Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2,3,4,5,6-Pentanitroaniline 1,2-dichloroethane disolvate: 'push–pull' deformation of aromatic rings by intramolecular charge transfer

Sergiy V. Rosokha, Jian Jiang Lu, Sergey M. Dibrov and Jay K. Kochi*

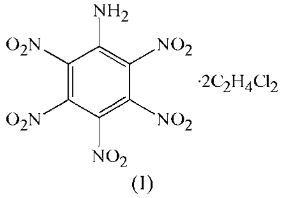
Department of Chemistry, University of Houston, 4800 Calhoun, Houston, TX 77204, USA
Correspondence e-mail: jkochi@uh.edu

Received 24 May 2006
Accepted 1 June 2006
Online 14 July 2006

The title compound, $C_6H_2N_6O_{10}{\cdot}2C_2H_4Cl_2$, forms layered stacks of pentanitroaniline molecules, which possess twofold symmetry. The voids between these stacks are occupied by dichloroethane molecules, which reside near a 2/*m* symmetry element and display pseudo-inversion symmetry. The C atoms in one of the two solvent molecules are threefold disordered. In the pentanitroaniline molecule, considerable distortion of the benzenoid ring, coupled with the short C—N(H_2) bond and out-of-plane NO_2 twistings, point to significant intramolecular 'push–pull' charge transfer at the amino- and nitro-substituted (*ortho* and *para*) positions, as theoretically quantified by natural bond orbital analysis of the π-electron density.

Comment

Organic molecules with pronounced intramolecular charge transfer have recently attracted significant attention owing to their potential solid-state applications (Lee *et al.*, 2001; Techert & Zachariasse, 2004; Perepichka *et al.*, 2001, 2002). Such 'push–pull' systems usually consist of bridged but relatively independent donor and acceptor constituents, and structural/spectroscopic studies have focussed on the effects of charge distribution between these parts, which vary between limiting neutral and ionic states (Yang *et al.*, 2002; Thallapally *et al.*, 2002).



(I)

In this communication, we turn to the structural effects of the intramolecular charge transfer in pentanitroaniline, which contains intimately bonded donor and acceptor parts. This molecule was prepared according to a literature procedure (Nielsen *et al.*, 1980) and crystallized as the dichloroethane disolvate, (I). As shown in Fig. 1, the pentanitroaniline molecule exhibits C_2 symmetry, with the C—N(amine) and C—N(*para*-nitro) bonds lying along the twofold rotation axis. Two crystallographically independent solvent molecules reside near a 2/*m* symmetry element and display pseudo-inversion symmetry. One of the two solvent moleules has ordered Cl atoms but threefold disorder amongst the C atoms, with C6 in a general position and C7 residing on a mirror plane. The packing diagram (Fig. 2) shows layers in which pentanitroaniline molecules are arranged in a rectangular fashion, with centroid-to-centroid distances of *c*/2 and *b*/2. Two adjacent layers, separated by 3.799 (3) Å, are shifted by $\frac{1}{2}$ along the *c* axis, which leads to the formation of stacks in which aromatic rings from every other layer are positioned directly below each other. Solvent molecules occupy the voids between these stacks in the *ac* plane.

The pentanitroaniline molecule contains an essentially planar but distorted aromatic ring (Fig. 1), in which the C1—C2 bond is significantly longer than the C2—C3 and C3—C4 bonds (Table 1), and the former is comparable to the average carbon–carbon bond length of 1.442 Å in 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965). It is notable that the structures of hexaaminobenzene (Dixon *et al.*, 1989) and hexanitrobenzene (Akopyan *et al.*, 1966) are both characterized by C—C bond lengths close to the standard aromatic value, *viz.* 1.39 Å. As such, the lengthening of the C—C bonds adjusted to the amine group in (I) is apparently related to the presence of both strong donor and strong acceptor substituents. Another feature of pentanitroaniline is the very short C1—N1 bond, compared with 1.432 Å in 1,3,5-triamino-2,4,6-trinitrobenzene, which is consistent with electron release from the amino group. On the other hand, the acceptor part of (I) shows that (i) the C3—N3 bond is longer than the C2—N2 and C4—N4 bonds (Table 1), and (ii) the twistings of the NO_2 groups relative to the benzene core are more pronounced in *meta* positions (torsion angle of 65.6°) than in *ortho* and *para* positions (the angles are 36.3 and 39.5°, respectively). The earlier studies of nitrobenzene derivatives showed that

