

## **Crystal Growth and Spectral Characterisation of P-[N, N-Bis(2-Chloroethyl) Aminobenzaldehyde**

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Synthesis and single crystal growth of organic compound p-[N, N-bis(2-chloroethyl)aminobenzaldehyde by slow evaporation technique is reported. Good quality single crystal of size 0.35 x 0.20 x 0.20 mm are grown for a period of seven days and characterized by spectral techniques. The grown crystal has been subjected to single crystal X-ray diffraction techniques and cell parameters of the crystal were determined. The title compound crystallizes in the monoclinic crystal system with space group Cc, Calculated density = 1.349Mg/m<sup>3</sup>, V = 1211.62(10) Å<sup>3</sup> with unit cell parameters a = 14.7579(8)Å,  $\alpha$  = 90°, b = 9.3470(4)Å,  $\beta$  = 116.333(2), c = 9.8005(4)Å,  $\gamma$  = 90°, final R<sub>1</sub> and wR<sub>2</sub> are 0.0326 and 0.0843 respectively.

**Key Words:** Crystal Structure; Conformation; P-[N,N-Bis(2-chloroethyl) Amino Benzaldehyde

### **Introduction**

The determination of the crystal structure and conformational aspects of p-[N,N-Bis(2-chloroethyl)aminobenzaldehyde has been undertaken by us in an attempt to correlate their structural features and material functions. This compound plays an important role in the preparation of Schiff bases (used as a precursor) [1] and most importantly Nonlinear optical (NLO) properties [2, 3] of organic molecular materials have received considerable attention recently due to their large second-order nonlinearities and relatively higher damage threshold. From the chemistry point of view, the title compound is an interesting compound. The carbonyl group is a strong electron absorber. When the para and/or ortho positions of an aromatic molecule have a relatively weak donor (e.g., methoxy, hydroxy, halides), a charge transfer interaction can also be established and will increase the molecular hyperpolarizability. Furthermore, conjugate molecules containing carbonyl and weak donors usually have their cutoff wavelength dramatically blue shifted from those containing strong

donors and acceptors such as the dimethylamino, diethylamino and nitro groups. This is very important in considering the trade-off between efficiency and transparency; similarly, three isomers exist with aldehyde and diethyl amino groups in the p-, m-, and o- positions with respect to each other. If structural studies of all three isomers i.e. p-, m- and o- could be made, they might furnish useful information. Thus both from structural and functional points of view the study of this compound are indeed significant. The present communication deals with the complete solution of the crystal and molecular structure of p-[N,N-Bis(2-chloroethyl) amino benzaldehyde.

### **Experimental Procedure**

The p-[N, N-bis(2-chloroethyl) amino benzaldehyde was prepared as per the reported procedure [4] by the formylation of dimethylaniline using phosphorousoxychloride and dimethylformamide taken into a 250 mL round bottom flask. The mixture was refluxed at around 40°C for around 2 hrs and cooled, after cooling, a purple white precipitate

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appeared, filtered, washed with ethanol followed by ether. Crystals suitable for X-ray diffraction studies were obtained by using small amount of ethanol with decolorizing charcoal give 58% of the colourless crystals melting at 85-88°C. The purity of the compound was checked by the elemental analysis and by melting point (87.5°C). [Analysis results for  $C_{11}H_{13}Cl_2NO$ . Found (Actual) C:53.66 % (53.65 %), H:5.30 % (5.28 %), N:5.70 % (5.69 %), O: 6.53 % (6.50 %), rest Chlorine, IR(KBr,  $cm^{-1}$ )  $-C=O$ : 1682  $cm^{-1}$ ,  $\nu_{C-H}$  (Ar-H): 2984  $cm^{-1}$ ,  $-C-N$  Stretching: 1604  $cm^{-1}$ ,  $-C-Cl$ : 894  $cm^{-1}$ ,  $-N(CH_2CH_2Cl)$ : 626  $cm^{-1}$ ,  $H^1$ -NMR (DMSO- $d_6$ ):  $\delta$  = 6.76-7.62 ppm (multiplet, 4H),  $-CH=O$ , 7.92 ppm (singlet, 1H)  $-CH_2-CH_2$ -protons-multiplets at  $\delta$  = 3.00-3.80 ppm].

