Fig. 3. Overlap of ring systems. Three molecules in parallel planes 3·4 Å apart are shown. The vertical stacking is indicated by the shading.

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The Crystal and Molecular Structures of Tetranactin*

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The structure of macrotetrolide antibiotic tetranactin, $C_{44}H_{72}O_{12}$, has been determined by the direct method with reflexion data collected on a 4-circle diffractometer. The crystals are monoclinic, space group $C2/c$ with four molecules in the unit cell of dimensions $a = 25·44$ (3), $b = 9·46$ (1), $c = 24·52$ (3) Å and $\beta = 129·83$ (8)°. The final R value for 3496 observed reflexions, obtained by the least-squares method with the block-matrix approximation, is 0·059, including anisotropic temperature factors for non-hydrogen atoms. The tetranactin molecule has a crystallographic twofold symmetry, and the molecular shape is fairly elongated and twisted. The outline of the molecule resembles that of a propeller which is remarkably different from that of nonactin. The intra- and intermolecular van der Waals contacts observed for tetranactin serve to stabilize the molecular and crystal structures.

Introduction

Tetranactin, $C_{44}H_{72}O_{12}$, is a macrotetrolide antibiotic (Ando *et al.*, 1971) and is one of the homologous compounds of nonactin (Dominguez, Dunitz, Gerlach & Prelog, 1962), which exhibit high K^+ selectivity for the alkali metal ion transport through the biological membranes. Physicochemical properties of the macrocyclic

antibiotics (nonactin, valinomysin, eniatin, gramicidin and others) as the alkali metal ion carriers have been investigated extensively (Ogata & Rasmussen, 1966; Graven, Lardy & Estrada-O, 1967; Mueller & Rudin, 1967). A correlation between the hydration energy of the cation and the origin of the cation specificity of the macrocyclic molecules on the formation of the alkali metal ion complexes in acetone-d_6($+ D_2O$) solution has been examined by proton magnetic resonance (p.m.r.) (Prestegard & Chan, 1970). However, the conformational changes of the molecules during the complex formation have remained unknown, except for those

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* Part of this work was presented at the 9th International Congress of Crystallography (31 August 1972, Kyoto) by Iitaka, Sakamaki & Nawata (1972*a*).

of valinomysin (Duax, Hauptman, Weeks & Norton, 1972) and monensin (Lutz, Winkler & Dunitz, 1971), and the assumption was made for those of nonactin on the basis of the p.m.r. spectra (Prestegard & Chan, 1969).

The purpose of this study is to elucidate the molecular structure of uncomplexed tetranactin in order to obtain information about the intramolecular motions and the complex formation mechanism of nonactin homologues. In the preliminary report (Iitaka, Sakamaki & Nawata, 1972*b*). the molecular structure of tetranactin and its alkali metal ion complexes, and also the several possible modes of intramolecular motions during the complex formation of tetranactin with the cation were described. In this paper are given detailed descriptions of the crystal and molecular structures of uncomplexed tetranactin in comparison with those of nonactin, which were published after completion of this work (Dobler, 1972).

Experimental

A single crystal of tetranactin, obtained from methanol solution as a transparent prism, was shaped to a specimen of size $0.42 \times 0.55 \times 0.52$ mm. Diffraction intensities were measured by a Rigaku computer-controlled 4-circle X-ray diffractometer with Ni-filtered Cu $K\alpha$ radiation and an ω–2θ scan to a maximum 2θ of 135°. The rate of scanning was 4° min^{-1}. No absorption correction was applied. 3496 structure factors having intensities above the 3σ level were obtained. The density was measured by flotation in an aqueous solution of potassium iodide.

Crystal data

Tetranactin, $C_{44}H_{72}O_{12}$, M.W. 792, monoclinic, $a = 25.44$ (3), $b = 9.46$ (1), $c = 24.52$ (3) Å and $\beta = 129.83$ (8)°, $U = 4527.8$ Å^3, $Z = 4$, $D_x = 1.16$, $D_m = 1.18$ g cm^{-3}, μ(Cu $K\alpha$) = 7.8 cm^{-1}, $F(000) = 1440$.
Absent spectra, hkl when $h + k$ is odd, $h0l$ when l is odd.
Space group, $C2/c$.
Statistical values for the normalized structure factors, E, are as follows:

		Theoretical values	
		Centrosymmetric	Noncentro-symmetric
$\langle |E|^2 \rangle$	$= 0.953$	1.000	1.000
$\langle |E| \rangle$	$= 0.737$	0.798	0.886
$\langle |E^2 - 1| \rangle$	$= 0.987$	0.968	0.736

Structure determination

The crystal structure analysis was started by the direct method. A $\sum_2$ correlation list was prepared for the 466 planes (16·7 times the number of non-hydrogen atoms in an asymmetric unit) with $|E|$ values greater than 1·6.

