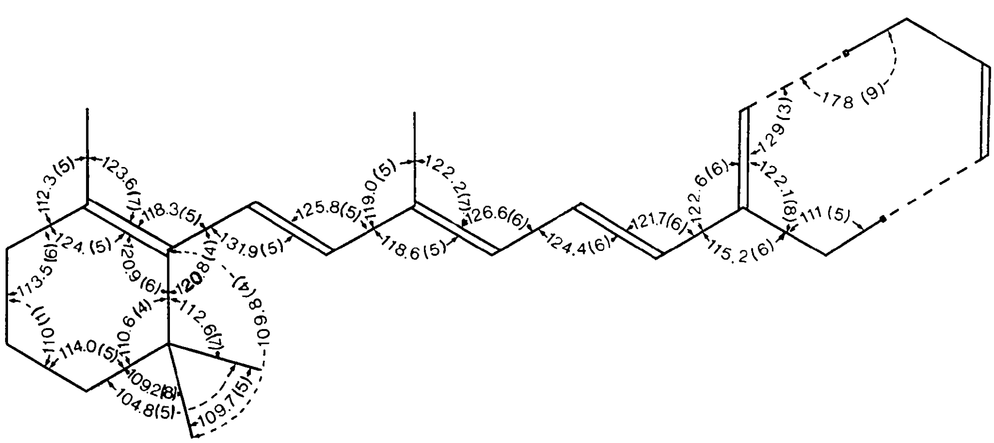


Fig. 3. Bond angles with e.s.d.'s in parentheses.

Table 2. *Intramolecular* H–C *distances and e.s.d.'s*

H(1)—C(12)	1·02 (6) Å	H(13)–C(14)	0·90 (14) Å
H(2)—C(11)	1·00 (6)	H(14)–C(14)	1·05 (7)
H(3)—C(10)	1·07 (7)	H(15)–C(17)	0·98 (8)
H(4)—C(8)	1·04 (5)	H(16)–C(17)	0·91 (8)
H(5)—C(7)	1·01 (5)	H(17)–C(17)	0·92 (10)
H(6)—C(4)	0·98 (9)	H(18)–C(15)	0·94 (7)
H(7)—C(4)	1·03 (7)	H(19)–C(15)	1·03 (9)
H(8)—C(3)	1·08 (10)	H(20)–C(15)	1·09 (8)
H(9)—C(3)	1·19 (10)	H(21)–C(16)	1·00 (9)
H(10)–C(2)	1·11 (6)	H(22)–C(16)	1·02 (8)
H(11)–C(2)	1·26 (10)	H(23)–C(16)	1·00 (9)
H(12)–C(14)	1·05 (10)		

Table 3. *Intramolecular angles* C–C–H *and* H–C–H *and e.s.d.'s*

C(1)—C(2)—H(10)	107 (4)°
C(1)—C(2)—H(11)	106 (6)
C(3)—C(2)—H(10)	115 (5)
C(3)—C(2)—H(11)	99 (5)
H(10)–C(2)—H(11)	116 (5)
C(2)—C(3)—H(8)	113 (4)
C(2)—C(3)—H(9)	101 (5)
C(4)—C(3)—H(8)	107 (4)
C(4)—C(3)—H(9)	110 (5)
H(8)—C(3)—H(9)	115 (9)
C(3)—C(4)—H(6)	118 (6)
C(3)—C(4)—H(7)	114 (5)
C(5)—C(4)—H(6)	108 (9)
C(5)—C(4)—H(7)	103 (5)
H(6)—C(4)—H(7)	99 (7)
C(6)—C(7)—H(5)	116 (3)
C(8)—C(7)—H(5)	112 (4)
C(7)—C(8)—H(4)	117 (4)
C(9)—C(8)—H(4)	118 (4)
C(9)—C(10)–H(3)	113 (5)
C(11)–C(10)–H(3)	120 (4)
C(10)–C(11)–H(2)	119 (4)
C(12)–C(11)–H(2)	116 (4)
C(11)–C(12)–H(1)	123 (5)
C(13)–C(12)–H(1)	115 (5)
C(5)—C(14)–H(12)	110 (6)
C(5)—C(14)–H(13)	111 (5)
C(5)—C(14)–H(14)	109 (4)
H(12)–C(14)–H(13)	109 (8)
H(12)–C(14)–H(14)	109 (6)
H(13)–C(14)–H(14)	109 (10)
C(1)—C(15)–H(18)	111 (4)
C(1)—C(15)–H(19)	108 (4)
C(1)—C(15)–H(20)	110 (4)
H(18)–C(15)–H(19)	114 (8)
H(18)–C(15)–H(20)	103 (6)
H(19)–C(15)–H(20)	111 (5)
C(1)—C(16)–H(21)	107 (5)
C(1)—C(16)–H(22)	108 (6)
C(1)—C(16)–H(23)	107 (4)
H(21)–C(16)–H(22)	111 (6)
H(21)–C(16)–H(23)	112 (9)
H(22)–C(16)–H(23)	111 (6)
C(9)—C(17)–H(15)	115 (5)
C(9)—C(17)–H(16)	116 (3)
C(9)—C(17)–H(17)	107 (6)
H(15)–C(17)–H(16)	115 (9)
H(15)–C(17)–H(17)	98 (7)
H(16)–C(17)–H(17)	104 (7)

