

X-ray analysis of 2-aniline benzo(2,3-*b*) cyclopentane-1,3-dione

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Abstract. The molecular and crystal structure of 2-aniline benzo(2,3-*b*) cyclopentane-1,3-dione has been determined by X-ray crystallographic techniques. This compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit cell parameters: $a = 5.467(1)$, $b = 10.657(3)$, $c = 19.602(6)$ Å; $V = 1142.01(5)$ Å³, $Z = 4$. The crystal structure has been resolved up to an R -factor 0.050 for 1129 reflections. All the three rings in the structure are planar. However, the dihedral angle between the phenyl ring and the moiety comprising of a five-membered and six-membered ring is 92.4°. The oxygen atom O1 acts as a trifurcated acceptor and is involved in the formation of three intermolecular interactions.

Keywords. Crystal structure; molecular interactions; X-ray diffraction; X-ray diffractometer; trifurcated acceptor.

1. Introduction

Alkaloids are used for the treatment of asthma, cough, tuberculosis, etc (Thappa *et al* 1996). They are also widely being abused as a recreational drug. It causes a variety of pharmacological effects on the central nervous system. The well known example is that of cocaine which when inhaled results in increased heart rate and blood pressure (Byke and Vandyke 1997). Carpaine is another such substance which is reported to be a kind of heart poison and it lowers the pulse frequency and depresses the central nervous system (Joshi *et al* 1996; Rajnikant *et al* 1998).

As a part of our on-going investigations on the preparation of X-ray diffraction quality single crystals and determination of some nitrogen containing molecules (Rajnikant *et al* 2002, 2003), the title compound has been investigated which shows antibacterial activity against a number of test organisms (Nedev *et al* 1989) and has been synthesized by heating N-phenyl phthalahydrazide with ethyl chloroformate in acetone in presence of K₂CO₃. The chemical structure as shown in figure 1 has been assigned on the basis of IR, UV, NMR and mass spectral data (Deshmukh 2002).

2. Experimental

Three-dimensional intensity data of transparent rectangular plate shaped single crystal of 2-aniline benzo(2,3-*b*) cyclopentane-1,3-dione were collected on an Enraf-Nonius

CAD-4 diffractometer. $w/2\theta$ scan mode was employed for data collection by using MoK α radiation ($\lambda = 0.71069$ Å). The cell parameters were refined from accurately determined 25 reflections in the range of $8.21 < \theta < 13.45^\circ$. The cell measurement was carried out at room temperature, 293(2) K and CAD-4 programs were used for the refinement of unit cell parameters. A total of 1431 reflections were recorded in the θ range, $2.08 < \theta < 24.98^\circ$. Of the total number of reflections, 1309 were found unique (index range: $-2 \leq h \leq 6$, $-5 \leq k \leq 12$, $-11 \leq l \leq 23$) and 1129 reflections were treated as observed [$F_0 > 4\sigma(F_0)$]. Two standard reflections, $(1\ 1\ 9)$ $(1\ 2\ 6)$, measured after every 100 reflections showed no significant variation in the intensity data which means that the crystal remained stable during exposure to X-rays. The reflection data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied.

The structure was elucidated by direct methods using SHELXS86 program (Sheldrick 1986). All non-hydrogen atoms of the molecule were located from the E -map. The R -factor was based on E -values, $R_E = 0.183$. Full-matrix

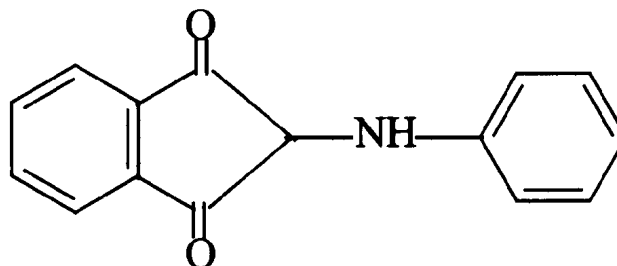


Figure 1. The chemical structure of the molecule.

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least-squares refinement of the structure was carried out by using SHELXL93 program (Sheldrick 1993). The positional and thermal parameters of non-hydrogen atoms were refined isotropically. All hydrogen atoms were fixed stereochemically. Further refinement with anisotropic thermal parameters resulted into a final value of the reliability index, $R = 0.050$. The maximum and minimum values for the residual electron density were 0.36 and $-0.48 \text{ e}\text{\AA}^{-3}$, respectively. Atomic scattering factors were obtained from International tables for Crystallography (1992, Vol. C tables 4.2.6.8 and 6.1.1.4). The crystallographic data are listed in table 1.

