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Structure of Phenacetin, $C_{10}H_{13}NO_2$ *

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Abstract. $M_r = 179.21$, monoclinic, $P2_1/c$, $a = 13.25$ (2), $b = 9.65$ (1), $c = 7.81$ (1) Å, $\beta = 104.9$ (5)°, $V = 965$ (2) Å³, $Z = 4$, $D_m = 1.240$ (4), $D_x = 1.234$ (3) Mg m⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.66$ mm⁻¹, $F(000) = 384$, $T = 300$ K, $R = 0.088$ for 1459 observed reflections. The planes of the side groups O(7)C(8)C(9) and N(10)C(11)C(12)O(13) are tilted with respect to the plane of the benzene ring by 9 (1) and 29 (1)°, respectively. The nitrogen and oxygen atoms of the acetamido group from two symmetry-related molecules are hydrogen bonded. The crystal structure is stabilized by hydrogen bonds and van der Waals forces.

Introduction. Phenacetin is the most prominent pain-relieving drug among acetanilide derivatives. We determined the structure of phenacetin as a part of our programme of structure analysis of drugs (Tiwari, Patel & Singh, 1982). A preliminary account of the structure has already been made (Patel, Patel & Singh, 1982) and the structure refinement and discussion are reported here.

Experimental. Hexagonal plate-shaped crystals from solution in methanol at 277 K; unit-cell parameters from 34 reflections on oscillation and Weissenberg photographs, systematic absences indicated $P2_1/c$, D_m by flotation in a mixture of benzene and carbon tetrachloride; crystals elongated along [001]; crystal $0.33 \times 0.10 \times 0.09$ mm, multiple films, equi-inclination Weissenberg technique, Ni-filtered Cu radiation; 1459 independent reflections, reciprocal levels hkL , $L = 0-7$, $2\theta_{max} = 154$ °, 455 unobserved reflections $I < 3\sigma(I)$; intensities estimated visually with calibrated film strips, corrected for Lorentz and polarization effects and spot-shape distortions but not for absorption ($\mu r = 0.07$); programs used in the above calculations were written by the authors.

The positions of 10 out of 13 non-hydrogen atoms in the asymmetric unit obtained with *MULTAN* (Germain, Main & Woolfson, 1971), Fourier methods revealed remaining three atoms; subsequent isotropic and anisotropic refinement cycles, on F , of non-hydrogen atoms by block-diagonal least squares [program originally written by Shiono (1968–1971) and modified by the authors], $R = 0.098$; all hydrogen atoms located from difference Fourier, positional and isotropic thermal parameters of hydrogen refined, $R = 0.088$ for 1459 observed reflections; in final cycles, Δ_{av} and Δ_{max} for non-hydrogen and hydrogen atoms were 0.04σ and 0.12σ , and 0.11σ and 0.3σ , respectively; $w = 1/(a + bF_{obs} + cF_{obs}^2)$ (Cruickshank, 1961), adjusted to make the average $w\Delta^2$ independent of F_{obs} , $a = 1.0$, $b = 0.05$ and $c = 0.001$, $R_w = 0.091$; atomic scattering factors from Cromer & Waber (1965) for non-H atoms, and from Stewart, Davidson & Simpson (1965) for H atoms; $\Delta\rho$ excursions $< 0.13 e \text{ \AA}^{-3}$.† All calculations were performed on the IBM 360/44 computer system of the M. S. University of Baroda, Baroda.

Discussion. Final positional and equivalent isotropic thermal parameters are listed in Table 1.

Fig. 1 shows a stereoscopic illustration and the numbering scheme of the molecule (*ORTEP*: Johnson, 1965). Bond distances and angles of non-hydrogen atoms and relevant torsion angles are given in Table 2. The O(7) atom deviates from the plane of the benzene ring by 0.01 (2) Å, whereas N(10) is displaced by 0.04 (2) Å. The planes of the C_6H_5O moiety and that of the acetamido group are inclined with respect to the

* *p*-Ethoxyacetanilide.

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38687 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane of the benzene ring at 9 (1) and 29 (1) $^\circ$ respectively. Bond lengths and angles, in general, are in good agreement with those found in similar structures (Brown 1966; Pedersen, 1967; Tanimoto, Kobayashi, Nagakura & Saito, 1973; Haisa, Kashino & Maeda, 1974). The single bond C(8)–C(9) [Csp^3-Csp^3] distance of 1.50 (1) Å is significantly shorter than the standard value of 1.54 Å. The N(10)–C(11) bond distance of 1.34 (1) Å shows an appreciable double-bond character similar to that observed in other amides (Brown, 1966; Subramanian, 1966; Pedersen, 1967; Haisa, Kashino & Maeda, 1974). The C(4)–N(10) distance is 1.40 (1) Å and is considerably shorter than that observed in *N*-methylacetanilide [1.481 (9) Å] (Pedersen, 1967) but is in good agreement with those observed in acetanilide [1.413 (3) Å] (Brown, 1966) and *p*-hydroxyacetanilide [1.422 (5) Å] (Haisa, Kashino & Maeda, 1974). The C(4)–N(10)–C(11) angle [127.0 (7) Å] is considerably larger than the corresponding angle (123 $^\circ$) in polypeptides (Corey & Pauling, 1953) but is comparable to those observed in acetanilide [127.6 (2) Å] (Brown, 1966) and *p*-hydroxyacetanilide [129.8 (4) Å] (Haisa, Kashino & Maeda, 1974).