photographs is consistent with some disorder in the crystal so we can postulate that both the possible chair conformations are present but one is preferred (other-

Table 4. *R.m.s. amplitudes parallel to the principal axes of the individual thermal vibration ellipsoids and angles relative to the crystal axes*

	R.m.s. ampl. (Å × 10⁴)	Angles with respect to *a*	*b*	*c*
C(1)	2855	105	39	77
	2303	97	84	135
	2221	163	128	48
C(2)	3900	78	12	97
	2895	76	81	156
	2338	19	82	113
C(3)	4202	74	9	100
	2875	109	86	123
	2408	155	98	35
C(4)	3297	39	34	109
	2774	108	58	113
	2213	124	79	31
C(5)	2719	11	67	117
	2204	83	137	115
	2134	98	125	39
C(6)	2032	76	119	60
	2426	162	130	50
	2261	78	126	126
C(7)	2208	65	93	63
	2493	130	71	46
	2364	50	20	124
C(8)	2234	54	77	74
	2570	91	23	93
	2498	36	71	164
C(9)	2185	67	130	83
	2506	61	48	78
	2414	39	68	166
C(10)	2805	143	148	52
	2462	85	102	142
	2321	53	119	95
C(11)	2132	129	62	65
	2710	42	37	102
	2471	78	68	152
C(12)	2360	124	61	55
	2750	138	151	50
	2618	112	88	120
C(13)	2709	55	25	98
	2460	107	65	118
	2388	140	89	29
C(14)	2160	75	62	60
	3214	161	94	48
	3028	78	28	124
C(15)	3647	132	66	58
	2909	73	52	148
	2311	47	47	91
C(16)	3430	89	29	79
	2815	26	62	152
	2060	64	98	65
C(17)	3163	102	151	56
	2663	93	117	128
	2208	12	80	123
O(1)	3570	95	149	61
	2537	160	116	71
	2353	110	73	35
O(2)	3301	101	152	58
	2729	163	108	70
	2237	104	70	40

wise the apparent ring conformation would be planar). The preference for one conformation may easily be caused by intramolecular steric hindrance (Fig. 4) and intermolecular (packing) influences. The postulate would explain the persistent and significant residual electron density maxima in the neighbourhood of the ring atoms. Such effects, but more pronounced, had been noticed in canthaxathin (Bart & MacGillavry, 1968*b*). In that case they could in fact be interpreted in terms of an alternate conformation. The canthaxanthin ring has an extra substituent in the form of a carboxyl oxygen attached to C(4). The conformation is accordingly 'sofa' at C(2). This means that only C(2) can flip from one side of the planar conjugated system C(1)–C(6)–C(5)–C(4)–C(3) to the other. Accordingly, the change of position of C(2) in flipping over is much larger than in the ordinary cyclohexene ring (in any case more pronounced). As a consequence, the movement of the *gem*-methyl groups at C(1) is also larger than can be expected in β-ionylidene crotonic acid. In rings like the present one which are without an exocyclic double bond and so more flexible, no clear distinction can be made between either large (anharmonic, asymmetric) vibrations of the ring and substituent carbon atoms or the existence of two separate ring conformations within one single crystal. The e.s.d.'s in the distances (Fig. 2 and Table 2) have been calculated from variances only; if the coordinate errors of two atoms are not uncorrelated, the e.s.d.'s in these lengths are not correct (too small), as is probably the case for the bonds C(1)–C(2), C(2)–C(3) and C(3)–C(4). The same holds for the corresponding values in Fig. 3 and Table 3 for the angles. Those in the chain show a trend like others collected in Table 14 of Bart & MacGillavry (1968*b*) but C(6)–C(7)–C(8) and C(1)–C(6)–C(7) are abnormally large (Bart & MacGillavry, 1968*b*, Table 18). Fig. 4 gives the shortest H···H distances between hydrogen atoms attached to different carbon atoms; no unusual values are found, although 2·0 Å at a few places is rather short, but the e.s.d.'s range from 0·08 to 0·16 Å so deviations from the mean 2·3 Å (20 values averaged) may be hardly significant.