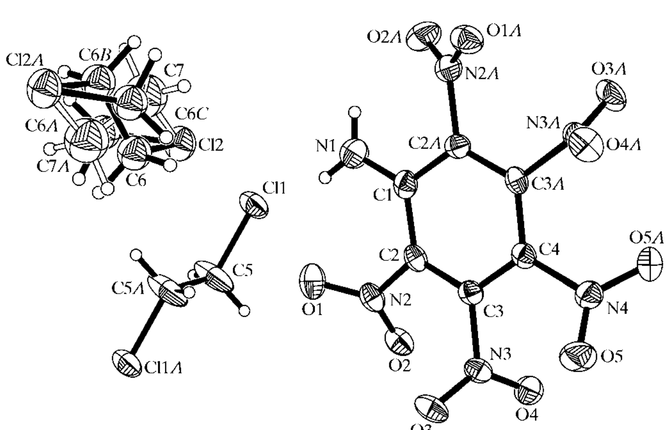


Figure 1
The molecular components of pentanitroaniline disolvate. Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270106020804

(partial) reduction of a nitro group results in its planarization and the elongation of the C—N bond (Lü *et al.*, 2005; Akopyan *et al.*, 1966; Cady & Larson, 1965). Therefore, the features are consistent with preferential charge transfer to the *ortho* and (to a slightly lesser extent) the *para* positions of (I). [Note that N—H···O—N hydrogen bonding (Table 2) may also affect the twisting of the NO_2 group in the *ortho* position.]

To quantify this conclusion, we carried out the natural bond orbital (NBO) analysis of the electron distribution within (I). Thus, density functional theory (B3LYP/6-11G*) computations with *GAUSSIAN98* (Frisch *et al.*, 1998) produced a geometry in good agreement with the experimentally obtained structure. The NBO analysis (Table 3) indicates that the negative charge in pentanitroaniline is concentrated mostly on the O atoms, which leads (together with some positive charge on N atoms) to overall negative charges on the *ortho*-, *meta*- and *para*-nitro groups of −0.20, −0.11 and −0.15, respectively. All the C_6 core atoms bear positive charges, and the electrostatic interaction leads to a very short intermolecular N—O···C distance between the negatively charged O2 atom and the electron deficient C3 atom. As such, all the data indicate significant contributions of the resonance structures in Fig. 3 that result from charge transfer *via* the amino- to the nitro-containing fragments and lead to the molecular geometry of (I).

Thus, the analysis of the structure of pentanitroaniline along with other polynitroaminobenzenes indicates that (i) the deformation of the aromatic ring results mainly from favorable resonance structures related to the asymmetrical presence of both donor and acceptor substituents as opposed to any symmetrical release or withdrawal of electron density, and (ii) the twistings of and bond lengths to NO_2 groups are determined by the charges on the entire C—NO_2 fragment, not merely on the constituent C—NH_2 or NO_2 parts.

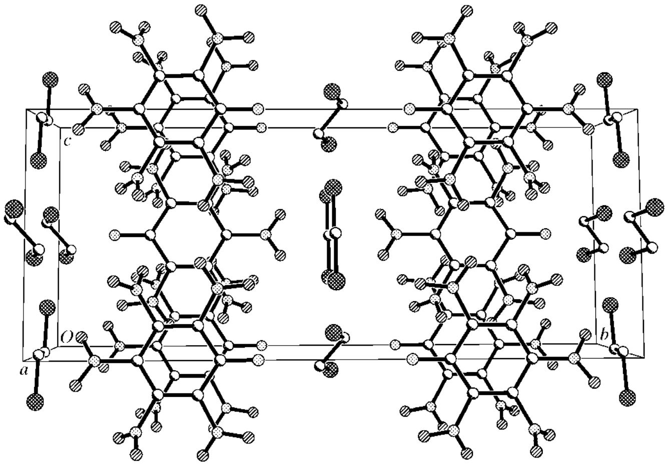


Figure 2
A view of the molecular arrangement of (I) along the *a* axis. H atoms have been omitted for clarity. For the disordered solvent molecule, only one set of its three possible conformations is shown.

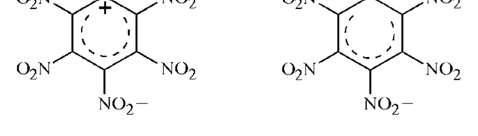


Figure 3
The principal resonance structures in (I), resulting in significant charge transfer.

Experimental

Pentanitroaniline was prepared by nitration of 3,5-dinitroaniline with nitric acid in 100% sulfuric acid according to the literature procedure of Nielsen *et al.* (1980). Dissolution of the yellow solid in dichloroethane followed by slow cooling to 243 K resulted in the precipitation of clear yellow plates suitable for X-ray analysis.

