result of the *D/E* cis-fusion. Ring *E* has a regular chair conformation, but ring *D* is a flattened chair [at C(13b)] with C(13b) and N at distances of 0·15 and −0·66 Å respectively from the seat formed by the other four atoms. The mean planes of rings *D* and *E* form an angle of 125·1°. The cycloheptane ring *B* is folded along the C(8)···C(13a) diagonal, with C(8), C(8a), C(12a), C(13) and C(13a) forming one approximate plane (within ±0·047 Å), and C(8), C(7a), C(13b) and C(13a) another (within ±0·021 Å). The angle between these two planes is 118·5°. H(8,1) and H(13a) exhibit a flagpole—bowsprit interaction between them, and their parent C atoms are separated by 2·876 Å.

At C(3), OH is axial and the *tert*-butyl is equatorial. The H atoms at O, C(4a) and N are *cis* to each other and *trans* to that at C(13a).

Intermolecular hydrogen-bonding

Each Br is involved in two intermolecular hydrogen bonds of the form N—H···Br···H—O that link the molecules into continuous chains parallel to **c** (Fig. 4). The separate chains do not have linkages between them. The geometrical entities of the hydrogen bonds are presented in Fig. 3(*a,b*). Similar N—H···Br··· H—O hydrogen bonds are also present in (±)-butaclamol.HBr and (+)-dexclamol.HBr, with N···Br and O···Br distances of 3·245 and 3·245 Å in the former and 3·210 and 3·192 Å in the latter respectively.

The authors thank Dr L. G. Humber of AYERST Research Laboratories, Montreal, for supplying the crystal samples and commenting on the biochemical aspects of the paper, Mrs M. E. Pippy for assistance with the computations, and Mrs H. M. Sheppard for technical assistance.

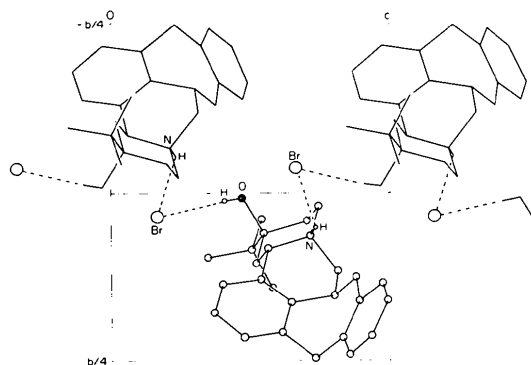
Fig. 4. Projection along **a** of part of the unit-cell contents, showing the intermolecular hydrogen bonding.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC Crystallographic Programs for the IBM 360 System. Accession Nos. 133–147 in *J. Appl. Cryst.* **6**, 309–346.

BIRD, P. H., BRUDERLEIN, F. T. & HUMBER, L. G. (1976). *Can. J. Chem.* **54**, 2715–2722.

BRUDERLEIN, F. T., HUMBER, L. G. & PELZ, K. (1974). *Can. J. Chem.* **52**, 2119–2122.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HUMBER, L. G., BRUDERLEIN, F. T., PHILIPP, A. H., GÖTZ, M. & VOITH, K. (1979). *J. Med. Chem.* **22**, 761–767.

HUMBER, L. G., BRUDERLEIN, F. T. & VOITH, K. (1975). *Mol. Pharmacol.* **11**, 833–840.

HUMBER, L. G., PHILIPP, A. H., VOITH, K., PUGSLEY, T., LIPPMANN, W., AHMED, F. R. & PRZYBYLSKA, M. (1979). *J. Med. Chem.* In the press.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

PHILIPP, A. H., HUMBER, L. G. & VOITH, K. (1979). *J. Med. Chem.* **22**, 768–773.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

The Structure of an Unknown Triterpane from a Californian (Monterey, USA) Shale Oil, 28,30-Dinor-17α(H),18α(H),21β(H)-hopane, C28H48

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Abstract

An unknown triterpane, $C_{28}H_{48}$, extracted from a Californian shale oil, has been identified as 28,30-dinor-17α(H),18α(H),21β(H)-hopane by the determination of its crystal structure. The compound is orthorhombic, space group $P2_12_12_1$, with $a = 11·262$ (4), $b = 7·360$ (6), $c = 28·378$ (11) Å, $Z = 4$. Refinement

reduced R to 0·068 for 2242 observed reflexions and included the isotropic refinement of all H atoms. The molecule consists of four fused all-chair all-*trans* six-membered rings A, B, C, D with a five-membered E ring *cis*-fused to D. The C(23) and C(24) geminal dimethyl pair is sited at C(4). Methyls C(25), C(26) are found with β configurations at C(10) and C(8) whilst C(27) is attached α at C(14) and the C(22), C(29) ethyl group adopts an α configuration at C(21).