3. Results and discussion

The final atomic positions and equivalent isotropic displacement parameters for all the non-hydrogen atoms are listed in table 2. Bond lengths and bond angles for non-hydrogen atoms are given in table 3. A general view of the molecule indicating atomic numbering scheme (thermal ellipsoid drawn at 50% probability) is shown in figure 2 (Farrugia 1997). The geometrical calculations were performed using PARST program (Nardelli 1995).

The bond distances within the aromatic nucleus of the phenyl rings are in agreement with some related structures (Hunter *et al* 1985; Johnson *et al* 1989; Selladurai *et al* 1996). The C1=O1 and C3=O2 bonds have distances which depict their double bond character. The C2–N1 and N1–C10 bonds linking the phenyl ring with rest of the molecule have distances slightly smaller and greater than the standard value of 1.41 \AA . This phenomenon is

quite prevalent in the molecules where nitrogen is bridged between two rings (Meurisse *et al* 1992). The exocyclic bond angles at the ring junction i.e. at C8 and C9, are $130.6(4)^\circ$ and $130.3(4)^\circ$, respectively. The large value of the bond angle could be attributed to the stretching of the molecule along its mean molecular axis. The endocyclic bond angles at C2 and C10 have values slightly greater and smaller than the standard values.

Table 2. Atomic coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses, for the non-hydrogen atoms.

Atom	X	Y	Z	U_{eq}^*
N1	0.4449(7)	0.0219(3)	0.9546(2)	0.0647(1)
O1	0.6168(6)	0.1164(3)	0.8285(2)	0.0848(1)
O2	-0.0033(5)	0.1526(3)	0.9841(1)	0.0684(1)
C1	0.4314(8)	0.1588(4)	0.8546(2)	0.0630(1)
C2	0.3660(6)	0.1157(3)	0.9166(2)	0.0414(1)
C3	0.1218(8)	0.1766(4)	0.9348(2)	0.0563(1)
C4	-0.0953(8)	0.3622(4)	0.8743(2)	0.0608(1)
C5	-0.0876(9)	0.4391(4)	0.8174(2)	0.0683(1)
C6	0.0964(10)	0.4269(4)	0.7686(2)	0.0724(2)
C7	0.2757(9)	0.3365(4)	0.7756(2)	0.0709(2)
C8	0.2674(8)	0.2598(4)	0.8326(2)	0.0589(1)
C9	0.0836(8)	0.0105(3)	0.8809(2)	0.0532(1)
C10	0.4337(7)	-0.1013(4)	0.9268(2)	0.0540(1)
C11	0.6141(8)	-0.1872(4)	0.9448(2)	0.0647(2)
C12	0.8970(9)	-0.3095(4)	0.9222(2)	0.0705(2)
C13	0.4062(9)	-0.3474(4)	0.8821(2)	0.0690(2)
C14	0.2303(8)	-0.2619(4)	0.8639(2)	0.0686(2)
C15	0.2428(8)	-0.1391(4)	0.8866(2)	0.0611(1)

$$U_{\text{eq}}^* = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i a_j).$$

Table 1. Crystal data and structure refinement details.

Crystal description	Pale yellow rectangular plates
Empirical formula	$\text{C}_{15}\text{H}_{11}\text{NO}_2$
Formula weight	236.24
Temperature	293(2) K
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 5.467(10)$, $b = 10.657(3)$, $c = 19.602(6) \text{ \AA}$
Z, volume, calculated density	4, $1142.01(5) \text{ \AA}^3$, 1.374 Mg/m^3
Absorption coefficient	0.092 mm^{-1}
$F(000)$	492
Crystal size	$0.30 \times 0.3 \times 0.2 \text{ mm}$
Radiation, wavelength(λ)	MoK α , 0.71069 \AA
θ range for data collection	2.08 to 24.98°
Index ranges	$-2 \leq h \leq 6$, $-5 \leq k \leq 12$, $-11 \leq l \leq 23$
No. of reflections collected/unique	1431/1309 [$R(\text{int}) = 0.0058$]
Largest diff. peak and hole	$0.36 < \Delta r < -0.48 \text{ e}\text{\AA}^{-3}$
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	1309/0/164
Final R indices [$F_0 > 4 \sigma F_0$]	$R_1 = 0.050$, $wR_2 = 0.166$
R indices (all data)	$R_1 = 0.062$
Goodness of fit	1.337

Table 3. Bond distances (\AA) and bond angles ($^\circ$) for non-hydrogen atoms (e.s.d.'s are given in parentheses).

