

would be expected to show true *N*-carbonyl character; this is indeed the case as its bond length is 0.025 Å shorter than in (II). The similarly somewhat shortened N(1)–N(2) bond in (I) is not observed. This is presumably on account of the loss of in-plane delocalization with the aryl group (see below).

The carboxamide group at C(4) in (I) is closely coplanar, with the five-atom group O(2), C(7), N(4), H(4A), H(4B) having a χ^2 of 2. This plane is inclined at 25.0 (5)° to the phenyl group, and compares well with the 27° value found in (II). In both cases the deviation from coplanarity can best be ascribed to the relief of otherwise close contacts between hydrogen atoms on the phenyl ring and –N(4)H₂ group.

The triazene oxide system [N(1), N(2), N(3), O(1)] is closely coplanar ($\chi^2 = 7$), as found in (II). The O(1) atom and the methyl group on N(1) are in a *cis* configuration. However, in contrast to (II), this N(1) substituent is markedly out of the triazene plane [C(9) is out of the four-atom plane by 1.175 (5) Å] and the N(2)–N(3)–O(1) angle is distorted. The triazene plane itself is at an angle of 42.3 (5)° with the phenyl ring, compared to 11° in (II). These out-of-plane distortions are probably due to the relief of steric hindrances arising from the methyl group at N(1). These factors

result in the title compound having a significantly different bonding geometry for the triazene moiety from (II).

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Structure of the 2:1 Complex of Phenol and Urea

BY ALISTAIR L. MACDONALD, ALISTAIR MURRAY AND SANDRA TOWNSLEY

Chemistry Department, Clydebank High School, Shelley Drive, Clydebank G81 3EJ, Scotland

AND PAUL R. MALLINSON

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

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Abstract. (NH₂)₂CO.2C₆H₅OH, *M_r* = 248.3, monoclinic, *Cc*, *a* = 26.933 (4), *b* = 6.646 (3), *c* = 7.428 (3) Å, β = 92.38 (3)°, *V* = 1328 (1) Å³, *Z* = 4, *D_m* = 1.23, *D_x* = 1.24 g cm⁻³, λ (Mo *K*α) = 0.71069 Å, μ = 0.83 cm⁻¹, *F*(000) = 528, *T* = 293 K, *R* = 0.053 for 562 unique observed [*I*/σ(*I*) ≥ 2.0] reflections. The two phenol molecules are linked by hydrogen bonds [O...O 2.61 (1) and 2.70 (1) Å] to the carbonyl oxygen of the urea. The urea is further linked to two separate phenol molecules by NH...O hydrogen bonds [N...O 2.95 (1) and 3.05 (1) Å], forming infinite chains. NH...O hydrogen bonds [N...O 3.08 (1) Å] link these chains into stacks along *c*. There is no hydrogen bonding between stacks.

Introduction. Phase equilibrium studies of the phenol–urea system by thermal analysis reveal the existence of a compound having 2:1 stoichiometry (Philip, 1903; Puschin & Konig, 1928; Palobekov & Bergman, 1966). Evidence has been adduced from IR spectra for the participation of all of the N and O atoms in hydrogen bonding (Chesnokov & Bokhovkin, 1966). We have determined the crystal structure of the complex in order to ascertain conclusively the nature of the bonding between the constituent molecules.

Experimental. The compound was obtained by melting together a mixture of phenol and urea (66 mol% phenol and 33 mol% urea). Very thin plates developed on

cooling. The sample for X-ray analysis, m.p. 333.8 K, was obtained by recrystallization from ethanol/water. D_m was measured by flotation in heptane/chloroform. The crystals lose phenol on exposure to air and gradually change into a white powder (urea). A thin, platy crystal ($0.25 \times 0.20 \times 0.01$ mm) was sealed in a thin-walled glass capillary and used for the measurement of 1450 unique X-ray intensities by θ - ω scan on a Nonius CAD-4 diffractometer, these comprising all possible reflections with $\sin\theta/\lambda < 0.64 \text{ \AA}^{-1}$ in the index ranges $0 \leq h \leq 34$, $0 \leq k \leq 8$, $-9 \leq l \leq 9$. Two standard reflections showed no appreciable intensity variation. 562 reflections having $I > 2\sigma(I)$ were considered observed. $R_{\text{int}} = 0.025$ from merging 138 pairs of equivalent reflections. Intensities were not corrected for absorption. Lattice parameters were determined from setting angles for 24 reflections with $8 < \theta < 13^\circ$. The structure was solved by the *MITHRIL* program with use of quartets (Gilmore, 1984). Anisotropic least-squares refinement gave a final R value (on F) of 0.053, with $wR = 0.059$, $S = 2.8$, $w = 1/\sigma^2(F_o)$. The origin was defined by fixing the x and z coordinates of

