Designing a Non-centrosymmetric Crystal: Structure of 4′-Cyano-2,6-dimethyl-4-hydroxyazobenzene†

Jagarlapudi A. R. P. Sarma,*[a] Mudigonda S. K. Dhurjati,[a] K. Bhanuprakash*[a] and K. Ravikumar[b]

[a] *Inorganic and Physical Chemistry Division and* [b] *Laboratory of Crystallography, Indian Institute of Chemical Technology, Hyderabad, 500 007, India*

Utilising the preferential adoption of hydroxy–cyano hydrogen bond over the hydroxy–hydroxy hydrogen bond in molecular crystals, the crystal structure of 4′-cyano-2,6-dimethyl-4-hydroxyazobenzene is designed into an acentric space group.

Designing a non-centrosymmetric crystal to possess high second-harmonic generation properties using weak molecular interactions is yet to become a routine exercise for the solid-state chemist.[1] The recent literature on non-linear optical materials has hinted that substituted stilbenes, azobenzenes and benzylidines are potential candidates for obtaining high β values (high hyperpolarizability).[2] In general, a molecule with electron-withdrawing groups and electron-donating groups on either side, prefers to crystallise in a centrosymmetric space group owing to its high dipole moment. The generation of a non-centrosymmetric crystal structure by such a molecule using well recognised intermolecular interactions is the point of our interest here.

The literature on the O–H···N hydrogen bonding suggests that it is almost equal to if not slightly stronger than O–H···O bonding and a number of studies were carried out to correlate the O–H stretching frequencies to the hydrogen bond strengths.[3,4] To study the nature of O–H···N hydrogen bonding in organic crystal structures, a search on the Cambridge Structural Database (CSD) (1990 June version) excluding metal and transition elements, was performed which yielded 106 crystal structures containing both cyano and hydroxy groups.[5] Incidentally, 51 of these crystal structures adopt a non-centrosymmetric space group,‡ which is rather a large number (48%) compared with the normal value of *ca.* 28% for all the structures of CSD.[6] However, no direct correlation between the presence of the cyano and hydroxy groups and the crystallographic non-centrosymmetry was so far observed. Geometrical searches were carried out on 91 of these 106 structures. Structures containing polymer, error and disordered units were omitted. The fragment –C–C≡N···H–O–C– yielded 19 hits; mean N···H (O···N) distance is 2.07 (2.88) Å and mean O–H···N and H···N≡C angles are 160 and 150.5°, respectively. A similar search for the H–O′···H–O′ fragment (hydroxy group as a part of phenols and alcohols only) produced 15 hits; mean O···H (O···O) distance is 1.87 (2.76) Å and mean O–H···O angle is 164°.

In general, the crystal structure of planar aromatic molecules with sufficient nitrogen and/or oxygen atoms constitutes layers characterised by weakly attractive yet directional non-bonded interactions.[7,8] Such layers stack together by optimising a large number of van der Waals interactions.[1] If the crystal packing of a molecule containing both hydroxy and cyano groups is considered, the hydroxy group (alcohols/phenols) prefers to orient along the twofold/screw axis optimising O–H···O interactions,[9] and cyano groups adopts

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† IICT communication number 3129.

‡ 21 of these 106 structures are chiral molecules.

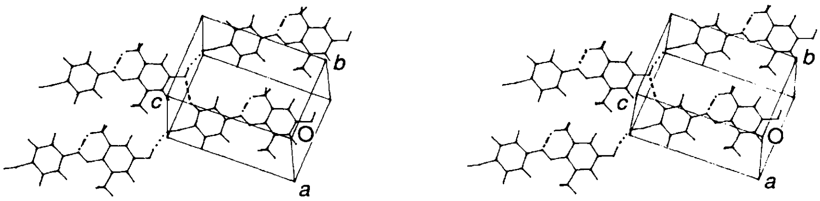
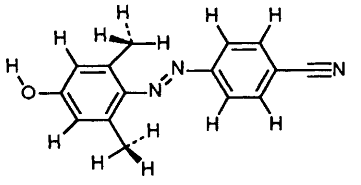


Fig. 1 Stereo diagram of **1**, showing a molecular sheet generated by translational molecules of one of the two independent molecules in the asymmetric unit. The intermolecular O–H···N (···), C–H···O (– – –) and intramolecular C–H···N (– · · – · · –) hydrogen bonding interactions are indicated.