### Crystal Growth

It was found from the solubility study that ethanol was found to be the best solvent for the single crystal growth of CEAB. A super saturated solution of CEAB was obtained by dissolving the sample in the ethanol at ambient temperature. The prepared solution was filtered, slightly warmed and allowed to evaporate slowly at room temperature. After about 10 days good quality crystals appeared of dimension. 0.35 x 0.20 x 0.20 mm suitable for XRD studies within a period of 10 days by slow evaporation technique. The grown crystals are depicted in Fig. 1.



Fig. 1: Photograph of CEAB crystal

### UV Spectral Studies

The UV-Visible studies of the compound CEAB were done in ethanol solvent. The electronic spectrum of compound shows absorbance maximum at 340 nm ( $29411\text{ cm}^{-1}$ ) in ethanol exhibits intense bands in the range  $4,000$ - $27,000\text{ cm}^{-1}$  which are assigned to  $-C=O$   $n-\pi^*$  transition [5].

### IR Spectral Studies

The Fourier transform infrared (FTIR) analysis of CEAB was carried out between  $400$ - $4000\text{ cm}^{-1}$  using KBr pellet. The characteristic IR absorption bands observed are consistent with the functional groups present in the compound and the assigned values are recorded in Table 1. Since it contains a  $-HC=O$ -functional group of aldehyde in CEAB has the frequencies of  $1682$  and  $1443\text{ cm}^{-1}$  respectively indicate the  $-C=O$  and  $-C-H$  stretching. Aromatic  $-C-H$  stretching,  $-C-N$  and  $-C-Cl$  stretching appeared at  $2984\text{ cm}^{-1}$ ,  $1604\text{ cm}^{-1}$ ,  $894\text{ cm}^{-1}$  respectively.

Table 1: Assigned values in IR spectral studeis

IR ( $cm^{-1}$ )	Mode assignments
2984	$\nu_{C-H}$ (Ar-H)
1682	$-C=O$
1604	$-C-N$ Stretching
894	$-C-Cl$
626	$-N(CH_2CH_2Cl)$

### $H^1$ NMR Spectral Studies

The structures of thiosemi carbazones were further confirmed from the  $^1H$ -NMR spectra, which provide diagnostic tools for the positional elucidation of the protons. Assignments of the signals are based on the chemical shifts and intensity patterns. The  $H^1$ -NMR studies of the compound CEAB were done in DMSO- $d_6$ . The  $H^1$ -NMR data for compound show that the phenyl protons of the compound gave a multiplets at  $\delta$  = 6.76-7.62 ppm. The signals due to the  $-CH_2-CH_2$ -protons gave a multiplets at  $\delta$  = 3.00-3.80 ppm. The signals due to  $-CH=O$  proton gave singlet at  $\delta$  = 7.92 ppm strongly confirm aldehydic group present in CEAB.

### Unit Cell Determination

X-ray diffraction study was carried out using a Bruker axs kappa Apx II single crystal CCD diffractometer equipped with Mo ( $K\alpha$ ) ( $\lambda = 0.7107\text{\AA}$ ) radiation. The goniometer equipped with the diffractometer is four circle goniometer with  $\phi$ ,  $\chi$ ,  $\omega$  and  $2\theta$  axes by which the crystal is rotated. A crystal specimen of size 0.30 x 0.20 x 0.15 mm was cut and mounted on a glass fiber using cyanoacrylate. The unit cell parameters were determined by collecting the diffracted intensities from 36 frames measured in three different crystallographic zones and using the method of difference vectors followed by data collection at 293 K using  $\omega\phi$  scan modes.