Fig. 2 shows the crystal structure projected onto the *ab* plane. It is seen that the molecules lie parallel to the *a* axis. The molecules are stacked together in such a way that the acetamido moieties lie close to each other at $a = \frac{1}{2}$ while C_2H_5O groups lie at $a = 0$ and $a = 1$. The molecules in the crystal structure are held together by intermolecular hydrogen bonds of the type N–H...O. The hydrogen-bond parameters are given in Table 2. All other intermolecular contacts correspond to van der Waals interactions.

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms

$U_{eq} = (U_{11} U_{22} U_{33})^{1/3}$, where U_{ii} are the principal axes of the thermal ellipsoids.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	1424 (6)	3987 (8)	3846 (11)	5.4 (8)
C(2)	2177 (7)	3159 (10)	3453 (12)	7.3 (10)
C(3)	3195 (6)	3264 (9)	4454 (11)	6.0 (9)
C(4)	3462 (6)	4206 (8)	5821 (10)	4.6 (7)
C(5)	2688 (6)	5034 (9)	6201 (11)	5.8 (9)
C(6)	1685 (6)	4926 (9)	5249 (14)	6.6 (9)
O(7)	402 (4)	3981 (7)	2969 (9)	7.8 (7)
C(8)	96 (7)	3145 (11)	1387 (13)	7.8 (11)
C(9)	–1021 (8)	3503 (12)	556 (16)	10.0 (1)
N(10)	4486 (5)	4399 (7)	6854 (9)	5.6 (7)
C(11)	5249 (6)	3446 (9)	7247 (11)	5.7 (9)
C(12)	6249 (7)	3944 (11)	8414 (14)	8.0 (1)
O(13)	5134 (5)	2234 (6)	6700 (9)	8.3 (7)

Table 2. Bond lengths (Å) and angles ($^\circ$) for non-hydrogen atoms, hydrogen-bond parameters (Å, $^\circ$), some relevant intermolecular contact distances <3.5 Å and some selected torsion angles ($^\circ$)

C(1)–C(2)	1.37 (1)	C(5)–C(6)	1.35 (1)
C(1)–C(6)	1.40 (1)	C(8)–O(7)	1.44 (1)
C(1)–O(7)	1.35 (1)	C(8)–C(9)	1.50 (1)
C(2)–C(3)	1.38 (1)	C(11)–N(10)	1.34 (1)
C(3)–C(4)	1.38 (1)	C(11)–C(12)	1.48 (1)
C(4)–C(5)	1.39 (1)	C(11)–O(13)	1.24 (1)
C(4)–N(10)	1.40 (1)		
C(2)–C(1)–C(6)	120.3 (8)	C(4)–C(5)–C(6)	120.9 (8)
C(2)–C(1)–O(7)	125.1 (8)	C(5)–C(6)–C(1)	119.6 (8)
C(6)–C(1)–O(7)	114.5 (8)	C(1)–O(7)–C(8)	117.4 (7)
C(1)–C(2)–C(3)	119.5 (8)	C(9)–C(8)–O(7)	105.7 (8)
C(2)–C(3)–C(4)	120.5 (8)	C(4)–N(10)–C(11)	127.0 (7)
C(3)–C(4)–C(5)	119.2 (7)	C(12)–C(11)–N(10)	114.9 (7)
C(3)–C(4)–N(10)	123.5 (7)	C(12)–C(11)–O(13)	121.9 (8)
C(5)–C(4)–N(10)	117.3 (7)	O(13)–C(11)–N(10)	123.2 (8)
Hydrogen bonding			
N(10)–H(10)	0.7 (1)		
H(10)...O(13 ^b)	2.3 (1)		
N(10)...O(13 ^b)	2.954 (9)		
\angle N(10)–H(10)...O(13 ^b)	180 (7)		
Intermolecular contacts			
O(7)...C(8 ^b)	3.47 (1)		
C(12)...O(13 ^b)	3.47 (1)		
Torsion angles ($^\circ$)			
C(9)–C(8)–O(7)–C(1)	172 (1)		
C(4)–N(10)–C(11)–C(12)	178 (1)		
C(4)–N(10)–C(11)–O(13)	–1 (1)		

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$.

