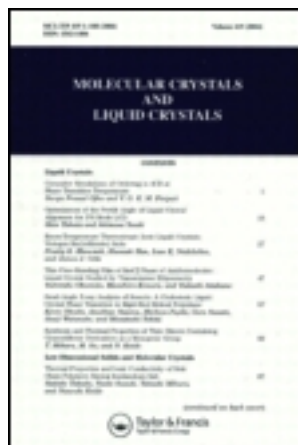


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Prediction of Non-Centrosymmetric Packing for 1,3-Disubstituted Nitro Aromatics. Crystal and Molecular Structure of 3-Hydroxy-6-(3'-nitro)-phenylazopyridine

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The crystal and molecular structure of 3-hydroxy-6-(3'-nitro)-phenylazopyridine is reported. The crystals are non-centrosymmetric, $Pna2_1$, $Z = 4$, $a = 16.522(3)$, $b = 8.402(2)$, $c = 7.945(1)$ Å, and the structure refined to an R-value of 0.046 on 1086 non-zero reflections. The molecule exists as the hydroxyazo tautomer and is intermolecularly O—H . . . N hydrogen bonded in the crystal. The title compound is one of several 1,3-disubstituted benzenes which adopt non-centrosymmetric packing, a necessary prerequisite for nonlinear second harmonic generation. Analysis of nearly 600 nitroaromatic crystal structures retrieved from the Cambridge Structural Database shows that 1,3-disubstitution significantly increases the probability of non-centrosymmetric space group adoption when compared to 1,2 or 1,4-disubstitution. Similar though less pronounced trends are observed for trisubstituted and higher derivatives.

INTRODUCTION

There has been much interest in obtaining single crystals of organic compounds which lack a centre of symmetry since such crystals are expected to show a non-linear Second Harmonic Generation (SHG) effect upon suitable irradiation.^{1,2} Although early demonstrations of SHG involved inorganic materials like quartz, it has been realised that organic compounds have SHG efficiencies that are greater by several orders of magnitude. A trivial means of ensuring crystallization in a non-centrosymmetric space group is to use a resolved material but such substances are, in general, neither very common

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nor need they exhibit sizable SHG effects since non-centrosymmetry is a necessary though not a sufficient condition for good SHG.

For these reasons, it is useful to be able to predict if a given substance, which is not optically active in solution, would spontaneously resolve and pack in an enantiomorphous (and necessarily non-centrosymmetric) space group.³ However, correlations between molecular structure and the tendency to adopt non-centrosymmetric packing are sparse and empirical.

This study was prompted by the observation that the meta-nitro azo dye 1 crystallizes in the non-centrosymmetric space group $Pna2_1$, while the corresponding para-derivative 2 adopts a centrosymmetric packing ($P2_1/n$).⁴ This observation is seemingly in accord with a well-known generalisation that for disubstituted benzenes, the meta isomer may have a greater tendency for non-centrosymmetric space group adoption than the ortho or para derivatives.⁵

Additionally, we note that the nitro group is expected to enhance the SHG effect in organic molecules through electron delocalisation. In fact, this group is present in many molecules which are known to have good SHG properties.⁶⁻⁸ This paper therefore describes the crystal structure of azo dye 1 and seeks to establish systematically, using the Cambridge Structural Database, whether 1,3-substitution in an aromatic nitro compound is expected to significantly increase the likelihood of non-centrosymmetric space group adoption.

Experimental

Dye 1 was prepared by diazotisation of 3-nitroaniline and coupling into 3-hydroxypyridine, orange-red needles from ethanol, data collected on an Enraf-Nonius CAD-4, $M_r = 244$, $Pna2_1$, $a = 16.522(3)$, $b = 8.402(2)$, $c = 7.945(1)$ Å, $V = 1102.9(6)$ Å³, $Z = 4$, $D_x = 1.49$ Mg m⁻³, λ (Cu K_α) = 1.54178 Å, μ (Cu K_α) = 8.44 mm⁻¹, maximum $\sin \theta/\lambda = 0.62$ Å⁻¹, standards ($-1 -1 3$, $-1 -2 2$) did not vary more than 6%, 1376 reflections measured, 1086 unique non-zero reflections at the 1.5σ significance level, structure solution with SHELXS-86,⁹ least-squares refinement using F^2 's, hydrogens located and refined isotropically, all other atoms refined anisotropically, $R = 0.046$, $R_w = 0.048$, $w = 0.73 \{[\sigma(F_o)]^2 + (0.03F_o)^2\}$ where $\sigma(F_o)$ is the standard deviation based on counting statistics, maximum least-squares shift-to-error in final refinement cycle 0.02, maximum peak height in final difference Fourier synthesis $0.21e$ Å⁻³, $F(000) = 504$, scattering factors from 'International Tables for X-ray Crystallography' (1974), refinements carried out with SHELX-76 (Sheldrick, 1976).

