

3-Hydroxyphthalimidine

BY JEAN M. OHRT

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263, USA

AND DANITA TSOUCARIS-KUPFER AND PAUL LECHAT

Laboratoire de Pharmacologie, UER Biomédical des Cordeliers, Paris 75270, France

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Abstract. $C_8H_7NO_2$, triclinic, $P\bar{1}$, $a = 9.159(5)$, $b = 7.580(4)$, $c = 5.224(4)$ Å, $\alpha = 98.46(7)$, $\beta = 102.85(8)$, $\gamma = 96.10(8)^\circ$, $Z = 2$, $V = 346.1$ Å³, $D_c = 1.43$, $D_m = 1.43$ g cm⁻³, $M_r = 149.15$, $\mu = 8.80$ cm⁻¹. The molecule is nearly planar; the hydroxyl O, which is almost perpendicular to this plane, hydrogen bonds to the keto O of a neighboring molecule, related by a center of inversion.

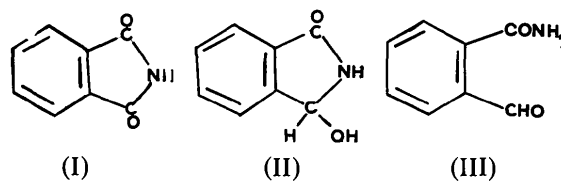
Introduction. Needle-shaped crystals were grown from aqueous methanol solution by slow evaporation at room temperature. A crystal of dimensions ($\sim 0.3 \times 0.1 \times 0.3$ mm) was mounted with the c^* axis along the φ axis of the goniometer and three-dimensional intensity data (1324 reflections, $337 < 2\sigma$) were measured to the limit $2\theta = 140^\circ$ for Cu $K\alpha_1$ on a GE XRD-6 diffractometer equipped with a scintillation counter, using the stationary crystal-stationary counter technique and Ni-Co balanced filters for monochromatization. The difference in absorption (maximum 10% at a^*) as a function of φ was measured for the axial reflections and was used for correcting approximately for the anisotropy of absorption. No additional absorption corrections were applied and the data were processed in the usual manner. The 11 non-hydrogen atoms were located in an E map ($260 E's > 1.2$) based on phases determined by the application of the multisolution technique (Germain, Main & Woolfson, 1971). The positional and thermal parameters of these atoms were refined by several cycles of block-diagonal least squares and the H atoms then located from an electron density difference map. Anisotropic refinement of non-hydrogen atoms and isotropic refinement of the H atoms was terminated when $R(\sum |F_o| - |F_c| / \sum |F_o|)$ was 0.049 and none of the shifts was greater than one-tenth of the corresponding standard deviations for the non-hydrogen atoms and one-fourth of the standard deviations for the H atoms. The observations were weighted according to the scheme of Evans (1961) and the refinement was carried out by minimizing $\sum [w|F_o| - (1/k)|F_c|]^2$. Atomic scattering factors for O, N and C were taken from *International Tables for X-ray Crystallography* (1962).

Table 1. Fractional coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms), with estimated standard deviations in parentheses

	x	y	z
O(1)	5438 (2)	3092 (2)	12602 (3)
O(3)	1986 (2)	6572 (2)	9518 (3)
C(1)	4222 (2)	3448 (3)	11324 (4)
N(2)	3488 (2)	4779 (2)	12123 (4)
C(3)	2060 (2)	4864 (3)	10258 (5)
C(3a)	2035 (2)	3343 (3)	8040 (4)
C(4)	978 (3)	2754 (4)	5639 (5)
C(5)	1238 (3)	1315 (4)	3944 (5)
C(6)	2493 (3)	456 (4)	-4602 (5)
C(7)	3560 (3)	1042 (3)	7002 (5)
C(7a)	3300 (2)	2497 (3)	8676 (4)
H(N2)	382 (2)	549 (3)	1375 (4)
H(O3)	273 (2)	687 (3)	879 (5)
H(C3)	116 (2)	465 (3)	1118 (4)
H(C4)	12 (2)	340 (3)	519 (4)
H(C5)	50 (2)	87 (3)	227 (4)
H(C6)	261 (2)	-51 (3)	346 (4)
H(C7)	448 (2)	38 (3)	747 (4)

