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(−)-3-(1-Phenylpropyl)-4-hydroxycoumarin

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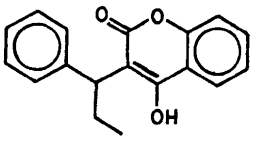
Abstract. The title compound [generic name: (−)-phenprocoumon], $C_{18}H_{16}O_3$, monoclinic, $P2_1$, $Z=4$ with two molecules/asymmetric unit, $a=7{\cdot}171$ (1), $b=17{\cdot}751$ (5), $c=11{\cdot}752$ (2) Å, $\beta=92{\cdot}58$ (2)°, $V=1494$ Å^3, $D_c=1{\cdot}28$, $d_o=1{\cdot}30$ (2) g cm^{-3} is pseudoisostructural with the crystalline racemate as suggested by a similarity in cell constants and symmetry. Structural differences involve small translations and where the racemate crystal contains layers of (−) and layers of (+) enantiomers, the (−) crystal contains one layer nearly identical with the (−) layer in the racemate while the molecules in the other layer adopt a different conformation so that packing is similar to that in the (+) layer of the racemate. Already high thermal motion in the racemate is dramatically increased in the enantiomeric structure which has a larger cell volume. Hydrogen bonding occurs along the *a* direction with O···O distances of 2·617 (5) and 2·587 (6) Å. The final *R* is 0·094 on 3060 counter-collected data.

Introduction. The title compound was resolved from the racemate by a known method (West & Link, 1965; Preis, West & Link, 1966) with an $[\alpha]_D^{25}=-120{\cdot}5$ (2·0)° conc. 1·2 g/100 ml EtOH. Crystals from ethanol were clustered, and an individual crystal with dimensions $0{\cdot}7\times0{\cdot}3\times0{\cdot}3$ mm was separated. Precession photographs on a specimen mounted along *a* revealed monoclinic symmetry, space group $P2_1$, systematic absences $0k0$, $k=2n+1$. Cell constants were determined by least-squares refinement of the 2θ values of 12 reflections for which $2\theta>25°$. Three-dimensional data collection using a Picker card-controlled diffractometer to $\sin\theta/\lambda=0{\cdot}70$ Å^{-1} (Nb-filtered Mo $K\alpha$) yielded 3600 data of which 3060 measured $>2\sigma(F)$ and were included in subsequent calculations. Standard reflections were measured at frequent intervals and a small (~3%) intensity decrease was noted and the data were scaled appropriately.



A similarity between the cell constants and symmetry of the racemate [$a=11{\cdot}407$, $b=18{\cdot}005$, $c=7{\cdot}177$ Å, $\beta=95{\cdot}30°$, $V=1468{\cdot}3$, $P2_1/n$, Bravic, Gaultier & Hauw, (1971)] and the (−) isomer was noticed. Another example in which optical isomers and racemates are isostructural occurs in amino acids exhibiting some dominant packing feature (Benedetti, Pedone & Sirigu, 1973; Di Blasio, Pedone & Sirigu, 1975) and it was therefore decided to attempt to solve the (−) structure with the racemate as a starting point. The structure

Table 1. *Atom positions* (×10^4) *and thermal factors* (×10^3) *for the non-hydrogen atoms in conformation* 1 (*e.s.d.'s are given in parentheses*)

