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## The Crystal and Molecular Structure of 3,3'-(1-Naphthylmethylene)bis(4-hydroxycoumarin) ( $\alpha$ -Naphthyldicoumarol) in Two Crystal Modifications

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### Abstract

The crystal structure of 3,3'-(1-naphthylmethylene)-bis(4-hydroxycoumarin)-acetone,  $C_{29}H_{18}O_6 \cdot C_3H_6O$ , has been determined by direct methods from three-dimensional diffractometer data collected with Cu  $K\alpha$  radiation. The unit-cell parameters are  $a = 12.776$  (7),  $b = 11.323$  (6),  $c = 10.149$  (5) Å,  $\alpha = 97.70$  (5),  $\beta = 109.41$  (4),  $\gamma = 105.97$  (6)° and  $Z = 2$  in the triclinic, and  $a = 17.615$  (3),  $b = 16.434$  (3),  $c = 9.001$  (3) Å,  $Z = 4$  in the orthorhombic crystals. Full-matrix least-squares refinement of the structural parameters gave unweighted linear  $R$  values of 0.041 (3463 reflexions) and 0.038 (1505 reflexions) for the triclinic and orthorhombic modifications respectively. The triclinic crystal structure consists of hydrogen-bonded  $\alpha$ -naphthyldicoumarol dimers and space-filling acetone molecules held together by van der Waals forces. The orthorhombic crystal structure is built up from hydrogen-bonded  $\alpha$ -naphthyldicoumarol-acetone complexes. The molecular geometries are slightly different in these two modifications.

### Introduction

The present investigation is part of a research program for structural studies of some anticoagulants (for example, different coumarin and indandione derivatives).  $\alpha$ -Naphthyldicoumarol belongs to a group of coumarin derivatives with an anticlotting effect. This substance shows a fairly high activity and a mode of

action of the dicoumarol type (Guminska & Eckstein, 1961).

Crystals of  $\alpha$ -naphthyldicoumarol, grown from acetone solution, show two different crystal forms, with triclinic and orthorhombic symmetry respectively. There is one molecule of acetone per asymmetric unit in both cases. The X-ray analysis of these two crystal modifications was undertaken in order to elucidate the possible conformational differences.

### Experimental

The title compound was synthesized at the Department of Technology of Drugs in Kraków (Eckstein, Kocwa & Pazdro, 1958). Suitable single crystals were obtained by recrystallization from acetone solutions. The crystals were examined first by oscillation and De Jong-Bouman photographic techniques. The unit-cell parameters were refined by least-squares fitting to powder photograph data, taken in a Guinier-Hägg focusing camera at 298 K with Cu  $K\alpha$  radiation and KCl ( $a = 6.2930$  Å) as internal standard.

X-ray diffraction intensities were measured with an automatic four-circle diffractometer and graphite-monochromatized Cu  $K\alpha$  radiation. The approximate dimensions of the selected single crystals were  $0.18 \times 0.25 \times 0.20$  mm for the triclinic form and  $0.16 \times 0.08 \times 0.58$  mm for the orthorhombic. 4618 and 2367 independent reflexions with  $0 \leq 65^\circ$  were measured and corrected for Lorentz and polarization effects for the triclinic and orthorhombic structures respectively. The rather low absorption effects ( $\mu = 0.73\text{--}0.74$  mm<sup>-1</sup>) were neglected.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the C and O atoms

The estimated standard deviations are given in parentheses.

