There are no intermolecular C—C distances less then 3·6 Å and the shortest H—H contact is 2·182 (3) Å. The distance between the O atoms involved in a hydrogen bond [2·749 (2) Å] as well as the O—H···O angle [154 (2)°] are in the normal range.

The position of the phenyl ring [OC(2)C(11)C(12) = −98·1 (2)°] causes short intramolecular distances between the hydrogen atoms at C(1) and C(16) [1·984 (3) Å] and between the hydrogen atoms at C(3) and C(12) [1·972 (3) Å]. The deviations of the angles C(1)C(2)C(11), C(1)C(2)C(3) and C(3)C(2)C(11) can be ascribed, therefore, to the substitution of the phenyl ring at C(2). As can be expected, this effect is not found in 1-phenylcyclohexanol, where the steric hindrance can be relieved by a more or less planar arrangement of the O atom and the phenyl group. In our compound this conformation would be impossible owing to further steric hindrance. Thus in contradistinction to 1-phenylcyclohexanol, the adamantane skeleton fixes the phenyl ring in a position where OH···$\pi$ interaction is possible.

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# Structure of 4-Hydroxymonophenylbutazone

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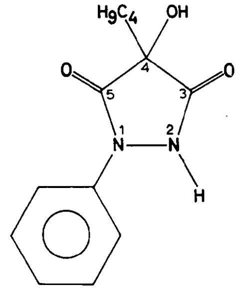
**Abstract.** 4-Butyl-4-hydroxy-1-phenyl-3,5-pyrazolidinedione, $C_{13}H_{16}N_2O_3$, $M_r = 248{\cdot}3$, monoclinic, $P2_1/n$, $a = 22{\cdot}357\ (5)$, $b = 5{\cdot}014\ (2)$, $c = 11{\cdot}350\ (4)$ Å, $\beta = 91{\cdot}88\ (3)°$, $V = 1272\ (1)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}296\ (3)$, $D_x = 1{\cdot}297$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}777$ mm$^{-1}$, $F(000) = 528$, $T = 293$ K. Final $R = 0{\cdot}059$ for 1668 observed reflections. The hetero nitrogen which carries the six-membered ring is planar in the structure while the other unsubstituted one is pyramidal. The five- and six-membered rings are almost coplanar. The crystal is made up of infinite columns of hydrogen-bonded molecules.

**Introduction.** Non-steroidal anti-inflammatory antipyretic analgesics, in spite of their diverse chemical structures, are believed to act through the inhibition of prostaglandin biosynthesis (Flower, 1974). With the objective of understanding their molecular geometry, the nature of their interactions, and the geometric and electronic consequences of such interactions, we have analysed the structures of several analgetic pyrazole derivatives, fenamates and their complexes (Dhanaraj & Vijayan, 1983; Vijayan, 1983, and the references therein). Monophenylbutazone is a drug belonging to the family of pyrazolidinedione derivatives. The crystal structures of the other important members of this family, phenylbutazone and oxyphenbutazone, have already been reported (Singh & Vijayan, 1977; Krishna Murthy & Vijayan, 1981). During attempts to crystallize monophenylbutazone from a commercial sample, a hydroxy derivative of the compound, present as an impurity, readily crystallized. The crystal structure of this derivative (I) is reported here.



(I)

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**Experimental.** The sample of monophenylbutazone used in the crystallization experiments was obtained from Sigma Chemical Co., USA. Colourless thin crystals were obtained by slow evaporation of a solution of the sample in an equivolume mixture of ethanol and methanol. The crystal system and the unit-cell dimensions were determined by preliminary X-ray diffraction photographs. $D_m$ measured by flotation in water–potassium iodide mixture. The density measured was higher than expected for monophenylbutazone. Subsequent analysis of $^1H$ NMR spectra indicated that the crystals were of the oxidized form. Chromatographic analysis of the crystals and the sample used for crystallization, using a solvent mixture containing 10% MeOH in $CHCl_3$, showed that the oxidized form was present in the sample as an impurity. Crystal of dimensions 0·18 × 0·50 × 0·75 mm, CAD-4 diffractometer, $\omega$–$2\theta$ scan to a maximum Bragg angle of 60° (max. $\sin\theta/\lambda = 0{\cdot}5617$ Å$^{-1}$), graphite-monochromated Cu $K\alpha$ radiation. 21 reflections in $\theta$ range 11·3–45·3° used for refining lattice parameters. Intensities not corrected for absorption, $h$ −24→0, $k$ −5→0, $l$ −12→12. Two standard reflections (622, 013) both showed 4% variation in intensity. 1882 unique reflections measured, 1668 having $I > 3\sigma(I)$ used in refinement.

