Table 4. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor (X)	Acceptor (O)	$X\cdots$O	X–H	H$\cdots$O	X–H$\cdots$O
Molecule (I)					
N(1)	O(12)	2·743 (6)	0·92 (7)	1·87 (7)	156 (6)
N(1)	H_2O	2·724 (7)	0·93 (7)	1·80 (7)	170 (5)
H_2O	O(13)	2·976 (7)	0·88 (7)	2·10 (7)	171 (6)
H_2O	O(13)	2·858 (6)	0·89 (7)	1·98 (7)	170 (6)
Molecule (II)					
N(1)	O(13)	2·746 (6)	0·99 (7)	1·76 (7)	169 (6)

packing is influenced by hydrogen bonding. In both molecules all available H atoms participate in intermolecular hydrogen bonds (parameters are given in Table 4). In (I) water crystallized with the quinoline. The H_2O acts as a donor in hydrogen bonds to two different O(13) atoms and as an acceptor from one of the H atoms on N(1). The remaining H on N(1) acts as a donor to O(12). In addition to the hydrogen bonds there is one intermolecular approach less than van der Waals distances, C(2)$\cdots$C(2) at 3·42 Å. In (II) there is only one H available for hydrogen bonding and it acts as a donor to O(13). There are no other approaches in (II) which are less than van der Waals separations.

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A Structure Containing Diastereomers, (2*S*,4*R*)-*trans*- and (2*R*,4*R*)-*cis*-2-Hydroxy-2,4-dimethyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one, $C_{14}H_{14}O_4$

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Abstract. $M_r = 246{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}804\ (3)$, $b = 18{\cdot}248\ (8)$, $c = 8{\cdot}752\ (5)$ Å, $\beta = 99{\cdot}59°$, $V = 1233$ Å^3, $Z = 4$ (2 molecules/asymmetric unit), $D_x = 1{\cdot}33$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71067 Å, $\mu = 0{\cdot}91$ cm^{-1}, $F(000) = 520$, $T = 293$ K. Final $R = 0{\cdot}066$ for 1123 observed independent intensities. The structure consists of diastereomers approximately inversion-related through a pseudocenter of symmetry at $x = 0{\cdot}241\ (4)$, $z = 0{\cdot}281\ (3)$ except the 4-methyl groups. The dihydropyran rings are half chairs distorted towards the e_f-diplanar conformation. Like molecules are hydrogen-bonded between hydroxyl and carbonyl groups along **a**, O$\cdots$O distances being 2·781 (7) (*trans*) and 2·780 (7) Å (*cis*).

Introduction. Michael-type addition of certain α,β-unsaturated ketones with 4-hydroxycoumarin leads to 3-substituted 4-hydroxycoumarins. In solution these products exist in a dynamic equilibrium between diastereomeric hemiketals and the open (keto) form of the molecule. The compound so obtained using 3-penten-2-one ($R = CH_3$) consists of about equal parts of each isomer in chloroform solution (Valente, Santarsiero & Schomaker, 1979), and its crystalline racemate consists of *cis* diastereomeric forms. As part of a structural study of this Michael addition product, we resolved the optical isomers and undertook a crystallographic investigation. In crystallizing the compound under different conditions, we hoped to observe another of the isomeric forms apparently present in solution.

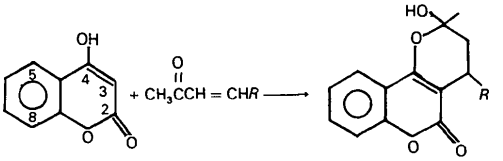

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Table 1. *Positional parameters* ($\times 10^4$) *and* U_{eq}*'s for cis- and trans-2-hydroxy-*2,4-*dimethyl-*3,4-*dihydro-*2*H*,5*H*-*pyrano*[3,2-*c*][1]*benzopyran-*5-*one*

E.s.d.'s are in parentheses.

