

Conformational polymorphism of (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)- benzene-1,4-diamine

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Received 26 January 2011

Accepted 17 March 2011

Online 14 April 2011

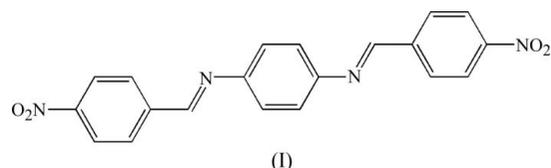
Two polymorphs of (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)benzene-1,4-diamine, C₂₀H₁₄N₄O₄, (I), have been identified. In each case, the molecule lies across a crystallographic inversion centre. The supramolecular structure of the first polymorph, (I-1), features stacking based on π - π interactions assisted by weak hydrogen bonds involving the nitro groups. The second polymorph, (I-2), displays a perpendicular arrangement of molecules linked *via* the nitro groups, combined with weak C—H \cdots O hydrogen bonds. Both crystal structures are compared with that of the carbon analogue (*E,E*)-1,4-bis[2-(4-nitrophenyl)ethenyl]benzene, (II).

Comment

Oligomers of poly(*p*-phenylenevinylene) (PPV) and its isoelectronic counterpart poly(1,4-phenylenemethyldiene-nitrilo-1,4-phenylenenitrilomethyldiene) (PPI) constitute an interesting class of organic semiconductors, mainly because these materials display useful opto-electronic properties. Using oligomers instead of polymers has proved to be a worthwhile endeavour, as the former are far more straightforward to produce, characterize and process than the latter (Müllen & Wegner, 1998). Also, such low-molecular-weight compounds can be subtly tailored to enhance the molecular properties desired for a specific application, by substituting them with functional groups such as electron donors and/or acceptors, thereby making optimal use of their potential as new materials for a variety of applications. However, since these materials are often used in the solid state, it is of equal importance to gain insight into their solid-state structures to correlate their structural characteristics with the experimentally determined optoelectronic properties of interest. In this paper, we present two conformational polymorphs of (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)benzene-1,4-diamine, (I), a nitro-substituted PPI oligomer.

The first polymorph, (I-1), crystallizes in the triclinic space group $P\bar{1}$, with one molecule per unit cell lying across a

crystallographic inversion centre. Its central ring (*B*) is twisted out of the plane defined by the peripheral nitro-substituted aromatic ring (*A*) by 56.99 (7)° (Fig. 1); this is further illustrated by the torsion angles presented in Table 1. These twisted conformations are well known within this class of compounds and originate from electronic effects rather than



from steric hindrance (Collas *et al.*, 2011). The supramolecular structure of (I-1) is based on extended chains of molecules, generated by a mutual weak hydrogen bond involving the relatively acidic aromatic atom H5 and an O atom from the nitro group in the 4-position of a neighbouring molecule (Fig. 2 and Table 2, entry 1). π - π stacks of nitro-substituted rings extend along the direction of the *a* axis (Fig. 2 and Table 2, entries 2 and 3). Within these stacks, an additional weak hydrogen bond involving atom H10 of the central ring [C10—H10 \cdots O1(-*x*, -*y* + 1, -*z* + 1)] operates in the same direction

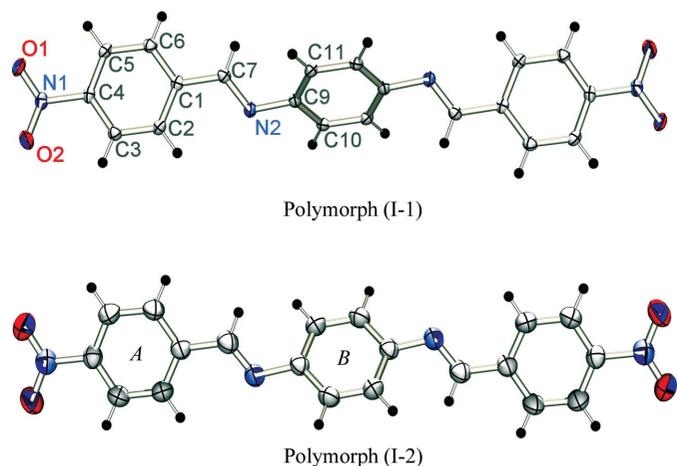


Figure 1

The molecular structures of the two polymorphs of (I), showing the atom-numbering schemes [note that, in (II), C8 replaces N2]. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii and they bear the same number as the C atom to which they are attached.

