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N,*N*-Dimethyl-*N*′-[(1*E*,2*E*)-3-(4-nitrophenyl)prop-2-enylidene]benzene-1,4-diamine and *N*,*N*-dimethyl-4-[(1*E*,3*E*)-4-(4-nitrophenyl)buta-1,3-dienyl]-1-naphthylamine

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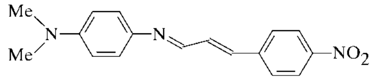
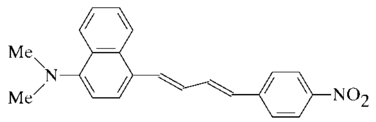
Syntheses and X-ray structural investigations have been carried out for the two title compounds, *viz.* $C_{17}H_{17}N_3O_2$, (I), and $C_{22}H_{20}N_2O_2$, (II). The molecular skeleton of (I) is slightly non-planar; the dihedral angles between the conjugated linkage and the *p*-(dimethylamino)phenyl ring, and between the linkage and the *p*-nitrophenyl ring are 13.0 (2) and 13.8 (2)°, respectively. The dihedral angle between the slightly pyramidal dimethylamine substituent and the aromatic ring is 23.3 (1)°. The molecular skeleton of (II) is not planar; the dihedral angles between the conjugated linkage and the naphthalene ring, and between the linkage and the substituted phenyl ring are 36.1 (2) and 2.7 (3)°, respectively. The dimethylamine substituent in (II) has a pyramidal geometry; the dihedral angle between this substituent and the naphthalene ring is 71.7 (1)°. The dihedral angle between the nitro group and the plane of the substituted phenyl ring is 9.0 (3)°. There is a weak intermolecular C—H⋯O hydrogen bond in the crystal structure of (II), which links the molecules into centrosymmetric dimers. Molecular mechanics calculations of molecular conformations have shown that the crystal environment influences the conformation more in (I) than in (II).

Comment

The present investigation is a continuation of a project that includes the syntheses and structural studies of polar conjugated organic molecules (Antipin *et al.*, 1997, 1998; Nesterov *et al.*, 2000). These compounds have applications in non-linear optical, electro-optical, photorefractive and optical limiting materials (Zyss *et al.*, 1994; Kuzyk & Dirk, 1998).



(I)



(II)

Synthesis and X-ray structural investigations have been carried out for the title compounds, (I) and (II) (Figs. 1 and 2). Most of the geometric parameters for (I) and (II) are similar to the standard values (Allen *et al.*, 1987) and very close to literature data for similar polyene derivatives (Childs *et al.*, 1989; Ercan *et al.*, 1996; Nesterov *et al.*, 2000). The title compounds have a *trans–trans* geometry about conjugated linkages. The molecular skeleton of (I) is slightly non-planar; the dihedral angles between the conjugated linkage and the *p*-(dimethylamino)phenyl ring, and between the linkage and the *p*-nitrophenyl ring are 13.0 (2) and 13.8 (2)°, respectively. Moreover, the dihedral angle between the slightly pyramidal dimethylamine substituent [the sum of the bond angles around the N atom is 353.5 (1)°] and the phenyl ring is 23.3 (1)°. The length of the C4—N2 bond is 1.388 (2) Å; although this bond is slightly longer than an average conjugated C—N single bond (1.370 Å), it is significantly shorter than an average non-conjugated C—N single bond (1.430 Å) found in the Cambridge Structural Database (CSD; Allen, 2002). As a result of the strong conjugation between the donor and acceptor parts of the molecule in (I), the substituted phenyl rings have a noticeable quinoid structure, which is most pronounced in the dimethylaniline phenyl ring (Table 1). The nitro group is essentially coplanar with the aromatic ring; the dihedral angle between the planes of these fragments is 1.0 (2)°.

