Crystal Structure of 2-Hydroxy-5-*t*-butylazobenzene

M. Murat CANDAN*1†, Engin KENDİ*1, Hasan KOCAOKUTGEN*2, Muhittin AYGÜN*3 and Şamil IŞIK*4

*1 *Department of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey*
*2 *Department of Chemistry, Ondokuz Mayıs University, 55139, Samsun, Turkey*
*3 *Department of Physıcs, Faculty of Buca Education, Dokuz Eylül University, Buca 35510, Izmir, Turkey*
*4 *Department of Physics, Ondokuz Mayıs University, 55139, Samsun, Turkey*

Azo compounds are the most widely used class of dyes due to their versatile application in various fields, such as the dyeing of textiles, an fibers, to coloring of different materials, and high-technology areas, such as electro-optical devices and ink-jet printers. The title compound (I) (Fig. 1) was obtained and its structure analyzed by standart analytical techniques (UV, IR, NMR).[1] In order to obtain information about the stereochemistry of the molecule and to confirm the assigned structure, an X-ray analysis of (I) was undertaken.

A mixture of analine (0.01 mol) water and concentrated hydrochloric acid (0.04 mol) was stirred until a clear solution was obtained. This solution was cooled down to 0 – 5˚C and a solution of sodium nitrite (0.011 mol) in 5 ml of water was than added dropwise, while maintaining the temperature below 5˚C. The resulting mixture was stirred for an additional 30 min in an ice bath, and excess nitrite was destroyed by the addition of urea. This solution was buffered with solid sodium acetate.

4-*t*-Butylphenol (0.01 mol), dissolved 5 ml ethanol, was cooled down to 0 – 5˚C in an ice bath, and then gradually added to a solution of the benzenediazonium chloride; to resulting mixture was continually stirred for 60 min. The crude precipitate was filtired, washed several times with water and recrystallized from glacial

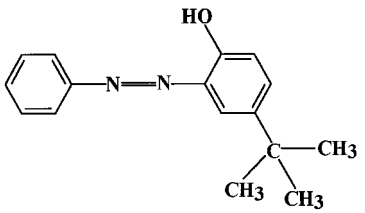

Fig. 1 Chemical structure.

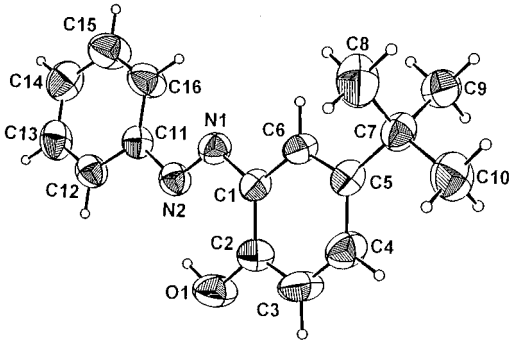

Fig. 2 An ORTEP drawing of the title compound with atomic labeling. The displacement ellipsoids are drawn at the 50% probability level.

† To whom correspondence should be addressed.

Table 1 Crystal and experimental data

Formula: $C_{16}H_{18}N_2O$	
Formula weight=254.33	
Crystal system: monoclinic	
Space group: $P2_1/c$	Z=4
a=14.002(3)Å	
b=5.930(1)Å	β=99.82(2)˚
c=17.331(5)Å	
V=1417.9(6)Å^3	
D_c=1.191 g/cm^3	
μ(Mo K$_\alpha$)=0.070 mm^{-1}	
T=295 K	
Orange	
F(0 0 0)=544	
Crystal size: 0.30×0.24×0.15 mm	
$2\theta_{max}$=52.6˚ with Mo K$_\alpha$	
R=0.037	
Rw=0.055	
No. of reflection used=1383	($I>3\sigma(I)$)
No. of parameters=172	
Goodness-of-fit=1.10	
$(\Delta/\sigma)_{max}$=0.0002	
$(\Delta\rho)_{max}$=0.14 eÅ^{-3}	
$(\Delta\rho)_{min}$=–0.12 eÅ^{-3}	
Measurements: Enraf Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: MolEN	
Treatment of hydrogen atoms: geometric calculation	
Refinement: full matrix least-squares (MolEN)	

