

*Acta Cryst.* (1996). **C52**, 2548–2552

## Conformational Flexibility in *N*-Benzylideneanilines

WILLIAM CLEGG, MARK R. J. ELSEGOOD, SARAH L. HEATH, ANDREW HOULTON AND MICHELLE A. SHIPMAN

*Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England. E-mail: w.clegg@ncl.ac.uk*

(Received 14 June 1996; accepted 8 July 1996)

### Abstract

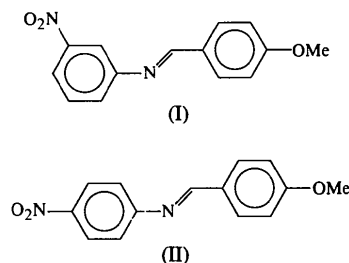
Molecules of *N*-(*p*-methoxybenzylidene)-*m*-nitroaniline, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>, (I), are essentially planar in the solid state, with average torsion angles of 15.7 (6), −179.6 (4) and −8.3 (6)° about the C—N, N=C and C—C bonds, respectively, of the central unit joining the two aromatic rings. The crystal packing consists of stacks of identically oriented molecules related by pure translation symmetry, with a perpendicular spacing of 3.490 (2) Å. Two different conformations (*A* and *B*) of the positional isomer *N*-(*p*-methoxybenzylidene)-*p*-nitroaniline, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>, (II), exist together in the solid state, one much more planar than the other; average torsion angles about C—N, N=C and C—C are 14.7 (2), −178.0 (1) and 1.0 (2)°, respectively, for (IIA), and 40.6 (2), −177.5 (1) and 5.7 (2)°, respectively, for (IIB). Molecules of (IIA) form stacks with an alternating head-to-tail arrangement and spacings of 3.319 (2) and 3.446 (2) Å; molecules of (IIB) also stack head-to-tail with parallel rings 3.277 (2) Å apart.

### Comment

*N*-Benzylideneaniline and its derivatives are of considerable interest as a class of compounds, not least for their non-linear optical properties. The optical electronic spectrum of *N*-benzylideneaniline differs markedly from that of the isoelectronic analogues *trans*-azobenzene and *trans*-stilbene because of differences in molecular geometry (Bernstein, Engel & Hagler, 1981). Whereas *trans*-azobenzene and *trans*-stilbene are essentially planar, *N*-benzylideneaniline is non-planar in the solid state (Bürgi & Dunitz, 1970), gas phase and in solution. *Ab initio* calculations on benzylideneaniline and related molecules have shown that rotations about the Ph—N bond of up to 45° from a planar conformation are stabilizing, while rotations about the Ph—C bond are destabilizing, and the most stable free-molecule conformation is non-planar (Bernstein, Engel & Hagler, 1981). By contrast, benzylideneaniline derivatives with substituents on one or both aromatic rings display a range of conformations in the solid state, and polymorphism is well established for this class of compounds. A total of 132 structures

of this kind have been extracted from the Cambridge Structural Database (Allen & Kennard, 1993). They generally show Ph—C torsion angles within 20° of planarity but a wide range of Ph—N torsion angles, while the central C—N=C—C unit is almost invariably close to planar, with torsion angles not exceeding 10°. As a consequence, these materials serve as useful models for the investigation of the effects of crystal packing forces on molecular geometry (Bürgi & Dunitz, 1970; Bar & Bernstein, 1984, 1987; Bernstein, Anderson & Eckhardt, 1979; Hagler & Bernstein, 1978; Bernstein & Izak, 1976; Bernstein, 1972; Zamir *et al.*, 1994).

Interest in the optical properties of benzylideneaniline derivatives has developed and has focused on potential applications, in particular through the liquid-crystalline and non-linear-optical properties of particular derivatives (Tsunekawa *et al.*, 1990; Leadbetter, Mazid, Kelly, Goodby & Gray, 1979; Bryan & Forcier, 1980; Gane & Leadbetter, 1981; Sato, Nakano & Mukaida, 1995; Kurogoshi & Hori, 1996). Of these latter effects, second-harmonic generation has been the most widely studied; this is due in part to the predicted small dipole and large hyperpolarizability of these compounds (Tsunekawa *et al.*, 1990). We have recently reported a series of compounds containing the required donor-π-acceptor framework for second-harmonic generation and have described the structure of *p*-bromo-*N*-(*p*-dimethylaminobenzylidene)aniline (Houlton *et al.*, 1992; Ahmet, