

Waals radii for S and N atoms (3.35 Å) (Bondi, 1964). Probably due to this shorter contact the Ps|Ar| cation is well anchored in the crystal. Consequently, the accuracy of bond-length estimations for this fragment is on the same level as for TCNQ (Table 2).

Fig. 1 presents the mutual positions of *A*, *B* and *B'* TCNQ species in the stack. One TCNQ ring (*A*) lies on a centre of symmetry, whereas the other two (*B* and *B'*) are related by it. The atom deviating most from the TCNQ plane is N(34) in the *B* species, 0.258 (3) Å. As mentioned above, this atom is closest to the S atom. It should be noted that TCNQ (*B*) deviates much more from planarity than TCNQ (*A*).

The Ps|Ar| cation belongs to the symmetrically *p*-disubstituted benzenes and may be analysed in terms of the Walsh rule (Walsh, 1948; Coulson, Domenicano & Vaciego, 1975; Krygowski, 1984). When the difference of the bonds C(45)–C(42)–C(41)–C(45) = *b* – *a* = Δ = 0.004 Å is plotted against α which is the angle O(45)–C(41)–O(42) = 118.7 (3)° the point lies very well on the line Δ vs α proposed by Krygowski (1984), slightly pushed towards greater Δ and α values. This effect may be interpreted as a result of positive charge at the cation species.

Application of the HOSE model (Krygowski *et al.*, 1983) allows estimation of the percentage of quinoid-form contribution, and in consequence the charge at the TCNQ species, with an accuracy of 0.18 e (Krygowski & Anulewicz, 1984). Thus in our study we have estimated *q* at *A* and *B* molecules of TCNQ by use of this model and that proposed by Flandrois & Chasseau (1977). The results are *q*(*A*) = –0.66 e and *q*(*B*) = –0.79 e in comparison with values –0.60 and –0.66 e respectively from the Flandrois & Chasseau (1977) model. The rather comparable charges at TCNQ *A* and *B* molecules in the Ps|Ar|.3TCNQ

complex explain its high electrical conductivity (Pęcherz *et al.*, 1984).

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Structure of Benoxaprofen, 2-[2-(4-Chlorophenyl)-1,3-benzoxazol-5-yl]propionic Acid

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Abstract. C₁₆H₁₂ClNO₃, *M_r* = 301.7, monoclinic, *A*2/*a*, *a* = 12.557 (8), *b* = 4.941 (11), *c* = 48.478 (32) Å, β = 101.5 (1)°, *U* = 2947.4 Å³, *Z* = 8, *D_m* =

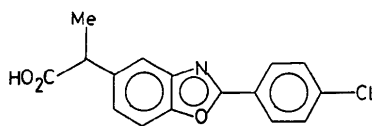
1.36, *D_x* = 1.36 g cm^{–3}, λ(Mo Kα) = 0.7107 Å, μ = 2.72 cm^{–1}, *F*(000) = 1248, room temperature, final *R* = 0.072 for 1303 independent observed reflections.

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The bond lengths and angles are normal. The molecule is planar apart from the carboxylic group which is rotated by $75.8(1)^\circ$ out of the plane of the adjacent ring. A strong pair of intermolecular hydrogen bonds connects two $-\text{CO}_2\text{H}$ groups across a centre of symmetry with $\text{O}\cdots\text{O}$ $2.67(1)$ Å.

Introduction. The title compound, known as benoxaprofen, is one of a series of related compounds prepared by Dunwell, Evans, Hicks, Cashin & Kitchen (1975) that have some anti-inflammatory activity. Subsequent work by Cashin, Dawson & Kitchen (1977) and Chatfield, Cashin, Kitchen & Green (1977) and others established its use as a non-steroidal anti-inflammatory agent. Benoxaprofen was marketed as a drug but subsequently withdrawn in 1982.



The crystal structure of benoxaprofen has now been determined to assist in the evaluation of structure-activity relationships. Crystals were prepared following the method of Dunwell *et al.* (1975).