Triclinic modification				Orthorhombic modification			
	x	y	z		x	y	z
O(1)	7689 (2)	2313 (2)	2432 (2)	O(1)	1266 (2)	1458 (3)	2500 (0)
C(2)	8117 (2)	3207 (2)	3705 (2)	C(2)	1975 (3)	1557 (3)	3103 (7)
O(2)	8797 (2)	4232 (2)	3775 (2)	O(2)	2005 (2)	1684 (3)	4422 (6)
C(3)	7779 (2)	2886 (2)	4875 (2)	C(3)	2631 (3)	1504 (3)	2127 (7)
C(4)	6972 (2)	1715 (2)	4638 (3)	C(4)	2520 (3)	1343 (3)	656 (7)
O(4)	6547 (2)	1345 (2)	5613 (2)	O(4)	3075 (2)	1251 (3)	-326 (6)
C(5)	5770 (2)	-474 (2)	3010 (3)	C(5)	1614 (4)	1111 (4)	-1451 (8)
C(6)	5437 (3)	-1319 (3)	1719 (4)	C(6)	880 (5)	1037 (4)	-1941 (11)
C(7)	5856 (3)	-962 (3)	681 (4)	C(7)	282 (5)	1123 (5)	-963 (11)
C(8)	6609 (3)	252 (3)	916 (3)	C(8)	398 (4)	1283 (4)	537 (10)
C(9)	6943 (2)	1107 (2)	2228 (3)	C(9)	1150 (3)	1339 (3)	998 (8)
C(10)	6546 (2)	771 (2)	3291 (3)	C(10)	1766 (3)	1267 (3)	50 (7)
O(1')	6147 (2)	5282 (2)	6710 (2)	O(1')	4050 (2)	-518 (2)	3328 (6)
C(2')	6716 (2)	4436 (2)	6594 (3)	C(2')	3854 (3)	207 (3)	2693 (7)
O(2')	6197 (2)	3365 (2)	6618 (2)	O(2')	3835 (2)	200 (2)	1337 (6)
C(3')	7847 (2)	4855 (2)	6462 (2)	C(3')	3691 (3)	896 (3)	3622 (7)
C(4')	8297 (2)	6083 (2)	6424 (2)	C(4')	3774 (3)	824 (3)	5120 (7)
O(4')	9308 (2)	6587 (2)	6252 (2)	O(4')	3682 (2)	1411 (2)	6124 (5)
C(5')	8140 (3)	8263 (2)	6604 (3)	C(5')	4037 (4)	-79 (4)	7310 (8)
C(6')	7516 (3)	9049 (3)	6762 (3)	C(6')	4212 (5)	-828 (4)	7865 (8)
C(7')	6447 (3)	8580 (3)	6905 (3)	C(7')	4325 (4)	-1483 (4)	6908 (10)
C(8')	5993 (3)	7326 (3)	6895 (3)	C(8')	4274 (4)	-1373 (3)	5391 (9)
C(9')	6630 (2)	6540 (2)	6729 (3)	C(9')	4100 (3)	-612 (3)	4851 (8)
C(10')	7698 (2)	6978 (2)	6587 (2)	C(10')	3976 (3)	48 (3)	5767 (7)
C(11)	8456 (2)	3889 (2)	6312 (2)	C(11)	3388 (3)	1669 (3)	2889 (7)
C(12)	8863 (2)	3355 (2)	7640 (2)	C(12)	3956 (3)	2149 (3)	1938 (7)
C(13)	8635 (3)	3686 (3)	8837 (3)	C(13)	4665 (3)	1862 (3)	1620 (8)
C(14)	9000 (3)	3190 (3)	10055 (3)	C(14)	5166 (3)	2318 (5)	696 (9)
C(15)	9600 (3)	2389 (3)	10069 (3)	C(15)	4962 (4)	3041 (5)	155 (8)
C(16)	9927 (2)	2062 (2)	8904 (3)	C(16)	4254 (4)	3373 (4)	490 (7)
C(17)	10621 (3)	1267 (3)	8934 (4)	C(17)	4050 (6)	4161 (5)	-14 (10)
C(18)	10945 (3)	968 (3)	7824 (5)	C(18)	3377 (6)	4518 (4)	391 (11)
C(19)	10622 (3)	1469 (3)	6633 (4)	C(19)	2888 (4)	4103 (4)	1346 (10)
C(20)	9954 (2)	2243 (2)	6551 (3)	C(20)	3057 (3)	3339 (3)	1827 (8)
C(21)	9567 (2)	2556 (2)	7670 (3)	C(21)	3742 (3)	2939 (3)	1416 (7)
C(22)	6943 (6)	5326 (9)	529 (6)	C(22)	3010 (6)	4277 (4)	5966 (12)
C(23)	6388 (3)	4955 (3)	1531 (3)	C(23)	3049 (3)	3386 (3)	6276 (7)
O(23)	5816 (3)	3876 (3)	1369 (4)	O(23)	3532 (2)	2999 (2)	5640 (5)
C(24)	6559 (5)	5927 (5)	2751 (5)	C(24)	2522 (5)	3022 (4)	7355 (10)

### Structure determination

The crystal structures were solved by direct phase determination with the *MULTAN* program system (Main, Lessinger, Woolfson, Germain & Declercq, 1974). 2000 best triple relations among the 350 highest normalized structure factors were used to generate 64 different phase sets for the triclinic and 128 trial phase sets for the orthorhombic structures.