Origin specification and unknown symbol assignments were made as follows:

h	k	l	$|E|$	Sign or symbol
-19	1	21	3·87	$+$
-18	2	21	3·30	$+$
-19	1	14	3·71	A
-7	3	21	3·70	B
-9	3	8	3·22	C
-18	0	18	3·30	D
-8	4	18	3·29	E

In five cycles of iterative calculation by means of the symbolic addition procedure (Karle & Karle, 1966) for the 233 planes ($|E| \geq 1.92$), several relations among the symbols, such as $A = D \sim -$ and $B = E = -C$, were obtained with a probability greater than 0·91. Four sets of trials to determine the signs of 344 planes ($|E| \geq 1.753$) were then carried out by use of the tangent formula. The R index for the normalized structure factors converged to 0·159 for the starting set I ($A = -$ and $B = +$) and the signs of 342 planes were determined. On the E map computed with these phases the correct structure consisting of all the 28 non-hydrogen atoms was readily recognized (Fig. 1).

The refinement of the structure was carried out by the block-matrix least-squares method. Five cycles of calculations with isotropic temperature factors reduced the R value from 0·339 to 0·156, and a further three cycles of calculations with anisotropic temperature factors gave an R value of 0·117. At this stage, the locations of all the 36 hydrogen atoms were recognized on the difference Fourier map, the average peak height of electron density being 0·3 e Å^{-3}. In the final calculation in the refinement, the following weighting system was adopted:

$$\sqrt{w} = 30/F_o \quad \text{when} \quad F_o > 30,$$
$$\sqrt{w} = 1.0 \quad \text{when} \quad 30 \geq F_o > 1.7,$$
$$w = 0 \quad \text{when} \quad 1.7 \geq F_o.$$

The atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1962). The final R value, for 3496 independent reflexions, is 0·059 including anisotropic temperature factors for non-hydrogen atoms. The final atomic parameters with their estimated standard deviations are listed in Table 1.
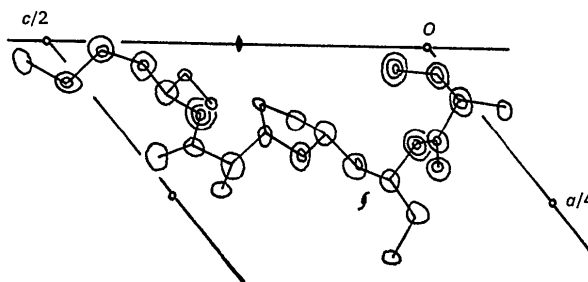

Fig. 1. E map, computed with 342 reflexions ($|E| > 1.753$).