The hydrogen scattering factors were those given by Stewart, Davidson & Simpson (1965). The final positional parameters and their e.s.d.'s (as obtained from the inverse of the block-diagonal matrix) are given in Table 1.*

Discussion. The reduction of (I) leads to hydroxyphthalimide for which two tautomeric formulas (II) and (III) have been considered. Further chemical work



* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33338 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

performed by Lechat (1957) on different chemical properties (hydrolysis, reduction, oxidation) has shown that both forms are compatible with the chemical reactions. This investigation shows that form (II) is the only one existing in the crystalline state. Figs. 1 and 2 show bond distances and angles for this structure. The average value of the standard deviation is 0.003 Å for bond distances and 0.2° for bond angles. The average value of the C—H bond is 0.96 Å. The thermal motion of various groups of atoms was analyzed using the method of Schomaker & Trueblood (1968) to check whether the individual anisotropic thermal motions of the atoms in these groups could be explained in terms of rigid-body librations. For the 11 atoms comprising the entire molecule the r.m.s. difference between the observed and calculated u_{ij} values was 0.0024. The corrections due to thermal libration ranged from 0.003 to 0.005 Å or of the same magnitude as the above-mentioned e.s.d. (or less than 2σ).

The nine atoms comprising the two rings are essentially planar (r.m.s. 0.010 Å); the substituents at C(3), *i.e.* O(3) and H(C3), deviate by 1.04 and -0.89 Å from this plane. The best plane for the five-membered ring is that consisting of C(3a), C(7a), C(1) and N(2). C(3) lies 0.023 Å out of this plane. None of the torsion

angles about the five- or six-membered rings is greater than 1.5°. The torsion angles about the C(3)—N(2) bond are -125.4° for O(3)—C(3)—N(2)—C(1) and 117.8° for H(C3)—C(3)—N(2)—C(1).

The molecules are symmetrically paired in an anti-parallel fashion *via* hydrogen bonds [H(O3)···O(1) of 1.97 Å] which join the five-membered ring of the reference molecule with that of the one at $1-x, 1-y,$

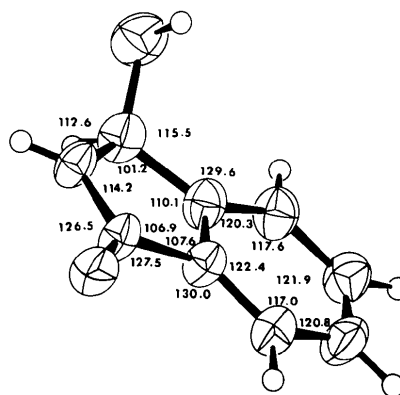


Fig. 2. Bond angles (°).

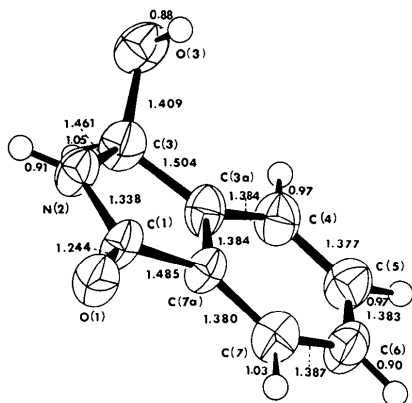


Fig. 1. Bond distances (Å).

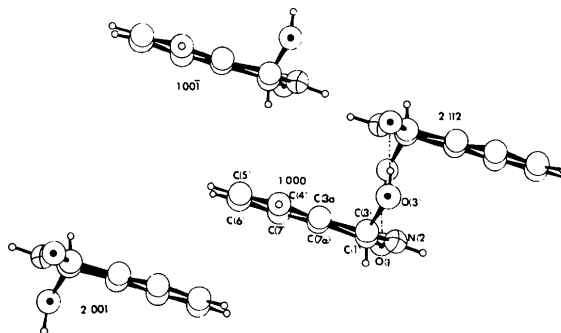


Fig. 3. Edge view of molecules showing stacking and hydrogen bonding. The numbers adjacent to the molecules indicate the equivalent molecules related by symmetry and translations.