Experimental. Density measured by flotation in CCl_4 /ligroin. Precession photograph established preliminary cell constants. Crystal of approximate size $0.2 \times 0.3 \times 0.3$ mm obtained as described above mounted on Stoe STADI2 diffractometer to rotate about (110) planes. Cell dimensions by measurement of *ca* 20 high-angle axial reflections. Intensity data collected *via* variable-width ω scan, background counts 20 s, step-scan rate $0.033^\circ \text{ s}^{-1}$, width $(1.5 + \sin\mu/\tan\theta)^\circ$. Absorption and extinction corrections not applied. Standard reflections *hh2* measured every 20 measurements for each layer: no significant change in intensity. 3317 ($0 \leq h \leq 12$, $0 \leq k < 6$, $-56 < l < 54$) data measured with $2\theta_{\text{max}} 50^\circ$. 1303 data with $I > 3\sigma(I)$ used in subsequent calculations. Structure solved by direct methods using *SHELX76* (Sheldrick, 1976). Cl, O, N, C atoms refined anisotropically; H atoms bonded to C placed in tetrahedral or trigonal positions, thermal parameters allowed to refine but those on same atom constrained to be equivalent. H atoms on methyl group refined as rigid group with common thermal parameter. Hydrogen atom on O(19) located in difference Fourier map and refined with constrained O-H distance. Weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$, $\sigma(F)$ taken from counting statistics. In final cycle of refinement (on *F*) no shift $> 0.1\sigma$. Final *R* 0.072 (*wR* 0.077, *S* 1.72). In final difference map, max. and min. peaks 0.33, $-0.36 \text{ e } \text{Å}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations

using *SHELX76* (Sheldrick, 1976) on the CDC7600 computer at the University of Manchester Regional Computer Centre. Atomic coordinates are given in Table 1. Details of interatomic distances and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42529 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$\bar{U}(\text{Å}^2 \times 1000)^*$
Cl(1)	6680 (2)	-1816 (4)	2637.8 (3)	100 (3)
C(1)	6407 (5)	507 (12)	2886 (1)	75 (8)
C(2)	5368 (5)	1534 (14)	2883 (1)	76 (8)
C(3)	5186 (4)	3389 (13)	3082 (1)	75 (8)
C(4)	6024 (4)	4254 (11)	3297 (1)	59 (7)
C(5)	7088 (5)	3232 (11)	3297 (1)	70 (7)
C(6)	7263 (5)	1382 (14)	3094 (1)	91 (8)
C(7)	5880 (5)	6211 (12)	3511 (1)	71 (7)
O(8)	4846 (3)	7407 (8)	3492 (1)	66 (5)
C(9)	4972 (4)	9082 (12)	3725 (1)	65 (7)
C(10)	6032 (4)	8868 (11)	3873 (1)	53 (7)
N(11)	6590 (3)	6955 (9)	3728 (1)	54 (6)
C(12)	4211 (5)	10857 (14)	3811 (1)	78 (8)
C(14)	5623 (5)	12055 (12)	4209 (1)	75 (8)
C(13)	4531 (5)	12290 (14)	4053 (1)	77 (8)
C(15)	6367 (4)	10327 (12)	4112 (1)	68 (7)
C(16)	5921 (5)	13668 (14)	4480 (1)	79 (8)
C(17)	5537 (5)	12003 (15)	4711 (1)	78 (9)
O(18)	6081 (4)	10313 (13)	4854 (1)	144 (7)
C(20)	7175 (5)	14336 (16)	4565 (1)	92 (10)
O(19)	4537 (4)	12581 (13)	4739 (1)	188 (9)

$$* U_{\text{eq}} = \frac{1}{3} \sum_j \sum_l a_j a_l U_{jl}$$

Table 2. Molecular dimensions (Å, °)

