4-Dimethylamino-β-nitrostyrene and 4-dimethylamino-β-ethyl-β-nitrostyrene at 100 K

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The structures of 4-dimethylamino-β-nitrostyrene (DANS), $C_{10}H_{12}N_2O_2$, and 4-dimethylamino-β-ethyl-β-nitrostyrene (DAENS), $C_{12}H_{16}N_2O_2$, have been solved at $T = 100$ K. The structure solution for DANS was complicated by the presence of a static disorder, characterized by a misorientation of 17% of the molecules. The molecule of DANS is almost planar, indicating significant conjugation, with a push–pull effect through the styrene skeleton extending up to the terminal substituents and enhancing the dipole moment. As a consequence of this conjugation, the hexagonal ring displays a quinoidal character; the lengths of the C—N [1.3595 (15) Å] and C—C [1.448 (2) Å] bonds adjacent to the benzene ring are shorter than single bonds. The molecules are stacked in dimers with antiparallel dipoles. In contrast, the molecule of DAENS is not planar. The ethyl substituent pushes the nitropropene group out of the benzene plane, with a torsion angle of −21.9 (3). Nevertheless, the molecule remains conjugated, with a shortening of the same bonds as in DANS.

Comment

A large number of conjugated organic compounds have been studied experimentally and theoretically in order to establish the structure–property relationships inducing large non-linear optical (NLO) properties. Among these, β-nitrostyrene derivatives have been very attractive (Oudar, 1977; Zyss, 1979; Dulcic et al., 1981; Cheng, Tam, Marder et al., 1991; Keshari et al., 1993). Such work has tried to determine the role and importance of the number of conjugated double bonds, the electronic biasing strengths of various donor and acceptor groups, charge-transfer enhancement, and the pattern and polarity of multiple substituents. The results of these studies reveal that very large second-order non-linearities can be

obtained with relatively long conjugated molecules containing strongly interacting donor–acceptor groups. For 4-dimethylamino-β-nitrostyrene, denoted DANS, the NLO properties found for dilute solutions are very close to those for 4-dimethylamino-4′-nitrostilbene, usually quoted as an example of a conjugated molecule which exhibits very large non-linearities (Chemla & Zyss, 1987; Cheng, Tam, Stevenson et al., 1991). However, a strong steric effect of the methyl substituent was observed in a series of β-methyl-β-nitrostyrene derivatives (Cho et al., 1996). In particular, the distortion from planarity caused by steric repulsion is able to reduce the optical non-linearities to nearly zero.
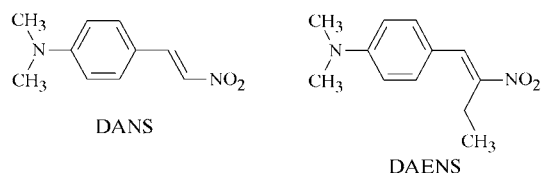
We present here the structure of DANS in order to establish the influence of charge transfer upon the molecular geometry, which affects the strength of the NLO properties. In parallel, in order to analyse the importance of steric effects upon conjugation, we also report the structure of 4-dimethylamino-β-ethyl-β-nitrostyrene, denoted DAENS (Pianka, 1963). For both compounds, data collection at 100 K has allowed an
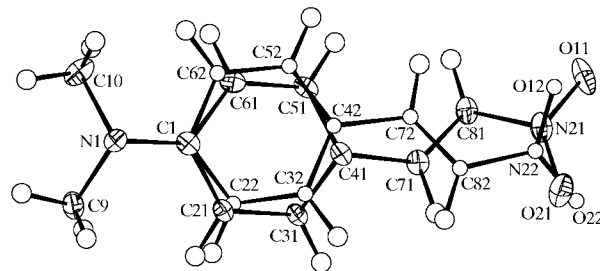

Figure 1
A composite view of the disordered molecule of DANS at 100 K, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii. The labels of the H atoms have been omitted for clarity.
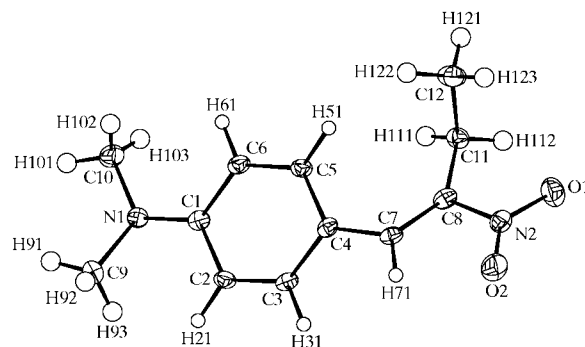

Figure 2
A view of the molecular unit of DAENS at 100 K, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary radii.

organic compounds

increase up to an acceptable level of the ratio of the number of independent observable reflections to the number of least-squares parameters, compared with the data collection at 293 K. Furthermore, for DANS it appears that the structure is disordered. The static disorder consists of a 180° rotation of 17% of the molecules around their long axis and is similar to that found in *trans*-stilbene and *trans*-azobenzene (Brown, 1966*a*,*b*; Bouwstra *et al.*, 1983; Finder *et al.*, 1974). In this paper, we report the molecular geometry and crystal packing of DANS, obviously only with regard to the molecule with the most probable orientation, for which atomic displacement parameters have been refined anisotropically.