Table 1. *Final atomic parameters and their standard deviations*

Quantities given are: fractional coordinates ($\times 10^4$) and β_{ij} ($\times 10^4$) for non-hydrogen atoms, where the temperature factor = exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; fractional coordinates ($\times 10^3$) and isotropic temperature factors (Å^2) for hydrogen atoms; r.m.s. displacements D_i along principal axes of vibration ellipsoids, in Å.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1660 (1)	1668 (3)	4217 (2)	25 (1)	102 (4)	26 (1)	−7 (1)	18 (1)	−5 (2)
C(2)	1966 (2)	1067 (3)	3901 (2)	24 (1)	116 (4)	30 (1)	1 (2)	19 (1)	−2 (2)
C(3)	1440 (2)	849 (3)	3101 (2)	27 (1)	120 (4)	28 (1)	5 (2)	21 (1)	2 (2)
O(4)	1812 (1)	579 (2)	2854 (1)	33 (1)	115 (3)	37 (1)	−12 (1)	29 (1)	−15 (1)
C(5)	1453 (1)	−483 (3)	2306 (1)	23 (1)	108 (4)	22 (1)	3 (1)	14 (1)	2 (1)
C(6)	1958 (1)	−1139 (3)	2252 (1)	25 (1)	93 (3)	22 (1)	8 (1)	16 (1)	6 (1)
C(7)	2184 (1)	−159 (3)	1949 (1)	20 (1)	89 (3)	18 (1)	5 (1)	12 (1)	1 (1)
O(8)	1574 (1)	21 (2)	1202 (1)	20 (1)	79 (2)	19 (1)	0 (1)	12 (0)	2 (1)
C(9)	1518 (1)	1229 (3)	886 (1)	21 (1)	83 (3)	22 (1)	−3 (1)	16 (1)	−5 (1)
C(10)	835 (1)	1346 (3)	148 (1)	23 (1)	78 (3)	20 (1)	−2 (1)	15 (1)	0 (1)
C(11)	422 (1)	2468 (3)	173 (1)	22 (1)	71 (3)	21 (1)	−5 (1)	15 (1)	0 (1)
O(12)	377 (1)	2075 (2)	704 (1)	21 (1)	102 (2)	19 (1)	5 (1)	14 (1)	3 (1)
C(13)	135 (1)	2987 (3)	4409 (1)	22 (1)	82 (3)	23 (1)	1 (1)	16 (1)	2 (1)
C(14)	346 (2)	2364 (3)	4003 (2)	28 (1)	96 (4)	29 (1)	−4 (1)	21 (1)	−6 (2)
C(15)	841 (2)	3312 (3)	4023 (2)	28 (1)	101 (4)	28 (1)	−4 (1)	22 (1)	−7 (2)
O(16)	1130 (1)	2526 (2)	3758 (1)	27 (1)	117 (3)	25 (1)	5 (1)	19 (1)	−1 (1)
O(17)	1870 (1)	1437 (3)	4809 (1)	35 (1)	118 (3)	27 (1)	9 (1)	22 (1)	9 (1)
C(18)	2396 (2)	−237 (4)	4304 (2)	32 (1)	176 (6)	33 (1)	26 (2)	18 (1)	9 (2)
C(19)	952 (2)	−411 (4)	2851 (2)	27 (1)	184 (5)	31 (1)	−11 (2)	21 (1)	−8 (2)
C(20)	1164 (2)	−1453 (4)	2550 (2)	30 (1)	139 (4)	30 (1)	−19 (2)	21 (1)	−13 (2)
C(21)	2765 (2)	−749 (4)	1993 (2)	24 (1)	159 (5)	30 (1)	13 (2)	18 (1)	4 (2)
O(22)	1949 (1)	2129 (2)	1157 (1)	28 (1)	119 (3)	29 (1)	−20 (1)	15 (1)	0 (1)
C(23)	935 (2)	1750 (4)	−387 (2)	35 (1)	133 (4)	26 (1)	4 (2)	23 (1)	7 (2)
C(24)	321 (1)	2653 (3)	5499 (1)	25 (1)	113 (4)	21 (1)	−5 (2)	15 (1)	9 (1)
C(25)	691 (1)	3068 (3)	5217 (2)	23 (1)	110 (4)	24 (1)	−7 (1)	14 (1)	−6 (2)
C(26)	495 (2)	4597 (4)	3540 (2)	40 (1)	109 (4)	42 (1)	4 (2)	32 (1)	6 (2)
C(27)	3443 (2)	−703 (5)	2737 (2)	22 (1)	204 (6)	39 (1)	14 (2)	16 (1)	11 (2)
C(28)	966 (2)	5507 (4)	3507 (2)	50 (1)	138 (5)	45 (1)	−8 (2)	36 (1)	3 (2)