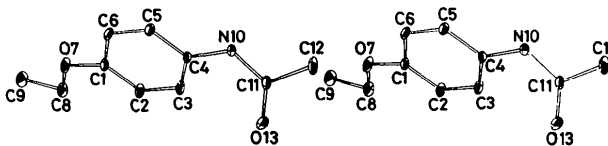


Fig. 1. Stereoscopic illustration of the molecule with thermal ellipsoids drawn to enclose 60% probability and numbering scheme.

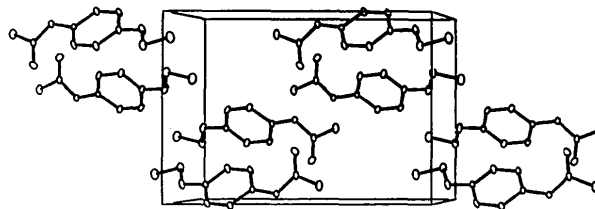


Fig. 2. Projection of the crystal structure onto the *ab* plane.

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Structure of (*E*)-Benzaldehyde Oxime, C₇H₇NO, at 100 K and Systematics of Molecular Structures of Aromatic Aldoximes

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Abstract. $M_r = 121.14$, monoclinic, $C2/c$, $a = 18.50$ (1), $b = 8.272$ (1), $c = 17.224$ (7) Å, $\beta = 101.38$ (5)°, $V = 2584$ (4) Å³, $Z = 16$, D_m (291 K) = 1.196, D_x (100 K) = 1.245 (2) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.0792$ mm⁻¹, $F(000) = 1024$. Final $R = 0.045$ for 3477 observed unique reflections. The molecules are linked by hydrogen bonds, O–H...N, into cyclic tetramers. No other short intermolecular distances are present. The tetramers are stacked in columns along the **b** direction around the twofold axes. The variability of the oxime moiety in aromatic aldoximes, Ar–CH=N–OH, found in the literature has been systematized and to some extent explained by studying the geometry as a function of oxime type (*E* versus *Z*) and of the nature of the aromatic moiety (unsubstituted or substituted benzene and heteroaromatic rings). The influence of (*E*)- and of (*Z*)-oxime moieties on the geometry of the aromatic ring has also been studied. The available data for *N*- and *O*-alkylated oximes are compared with the results obtained for non-alkylated oximes.

Introduction. The crystal structure of the prototype of aromatic (*E*)-aldoximes, (*E*)-benzaldehyde oxime, was determined at low temperature in order to obtain reliable data for comparison with the result of a similar study of an *O*-alkylated, aromatic (*E*)-aldoxime (Jerslev, Lerche & Larsen, 1983). The aim of the structure determination was furthermore to obtain direct information on the influence of an (*E*)-aldoxime moiety on the geometry of the aromatic ring.

Numerous room-temperature crystal-structure determinations of compounds containing the oxime moiety, >C=N–OH, have been published, and a comprehensive survey of the dimensions of the oxime moieties and of the hydrogen-bonding schemes has recently been

given (Bertolasi, Gilli & Veronese, 1982). Direct comparisons between dimensions of oxime moieties found in oximes of different types are common in the literature, although the dimensions of an oxime moiety are likely to be influenced by the nature of the attached atomic groups. Thus, the geometry of the oxime moiety in esters or amides of hydroxamic acid, $\text{>C} \begin{array}{l} \text{N-OH} \\ \text{OH} \end{array}$

presumably differs from that in ketoximes, $\text{R} \begin{array}{l} \text{R} \\ \text{R} \end{array} \text{>C=N-OH}$, or aldoximes, $\text{R} \begin{array}{l} \text{R} \\ \text{H} \end{array} \text{>C=N-OH}$; also, the dimensions of the oxime moiety in aldoximes may well be different from those in ketoximes, and even between (*E*)- and (*Z*)-isomers systematic variations may occur. Likewise, the geometry of an *O*-alkylated oxime, >C=N–OR, or of an *N*-alkylated oxime (a nitron), $\text{>C=N} \begin{array}{l} \text{O} \\ \text{R} \end{array}$, certainly deviates from that of the

corresponding non-alkylated oxime. So far it has not been systematically explored, whether the differences thus expected are discernible with the present accuracy of crystal-structure determinations; a part of this problem is elucidated in the present study. The structural data for aromatic (*E*)-aldoximes, $\text{Ar} \begin{array}{l} \text{R} \\ \text{H} \end{array} \text{>C=N} \begin{array}{l} \text{O} \\ \text{OH} \end{array}$, are analysed, and the dimensional features found are compared with the available data for aromatic (*Z*)-aldoximes and for *O*- and *N*-alkylated, aromatic aldoximes.

The influence of a number of different atomic groups on the geometry of an attached aromatic ring has been studied by several authors. Based upon the latest and most comprehensive analysis (Norrestam & Schepper, 1981), an attempt has been made to derive such data for oxime moieties.