The molecular skeleton of (II) is not planar; the dihedral angles between the conjugated linkage and the naphthalene ring, and between the linkage and the substituted phenyl ring are 36.1 (2) and 2.7 (3)°, respectively. The dimethylamine substituent in this molecule is more pyramidal [the sum of the bond angles around the N atom is 337.6 (2)°] than that in (I). Furthermore, the dihedral angle between this substituent and the naphthalene ring is 71.7 (1)°, and the C4—N1 bond is

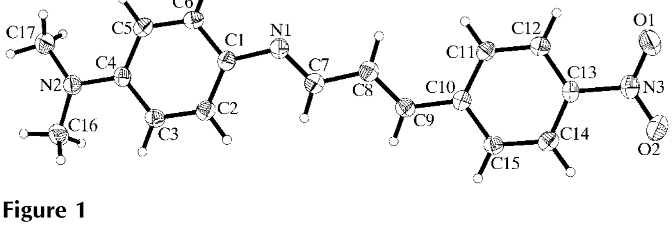


Figure 1
A view of (I), showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids at the 50% probability level.

much longer than the corresponding C4—N2 bond in (I); the C4—N1 bond length [1.428 (2) Å] agrees with the standard length of a non-conjugated C—N single bond (Allen *et al.*, 1987). These torsion angles and bond lengths indicate that the donor–acceptor interactions in (II) are considerably less effective than those in (I). The elongation of the C4—N1 bond (Table 2) from the average value for conjugated C—N single bonds (1.370 Å; CSD; Allen, 2002) and the increase of the dihedral angle between such fragments of molecules can be explained by the steric interactions between the dimethylamine group and the H atom of the naphthalene ring. Similar values of bond lengths and dihedral angles have been found for substituted *N*,*N*-dimethylanilines and 1,8-naphthalenedicarboximide derivatives (Kovalevsky *et al.*, 2000; Borbulevych *et al.*, 2002). It can be concluded that compounds with aromatic systems, such as naphthalene or anthracene, do not have as strong a conjugation as similar compounds with benzene rings because of stronger steric interactions between the bridging and aromatic parts of the molecules. The deviation of the nitro group from the plane of the substituted phenyl ring in (II) is more significant than the deviation in (I); the dihedral angle between these fragments is 9.0 (3)°. A weak intermolecular C9—H9*A*···O1 hydrogen bond in (II), between an H atom of a benzene ring and an O atom of the nitro group (Table 3), links the molecules into centrosymmetric dimers. Similar hydrogen bonds have been reported previously (Zhang *et al.*, 1998; Desiraju & Steiner, 1999; Huang *et al.*, 2002). Molecules of both (I) and (II) form stacks in which the molecules are located in parallel planes that are not exactly one above another.

In order to investigate the influence of the crystal packing on the geometry of molecules in the crystal structure, a theoretical search for possible conformations by the molecular mechanics method (*MM*3; Allinger *et al.*, 1989; Lii & Allinger, 1989) has been completed. It was confirmed that molecules of both (I) and (II) have to be non-planar in order to avoid steric interactions between neighboring H atoms of aromatic substituents and the conjugated bridge. The planarity of the molecules of (I) and (II) would lead to shortened intramolecular H···H distances (< 2 Å), *viz.* H2*A*···H7*A* and H8*A*···H11*A* in (I), and H2*A*···H12*A*, H13*A*···H16*A* and H9*A*···H11*A* in (II). A search for the optimal geometries of the molecules of (I) and (II) was performed using the stochastic search option in the *MM*3 program package. The results are summarized in Table 4. The conformation of the molecule of (II) corresponds to the second energy minimum found by *MM*3. The energy of the preferred conformation in this case is only slightly lower than that of the second minimum, which corresponds to the X-ray structure. However, the energy of the conformation that corresponds to the X-ray structure is higher above the global minimum in (I) than it is in (II) (Table 4). This result shows that the crystal environment influences the conformation in (I) more than in (II).

