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The Crystal and Molecular Structure of Nagilactone A Diacetate[1]

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The title compound crystallizes in the orthorhombic space group $P2_12_12_1$, with cell dimensions of $a=10.43$, $b=15.45$, $c=13.65$ Å, and $Z=4$. The structure was determined by direct methods from photographic data, and was refined by the least-squares method to a final R of 0.098 for 2581 reflections. Rings A and B are subject to steric strains resulting from the formation of a lactone ring. This is reflected in the abnormal values for some bond lengths, angles, and dihedral angles.

Nagilactones were the first reported compounds of novel tricyclic nor- or bisnor-diterpenoid constituents which originate in *Podocarpus* plants. Since four nagilactones, A, B, C, and D, were isolated from *P. nagi* zoll. et Moritzi in 1968,[2] more than twenty components have been found in various *Podocarpus* species as important biologically active principles: plant-growth regulators,[3] anti-termite substances,[4] and insect toxins for house-fly larvae.[5] Although the structures of all the lactones have been assigned and correlated on the basis of chemical or spectral evidence, it has become increasingly important to determine the exact structure of any congener in this group of compounds by means of X-ray crystallography. This article will report the details of the X-ray analysis of nagilactone A diacetate. The present results completely support the structure as assigned in the preliminary communication.[1]

Experimental

Nagilactone A diacetate crystallizes from chloroform as colorless prisms. All the data were obtained from a specimen with dimensions of 0.2×0.3×0.4 mm, cut from the above crystal.

Crystal Data. $C_{23}H_{28}O_8$, $M=432.5$, orthorhombic, $a=10.43(1)$, $b=15.45(1)$, $c=13.65(1)$ Å, $U=2200$ Å^3, $D_c=1.32$ g·cm^{-3} $Z=4$, $F(000)=920$, $\mu=$(Cu-$K\alpha$, $\lambda=1.542$ Å)$=6.9$ cm^{-1}; space group $P2_12_12_1(D_2^4)$; systematic absences: $h\,0\,0$ when $h\neq 2n$, $0\,k\,0$ when $k\neq 2n$, and $0\,0\,l$ when $l\neq 2n$.

Crystallographic Measurements. The unit-cell dimensions were evaluated from zero-layer Weissenberg photographs, the spacings of the reflections being calibrated with superimposed Al powder lines. The intensity data for the $0\,k\,l \sim 10\,k\,l$ and $h\,0\,l \sim h\,3\,l$ layers were recorded by equi-inclination Weissenberg photography using Cu-$K\alpha$ radiation. The intensities were estimated visually and corrected for spot shape and for Lorentz and polarization factors. No correction was applied for absorption and extinction. The resulting data were correlated and reduced to structure-factor amplitudes using the method of Hamilton, Rollet, and Sparks.[6] A total of 2581 independent structure factors were obtained; 292 were too weak to be measured.

Structure Determination and Refinement. The normalized structure factors, E's, were calculated with a scale factor and a mean isotropic temperature factor derived from a Wilson plot.[7] The structure was solved by direct phase-determining methods.[8] Using 600 reflections with $E>1.21$, the $\sum_2$ relations were listed. Four zonal reflections (Table 1), having large $|E|$ values and appearing in many $\sum_2$ interactions, were chosen to define the origin and the enantiomorph. In addition, three symbolic phases (A, B, and C) were assigned. The starting set, together with the final refined values of A and B, is listed in Table 1. The manual symbolic addition procedure indicated that $B=\pi/2$ and $C=-\pi/2$, or that $B=-\pi/2$ and $C=\pi/2$. No information was obtained for the A symbol. In order to apply the tangent formula,[9] the numerical phases from 0° to 315°, in steps of 45°, were assigned to the A symbol. Tangent refinement was carried out for each of the 16 possible phase combinations. The values of R_{Karle}[8] ranged from 0.25 to 0.33, and those of Z,[10] from 5602 to 7710. A reasonable structure was obtained from an E-map calculated with the phases in the most consistent set ($R_{Karle}=0.25$ and $Z=7710$). All the atoms, except for C(16) and C(17) of the isopropyl group, were located. Three cycles of block-diagonal least-squares refinement of the positions and isotropic thermal parameters for these 29 atoms reduced the R from 0.402 to 0.243. The two remaining carbon atoms were located in a difference synthesis. A further five cycles including all the non-hydrogen atoms reduced the R to 0.135. In the anisotropic least-squares calculations, the following weighting scheme was used:

$$w = 0.1 \quad \text{for } |F_o| \leq 2.0$$
$$w = 1.0 \quad \text{for } 2.0 < |F_o| \leq 12.0$$
$$w = (12.0/F_o)^2 \quad \text{for } |F_o| > 12.0.$$

Seven rounds of least-squares with block-diagonal approximation brought the refinement to convergence at 0.112. The hydrogen atoms, except for those bonded to C(22),

Table 1. Starting set of reflections, together with final refined phases for the symbols

h	k	l		$\phi(h)$ initial	$\phi(h)$ final
0	10	5		0	fixing origin and enantiomorph
0	3	6		$\pi/2$	
9	2	0		$\pi/2$	
2	0	1		$\pi/2$	
4	1	10	A	$\pm\pi/4$, $\pm 3\pi/4$, 0, π, $\pm\pi/2$	-2.83
4	1	11	B	$\pi/2$, $-\pi/2$	1.85
1	14	0	C	$-\pi/2$, $\pi/2$	$-\pi/2$

[†] Deceased 5 August 1973.

Table 2. Fractional atomic co-ordinates and anisotropic thermal parameters with estimated standard deviations in parentheses

(a) Fractional co-ordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C (1)	−0.0776(7)	0.0602(5)	−0.1621(5)	C (22)	0.1238(9)	0.0035(7)	−0.3784(6)
C (2)	−0.0507(9)	0.1582(5)	−0.1506(6)	C (23)	0.0020(7)	−0.0705(4)	0.2769(5)
C (3)	−0.1358(9)	0.2010(5)	−0.0792(6)	C (24)	0.1356(7)	−0.0846(5)	0.3213(5)
C (4)	−0.1627(8)	0.1525(4)	0.0168(5)	O (25)	0.0101(6)	0.2198(3)	0.1152(4)
C (5)	−0.1704(6)	0.0544(4)	0.0052(4)	O (26)	−0.0599(5)	0.0870(3)	0.1513(3)
C (6)	−0.1550(6)	0.0267(4)	0.1112(4)	O (27)	−0.1681(7)	−0.2683(3)	−0.2052(4)
C (7)	−0.1140(6)	−0.0691(5)	0.1270(4)	O (28)	0.0249(4)	0.0259(3)	−0.2262(3)
C (8)	−0.1098(7)	−0.1224(4)	0.0331(5)	O (29)	−0.0844(5)	0.0700(4)	−0.3588(4)
C (9)	−0.0951(6)	−0.0817(4)	−0.0616(4)	O (30)	0.0084(5)	−0.0781(3)	0.1778(3)
C (10)	−0.0619(6)	0.0136(4)	−0.0610(4)	O (31)	−0.0948(5)	−0.0554(4)	0.3195(3)
C (11)	−0.1129(7)	−0.1306(4)	−0.1440(5)	H (C1)	−0.169(9)	0.048(6)	−0.188(7)
C (12)	−0.1437(7)	−0.2193(5)	−0.1368(5)	H (C2)	−0.061(8)	0.183(6)	−0.226(6)
O (13)	−0.1418(6)	−0.2553(3)	−0.0461(3)	H (C2a)	0.044(8)	0.154(6)	−0.116(6)
C (14)	−0.1296(8)	−0.2059(4)	0.0383(5)	H (C3)	−0.229(8)	0.199(6)	−0.110(7)
C (15)	−0.1344(10)	−0.2641(5)	0.1267(6)	H (C3a)	−0.100(8)	0.248(6)	−0.061(6)
C (16)	−0.2684(13)	−0.3104(7)	0.1332(8)	H (C5)	−0.245(8)	0.036(6)	−0.026(7)
C (17)	−0.0136(13)	−0.3284(7)	0.1223(8)	H (C6)	−0.240(7)	0.031(5)	0.147(6)
C (18)	−0.2922(8)	0.1882(6)	0.0592(7)	H (C7)	−0.190(8)	−0.102(6)	0.182(7)
C (19)	−0.0604(7)	0.1609(5)	0.0944(5)	H (C11)	−0.103(8)	−0.115(6)	−0.213(7)
C (20)	0.0772(6)	0.0217(5)	−0.0213(5)	H (C15)	−0.125(7)	−0.226(5)	0.187(6)
C (21)	0.0062(8)	0.0373(5)	−0.3227(5)				