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4468 (5)	5294 (3)	8927 (4)	22 (2)	66 (3)	83 (3)	10 (2)	−2 (2)	10 (3)
O(2)	2787 (6)	4503 (3)	9882 (5)	19 (2)	82 (4)	163 (6)	−2 (3)	9 (3)	35 (4)
C(4)	9276 (6)	4306 (3)	10208 (4)	24 (2)	57 (3)	64 (3)	2 (2)	11 (2)	10 (2)
C(2)	4386 (8)	4700 (4)	9680 (5)	45 (4)	60 (5)	45 (4)	−1 (3)	9 (3)	11 (3)
C(3)	6051 (7)	4382 (3)	10109 (5)	18 (3)	50 (4)	51 (4)	2 (3)	0 (2)	1 (3)
C(4)	7711 (7)	4646 (3)	9796 (4)	21 (3)	43 (4)	40 (3)	3 (3)	4 (2)	1 (3)
C(5)	9481 (9)	5635 (4)	8767 (5)	39 (4)	55 (5)	57 (4)	−3 (4)	12 (3)	14 (4)
C(6)	9458 (10)	6266 (4)	8062 (6)	55 (5)	67 (6)	78 (5)	−11 (4)	8 (4)	−12 (5)
C(7)	7715 (12)	6555 (4)	7594 (4)	91 (6)	41 (5)	65 (5)	−9 (4)	31 (4)	3 (4)
C(8)	6098 (10)	6232 (4)	7914 (6)	41 (4)	60 (5)	90 (5)	9 (4)	2 (4)	13 (4)
C(9)	6160 (8)	5596 (4)	8645 (5)	35 (3)	47 (4)	61 (4)	1 (3)	9 (3)	2 (3)
C(10)	7841 (7)	5296 (3)	9083 (5)	27 (3)	43 (4)	5 (3)	2 (3)	48 (3)	−3 (3)
C(11)	5952 (8)	3716 (4)	10939 (5)	26 (3)	52 (4)	64 (4)	−1 (3)	11 (3)	17 (4)
C(12)	4683 (7)	3813 (4)	11985 (5)	51 (3)	69 (4)	60 (4)	−18 (3)	17 (3)	−5 (4)
C(13)	5196 (9)	4494 (4)	12659 (5)	74 (5)	95 (6)	50 (4)	−7 (4)	14 (4)	−5 (4)
C(14)	5560 (8)	3984 (3)	10292 (5)	71 (4)	52 (4)	40 (3)	−11 (3)	7 (3)	14 (3)
C(15)	7023 (10)	2492 (4)	10082 (6)	105 (6)	58 (5)	70 (5)	0 (4)	27 (4)	11 (4)
C(16)	6727 (16)	1840 (5)	9520 (7)	164 (10)	58 (5)	74 (6)	14 (6)	26 (6)	−10 (5)
C(17)	4965 (25)	1677 (5)	9090 (8)	295 (19)	40 (5)	77 (6)	15 (8)	−26 (9)	−11 (5)
C(18)	3554 (16)	2141 (5)	9260 (8)	184 (11)	59 (6)	119 (7)	−9 (7)	−56 (7)	−9 (6)
C(19)	3799 (11)	2795 (4)	9904 (6)	96 (6)	75 (5)	73 (5)	−21 (5)	−21 (4)	−12 (4)

was solved by assuming that the coumarin location in both the enantiomer and the racemate were the same.

After accounting for the origin shift from $P2_1/n$ to $P2_1$, positions for the coumarin rings were generated and an initial Fourier map ($R=0{\cdot}55$) indicated that a shift of one coumarin ring by about $+0{\cdot}08$ in x was desired. A second map ($R=0{\cdot}47$), phased on the shifted coumarin rings, revealed the remainder of the structure. Three cycles of least-squares refinement on all non-hydrogen atoms and their isotropic thermal factors lowered R to 0·149. Introduction of anistorpic thermal factors retarded the refinement due to the necessity for blocking in our calculations, as well as the appearance of large but not unexpected, thermal motion. Six refinement cycles [using weights of $1/\sigma^2(F)$], the last two including a partial contribution from the

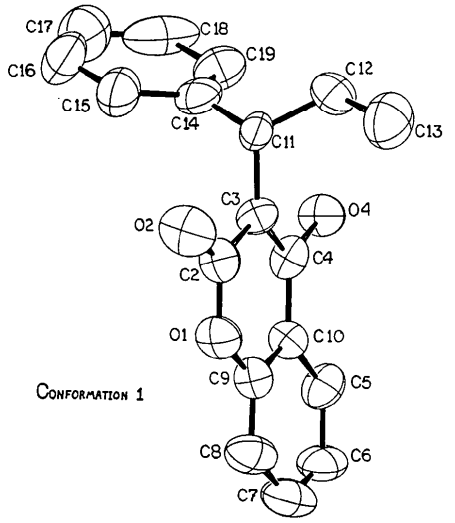


Fig. 1. An *ORTEP* plot of (−)-phenprocoumon in conformation 1 (see text).

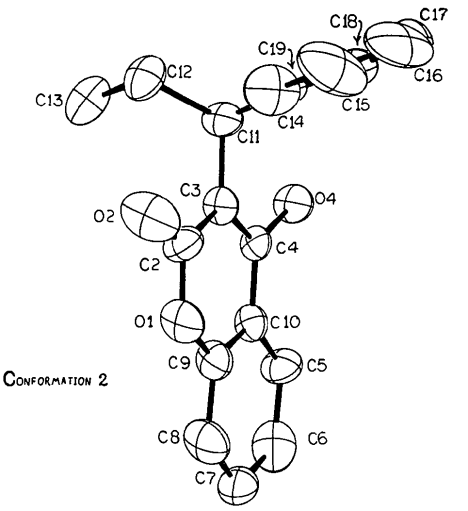


Fig. 2. An *ORTEP* plot of (−)-phenprocoumon in conformation 2 (see text), in the same projection with respect to the coumarin ring as conformation 1.