The studies on space group statistics were carried out with the 1985 version of the Cambridge Structural Database and the accompanying program GEOM78.¹⁰

All calculations were carried out with the OMC 58000 and ICIM 6000 computers at the University of Hyderabad.

RESULTS AND DISCUSSION

Molecular and crystal structure of compound 1

The atomic coordinates are reported in Table I. Figure 1 shows the atom-numbering scheme. Intramolecular bond lengths and angles are given in Table II. The phenyl and pyridyl rings are nearly planar and

TABLE I

Atomic coordinates in fractional crystal coordinates and equivalent isotropic values of the anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Estimated standard deviations are given in parentheses.

$$U = \sqrt[3]{U_{11}U_{22}U_{33}}$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i>
C(1)	0.2506(4)	0.4017(6)	0.0869(1)	0.040(3)
C(2)	0.2545(3)	0.3244(5)	0.2409(9)	0.034(5)
C(3)	0.2944(3)	0.3994(6)	0.3717(9)	0.038(3)
C(4)	0.3287(3)	0.5488(6)	0.3437(9)	0.038(3)
C(5)	0.3220(3)	0.6146(5)	0.1854(9)	0.035(3)
C(6)	0.4075(3)	1.0035(5)	0.1970(10)	0.037(3)
C(7)	0.3966(3)	0.0617(5)	0.0359(10)	0.041(3)
C(8)	0.4298(3)	0.2095(5)	−0.0003(10)	0.041(3)
C(9)	0.4729(4)	0.2943(7)	0.1183(12)	0.050(4)
C(10)	0.4811(4)	0.2355(7)	0.2727(12)	0.062(4)
C(11)	0.4467(4)	0.0888(7)	0.3186(11)	0.055(4)
N(1)	0.3522(3)	0.7684(4)	0.1352(8)	0.039(2)
N(2)	0.3777(3)	0.8483(5)	0.2537(9)	0.044(2)
N(3)	0.2845(3)	0.5433(4)	0.0582(8)	0.036(2)
N(4)	0.4206(3)	0.2724(5)	−0.1705(10)	0.060(3)
O(1)	0.3796(4)	0.1992(6)	−0.2691(10)	0.100(4)
O(2)	0.4520(4)	0.3974(5)	−0.2050(10)	0.094(4)
O(3)	0.2184(4)	0.1812(4)	0.2513(8)	0.047(2)
H(1)	0.219(3)	0.357(6)	−0.008(7)	0.05(2)
H(3)	0.297(3)	0.351(5)	0.472(7)	0.03(1)
H(4)	0.366(3)	0.595(5)	0.438(6)	0.03(1)
H(7)	0.373(2)	0.016(5)	−0.061(7)	0.03(1)
H(9)	0.497(4)	0.368(7)	0.087(9)	0.07(2)
H(10)	0.496(4)	0.271(8)	0.375(10)	0.09(3)
H(11)	0.445(3)	0.046(7)	0.444(9)	0.06(2)
H(0)	0.217(4)	0.143(8)	0.369(10)	0.07(2)

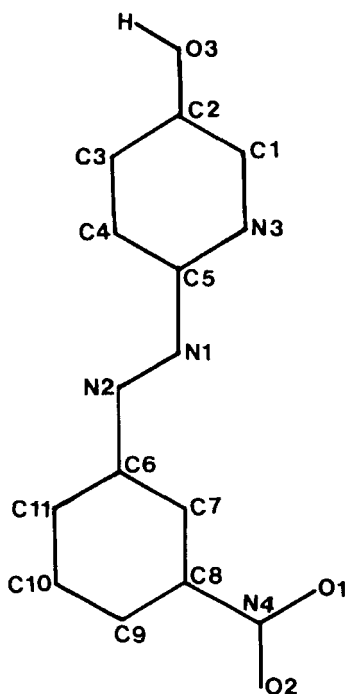


FIGURE 1 Atom—labelling scheme for the title compound.