The molecular structure of DANS is shown in Fig. 1, while selected geometric parameters are given in Table 1. The molecule is almost planar, indicating a high degree of conjugation, with a strong push–pull effect between the nitro and dimethylamine groups through the styrene skeleton. Excluding the dimethylamine group (atom N1 has slightly pyramidal bonds), the highest mean square deviation from the calculated mean plane is 0.014 (2) Å. The dihedral angle between the mean planes of these two parts of the molecule is 1.4 (2)°. The sum of the bond angles around N1 is 359.2 (3)°, close to 360°, revealing the delocalization of the lone pair toward the N1—C1 bond, which is too short [1.3595 (15) Å] for a single N—C bond. Conjugation through the styrene induces the quinoidal character of the hexagonal ring; the C21—C31 [1.390 (2) Å] and C51—C61 [1.373 (2) Å] bond lengths, roughly parallel to the molecular dipole, are significantly shorter than C1—C21 [1.418 (2) Å], C1—C61 [1.423 (2) Å], C31—C41 [1.4045 (17) Å] and C41—C51 [1.4057 (19) Å]. For the same reason, the C41—C71 bond [1.448 (2) Å] is shorter than a single bond.

A perspective view of DAENS is shown in Fig. 2 and selected geometric parameters are given in Table 3. Several differences from the conformation of DANS are found. The most striking feature is the C5—C4—C7—C8 torsion angle of −21.9 (3)°, which pushes the nitro and ethyl substituent groups out of the benzene ring plane. The main consequence of this torsion is to decrease the conjugation between the C7=C8 double bond and the dimethylaminobenzene moiety, and hence explains the hypsochromic effect for DAENS,

which is yellow, not red like DANS. Nevertheless, a noticeable conjugation remains, evidenced by the shortening of several bonds [C2—C3 = 1.383 (2) Å, C5—C6 = 1.391 (3) Å, N1—C1 = 1.369 (2) Å and C4—C7 = 1.450 (2) Å]. The conjugation also explains why the N atom of the dimethylamine moiety has lost all pyramidal character [the sum of the bond angles around atom N1 is 359.02 (5)°].

The aforementioned steric hindrance of the ethyl group on the molecular planarity of DAENS must be compared with that of the methyl group in β-methyl-β-nitrostyrene compounds substituted by donors of various strengths on the benzene ring. The value of the torsion angle between the benzene and nitropropene groups in 4-dimethylamino-β-methyl-β-nitrostyrene, with the same donor as in DAENS, is only 1.6 (8)° (Brito *et al.*, 1991), while it is 27.1° in the 4-methoxy analogue (Boys *et al.*, 1993) and 23.7° in the 4-hydroxy-3-methoxy (Zabel *et al.*, 1980) analogue. These values illustrate how molecular conjugation, or in other words the planarity of the molecule, is counter-balanced between steric effects and the strength of donors.

In the crystal structure, molecules of DANS are stacked as dimers, interacting in an antiferroelectric manner, and consequently no second-order NLO effect is observed in the solid state. The distance between the mean planes of the dimer is 3.276 (2) Å, while the smallest distance is between atoms C1 and N21 of 3.322 (2) Å. The dimers are organized in chains along the *c* axis (Fig. 3) *via* C—H⋯O interactions between donor and acceptor groups (Table 2). Each chain of dimers is symmetrically surrounded by four other chains, within which the molecular planes are almost perpendicular to the molecular plane of the central chain.

The packing of molecules of (II) in the crystal structure displays short contacts between O atoms and methyl groups (see Table 4 and Fig. 4). The asymmetric interactions of the O atoms with the methyl groups of the dimethylamine group explain the difference between torsion angles C2—C1—N1—C9 [10.4 (3)°] and C6—C1—N1—C10 [−1.4 (3)°]. Unfortunately in this non-centrosymmetric structure, the non-planarity of the molecules does not allow an efficient NLO effect.
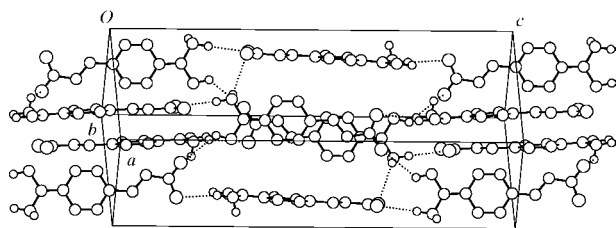