	x	y	z	B
H(C2)	226 (2)	188 (4)	398 (2)	6·1 (0·9)
H(C3)	119 (2)	175 (4)	289 (2)	5·4 (0·8)
H(C5)	106 (2)	−7 (3)	184 (2)	4·9 (0·7)
H(C6)	234 (2)	−149 (3)	271 (2)	4·7 (0·7)
H'(C6)	173 (1)	−204 (3)	192 (2)	4·2 (0·7)
H(C7)	233 (1)	77 (3)	218 (1)	3·4 (0·6)
H(C10)	57 (1)	39 (3)	1 (1)	3·4 (0·6)
H(C11)	68 (1)	332 (3)	33 (2)	4·5 (0·7)
H(C13)	8 (1)	390 (3)	80 (1)	3·7 (0·6)
H(C14)	57 (1)	146 (3)	424 (2)	4·2 (0·7)
H'(C14)	−8 (2)	225 (3)	348 (2)	4·9 (0·7)
H(C15)	123 (1)	362 (3)	451 (2)	3·9 (0·7)
H(C18)	272 (2)	−2 (4)	477 (2)	7·4 (0·9)
H'(C18)	218 (2)	−106 (4)	432 (2)	6·7 (0·9)
H''(C18)	266 (2)	−49 (4)	415 (2)	6·3 (0·9)
H(C19)	100 (2)	−87 (4)	324 (2)	5·3 (0·8)
H'(C19)	46 (2)	−4 (4)	244 (2)	8·3 (1·1)
H(C20)	76 (2)	−210 (4)	214 (2)	6·1 (0·8)
H'(C20)	156 (2)	−207 (3)	293 (2)	5·4 (0·8)
H(C21)	280 (2)	−25 (4)	168 (2)	6·6 (0·9)
H'(C21)	262 (2)	−169 (4)	173 (2)	6·2 (0·8)
H(C23)	49 (2)	164 (5)	−85 (2)	7·8 (1·1)
H'(C23)	123 (2)	102 (4)	−38 (2)	6·9 (0·9)
H''(C23)	116 (2)	262 (3)	−27 (2)	5·1 (0·7)
H(C24)	50 (1)	172 (3)	577 (1)	4·0 (0·6)
H'(C24)	38 (2)	335 (3)	583 (2)	4·7 (0·7)
H(C25)	94 (2)	404 (4)	541 (2)	5·6 (0·8)
H'(C25)	107 (2)	242 (3)	539 (2)	4·8 (0·7)
H(C26)	13 (2)	426 (4)	308 (2)	5·5 (0·8)
H'(C26)	32 (2)	517 (4)	372 (2)	6·1 (0·8)
H(C27)	380 (2)	−110 (4)	273 (2)	8·4 (1·0)
H'(C27)	354 (2)	14 (4)	293 (2)	8·5 (1·1)
H''(C27)	345 (2)	−138 (4)	305 (2)	7·7 (0·9)
H(C28)	68 (2)	627 (4)	316 (2)	7·0 (0·9)
H'(C28)	139 (2)	586 (4)	397 (2)	7·0 (0·9)
H''(C28)	116 (2)	492 (4)	334 (2)	7·4 (0·9)

	D_1	D_2	D_3
C(1)	0·18	0·19	0·21
C(2)	0·17	0·19	0·21
C(3)	0·17	0·19	0·21
O(4)	0·18	0·20	0·22
C(5)	0·19	0·19	0·21
C(6)	0·19	0·21	0·24
C(7)	0·18	0·21	0·24
O(8)	0·18	0·22	0·24
C(9)	0·20	0·21	0·23
C(10)	0·20	0·23	0·23
C(11)	0·18	0·23	0·24
O(12)	0·18	0·21	0·28
C(13)	0·20	0·21	0·22
C(14)	0·19	0·20	0·23
C(15)	0·18	0·19	0·21
O(16)	0·18	0·19	0·20
O(17)	0·18	0·23	0·29
C(18)	0·18	0·24	0·26
C(19)	0·18	0·22	0·23
C(20)	0·20	0·22	0·23
C(21)	0·21	0·22	0·29
O(22)	0·20	0·25	0·29
C(23)	0·21	0·26	0·32
C(24)	0·20	0·23	0·29
C(25)	0·20	0·21	0·28
C(26)	0·19	0·23	0·28
C(27)	0·22	0·26	0·31
C(28)	0·20	0·29	0·31

The interatomic distances and angles are given in Fig. 2.*

Discussion

Molecular structure

A stereoscopic drawing of the molecule of tetranactin is shown in Fig. 3. The molecule has a diad axis coinciding with a crystallographic diad. The shape of the molecule is fairly elongated and twisted, and the outline resembles that of a propeller. The shape is markedly different from that of nonactin which resembles a torus of approximate symmetry $\bar{4}$, having a crystallographic diad axis coinciding with the approximate $\bar{4}$ axis. Conformations of the tetrahydrofuran (THF) rings in the tetranactin molecule are all of the envelope type and