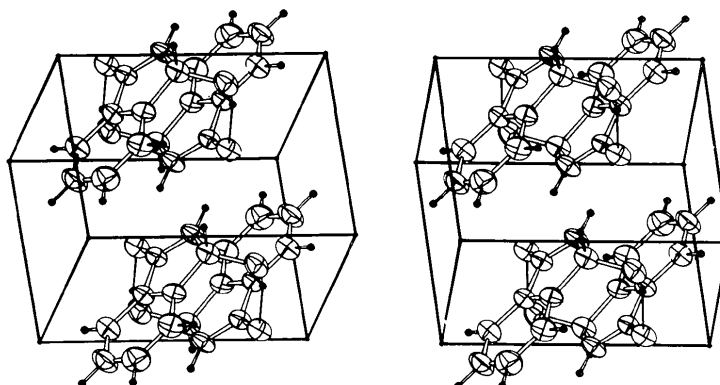


Fig. 4. Stereoview of unit cell with hydrogen bonding.

$2 - z$; the $O(3) \cdots O(1)$ distance is 2.82 Å and the angle $O(3)-H(O3) \cdots O(1)$ equals 164.2°. These 'dimers', 3.24 Å apart, are stacked on each other 3.47 Å along the **b** axis (Figs. 3 and 4). The H attached to N(2) is not involved in hydrogen bonding, its closest contacts being 3.48 Å to C(7a) of the hydrogen-bonded molecule and 3.10 Å to H(O3) of the molecule translated along the *z* axis. The closest contacts are between the five-membered portions of the bonded molecules, $C(1) \cdots C(1) = 3.257$, $C(1) \cdots N(2) = 3.354$ plus $C(5) \cdots C(5)(\bar{x}, \bar{y}, 1 - z) = 3.338$ Å.

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Hexamethylenetetramine-*m*-Cresol (1:2)

BY THOMAS C. W. MAK, WAI-HING YU AND YIU-SHING LAM

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract. $(CH_2)_6N_4 \cdot 2m\text{-CH}_3C_6H_4OH$, orthorhombic, space group *Ccc2*, $a = 10.63$ (1), $b = 26.33$ (2), $c = 7.199$ (5) Å; $Z = 4$, $D_m = 1.19$ (1) by flotation in hexane/ CCl_4 , $D_x = 1.175$ g cm⁻³. The structure was determined from film data and refined to $R = 0.109$. The hexamethylenetetramine molecule occupies a site of symmetry 2, and is linked to two *m*-cresol molecules by $N \cdots H-O$ hydrogen bonds.

Introduction. Hexamethylenetetramine (HMT) forms a variety of crystalline complexes with phenol and substituted phenols (Tse, Wong & Mak, 1977; Mak, Tse, Chong & Mok, 1977). As part of our investigation on hydrogen-bonded molecular compounds of HMT, we have carried out an X-ray analysis of its 1:2 adduct with *m*-cresol to determine the nature of the molecular association.

Colourless elongated prisms of the adduct were prepared as described by Tse, Wong & Mak (1977). As the compound slowly crumbles into powder in air, specimens for diffraction study were sealed in Lindemann-glass capillaries of mean diameter 0.5 mm. Even with this precaution, the crystals deteriorated appreciably upon irradiation by X-rays, judged from the appearance of streaks and the general increase in background on the photographs. Cell dimensions were

determined from high-angle reflections on all three zero-layer Weissenberg photographs calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2 \theta_m - \sin^2 \theta_c|$. Seven different crystals were used to record the intensities of reflections $0kl-9kl$ and $hk0-hk7$ by the multiple-film equi-inclination Weissenberg method with $Cu K\alpha$ radiation ($\lambda = 1.5418$ Å). The intensities were estimated visually by comparison with a calibrated strip. They were corrected for Lorentz and polarization factors but not for absorption ($\mu = 6.29$ cm⁻¹). A set of scaled structure amplitudes was derived by least squares (Hamilton, Rollett & Sparks, 1965). The data after reduction consisted of 573 independent reflections of measurable amplitude and 393 unobserved reflections.

Of the two space groups, *Ccc2* and *Cccm*, which are consistent with the systematic absences, the latter was considered unlikely from packing considerations. The correct structure was deduced from model building in space group *Ccc2*. In view of the unfavourable data-to-parameter ratio, least-squares refinement was carried out by treating the *m*-cresol molecule as a rigid group (Doedens, 1970). The phenyl ring was taken as a regular hexagon of side 1.390 Å, the C—OH and C—CH₃ bonds were assigned lengths of 1.390 and