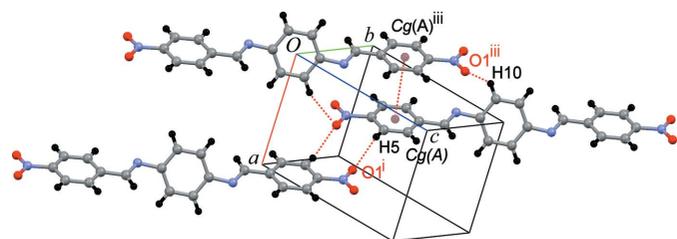


Figure 2

View of the π - π stacking and hydrogen bonding in polymorph (I-1). [Symmetry codes: (i) -*x* + 1, -*y*, -*z* + 1; (iii) -*x*, -*y* + 1, -*z* + 1.]

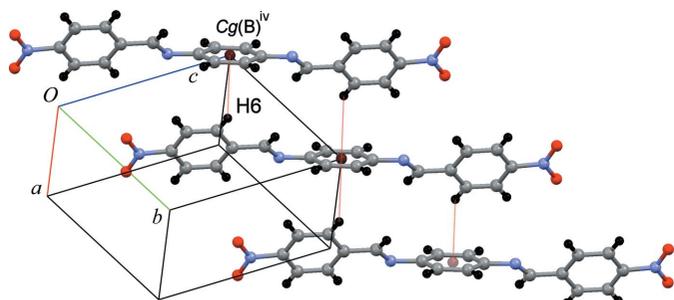


Figure 3
View of the C—H... π contacts in polymorph (I-1). [Symmetry code: (iv) $x, -1 + y, z$.]

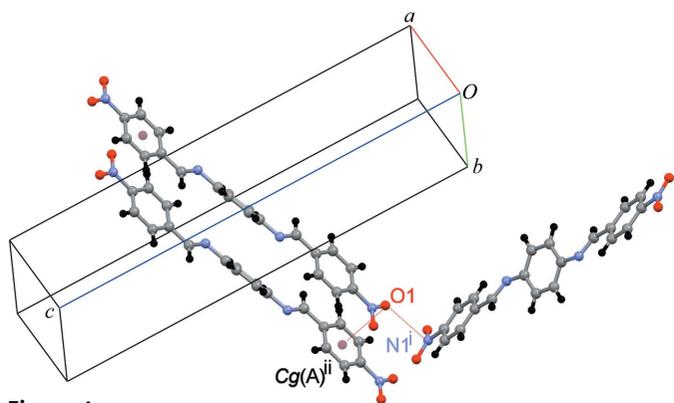


Figure 4
Interactions involving the nitro group generating a herringbone pattern in polymorph (I-2). [Symmetry codes: (i) $-x - 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y + 1, z$.]

(Fig. 2 and Table 2, entry 4). Finally, a mutual weak hydrogen bond, linking atom H6 to the π -system of the central ring of another molecule, holds the stacks together (Fig. 3 and Table 2, entry 5). It is interesting to note that the most acidic H atom, H7, is not involved in the crystal packing.

The second polymorph, (I-2), crystallizes in the monoclinic space group $P2_1/c$, with two molecules per unit cell lying across