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30328 (21 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
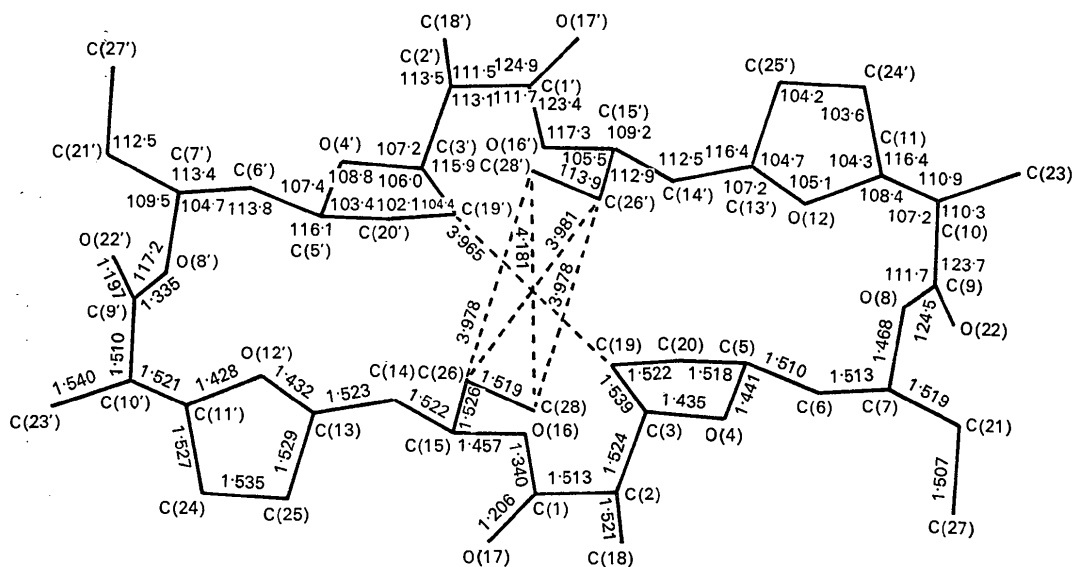
approximate symmetry planes lie on the atoms C(5) and O(12) (see Fig. 4), while in the nonactin molecule carbon atoms C(5) and C(13) deviate from the planes of the other four atoms. In the tetranactin molecule four keto oxygen atoms turn outward, just as in nonactin, but two ethyl groups $C(26^i)$–$C(28^i)$ and $C(26^{vi})$–$C(28^{vi})$, and two carbon atoms of the THF rings, $C(19^i)$ and $C(19^{vi})$, approach each other in pairs and give rise to intramolecular van der Waals contacts which may stabilize the molecular conformation (Fig. 2). The comparison of the corresponding dihedral angles (Φ) along the 32-membered rings of the molecules of tetranactin and nonactin in each crystal revealed that the conformations around the successive seven bonds within one unit of the constituent acids (in Figs. 5 and 6, Φ's for (+)-homononactic acid are shown) are very similar ($|\Delta\Phi| < 7°$), while those involved in the other unit in the immediate vicinity are quite different (where three $|\Delta\Phi|$s exceed 100°). It should be noted here that while the conformation of the nonactin molecule in the uncomplexed state is very

Fig. 2. Bond distances (Å) and angles (°). The estimated deviations are about 0·006 Å and 0·3°, respectively. The atoms with a single prime correspond to those of the equivalent position vi given in Table 2.
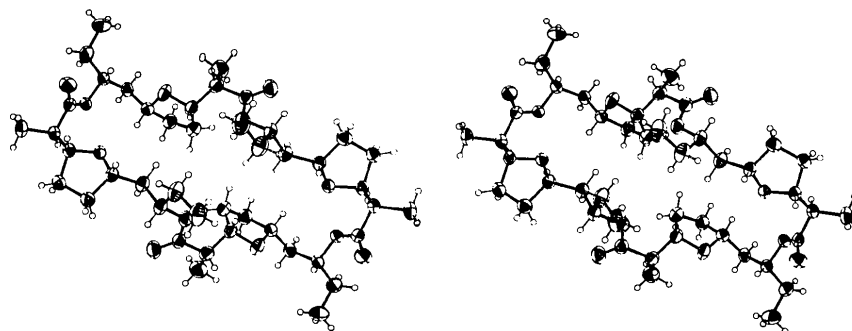

Fig. 3. Stereoscopic drawing of the molecule along [010]. The ellipsoid encloses the region in which the centre of the atom is found with probability 50%. The thermal motions of the hydrogen atoms are reduced to 0·6 Å².

