The Crystal and Molecular Structure of 3-Phenyl-5-benzyl-6-oxo-1,6-dihydro-1,2,4-triazine

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Received 26 October 1994

The crystal and molecular structure of the title compound was elucidated. The structure was solved by direct methods and refined anisotropically to $R = 0.0393$ for 1577 unique observed reflections. The crystal is monoclinic, $P2_1/c$, $a = 12.036(2)\ 10^{-10}$ m, $b = 12.3257(11)\ 10^{-10}$ m, $c = 9.3466(12)\ 10^{-10}$ m, $\beta = 102.719(12)°$, $Z = 4$. The presence of one from possible tautomeric structures has been proved using X-ray diffraction. The structure is stabilized by intermolecular hydrogen bonds.

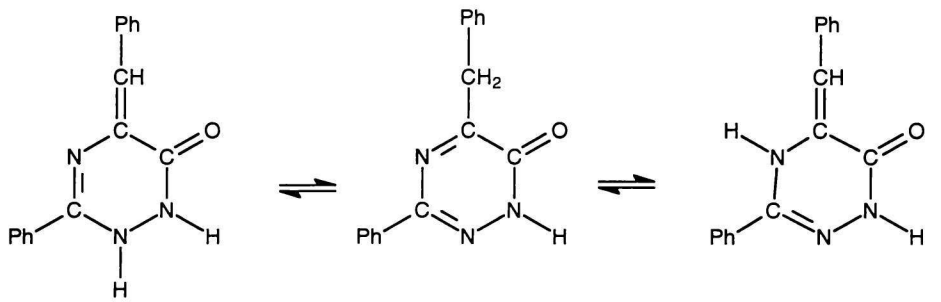
On the basis of the systematic study of nitrogenous heterocyclic compounds we were concerned with preparation and reactions of 3,5-disubstituted 6-oxo-1,6-dihydro-1,2,4-triazines in our previous works [1—6]. From reactions of these substances it is evident that they exist in a few tautomeric forms [7]. Some of possible tautomeric structures are shown in Scheme 1. For this reason we decided to solve the crystal and molecular structure of 3-phenyl-5-benzyl-6-oxo-1,6-dihydro-1,2,4-triazine (*I*) as a starting substance.

EXPERIMENTAL

3-Phenyl-5-benzyl-6-oxo-1,6-dihydro-1,2,4-triazine (*I*) was synthesized according to the procedure described in [8]. Crystals for X-ray structural analyses were obtained by recrystallization from an ethanol—benzene (1 : 1) mixture. The experimental density was estimated by the flotation method in a H_2O—KI mixture.

Diffraction experiment was performed on a KUMA KM-4 four-circle diffractometer at 293 K using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073\ 10^{-10}$ m) and a crystal with dimensions of 0.60 mm × 0.45 mm × 0.30 mm. Lattice parameters were refined using 50 reflections in the range $23.8° < 2\theta < 41.0°$. Intensities were measured with ω-2θ scan technique within the $4.8° < 2\theta < 50.2°$ region. Index ranges: $-14 \le h \le 14$, $0 \le k \le 14$, $-11 \le l \le 0$. The three standard reflections (4 3 0, −2 4 −3, −2 4 4) were checked after every 80 measurements (the e.s.d.'s were slighter than 1.5%). Extinction and absorption corrections were not applied.

The phase problem was solved by direct methods and the structure was anisotropically refined by the full-matrix least-squares procedure with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.25P]$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atom positions were found from the difference Fourier synthesis and were refined isotropically. The maximum and minimum electron densities on the final difference Fourier map were 1.50 ×



Scheme 1

10^{29} and -1.30×10^{29} e m^{-3}. Other maxima were found inside the phenyl, benzyl, and triazine ring, respectively. Refinement of the structure was based on F^2. The weighted R-factor, wR, and goodness of fit, S, were based on F^2 The conventional R-factor, R, was based on F. The observed criterion of $I > 2\sigma(I)$ was used only for calculation of R_{obs} and wR_{obs}, respectively, and is not relevant to the choice of reflections for refinement. The following programs were used: SHELXS-86 [9], SHELXL-93 [10], PARST [11], and ORTEP [12].

RESULTS AND DISCUSSION

The basic crystallographic data and structure refinement parameters are given in Table 1. The final coordinates and equivalent isotropic thermal parameters of non-H atoms are summarized in Table 2. Complete set of bond distances and angles is listed in Tables 3 and 4.

The molecular structure of the compound studied (Fig. 1) confirms the presence of a single tautomer in solid state. The distance C(6)—O(7) (1.233(2) 10^{-10} m) is typical for the double bond [13] (Table 3) and the same is valid for the bond lengths N(2)—C(3) (1.306(2) 10^{-10} m) and N(4)—C(5) (1.290(2) 10^{-10} m), respectively.