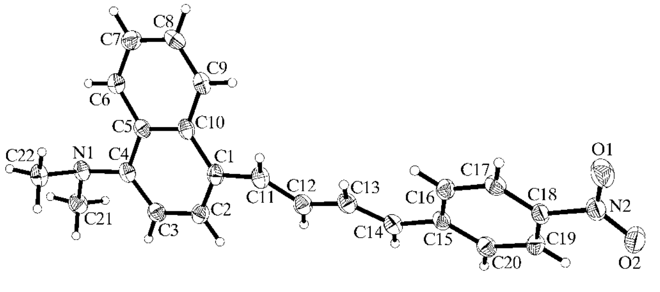


Figure 2
A view of (II), showing the atom-numbering scheme. Non-H atoms are shown with displacement ellipsoids at the 50% probability level.

Experimental

Compound (I) was synthesized according a literature procedure (Nesterov *et al.*, 2000) and recrystallized from acetonitrile (m.p. 503 K). Compound (II) (m.p. 411 K) was synthesized by the Wittig reaction of 1-(dimethylamino)-4-formylnaphthalene and (4-nitrocinnamyl)triphenylphosphonium chloride using sodium methoxide in methanol as a base. For (I), ^{1}H NMR (CDCl$_3$, 300 MHz): δ 8.38 (*d*, 1H, J = 8.83 Hz), 8.24 (*d*, 2H, J = 8.83 Hz), 7.64 (*d*, 2H, J = 8.82 Hz), 7.27 (*d*, 2H, J = 9.19 Hz), 7.25 (overlapping *m*, 1H), 7.08 (*d*, 1H, J = 15.81 Hz), 6.74 (*d*, 2H, J = 9.19 Hz), 3.01 (*s*, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 154.9, 150.1, 147.5, 142.5, 139.6, 137.8, 133.4, 127.5, 124.2, 122.7, 112.6, 40.5; GC–MS calculated for $C_{17}H_{17}N_3O_2$: 295.34; found 295.34. For (II), ^{1}H NMR (CDCl$_3$, 250 MHz): δ 8.27 (*m*, 1H), 8.21 (*d*, 2H, J = 7.5 Hz), 8.18 (*m*, 1H), 7.69 (*d*, 1H, J = 8.0 Hz), 7.57 (*d*, 2H, J = 7.5 Hz), 7.55 (overlapping *m*, 3H), 7.26 (*dd*, 1H, J = 15.5, 10.8 Hz), 7.08 (*d*, 1H, J = 8.0 Hz), 6.99 (*dd*, 1H, J = 15.0, 10.8 Hz), 6.72 (*d*, 1H, J = 15.5 Hz), 2.93 (*s*, 6H); high resolution FAB mass spectrometry calculated for $C_{22}H_{20}N_2O_2$: 344.1525; found 344.1527. Crystals of (I) and (II) suitable for X-ray diffraction analysis were grown by slow isothermal evaporation from ethanol.

Compound (I)

Crystal data

$C_{17}H_{17}N_3O_2$
M_r = 295.34
Monoclinic, $P2_1/n$
a = 6.1191 (18) Å
b = 7.168 (2) Å
c = 33.449 (10) Å
β = 91.408 (9)°
V = 1466.7 (7) Å^3
Z = 4

D_x = 1.337 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 320 reflections
θ = 4–24°
μ = 0.09 mm^{-1}
T = 110 (2) K
Plate, dark red
0.50 × 0.40 × 0.10 mm