close to that of the potassium complex and also very similar to that of tetranactin in the complexed state, it greatly differs from that of the uncomplexed tetranactin molecule. It is interesting to see that the uncomplexed molecule of tetranactin changes its conformation quite easily in the presence of alkali ions in solution. Interconversion of the two types of conformation may possibly be readily achieved by intramolecular motions in which the rotation around the bonds C(10)–C(11), C(13)–C(14), C(14)–C(15) and C(15)–O(16) may be important (where $|\Delta\Phi| > 78°$). The modes of intramolecular motion in the complex formation with alkali metal ions have been discussed for tetranactin (Iitaka, Sakamaki & Nawata, 1972b).

Also noteworthy in this connexion are the structures of the molecules in solution. The molecular conformation of nonactin in the crystal possesses an approximate symmetry of $\overline{4}$. This is in accordance with the result of the p.m.r. study which showed that the four constituent acids are magnetically equivalent in solution (Prestegard & Chan, 1969). On the other hand, the present study suggests that the two sets of subunits in

Fig. 4. Dihedral angles ($\Phi°$) around THF rings and deviations (Å) from the planes of four atoms (marked with *).

tetranactin should be magnetically non-equivalent in the crystal. This may be apparent on examining the environments of the methine protons involved in each of the non-equivalent THF rings: H(C11) is nearly on the carbonyl plane [$X - Y$ plane defined by Pople (1962)] and is in proximity to O(22), while H(C3) lies nearly on the axis of C(1)=O(17) [the X axis defined by Pople (1962)] and is in proximity to the carbon end of the carbonyl group. Therefore it is to be expected that H(C11) will experience an intense deshielding effect, but H(C3) a positive long-range shielding effect. This was not the case in the n.m.r. spectra, which showed the four subunits to be magnetically equivalent in $CDCl_3$ solution at ambient temperature (Ando, Murakami & Nawata, 1971) and even at $-110°C$ in the mixed solvent $CS_2 + CD_3C_6D_5(2:1)$ (Kyogoku, Akutsu, Kobayashi, Kawano & Ueno, 1973). The infrared spectrum (KBr disc) of tetranactin, on the other hand, exhibited distinct differences from that of nonactin which could be ascribed to the difference in crystal structures. In the solutions ($CHCl_3$ and CCl_4), however, they showed similar infrared spectra with broad absorption bands, which also resemble the spectrum of nonactin in the solid state (Ueno, Akutsu, Kyogoku & Nawata, 1973). These facts suggest that in solution the tetranactin molecule may be very flexible and may possess the molecular symmetry $\overline{4}$.
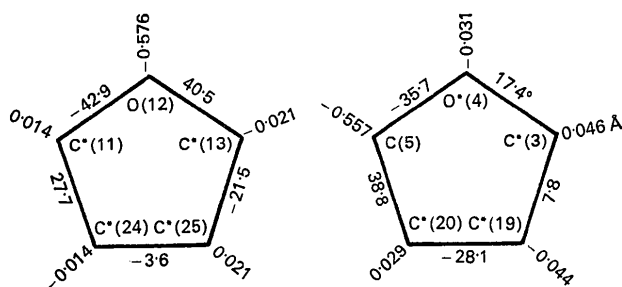
Crystal structure

In the crystal, as shown in Fig. 7, the molecules are packed along [101], and held together by intermolecular short contacts to form a wave-shaped strip, the shortest intermolecular distances being $C(2^i)-O(17^{vii})$ $= 3.511$ and $C(1^i)-O(17^{vii}) = 3.385$ Å, where the dipole moments of the two carbonyl groups are arranged in antiparallel fashion. The strips are arranged along [100]
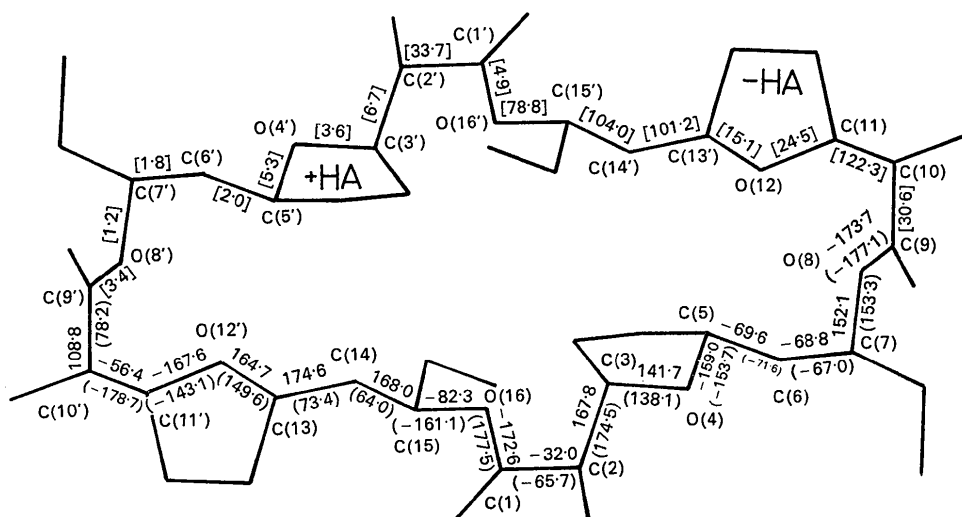