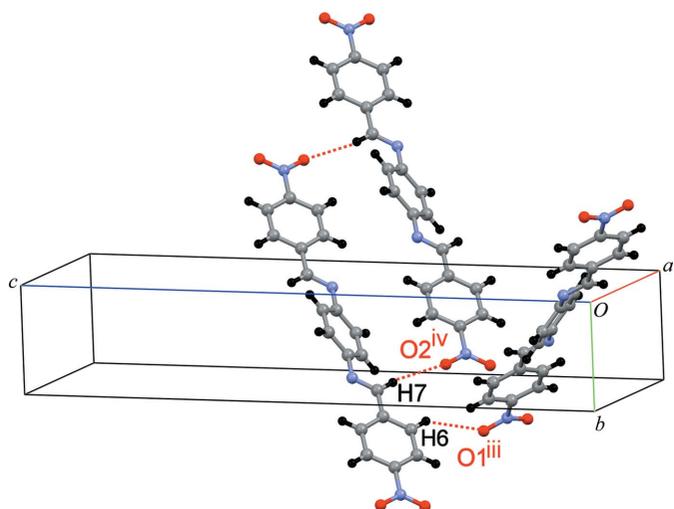


Figure 5
View of the weak hydrogen bonds in polymorph (I-2). [Symmetry codes: (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + 1, -1 + y, z$.]

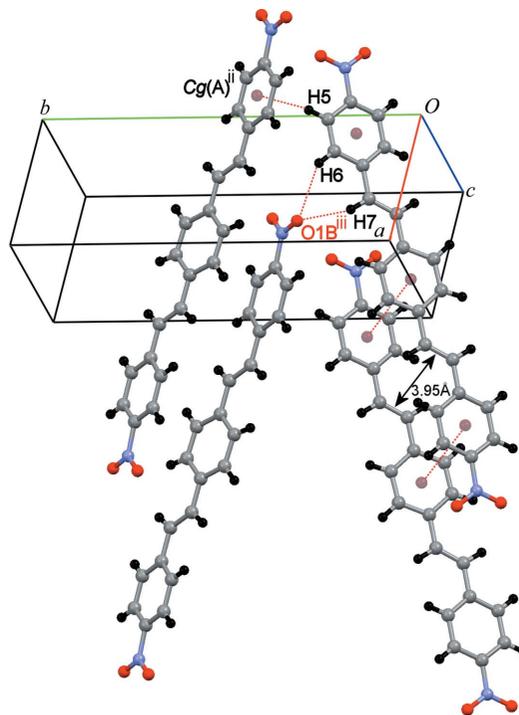


Figure 6
View of the relevant interactions in MUBTEJ, (II). [Symmetry codes: (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$.]

crystallographic inversion centres ($Z' = 0.5$). In its structure one can also easily see that the central ring is twisted out of the plane of the peripheral ring (Fig. 1), but to a lesser extent than for (I-1); the angle between the two planes through rings *A* and *B* is $36.29(8)^\circ$. As can be seen from Table 1, the torsion angle τ (C11—C9—N2—C7) is the largest contributor to the twists in both structures. The crystal packing of (I-2) is quite different from that of (I-1), as contacts between the nitro groups dominate the supramolecular structure. A T-shaped contact between the partially positively charged N atom and the partially negatively charged O atom of the nitro groups results in a herringbone pattern (Fig. 4 and Table 3, entry 1). This type of stacking is reinforced by mutual N—O... π interactions (Fig. 4 and Table 3, entries 2 and 3). Further stacking of the molecules is achieved by two additional weak C—H...O hydrogen bonds involving atoms H6 and H7 (Fig. 5 and Table 3, entries 4 and 5).

The distyrylbenzene (DSB) analogue of the title compounds, namely (*E,E*)-1,4-bis[2-(4-nitrophenyl)ethenyl]benzene, (II), originally reported by Pham (2009) [Cambridge Structural Database (CSD; Allen, 2002) refcode MUBTEJ], is quasi-planar, with a dihedral angle of $11.86(7)^\circ$ between the planes through the peripheral and central rings. The dihedral angle is only $2.29(10)^\circ$ in the previously reported dimethylformamide (DMF) solvate (Bartholomew *et al.*, 2000; CSD refcode REGBEK), but as the solvent molecules interfere in the inter-oligomer contacts we will only consider the crystal packing of MUBTEJ (Fig. 6). Here, π - π stacking is present but, unlike in the structure of (I-1), it occurs between the two different rings *A* and *B* (Table 4, entry 1), which leads to a photoreactive structure that may undergo a topochemical

polymerization. Indeed, the distance between the vinyl spacers is 3.95 Å, which is smaller than the experimentally determined limit of 4.2 Å (Schmidt, 1971). Perpendicular to these photoreactive stacks, molecules are connected through three weak hydrogen bonds (Table 4, entries 2, 3 and 4), one in which aromatic atom H5 contacts the π -system of an adjacent ring *A* and two in which one of the O atoms of the nitro group, O2, acts as an acceptor for aromatic atoms H6 and H7 from another molecule.