Introduction

This compound which occurs abundantly in a Monterey (California) shale oil (Seifert & Moldowan, 1979) and in a crude petroleum from Northern Volga Ural (Siva) Region (USSR) (Petrov, Pustil'nikova, Abriutina & Kagramanova, 1976), was extracted, purified and crystallized by Drs Seifert and Moldowan (Chevron Oil Company) who produced a large plate-like single crystal ~3·0 × 2·0 × 0·15 mm. Preliminary mass spectrometry and NMR measurements indicated either a hopane- or lupane-type structure probably lacking the usual methyl group at the C(18) position. The X-ray results show the molecule to have the structure (I).

(I)
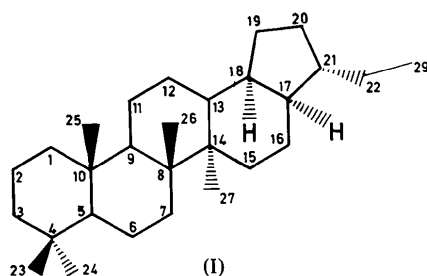
Experimental

A fragment ~0·5 mm square cut from the original crystal was examined by Weissenberg photography with Cu $K\alpha$ radiation, which showed it to be ortho-rhombic. Cell parameters were refined from the angles of 17 reflexions measured on a Stoe four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

Crystal data

$C_{28}H_{48}$, $M_r = 384.38$, orthorhombic, $a = 11.262$ (4), $b = 7.360$ (6), $c = 28.378$ (11) Å, $U = 2352.2$ Å^3, $D_x = 1.086$ Mg m^{-3}, $F(000) = 864$, space group $P2_12_12_1$, $Z = 4$, optic sign positive, μ(Mo $K\alpha$) = 0·065 mm^{-1}.

Owing to the precious nature of the crystal which was required for other examinations, no attempt was made to measure the density.

Intensities were collected on the Stoe instrument by courtesy of Dr R. Fenn (Portsmouth Polytechnic) with β-filtered Mo $K\alpha$ radiation in the $\omega/2\theta$ scan mode. Background measurements were taken on either side of the peak for half the scan time. The intensities of three standard reflexions, monitored after every 30 reflexions, showed a linear decrease with time. Tube failure occurred after collecting 2300 reflexions when tube output had fallen by 50% and subsequent data were collected on a reserve tube whose output was only 20% of the former. Extensive scaling of the data was therefore necessary. 3090 independent reflexions were measured for $2\theta \leq 55°$ of which 2243 were taken to be observed according to the criterion $I \geq 1.5\sigma(I)$ where $\sigma^2 = I(\text{peak}) + I(\text{background})$. No correction for instrumental stability was applied. The 002 reflexion could not be adequately measured because of its proximity to the beam stop.

Net intensities were corrected for Lp factors and those with zero-net values were given an arbitrary F_o value of 1·0. Overall scale and temperature factors ($\bar{B} = 4.86$ Å^2) were obtained from a Wilson plot, and normalized structure amplitudes were calculated.

Structure determination

Similarities between the cell dimensions and the $h0l$ intensities of this compound and those of triterpane D (Smith, 1975a) indicated that the structures could be closely related. The c dimension strongly suggested that the D/E ring junction would be *cis* whilst it was inferred from the b dimension that the ethyl group, if present, would be at C(21) implying a hopane rather than a lupane derivative.

The structure was solved from 208 reflexions with $E \geq 1.5$ by $MULTAN$ (Germain, Main & Woolfson, 1971). The E_o map phased upon the set having the highest figure of merit and lowest residual showed 23 C atoms clearly, while C(19), C(20), C(21) and C(22) were inferred from weak peaks on the basis of the suspected *cis* junction. C(29) was initially wrongly placed. As the refinement showed, these atoms have an average isotropic temperature factor of 7·25 Å^2 compared with the mean for the other 24 C atoms of 4·51 Å^2.