N1–C2	1.380(5)	N1–C10	1.423(5)
C1–C2	1.399(6)	C1–C8	1.465(6)
C1–O1	1.221(6)	C2–C3	1.388(5)
C3–C9	1.489(6)	C3–O2	1.211(5)
C4–C5	1.385(6)	C4–C9	1.369(6)
C5–C6	1.394(7)	C6–C7	1.381(7)
C7–C8	1.385(6)	C8–C9	1.388(6)
C10–C11	1.391(6)	C10–C15	1.368(6)
C11–C12	1.380(6)	C12–C13	1.367(6)
C13–C14	1.372(6)	C14–C15	1.384(6)
C2–N1–C10	116.3(3)	C8–C1–O1	131.0(4)
C2–C1–O1	123.3(4)	C2–C1–C8	105.7(3)
N1–C2–C1	123.2(4)	C1–C2–C3	112.5(3)
N1–C2–C3	124.3(3)	C2–C3–O2	125.7(4)
C2–C3–C9	105.0(3)	C9–C3–O2	129.3(4)
C5–C4–C9	117.7(4)	C4–C5–C6	121.3(4)
C5–C6–C7	121.2(5)	C6–C7–C8	117.9(4)
C1–C8–C9	130.6(4)	C7–C8–C9	120.9(4)
C1–C8–C3	108.5(4)	C4–C9–C8	121.6(4)
C3–C9–C8	108.2(3)	C3–C9–C4	130.3(4)
N1–C10–C15	121.7(4)	N1–C10–C11	118.7(4)
C11–C10–C15	119.5(4)	C10–C11–C12	119.5(4)
C11–C12–C13	121.0(4)	C12–C13–C14	119.2(4)
C13–C14–C15	120.7(4)	C10–C15–C14	120.1(4)

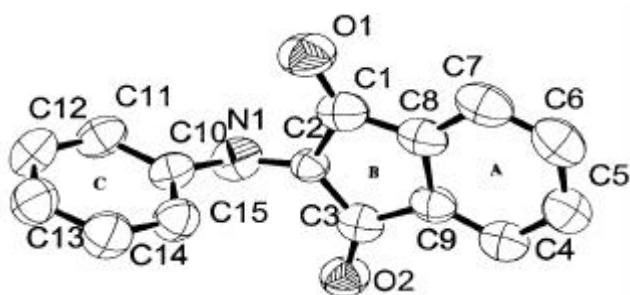


Figure 2. General view of the molecule indicating atomic numbering scheme.

Ring A containing atoms C4–C9 define a plane in which maximum deviation has been found for atom C6 [–0.003(5) Å]. The atoms C1 and C3 which have not been included in the calculation of the least square plane are found to have a deviation of –0.023(4) and 0.022(4) Å, respectively. This indicates that the atom C1 is lying below the plane and C3 is lying above the plane of ring A. The average value of torsion angles in this ring is 0.37(6)°. In ring B, maximum deviation has been obtained for atom C3 [0.022(4) Å]. The atoms O1, O2 and N1 which have not been included in the least squares plane calculation have a deviation of 0.009(3), 0.081(4) and –0.051(4), respectively. This shows that O1 and O2 atoms are lying above the plane and N1 is lying below the plane comprising of ring B atoms. The average value of torsion angles in this ring is 2.2(5)°. The ring C with atoms C10, C11, C12, C13, C14, and C15 define a plane from which the largest deviation is observed in case of atom C14 (0.006(4) Å). The atom N1 which has not been included in the calculation of the least square plane is found to be deviated below the plane of ring C by –0.086(4) Å. The average value of torsion angles in this ring is 0.57(6)°.