The *E* map computed with the signs of the phase set with the best figure of merit showed 37 of the 39 non-hydrogen atoms in the asymmetric unit for the centrosymmetric triclinic structure. The remaining two C atoms and 24 H atoms were located from two subsequent difference electron density calculations. Full-matrix least-squares refinement, with all non-hydrogen atoms having anisotropic temperature factors

and the H atoms isotropic, yielded a conventional linear *R* value of 0.041 for the 3463 reflexions with  $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0.25$  [where  $\sigma(I_{\text{net}})$  is the estimated

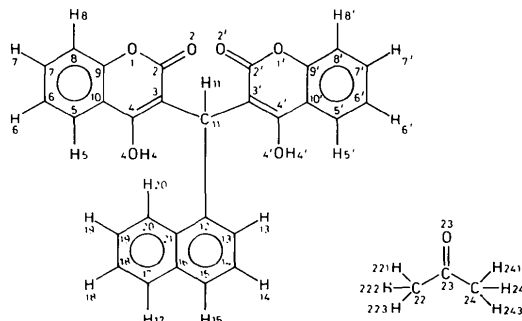


Fig. 1. Schematic drawing of the  $\alpha$ -naphthylidicoumarol and solvent acetone molecules with atoms numbered as in the text.

standard deviation based on conventional counter statistics]. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1974).

In the *E* map derived for the solution with the best figure of merit for the noncentrosymmetric ortho-

rhombic form, 23 of the highest peaks could be recognized as forming an image of a molecular fragment. A difference electron density map, calculated for the partial structural model consisting of 23 isotropically refined atoms, showed all the remaining 16 non-hydrogen positions. The 18 H positions of the  $\alpha$ -

Table 2. *Fractional atomic coordinates ( $\times 10^3$ ) and isotropic temperature factors for the hydrogen atoms, with estimated standard deviations in parentheses*

Triclinic modification					Orthorhombic modification				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ( $\text{\AA}^2 \times 10^3$ )		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ( $\text{\AA}^2 \times 10^3$ )
H(4)	652 (3)	205 (3)	616 (3)	35 (6)	H(4)	354 (3)	116 (3)	12 (6)	72
H(5)	547 (3)	-73 (3)	377 (3)	44 (7)	H(5)	208 (3)	110 (3)	-213 (6)	70
H(6)	487 (3)	-217 (3)	151 (3)	49 (7)	H(6)	73 (3)	94 (4)	-290 (7)	96
H(7)	563 (3)	-157 (3)	-17 (4)	46 (7)	H(7)	-26 (3)	114 (4)	-112 (7)	92
H(8)	690 (2)	55 (3)	25 (3)	30 (6)	H(8)	-1 (3)	126 (3)	137 (7)	75
H(4')	956 (3)	597 (3)	594 (4)	71 (9)	H(4')	358 (3)	201 (3)	568 (6)	65
H(5')	893 (3)	860 (3)	655 (3)	37 (6)	H(5')	393 (3)	40 (3)	799 (6)	74
H(6')	781 (3)	995 (3)	676 (3)	37 (6)	H(6')	435 (3)	-94 (3)	892 (7)	85
H(7')	599 (3)	911 (3)	703 (3)	44 (6)	H(7')	443 (3)	-203 (4)	741 (6)	81
H(8')	524 (3)	694 (3)	694 (3)	44 (7)	H(8')	442 (3)	-180 (3)	473 (6)	63
H(11)	918 (2)	434 (2)	625 (2)	7 (4)	H(11)	321 (2)	204 (3)	372 (5)	45
H(13)	821 (2)	423 (3)	886 (3)	28 (5)	H(13)	481 (3)	134 (3)	225 (6)	62
H(14)	877 (3)	346 (3)	1082 (4)	49 (7)	H(14)	569 (3)	205 (3)	63 (6)	72
H(15)	985 (3)	202 (3)	1089 (4)	53 (7)	H(15)	535 (3)	335 (3)	-50 (7)	81
H(17)	1087 (3)	98 (3)	978 (4)	48 (7)	H(17)	441 (3)	442 (3)	-54 (7)	85
H(18)	1140 (3)	39 (3)	787 (4)	56 (7)	H(18)	315 (3)	508 (4)	26 (7)	92
H(19)	1092 (3)	131 (3)	584 (4)	54 (8)	H(19)	239 (3)	435 (3)	175 (7)	77
H(20)	976 (2)	260 (2)	572 (3)	23 (5)	H(20)	267 (3)	311 (3)	246 (6)	59
H(221)	776 (5)	574 (5)	99 (6)	105 (14)	H(221)	257 (1)	448 (1)	670 (2)	111
H(222)	690 (6)	605 (5)	38 (7)	180 (26)	H(222)	286 (1)	440 (1)	483 (2)	111
H(223)	670 (7)	468 (7)	-13 (8)	97 (26)	H(223)	353 (1)	459 (1)	624 (2)	111
H(241)	731 (4)	645 (4)	323 (5)	79 (11)	H(241)	211 (1)	339 (1)	792 (1)	94
H(242)	622 (5)	647 (5)	226 (6)	131 (19)	H(242)	288 (1)	271 (1)	813 (1)	94
H(243)	606 (6)	567 (5)	328 (7)	123 (19)	H(243)	222 (1)	257 (1)	667 (1)	94

Table 3. *Equations of the least-squares planes, and deviations of the atoms from the planes*

The planes are expressed as  $Ax + By + Cz = D$ , where *x*, *y* and *z* are in  $\text{\AA}$  relative to the axes  $a^*$ ,  $b^*$ , and *c* in the triclinic crystals and *a*, *b*, and *c* in the orthorhombic structure. Atoms marked with asterisks were omitted from the calculations of the least-squares planes. A negative sign means that the atom lies between the plane and the origin.