32 H atoms at positions calculated to be 1·0 Å from the bound heavy atom, reduced R to 0·094 ($wR=0{\cdot}071$).* A difference synthesis calculated at this point had no peak higher than 0·5 e Å^3 except in the regions occupied by the atoms with large thermal motion. Atom positions and thermal parameters for the non-hydrogen atoms are given in Tables 1 and 2. The corresponding molecules are shown in *ORTEP* plots (Fig. 1 and 2; Johnson, 1965) and display the conformational differences between the non-equivalent molecules.

* Structure factor tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31346 (16pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atom positions* ($\times 10^4$) *and thermal factors* ($\times 10^3$) *for the non-hydrogen atoms in conformation* 2 *(e.s.d.'s are given in parentheses)*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	11662 (5)	4715 (2)	6259 (3)	38 (2)	65 (3)	70 (3)	8 (2)	−7 (2)	11 (2)
O(2)	13351 (5)	5541 (3)	5383 (4)	25 (2)	111 (4)	98 (3)	1 (2)	3 (2)	22 (3)
O(4)	6857 (4)	5693 (2)	4897 (3)	24 (2)	68 (3)	76 (3)	−3 (2)	−5 (2)	14 (2)
C(2)	11766 (7)	5311 (4)	5561 (5)	30 (3)	64 (4)	60 (4)	3 (3)	−1 (3)	−1 (3)
C(3)	10088 (7)	5657 (3)	5044 (4)	38 (3)	45 (4)	54 (3)	−2 (3)	11 (2)	3 (3)
C(4)	8394 (6)	5353 (3)	5353 (5)	31 (3)	46 (4)	64 (4)	2 (3)	4 (3)	−9 (3)
C(5)	6681 (7)	4339 (4)	6387 (5)	48 (3)	59 (4)	70 (4)	−10 (3)	12 (3)	−6 (4)
C(6)	6703 (9)	3723 (4)	7060 (5)	80 (5)	58 (5)	56 (4)	−8 (4)	20 (3)	16 (3)
C(7)	8354 (11)	3436 (4)	7439 (5)	105 (6)	64 (5)	54 (4)	19 (4)	19 (4)	16 (4)
C(8)	10036 (9)	3791 (4)	7200 (5)	85 (5)	53 (4)	63 (4)	24 (4)	13 (3)	10 (4)
C(9)	9962 (8)	4403 (4)	6517 (5)	52 (3)	54 (4)	48 (3)	0 (3)	0 (3)	−3 (3)
C(10)	8331 (6)	4707 (3)	6092 (4)	35 (3)	52 (4)	44 (3)	1 (3)	7 (2)	2 (3)
C(11)	10326 (7)	6316 (3)	4271 (4)	49 (3)	43 (3)	46 (3)	−10 (3)	0 (2)	−7 (3)
C(12)	9470 (8)	6239 (4)	3106 (5)	57 (4)	71 (4)	47 (4)	3 (3)	9 (3)	5 (3)
C(13)	10124 (10)	5571 (5)	2467 (6)	103 (6)	89 (7)	84 (5)	−5 (5)	10 (4)	−19 (5)
C(14)	9790 (8)	7055 (3)	4855 (5)	54 (3)	52 (4)	73 (4)	−15 (3)	6 (3)	15 (3)
C(15)	11106 (9)	7422 (4)	5593 (6)	96 (5)	71 (5)	66 (5)	−17 (4)	9 (4)	−12 (4)
C(16)	10654 (14)	8108 (6)	6129 (8)	137 (7)	72 (8)	90 (7)	−46 (7)	4 (6)	−15 (6)
C(17)	8973 (16)	8404 (5)	6014 (8)	156 (9)	97 (7)	77 (6)	−23 (7)	23 (6)	−17 (5)
C(18)	7663 (12)	8075 (5)	5302 (8)	129 (7)	70 (6)	117 (7)	30 (5)	69 (5)	37 (5)
C(19)	7986 (8)	7384 (4)	4733 (6)	66 (4)	56 (4)	85 (5)	5 (3)	17 (3)	3 (4)