	x	*y*	*z*	U_{eq}(Å^2)
cis Isomer				
O(1*A*)	−5465 (6)	3950 (3)	−661 (6)	7·2 (4)
O(2*A*)	−6192 (6)	5016 (3)	165 (7)	9·4 (5)
O(3*A*)	635 (6)	5317 (3)	1072 (6)	6·3 (4)
O(4*A*)	−385 (6)	4172 (3)	1560 (6)	5·3 (4)
C(2*A*)	−5011 (11)	4584 (5)	166 (10)	6·0 (7)
C(3*A*)	−3293 (12)	4670 (3)	962 (11)	5·4 (7)
C(4*A*)	−2103 (11)	4156 (5)	835 (9)	4·9 (6)
C(5*A*)	−1370 (12)	2930 (5)	−226 (11)	6·3 (7)
C(6*A*)	−1863 (14)	2303 (6)	−1072 (12)	7·8 (8)
C(7*A*)	−3620 (18)	2275 (6)	−1772 (11)	8·6 (9)
C(8*A*)	−4854 (13)	2826 (7)	−1647 (12)	7·9 (9)
C(9*A*)	−4247 (13)	3410 (6)	−756 (11)	5·3 (8)
C(10*A*)	−2535 (13)	3482 (6)	−57 (11)	5·0 (8)
C(11*A*)	−2812 (12)	5336 (6)	1892 (11)	7·0 (8)
C(12*A*)	−1100 (9)	5222 (4)	3012 (9)	5·4 (6)
C(13*A*)	275 (11)	4865 (4)	2281 (9)	5·5 (6)
C(14*A*)	1872 (10)	4641 (4)	3360 (10)	6·8 (7)
C(15*A*)	−2813 (9)	6058 (4)	932 (8)	5·3 (7)
trans Isomer				
O(1*B*)	10285 (6)	3199	6251 (5)	5·8 (4)
O(2*B*)	10992 (6)	2090 (3)	5570 (6)	7·3 (4)
O(3*B*)	4156 (6)	1852 (3)	4590 (6)	6·6 (4)
O(4*B*)	5258 (5)	2989 (3)	4077 (5)	5·2 (4)
C(2*B*)	9856 (11)	2562 (5)	5489 (9)	5·9 (6)
C(3*B*)	8080 (10)	2462 (5)	4662 (9)	4·9 (6)
C(4*B*)	6941 (8)	3018 (4)	4726 (8)	4·0 (5)
C(5*B*)	6260 (9)	4246 (5)	5748 (9)	5·9 (6)
C(6*B*)	6844 (13)	4837 (5)	6633 (11)	6·8 (7)
C(7*B*)	8533 (13)	4911 (5)	7345 (10)	6·2 (7)
C(8*B*)	9641 (13)	4354 (5)	7190 (9)	5·7 (6)
C(9*B*)	9059 (13)	3732 (5)	6326 (10)	5·7 (7)
C(10*B*)	7370 (12)	3668 (5)	5588 (9)	4·3 (6)
C(11*B*)	7541 (11)	1748 (5)	3810 (10)	5·4 (7)
C(12*B*)	5887 (11)	1902 (4)	2646 (10)	6·2 (7)
C(13*B*)	4554 (10)	2302 (5)	3429 (9)	5·5 (6)
C(14*B*)	2952 (11)	2540 (5)	2327 (10)	7·3 (7)
C(15*B*)	8831 (13)	1426 (6)	2952 (12)	10·2 (9)

Experimental. Synthesis reported (Ikawa, Stahmann & Link, 1944), resolved with brucine as more soluble salt and forms colorless crystals from ethanol:water. Crystal: 0·22 × 0·27 × 0·60 mm, mounted along long axis, **c**. D_m not measured. Weissenbergs: monoclinic with 0*k*0 absent for *k* odd. Picker FACS-1 diffractometer. Unit cell: least squares on 15 reflections '$\pm 2\theta$'. Intensity measurements by ω-scans, 1·0° min^{-1} in ω, 30s backgrounds at scan limits, width 4·1°, Mo *Kα* radiation with 0·76 mm Nb filter; 3200 reflections ($h \pm 8$, $k\, 0 \rightarrow 23$, $l\, 0 \rightarrow 10$), to $\sin \theta/\lambda = 0{\cdot}65$ Å^{-1}, in survey mode to pass by weak or absent reflections, 1247 measured exceeding their standard deviations, none requiring coincidence-loss correction. Four standards, for count and orientation, every 400 reflections, 1% decay over experiment. Structure discovered with *MULTAN* (Germain, Main & Woolfson, 1971), two molecules in the asymmetric unit. Refinement: C and O positions and U_{iso}'s by full-matrix least squares on all reflections except those with weighted $[\sigma^2(F)^{-1}]$ differences, $F_o - F_c$, exceeding six. U_{ij} for C and O included, then H's at calculated and fixed positions and their U_{iso}'s included; to $R = 0{\cdot}073$. Molecules refined individually in alternation to overcome model divergence owing to pseudocentrosymmetrical structure. Final cycles of least squares in blocks on *F*, final $R = 0{\cdot}066$, $wR = 0{\cdot}031$, $S = 1{\cdot}67$ for 326 variables, scale factor 0·78, with *f*'s for C and O from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965); $(\Delta/\sigma)_{ave} = 0{\cdot}06$, $(\Delta/\sigma)_{max} = 0{\cdot}25$ {*y*[O(4*A*)]}, subsequent $\Delta\rho$ excursions $< 0{\cdot}4$ e Å^{-3}.

No corrections for anomalous dispersion, extinction or absorption. Crystals dissolved in acetonitrile give circular dichroism spectra with positive Cotton effects of increasing strength at 315, 220, and 210 nm, and a lone negative feature at 270 nm; the same solution gives a + optical rotation at 589 nm.