In Table 4 the r.m.s. amplitudes parallel to the principal axes of the individual thermal vibration ellipsoid and angles relative to the crystal axes are listed.

The average for H···H in the chain only is $2{\cdot}2_2$ Å (9 values averaged). The *syn*-planar carboxyl-hydrogen bond system is displayed in Figs. 2 to 4 and in the Newman projection of the end of the chain (*B* molecule), Fig. 5(*e*).

Table 5 is a comparison of the endocyclic torsion angles of the tetrakis-substituted ring system found in this work and those of a carotenoidal compound (Braun Hornstra & Leenhouts, 1971), those of cyclohexene from electron-diffraction measurements in the vapour phase (Chiang & Bauer, 1969; Geise & Buys, 1970) and calculated values (Bucourt & Hainaut, 1967). Fig. 5(*a*) to (*c*) show some of the dihedral angles in TBIC. Table 5 demonstrates the expected loss of *C*2 symmetry of the ring itself because of substitution at C(1) and C(5), which must have introduced some extra strain compared with the most 'favourable' conformation of cyclohexene, but the changes in the endocyclic torsion angles are small.

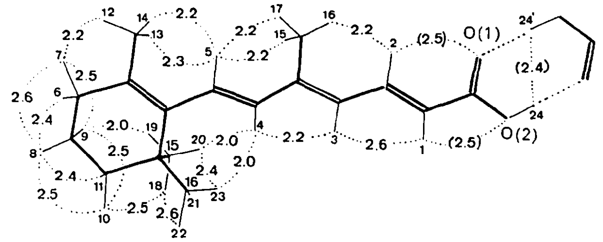


Fig. 4. Intramolecular H···H contacts. The e.s.d.'s are about 0·1 Å.

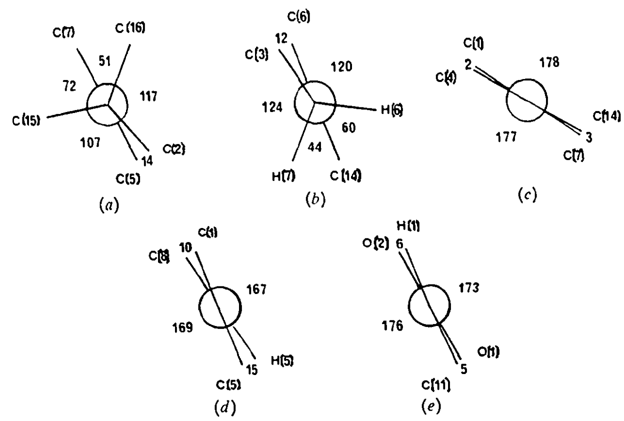


Fig. 5. Newman projections. The rotation directions of the torsion angles φ (see also Table 5 for some of them) hold for an inverted molecule *B* with atomic positions $\bar{x}$, $\bar{y}$, $\bar{z}$. (*a*) along C(1)–C(6); (*b*) along C(4)–C(5); (*c*) along C(5)–C(6); (*d*) along C(6)–C(7); (*e*) along C(12)–C(13).