(b) Anisotropic thermal parameters $(\times 10^4)$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	40(7)	28(3)	33(4)	0(8)	4(8)	11(7)
C (2)	121(11)	17(3)	43(5)	−31(9)	34(12)	5(7)
C (3)	138(12)	25(3)	36(4)	−2(11)	12(13)	23(7)
C (4)	83(8)	12(3)	32(4)	13(8)	11(10)	−6(6)
C (5)	39(6)	13(3)	22(3)	3(7)	−3(7)	−8(5)
C (6)	36(6)	16(3)	26(3)	−15(7)	−5(8)	5(6)
C (7)	37(6)	30(3)	15(3)	−3(8)	−3(7)	−7(6)
C (8)	62(7)	17(3)	20(3)	−7(7)	−7(9)	3(5)
C (9)	32(6)	24(3)	19(3)	3(7)	4(7)	−5(6)
C (10)	20(5)	17(3)	21(3)	−2(7)	1(7)	3(5)
C (11)	65(7)	19(3)	24(3)	−3(8)	16(9)	−8(6)
C (12)	66(8)	28(3)	28(4)	−15(9)	−21(9)	−16(6)
O (13)	114(7)	19(2)	30(3)	−28(7)	−15(8)	−10(4)
C (14)	94(9)	20(3)	34(4)	−34(9)	2(11)	−18(7)
C (15)	213(15)	22(3)	30(4)	−54(13)	−35(14)	8(7)
C (16)	261(20)	64(6)	79(8)	−191(20)	73(23)	15(12)
C (17)	281(20)	60(6)	74(8)	185(20)	−47(23)	40(11)
C (18)	90(9)	41(4)	68(6)	95(10)	13(13)	−28(9)
C (19)	73(8)	21(3)	34(4)	0(9)	13(10)	5(7)
C (20)	11(5)	32(3)	30(3)	−22(7)	−17(7)	−9(6)
C (21)	81(8)	45(4)	29(4)	−31(11)	37(10)	15(8)
C (22)	94(10)	70(6)	44(5)	68(13)	76(11)	−20(9)
C (23)	75(7)	19(3)	23(3)	−4(9)	−11(9)	−2(6)
C (24)	60(8)	43(4)	35(4)	3(9)	−38(9)	−7(8)
O (25)	125(8)	24(2)	58(4)	−61(7)	−22(10)	−13(5)
O (26)	72(5)	13(2)	25(2)	−19(5)	−21(6)	−6(4)
O (27)	132(8)	31(2)	37(3)	−21(7)	−21(8)	−34(5)
O (28)	47(5)	33(2)	22(2)	−12(5)	19(6)	5(5)
O (29)	61(6)	80(4)	33(3)	−21(8)	−21(8)	31(6)
O (30)	45(4)	22(2)	23(2)	3(5)	−7(6)	2(4)
O (31)	63(6)	57(3)	25(2)	13(7)	19(7)	−28(5)

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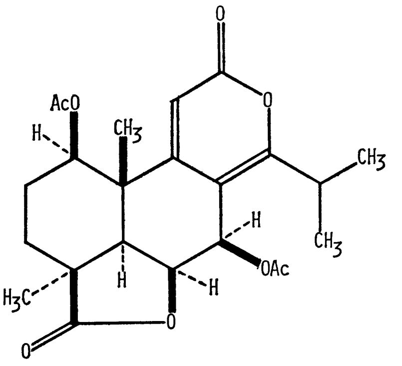
a) in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

C(16), C(17), C(24), and C(20), appeared in a difference map.