make an angle of 0.65° with each other and angles of 9.25° and 9.78° respectively with the plane formed by the central atoms C(5), N(1), N(2), and C(6). The bond lengths show that the compound definitely exists as the hydroxyazo tautomer. Not only is the N(1)—N(2) distance ($1.231(6)\text{\AA}$), typical of an azo group (1.24 \AA in azobenzene) but the C(2)—O(3) distance ($1.346(5)\text{\AA}$) is indicative of a pyridinol. In the azo form, one could also expect the C(5)—N(1) and C(6)—N(2) distances to be nearly the same. That this is the case is evident from the respective bond lengths [C(5)—N(1) $1.442(6)\text{\AA}$, C(6)—N(2) $1.465(6)\text{\AA}$].

Clear evidence that the compound is a hydroxyazo tautomer was also provided by the location of the phenolic hydrogen H(O) in the difference Fourier synthesis and its successful refinement to give an O(3)—H(O) bond length of $0.99(7)\text{\AA}$. Indirect evidence of the presence of the hydroxyazo form is the intermolecular hydrogen bonding arrangement where the phenolic O(3) of (x, y, z) is situated at 2.70 \AA from the heterocyclic N(3) of $(1/2 - x, 1/2 + y, -1/2 + z)$. Such a hydrogen-bonding scheme is consistent only with $-\text{O}-\text{H} \cdots \text{N}$

TABLE II

Bond lengths in Å and bond angles in degrees (e.s.d.'s in parentheses) for compound 1

Bond	Bond length	Bond	Bond length
C(1)—C(2)	1.387(6)	C(2)—C(3)	1.383(7)
C(3)—C(4)	1.395(7)	C(4)—C(5)	1.378(7)
C(6)—C(7)	1.382(8)	C(7)—C(8)	1.387(6)
C(8)—C(9)	1.380(8)	C(9)—C(10)	1.330(11)
C(10)—C(11)	1.405(9)	C(1)—N(3)	1.334(6)
C(5)—N(3)	1.329(6)	C(5)—N(1)	1.442(6)
N(1)—N(2)	1.231(6)	C(6)—N(2)	1.465(6)
C(8)—N(4)	1.459(8)	N(4)—O(1)	1.205(7)
N(4)—O(2)	1.203(5)	C(2)—O(3)	1.346(5)
O(3)—H(0)	0.99(7)		
Bond angle			
C(2)—C(1)—N(3)			123.3(5)
C(1)—C(2)—C(3)			118.2(4)
C(1)—C(2)—O(3)			116.9(4)
C(3)—C(2)—O(3)			124.9(4)
C(2)—C(3)—C(4)			118.9(5)
C(3)—C(4)—C(5)			118.3(5)
C(4)—C(5)—N(3)			123.4(4)
C(4)—C(5)—N(1)			125.8(5)
N(3)—C(5)—N(1)			110.8(4)
C(7)—C(6)—C(11)			122.1(5)
C(7)—C(6)—N(2)			123.8(5)
C(11)—C(6)—N(2)			114.2(5)
C(6)—C(7)—C(8)			117.3(5)
C(7)—C(8)—C(9)			121.6(6)
C(7)—C(8)—N(4)			118.4(5)
C(9)—C(8)—N(4)			119.9(5)
C(8)—C(9)—C(10)			119.4(6)
C(9)—C(10)—C(11)			121.6(7)
C(10)—C(11)—C(6)			117.9(6)
C(5)—N(1)—N(2)			113.3(4)
C(6)—N(2)—N(1)			111.5(5)
C(1)—N(3)—C(5)			117.9(4)
C(8)—N(4)—O(1)			118.4(5)
C(8)—N(4)—O(2)			118.9(6)
O(1)—N(4)—O(2)			122.7(6)

bonding, that is with the molecule existing as the hydroxyazo tautomer.