The six-membered triazine ring deviates significantly from planarity (the value of $\sum(d/s)^2$ for the N(1), N(2), C(3), N(4), C(5), and C(6) atoms is 214.8; the value of χ^2 at 95 % probability level is 7.8). The N(1), N(2), C(3), C(5), and C(6) atoms displaced by $-0.005(2)\ 10^{-10}$ m, $-0.006(2)\ 10^{-10}$ m, $0.012(3)\ 10^{-10}$ m, $-0.014(2)\ 10^{-10}$ m, and $0.016(2)\ 10^{-10}$ m, respectively, from the least-squares plane fitted through the N(1)—N(2)—C(3)—N(4)—C(5)—C(6) atoms (plane 1). The N(4) atom lies

Table 1. Basic Crystallographic Data and Refinement Parameters

Formula unit	$C_{16}H_{13}N_3O$
Relative molecular mass	263.29
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 12.036(2)\ 10^{-10}$ m $\alpha = 90°$
	$b = 12.3257(11)\ 10^{-10}$ m $\beta = 102.719(12)°$
	$c = 9.3466(12)\ 10^{-10}$ m $\gamma = 90°$
Volume	$1352.6(3)\ 10^{-30}$ m^3
Z	4
Density (calc./exp.)	1.293 g cm^{-3}/1.29 g cm^{-3}
Absorption coefficient	0.084 mm^{-1}
$F(000)$	552
Reflections collected	2569
Independent reflections	2408 ($R_{int} = 0.0161$)
Reflections observed	1577
Data/parameters	2395/220
$S_{obs./all}$	1.036/1.827
$R_{obs.}$ ($I > 2\sigma(I)$)	$R = 0.0393$, $wR = 0.1080$
R_{all}	$R = 0.1127$, $wR = 0.2413$

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (10^{-20} m^2 × 10^3)

Atom	$10^4\ x$	$10^4\ y$	$10^4\ z$	U_{eq}
N(1)	681(1)	6125(1)	1183(2)	51(1)
N(2)	1412(1)	6621(1)	2298(2)	51(1)
C(3)	1413(1)	7680(1)	2266(2)	46(1)
N(4)	713(1)	8304(1)	1213(2)	48(1)
C(5)	13(1)	7815(1)	169(2)	46(1)
C(6)	−32(1)	6628(1)	61(2)	49(1)
O(7)	−651(1)	6130(1)	−953(1)	64(1)
C(8)	−806(2)	8448(2)	−963(2)	51(1)
C(9)	2230(1)	8250(1)	3429(2)	50(1)
C(10)	2353(2)	9357(2)	3384(3)	79(1)
C(11)	3121(3)	9895(2)	4453(3)	96(1)
C(12)	3783(2)	9341(2)	5588(3)	80(1)
C(13)	3664(2)	8233(2)	5656(2)	75(1)
C(14)	2899(2)	7689(2)	4589(2)	63(1)
C(15)	−1951(1)	8536(1)	−560(2)	47(1)
C(16)	−2834(2)	7841(2)	−1142(2)	68(1)
C(17)	−3880(2)	7950(2)	−746(3)	83(1)
C(18)	−4038(2)	8748(2)	217(3)	79(1)
C(19)	−3165(2)	9429(2)	789(3)	74(1)
C(20)	−2130(2)	9323(2)	421(2)	59(1)
H(1)	683(16)	5312(18)	1188(21)	72(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Lengths in Substance *I*

	Bond length/10^{-10} m		
N(1)—C(6)	1.351(2)	C(9)—C(14)	1.385(3)
N(1)—N(2)	1.352(2)	C(10)—C(11)	1.374(3)
N(2)—C(3)	1.306(2)	C(11)—C(12)	1.362(4)
C(3)—N(4)	1.380(2)	C(12)—C(13)	1.377(4)
C(3)—C(9)	1.474(2)	C(13)—C(14)	1.373(3)
N(4)—C(5)	1.290(2)	C(15)—C(16)	1.380(2)
C(5)—C(6)	1.467(2)	C(15)—C(20)	1.383(2)
C(5)—C(8)	1.497(2)	C(16)—C(17)	1.394(3)
C(6)—O(7)	1.233(2)	C(17)—C(18)	1.374(3)
C(8)—C(15)	1.511(2)	C(18)—C(19)	1.359(3)
C(9)—C(10)	1.374(3)	C(19)—C(20)	1.370(3)
N(1)—H(1)	1.00(2)		