The inclusion of these in a structure-factor calculation, with each assigned an isotropic temperature factor of 4.0 Å^2, followed by six cycles, gave an R value of 0.098. The atomic scattering factors were taken from Ref. 11. At the end of the refinement, an analysis of the distribution of $<W\Delta^2>$ against $|F_o|$ and $\sin\theta$ confirmed that the weighting scheme was adequate. The final positional and thermal parameters for the atoms are listed in Table 2. The final structure factors are given in Table 3.*

Results and Discussion

A perspective view of the molecule, together with the numbering scheme, is shown in Fig. 1. The molecular structure of nagilactone A diacetate derived from X-ray analysis, as shown in (I), was consistent with that previously proposed on the basis of the chemical and spectroscopic data.[5]



(I)

The A/B ring junction is *trans*, and H(5)/H(6) and H(6)/H(7) are *cis*. The O(30) atom at the 7-position is *cis* to C(20) at the 10-position and the γ-lactone ring. O(28) is in an equatorial position.

The equations of the least-squares planes and the deviations of individual atoms from these planes are given in Table 4. The torsional angles are shown in Fig. 2.

Ring A adopts a distorted chair conformation. The deviations from the least-squares plane (Plane I of Table 4) range from 0.096 Å (C(3)) to 0.324 Å (C(10)). For a closer examination of the chair, several planes consisting of four atoms and the deviations of the atoms from them are given in Table 4. These results and the torsional angles indicate that a flattening of the chair conformation occurs at C(3) and C(4), while puckering occurs at C(1) and C(10). The distortion of Ring A from a chair conformation may be mainly attributed to the formation of a lactone ring and to the 1,3-diaxial steric strains between C(20) and C(19), and between C(20) and O(26). In spite of the deformation, the C(20)···C(19) and C(20)···O(26) distances (3.028 Å and 2.934 Å respectively) are still shorter than the sum of the van der Waals radii, although these are larger from those expected from the dreiding molecular models.

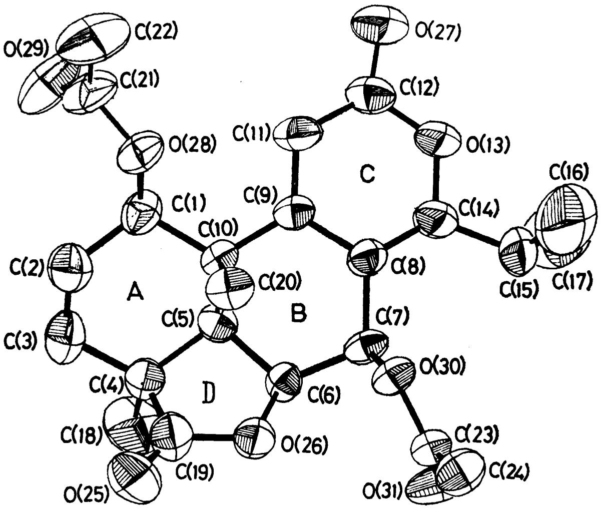


Fig. 1. Molecular structure and atomic numbering in nagilactone A diacetate. The thermal ellipsoids are scaled to include 50% probability.