Plane 1				Plane 2			
		Deviation ( $\text{\AA}$ ) (triclinic)	Deviation ( $\text{\AA}$ ) (orthorhombic)			Deviation ( $\text{\AA}$ ) (triclinic)	Deviation ( $\text{\AA}$ ) (orthorhombic)
Triclinic	O(1)	-0.038	-0.044	Triclinic	O(1')	0.025	-0.028
<i>A</i> = -0.026	C(2)	-0.004	-0.003	<i>A</i> = 0.971	C(2')	-0.006	0.003
<i>B</i> = 0.985	O(2)	-0.004	0.005	<i>B</i> = 0.234	O(2')	0.015	0.007
<i>C</i> = -0.172	C(3)	0.032	0.066	<i>C</i> = -0.045	C(3')	-0.058	0.034
<i>D</i> = 1.952	C(4)	0.005	-0.002	<i>D</i> = 6.568	C(4')	-0.005	-0.001
	O(4)	-0.017	-0.023		O(4')	0.023	-0.029
Orthorhombic	C(5)	-0.003	-0.009	Orthorhombic	C(5')	0.008	0.011
<i>A</i> = 0.777	C(6)	-0.013	0.013	<i>A</i> = 0.485	C(6')	-0.003	0.012
<i>B</i> = -0.606	C(7)	0.002	0.026	<i>B</i> = 0.067	C(7')	-0.022	0.003
<i>C</i> = 0.169	C(8)	0.023	0.007	<i>C</i> = 0.872	C(')	-0.005	-0.003
<i>D</i> = 6.966	C(9)	0.008	-0.018	<i>D</i> = 6.596	C(9')	0.012	-0.009
	C(10)	0.010	-0.018		C(10')	0.016	0.002
	C(11)*	0.146	0.322		C(11)*	-0.249	0.048

The r.m.s. deviations from the planes of the atoms without asterisks are 0.017  $\text{\AA}$  in the triclinic and 0.027  $\text{\AA}$  in the orthorhombic forms.

The r.m.s. deviations from the planes of the atoms without asterisks are 0.022  $\text{\AA}$  in the triclinic and 0.016  $\text{\AA}$  in the orthorhombic forms.

Table 3 (cont.)

Plane 3

		Deviation (Å) (triclinic)	Deviation (Å) (orthorhombic)
Triclinic	C(11)*	-0.111	-0.065
	C(12)	-0.054	-0.048
	C(13)	0.042	0.033
	C(14)	0.052	0.039
	C(15)	0.003	-0.016
	C(16)	-0.050	-0.023
Orthorhombic	C(17)	-0.029	-0.008
	C(18)	0.012	0.002
	C(19)	0.062	0.030
	C(20)	0.014	0.018
	C(21)	-0.052	-0.029

The r.m.s. deviations from the planes of the atoms without asterisks are 0.042 Å in the triclinic and 0.028 Å in the orthorhombic forms.

Angles between the least-squares-plane normals (with the estimated standard deviations in parentheses)

Planes	Angle (°) (triclinic)	Angle (°) (orthorhombic)
1-2	61.1 (4)	77.7 (4)
1-3	70.7 (6)	75.0 (7)
2-3	61.6 (5)	62.1 (7)

naphthyldicoumarol molecule were derived from difference electron density maps; the six methyl H positions of the acetone molecule were calculated geometrically. A blocked-full-matrix least-squares procedure (*SHELX 76*, Sheldrick, 1976) was used for the final refinement of the structural model. The non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms, each with the same isotropic temperature factor as the C or O atom to which it is linked, had only the positional parameters refined. The methyl groups of the solvent molecule were refined as rigid groups. The final linear *R* value reduced to 0.038 for the 1505 reflexions with  $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0.33$ . The atomic scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965), and for the non-hydrogen atoms from Cromer & Mann (1968) and Cromer & Liberman (1970).\*

## Results and discussion

The final atomic coordinates are given in Tables 1 and 2. The atomic labels used are given in Fig. 1. The intramolecular bond lengths and bond angles involving the O and the C atoms are shown in Fig. 2. The geometries