Refinement

Block-diagonal isotropic least-squares refinement was started for the C atoms alone, with scattering factors given in *International Tables for X-ray Crystallography* (1962). It became clear that C(29) was wrongly placed and its true position was extracted from electron density and difference maps. Subsequent cycles reduced R from 0·29 to 0·16 with weights $w = 1$ for $F \leq 7.0$ and $w = 7.0/F$ for $F > 7.0$. The positions of the 30 H atoms fixed by geometry were calculated

with C—H = 1·08 Å, and included as fixed parameters until R converged at 0·13. The positions of the methyl H atoms were obtained from another pair of electron density and difference maps and, following their inclusion as fixed parameters, R was reduced to 0·11 with weights $w^{-1} = [1 + (F - 6)^2/64]^{1/2}$. Anisotropic refinement of the C atoms alone reduced R to 0·07. Finally, isotropic refinement of all H parameters was attempted in which unobserved reflexions were included providing $\Delta F/F \leq 1\cdot0$. R converged at 0·079 (2837 reflexions) with $R = 0\cdot068$ for 2242 observed reflexions (002 excluded). Attempts to refine beyond this point resulted in divergence and a worsening of the C—H bond geometry.

The coordinates of the C atoms are given in Table 1.*

Discussion

The bond lengths between C atoms, Table 2, yield a mean C—C distance, over 32 lengths, of 1·536 (21) Å which may be compared with 1·542 (28) and 1·532 (30) Å for triterpanes D and H respectively (Smith, 1975a,b). Seven distances lie outside the 1σ limit but only one outside the 2σ limit. This distance, C(8)—C(14), is just on the 3σ limit and has been observed to be >1·6 Å for a number of other triterpenoids, e.g. the equivalent distances in triterpanes D and H are 1·622 and 1·624 Å respectively, both of which have the same ring skeleton as this

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* Lists of structure factors, thermal parameters, H atom positional parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34523 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

compound. It probably accounts for the mid-molecule strain common in triterpanes which appears to be a principal determinant in the regular mode spectral splitting of these hydrocarbons.

The C—H distances* have a mean of 1·02 (5) Å with only two distances outside the 2σ limit; in view of the difficulty in refining large numbers of H atoms, these results appear satisfactory. Bond angles for the C atom skeleton are listed in Table 3; all angles lie inside the 2σ limit of the mean of 110·8 (3·2)°. There appears to be some strain associated with the B ring arising from the steric effects of the methyl groups C(24), C(25) and C(26) which cause C(4)—C(5)—C(10) and C(8)—C(9)—C(10) to show the largest deviations from the mean. As a result the C(24)—C(25) distance increases to 3·17 Å compared with 2·64 Å for C(4)—C(10); likewise C(25)—C(26) is increased to 3·16 Å compared with 2·66 Å for C(8)—C(10).

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* See deposition footnote.

Table 2. C—C *bond lengths* (Å)

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

C(1)—C(2)	1·509 (7)	C(10)—C(25)	1·547 (5)
C(1)—C(10)	1·540 (5)	C(11)—C(12)	1·538 (7)
C(2)—C(3)	1·508 (7)	C(12)—C(13)	1·503 (6)
C(3)—C(4)	1·523 (7)	C(13)—C(14)	1·553 (6)
C(4)—C(5)	1·564 (5)	C(13)—C(18)	1·552 (6)
C(4)—C(23)	1·528 (8)	C(14)—C(15)	1·553 (6)
C(4)—C(24)	1·538 (7)	C(14)—C(27)	1·534 (5)
C(5)—C(6)	1·505 (6)	C(15)—C(16)	1·531 (6)
C(5)—C(10)	1·550 (5)	C(16)—C(17)	1·522 (7)
C(6)—C(7)	1·528 (5)	C(17)—C(18)	1·532 (7)
C(7)—C(8)	1·531 (5)	C(17)—C(21)	1·534 (7)
C(8)—C(9)	1·550 (5)	C(18)—C(19)	1·538 (8)
C(8)—C(14)	1·600 (5)	C(19)—C(20)	1·533 (10)
C(8)—C(26)	1·544 (5)	C(20)—C(21)	1·519 (9)
C(9)—C(10)	1·573 (5)	C(21)—C(22)	1·512 (8)
C(9)—C(11)	1·537 (6)	C(22)—C(29)	1·513 (10)