Figure 3
A crystal packing diagram of part of DANS at 100 K, along the [3̄21] direction, showing the formation of a chain of dimers surrounded by half a chain of two neighbours. C—H⋯O contacts are represented by dotted lines. For the sake of clarity, the molecule with 17% of the disorder and H atoms not involved in hydrogen bonding have been omitted.
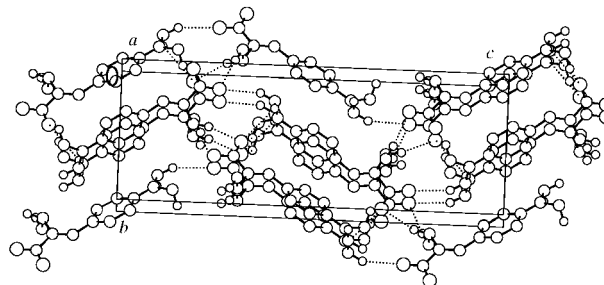

Figure 4
A crystal packing diagram of DAENS at 100 K, viewed along [100] and slightly rotated around the *c* axis, showing asymmetric C—H⋯O hydrogen-bond interactions (dotted lines). For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

Experimental

The syntheses of both materials consists of the condensation of 4-dimethylaminobenzaldehyde (DABA) with a nitroolefin. To obtain DANS, a mixture of DABA (0.01 mol) and nitromethane (0.03 mol) was used at 373 K, with a few drops of butylamine. For DAENS, the synthesis begins with the condensation of DABA with butylamine to obtain the 4-dimethylaminobenzylidene butylamine. After separation, this butylamine reacts with nitromethane in the presence of acetic acid to give the nitrostyrene. Single crystals of DANS were grown by slow evaporation of a solution in toluene. Single crystals of DAENS were obtained from a saturated solution in ethanol prepared at room temparature and slowly evaporated in a refrigerator [m.p. 390 K for DANS and 361 K for DAENS].

DANS

Crystal data

$C_{10}H_{12}N_2O_2$
$M_r = 192.22$
Orthorhombic, $Pbca$
$a = 10.1460 (2)$ Å
$b = 7.3091 (2)$ Å
$c = 25.1662 (7)$ Å
$V = 1866.28 (8)$ Å^3

$Z = 8$
$D_x = 1.368$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 100 (1)$ K
Plate, dark red
$0.26 \times 0.18 \times 0.16$ mm

Data collection

Bruker APEX-II diffractometer
CCD scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 2002)
  $T_{min} = 0.975$, $T_{max} = 0.985$

20691 measured reflections
2137 independent reflections
1488 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.037$
$S = 1.17$
1488 reflections
161 parameters
H-atom parameters constrained

Prince (1982) modified Chebychev polynomial with five parameters (Watkin, 1994): 1.34, 1.99, 1.39 0.636 0.244
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O11—N21	1.2394 (19)	C1—C61	1.423 (2)
O21—N21	1.240 (2)	C21—C31	1.390 (2)
N1—C1	1.3595 (15)	C31—C41	1.4045 (17)
N1—C9	1.4554 (15)	C41—C51	1.4057 (19)
N1—C10	1.4554 (15)	C41—C71	1.448 (2)
N21—C81	1.4313 (19)	C51—C61	1.373 (2)
C1—C21	1.418 (2)	C71—C81	1.336 (2)
C1—N1—C9	120.35 (10)	C1—C21—C31	120.75 (13)
C1—N1—C10	120.11 (10)	C21—C31—C41	122.46 (13)
C9—N1—C10	118.73 (10)	C31—C41—C51	116.55 (12)
O21—N21—O11	122.53 (15)	C31—C41—C71	119.10 (13)
O21—N21—C81	119.86 (16)	C51—C41—C71	124.35 (13)
O11—N21—C81	117.61 (16)	C41—C51—C61	121.93 (13)
N1—C1—C21	119.90 (11)	C1—C61—C51	121.91 (13)
N1—C1—C61	123.75 (11)	C41—C71—C81	126.72 (14)
C21—C1—C61	116.34 (12)	N21—C81—C71	120.71 (14)
C51—C41—C71—C81	1.148	C71—C81—N21—O21	−0.427
C31—C41—C71—C81	−179.887	C21—C1—N1—C9	−6.750
C41—C71—C81—N21	179.863	C61—C1—N1—C10	4.305
C71—C81—N21—O11	179.363		

Table 2
Short-contact geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H91$\cdots$O21^i	1.00	2.55	3.534 (2)	169
C9—H93$\cdots$O11^{ii}	1.00	2.78	3.419 (2)	122
C10—H101$\cdots$O11^{iii}	1.00	2.79	3.503 (2)	129