\* Lists of structure factors, anisotropic thermal parameters, and intramolecular bond distances and bond angles involving the non-hydrogen atoms for both modifications have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34000 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

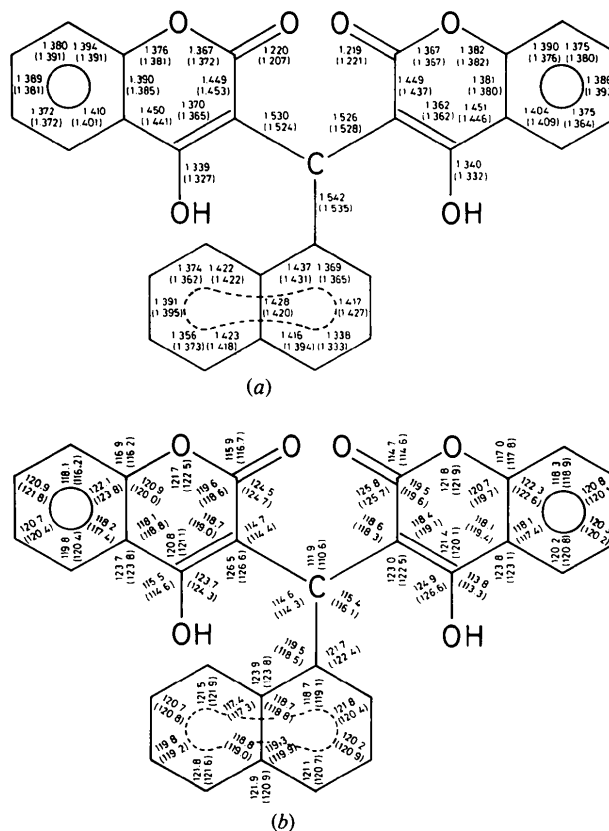


Fig. 2. (a) Interatomic distances (Å) and (b) bond angles (°) involving the non-hydrogen atoms of the  $\alpha$ -naphthyldicoumarol molecule in the triclinic crystal form. The corresponding values observed in the orthorhombic form are shown in parentheses. The e.s.d.'s of the bond lengths range between 0.002 and 0.005 Å in the triclinic form, and between 0.006 and 0.014 Å in the orthorhombic form. The estimated uncertainty in bond angles varies from 0.1 to 0.3° in the triclinic, and from 0.3 to 0.8° in the orthorhombic forms.

of the  $\alpha$ -naphthyldicoumarol molecules are displayed in Fig. 3. The inclined 'butterfly' molecular geometry of the dicoumarol moiety has been observed earlier in studies of the dicoumarol molecule itself (Bravic, Gaultier & Hauw, 1968) and of the corresponding bis(6-bromo) derivative (Alcock & Hough, 1972). However, this latter compound yielded less accurate bond distances and angles owing to the presence of the Br atoms, and the refinement of the structural model of dicoumarol had not been completed (linear *R* value 0.19) when the atomic coordinates were published. Since both these earlier studies gave comparatively low accuracy in bond distances and angles, no further comparison with the results found in the present study seems meaningful. Comparison between the results of the present two studies shows that these two sets of bond lengths and angles agree with each other within a few e.s.d.'s. However, the molecular conformations are not identical. The angles between the normals of the

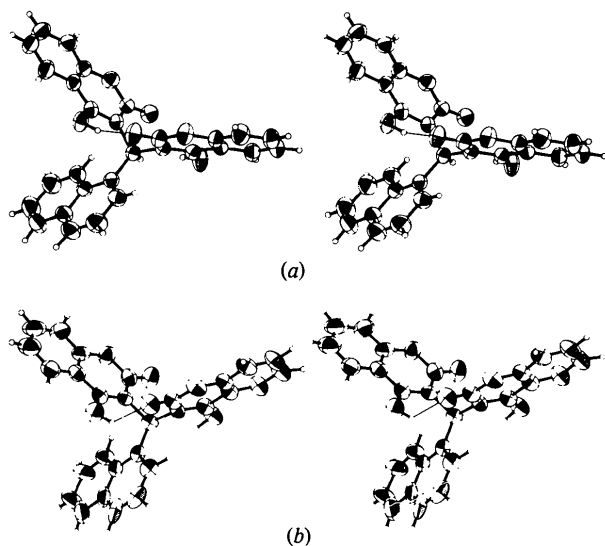


Fig. 3. Stereoscopic views of the  $\alpha$ -naphthylidicoumarol molecule in (a) the triclinic and (b) the orthorhombic crystal modifications. The non-hydrogen atoms are represented by their thermal ellipsoids while the H atoms are drawn as spheres.