Cl(1)-C(1)	1.745 (6)	C(9)-C(12)	1.418 (9)
C(1)-C(2)	1.397 (10)	C(10)-N(11)	1.442 (7)
C(1)-C(6)	1.388 (8)	C(10)-C(15)	1.359 (7)
C(2)-C(3)	1.382 (9)	C(12)-C(13)	1.362 (8)
C(3)-C(4)	1.390 (7)	C(14)-C(13)	1.431 (8)
C(4)-C(5)	1.427 (8)	C(14)-C(15)	1.413 (9)
C(4)-C(7)	1.456 (8)	C(14)-C(16)	1.520 (8)
C(5)-C(6)	1.393 (9)	C(16)-C(17)	1.541 (9)
C(7)-O(8)	1.414 (7)	C(16)-C(20)	1.581 (9)
C(7)-N(11)	1.289 (7)	C(17)-O(18)	1.206 (8)
O(8)-C(9)	1.385 (6)	C(17)-O(19)	1.322 (9)
C(9)-C(10)	1.383 (7)		
Cl(1)-C(1)-C(2)	123.0 (5)	C(9)-C(10)-N(11)	108.0 (5)
Cl(1)-C(1)-C(6)	118.4 (5)	C(9)-C(10)-C(15)	120.3 (5)
C(2)-C(1)-C(6)	118.6 (5)	N(11)-C(10)-C(15)	131.8 (5)
C(1)-C(2)-C(3)	121.2 (5)	C(7)-N(11)-C(10)	105.1 (4)
C(2)-C(3)-C(4)	121.3 (5)	C(9)-C(12)-C(13)	118.2 (5)
C(3)-C(4)-C(5)	117.5 (5)	C(13)-C(14)-C(15)	120.1 (5)
C(3)-C(4)-C(7)	123.6 (5)	C(13)-C(14)-C(16)	117.3 (5)
C(5)-C(4)-C(7)	118.9 (5)	C(15)-C(14)-C(16)	122.6 (5)
C(4)-C(5)-C(6)	120.7 (5)	C(12)-C(13)-C(14)	120.0 (5)
C(1)-C(6)-C(5)	120.6 (5)	C(10)-C(15)-C(14)	119.3 (5)
C(4)-C(7)-O(8)	118.4 (5)	C(14)-C(16)-C(17)	106.8 (5)
C(4)-C(7)-N(11)	127.4 (5)	C(14)-C(16)-C(20)	113.3 (5)
O(8)-C(7)-N(11)	114.2 (5)	C(17)-C(16)-C(20)	111.2 (5)
C(7)-O(8)-C(9)	104.1 (4)	C(16)-C(17)-O(18)	124.2 (6)
O(8)-C(9)-C(10)	108.6 (5)	C(16)-C(17)-O(19)	113.7 (6)
O(8)-C(9)-C(12)	129.3 (5)	O(18)-C(17)-O(19)	122.1 (6)
C(10)-C(9)-C(12)	122.0 (5)		

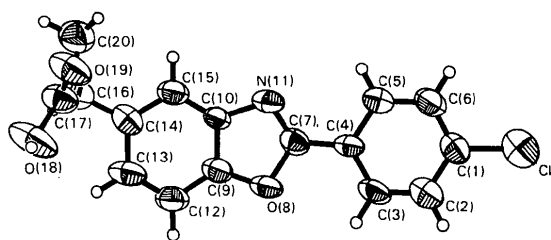


Fig. 1. The structure of benoxaprofen. Thermal ellipsoids are shown at 50% probability.

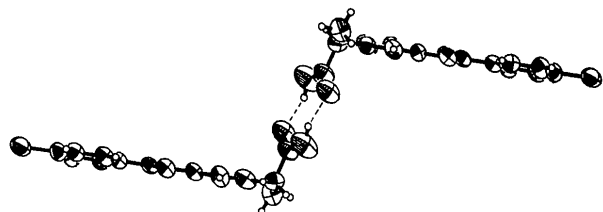


Fig. 2. Two molecules of benoxaprofen, connected *via* intermolecular hydrogen bonds (shown as dotted lines) over a centre of symmetry.

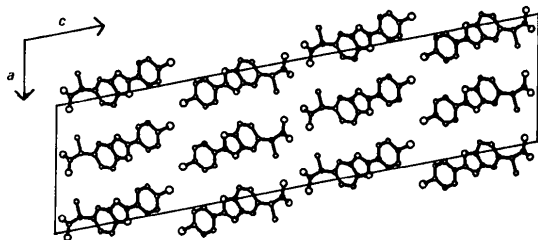


Fig. 3. The unit cell of benoxaprofen in the *b* projection.