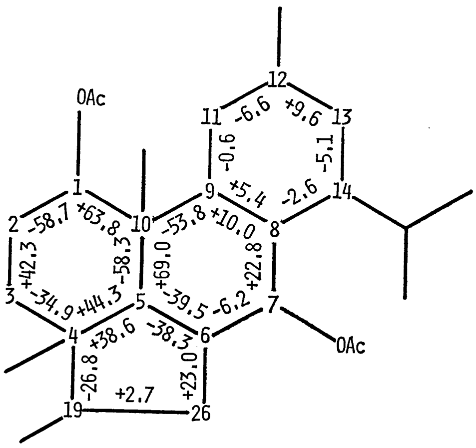


Fig. 2. Ring torsional angles in nagilactone A diacetate.

In Ring B, C(7), C(8), C(9) and C(10) are coplanar within 0.047 Å, with C(5) and C(6) deviating by 1.113 Å and 0.736 Å respectively in the same direction from this plane (Plane V). Upon the ABD ring fusion, Ring B adopts a conformation distorted from the energetically preferred half-chair form.[12] Ring C (α-pyrone ring) is nearly planar, although the deviations from Plane VI show a slight bending of the α-pyrone ring along the C(8)···C(12) vector. C(7) and O(27) deviate from Plane VI by +0.263 Å and +0.136 Å respectively in the same direction as C(12) and C(8), while C(10) and C(15) deviate by −0.093 Å and −0.090 Å respectively in the opposite direction.

In Ring D (γ-lactone ring), the C·C(O)·O·C moiety is planar with C(5), by 0.626 Å out of the plane.

The bond lengths and angles, together with their estimated standard deviations, are listed in Table 5. The mean C(sp^3)–C(sp^3) bond is 1.546 Å; however, there are a number of significant departures from

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* Table 3 has been submitted to, and is kept by, the office of the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 113. (Document No. 7509).

Table 4. Least-squares planes and deviations

The atoms indicated with asterisks were included in the calculation of the least-squares planes.

Plane I $-0.8956x-0.1300y-0.4254z=1.2292$
Plane II $-0.8957x+0.1506y-0.4145z=1.7385$
Plane III $-0.7386x-0.2514y-0.6255z=1.0017$
Plane IV $-0.9448x-0.2694y-0.1867z=0.8165$
Plane V $-0.9780x+0.1844y-0.0976z=0.7739$
Plane VI $-0.9822x+0.1865y+0.0237z=0.7486$
Plane VII $-0.6829x+0.3907y+0.6173z=2.2116$

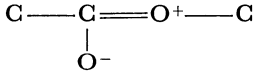
Deviations from planes

Plane I		Plane II		Plane III		Plane IV	
C (1)*	0.316 Å	C (1)*	0.045 Å	C (1)	0.747 Å	C (1)*	0.111 Å
C (2)*	−0.199	C (2)*	−0.044	C (2)*	0.060	C (2)	−0.592
C (3)*	0.096	C (3)	0.449	C (3)*	−0.060	C (3)*	−0.113
C (4)*	−0.113	C (4)*	0.044	C (4)	−0.484	C (4)*	0.109
C (5)*	0.224	C (5)*	−0.046	C (5)*	0.056	C (5)	0.624
C (10)*	−0.324	C (10)	−0.782	C (10)*	−0.056	C (10)*	−0.107

Plane V		Plane VI				Plane VII	
C (5)	1.113 Å	C (7)	0.263 Å	C (15)	−0.090 Å	C (4)*	0.009 Å
C (6)	0.736	C (8)*	0.036	O (27)	0.136	C (5)	−0.626
C (7)*	0.023	C (9)*	−0.028	C (5)	1.158	C (6)*	−0.009
C (8)*	−0.047	C (10)	−0.093	C (6)	0.955	C (19)*	−0.015
C (9)*	0.046	C (11)*	−0.013			O (26)*	0.015
C (10)*	−0.022	C (12)*	0.050			O (25)	0.014
C (11)	0.197	O (13)*	−0.044				
C (14)	−0.090	C (14)*	0.000				