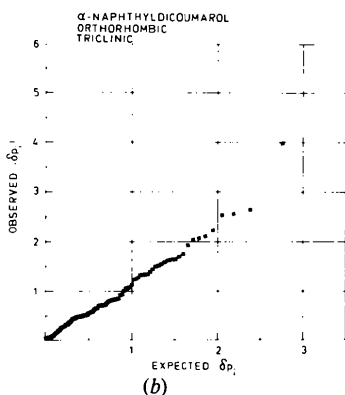
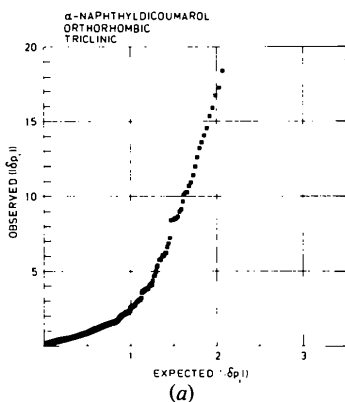


Fig. 4. Half-normal probability plots comparing intramolecular distances (a)  $< 4.65 \text{ \AA}$  and (b)  $< 2.5 \text{ \AA}$  between the non-hydrogen atoms of the  $\alpha$ -naphthylidicoumarol molecule in two different crystal modifications.

Table 4. Intermolecular distances less than  $3.6 \text{ \AA}$  between the non-hydrogen atoms in the triclinic structure of  $\alpha$ -naphthylidicoumarol-acetone

The estimated standard deviations are given in parentheses. Atom B is generated from the coordinates of Table 1 using the unit-cell translation shown, together with the following symmetry operation:

Superscript	
None	$x, y, z$
(i)	$-x, -y, -z$

Distances between the  $\alpha$ -naphthylidicoumarol molecules

Atom A	Atom B	Unit-cell translation along axes			Distances ( $\text{\AA}$ )
		a	b	c	
O(4')	O(2) <sup>i</sup>	2	1	1	2.828 (4)
O(2)	O(2) <sup>i</sup>	2	1	1	3.078 (5)
C(2)	O(4') <sup>i</sup>	2	1	1	3.219 (4)
O(4)	C(6') <sup>i</sup>	0	-1	0	3.358 (4)
C(7)	C(8) <sup>i</sup>	1	0	0	3.397 (5)
O(1)	O(4') <sup>i</sup>	2	1	1	3.402 (4)
O(4')	C(15) <sup>i</sup>	2	1	2	3.423 (4)
O(1)	C(14)	0	0	1	3.467 (4)
C(4')	C(15) <sup>i</sup>	2	1	2	3.509 (5)
O(4)	C(7') <sup>i</sup>	0	-1	0	3.540 (4)
O(2')	C(8') <sup>i</sup>	1	1	1	3.545 (4)
O(1')	O(1') <sup>i</sup>	1	1	1	3.558 (5)
O(4')	C(20) <sup>i</sup>	2	1	1	3.584 (4)
O(4')	C(14) <sup>i</sup>	2	1	2	3.584 (4)
C(7)	C(7) <sup>i</sup>	1	0	0	3.586 (7)

Distances between  $\alpha$ -naphthylidicoumarol and acetone molecules

Atom A	Atom B	Unit-cell translation along axes			Distances ( $\text{\AA}$ )
		a	b	c	
C(7)	O(23) <sup>i</sup>	1	0	0	3.333 (6)
O(1)	O(23)	0	0	0	3.339 (4)
C(2)	O(23)	0	0	0	3.451 (5)
C(8')	O(23) <sup>i</sup>	1	1	1	3.452 (5)
C(6)	O(23) <sup>i</sup>	1	0	0	3.529 (6)
O(2)	C(23)	0	0	0	3.544 (4)
C(10')	C(24)	0	0	0	3.568 (6)

two 4-hydroxycoumarin parts of the molecule are  $61.1 (4)^\circ$  in the triclinic and  $77.7 (4)^\circ$  in the orthorhombic forms of  $\alpha$ -naphthylidicoumarol-acetone. The angles between the normals of the naphthyl rings and the 4-hydroxycoumarin rings also show significant differences in the two crystal modifications (*cf.* Table 3). These differences are also evident from the half-normal probability plot calculated for the intramolecular distances shorter than  $4.65 \text{ \AA}$  between the 35 non-hydrogen atoms in these two crystal modifications (*cf.* Fig. 3a) (Abrahams & Keve, 1971; De Camp, 1973; Abrahams, 1974). Random errors in interatomic distances should be normally distributed and result in a linear plot. Conversely, the non-linearity of the plot of Fig. 4(a) obviously reflects the minor changes in conformation. The least-squares line through the 157 points (out of a total of 248 points)

with  $\delta p < 2.0$  has a slope of  $1.90 \pm 0.02$ , an intercept of  $-0.01 \pm 0.01$  on the ordinate and a correlation coefficient of 0.9912. Comparison of the intramolecular distances shorter than 2.5 Å between the non-hydrogen atoms results in a half-normal probability plot (*cf.* Fig. 4*b*) indicating a normal error distribution. The least-squares line of this plot has a slope of  $1.12 \pm 0.01$ , an intercept of  $0.014 \pm 0.009$  and a correlation coefficient of 0.9962.