Discussion. The structure is shown in Fig. 1 together with the atomic numbering system. The bond lengths and angles in the molecule are unexceptional. The molecule is closely planar apart from the carboxylic acid group (least-squares planes in Table 3). Thus there is a small twist between planes 1 and 2 of 5.3 (1)° but planes 2 and 3 are coplanar. The carboxylic acid group (plane 4) is twisted well out of the plane of the other atoms in the molecule, making an angle of 75.8 (1)° with plane 3. This twist clearly maximizes intramolecular distances between the C(20) methyl group and the carboxylic acid group and plane 3 but it also facilitates the formation of a pair of intermolecular hydrogen bonds with another molecule (1 - *x*, 2 - *y*, 1 - *z*) across a centre of symmetry. Dimensions of these bonds are O(18)···O(19) 2.676 (8) Å, O(18)···H(19)—O(19) 157 (9)°, O(18)···H(19) 1.83 (11) Å. This hydrogen-bonded dimer is shown in Fig. 2 and the overall packing is illustrated in Fig. 3.

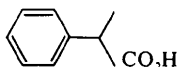
Table 3. *Least-squares planes for (1)*

Distances of atoms from the planes are given in Å. Atoms not contributing to the plane are marked with an asterisk.

Plane 1.	C(1) -0.00 (1), C(2) -0.00 (1), C(3) 0.01 (1), C(4) -0.01 (1), C(5) 0.00 (1), C(6) 0.00 (1), Cl(1)* -0.01 (1), O(8)* 0.12 (1), N(11)* -0.11 (1)
Plane 2.	C(7) 0.01 (1), O(8) -0.00 (1), C(9) -0.00, C(10) -0.00, N(11) -0.01 (1), C(4)* -0.02 (1), C(3)* -0.12 (1), C(5)* 0.11 (1), C(12)* 0.03 (1), C(15)* 0.01 (1)
Plane 3.	C(9) -0.01 (1), C(10) 0.00 (1), C(12) 0.01 (1), C(14) -0.01 (1), C(13) -0.01 (1), C(15) 0.01 (1), C(16)* -0.05 (1), C(17)* -1.48 (1), C(20) 0.54 (1)
Plane 4.	C(16) -0.00 (1), C(17) 0.00 (1), O(18) -0.01 (1), O(19) -0.00 (1)

Angles between planes (°): 1/2 5.3 (1), 1/3 5.6 (1), 1/4 77.8 (1), 2/3 0.4, 2/4 75.8 (1), 3/4 75.8 (1)

Table 4. *Selected dimensions for molecules containing the 2-phenylpropionic acid fragment*



Dimensions*	(1)	(2)	(3)	(4)	(5)	(6)†	
Torsion angles (°)							
C(13)—C(14)—C(16)—C(17)	82.4 (1)	87.8	109.2	130.5	140.9	158.2	119.3
C(13)—C(14)—C(16)—H(17)	-38.4 (1)	-30.5	-6.3	0.8	16.6	40.4	-1.1
C(13)—C(14)—C(16)—C(20)	-154.7 (1)	-148.8	-124.6	-107.7	-96.5	-79.7	-116.4
Angle between Ph ring and -CO ₂ H (°)	75.8 (1)	79.2	82.9	71.7	75.2	70.2	59.1
C(14)—C(16)—C(17)—O (°)	88.9 (1)	67.3	97.7	77.3	89.3	79.7	109.7
	-90.7 (1)	-114.7	-80.6	-102.0	-88.7	-102.2	-69.9
Type of intermolecular hydrogen bonding	Dimer	‡	Dimer	Dimer	Dimer	§	
O···O distance (Å)	2.68 (1)	2.68	2.66	2.65	2.66	2.68	2.65

References: (1) this molecule; (2) 2-(4-cyclohexyl-1-naphthyl)propionic acid (Dupont, Dideberg, Dive, Godfroid & Steiner, 1982); (3) 2-methyl-4-(2-thenoyl)benzenoacetic acid (Peeters Bleton & de Ranter, 1983); (4) (±)-2-(2-fluoro-4-biphenyl)propionic acid (Flippen & Gilardi, 1975); (5) 2-(4-isobutylphenyl)propionic acid (McConnell, 1974); (6) (+)-(2*R*,*αS*)-2-isopropyl-*α*-methyl-5-indanacetic acid (Foulon, Baert, Fourret, Brienne & Jacques, 1979).