Discussion. Final atomic positional and thermal parameters are given in Table 1.*

The chief feature of the crystal structure is alternating layers of loosely packed molecules in the *ac* planes. Roughly planar molecules are approximately parallel with all others in a layer, and pack without close interaromatic contacts. In this motif, adjacent layers are inclined oppositely and related to one another by the screw axis along **b**. Fig. 1 shows a unit-cell view normal to these layers in the *bc* plane. In detail, the molecules are of two configurational types, corresponding to a diastereomeric pair, in an ordered structure. This relatively rare result has also recently been observed in a cyclic tetrapetide (Chiang & Karle, 1982). Along **a**, like molecules are hydrogen-bonded between hydroxyl and carbonyl groups. The O···O distances are 2·781 (7) (*trans*) and 2·780 (7) Å (*cis*). The cell volume is 1233 Å^3 compared with 1206 Å^3 for the racemate (Valente *et al.*, 1979) and the melting point and density (404 K, 1·32 g cm^{-3}) are lower than for the racemate (414 K, 1·35 g cm^{-3}), which also contains two molecules in its asymmetric unit but has closer interaromatic contacts.

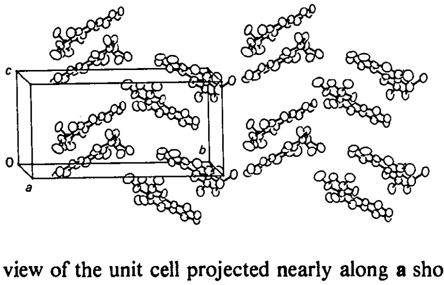

Fig. 1. A view of the unit cell projected nearly along **a** showing the layers in *ac*.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39265 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, Chester CH1 2HU, England.

Two distinct molecular types are contained in the crystal and are grossly related by an approximate center of symmetry. The crystal structure therefore resembles a racemic structure in space group $P2_1/n$, as if the molecules were centrosymmetrically related. The molecules differ, however, in both configuration and conformation. Both display an axial hydroxyl group corresponding to the more stable anomeric form and the configurations at their hemiketal carbons [C(13)] are opposite. This is consistent with pseudo-inversion symmetry between the two molecules and is possible in an enantiomorphic compound such as this because the hemiketal inversion is labile in the solution from which the crystals form. The configuration at the other asymmetric center [C(11)] determines the enantiomorphic form of the molecules. Brucine, the resolving agent, forms a salt with the coumarin 4-hydroxyl group of the molecule in the open side-chain form in which C(11) is the only asymmetric center, and the hemiketals are formed later upon liberating the resolved compound. The configuration at C(11) in the two molecules is the same and, referring to the spatial relationship of the 2-hydroxyl and 4-methyl groups, both *cis* and *trans* diastereomeric forms are present in the crystal. From a comparison of its circular dichroism spectrum with those from similar compounds of known absolute configuration, we can assign the *cis* isomer as 2*R*,4*R* and the *trans* isomer as 2*S*,4*R* (Valente & Trager, 1978), where the 2 position is C(13) and the 4 position is C(11) in Fig. 2. The *cis* isomer has the methyl [C(15)] disposed in a pseudoequatorial conformation. All other atoms in the structures are nearly inversion-related except these methyls and hydrogen atoms bonded to C(11). A drawing of both molecules and this relationship is given in Fig. 2.

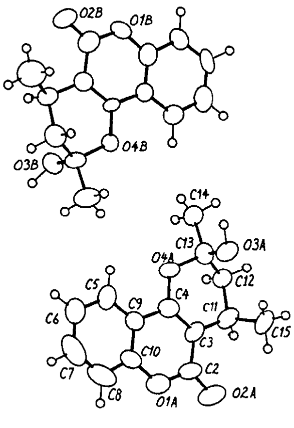
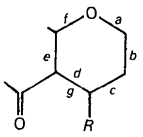


Fig. 2. A view of the two molecules in projection along **c**, showing the near inversion symmetry and giving the atom-numbering scheme.

Table 2. *Torsion angles* (°) *in the dihydropyran rings*

E.s.d.'s are about 1·0°.



	a	*b*	*c*	*d*	*e*	*f*	*g*
cis	38	−55	45	−18	2	−12	−68
trans	−38	59	−49	21	1	8	−40

The conformations of the dihydropyran rings in the molecules are half-chairs distorted towards the *e*,*f*-diplanar form. Intraring torsion angles are presented in Table 2. The flattening of the dihydropyran rings may also be seen in the deviation of C(12) and C(13) from the mean plane described by the four remaining ring atoms. In the *cis* molecule, they are −0·42 and 0·24 Å from the mean plane; in the *trans* molecule, −0·54 and 0·19 Å. In general the average bond lengths and angles for the structure agree with those from similar structures (Valente *et al.*, 1979). Average and maximal differences in bond lengths between the two different molecules are 0·030 and 0·052 Å, and in bond angles 2·2 and 7·7°. Considering the small data set, the parameter correlations, and anisotropy of many of the coumarin ring atoms, we consider the accuracy of individual structural dimensions to be no better than the average differences just quoted. This may still be an underestimation.

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