Crystal data

$C_6H_2N_6O_{10}\cdot C_2H_4Cl_2$
$M_r = 417.09$
Monoclinic, $C2/m$
$a = 11.327$ (4) Å
$b = 21.621$ (7) Å
$c = 7.911$ (3) Å
$\beta = 128.941$ (6)°
$V = 1506.9$ (9) Å^3
$Z = 4$
$D_x = 1.838$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.50$ mm^{-1}
$T = 173$ (2) K
Plate, yellow
0.5 × 0.5 × 0.01 mm

Data collection

Bruker SMART diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{\min} = 0.800$, $T_{\max} = 0.995$
10284 measured reflections
2294 independent reflections
1574 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\max} = 30.6°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.148$
$S = 1.09$
2294 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2 + 0.3853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—N1	1.325 (4)	C4—N4	1.474 (4)
C1—C2	1.429 (3)	N2—O1	1.226 (3)
C2—C3	1.378 (3)	N2—O2	1.227 (3)
C2—N2	1.468 (3)	N3—O4	1.217 (2)
C3—C4	1.382 (3)	N3—O3	1.227 (2)
C3—N3	1.480 (3)	N4—O5	1.214 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.81	2.08	2.690 (2)	132

The disordered 1,2-dichloroethane molecule has two crystallographically independent C atoms, *viz.* C6 and C7. They were located in a difference Fourier map and their site-occupancy factors of 0.36 (1) and 0.28 (2), respectively, were obtained by *SHELXTL* (Bruker, 2003). These two C atoms were refined isotropically. The H atoms of the solvent molecules were placed in calculated positions

Table 3
Natural bond orbital analysis of electron population in (I) – fragments and charges on atoms and groups.

	C	N	O(H)[a]	O(H)[a]	$NO_2(NH_2)$[a]
$C-NH_2$	0.24	−0.69	0.42	0.42	0.15
o-$C-NO_2$	0.03	0.52	−0.40	−0.32	−0.20
m-$C-NO_2$	0.15	0.52	−0.31	−0.31	−0.11
p-$C-NO_2$	0.03	0.52	−0.33	−0.33	−0.15

Note: (*a*) in the first row, charges on H atoms or amine group.

and were treated as riding atoms, with C—H distances of 0.99 Å (CH_2). H atoms in the NH_2 group, which are involved in hydrogen bonds, were located in a difference Fourier map and subsequently allowed to refine as riding atoms. All H atoms were refined isotropically with $U_{iso}(H) = 1.2U_{eq}(N,C)$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Bruker, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *XCIF* (Bruker, 1999).

The authors thank D. Sun for assistance in the synthesis of the title compound and the R. A. Welch Foundation and National Science Foundation for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3030). Services for accessing these data are described at the back of the journal.

References

Akopyan, Z. A., Struchkov, Yu. T. & Dashevii, V. G. (1966). *Zh. Strukt. Khim. (J. Struct. Chem.)*, **7**, 408–416. (In Russian.)

Bruker (1999). *XP* and *XCIF*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2003). *SHELXTL* (Version 6.12), *SMART* (Version 5.630), *SAINT* (Version 6.28) and *SADABS* (Version 2.06). Bruker AXS Inc., Madison, Wisconsin, USA.

Cady, H. H. & Larson, A. C. (1965). *Acta Cryst.* **18**, 485–496.

Dixon, D. A., Calabrese, J. C. & Miller, J. S. (1989). *Angew. Chem. Int. Ed.* **28**, 90–92.

Frisch, M. J. *et al.* (1998). *GAUSSIAN98*. Revision A.1. Gaussian Inc., Pittsburgh, PA, USA.

Lee, J. Y., Kim, K. S. & Mhin, B. J. (2001). *J. Chem. Phys.* **115**, 9484–9489.

Lü, J.-M., Rosokha, S. V., Lindeman, S. V., Neretin, I. S. & Kochi, J. K. (2005). *J. Am. Chem. Soc.* **127**, 1796–1809.

Nielsen, A. T., Atkins, R. L., Norris, W. P., Coon, C. L. & Sitzmann, M. E. (1980). *J. Org. Chem.* **45**, 2341–2347.

Perepichka, D. F., Bryce, M. R., Batsanov, A. S., Howard, J. A. K., Cuello, A. O., Gray, M. & Rotello, V. M. (2001). *J. Org. Chem.* **66**, 4517–4524.

Perepichka, D. F., Bryce, M. R., Perepichka, I. F., Lyubchik, S. B., Christensen, C. A., Godbert, N., Batsanov, A. S., Levillain, E., McInnes, E. J. L. & Zhao, J. P. (2002). *J. Am. Chem. Soc.* **124**, 14227–14238.

Techert, S. & Zachariasse, K. A. (2004). *J. Am. Chem. Soc.* **126**, 5593–5600.

Thallapally, P. K., Desiraju, G. R., Bagieu-Beucher, M., Masse, R., Bourgogne, C. & Nicoud, J.-F. (2002). *Chem. Commun.* pp. 1052–1053.

Yang, M., Jacquemin, D. & Champagne, B. (2002). *Phys. Chem. Chem. Phys.* **4**, 5566–5571.