Fig. 2 Stereo diagram of two independent molecules in the asymmetric unit of **1**, and are related by a pseudocentre of symmetry

an 'antiparallel' arrangement (usually leading to centrosymmetry) to optimise the dipole–dipole interactions along the layers.[10] However, if O–H···N≡C hydrogen bonding is preferred over O–H···O hydrogen bonding, then the crystal packing is more compatible with a layered structure. The centre of symmetry within a molecular layer could be removed by placing the -OH and -CN groups in 4 and 4′ positions of an azobenzene molecule so as to optimise the O–H···N≡C only by translationally related molecules. The centre of symmetry between the successive layers could be removed by making the molecule slightly non-planar, which could be achieved by placing one or two bulky substituents on one or two *ortho* positions of the phenyl ring. In accordance with this scheme, 4′-cyano-2,6-dimethyl-4-hydroxyazobenzene, **1** was synthesised and its crystal structure was solved.[§]

The compound, **1** was prepared by diazotization of 4-cyanoaniline and subsequent coupling with 3,5-dimethylphenol at 0 °C and characterized by UV, IR, ^{1}H NMR and mass spectral data. UV (MeOH) peak A (λ_{max} 368 nm, ε 34966 π–π^*), peak B (α_{max} 466 nm, ε 2913 n–π^*); IR (KBr) 3362–2325, 2240, 1590, 1435, 1310, 1220, 1140 and 850 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.55 (s, 6H), 5.45 (s, 1H), 6.6 (d, 2H), 7.85 (dd, 8 Hz, 4H); *m/z*(%) 251 ($M^{+\cdot}$) (15), 149 ($M^{+\cdot}$ – $C_7H_4N_1$)(5), 121 (149 – N_2) (100). The UV spectra were recorded in various solvents of different polarities, such as methanol, ethanol, acetone, chloroform, dichloromethane, benzene and hexane. A shift of 9 nm for π–π^* (bathchromic) and n–π^* (hypsochromic) transitions were observed from methanol to hexane. The compound was recrystallized from methanol to yield red, long and thick needles.[¶]



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There are two independent molecules in the asymmetric unit which are related only by a pseudocentre of symmetry. They are mutually opposite in their conformation, the difference is mainly around the central >C–N=N–C< region (Fig. 1). Cyanobenzene and phenol ring planes make an angle of 17.4; 11.14° (molecule 1) and −15.88; −10.22° (molecule 2), respectively with the central azo plane. The near planarity of the molecule could be a result of an intramolecular N···H–CH$_2$– weak hydrogen bonding (H···N 2.04 and 2.08 Å and C···N 2.81 and 2.85 Å for molecules 1 and 2, respectively) resembling a six-membered ring (Fig. 2). In these two molecules, the conformations are locked in two minima of a double well potential surface. In addition to the different molecular geometry between two molecules in the asymmetric unit, the non-centrosymmetric space group *P*1 was also confirmed by (*a*) unsuccessful refinement in *P*$\bar{1}$ space group,[||] (*b*) a nearly identical match was observed between experimental and calculated X-ray powder spectra in *P*1 space group and (*c*) a total mismatch between these two spectra when the calculated spectrum was computed in the *P*$\bar{1}$ space group.[11]

As predicted previously, the crystal structure lacks the centre of symmetry. Each independent molecule of the asymmetric unit generates a layer with its own translational molecules and one such layer is shown in Fig. 2. However, two successive layers are formed along [1 0 0] by two independent molecules in the asymmetric unit and hence the layers are again related by a pseudocentre of symmetry. In a layer, each molecule is held firmly by two strong O–H···N (H···N 1.94 Å, O···N 2.88 Å in layer 1; H···N 1.95 Å, O···N 2.88 Å in layer 2) and two relatively weak C–H···O (H···O 2.61 Å, C···O 3.52 Å in layer 1; H···O 2.71 Å, C···O 3.58 Å in layer 2) hydrogen bonding interactions by molecules *x*, −1 + *y*,1 + *z* and *x*,1 + *y*, −1 + *z* along the long axis ends, as shown in Fig. 2. Thus the deviation from real centre of symmetry is due to non-planarity of the molecule as predicted previously. The mutually opposite conformations in the two independent molecules is probably an attempt to optimise the stacking and/or charge-transfer interactions along the stack direction as shown in Fig. 1. The lack of any other short contacts of considerable importance especially sideways in a sheet, resulted in low packing coefficient of 0.71 and density of 1.24 g cm^{-3}. The packing energy calculations using Williams potentials,[12] gave

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[§] *Crystal data* for **1**: $C_{15}H_{13}N_3O$, M = 173, m.p. 182 °C, triclinic, space group *P*1, 298 K, a = 7.523(2), b = 8.099(2), c = 12.097(3) Å, α = 92.76(2), β = 91.68(2), γ = 116.72(2)°, V = 656.5(2) Å^3, $F(000)$ = 264, Z = 2, D_c = 1.27 g cm^{-3}, D_m = 1.24 g cm^{-3}, μ(Mo-Kα) = 0.08 mm^{-1}, crystal size 0.20 × 0.18 × 0.25 mm. 1518 Independent reflections with $I > 3\sigma(I)$ from 1828 observed reflections. C, N, O anisotropic, R = 0.0473; R_w = 0.0547 $w = 1.0/[\sigma^2(F) + (0.029\ F)^2]$. Even though all hydrogen atoms could be located in the difference Fourier map and refined satisfactorily, their positions were fixed at 1.00 Å to assist in further calculations and their thermal parameters to a value of 0.08 Å^2. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[¶] Some crystals are as large as 3 × 0.7 × 0.4 cm.

