Crystal structure of hexahydro-1,3,5-tri (p-chloro-phenyl)-s-triazine

Pratyush Purkayastha and A N Talukdar*

Department of Physics,
Gauhati University, Guwahati-781 014, Assam

E-mail . kkhlgu@gwl dot net/in

Abstract   The crystal structure of hexahydro-1,3,5-tri (p-chloro-phenyl)-s-triazine, $C_{21}H_{18}N_3Cl_3$ has been determined from intensity data collected using a CAD-4 diffractometer with $CuK\alpha$ radiation. The non-centrosymmetric molecule adopts a chair conformation with an equatorial – axial orientation of the p-chloro-phenyl group There is no hydrogen bond in the molecule and the crystal packing is determined by van der Waals interactions.

1. Introduction

A variety of chair, twist-boat and boat conformations can be considered for triazine with a pyramidal arrangement of bonds at the N atoms. The structure determination of the title compound was undertaken in order to see the influence of substituents as well as molecular conformation. The structural formula of the title compound is given below.
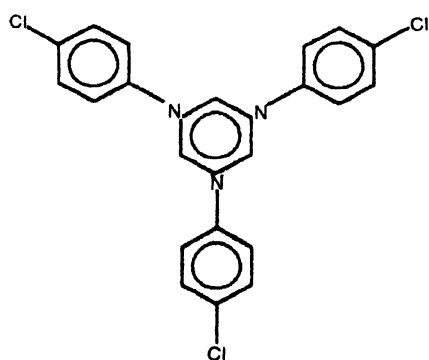
2. Experimental details

Synthesis of the title compound was carried out by the reaction of p-chloro aniline and formaldehyde in ethanol solution at room temperature and purification was done with the help of boiling petroleum ether. The insoluble high polymer was then removed by hot filtration. Table 1 shows the experimental data. Preliminary

oscillation and Weissenberg photographs indicated an orthorhombic crystal system, with systematic absences $k = 2n + 1$ for 0 k l, $k = 2n + 1$ for 0 k 0, $l = 2n + 1$ for h 0 l and $l = 2n + 1$ for 0 0 l reflections consistent with the space group Pbcm or Pbc2$_1$. Space group Pbcm although consistent with observed systematic absences, is not a correct space group. Because, introduction of mirror plane and inversion centre is not justified by the data presented in the Table 2. Hence, space group Pbc2$_1$ has been accepted as a correct one. 25 high angle reflections were used for refining the unit cell constants by the least-squares refinement method which are lying in the range $10^0 \le \theta \le 30^0$. Data were recorded up to 75^0 in 2θ by the $\omega - 2\theta$ scan technique. The intensities were corrected for the Lorentz and polarization factors and also for absorption.

3. Structure solution and refinement

The structure was solved by direct methods using the program SHELXS-97 [1]. The structure refinement was carried out using program SHELXL - 97 [2]. Full matrix least squares refinement, first isotropic and then anisotropic thermal parameters, gave an R value of 0.1225. At this stage all the hydrogen atoms were generated using a riding model and the final R value was found to be 0.0718. The function was minimized with weight $w = 1/[sigma^2(F_0^2) + (0.2000*P)^2]$ where $P = [$ Max $(F_0^2, 0) + 2*Fc^2]/3$.

Corresponding Author.

Table 1. The experimental data.

Chemical formula	$C_{21}H_{18}N_3Cl_3$
Colour	White
M_r	418 75
Melting point	410 K
Crystal system	Orthorhombic
Space group	$Pbc2_1$
Unit cell dimensions	a = 5 699(2) Å
	b = 21 879(3) Å
	c = 15 785(2) Å
Volume	1968.2(7) Å³
Z	4
Temperature	293(2) K
Crystal size	0 563 × 0 578 × 0 135 mm³
Density (calculated)	1 413 Mg /m³
F (000)	864
Absorption coefficient (mu)	0 43 mm⁻¹
Radiation	CuKα
Wavelength	1 5418 Å
θ (Theta) max	75°
Index ranges	0≤h≤7, -27≤k≤0, 0≤l≤19
Number of reflections collected	364
Number of independent/observed refls.	1999 / 1477 [$F_o > 4\sigma (F_o)$]
Absorption correction	Psi plot, using method of North *et al.*
Number of standard reflections	3
Standard interval count	100
Diff. standard interval time	60 min.
% decrease in intensity	none
Range of relative transm. factor	0 99 and 0 81
Refinement method	Full matrix least squares on F^2
Parameter	245
Goodness of fit on F^2	1.052
Final R	0 071
wR	0.2667
$\Delta\rho_{max}$	0 53 eÅ⁻³
$\Delta\rho_{min}$	- 0.41 eÅ⁻³
$(\Delta/\sigma)_{max}$	0 069

The final difference Fourier map showed peaks lying between 0.53 to - 0.41 eÅ⁻³. The atomic scattering factors used were taken from the International Tables for X-ray Crystallography Vol. IV [3].