C(7). The phenyl hydrogen atoms were placed in theoretical positions and allowed to ride on their attached carbon atoms. Only one of the remaining hydrogen atoms, H(1') [attached to O(1')], was located in difference maps. It was refined isotropically. Refinement of the η parameter (Rogers, 1981) failed to give a reliable indication of the absolute structure, presumably because of the low number of observed reflections from the small crystal. After the final refinement cycle $(\Delta/\sigma)_{\text{max}} = 0.2$, $(\Delta\rho)_{\text{max}} = 0.5$, $(\Delta\rho)_{\text{min}} = -0.6 \text{ e \AA}^{-3}$. Computations were carried out with the *GX* crystallographic package (Gilmore, 1984; Mallinson & Muir 1985). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Atomic coordinates and bond lengths are in Tables 1 and 2.* Fig. 1 shows the 2:1 phenol-urea unit packing with atom labels and Fig. 2 is a view of the crystal packing.

Discussion. The two independent phenol molecules are hydrogen-bonded to the same urea oxygen atom [O(1)···O(2) 2.61 (1), O(1')···O(2) 2.70 (1) Å]. The

Table 1. Refined fractional atomic coordinates and isotropic displacement parameters (\AA^2), with standard deviations in the least significant digits in parentheses

For anisotropic atoms, the equivalent isotropic displacement parameters are shown. The hydrogen atom has the number of the oxygen atom to which it is attached.

	x	y	z	$U/U_{\text{eq}} (\text{\AA}^2)$
C(1)	0.1048 (6)	0.2554 (19)	0.6559 (22)	0.043
C(2)	0.1194 (6)	0.3877 (17)	0.5252 (21)	0.051
C(3)	0.1684 (6)	0.3852 (20)	0.4713 (22)	0.058
C(4)	0.2023 (6)	0.2520 (22)	0.5444 (24)	0.056
C(5)	0.1882 (6)	0.1198 (22)	0.6762 (23)	0.055
C(6)	0.1386 (6)	0.1213 (19)	0.7325 (21)	0.050
C(1')	0.3838 (6)	0.2473 (19)	0.2068 (20)	0.042
C(2')	0.3506 (6)	0.3899 (19)	0.2646 (24)	0.052
C(3')	0.3025 (6)	0.3905 (22)	0.1922 (24)	0.057
C(4')	0.2859 (6)	0.2488 (20)	0.0697 (22)	0.057
C(5')	0.3188 (6)	0.1091 (20)	0.0123 (21)	0.058
C(6')	0.3675 (6)	0.1044 (17)	0.0797 (22)	0.051
C(7)	0.4938	0.2243 (14)	0.6783	0.046
O(1)	0.0564 (5)	0.2519 (11)	0.7156 (19)	0.050
O(1')	0.4319 (5)	0.2542 (13)	0.2773 (19)	0.054
O(2)	0.4912 (6)	0.0344 (9)	0.6488 (20)	0.047
N(1)	0.5238 (6)	0.3481 (16)	0.5979 (22)	0.066
N(2)	0.4641 (6)	0.3064 (14)	0.8035 (21)	0.073
H(1')	0.454 (3)	0.822 (14)	0.761 (14)	0.04 (4)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Table 2. Bond lengths (\AA)

C(1)–C(2)	1.38 (2)	C(1)–C(6)	1.38 (2)
C(1)–O(1)	1.39 (2)	C(2)–C(3)	1.39 (2)
C(3)–C(4)	1.37 (2)	C(4)–C(5)	1.38 (2)
C(5)–C(6)	1.42 (2)	C(1')–C(2')	1.38 (2)
C(1')–C(6')	1.40 (2)	C(1')–O(1')	1.38 (2)
C(2')–C(3')	1.38 (2)	C(3')–C(4')	1.37 (2)
C(4')–C(5')	1.36 (2)	C(5')–C(6')	1.39 (2)
C(7)–O(2)	1.28 (2)	C(7)–N(1)	1.31 (2)
C(7)–N(2)	1.37 (2)	O(1')–H(1')	.79 (9)

* Lists of structure factors, unrefined H-atom coordinates and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43527 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

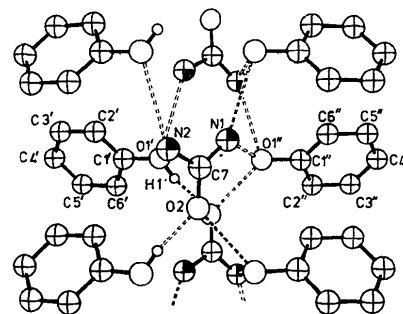


Fig. 1. A view of part of the complex showing hydrogen bonds (broken lines) and the atom-numbering scheme. (Double-primed atoms are related to the corresponding unprimed ones in Table 1 by the operation $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$.)