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

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

	x	y	z		x	y	z
C(1)	3660 (5)	8114 (5)	4570 (2)	C(15)	4372 (4)	2108 (6)	6204 (1)
C(2)	3649 (5)	8382 (6)	4042 (2)	C(16)	4817 (4)	2105 (7)	6714 (2)
C(3)	4527 (7)	7159 (7)	3797 (2)	C(17)	4096 (4)	3368 (7)	7027 (1)
C(4)	4351 (4)	5150 (6)	3904 (1)	C(18)	3885 (5)	5263 (7)	6821 (2)
C(5)	4327 (3)	4909 (5)	4452 (1)	C(19)	2866 (6)	5961 (8)	7133 (2)
C(6)	4258 (4)	2965 (6)	4614 (1)	C(20)	2072 (6)	4304 (10)	7220 (2)
C(7)	4596 (4)	2838 (5)	5135 (1)	C(21)	2860 (4)	2647 (7)	7157 (1)
C(8)	3807 (3)	3978 (5)	5460 (1)	C(22)	2857 (6)	1381 (10)	7577 (2)
C(9)	3742 (3)	5936 (5)	5261 (1)	C(23)	5448 (5)	4178 (10)	3713 (2)
C(10)	3439 (3)	6135 (5)	4722 (1)	C(24)	3249 (5)	4405 (8)	3649 (2)
C(11)	3002 (5)	7178 (6)	5582 (2)	C(25)	2121 (3)	5709 (7)	4616 (2)
C(12)	3457 (5)	7134 (6)	6093 (2)	C(26)	2576 (3)	3059 (6)	5473 (1)
C(13)	3531 (4)	5246 (5)	6292 (1)	C(27)	5622 (4)	4761 (7)	5974 (2)
C(14)	4346 (3)	4035 (5)	5982 (1)	C(29)	1691 (6)	0426 (10)	7668 (2)

There are 114 angles involving the H atoms;* the mean is 108·8 (3·4)° with all but four inside the 2σ limit. These are C(10)—C(9)—H(109) = 99·9, H(115)—C(15)—H(215) = 98·4, H(123)—C(23)—H(223) = 116·4 and C(22)—C(29)—H(329) = 116·3°.

The packing of the molecules is shown in Fig. 1. Comparison with the structure of triterpane D shows that the packing arrangements are closely similar and that the absence of the methyl C(28) at the C(18) position has had little effect. It bears out the similarity first noticed in the X-ray diffraction photographs, while comparison of the z coordinates of the equivalent atoms of both molecules shows that the average difference between coordinates is only 0·0052 = 0·15 Å. The x coordinates (when transformed by ½a) are also consistently related with an average displacement between respective atoms of 0·0465 = 0·54 Å. The major difference in the packing occurs in the y coordinates where it appears as though this molecule is tilted about the centre of C(8)—C(14), relative to triterpane D, such that the A and B rings are displaced upwards while rings D and E are displaced downwards. The displacements are not great, being ~0·32 Å for C(3) at one end and ~0·28 Å for C(16) at the other.

The similarity between the two structures is further displayed by the angles between the mean planes through the atoms of rings A, B, C, D and E. For this compound the values are AB = 13·3, BC = 171·4, CD = 177·2 and DE = 64·1°; corresponding values for triterpane D are 15·0, 169·7, 173·7 and 69·5°.
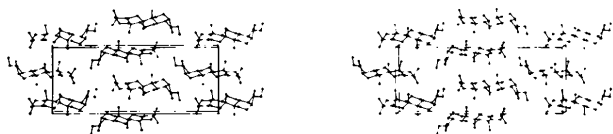
* See deposition footnote.

Fig. 1. Unit-cell packing diagram viewed down b (Johnson, 1965).

The van der Waals distances between C atoms are normal. There are twelve distances <4·0 Å of which ten lie in the range 3·71–3·97 Å. Two other shorter values correspond to the distances C(1)—C(6), 3·64 Å, where C(6) is in a molecule translated by +b, and C(2)—C(27), 3·67 Å, where C(27) is in the molecule related by the operation x − 0·5, 1·5 − y, 1 − z.