* The numbering scheme is given for (1). The equivalent dimensions are given for molecules (2)–(6).

† Two molecules in the asymmetric unit.

‡ Intermolecular hydrogen bond.

§ Intramolecular hydrogen bonds between the -CO₂H groups of the two molecules in the asymmetric unit.

Search of the Cambridge Data Centre files shows only five other molecules that contain a C(Me)COOH group attached to a benzene ring. These compounds are listed in Table 4 together with selected dimensions. Three of these five structures contain intramolecular hydrogen bonds formed between two molecules over a centre of symmetry in an equivalent manner to (1). The conformation of the propionic acid moiety relative to the benzene ring can be described by a number of torsion angles. These are listed for all these molecules in Table 4. The C(13)–C(14)–C(16)–C(17) torsion angle varies considerably in the molecules, ranging from 82.4 (1)° in (1) to 158.2° in (6). However, there is more agreement in the position of the –CO₂H group relative to the phenyl ring measured either by the angle of intersection or by the C–C–C–O torsion angles, which fall within a 30° spread if sign variations are ignored. The considerable range of values for both these dimensions indicates that no particular conformation is favoured and that overall packing effects may well decide the exact molecular conformation.

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4-O-β-D-Galactopyranosyl-α-D-mannopyranose Hemiethanol Dihydrate

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Abstract. C₁₂H₂₂O₁₁·½C₂H₆O·2H₂O, *M_r* = 401.4, tetragonal, *P*4₂, *a* = 9.2351 (13), *c* = 42.2158 (30) Å, *V* = 3600.46 Å³, *Z* = 8, *D_x* = 1.48 g cm⁻³, λ(Cu *K*α) = 1.5418 Å, μ = 11.84 cm⁻¹, *F*(000) = 1720, *T* = 293 K, *R* = 0.0636 for 1999 observed reflections. The material was prepared by recrystallization from an ethanol/water mixture of a commercially prepared sample. The results have confirmed the disaccharide structure, showing two molecules of water per oligomer plus ethanol of crystallization.

Introduction. Great importance has been placed on carbohydrates which exhibit the properties of gelation because of their commercial applications. In this context, work on the structure of galactomannans, which form synergistic gels with other polysaccharides such as carrageenan (Dea & Morrison, 1975), is of interest. Thus, the crystal structure of any galactomanan oligomer is useful as a model for conformational analysis of the polymer. The present study has shown that the recrystallized compound is the free reducing disaccharide which contains ethanol of crystallization.

Experimental. Crystals prepared by slow evaporation from an ethanol/water mixture; crystal 0.2 × 0.2 × 0.25 mm, Enraf–Nonius CAD-4F diffractometer, Cu *K*α radiation, cell dimensions calculated from θ measurements of 32 reflections. 6476 reflections measured, 2θ_{max} = 70°, *h* 0 to 8, *k* 0 to 11, *l* 0 to 52, data merged using *SHELX76* (Sheldrick, 1976) giving 2060 unique reflections, *R*_{int} = 0.0532, 1999 [*F* > 3σ(*F*)] used in analysis. As an intensity check the 5,5,18 reflection was used: average count 455.1 and σ (calculated from the distribution) = 63.0 (13.8%). No absorption correction applied. *MULTAN80* (Main *et al.*, 1980) used to solve structure and least-squares refinement carried out, with *SHELX*, for positional parameters and anisotropic thermal parameters for all non-H atoms; ∑*w*(Δ*F*)² minimized, *w* = 1/(σ²*F* + 0.001159*F*²); H atoms located from difference Fourier synthesis except for ethanolic H atoms but not refined; *R* = 0.0636, *wR* = 0.0940. In final cycle max. Δ/σ 0.084, av. 0.006; on final difference Fourier synthesis max. and min. electron densities 0.37 and –0.35 e Å⁻³; scattering factors from *International Tables for X-ray*