Molecular geometry calculations were carried out using the program PARST [4]. The final value of fractional coordinates

and equivalent isotropic thermal parameters for all refined atoms are given in Table 2.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters (Å²) for non hydrogen atoms with e.s d 's in parenthesis

Atom	x	y	z	Uequiv*
Cl1	0.3727(9)	0.3349(3)	0.0808(3)	0 0972(8)
Cl2	0 6259(6)	0 8077(1)	0.3218(5)	0 0902(4)
Cl3	0 3652(9)	0 3351(2)	0.5618(3)	0 093(8)
N2	-0.0299(5)	0.5963(3)	0 3213(9)	0 0582(7)
C10	0 1104(6)	0.6501(3)	0 3232(9)	0 0541(9)
N3	-0 2428(3)	0 5199(6)	0 4008(8)	0 0617(8)
N1	-0.2493(5)	0.5186(7)	0 2479(9)	0 0701(3)
C1	0 1964(5)	0 3901(5)	0 1321(8)	0 0674(5)
C17	0 1272(2)	0 4936(6)	0 4624(9)	0 0548(4)
C4	-0.0841(3)	0.4751(5)	0.2124(7)	0 0562(4)
C2	0 2613(9)	0.4487(7)	0 1381(9)	0 0708(5)
C9	0 1974(9)	0 6743(7)	0.3954(3)	0 091(5)
C16	-0.0925(3)	0 4776(7)	0 4325(9)	0 0592(6)
C13	0 1958(7)	0 3884(6)	0 5106(7)	0 0745(5)
C20	-0 1849(3)	0 5797(9)	0 4032(9)	0 0699(7)
C19	-0.1663(9)	0 5844(6)	0 2508(9)	0 0608(5)
C3	0.1299(4)	0 4882(8)	0.1771(9)	0 0669(8)
C18	0.2740(6)	0 4480(6)	0 5051(9)	0 068(8)
C14	-0 0213(6)	0 3729(7)	0.4795(9)	0 0874(7)
C21	-0.3751(6)	0 5056(6)	0.3185(6)	0 0711(6)
C11	0 1864(5)	0 6764(8)	0 2464(9)	0 0773(7)
C15	-0 1626(9)	0 4143(6)	0 4372(9)	0 0719(9)
C5	-0 1531(3)	0 4148(7)	0 2021(6)	0 1051(8)
C7	0 4263(8)	0.7472(4)	0 3224(9)	0 0671(4)
C6	-0 0095(9)	0.3714(5)	0 1681(3)	0 0852(8)
C12	0.3292(3)	0.7276(8)	0 2457(9)	0 0804(4)
C8	0.3594(8)	0.7199(7)	0.3940(9)	0 0881(2)

* Uequiv = $1/3\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

4. Results and discussions

The ORTEP [5] diagram showing the numbering scheme of atoms and the thermal ellipsoids are given in the Figure 1. The packing of the molecule in the unit cell as viewed down the b axis is shown in the Figure 2.

The N - C ring bond lengths and the exocyclic N - C bond lengths are in the range 1.41(2) - 1.48(2)Å and 1.40(2) - 1.46(2)Å respectively. The CH₂-N-CH₂ angles and N-CH₂-N angles are 107.3(7)-109.9(1)° and 111.3(1)-113.2(7)° respectively, which are

in agreement with those observed for other triazine derivatives [10-11] From the analysis of the least squares planes, it has been observed that the three p-chloro phenyl rings are almost planar with maximum deviations of the atoms lying in the range – 0.006(2)Å to + 0.001(3)Å.
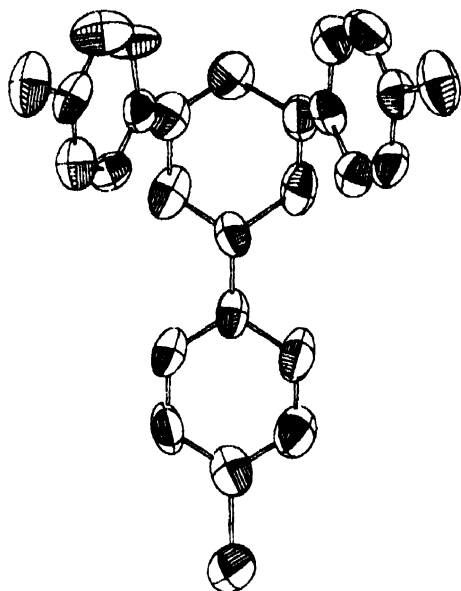