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2
O1	0.1662(1)	0.3233(3)	0.16488(8)	5.68(4)
N1	0.2985(1)	0.2004(3)	0.05592(9)	3.79(4)
N2	0.2993(1)	0.0806(3)	0.11645(9)	3.85(4)
C1	0.2301(1)	0.3762(4)	0.0450(1)	3.49(4)
C2	0.1671(2)	0.4350(4)	0.0969(1)	4.12(5)
C3	0.1050(2)	0.6126(5)	0.0773(1)	5.23(6)
C4	0.1030(2)	0.7283(4)	0.0084(1)	4.82(5)
C5	0.1629(2)	0.6754(4)	-0.0455(1)	3.78(4)
C6	0.2265(1)	0.4981(4)	-0.0240(1)	3.69(4)
C7	0.1601(2)	0.7951(4)	-0.1238(1)	4.02(5)
C8	0.1349(2)	0.6254(4)	-0.1910(1)	6.24(7)
C9	0.2589(2)	0.8995(4)	-0.1279(1)	4.90(5)
C10	0.0848(2)	0.9845(5)	-0.1354(2)	5.90(6)
C11	0.3685(1)	-0.0969(4)	0.1255(1)	3.71(4)
C12	0.3633(2)	-0.2509(4)	0.1839(1)	4.23(5)
C13	0.4271(2)	-0.4279(4)	0.1964(1)	5.11(6)
C14	0.4961(2)	-0.4528(5)	0.1495(2)	5.69(6)
C15	0.5015(2)	-0.2999(5)	0.0911(2)	6.27(6)
C16	0.4388(2)	-01221(5)	0.0787(1)	5.44(6)

$B_{eq}=(8\pi^2/3)\Sigma_i\Sigma_j U_{ij}(a_i^* a_j^*)(\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Selected geometric parameters (Å, ˚)

O1 - C2	1.354 (3)	C5 - C7	1.526 (3)
N1 - N2	1.265 (2)	C7 - C8	1.534 (3)
N1 - C1	1.406 (3)	C7 - C9	1.528 (3)
N2 - C11	1.421 (3)	C7 - C10	1.530 (3)
C2 - O1 - H1′	107.8 (2)	C5 - C7 - C10	111.8 (2)
N2 - N1 - C1	115.9 (2)	C8 - C7 - C9	108.8 (2)
N1 - N2 - C11	114.6 (2)	C8 - C7 - C10	108.5 (2)
C5 - C7 - C9	110.1 (2)	C9 - C7 - C10	107.8 (2)
C4-C5-C7-C8	-119.3 (2)	C4-C5-C7-C9	121.0 (2)
C1-N1-N2-C11	179.4 (2)	N1-N2-C11-C12	-171.1 (2)
N2-N1-C1-C2	3.2 (3)	N1-N2-C11-C16	8.4 (3)
N2-N1-C1-C6	-176.6 (2)		

acetic acid to give a product of m.p. 57 – 58˚C. Yield 55%. Its purity was monitored by TLC.

The structure of the molecule is shown in Fig. 2 (ORTEP-MolEN).[2] Table 1 gives the crystal and relevant X-ray data. The fractional coordinates and mean-temperature factors with estimated standart deviations for non-hydrogen atoms are listed in Table 2; selected geometric parameters are given in Table 3.

The dihedral angle between two benzene rings is 3.4 (5)˚. The torsion angle, C1–N1=N2–C11, in the azo moiety is 179.4 (2)˚.

The crystal structure of the title compound is stabilized by inter-molecular hydrogen bonds. As shown in other *t*-butylazobenzene compounds (3-*t*-butyl-2′-chloro-2-hydroxy-5-methyl-azobenzene[3] and 3-*t*-butyl-2-hydroxy-5-methoxyazo-benzene[4]), in this compound there is also an intra-molecular O–H···N hydrogen bond between the hydroxy H1 atom and the N2 atom. In addition, the C–H···N hydrogen bond between the H16 and N1 atoms contributes to the planarity of the molecule as a whole.

References

1. H. Kocaokutgen and I. E. Gümrükçüoòlu, *Spectrosc. Lett*., **29**, 185 (1996).
2. C. K. Fair, "MolEN. *An Interactive Intelligent System for Crystal Structure Analysis*", Enraf-Nonius, Delft, The Netherlands (1990).
3. Ş. Işık, M. Aygün, H. Kocaokutgen and M. N. Tahir, *Acta Crystallogr*., **C54**, 1145 (1998).
4. Ş. Işık, M. Aygün, H. Kocaokutgen, M. N. Tahir, O. Büyükgüngör and A. Erdönmez, *Acta Crystallogr*., **C54**, 859 (1998).

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