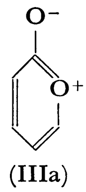
this mean. The C(2)–C(3) bond length (1.478 Å) is shorter by 6σ than the average value of the other C–C distances of Ring A. The lengthening of the C(5)–C(10) bond (1.580 Å) may be due to intramolecular steric strains between C(20) and C(19) and between C(20) and O(26). The same type of bond lengthening has been found in the crystal structures of levopimaric acid,[13] mebadonin,[14] and prerotundifuran.[15]

In Ring D, C(19)–O(26) [1.380 Å] is short and C(6)–O(26) [1.467 Å] long. Differences between C(sp^2)–O and C(sp^3)–O single-bond lengths in lactone groups have been found in many other structures.[16] A similar trend is found between C(21)–O(28) and C(1)–O(28), and between C(23)–O(30) and C(7)–O(30). The geometry observed in the C·C(O)·O·C moiety of Ring D or OAc may be ascribed to the contribution from the resonance form (II):

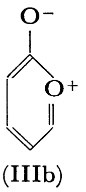


$$\mathrm{C{-}\!\!-\underset{\underset{\displaystyle O^-}{|}}{C}{=\!=}O^+{-}\!\!-C} \qquad \text{(II)}$$

In Ring C (α-pyrone ring), the two C–O lengths (C(12)–O(13) and C(14)–O(13)) indicate a contribution from two resonance forms (IIIa and IIIb):



(IIIa)



(IIIb)

The slight shortening of C(12)–O(13) is probably due to the larger electronegativity of the C(12) bonded to O(27) than that of C(14).

The C(8)–C(9), C(11)–C(12), C(12)–O(13), and C(14)–O(13) bond lengths show that considerable delocalization occurs in Ring C.

Most of the bond angles around the C(sp^3) atoms in Rings A and B deviate greatly from the tetrahedral angle as a result of the formation of the γ-lactone ring and the 1,3-diaxial interactions. The values range from 100.1° (C(4)–C(5)–C(6)) to 117.0° (C(2)–C(3)–C(4)). The C(4)–C(19)–O(25)=131.5° bond angle is largest for those around the C(19) atom of Ring D. The same trend was observed in the bond angles around the C(12) atom of the α-pyrone ring; C(11)–C(12)–O(27) is largest.

The shorter intermolecular contacts (less than 4.0 Å) are given in Table 6. The packing of nagilactone A diacetate molecules in the crystal structure is illustrated in Fig. 3. The mean plane of the four-ring nucleus is roughly parallel to the crystallographic bc plane. The intermolecular contacts correspond to van der Waals interactions.

Computer Programs

All the calculations were performed on a FACOM 270/30 computer at the Computer Center of Osaka City University using the following programs: RSLC-3,[17] RSSFR-3,[17] HBLS-IV,[17] SCALE (film factor, Lp and layer scaling),[18] TECS (stereoscopic drawing

TABLE 5. BOND LENGTHS (Å) AND ANGLES (deg.), WITH STANDARD DEVIATIONS IN PARENTHESES

(a) Bond distances

C (1)-C (2)	1.549(10)	C (5)-C (10)	1.580(9)	C (21)-C (22)	1.536(13)	O (30)-C (23)	1.361(8)
C (2)-C (3)	1.478(12)	C (10)-C (1)	1.565(9)	C (21)-O (29)	1.179(11)	C (23)-C (24)	1.535(11)
C (3)-C (4)	1.536(11)	C (9)-C (11)	1.367(9)	C (4)-C (19)	1.510(11)	C (23)-O (31)	1.188(10)
C (4)-C (5)	1.526(9)	C (11)-C (12)	1.410(11)	C (19)-O (26)	1.380(8)	C (10)-C (20)	1.554(9)
C (5)-C (6)	1.518(9)	C (12)-O (13)	1.358(9)	C (6)-O (26)	1.467(8)	C (12)-O (27)	1.229(9)
C (6)-C (7)	1.556(9)	O (13)-C (14)	1.389(9)	C (4)-C (18)	1.571(12)	C (14)-C (15)	1.506(11)
C (7)-C (8)	1.524(9)	C (8)-C (14)	1.308(10)	C (19)-O (25)	1.205(9)	C (15)-C (16)	1.572(18)
C (8)-C (9)	1.446(9)	C (1)-O (28)	1.480(8)	C (7)-O (30)	1.460(8)	C (15)-C (17)	1.606(17)
C (9)-C (10)	1.512(9)	O (28)-C (21)	1.344(9)				