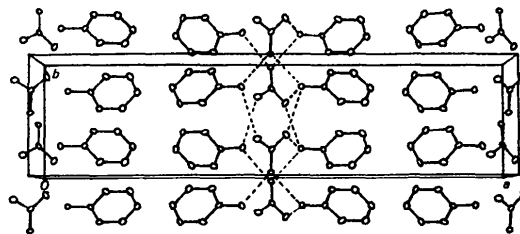


Fig. 2. The unit cell contents viewed along c . Hydrogen bonds are shown for two antiparallel chains only.

O...O...O angle is $79.9(3)^\circ$. Both urea nitrogen atoms are also bonded to two phenol molecules separated from the first by a *b* lattice translation [$N(1)\cdots O(1)$ 2.95 (1), $N(2)\cdots O(1')$ 3.05 (1) Å], thus forming infinite chains of phenol-urea moieties containing ten-membered hydrogen-bonded rings (Fig. 2). Each chain is in contact with parallel and antiparallel chains related by lattice centring and the *c* glide plane respectively. The antiparallel chains are linked into stacks along *c* by $NH\cdots O$ hydrogen bonds [$N\cdots O$ 3.08 (1) Å] involving the phenol O atoms. These atoms are thus involved in three hydrogen bonds while one N and the other O atom are involved in two each. There is no hydrogen bonding between adjacent parallel chains. The absence of hydrogen bonding between stacks probably accounts for the ready decomposition of the crystals. The hydrogen-bonding distances are similar to those found by Mahmoud & Wallwork (1975) in the quinol complex and by Pickering & Small (1982) in the resorcinol complex of urea. The distances in those compounds are in the ranges 2.633 (2)–2.702 (2) Å for O...O and 2.944 (4)–3.128 (4) Å for N...O.

The atoms of both the urea and the phenol molecules do not deviate significantly from planarity. The phenol molecular planes containing O(1) and O(1') are inclined to the urea molecule at $57(2)$ and $65(2)^\circ$ respectively, and to each other at $87(2)^\circ$.

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Structure en Série Mutagène: les Nitro-2 Naphto[2,1-*b*]- et [2,3-*b*]furannes

PAR A. AJANA, J. P. BIDEAU ET M. COTRAIT

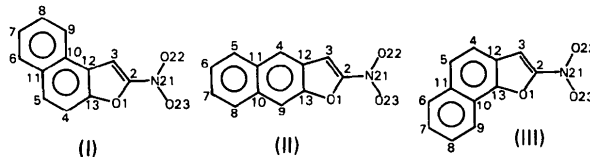
Laboratoire de Cristallographie et de Physique Cristalline, UA 144 du CNRS, 351 Cours de la Libération, 33405 Talence CEDEX, France

(Reçu le 23 mai 1986, accepté le 27 octobre 1986)

Abstract. (I) 2-Nitronaptho[2,1-*b*]furan-benzene (2/1), $C_{12}H_7NO_3 \cdot 0.5C_6H_6$, $M_r = 252.2$, monoclinic, $P2_1/c$, $a = 8.865(2)$, $b = 16.159(3)$, $c = 8.500(5)$ Å, $\beta = 100.58(5)^\circ$, $V = 1197.0$ Å³, $Z = 4$, $D_m = 1.37$, $D_x = 1.399$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.107$ cm⁻¹, $F(000) = 524$, $T = 298$ K, $R = 0.029$ for 1141 observed reflexions. (II) 2-Nitronaptho[2,3-*b*]furan, $C_{12}H_7NO_3$, $M_r = 213.2$, triclinic, $P\bar{1}$, $a = 7.850(2)$, $b = 9.191(1)$, $c = 7.369(4)$ Å, $\alpha = 92.09$, $\beta = 116.79(3)$, $\gamma = 86.42(2)^\circ$, $V = 473.7$ Å³, $Z = 2$, $D_m = 1.48$, $D_x = 1.495$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.121$ cm⁻¹, $F(000) = 220$, $T = 298$ K, $R = 0.040$ for 1197 observed reflexions. Mutagenic agents. The nitro group is practically coplanar with the benzofuran ring. Stacking forces result in π - π interactions between parallel molecules and play an important role in crystal cohesion.

Introduction. Un nombre important de molécules appartenant à la série des nitro-2 naphtofurannes a été

synthétisé (Royer & Buisson, 1980; Royer, 1986; Royer & Buisson, 1986). Elles peuvent être classées en trois groupes, suivant la position de l'hétérocycle nitré sur son support naphthalénique: les groupes (I), (II) et (III) correspondent à des naptho[2,1-*b*]-, naptho[2,3-*b*]- et naptho[1,2-*b*]furannes respectivement. Divers substituants ont été introduits, notamment en position β du cycle furanne et en diverses positions sur l'homocycle extérieur et plus rarement sur l'homocycle intérieur.



Certaines de ces molécules présentent des propriétés bactéricides et protozoocides remarquables (Cavier, Buisson, Lemoine & Royer, 1981). Elles sont, par