Table 5. *Torsion angles* φ_{ij} *for cyclohexene (vapor phase) and two trimethyl substituted cyclohexenyl compounds (solid phase)*

φ_{ij}	This work	Braun *et al.* (1971)	Chiang & Bauer (1969)	Geise & Buys (1970)	Bucourt & Hainaut (1967)
φ_{61}	+14·8	+14·5	+15·2	+15·3	+15·0
φ_{12}	−46·1	−49·8	−44·9	−44·8	−44·4
φ_{23}	+61·0	+64·3	+60·2	+61·2	+60·6
φ_{34}	−42·6	−41·4	−44·9	−44·8	−44·4
φ_{45}	+12·2	+7·0	+15·2	+15·3	+15·0
φ_{56}	+2·5	+6·4	+0	+0	+0

The dihedral angle between the ring plane $P1$ and the overall chain plane $P3$ [C(17) inclusive] is 6·2°, the dihedral angle between $P1$ and $P2$ is 10·4 [Table 6 and Fig. 5(*d*)].

Table 6. *Planes* (P) *through parts of molecule* A 000 *and hydrogen-bond system; equations* $Ax_0+By_0+Cz_0+D=0$*

The lower part of the Table contains the distances of the atoms, used for calculation of the equation, to this plane; distances of non-plane atoms are given between brackets.

Plane Coefficient	$P1$	$P2$	$P3$	$P4$
A	−0·20333	−0·21512	−0·26206	+0·28829
B	+0·91538	+0·83346	+0·85359	−0·83341
C	−0·34748	−0·50899	−0·45022	+0·47151
D	−1·0340	−0·1533	−0·4729	+0·2416
Atom				
C(1)	−0·02			
C(2)	(−0·38)			
C(3)	(+0·35)			
C(4)	+0·03			
C(5)	−0·00			
C(6)	−0·01	(−0·01)	(−0·20)	
C(7)	+0·03	0	−0·10	
C(8)		0	+0·02	
C(9)		0	+0·08	
C(10)		(−0·11)	+0·07	
C(11)		(−0·21)	+0·06	
C(12)		(−0·38)	−0·02	
C(13)		(−0·53)	−0·08	−0·01
C(13′)				+0·01
C(14)	−0·03			
C(15)	(+1·37)	(+1·00)	(+0·88)	
C(16)	(−1·10)	(−1·49)	(−1·58)	
C(17)		(+0·02)	(+0·06)	
O(1)		(−0·58)	(−0·15)	+0·01
O(1′)				−0·01
O(2)		(−0·61)	(−0·07)	+0·01
O(2′)				−0·01

* The coordinates (x, y, z) from Table 1 are transformed to (x_0, y_0, z_0) with reference to an orthogonal standard system a_0, b_0, c_0 (retaining the origin of the triclinic system a, b, c) in such a way that $\mathbf{b}_0$ is parallel to $\mathbf{b}$ and $\mathbf{c}_0$ to $\mathbf{c}^*$.

Packing of the molecules

The intermolecular arrangement was already known, but more details can be given after locating the hydrogen atoms. Fig. 6 shows the parallel layer packing in planes (0$\bar{3}$1) in a-axis projection. The interlayer distance is 3·586 Å. All atoms of the chain and carboxyl group lie within 0·13 Å from this plane, except C(17) which deviates by 0·2 Å.

The basic molecule A 000 is surrounded by 14 translation equivalent (A) and inverted (B with atomic positions $\bar{x}$, $\bar{y}$, $\bar{z}$) molecules. Fig. 7(*a*) and (*b*), showing the (0$\bar{3}$1) projection of the molecular contents indicate some packing details; for the sake of clearness parts of molecules and overlapping atoms have been left out. The reference molecule A 000 has only two shorter intermolecular H···H contacts of 2·5 Å, *viz.* H(6) {A 000} ···H(12) {B 100} and H(6) {A 000}···H(15) {B 101} and one contact of 2·4 Å in the hydrogen bridge between A 000 and B 013 (see Fig. 4). All these contacts are usual values and the molecules seem to fit together in a very orderly way.

Discussion

Langlet, Pullman & Berthod (1970) calculated for the most stable form of an isolated TBIC molecule an angle between the ring ethene and chain planes of 55°. This deviates largely from the experimental value of 6° (with respect to $P3$) or 10° (with respect to $P2$). The authors pointed out the specific role, in the case of TBIC, of the intermolecular forces in the crystal. Consistent with an assumed flexibility of the cyclohexenic system (or presence of more than one, preferred, conformation) at room temperature the positions of the hydrogen atoms attached to C(2), C(3), C(4), C(14), C(15), C(16) are equivocal as well. This may also affect the evalution of the ring/chain torsion angle in the case of TBIC.