The molecule, which has been named as 28,30-dinor-17α(H),18α(H),21β(H)-hopane, is the first positively identified fossil fuel, C_{28} triterpane. The presence of pentacyclic hydrocarbons in petroleum is taken as strong evidence of the diagenetic conversion of natural products to fossil fuel and whilst several triterpanes have been discovered with carbon numbers 27, 29, 30 and 31, the apparent absence of a C_{28} member has been attributed to the unlikely scission of the two C—C bonds at C(22). Its large abundance in the shale oils already mentioned suggests the operation of a specific diagenetic mechanism for which three possible routes have been proposed (Seifert, Moldowan, Smith & Whitehead, 1978). A favoured precursor is the fern triterpenoid adipedatol which has a hemiacetal link between C(22) and C(28). After hydrolysis, a CH_2OH group would be left at C(18) which, upon oxidation to a carboxylic acid and subsequent decarboxylation and isomerization to 17α(H) at C(17), would lead to (I). Alternatively, adiantone, which has been suggested as the precursor of some partially aromatized hopanes in fossil fuels, could be a precursor for (I). Reduction of the keto group at C(22) in adiantone and subsequent dehydration, would introduce the first double bond which under strongly acidic conditions would be expected to migrate to the most stable C(13)—C(18) position; this shift might well result in the removal of the usual methyl C(28), at C(18), and subsequent hydrogenation would yield (I) (Whitehead, 1971).

As a third possibility, the fern constituent 21-hydroxyadiantone could, by the formation of a conjugated diene with associated loss of C(28) and isomerization at C(17) and subsequent hydrogenation, yield (I).

Table 3. Bond angles (°) for the C atom skeleton

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

C(2)—C(1)—C(10)	113·6 (0·4)	C(7)—C(8)—C(9)	108·5 (0·3)	C(9)—C(10)—C(25)	112·2 (0·3)	C(15)—C(16)—C(17)	112·1 (0·4)
C(1)—C(2)—C(3)	112·0 (0·4)	C(7)—C(8)—C(14)	110·6 (0·3)	C(9)—C(11)—C(12)	111·5 (0·4)	C(16)—C(17)—C(18)	114·5 (0·4)
C(2)—C(3)—C(4)	113·7 (0·4)	C(7)—C(8)—C(26)	107·2 (0·3)	C(11)—C(12)—C(13)	113·1 (0·4)	C(16)—C(17)—C(21)	114·4 (0·4)
C(3)—C(4)—C(5)	108·1 (0·3)	C(9)—C(8)—C(14)	109·4 (0·3)	C(12)—C(13)—C(14)	110·5 (0·3)	C(18)—C(17)—C(21)	105·5 (0·4)
C(3)—C(4)—C(23)	106·2 (0·4)	C(9)—C(8)—C(26)	111·9 (0·3)	C(12)—C(13)—C(18)	111·7 (0·3)	C(13)—C(18)—C(17)	113·7 (0·4)
C(3)—C(4)—C(24)	111·0 (0·4)	C(14)—C(8)—C(26)	109·3 (0·3)	C(14)—C(13)—C(18)	113·6 (0·3)	C(13)—C(18)—C(19)	111·6 (0·4)
C(5)—C(4)—C(23)	108·3 (0·4)	C(8)—C(9)—C(10)	116·9 (0·3)	C(8)—C(14)—C(13)	108·4 (0·3)	C(17)—C(18)—C(19)	101·5 (0·4)
C(5)—C(4)—C(24)	114·4 (0·4)	C(8)—C(9)—C(11)	111·2 (0·3)	C(8)—C(14)—C(15)	111·1 (0·3)	C(18)—C(19)—C(20)	105·2 (0·5)
C(23)—C(4)—C(24)	108·6 (0·4)	C(10)—C(9)—C(11)	113·8 (0·3)	C(8)—C(14)—C(27)	110·6 (0·3)	C(19)—C(20)—C(21)	106·2 (0·5)
C(4)—C(5)—C(6)	114·4 (0·3)	C(11)—C(10)—C(5)	107·9 (0·3)	C(13)—C(14)—C(15)	107·8 (0·3)	C(17)—C(21)—C(20)	106·3 (0·4)
C(4)—C(5)—C(10)	115·9 (0·3)	C(1)—C(10)—C(9)	109·1 (0·3)	C(13)—C(14)—C(27)	111·2 (0·3)	C(17)—C(21)—C(22)	113·8 (0·4)
C(6)—C(5)—C(10)	111·6 (0·3)	C(1)—C(10)—C(25)	107·0 (0·3)	C(15)—C(14)—C(27)	107·8 (0·3)	C(20)—C(21)—C(22)	113·7 (0·5)
C(5)—C(6)—C(7)	110·0 (0·3)	C(5)—C(10)—C(9)	106·7 (0·3)	C(14)—C(15)—C(16)	113·1 (0·3)	C(21)—C(22)—C(29)	115·1 (0·5)
C(6)—C(7)—C(8)	113·9 (0·3)	C(5)—C(10)—C(25)	113·9 (0·3)				

