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Structure of Fenpropimorph Picrate

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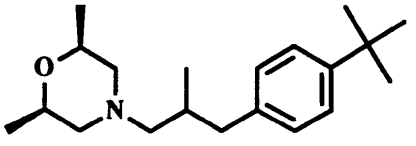
Abstract. $C_{20}H_{34}NO^+.C_6H_2N_3O_7^-$, $M_r = 532{\cdot}6$, monoclinic, Cc, $a = 23{\cdot}890\ (8)$, $b = 7{\cdot}637\ (3)$, $c = 17{\cdot}329\ (7)$ Å, $\beta = 118{\cdot}43\ (3)°$, $V = 2780\ (3)$ Å^3, $Z = 4$, $D_x(105\ K) = 1{\cdot}272$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}088$ mm^{-1}, $F(000) = 1136$, $T = 105$ K, final $R = 0{\cdot}044$ for 1728 observed reflections. The fenpropimorph ion adopts a rather open conformation and is linked to one picrate ion by a hydrogen bond N—H···O; the shape of the fenpropimorph ion in the structure is roughly that of the letter L.

Introduction. Fenpropimorph, (±)-*cis*-4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine (I) is an agricultural fungicide, which is particularly useful against powdery mildews (Himmele & Pommer, 1980). Fenpropimorph and related 3-phenylpropylamines are inhibitors of the ergosterol biosynthesis, the target enzymes being the Δ^{14} reductase and the Δ^8–Δ^7 isomerase (Baloch, Mercer, Wiggins & Baldwin, 1984; Baloch & Mercer, 1987). The determination of the crystal and molecular structure of fenpropimorph picrate was undertaken as part of a study of the conformational properties of fenpropimorph.



(I)

Experimental. Title compound prepared from commercially available fenpropimorph (BASF) *via* the iodide (very fine needles, unusable for structure determination) and picric acid. M.p. 419–422 K. Yellow transparent triangular plate-like crystals from aqueous ethanol. Triangular crystals invariably twins. Single crystal for data collection, 0·12 × 0·2 × 0·4 mm, cut from a twinned crystal. Enraf–Nonius CAD-4 diffractometer and low-temperature device, graphite-monochromatized Mo $K\alpha$ radiation. Temperature (105 K) recorded with a thermocouple, variation within 1 K. Cell parameters and orientation matrix from 18 reflections ($10 \le \theta \le 19°$). No corrections for absorption or secondary extinction. Three intensity control reflections measured every 10^4 s; no systematic variation. Intensity data measured by ω–2θ scan, $\theta_{max} = 29°$; $0 \le h \le 32$, $-10 \le k \le 10$, $-23 \le l \le 20$. 3700 unique reflections measured (Friedel pairs averaged). $R_{int} = 0{\cdot}04$. Most non-H atoms localized by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Remaining non-H atoms localized from difference electron density maps, in which peaks for H atoms could also be found. No refinement of H atoms, which were kept in calculated positions. Structure refinement by least squares minimizing $\sum w(|F_o| - k|F_c|)^2$, with $w^{-1} = \sigma^2(F_o) + 0{\cdot}0175F_o^2$. Final $R = 0{\cdot}044$, $wR = 0{\cdot}054$, $S = 1{\cdot}01$, for 1728 observed reflections ($I \ge 3{\cdot}0\sigma I$) and 211 variables, $(\Delta/\sigma)_{max} = 0{\cdot}34$. Only 12 of the 38 non-H atoms refined anisotropically. $\Delta\rho_{max}/\Delta\rho_{min} = 0{\cdot}3/-0{\cdot}3$ e Å^{-3}. Structure factors for uncharged atoms as implemented in the *SDP* program package (Frenz, 1982), which was used for all calculations.

Discussion. Final atomic coordinates and thermal parameters for non-H atoms are given in Table 1.* The atomic numbering scheme is given in Fig. 1, which shows the biologically most active *S*-enantiomer (Himmele & Pommer, 1980). Bond lengths and valency angles are given in Table 2 together with selected torsion angles and interplanar angles. A few of the chemically equivalent pairs of angles and bonds deviate significantly from each other. These deviations are undoubtedly a function of the actual conformation of the ions. In the fenpropimorph ion C3—N4—C11 and C5—N4—C11 are 113·5 (3) and 108·6 (4)° respectively, and the torsion angles C3—N4—C11—C12 and C5—N4—C11—C12 are ±55·4 (6) and ±177·9 (4)° respectively. Furthermore, the angles C23—C24—C27 and