[||] The lowest R factor obtained was 0.36 at which all the bond lengths and angles changed to unacceptable values.

an estimated lattice energy as -222.25 kJ mol^{-1} in which the coulombic contribution is -14.98 kJ mol^{-1}.

The O–H stretching frequencies of **1** obtained by FTIR are 3596 (solvent CCl_4) and 3362 cm^{-1} (Nujol or KBr). Hence, a shift of 234 cm^{-1} (strength *ca.* 23 kJ mol^{-1}) is attributed to the intermolecular O–H···N hydrogen bonding.[13] MACROMODEL[14] using MM2 force field gave an estimated energy of 17.99 kJ mol^{-1} for the same intermolecular hydrogen bond. Semi-empirical AM1 calculations failed to reproduce the experimental geometry (optimised H···N distance is 2.72 Å) and the estimated hydrogen bonding energy is only 5.44 kJ mol^{-1}. However, the calculations with the recently developed PM3 parameters produced the hydrogen bonding distance of 1.83 Å and an energy of 5.86 kJ mol^{-1}.[6] Finite Field approach of the energy expansion was used to calculate the hyperpolarizabilities.[15] The MNDO hamiltonian using the PM3 parameters yielded a β_o value of *ca.* 10.3×10^{-30} esu units which is nearly of the same magnitude as that of *p*-nitroaniline. Efforts to measure the β value for this compound and other related compounds are in progress.

While there have been some reports on designing organic mixed crystals using hydrogen bonding and other weakly attractive interactions,[16,17] this attempt to design an organic crystal of a molecule containing both electron-donating and withdrawing groups (large hyperpolarizability) into an acentric space group is the first example though it was met with a partial success. In the sense that a real crystallographic non-centrosymmetric structure could not be obtained, instead a geometrically non-centrosymmetric (pseudo-centrosymmetric) structure was obtained. Such a structure may not be compatible with the requirements of the above mentioned physical properties.

We thank Dr A. V. Rama Rao, Director, IICT and Professor G. R. Desiraju, University of Hyderabad for their interest in this work. We also thank Dr A. Krishna Murthy, IICT for recording FTIR spectra and Dr M. W. Pandit, Coordinator, DIC-Bioinformatics, CCMB for extending the facility of a microVAX computer. One of us (M. S. K. D.) thanks CSIR for a Junior Research Fellowship.

Received, 30th October 1992; Com. 2/05821I

References

1 G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989, pp. 225–260.
2 A. Ulman, C. S. Willand, W. Kohler, D. R. Robello, D. J. Williams and L. Handley, *J. Am. Chem. Soc.*, 1990, **112**, 7083.
3 H. H. Freedman, *J. Am. Chem. Soc.*, 1961, **83**, 2900.
4 R. S. Drago, *Physical Methods in Inorganic Chemistry*, Litton Educational Publishing, New York, 1965.
5 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320; and references cited therein.
6 P. Camilleri, C. A. Marby, B. Odell, H. S. Rzepa, R. N. Sheppard, J. J. P. Stewart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1989, 1722.
7 J. F. Nicoud and R. Tweig, in *Non-linear Optical Properties of Organic Molecules and Crystals*, ed. J. Zyss and D. S. Chemla, Academic, Orlando, 1987, vol. 1, p. 242.
8 J. A. R. P. Sarma and G. R. Desiraju, *Acc. Chem. Res.*, 1986, 220.
9 N. W. Thomas and G. R. Desiraju, *Chem. Phys. Lett.*, 1984, **110**, 99.
10 M. S. K. Dhurjati, J. A. R. P. Sarma and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1991, 1702.
11 LAZY PULVERIX, K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr.*, 1977, **10**, 73.
12 D. E. Williams, *A Crystal Molecular Packing Analysis Program*, QCPE No. 548, Indiana University, Bloomington, USA, 1983.
13 R. S. Drago and T. D. Epley, *J. Am. Chem. Soc.*, 1969, **91**, 2883.
14 C. Still, MACROMODEL, A *Molecular Modelling Program*, Version 2.5, Columbia University, New York, 1987.
15 H. A. Kurtz, J. J. P. Stewart and K. M. Dieter, *J. Comp. Chem.*, 1990, **11**, 82.
16 M. C. Etter and G. M. Frankenbach, *Chem. Mater.*, 1989, **1**, 10.
17 C. V. K. Sharma, K. Paneerselvam, T. Pilati and G. R. Desiraju, *J. Chem. Soc., Chem. Commun*, 1992, 832, and references cited therein.