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

N1—C7	1.283 (2)	C3—C4	1.411 (3)
N1—C1	1.418 (2)	C4—C5	1.416 (3)
N2—C4	1.388 (2)	C5—C6	1.384 (3)
C1—C6	1.396 (2)	C7—C8	1.439 (3)
C1—C2	1.407 (3)	C8—C9	1.341 (2)
C2—C3	1.385 (3)	C9—C10	1.464 (3)
C7—N1—C1	120.96 (16)	N1—C7—C8	122.00 (18)
C4—N2—C17	118.71 (15)	C9—C8—C7	122.30 (18)
C4—N2—C16	119.04 (16)	C8—C9—C10	126.89 (18)
C17—N2—C16	115.83 (15)		
C7—N1—C1—C2	11.6 (3)	N1—C7—C8—C9	178.88 (18)
C17—N2—C4—C3	−168.17 (17)	C7—C8—C9—C10	−174.95 (18)
C16—N2—C4—C3	−17.4 (3)	C8—C9—C10—C11	−12.6 (3)
C1—N1—C7—C8	175.97 (17)		

Table 2
Selected geometric parameters (Å, °) for (II).

N1—C4	1.428 (2)	C12—C13	1.440 (2)
C1—C11	1.461 (2)	C13—C14	1.338 (3)
C11—C12	1.341 (3)	C14—C15	1.465 (2)
C4—N1—C21	115.40 (15)	C11—C12—C13	121.65 (18)
C4—N1—C22	111.35 (14)	C14—C13—C12	126.32 (18)
C21—N1—C22	110.93 (14)	C13—C14—C15	125.83 (18)
C12—C11—C1	128.03 (18)		
C21—N1—C4—C3	−25.0 (2)	C11—C12—C13—C14	−172.96 (18)
C22—N1—C4—C3	102.6 (2)	C12—C13—C14—C15	176.48 (17)
C2—C1—C11—C12	32.6 (3)	C13—C14—C15—C16	−2.8 (3)
C1—C11—C12—C13	177.99 (17)		

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
7168 measured reflections
2740 independent reflections
1809 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.7°$
$h = -7 \rightarrow 6$
$k = -8 \rightarrow 8$
$l = -40 \rightarrow 32$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.145$
$S = 1.02$
2740 reflections
201 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Compound (II)

Crystal data

$C_{22}H_{20}N_2O_2$
$M_r = 344.40$
Triclinic, $P\overline{1}$
$a = 6.7383$ (10) Å
$b = 10.3948$ (16) Å
$c = 12.8735$ (19) Å
$\alpha = 79.933$ (8)°
$\beta = 81.754$ (8)°
$\gamma = 84.103$ (8)°
$V = 875.9$ (2) Å^3
$Z = 2$
$D_x = 1.306$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 320 reflections
$\theta = 4$–$24°$
$\mu = 0.08$ mm^{-1}
$T = 110$ (2) K
Prism, red
0.45 × 0.35 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
6053 measured reflections
3800 independent reflections
2589 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.0°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 12$
$l = -16 \rightarrow 12$

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O1$^{\rm i}$	0.95	2.46	3.395 (3)	166

Symmetry code: (i) $-1 - x, 1 - y, -z$.

Table 4
Selected torsion angles (°) and energies (kcal mol^{-1}) in the investigated molecules.

	C2—C1—N1—C7	C8—C9—C10—C11	Energy
Molecule (I)			
X-ray data	11.6	−12.6	
*MM*3 best conformation	29.1	−14.7	18.06
*MM*3 conformation (X-ray-like)	12.3	−13.8	19.24
Data range from *MM*3	1.43–29.1	−14.7–10.1	18.06–19.32
Molecule (II)			
X-ray data	32.6	−2.8	
*MM*3 best conformation	−35.4	−10.3	24.05
*MM*3 conformation (X-ray-like)	34.5	−2.1	24.36
Data range from *MM*3	−38.4–34.5	−12.5–7.2	24.05–24.70

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.187$
$S = 1.03$
3800 reflections
237 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1177P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

All H atoms were positioned geometrically and treated as riding, with C—H distances of 0.95–0.98 Å. $U_{\rm iso}$ values were assigned as $1.5U_{\rm eq}$(C) for methyl H atoms or $1.2U_{\rm eq}$(C) for other H atoms.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1994); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1427). Services for accessing these data are described at the back of the journal.

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