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52478 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final fractional coordinates and isotropic thermal parameters* (Å^2) *for non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{iso}
O1	1·0170	0·0105 (5)	0·7260	1·83 (6)
C2	1·0005 (2)	0·1032 (7)	0·6461 (3)	1·64 (8)
C3	0·9682 (2)	−0·0209 (7)	0·5686 (3)	1·70 (8)
N4	1·0109 (2)	−0·1760 (5)	0·5799 (2)	1·49 (7)
C5	1·0304 (2)	−0·2622 (7)	0·6676 (3)	1·85 (9)
C6	1·0600 (2)	−0·1294 (7)	0·7395 (3)	2·09 (9)
C7	0·9558 (2)	0·2486 (8)	0·6395 (3)	2·7 (1)*
C8	1·0767 (3)	−0·2096 (9)	0·8283 (4)	3·1 (1)*
C11	0·9808 (2)	−0·3108 (7)	0·5092 (3)	1·84 (9)
C12	0·9564 (2)	−0·2436 (7)	0·4166 (3)	2·04 (9)
C13	0·9301 (2)	−0·3997 (7)	0·3519 (3)	2·07 (9)
C14	1·0079 (2)	−0·1465 (8)	0·4028 (3)	2·8 (1)*
C21	0·8801 (2)	−0·5096 (7)	0·3587 (3)	1·77 (8)
C22	0·8815 (2)	−0·6911 (7)	0·3571 (3)	1·97 (9)
C23	0·8349 (2)	−0·7922 (7)	0·3619 (3)	1·94 (9)
C24	0·7861 (2)	−0·7149 (6)	0·3715 (3)	1·42 (8)
C25	0·7831 (2)	−0·5332 (7)	0·3710 (3)	1·72 (8)
C26	0·8299 (2)	−0·4315 (6)	0·3647 (3)	1·83 (8)
C27	0·7349 (2)	−0·8199 (7)	0·3819 (3)	1·71 (8)
C28	0·7485 (2)	−1·0185 (8)	0·3888 (4)	2·5 (1)*
C29	0·6699 (2)	−0·7908 (9)	0·3023 (4)	3·4 (1)*
C30	0·7348 (3)	−0·7626 (8)	0·4662 (3)	3·2 (1)*
C41	0·6608 (2)	0·4351 (6)	0·1027 (3)	1·23 (8)
C42	0·7142 (2)	0·5477 (6)	0·1353 (3)	1·41 (8)
C43	0·7732 (2)	0·5030 (7)	0·1451 (3)	1·52 (8)
C44	0·7811 (2)	0·3357 (6)	0·1223 (3)	1·28 (7)
C45	0·7331 (2)	0·2125 (7)	0·0914 (3)	1·50 (8)
C46	0·6755 (2)	0·2613 (6)	0·0825 (3)	1·33 (8)
O41	0·6055 (1)	0·4753 (5)	0·0865 (2)	2·09 (6)
N42	0·7101 (2)	0·7269 (5)	0·1634 (3)	1·88 (7)
O421	0·6623 (2)	0·7691 (5)	0·1688 (3)	3·96 (9)*
O422	0·7536 (2)	0·8281 (5)	0·1799 (2)	2·68 (8)*
N44	0·8428 (2)	0·2850 (6)	0·1316 (2)	2·01 (8)
O441	0·8853 (1)	0·3968 (6)	0·1556 (2)	3·00 (8)*
O442	0·8502 (1)	0·1329 (5)	0·1149 (3)	3·10 (8)*
N46	0·6254 (2)	0·1276 (6)	0·0502 (3)	2·10 (8)
O461	0·6251 (2)	0·0193 (5)	−0·0016 (2)	2·59 (8)*
O462	0·5870 (1)	0·1293 (6)	0·0791 (2)	3·66 (9)*

* Equivalent isotropic thermal parameters.

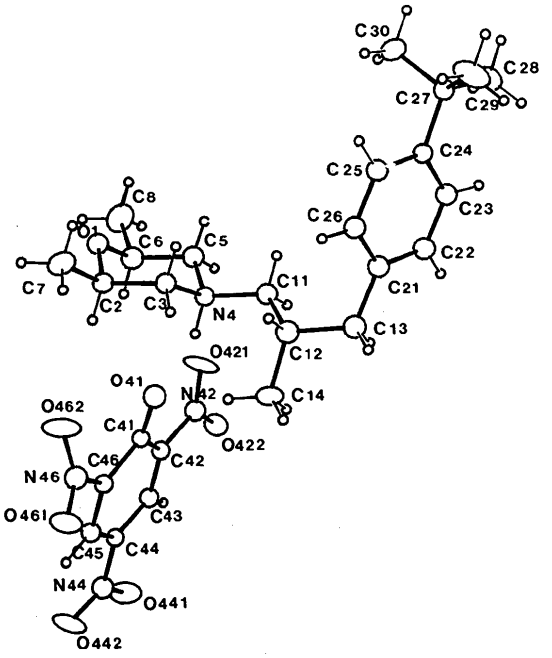

Fig. 1. A perspective view of the *S*-(−)-fenpropimorph ion and the picrate ion, with the numbering system. The drawing was produced by *ORTEP* (Johnson, 1976).