All C—H bond distances in the triclinic structure of  $\alpha$ -naphthyldicoumarol range between 0.93 and 1.01 Å, with estimated standard deviations of 0.03–0.04 Å. In the orthorhombic modification the observed C—H bonds are between 0.90 and 1.06 Å with estimated uncertainties of 0.05–0.07 Å. The mean values of 0.96 and 1.00 Å, respectively, are compatible with X-ray-determined C—H distances (Stewart, Davidson & Simpson, 1965).

In the crystal structures of dicoumarol and its dibromo derivative there are two intramolecular hydrogen bonds between the two 4-hydroxycoumarin parts of the molecule. The O...O contact distances are 2.62 Å in dicoumarol and 2.69 (1) Å in 6,6'-dibromodicoumarol. In each of the crystal structures of  $\alpha$ -naphthyldicoumarol there is only one intramolecular hydrogen bond between O(4) and O(2') (*cf.* Fig. 3). In

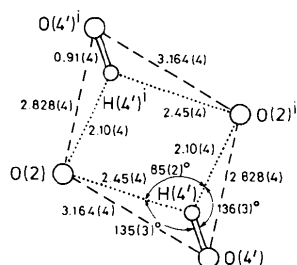


Fig. 5. Schematic picture of the O(4')—H(4')...O(2) contact distances in the triclinic crystals of  $\alpha$ -naphthyldicoumarol-acetone.

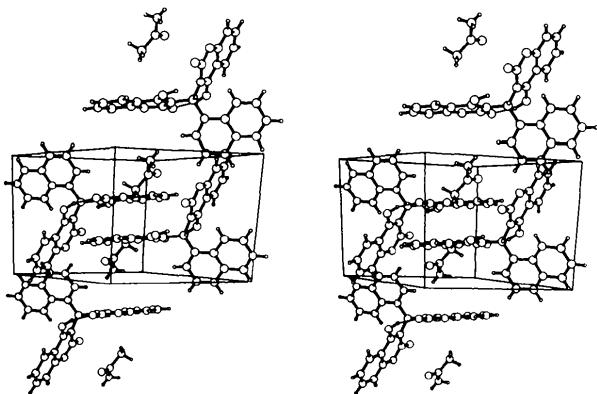


Fig. 6. Stereoscopic packing diagram of the triclinic crystal modification ( $z$  is vertical,  $y$  is to the right and  $x$  is out of the paper).

the triclinic crystal form this intramolecular O...O distance is as short as 2.59 (3) Å. The H...O distance is 1.70 (4) Å, and the O(4)—H(4)...O(2') angle is 161 (3)°. The other hydroxyl O atom [O(4')] lies 3.164 (4) Å from the carbonyl O(2) within the same molecule; however, the distance between O(4') and O(2) belonging to another  $\alpha$ -naphthyldicoumarol molecule ( $2-x, 1-y, 1-z$ ) is only 2.828 (4) Å (*cf.* Table 4), suggesting an intermolecular hydrogen bond. Fig. 5 shows a schematic picture of the O(4')—H(4')...O(2) contact distances. The intermolecular H(4')...O(2) distance, 2.10 (4) Å, is significantly shorter than the sum of the van der Waals radii (2.4 Å, Olovsson & Jönsson, 1976), while the intramolecular H(4')...O(2) distance, 2.45 (4) Å, is within 0.1 Å of the van der Waals approach. Donohue (1968) calls such bonds 'doubtful bifurcated hydrogen bonds'. However, according to the suggested geometrical criterion for hydrogen bonding (Olovsson & Jönsson, 1976) only the intermolecular contact OH(4')...O(2) is a hydrogen bond. It seems probable that this arrangement, in which H(4') is situated near two potential acceptor atoms, is a result of packing effects.