### Structure Solution and Refinement

The structure was solved by direct methods using the program SHELXS 97 [6], which revealed the position of all non-hydrogen atoms, and refined on  $F^2$  by a full matrix least squares procedure using SHELXL 97. The non hydrogen atoms were refined anisotropically and the hydrogen atoms were allowed to ride over their parent atoms. The final cycle of refinement converged to  $R_1 = 0.0326$  and  $wR_2 = 0.0843$  for the observed reflections. The maximum and minimum heights in the final difference Fourier map were found to be 0.220 and  $-0.198 \text{ e \AA}^{-3}$  respectively. Least squares planes and asymmetry calculations were done using the program PARST 97. The thermal ellipsoid plot and packing were done, respectively, using ORTEP and PLATON [7, 8]. Non bonded interaction graphics were created using the program PLATON. The crystallographic data and methods of data collection, solution and refinement are shown in Table 2 and selected bond distances and angles in Table 3. The atomic coordinates and equivalent isotropic displacement coefficients are included in the deposited material (CCDC 861226) as a complete list of bond distances and angles.

### Result and Discussion

In the title compound *p*-[*N*, *N*-bis (2-chloroethyl) amino benzaldehyde,  $C_{11}H_{13}Cl_2NO$ , crystallizes in the monoclinic crystal system with space group *Cc*, Calculated density =  $1.349 \text{ Mg/m}^3$ ,  $V = 1211.62(10)$

**Table 2: Crystal data and structure refinement of *p*-[*N*, *N*-bis(2-chloroethyl) amino benzaldehyde**

Parameters	<i>p</i> -[ <i>N</i> , <i>N</i> - bis(2-chloroethyl) aminobenzaldehyde
Empirical formula	$C_{11}H_{13}Cl_2NO$
Formula weight	246.12
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>Cc</i>
Unit cell dimensions	a = 14.7579(8) Å alpha = 90 deg b = 9.3470(4) Å beta = 116.333(2) c = 9.8005(4) Å gamma = 90 deg
Z, Calculated density	4, 1.349 Mg/m <sup>3</sup>
Crystal size	0.30 x 0.20 x 0.15 mm
F(000)	512
Theta range for data collection	2.67 to 23.70 deg
Limiting indices	$-16 \leq h \leq 16$ , $-10 \leq k \leq 10$ , $-11 \leq l \leq 9$
Reflections collected/unique	4636/1645 [R(int) = 0.0244]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1645/8/148
Goodness-of-fit on $F^2$	1.048
Final R-indices [I[2 $\sigma$ (I)]]	$R_1 = 0.0326$ , $wR_2 = 0.0843$
R-indices (all data)	$R_1 = 0.0371$ , $wR_2 = 0.0884$
Largest diff. peak and hole	0.220 and $-0.198 \text{ e \AA}^{-3}$

$\text{\AA}^3$  with unit cell parameters a = 14.7579(8) $\text{\AA}$ ,  $\alpha = 90^\circ$ , b = 9.3470(4) $\text{\AA}$ ,  $\beta = 116.333(2)$ , c = 9.8005(4) $\text{\AA}$ ,  $\gamma = 90^\circ$ , final  $R_1$  and  $wR_2$  are 0.0326 and 0.0843 respectively. The analysis of the crystal structure reveals the aldehyde and bis(2-chloroethyl)amino groups are essentially coplanar with the attached benzene ring.

The distances in the aromatic ring are not completely uniform. The longest bond (approx. 140 pm) was found between the carbon atoms carrying the *p*-substituent C2-C3-C7 and C4-C5-C6. The

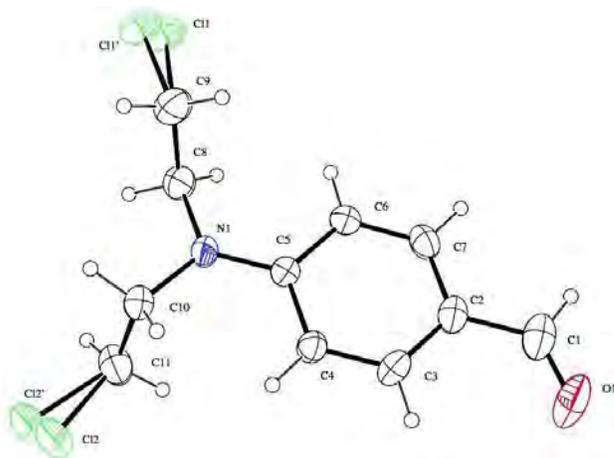
**Table 3: Selected Bond Lengths (Å) and Angles (deg) of p-[N, N-bis(2-chloroethyl)aminobenzaldehyde**