Fig. 5. Dihedral angles ($\Phi°$) around the 32-membered ring. The values in the parentheses are those for nonactin, and those in the brackets are the $|\Delta\Phi|$ between the two molecules at the corresponding bonds.

to form a rippled sheet, and are connected to each other mainly by van der Waals contacts $O(22^i)-C(6^{viii})$ $=3\cdot424$ Å. These sheets are then stacked along [010], through the van der Waals contacts, to complete the crystal structure $[C(28^i)-C(23^{ii})=3\cdot787$ and $C(27^i)-C(13^{iii'})=3\cdot775$ Å] (Table 2). In the crystal of nonactin, no close intermolecular van der Waals contacts involving the carbonyl group are observed and the molecules pack to form the disordered three-dimensional structure. The presence of the ethyl groups in tetranactin may serve to stabilize the molecular and crystal structures, which results in the distinct difference in structure between the two homologues in the crystalline state.

Computer program *SYMMAIN* (Matsuzaki & Iitaka, 1971) was used for the calculation of the symbolic addition procedure and the application of the tangent formula. The least-squares block-matrix calculations were carried out with the use of the program *HBLS* IV (Okaya & Ashida, 1967). The stereoscopic drawing was made with *ORTEP* (Johnson, 1965).

Table 2. *Packing distances shorter than* $3\cdot8$ Å

From molecule i (000)	To atom	Of molecule	Translation	Distance
C(27)	C(13)	iii	0$\overline{1}$0	3·775 Å
C(28)	C(23)	ii	000	3·787
C(1)	O(17)	vii	000	3·385
O(22)	C(6)	viii	000	3·424
C(2)	O(17)	vii	000	3·511
C(25)	O(8)	ii	0$\overline{1}$0	3·530
C(24)	O(8)	ii	0$\overline{1}$0	3·532
O(22)	C(18)	viii	000	3·557
O(4)	C(21)	viii	000	3·582
O(12)	C(27)	viii	000	3·651
O(17)	C(23)	ii	0$\overline{1}$0	3·673
O(4)	C(27)	viii	000	3·698

The coordinates of the equivalent positions are

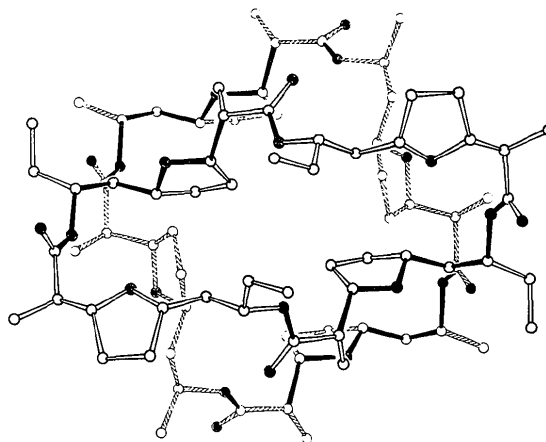|	x	y	z
i	x	y	z
ii	x	$1-y$	$\frac{1}{2}+z$
iii	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
iv	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$
v	$1-x$	$1-y$	$1-z$
vi	$-x$	y	$\frac{1}{2}-z$
vii	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$1-z$
viii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$