(b) Valency angles

C (2)-C (1)-C (10)	110.0(6)	C (3)-C (4)-C (19)	115.3(7)
C (2)-C (1)-O (28)	106.2(6)	C (5)-C (4)-C (18)	110.0(6)
C (10)-C (1)-O (28)	106.3(5)	C (5)-C (4)-C (19)	101.3(5)
C (1)-C (2)-C (3)	113.3(7)	C (18)-C (4)-C (19)	108.6(6)
C (2)-C (3)-C (4)	117.0(7)	C (4)-C (5)-C (6)	100.1(5)
C (3)-C (4)-C (5)	114.0(6)	C (4)-C (5)-C (10)	114.7(5)
C (3)-C (4)-C (18)	107.5(6)	C (6)-C (5)-C (10)	111.0(5)
C (5)-C (6)-C (7)	115.4(5)	O (13)-C (12)-O (27)	116.3(7)
C (5)-C (6)-O (26)	104.4(5)	C (12)-O (13)-C (14)	122.2(6)
C (7)-C (6)-O (26)	111.5(5)	C (8)-C (14)-O (13)	120.8(7)
C (6)-C (7)-C (8)	114.0(5)	C (8)-C (14)-C (15)	129.7(7)
C (6)-C (7)-O (30)	113.4(5)	O (13)-C (14)-C (15)	109.5(6)
C (8)-C (7)-O (30)	108.8(5)	C (14)-C (15)-C (16)	110.3(8)
C (7)-C (8)-C (9)	121.4(6)	C (14)-C (15)-C (17)	108.4(8)
C (7)-C (8)-C (14)	118.8(7)	C (16)-C (15)-C (17)	114.7(8)
C (9)-C (8)-C (14)	119.6(7)	C (4)-C (19)-O (25)	131.5(7)
C (8)-C (9)-C (10)	116.3(6)	C (4)-C (19)-O (26)	109.0(6)
C (8)-C (9)-C (11)	118.7(6)	O (25)-C (19)-O (26)	119.4(7)
C (10)-C (9)-C (11)	125.0(6)	C (22)-C (21)-O (28)	109.0(7)
C (1)-C (10)-C (5)	104.2(5)	C (22)-C (21)-O (29)	125.4(7)
C (1)-C (10)-C (9)	114.8(5)	O (28)-C (21)-O (29)	125.6(8)
C (1)-C (10)-C (20)	111.6(5)	C (24)-C (23)-O (30)	109.6(6)
C (5)-C (10)-C (9)	103.2(5)	C (24)-C (23)-O (31)	127.3(7)
C (5)-C (10)-C (20)	115.9(5)	O (30)-C (23)-O (31)	123.1(7)
C (9)-C (10)-C (20)	107.1(5)	C (6)-O (26)-C (19)	108.3(5)
C (9)-C (11)-C (12)	120.7(6)	C (1)-O (28)-C (21)	115.3(6)
C (11)-C (12)-O (13)	117.2(6)	C (7)-O (30)-C (23)	114.9(5)
C (11)-C (12)-O (27)	126.4(7)		