Table 4. Bond Angles in Substance *I*

	Bond angle/°		
C(6)—N(1)—N(2)	125.81(14)	C(14)—C(9)—C(3)	121.2(2)
C(3)—N(2)—N(1)	115.97(14)	C(11)—C(10)—C(9)	121.1(2)
N(2)—C(3)—N(4)	124.7(2)	C(12)—C(11)—C(10)	120.6(2)
N(2)—C(3)—C(9)	117.63(14)	C(11)—C(12)—C(13)	119.0(2)
N(4)—C(3)—C(9)	117.63(14)	C(14)—C(13)—C(12)	120.7(2)
C(5)—N(4)—C(3)	118.29(14)	C(13)—C(14)—C(9)	120.4(2)
N(4)—C(5)—C(6)	121.7(2)	C(16)—C(15)—C(20)	118.5(2)
N(4)—C(5)—C(8)	120.7(2)	C(16)—C(15)—C(8)	121.5(2)
C(6)—C(5)—C(8)	117.6(2)	C(20)—C(15)—C(8)	119.9(2)
O(7)—C(6)—N(1)	122.7(2)	C(15)—C(16)—C(17)	119.8(2)
O(7)—C(6)—C(5)	123.9(2)	C(18)—C(17)—C(16)	120.4(2)
N(1)—C(6)—C(5)	113.4(2)	C(19)—C(18)—C(17)	119.6(2)
C(5)—C(8)—C(15)	110.88(13)	C(18)—C(19)—C(20)	120.6(2)
C(10)—C(9)—C(14)	118.1(2)	C(19)—C(20)—C(15)	121.1(2)
C(10)—C(9)—C(3)	120.6(2)		

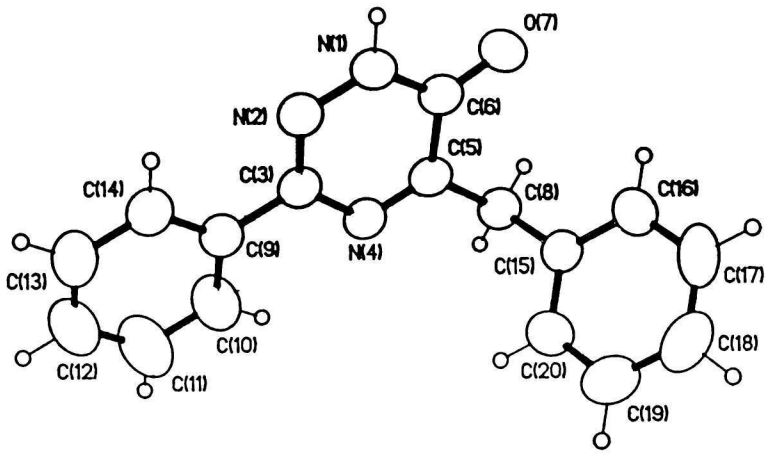


Fig. 1. View of a molecule of the triazine with atom numbering. Thermal motion is shown by ellipsoids at the 50 % probability level.

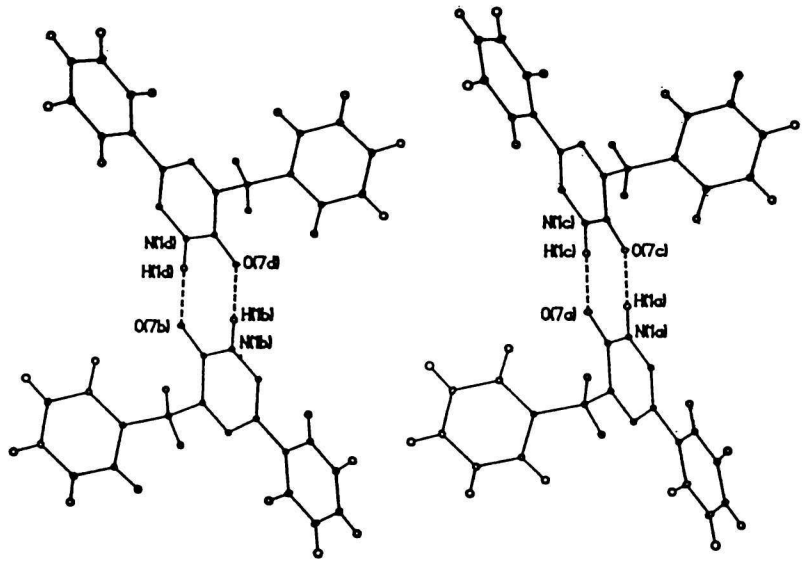


Fig. 2. A stereoscopic view showing molecular packing in crystal. Dashed lines indicate the hydrogen bonding.

in this plane. The remaining two six-membered rings, *i.e.* phenyl ring (plane 2) and benzyl ring (plane 3), are situated in different planes. The dihedral angles formed by least-squares planes are as follows: (plane 1—plane 2) 6.51(7)°, (plane 1—plane 3) 73.07(6)°, (plane 2—plane 3) 77.78(7)° The molecules are linked together by N—H...O hydrogen bonds involving the N(1) atom and the O(7) atom (the N(1)...O(7)^{i} interatomic contact is equal to 2.787(2) 10^{-10} m) of the neighbouring molecule (H(1)...O(7)^{i} = 1.79(2) 10^{-10} m; i: $-x, -y+1, -z$). The latter distance also represents the shortest intermolecular contact, which has been observed in this structure. A stereoscopic view showing the structure and crystal packing of the compound is displayed in Fig. 2. Intermolecular hydrogen bonds are indicated by dashed lines.

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Translated by Z. Trávníček