The torsion angle C3–C2–N1–C10 is 109.2(4)°, a rotation of nitrogen containing phenyl group that effectively takes it out of conjugation with the rest of the molecule. The dihedral angle between the plane consisting of atoms C1–C9 and the phenyl ring C is 92.40(1)° which clearly indicates that the phenyl ring is placed at almost right angle to the remaining molecule. There exists the following three intermolecular interactions (Jeffrey and Lewis 1978; Taylor and Kennard 1983):

D–H...A	H...A(Å)	D...A(Å)	D–H...A(°)
C5–H5...O1 ⁽ⁱ⁾	1.38(1)	1.91(1)	110.3(5)
C6–H6...O1 ⁽ⁱⁱ⁾	2.43(1)	3.19(1)	138.9(4)
C14–H14...O1 ⁽ⁱⁱⁱ⁾	1.59(1)	2.40(1)	144.0(5)

Equivalent position: (i) $-x + 1/2, +y + 1/2 + 1, +z$ (ii) $-x + 1/2, +y + 1/2, -z + 1/2 + 1$ (iii) $-x + 1/2, +y - 1/2, +z$

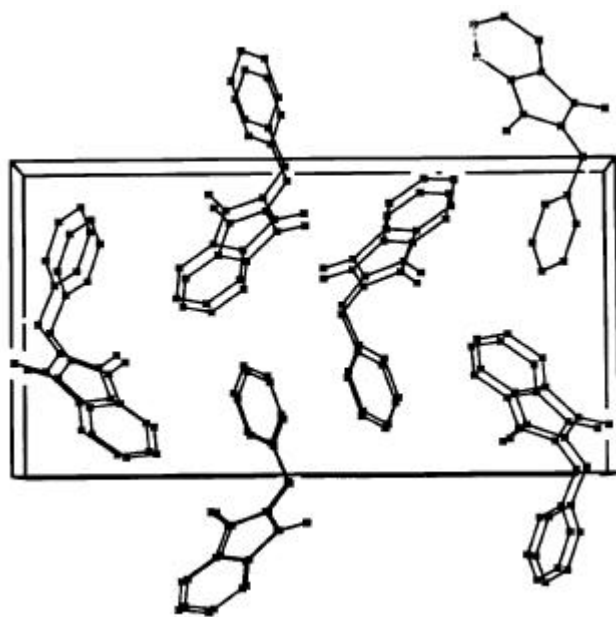


Figure 3. Unit cell molecular packing down a-axis.

The analyses of these interactions clearly indicate that the oxygen atom O1 acts as a trifurcated acceptor (Desiraju and Steiner 1999). Down the *a*-axis (figure 3), the molecule appears to be stacked one above another in the same orientation. The crystal structure is also stabilized by van der Waals interaction.

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References

- Byke R and Vandyke C 1997 *Cocaine* (eds) R C Peterson and R C Stillman (Washington) p. 97
- Deshmukh M B 2002 Private Communication, Shivaji University, Kolhapur, India
- Desiraju G J and Steiner T 1999 *The weak hydrogen bond* (New York: IUCr)
- Farrugia L J 1997 *J. Appl. Cryst.* **30** 565
- Hunter D, Neilson D G and Weakley T J R 1985 *J. Chem. Soc. Perkin Trans.* **1** 2709
- Jeffrey G A and Lewis L 1978 *Carbohydr. Res.* **60** 178
- Johnson A T, Keszler D A, Sakuma K and White J D 1989 *Acta Crystallogr.* **C45** 1114
- Joshi B S, Newton M G, Lee D W, Barber A D and Pelletier S W 1996 *Tetrahedron Asymmetry* **7** 25
- Meurisse R L, Blaton N M, Peeters O M and De Ranter C J 1992 *Acta Crystallogr.* **C48** 508
- Nardelli M 1995 *J. Appl. Cryst.* **28** 659

- Nedev K H, Minchev S and Noneva S 1989 *Dokl Bolg. Akad. Nauk.* **42** 31
- Rajnikant, Gupta V K, Lal M, Rangari V D, Belsare D P, Soni B S and Varghese B 1998 *Mol. Mater.* **9** 131
- Rajnikant, Dinesh, Mousmi, Deshmukh M B, Patil S S and Anshu Sawhney 2002 *J. Chem. Crystallogr.* [communicated]
- Rajnikant, Gupta V K, Dinesh, Mousmi, Deshmukh M B, Salunke D K, Dhondage S R and Anshu Sawhney 2003 *Asian J. Phys.* **12** 93
- Selladurai S, Subramanian K, Lakshmi S, Chen Y, Holt E J and Rao S N 1996 *Acta Crystallogr.* **C52** 94
- Sheldrick G M 1986 *SHELXS86 program for the solution of crystal structures* (Germany: University of Gottingen)
- Sheldrick G M 1993 *SHELXS93 program for the refinement of crystal structures* (Germany: University of Gottingen)
- Taylor R and Kenard O 1983 *Acta Crystallogr.* **B39** 133
- Thappa R K, Agarwal S G, Dhar K L, Gupta V K and Goswami K N 1996 *Phytochemistry* **42** 1485