The sample was kindly provided by Dr P. H. van Leeuwen (Philips-Duphar, Weesp, Netherlands). I am also indepted to D. Heijdenrijk and Charlotte Dik for their help in obtaining valuable data and am much obliged to the personnel of the Mathematical Centre of Amsterdam (Electrologica X8 Computer). Use has been made of the programs at the Laboratory. Plot programs have been written by Drs J. Beintema and H. Schenk. Finally, I have to express my gratitude to Professor MacGillavry for the opportunity given to perform this investigation and for the discussion on the manuscript.

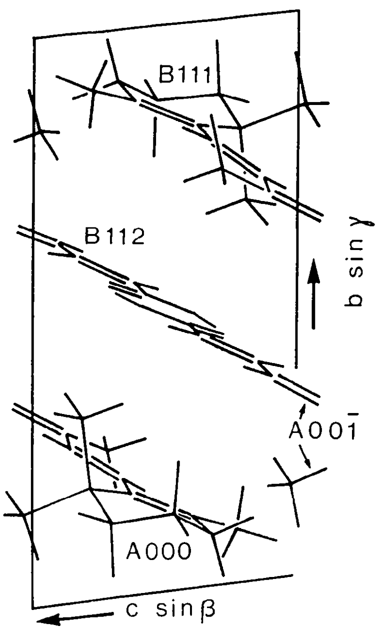
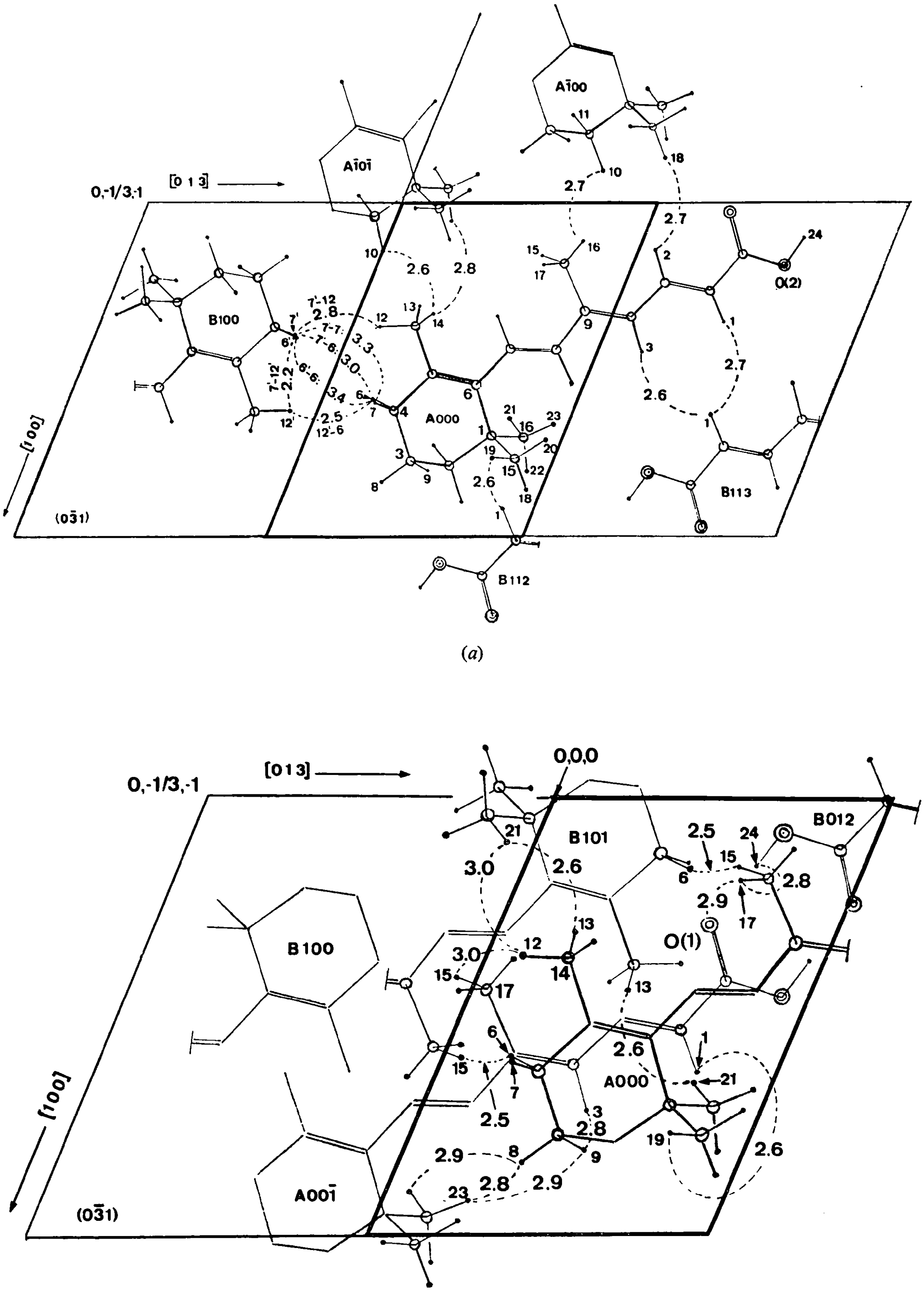