Fig. 6. Tetranactin and nonactin (shaded bonds) molecules viewed down the twofold axis. Oxygen atoms are shaded. $|\Delta\Phi|$'s at the dark bonds are less than 7° between the two molecules.
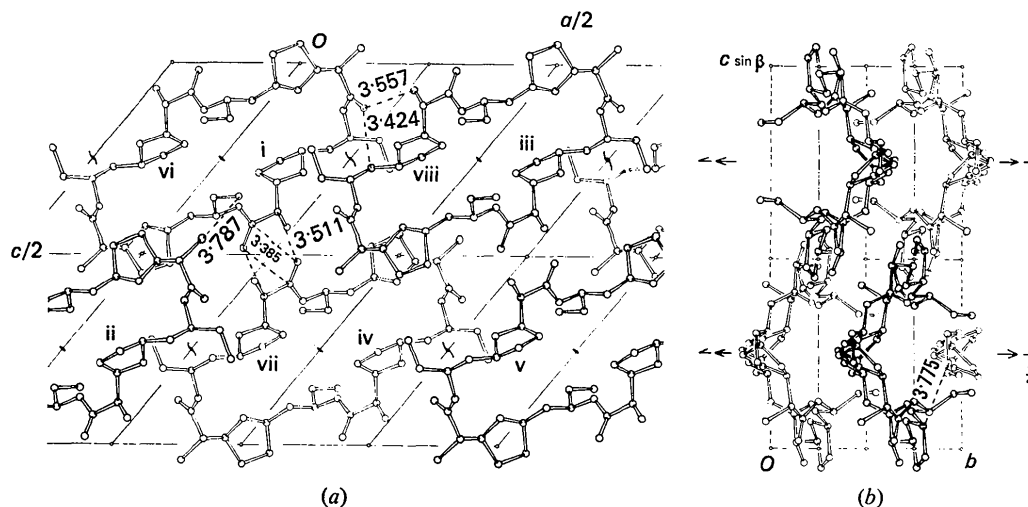

(a)   (b)

Fig. 7. (a) Projection of the crystal structure along [010]. The coordinates of the asymmetric units i, ii, iii, ..., viii are given in Table 2. (b) Projection of the crystal structure along [100].

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The High-Temperature Structure of CsCuCl₃

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The crystal structure of $CsCuCl_3$, above its transition temperature (423°K) has been determined at 466°K. The polar hexagonal space group $P6_3mc$ is the most probable one for this compound. The cell dimensions are $a = 7.245$ (7) and $c = 6.150$ (6) Å with $Z = 2$. Full-matrix least-squares refinement of 185 observed symmetry-independent three-dimensional diffractometer data (Mo $K\alpha$) led to a final R index on F of 0.041 and a weighted R index of 0.069. Above its transition temperature $CsCuCl_3$ is isostructural with $CsCrCl_3$ and $CsCrBr_3$. The Cu^{2+} ion is slightly displaced from the centre of a Cl^- octahedron along the trigonal axis (c axis) giving rise to a ferroelectric structure.

Introduction

In a previous communication (Kroese, Tindemans-van Eyndhoven & Maaskant, 1971) we reported a phase transition in $CsCuCl_3$ at 423°K; we also discussed the high-temperature structure as determined by single-crystal Weissenberg measurements. However, owing to the lack of sufficient data we could not determine unequivocally the space group of this compound. In order to solve this problem we performed single-crystal X-ray diffractometer measurements, the results of which are communicated here.

Experimental

Crystals of $CsCuCl_3$ were grown from an aqueous solution as described elsewhere (Schlueter, Jacobson &

Rundle, 1966). An irregularly shaped crystal of approximate size $0.2 \times 0.2 \times 0.6$ mm was mounted on an Enraf–Nonius three-circle single-crystal diffractometer with the hexagonal axis along the φ-axis. The diffractometer was equipped with an apparatus enabling us to heat the crystal with a continuous stream of hot nitrogen gas. The temperature of the crystal during the experiment was 466 ± 5°K. Precise unit-cell parameters were determined at this temperature by measuring nine carefully selected reflexions with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The cell parameters are: $a = 7.245$ (7), $c = 6.150$ (6) Å (numbers in parentheses here and in the tables are estimated standard deviations in the least significant digit). The calculated density at 466°K for $Z = 2$ and a molecular weight of 302.8, $d = 3.63$ g cm^{-3}, agrees with the measured density at room temperature, $d = 3.65$ g cm^{-3}. Intensities were