Thus, the three structures show completely different packing schemes. While in the structure of polymorph (I-1) the central ring *B* acts as an acceptor for aromatic atom H6 and as a hydrogen-bond donor to a nitro group [C10–H10 \cdots O1(–*x*, –*y* + 1, –*z* + 1), Table 2, entry 4], this ring does not take part in the crystal packing of (I-2). Besides the fact that (I-2) and (II) share the same space group, they also share two active sites on their carbon backbone; in both structures, atoms H6 and H7 are engaged in weak hydrogen bonds with the O atoms of the nitro groups of neighbouring molecules. However, in the latter only one O atom is available, while in the former both O atoms are used as acceptor sites. The presence of the N atom in (I), which results in a twist of the central ring, precludes the possibility of closer stacking and, as a result, a photosensitive supramolecular structure based on π – π interactions, as seen in (II), cannot be formed.

Experimental

Benzene-1,2-diamine (2.6 g, 25 mmol) and 4-nitrobenzaldehyde (3.8 g, 50 mmol) were dissolved in ethanol (200 ml) and the resulting solution was boiled under reflux for 2 h. The resulting precipitate was filtered off, yielding a yellow–orange powder, part of which was recrystallized from acetonitrile to produce needles of (I-1) with a golden lustre. Slow evaporation of a CHCl₃ solution yielded polymorph (I-2) as orange plates [m.p. (uncorrected) 512 and 502 K for (I-1) and (I-2), respectively]. UV–visible (CH₂Cl₂): λ_{max} = 391 nm (log ϵ = 4.45); ¹H NMR (CDCl₃, 400 MHz, TMS): δ 7.36 (*s*, 4H, H10 and H11), 8.10 (*d*, 4H, ³*J* = 8.8 Hz, H2 and H6), 8.35 (*d*, ³*J* = 8.8 Hz, H3 and H5), 8.62 (*s*, 2H, H7); ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 122.20 (C3 and C5), 124.09 (C10 and C11), 129.46 (C2 and C6), 141.53 (C1), 149.76 (C9), 149.76 (C4), 157.03 (C7).

Polymorph (I-1)

Crystal data

C ₂₀ H ₁₄ N ₄ O ₄	γ = 88.071 (1)°
M_r = 374.35	V = 427.20 (7) Å ³
Triclinic, $P\bar{1}$	Z = 1
a = 6.9357 (7) Å	Mo $K\alpha$ radiation
b = 7.3036 (7) Å	μ = 0.11 mm ^{–1}
c = 8.8768 (8) Å	T = 173 K
α = 73.295 (1)°	0.29 × 0.22 × 0.1 mm
β = 82.707 (1)°	

Data collection

Bruker SMART APEX CCD diffractometer	3748 measured reflections
Absorption correction: multi-scan (APEX2; Bruker, 2008)	1731 independent reflections
T_{min} = 0.973, T_{max} = 0.991	1496 reflections with $I > 2\sigma(I)$
	R_{int} = 0.018

Table 1

Dihedral angles (°) in the compounds under discussion.

	(I-1)	(I-2)	MUBTEJ, (II)	REGBEK
C2–C1–C7–N2/C8	12.3 (2)	–0.5 (3)	9.5 (2)	–5.1 (4)
C1–C7–N2/C8–C9	–174.49 (13)	–172.48 (15)	179.9 (1)	–178.4 (2)
C11–C9–N2/C8–C7	43.7 (2)	35.2 (2)	–177.6 (1)	–175.8 (2)

Table 2

Short contacts in the crystal packing of polymorph (I-1) (Å, °).

The angle related to a pair of centroids is defined as the angle between the $CgI \cdots CgJ$ vector and the normal to plane *I*.