Bond length (Å)			
C(1)-O(1)	1.198(5)	C(1)-C(2)	1.448(5)
C(1)-H(1)	0.952(11)	C(2)-C(7)	1.383(5)
C(2)-C(3)	1.393(4)	C(3)-C(4)	1.363(4)
C(3)-H(3)	0.9300	C(4)-C(5)	1.403(4)
C(4)-H(4)	0.9300	C(5)-N(1)	1.371(4)
C(5)-C(6)	1.410(4)	C(6)-C(7)	1.366(4)
C(6)-H(6)	0.9300	C(7)-H(7)	0.9300
C(8)-N(1)	1.456(4)	C(8)-C(9)	1.496(5)
C(8)-H(8A)	0.9700	C(8)-H(8B)	0.9700
C(9)-Cl(1)	1.765(9)	C(9)-Cl(1')	1.784(4)
C(9)-H(9A)	0.9700	C(9)-H(9B)	0.9700
C(10)-N(1)	1.456(4)	C(10)-C(11)	1.504(5)
C(10)-H(10A)	0.9700	C(10)-H(10B)	0.9700
C(11)-Cl(2)	1.745(9)	C(11)-Cl(2')	1.778(4)
C(11)-H(11A)	0.9700	C(11)-H(11B)	0.9700
Bond angles (deg)			
O(1)-C(1)-C(2)	126.1(5)	C(10)-N(1)-C(8)	116.2(2)
C(7)-C(2)-C(1)	120.8(3)	C(9)-C(8)-H(8B)	109.4
C(3)-C(4)-C(5)	121.5(3)	Cl(1)-C(9)-H(9B)	111.1
C(7)-C(6)-H(6)	119.8	H(10A)-C(10)-H(10B)	108.0
C(2)-C(7)-H(7)	118.7	Cl(2)-C(11)-H(11B)	110.9

shortest bonds present in the compound are C6-C7 and C3-C4 may be due to the influence of the 2-chloroethyl amino group substituted at para position. This pattern was also found in the crystal structure of the 4-chlorobenzaldehyde and its derivatives [9, 10]. The bond lengths C<sub>9</sub>-Cl<sub>1</sub> (1.784 Å) and C<sub>11</sub>-Cl<sub>2</sub> (1.778 Å) are also significantly different, these type of bond length variations are due to the electron releasing capability of the chlorine to the benzene ring.

There is no such hydrogen bonding in the

molecule, which was further confirmed by using the vibrational spectra, splitting of the carbonyl stretching mode,  $\nu_{C=O}$  was found to be  $1682\text{ cm}^{-1}$ , assigned to the free carbonyl group, indicates the compound does not involve any inter or intra molecular hydrogen bonding. In the title compound, Bis(2-chloroethyl) amino moiety is disordered at the position of the atom Cl<sub>2</sub> and its disordered component Cl<sub>2</sub>' has the percentage of occupancy 67 % and 33 % respectively. The Ortep diagram of the title compound with 40 % ellipsoid probability showing the disordered component in Fig. 2.

**Fig. 2: Crystal structure of p-[N, N-bis(2-chloroethyl)aminobenzaldehyde**

## Conclusion

The solubility of the organic p-[N, N-bis (2-chloroethyl) aminobenzaldehyde was found to be higher in ethanol. Optical quality crystals were grown. The lattice parameter values of the crystal were found out from single crystal XRD studies. The compound can be used as a donor group for the preparation of organic NLO molecules, since it has -N(CH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub> and -C=O group.

## Supplementary Material

All crystallographic data for this paper are deposited with the Cambridge Crystallographic Data Centre (CCDC-861226). The data can be obtained free of

charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from Cambridge Crystallographic Data

Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44 (0) 1223-336033, E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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