The triclinic crystal structure of the title compound is illustrated in Fig. 6. The  $\alpha$ -naphthyldicoumarol molecules, related by the symmetry operation ( $2-x, 1-y, 1-z$ ), form dimers by the intermolecular hydrogen bonds discussed above. This dimerization leads to fairly short intermolecular contact distances between the O(2) atoms [3.078 (5) Å] and between C(2) and O(4') [3.219 (4) Å] (*cf.* Table 4). All the other intermolecular distances listed in Table 4 are of

Table 5. Hydrogen-bond distances (Å) and angles (°) in the orthorhombic crystal modification

The estimated standard deviations are given in parentheses.

O—H...O	O...O	O—H	H...O	$\angle$ O—H...O
O(4)—H(4)...O(2')	2.649 (6)	0.92 (6)	1.99 (5)	127 (5)
O(4')—H(4')...O(23)	2.659 (5)	1.08 (5)	1.63 (5)	158 (5)

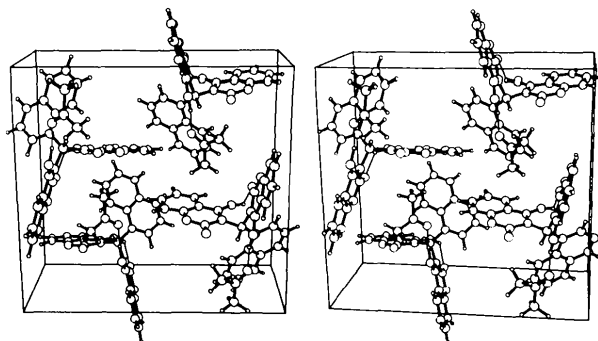


Fig. 7. Stereoscopic packing diagram of the orthorhombic crystal structure ( $y$  is vertical,  $x$  is to the right and  $z$  is out of the paper).

Table 6. *Intermolecular distances less than 3.6 Å between the C and O atoms in the orthorhombic structure of  $\alpha$ -naphthylidicoumarol-acetone*

Atom *B* is generated from the coordinates of Table 1 using the unit-cell translation shown, together with the following symmetry operation:

## Superscript

None	$x, y, z$
(i)	$-x, -y, z$
(ii)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$
(iii)	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$

Distances between the  $\alpha$ -naphthylidicoumarol molecules (with estimated standard deviations in parentheses)

Atom <i>A</i>	Atom <i>B</i>	Unit-cell translation along axes			Distances (Å)
		<i>a</i>	<i>b</i>	<i>c</i>	
O(4)	O(4')	0	0	-1	3.379 (7)
C(5')	C(5') <sup>i</sup>	1	0	0	3.402 (14)
O(1)	C(15) <sup>iii</sup>	-1	0	0	3.415 (8)
C(6)	C(15) <sup>iii</sup>	-1	0	-1	3.427 (12)
C(5')	C(6') <sup>i</sup>	1	0	0	3.462 (11)
O(4)	C(5') <sup>i</sup>	0	0	-1	3.489 (8)
C(13)	O(1') <sup>i</sup>	1	0	0	3.516 (7)
C(4')	C(8') <sup>i</sup>	1	0	0	3.563 (9)
O(1)	C(7') <sup>ii</sup>	0	0	-1	3.581 (8)
O(4')	C(7') <sup>i</sup>	1	0	0	3.584 (8)

Distances between the  $\alpha$ -naphthylcoumarol and acetone molecules (with estimated standard deviations in parentheses)

Atom <i>A</i>	Atom <i>B</i>	Unit-cell translation along axes			Distances (Å)
		<i>a</i>	<i>b</i>	<i>c</i>	
O(4')	O(23)	0	0	0	2.659 (5)
C(11)	O(23)	0	0	0	3.312 (7)
C(10)	C(22) <sup>ii</sup>	0	-1	-1	3.396 (9)
O(4')	C(23)	0	0	0	3.434 (6)
C(8)	O(23) <sup>iii</sup>	-1	0	-1	3.495 (8)
O(4')	C(24)	0	0	0	3.522 (8)
C(4)	C(22) <sup>ii</sup>	0	-1	-1	3.533 (9)
O(2)	C(24)	0	0	0	3.554 (10)
C(20)	O(23)	0	0	0	3.576 (8)

the same magnitude as van der Waals contact distances. The weakly bonded acetone molecules seem to have a space-filling role in this structure.

The packing in the orthorhombic modification of the  $\alpha$ -naphthylidicoumarol-acetone crystals is illustrated in Fig. 7. Every  $\alpha$ -naphthylidicoumarol molecule is involved in two hydrogen bonds: one intramolecular

[between O(4) and O(2')], and one intermolecular [from the hydroxyl group O(4')-H(4') to the carbonyl O(23) of an adjacent acetone molecule]. The bond distances and angles in the hydrogen bonds are listed in Table 5. Apart from this latter hydrogen bond, all the other intermolecular distances (Table 6) are of the same magnitude as van der Waals contact distances.

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