Entry	<i>D</i>	<i>X</i>	<i>A</i>	$X \cdots A$	$D-X \cdots A$
1	C5	H5	O1 ⁱ	2.55	153
2	CgA		CgA^{ii}	3.5212 (9)	15.64
3	CgA		CgA^{iii}	3.5981 (9)	24.53
4	C10	H10	O1 ⁱⁱⁱ	2.52	155
5	C6	H6	CgB^{iv}	2.83	129

Symmetry codes: (i) –*x* + 1, –*y*, –*z* + 1; (ii) –*x* + 1, –*y* + 1, –*z* + 1; (iii) –*x*, –*y* + 1, –*z* + 1; (iv) *x*, *y* – 1, *z*.

Table 3

Short contacts in the crystal packing of polymorph (I-2) (Å, °).

Entry	<i>D</i>	<i>X</i>	<i>A</i>	$X \cdots A$	$D-X \cdots A$
1	N1	O1	N1 ⁱ	2.982 (2)	121.20 (11)
2	N1	O1	CgA^{ii}	3.5301 (17)	86.14 (10)
3	N1	O2	CgA^{ii}	3.9359 (18)	67.91 (9)
4	C6	H6	O1 ⁱⁱⁱ	2.66	135
5	C7	H7	O2 ^{iv}	2.54	152

Symmetry codes: (i) –*x* – 1, *y* + $\frac{1}{2}$, –*z* + $\frac{1}{2}$; (ii) *x*, *y* + 1, *z*; (iii) –*x*, *y* – $\frac{1}{2}$, –*z* + $\frac{1}{2}$; (iv) *x* + 1, *y* – 1, *z*.

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042	127 parameters
$wR(F^2)$ = 0.106	H-atom parameters constrained
S = 1.08	$\Delta\rho_{\text{max}}$ = 0.20 e Å ^{–3}
1731 reflections	$\Delta\rho_{\text{min}}$ = –0.22 e Å ^{–3}

Polymorph (I-2)

Crystal data

C ₂₀ H ₁₄ N ₄ O ₄	V = 860.4 (2) Å ³
M_r = 374.35	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 6.567 (1) Å	μ = 0.10 mm ^{–1}
b = 5.0227 (7) Å	T = 293 K
c = 26.723 (5) Å	0.55 × 0.37 × 0.07 mm
β = 102.558 (4)°	

Data collection

Bruker SMART APEX CCD diffractometer	4451 measured reflections
Absorption correction: multi-scan (APEX2; Bruker, 2008)	1753 independent reflections
T_{min} = 0.955, T_{max} = 0.993	1181 reflections with $I > 2\sigma(I)$
	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040	127 parameters
$wR(F^2)$ = 0.106	H-atom parameters constrained
S = 1.02	$\Delta\rho_{\text{max}}$ = 0.12 e Å ^{–3}
1753 reflections	$\Delta\rho_{\text{min}}$ = –0.18 e Å ^{–3}

Table 4

Short contacts in the crystal packing of (II) (Å, °).

The angle related to a pair of centroids is defined as the angle between the $CgI \cdots CgJ$ vector and the normal to plane I .

Entry	D	X	A	$X \cdots A$	$D-X \cdots A$
1	CgA		CgB^i	3.8933 (11)	29.52
2	$C5$	H5	CgA^{ii}	2.764 (15)	160.2 (13)
3	$C6$	H6	$O1^{iii}$	2.659 (15)	146.0 (11)
4	$C7$	H7	$O1^{iii}$	2.419 (15)	161.8 (12)

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$.

In order to improve R statistics, the high-resolution data were truncated at a resolution of 0.8 Å; this value was chosen based on inspection of the analysis of the variance section in the `shelx.lst` output file. H atoms were placed in calculated positions and refined as riding, with C–H distances of 0.93 Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

AC wishes to thank the Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT) for

a predoctoral grant. The X-ray diffractometer was funded by NSF grant No. 0087210, Ohio Board of Regents grant No. CAP-491 and Youngstown State University. Financial support by the University of Antwerp under grant No. GOA-2404 is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3102). Services for accessing these data are described at the back of the journal.

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