The structure was solved using the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). The non-H atoms were refined anisotropically and the H atoms, located from a difference Fourier map with the aid of geometrical considerations, isotropically on $F$ using the block-diagonal least-squares method (9 × 9 and 4 × 4 matrices respectively for non-H and H atoms) employing the locally modified version of a program originally written by Dr R. Shiono. Refinement converged at $R = 0{\cdot}059$, $wR = 0{\cdot}099$, $S = 0{\cdot}6148$ when all the least-squares shifts were less than the corresponding standard deviations (max. $\Delta/\sigma = 0{\cdot}117$). Weighting scheme employed in the final cycles had the form $1/(a + bF_o + cF_o^2)$ with $a = 1{\cdot}290$, $b = -0{\cdot}0458$ and $c = 0{\cdot}0281$, $\Delta\rho = -0{\cdot}30$ to $0{\cdot}26$ e Å$^{-3}$. Form factors for non-H atoms taken from Cromer & Waber (1965), those for H from Stewart, Davidson & Simpson (1965). Computations performed on a DEC-1090 computer. The final positional parameters and equivalent isotropic thermal parameters (Hamilton, 1959) of the non-H atoms are given in Table 1.*

**Discussion.** A perspective view of the molecule seen normal to the mean plane of the pyrazolidinedione ring is given in Fig. 1. The bond lengths and angles in the structure are similar to those in the structures of phenylbutazone (Singh & Vijayan, 1977) and oxyphenbutazone (Krishna Murthy & Vijayan, 1981). For example, C—O lengths in phenylbutazone and oxyphenbutazone range from 1·20 (2) and 1·23 (2) Å whereas they are 1·222 (5) and 1·223 (4) Å in the present structure. An interesting difference between 4-hydroxymonophenylbutazone on the one hand and phenylbutazone and oxyphenbutazone on the other pertains to the hybridization state of the hetero nitrogen atoms. Both the nitrogens are pyramidal in phenylbutazone and oxyphenbutazone in the crystal structures containing them. In the present structure, however, N(1), which carries the phenyl ring, is nearly planar while the unsubstituted N(2) is pyramidal. N(1) deviates from the plane of the three surrounding atoms by 0·061 (3) Å whereas the corresponding value for N(2) is 0·214 (3) Å. Another point of interest pertains to the mutual orientations of the rings. In phenylbutazone and oxyphenbutazone, both the N atoms have phenyl rings as substituents and

Table 1. *Final positional coordinates* (× 10⁴) *and equivalent isotropic thermal parameters of the non-hydrogen atoms with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| N(1) | 5573 (1) | 6898 (6) | 2835 (2) | 3·2 (1) |
| N(2) | 5206 (1) | 7973 (6) | 3717 (2) | 3·6 (1) |
| C(3) | 4829 (2) | 9804 (7) | 3260 (3) | 3·4 (1) |
| C(4) | 4833 (2) | 9535 (7) | 1927 (3) | 3·1 (1) |
| C(5) | 5388 (2) | 7823 (7) | 1761 (3) | 3·2 (1) |
| O(6) | 4535 (1) | 11364 (6) | 3832 (2) | 4·6 (1) |
| C(7) | 4285 (2) | 7938 (8) | 1477 (3) | 3·7 (2) |
| O′(7) | 4889 (1) | 12048 (5) | 1413 (2) | 4·1 (1) |
| C(8) | 3692 (2) | 9387 (9) | 1558 (4) | 4·6 (2) |
| C(9) | 3176 (2) | 7733 (14) | 1080 (6) | 7·0 (3) |
| C(10) | 2587 (2) | 9115 (16) | 1097 (7) | 8·8 (4) |
| O(11) | 5619 (1) | 7338 (6) | 823 (3) | 4·2 (1) |
| C(12) | 5999 (1) | 4890 (7) | 3137 (3) | 3·2 (1) |
| C(13) | 6039 (2) | 3887 (9) | 4271 (3) | 4·2 (2) |
| C(14) | 6456 (2) | 1936 (10) | 4546 (4) | 5·2 (2) |
| C(15) | 6825 (2) | 961 (9) | 3721 (4) | 5·1 (2) |
| C(16) | 6780 (2) | 1952 (11) | 2600 (4) | 5·8 (2) |
| C(17) | 6375 (2) | 3901 (10) | 2295 (4) | 5·2 (2) |

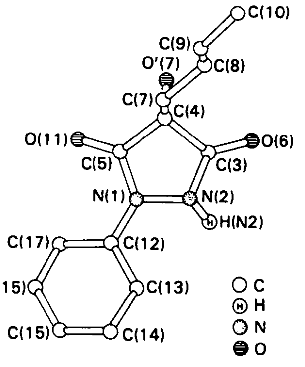

Fig. 1. A perspective view of the 4-hydroxymonophenylbutazone molecule. Only one hydrogen atom, H(N2), is indicated.