A stereodrawing of the molecular packing down [001] with the following symmetry elements: $x, y, z; 1 - x, 1 - y, 0.5 + z; 0.5 + x, 1.5 - y, z; 0.5 - x, -0.5 + y, 0.5 + z$; is shown in Figure 2. In accordance with the polar space group $Pna2_1$, molecules are packed such that all the $-\text{NO}_2$ groups point towards $+\underline{c}$, while all the $-\text{OH}$

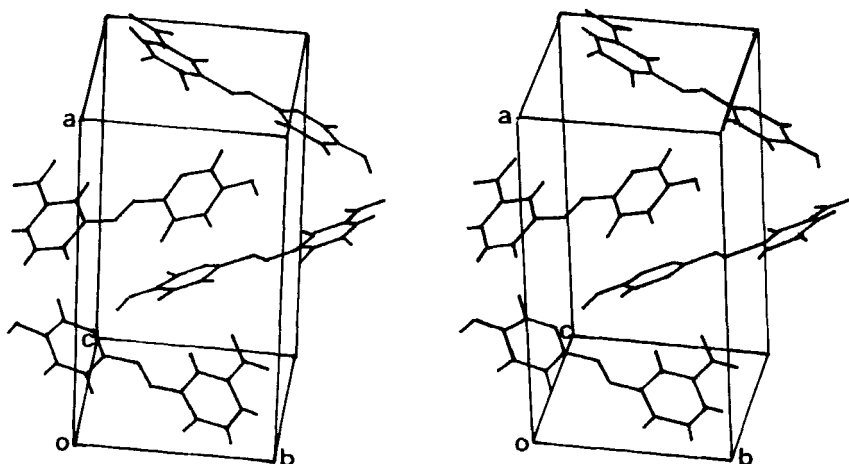


FIGURE 2 Stereodrawing of the crystal packing of the title compound down [001].

groups point towards $-c$. In this respect there is a certain resemblance to the crystal structure of 3-nitroaniline (space group $Pbc2_1$) where also the nitro groups point in the same sense along the polar direction c . This latter compound, incidentally, is known to show significant SHG properties and has been extensively studied.¹¹ Incidentally, the assignments $+c$ and $-c$ for the $-\text{NO}_2$ and $-\text{OH}$ groups are only relative. No attempt was made to determine the absolute direction of the polar axis.⁵

Adoption of non-centrosymmetric packing by nitro-aromatics

Of the 1218 nitro compounds in the Cambridge Structural Database (1985 version), 594 were found where at least one nitro group is substituted on an isocyclic or heterocyclic 6-membered aromatic ring which may or may not be part of a fused-system. These 594 compounds were analysed further whereupon 457 (77%) compounds were found to adopt centrosymmetric space groups while 137 (23%) adopt non-centrosymmetric space groups.

Of the 457 centrosymmetric crystals, 124 are racemates of chiral molecules, so only 333 are crystals containing molecules that would be achiral in fluid media. Of the 137 non-centrosymmetric crystals, 59 are composed of resolved molecules containing at least one asymmetric carbon atom; adoption of a non-centrosymmetric space group is inevitable in these cases. The remaining 78 compounds are the ones of interest to the problem at hand, namely the design of achiral

TABLE III

Space group distribution for 78 achiral nitroaromatic compounds adopting non-centrosymmetric space groups

	Number	Percentage
P2 ₁ 2 ₁ 2 ₁	21	26.9
Pna2 ₁	17	21.8
P2 ₁	12	15.4
Pca2 ₁	9	11.5
Pc	6	7.7
P4 ₁ 2 ₁ 2	3	3.9
others	10	12.8

molecules which are likely to adopt non-centrosymmetric packing arrangements. Table III gives the distribution by space group of these 78 compounds. Of the total of 411 (333 + 78) achiral molecules examined in the final study, 81% crystallise in a centrosymmetric arrangement while 19% are non-centrosymmetric.

More pertinent space group statistics for the 78 non-centrosymmetric and 333 centrosymmetric achiral compounds are given in Table IV from which it may be seen that the space groups P2₁/c and P $\bar{1}$ are common when the compound crystallises in a centrosymmetric arrangement, while P2₁2₁2₁ and Pna2₁ are common for non-centrosymmetric arrangements.