Table 2. *Bond distances* (Å), *angles and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O1—C2	1·437 (5)	C27—C28	1·545 (8)
O1—C6	1·424 (6)	C27—C29	1·526 (6)
C2—C3	1·516 (6)	C27—C30	1·524 (8)
C5—C6	1·495 (7)	C41—C42	1·417 (6)
C3—N4	1·514 (6)	C41—C46	1·460 (7)
N4—C5	1·515 (6)	C42—C43	1·378 (7)
C2—C7	1·508 (8)	C45—C46	1·361 (7)
C6—C8	1·525 (8)	C43—C44	1·379 (7)
N4—C11	1·492 (6)	C44—C45	1·381 (6)
C11—C12	1·515 (7)	C41—O41	1·251 (6)
C12—C13	1·546 (7)	C42—N42	1·474 (7)
C12—C14	1·551 (9)	C46—N46	1·469 (6)
C13—C21	1·510 (8)	C44—N44	1·457 (7)
C21—C22	1·387 (8)	N42—O421	1·232 (6)
C21—C26	1·387 (8)	N42—O422	1·217 (6)
C22—C23	1·391 (8)	N46—O461	1·222 (6)
C25—C26	1·407 (8)	N46—O462	1·235 (7)
C23—C24	1·387 (8)	N44—O441	1·238 (5)
C24—C25	1·389 (7)	N44—O442	1·232 (6)
C24—C27	1·543 (8)		

C2—O1—C6	112·2 (3)	C24—C27—C29	109·8 (4)
O1—C2—C3	109·6 (4)	C24—C27—C30	109·1 (4)
O1—C6—C5	110·6 (3)	C28—C27—C29	107·8 (4)
C2—C3—N4	110·1 (3)	C28—C27—C30	107·4 (5)
C6—C5—N4	109·7 (4)	C29—C27—C30	111·0 (5)
C3—N4—C5	109·9 (4)	C42—C41—C46	112·1 (4)
O1—C2—C7	107·3 (4)	C41—C42—C43	124·9 (5)
O1—C6—C8	107·1 (5)	C41—C46—C45	124·6 (4)
C3—C2—C7	110·4 (3)	C42—C43—C44	117·8 (4)
C5—C6—C8	111·1 (5)	C44—C45—C46	117·7 (5)
C3—N4—C11	113·5 (3)	C43—C44—C45	122·9 (5)
C5—N4—C11	108·6 (4)	C42—C41—O41	126·6 (5)
N4—C11—C12	115·3 (4)	C46—C41—O41	121·3 (4)
C11—C12—C13	109·0 (4)	C41—C42—N42	120·5 (4)
C11—C12—C14	113·2 (3)	C41—C46—N46	118·7 (4)
C13—C12—C14	109·5 (5)	C43—C42—N42	114·6 (4)
C12—C13—C21	115·6 (5)	C45—C46—N46	116·7 (4)
C13—C21—C22	121·7 (5)	C42—N42—O421	118·7 (4)
C13—C21—C26	120·8 (5)	C46—N46—O461	118·2 (5)
C22—C21—C26	117·5 (5)	C42—N42—O422	119·0 (4)
C21—C22—C23	121·8 (5)	C46—N46—O462	117·7 (4)
C25—C26—C21	121·0 (5)	O421—N42—O422	122·4 (4)
C22—C23—C24	121·0 (5)	O461—N46—O462	124·1 (4)
C24—C25—C26	120·8 (5)	O441—N44—O442	123·0 (4)
C23—C24—C25	117·9 (5)	C43—C44—N44	118·9 (4)
C23—C24—C27	123·4 (4)	C45—C44—N44	118·1 (4)
C25—C24—C27	118·7 (5)	C44—N44—O441	118·6 (4)
C24—C27—C28	111·8 (4)	C44—N44—O442	118·4 (4)