Discussion. Crystals of the (−)-enantiomer of phenprocoumon are essentially isostructural with the crystalline racemate. Where the racemate features hydrogen bonding along the short cell-axis between molecules of the same configuration, the enantiomer shows similar hydrogen bonding between molecules of the same conformation. Conformation 2 (Fig. 2), which differs from conformation 1 by a rotation of about 180° around the C(3)–C(11) bond, allows the H on C(11) to adopt the '*trans*' arrangement with respect to the C(3)–C(4) double bond, while in conformation1, and the racemate the arrangement is '*cis*'. Least-squares planes calculated for the 13 coumarin ring atoms and the 6 phenyl ring atoms in each molecule described planarity to within 0·04 and 0·02 Å respectively. The large thermal motion observed in the racemate in dramatically enhanced in the enantiomeric structure particularly at the extremities of the coumarin and phenyl rings. It can be inferred from the direction and magnitude of the thermal motion that the structure permits a large in-lane libration of the rings that increases towards the ends of the group. The bond lengths in the two independent molecules in the enantiomer agree to within 0·04 Å, and the average agrees to within 0·02 Å of those given for the racemate. Representative bond lengths in coumarin compounds are cited elsewhere (Valente, Trager & Jensen, 1975).

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References

BENEDETTI, E., PEDONE, C. & SIRIGU, A. (1973). *Acta Cryst.* B**29**, 730–733.

BRAVIC, G., GAULTIER, J. & HAUW, C. (1971). *C. R. Acad. Sci. Paris, Sér. C*, 1112–1114.

DI BLASIO, B., PEDONE, C. & SIRIGU, A. (1975). *Acta Cryst.* B**31**, 601–602.

JOHNSON, C. K (1965). *ORTEP Thermal Ellipsoid Plotting Program*, Oak Ridge National Laboratory Report ORNL-3794.

PREIS, S., WEST, B. D. & LINK, K. P. (1966). U.S.Patent 3,239,529, 8 March.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY System, Univ. of Maryland.

VALENTE, E., TRAGER, W. & JENSEN, L. (1975). *Acta Cryst.* B**31**, 954–960.

WEST, B. D. & LINK, K. P. (1965). *J. Hetero. Chem.* **2**, 93–94.

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Tetrakis(ethylamine)platinum(II)dibromotetrakis(ethylamine)platinum(IV) Tetrabromide Tetrahydrate

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Abstract. Monoclinic (pseudo-tetragonal), $a=13{\cdot}495$ (2), $b=13{\cdot}507$ (2), $c=11{\cdot}172$ (2) Å, $\beta=92{\cdot}7$ (1)°, $C_{16}H_{56}Br_6N_8Pt_2.4H_2O$, $Z=2$, $D_m=2{\cdot}08$, $D_c=2{\cdot}13$ g cm^{-3}. Only diffuse layer lines are observed corresponding to odd values of l; the subcell for which $c=5{\cdot}586$ Å has space group *Im*. The structure is interpreted in terms of chains of alternate square planar $[Pt(C_2H_5NH_2)_4]^{2+}$ and octahedral $[Pt(C_2H_5NH_2)_4Br_2]^{2+}$ ions, the disorder arising from stacking mistakes involving displacement of the chain by one half the repeat unit.

Introduction. Green needles were prepared as described by Drew & Tress (1935). Rotation photographs about **c** showed normal sharp reflexions on even layer lines, but the odd layer lines were diffuse and were continuous. Data for even values of l were collected on a Hilger–Watts automated diffractometer, with Mo $K\alpha$ radiation, for all reflexions $-h$ to h, 0 to k, $-l$ to l to θ_{max} of 30°. 1907 data were observed [$I>2\sigma(I)$], corrected for absorption and reduced to a set of 1009 on assumption of monoclinic symmetry. If these reflexions are indexed with respect to the subcell for which c is halved, systematic absences are in hkl with $h+k+l$ odd.

The subcell must contain two molecules of formula $Pt(C_2H_5NH_2)_4Br_3.2H_2O$; on analogy with the structures reported for other compounds of this type, it was expected to show half-weight Br atoms attached to the Pt, with Pt–Br bonds parallel to the needle axis. The positions of all atoms were readily deduced from the Patterson function, except for ambiguity of sign of the z coordinates of the C atoms. It was then apparent that adoption of $I2$ or $I2/m$ as the subcell space group would imply that the disorder extends to the signs of these coordinates. Space group *Im* permits all atoms other than the Br atoms above, and including the bromide ions, to occupy ordered positions. If all of the C atoms have z coordinates of the same sign, then