Figure 1. A view of the molecule with 50% probability anisotropic displacement ellipsoids for the non-H atoms and atomic numbering scheme
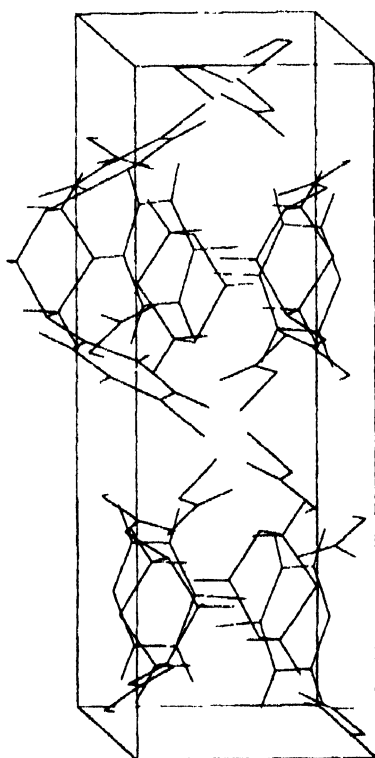

Figure 2. Packing of the molecules in the unit cell as viewed down the b-axis of the unit cell

From the analysis of the structure, it has been concluded that there is no triad axis to the central triazine ring which is similar to that observed in case of s-tri phenyl triazine [12] and 1,3,5 tri phenyl benzene [13]. This may be due to better packing and also for better gain in stability in the crystallization.

The dihedral angle between the planes defined by the atoms C1 – C6 and C7 – C12 is 114.2(6)° and that between C13 – C18 and C7 – C12 is 57.7(5)°. The dihedral angle between planes defined by the atoms N1 – C21 and C7 – C12 is 177.8(5)° from which it can be concluded that the lone pair of N2 forces the attached p-chloro phenyl unit in to an approximately equatorial position.

Similarly, the other lone pairs at N1 and N3 forces the respective p-chlorophenyl unit into the axial positon and thereby the structure confirms the comfortable accommodation and interconversions of p-chlorophenyl groups into equatorial – diaxial orientation. The same type of chair conformation with equatorial – axial configurations are also found in RDX [14] molecule.

Acknowledgments

References

[1] G M Sheldrick *SHELXS-97 Program for the Solution of Crystal Structures* (University of Gottingen, Germany) (1997)

[2] G M Sheldrick *SHELXL-97 Program for the Refinement of Crystal Structures* (University of Gottingen, Germany) (1997)

[3] *International Tables for X-ray Crystallography* IV (Birmingham Kynoch Press) (1974)

[4] M Nardelli *Comput Chem* 7 95 (1983)

[5] C K Johnson *ORTEPII, Report ORNL-5138* (Oak Ridge National Laboratory, Tennessee, USA) (1996)

[6] C S Choi, A Santoro and P L Marinkas *Acta Cryst* B31 2934 (1975)

[7] K Ogawa, S Yoshimura and Y Takeuchi *Acta Cryst* C48 1071 (1992)

[8] A Bouchemma, P H McCabe and G A Sim *Acta Cryst* C46 671 (1990)

[9] V R Thalladi, M Muthuraman, A Nangia and G R Desiraju *Acta Cryst* C55 698 (1999)

[10] V R Thalladi, A K Katz, H L Carrell, A Nangia and G R Desiraju *Acta Cryst* C54 86 (1998)

[11] M H Palmer, S Parsons, S Smith, A J Blake and M F Guest *Acta Cryst* C54 550 (1998)

[12] A Damiani, G Giglio and A Ripamonti *Acta Cryst* 19 161 (1965)

[13] M S Farag *Acta Cryst* 7 117 (1954)

[14] T M Haller, T B Brill and A L Rheingold *Acta Cryst* C40 517 (1984)