Fig. 6. Orthogonal projection of the contents of the unit cell, viewed along the a axis. Coordinates of the atoms in molecule A 000 are x, y, z and of B 111 are $1-x$, $1-y$, $1-z$ *etc.*



(*a*)

(*b*)

Fig. 7. Orthogonal projection on the plane of the strongest X-ray reflexion (0$\bar{3}$1); axis [013]=7·508 Å, angle between [100] and [013]=112°56′. The basic molecule *A* 000 (positions *x*, *y*, *z*) is surrounded by various translation and/or symmetry-related molecules to show shorter intermolecular H···H contacts. Irrelevant detail has mostly been omitted.

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Structure du Pentafluorodibéryllate* $TlBe_2F_5$

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The structure of $TlBe_2F_5$ has been studied by neutron diffraction. This pentafluorodiberyllate is monoclinic, space group $P2/c$. The unit cell with $a=8·06$; $b=4·65$, $c=12·63$ Å, $\beta=90°$ contains 4 $TlBe_2F_5$ molecules. It is a sheet structure with two $(Be_4F_{10})^{2-}$ sheets per unit cell lying parallel to (001) at $z=\frac{1}{4}$ and $\frac{3}{4}$ and two thallium ions lying half way between successive pairs of sheets. As in $RbBe_2F_5$, each sheet consists of linked six-membered rings of BeF_4 tetrahedra with hexagonal symmetry, and unshared vertices of the tetrahedra lie on both sides of each sheet. Successive pairs of sheets are related by symmetry centres, and thallium ions, lying on symmetry centres, are surrounded by six unshared fluorine ions, three of which belong to one sheet, and three belong to the next sheet.

Introduction

Bien que l'existence de pentafluorodibéryllates MBe_2F_5 avec $M=NH_4$, K, Rb et Cs ait été mise en évidence depuis 1957 [(Tamm & Novoselova, 1957; Breusov, 1958; Breusov & Simanov, 1959; Breusov, Vagurtova, Novoselova & Simanov, 1959; Toropov & Grebenshchikov, 1961)], seul le sel de rubidium a fait l'objet d'une étude cristallographique approfondie (Ilyukhin & Belov, 1962).

Il a pu être obtenu sous forme de monocristaux et l'observation d'un clivage très net parallèlement au plan (001) avait déjà conduit plusieurs auteurs à le considérer comme analogue à la sanbornite $BaSi_2O_5$ (Douglass, 1958). Sa structure est effectivement caractérisée par l'alternance de couches d'ions Rb^+ et de feuillets Be_4F_{10} constitués par des cycles liés de six tétraèdres $(BeF_4)^{2-}$. Sa maille triclinique de groupe spatial $P1$ et contenant 2 unités moléculaires aurait pour constantes:

$$a=7,98 \text{ Å},\quad b=4,69 \text{ Å},\quad c=6,12 \text{ Å}$$
$$\alpha=89°40',\quad \beta=91°,\quad \gamma=90°27'.$$

Ce qui révèle:

– l'existence d'une symétrie pseudohexagonale ($\alpha\neq\beta\neq\gamma\neq90°$; $a/b\neq\sqrt{3}$).

– et la présence, dans une maille, d'une seule couche de feuillet Be_4F_{10}, perpendiculaire à l'axe pseudohexagonal.

* Ce travail a été réalisé dans le cadre de la R.C.P. n° 219 'Structure et propriétés physiques de nouveaux composés fluorés'.