C6—O1—C2—C3	60·9 (5)	C2—O1—C6—C5	−62·1 (5)
O1—C2—C3—N4	−56·5 (5)	O1—C6—C5—N4	58·0 (5)
C2—C3—N4—C5	54·2 (5)	C6—C5—N4—C3	−54·6 (5)
C6—O1—C2—C7	−179·3 (4)	C2—O1—C6—C8	176·7 (4)
N4—C3—C2—C7	−174·5 (4)	N4—C5—C6—C8	176·7 (5)
C2—C3—N4—C11	176·1 (1)	C6—C5—N4—C11	−179·3 (4)
C3—N4—C11—C12	55·4 (6)	C5—N4—C11—C12	177·9 (4)
N4—C11—C12—C13	176·9 (4)	N4—C11—C12—C14	54·9 (6)
C11—C12—C13—C21	54·6 (6)	C14—C12—C13—C21	178·9 (4)
C12—C13—C21—C22	−135·6 (5)	C12—C13—C21—C26	45·9 (6)
C23—C24—C27—C28	5·3 (6)	C25—C24—C27—C28	−175·2 (4)
C23—C24—C27—C29	−114·2 (5)	C25—C24—C27—C29	65·3 (6)
C23—C24—C27—C30	123·9 (5)	C25—C24—C27—C30	−56·6 (6)

C25—C24—C27 are 123·4 (4) and 118·7 (5)° respectively, and the contact between the H atoms on C23 and C28 is thereby relieved. The torsion angle C23—C24—C27—C28 is ±5·3 (6)°. In the picrate ion the bonds C41—C42 and C41—C46 are found to have the lengths 1·417 (6) and 1·460 (7) Å respectively, a difference which can hardly be real. The angles C42—C41—O41 and C46—C41—O41 are 126·6 (5) and 121·3 (4)° respectively. The nitro group at C42 makes an angle of 10·0 (4)° with the benzene ring, while the nitro group at C46 is rotated 33·2 (2)° out of plane relative to the benzene ring.

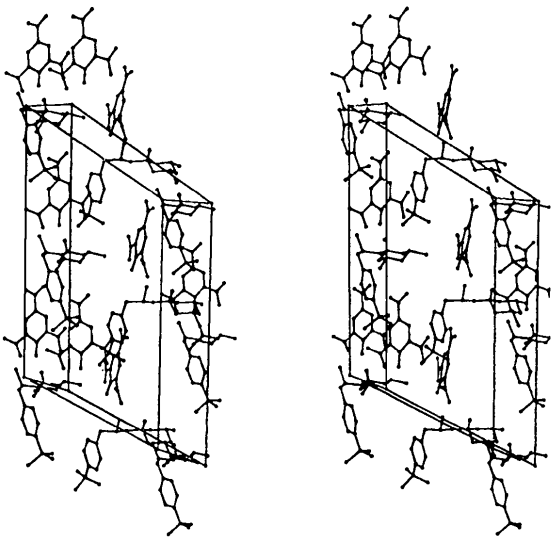

Fig. 2. Stereoview of the crystal packing. The H atoms except H4 have been omitted. The *a* axis points upward, the *b* axis out of the paper and the *c* axis from left to right.

The fenpropimorph ion forms a hydrogen bond N4—H4···O41 to one picrate ion. The distance N4···O41 is 2·687 (6) Å. A stereoview of the crystal packing is shown in Fig. 2. The shape of the fenpropimorph ion in the present structure is roughly that of the letter L. It has been mentioned (Himmele & Pommer, 1980) that the crystal structure of *S*-(−)-fenpropimorph hydrochloride has been examined, but the results have not been made available. Molecular mechanics calculations performed on the fenpropimorph molecule (Jensen, Pettersson, Jørgensen, Klemmensen & Hacksell, 1990) find a low energy conformation similar to that found in fenpropimorph picrate.

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Structure of a Synthetic Taxol Precursor: *N-tert*-Butoxycarbonyl-10-deacetyl-*N*-debenzoyltaxol

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Abstract. 4-Acetoxy-2-benzoyloxy-1,7,10-trihydroxy-9-oxo-5,20-epoxy-11-taxen-13-yl *β-tert*-butoxycarbonylamino-*α*-hydroxybenzenepropionate–methanol–water (1/1/1), $C_{43}H_{53}NO_{14}.CH_3OH.H_2O$, $M_r = 857{\cdot}9$, monoclinic, $P2_1$, $a = 20{\cdot}816$ (10), $b = 8{\cdot}758$ (5), $c = 12{\cdot}726$ (8) Å, $\beta = 101{\cdot}06$ (5)°, $V = 2277$ Å^3, $Z = 2$, $D_x = 1{\cdot}25$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}07$ cm^{-1}, $F(000) = 916$, room temperature, final $R = 0{\cdot}073$, $wR = 0{\cdot}084$, for 3438 observed reflexions. X-ray analysis of an intermediate in the hemisynthesis of taxol was performed; this is the first example of X-ray analysis of a taxane diterpenoid containing an oxetan ring and the taxol-type side chain, both of which are essential for biological activity.

Introduction. In 1971, antitumoral taxol (1) (see Fig. 1) was isolated from the stem bark of the yew *Taxus brevifolia* Nutt, and its structure and configuration were confirmed by the X-ray analysis of the bis-

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