The 411 (333 + 78) achiral compounds were next taken according to their substitution type: (a) disubstituted: 1,2; 1,3; 1,4; (b) trisubstituted (mono nitro): 1,2,3; 1,2,4; 1,3,5; (c) trisubstituted (dinitro):

TABLE IV

Space group distribution for 411 achiral nitroaromatic compounds adopting centrosymmetric and non-centrosymmetric space groups

	Number	Percentage
P2 ₁ /c	194	47.2
P1	76	18.5
C2/c	24	5.8
P2 ₁ 2 ₁ 2 ₁	21	5.1
Pna2 ₁	17	4.1
P2 ₁	12	2.9
Pca2 ₁	9	2.2
Pbcn	9	2.2
others	49	11.9

Total Centrosymmetric compounds = 333 (81%)

Total Non-centrosymmetric compounds = 78 (19%)

1,2,3; 1,2,4; 1,3,5; 1,2,3; 1,3,4; 1,2,4; (d) 1,3,5; trinitro, (e) tetra and higher substituted. Table V is a tabulation of the number of compounds adopting centrosymmetric and non-centrosymmetric packing in all these cases. The percentage of non-centrosymmetric structures (last column) must be compared with the overall figure of 19% for all achiral nitro-substituted compounds.

Table V shows some interesting trends. There is definitely a strong tendency for non-centrosymmetric space group adoption in 1,3-disubstituted benzenes, while 1,4-disubstituted compounds show no particular preference for centrosymmetric or non-centrosymmetric

TABLE V

Distribution of centrosymmetric and non-centrosymmetric space groups for 411 achiral nitroaromatics according to substitution type (does not include title compound)

Substitution type	Centro-symmetric structures	Non-centro-symmetric structures	% of non-centro-symmetric structures
-------------------	-----------------------------	---------------------------------	--------------------------------------

Disubstituted:

1,2	28	4	12.5
1,3	12	8	40.0
1,4	103	26	20.2

Trisubstituted (mono nitro):


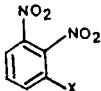
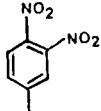
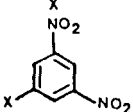
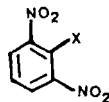
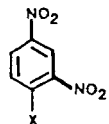
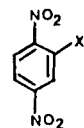
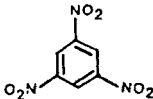
	1,2,3	9	3	25.0
	1,2,4	45	8	15.1
	1,3,5	0	0	—

TABLE V *Continued*

Substitution type	Centro-symmetric structures	Non-centro-symmetric structures	% of non-centro-symmetric structures	
<i>Trisubstituted (dinitro):</i>				
	<u>1,2,3</u>	0	0	—
	<u>1,2,4</u>	3	0	—
	<u>1,3,5</u>	3	0	—
	<u>1,2,3</u>	2	1	33.3
	<u>1,3,4</u>	32	3	8.6
	<u>1,2,4</u>	0	0	—
<i>Structures involving 1,3,5-trinitrobenzene:</i>				
	22	2	8.3	
<i>Tetra & higher substituted:</i>				
	78	20	20.4	

packing. However, 1,2-disubstituted compounds seem to distinctly prefer centrosymmetric space groups.

The trends for trisubstituted (mono-nitro) benzenes are more uncertain. While 1,2,4 substitution favours centrosymmetric packing, 1,2,3 derivatives seem to marginally prefer non-centrosymmetric space groups. But, there is a paucity of examples in these cases and it might be difficult to draw firm conclusions. Among the trisubstituted dinitro compounds 1,3,4 substitution strongly favours centrosymmetry which accounts for 32 out of 35 compounds in this group. This is also the case for 1,3,5-trinitrobenzene and some 20 odd molecular complexes involving this compound. Of the 24 structures found, 22 are centrosymmetric. The tetra and higher substituted compounds (one or more nitro groups) involve most of the fused ring derivatives and the trends are close to the average situation (19% non-centrosymmetric).

From these data it is possible to state that there is a much better chance for non-centrosymmetric packing in 1,3-disubstituted nitro aromatics as compared to 1,2 and 1,4 derivatives. Similar correlations may be applied to trisubstituted and higher derivatives.

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Supplementary Material

Atomic co-ordinates, thermal parameters and F_o/F_c tables for compound 1 (6 pages).

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