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*Lists of structure factors, anisotropic thermal parameters, hydrogen-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43348 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

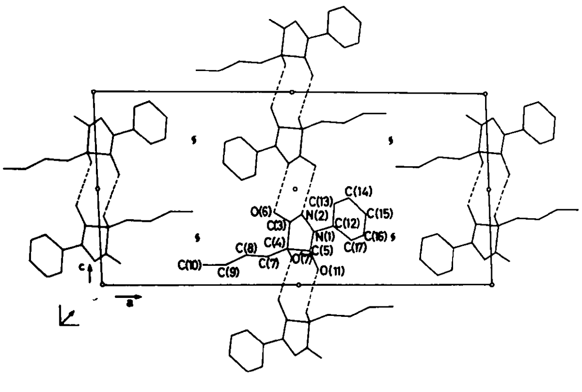

Fig. 2. The crystal structure of 4-hydroxymonophenylbutazone.

Table 2. *Hydrogen-bond parameters with e.s.d.'s in parentheses*

| $D\cdots A$ | | $l(D\cdots A)$ | $\theta(\mathrm{H}-D\cdots A)$ |
|---|---|---|---|
| N(2) | O(6$^{i}$) | 2·842 (4) Å | 8 (3)° |
| O'(7) | O(11$^{ii}$) | 2·763 (3) | 7 (3) |

Key to symbols: *D* donor atom, *A* acceptor atom; symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $1-x, 2-y, -z$.

steric interactions between these two rings prevent coplanarity of the five-membered ring with either of them. In 4-hydroxymonophenylbutazone, however, one phenyl ring is replaced by an H atom, thus enabling the five- and the six-membered rings to be nearly coplanar. The planes of the two rings are inclined with respect to each other at 11·2°. This coplanarity presumably leads to the planarity of the hetero nitrogen atom N(1) through interactions involving $\pi$ orbitals.

The crystal structure of the compound is shown in Fig. 2. The parameters of the hydrogen bonds that contribute to the stability of the structure are listed in Table 2. The molecules are arranged in infinite hydrogen-bonded columns parallel to the *c* axis. In these columns each molecule is involved in two pairs of parallel hydrogen bonds related by an inversion centre. One involves an N—H···O hydrogen bond between the hetero nitrogen atom N(2) and the carbonyl O atom O(6) [2·842 (4) Å], while the other contains an O—H···O hydrogen bond between the hydroxyl O'(7) and the carbonyl O(11) [2·763 (3) Å].

In the crystal, these hydrogen-bonded columns are packed together so that the crystal can be considered as made up of alternating hydrophilic and hydrophobic layers. The former contain primarily N and O atoms belonging to or attached to the five-membered rings whereas the latter contain phenyl and butyl groups.

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# Structure of Thiamin Dinitrate

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**Abstract.** $\mathrm{C_{12}H_{18}N_4OS^{2+}.2NO_3^-}$, $M_r = 390{\cdot}18$, triclinic, $P\bar{1}$, $a = 8{\cdot}9260\,(8)$, $b = 10{\cdot}201\,(1)$, $c = 10{\cdot}405\,(1)$ Å, $\alpha = 97{\cdot}897\,(8)$, $\beta = 105{\cdot}059\,(7)$, $\gamma = 104{\cdot}437\,(9)°$, $V = 865{\cdot}01$ Å$^3$, $Z = 2$, $D_m = 1{\cdot}494$, $D_x = 1{\cdot}498$ Mg m$^{-3}$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 2{\cdot}086$ mm$^{-1}$, $F(000) = 408$, $T = 296$ K, $R = 0{\cdot}050$ for 2619 unique observed reflections. The structure was found to be in the characteristic *F* conformation and is similar to that of

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* In partial fulfillment of the requirements for PhD degree, University of Pittsburgh.

† Deceased 31 August 1983.

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