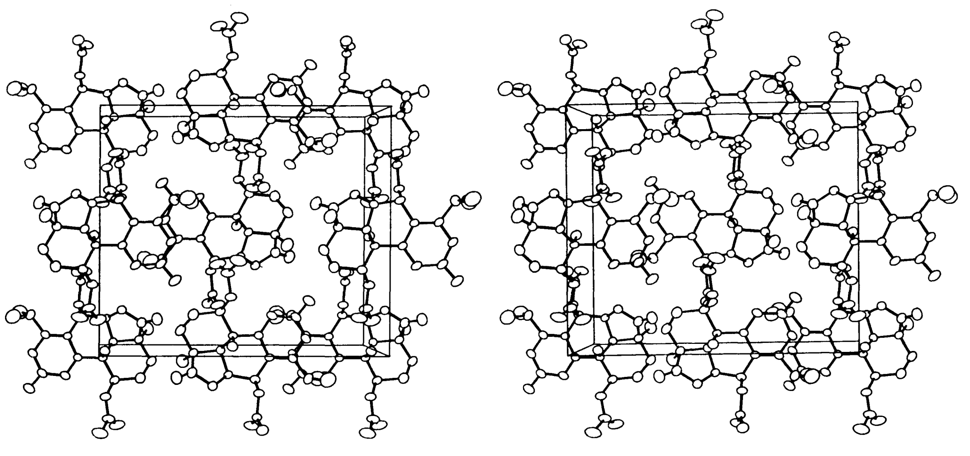


Fig. 3. Stereoscopic view of the packing in the crystal of nagilactone A diacetate looking along the a axis. The b axis is horizontal and the c axis is vertical. The atoms are represented by 50% probability thermal ellipsoids.

of crystal and molecular structure),[19] PHASE-I, II and III (direct method),[20] and BOND (bond length and angle, best plane, dihedral angle and intermolecular distance).[21]

Table 6. Intermolecular distances less than 4.0 Å

C (1)	O (31, a)	3.427 Å	C (3)	O (25, g)	3.922 Å
C (3)	O (31, a)	3.856	C (2)	C (18, h)	3.803
C (4)	O (31, a)	3.987	C (3)	C (18, h)	3.981
C (5)	O (31, a)	3.525	C (18)	O (25, g)	3.456
C (10)	O (31, a)	3.988	O (13)	C (21, i)	3.935
C (6)	C (21, b)	3.900	O (13)	C (22, i)	3.872
C (18)	O (27, b)	3.471	O (13)	O (29, i)	3.813
C (5)	O (29, b)	3.699	C (2)	O (27, j)	3.220
C (6)	O (29, b)	3.129	C (21)	O (27, j)	3.467
C (7)	O (29, b)	3.152	C (22)	O (27, j)	3.735
C (8)	O (29, b)	3.607	O (27)	O (28, i)	3.636
C (14)	O (29, b)	3.910	O (27)	O (29, i)	3.734
C (20)	C (24, c)	3.812	C (15)	O (25, k)	3.762
C (20)	C (22, d)	3.699	C (17)	C (19, k)	3.947
C (22)	C (24, c)	3.912	C (17)	C (23, k)	3.987
C (24)	O (28, d)	3.712	C (17)	O (25, k)	3.660
C (12)	C (17, e)	3.933	C (17)	O (26, k)	3.443
C (9)	C (16, f)	3.918	C (17)	O (31, k)	3.771
C (11)	C (16, f)	3.710	C (23)	O (25, k)	3.561
C (12)	C (16, f)	3.942	C (24)	O (25, k)	3.493
C (16)	C (20, e)	3.948	O (25)	O (31, k)	3.692
C (24)	O (27, f)	3.446			

The letters refer to the following transformation relative to the reference molecule at x, y, z:

(a)	$-1/2-x$,	$-y$,	$-1/2+z$
(b)	$-1/2-x$,	$-y$,	$1/2+z$
(c)	$1/2-x$,	$-y$,	$-1/2+z$
(d)	$1/2-x$,	$-y$,	$1/2+z$
(e)	$-1/2+x$,	$-1/2-y$,	$-z$
(f)	$1/2+x$,	$-1/2-y$,	$-z$
(g)	$-1/2+x$,	$1/2-y$,	$-z$
(h)	$1/2+x$,	$1/2-y$,	$-z$
(i)	$-x$,	$-1/2+y$,	$-1/2-z$
(j)	$-x$,	$1/2+y$,	$-1/2-z$
(k)	$-x$,	$-1/2+y$,	$1/2-z$

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