Symmetry codes: (i) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

DAENS

Crystal data

$C_{12}H_{16}N_2O_2$
$M_r = 220.27$
Orthorhombic, $P2_12_12_1$
$a = 5.9641 (1)$ Å
$b = 8.4492 (1)$ Å
$c = 23.1400 (4)$ Å
$V = 1166.07 (3)$ Å^3

$Z = 4$
$D_x = 1.255$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 100 (1)$ K
Plate, yellow
$0.45 \times 0.34 \times 0.28$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
CCD scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 2002)
  $T_{min} = 0.962$, $T_{max} = 0.976$

14807 measured reflections
5077 independent reflections
2017 reflections with $I > 3\sigma(I)$
$R_{int} = 0.04$
$\theta_{max} = 35.0°$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.039$
$S = 1.14$
2017 reflections
148 parameters
H-atom parameters constrained

Prince (1982) modified Chebychev polynomial with three parameters (Watkin, 1994): 3.54, −1.10, 3.21
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}
Absolute structure: Flack (1983), with 3060 Friedel pairs
Flack parameter: 0.7 (14)

Table 3
Selected geometric parameters (Å, °) for (II).

O1—N2	1.232 (2)	C2—C3	1.383 (2)
O2—N2	1.231 (2)	C3—C4	1.395 (2)
N1—C1	1.369 (2)	C4—C5	1.410 (2)
N1—C9	1.454 (2)	C4—C7	1.450 (2)
N1—C10	1.453 (2)	C5—C6	1.391 (3)
N2—C8	1.468 (2)	C7—C8	1.345 (3)
C1—C2	1.421 (2)	C8—C11	1.502 (2)
C1—C6	1.408 (2)	C11—C12	1.527 (3)
C1—N1—C9	121.12 (15)	C3—C4—C5	116.54 (16)
C1—N1—C10	120.01 (15)	C3—C4—C7	117.66 (15)
C9—N1—C10	117.89 (15)	C5—C4—C7	125.68 (16)
O1—N2—O2	122.23 (16)	C4—C5—C6	121.70 (16)
O1—N2—C8	117.74 (15)	C1—C6—C5	121.05 (15)
O2—N2—C8	120.01 (15)	C4—C7—C8	130.66 (16)
N1—C1—C2	120.82 (15)	N2—C8—C7	115.37 (16)
N1—C1—C6	121.69 (15)	N2—C8—C11	114.77 (16)
C2—C1—C6	117.50 (15)	C7—C8—C11	129.85 (16)
C1—C2—C3	120.11 (16)	C8—C11—C12	112.52 (14)
C2—C3—C4	123.06 (15)		
C5—C4—C7—C8	−21.9 (3)	C7—C8—N2—O2	−7.0 (3)
C3—C4—C7—C8	162.26 (19)	C2—C1—N1—C9	10.4 (3)
C4—C7—C8—N2	178.23 (17)	C6—C1—N1—C10	−1.4 (3)
C7—C8—N2—O1	174.21 (17)	C4—C7—C8—C11	−3.3 (3)

organic compounds

Table 4
Short-contact geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C10—H101$\cdots$O1[i]	1.00	2.47	3.401 (2)	154
C12—H121$\cdots$O1[ii]	1.00	2.50	3.499 (2)	175
C9—H92$\cdots$O2[iii]	1.00	2.77	3.283 (2)	112
C10—H102$\cdots$O2[iii]	1.00	2.82	3.310 (2)	111
C11—H112$\cdots$O2[iv]	1.00	2.58	3.539 (2)	161

Symmetry codes: (i) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + 2$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

The structure of (I) was first refined without consideration of any static disorder, giving a final R value of 0.067 and $\Delta\rho_{max} = 1.19$ e Å^{-3}. Fourier difference maps clearly reveal two peaks on both sides of the ethylenic C71═C81 double bond and approximately equidistant from it. These two peaks were interpreted as C atoms of the ethylenic double bond belonging to a second misoriented molecule of (I). The occupancy ratio was initially set at 0.85:0.15 for both disordered molecules and was refined at each refinement step. Geometric soft restraints were simultaneously applied on distances and angles of the disordered moieties, according to values found from density functional theory quantum chemistry calculations. For the final cycles of refinement, only the most probable molecule was refined anisotropically, and an equivalent isotropic displacement parameter was assigned for the atoms of the misoriented molecule. All H atoms were located geometrically and treated as riding, with C—H = 1.00 Å, and refined isotropically using equivalence constraints.

Data collection: *SMART* (Bruker, 2001) for DANS; *COLLECT* (Nonius, 2000) for DAENS. Cell refinement: *SMART* for DANS; *DIRAX* (Duisenberg *et al.*, 2000) for DAENS. Data reduction: *SAINT* (Bruker, 2001) for DANS; *EVALCCD* (Duisenberg *et al.*, 2003) for DAENS. For both compounds, program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Issue 12; Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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