Permission to publish this work has been given by Chevron Oil Field Research, California, and The British Petroleum Company Limited. Thanks are also due to E. V. Whitehead for help in the interpretation of these results.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
PETROV, A. A., PUSTIL'NIKOVA, S. D., ABRIUTINA, N. N. & KAGRAMANOVA, G. R. (1976). *Neftekhimiya*, **16**, 411–427.
SEIFERT, W. K. & MOLDOWAN, J. M. (1979). *Geochim. Cosmochim. Acta*, **42.** In the press.
SEIFERT, W. K., MOLDOWAN, J. M., SMITH, G. W. & WHITEHEAD, E. V. (1978). *Nature (London)*, **271**, 436–437.
SMITH, G. W. (1975*a*). *Acta Cryst.* B**31**, 526–530.
SMITH, G. W. (1975*b*). *Acta Cryst.* B**31**, 522–526.
WHITEHEAD, E. V. (1971). *Chem. Ind. (London)*, pp. 1116–1118.

Structural Studies of Benzene Derivatives.
VI.* Refinement of the Crystal Structure of *p*-Hydroxybenzoic Acid Monohydrate

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Abstract

The crystal structure of *p*-hydroxybenzoic acid monohydrate, $C_7H_6O_3.H_2O$, determined from photographic data [Fukuyama, Ohkura, Kashino & Haisa (1973). *Bull. Chem. Soc. Jpn*, **46**, 804–808], has been refined to $R = 0.0414$ on 1454 counter reflexions. Crystals are monoclinic, space group $P2_1/a$, with $a = 17.752$ (9), $b = 6.442$ (2), $c = 6.731$ (3) Å, $\beta = 105.48$ (6)°, $Z = 4$. The benzene ring has approximate C_{2v} (*mm*) symmetry and shows a slight quinoidal shortening of the central C–C bonds. The internal angles at the *ipso* positions of the ring are $\alpha_{OH} = 120.5$ (1)°, $\alpha_{COOH} = 119.4$ (1)°.

Introduction

As part of a research project aimed at measuring accurately the effect of various *para* substituents on the molecular geometry of benzoic acid (Colapietro & Domenicano, 1977, 1978; Colapietro, Domenicano & Marciante, 1978; Colapietro, Domenicano & Pela Ceccarini, 1979) we report the structure of *p*-hydroxybenzoic acid monohydrate. An X-ray diffraction study of this material was published by Fukuyama, Ohkura,

Kashino & Haisa (1973). The refinement, based on 806 reflexions from photographic records, was by block-diagonal least squares and led to a final R of 0.086. The e.s.d.'s of the bond lengths and angles of the heavy-atom skeleton (0.007–0.009 Å and 0.5–0.6° respectively) were too high to allow the measurement of the structural effects of substitution. Thus we have carried out a new refinement based on a set of counter intensities.

Experimental

Colourless tablets were grown from an acetone solution of the commercial product (Fluka). Oscillation and Weissenberg photographs confirmed the crystal data given by Fukuyama *et al.* (1973). A crystal *ca* 0.38 × 0.58 × 0.24 mm was sealed in a glass capillary to prevent the loss of water and mounted on a Syntex $P2_1$ diffractometer. The cell parameters were refined by least squares from the measured θ values for 22 accurately centred reflexions, lying in the θ range 18–24° and well distributed in reciprocal space. The values obtained are compared in Table 1 with those of Fukuyama *et al.* (1973).

Intensities were collected at room temperature in the θ–2θ scan mode with graphite-monochromatized Mo

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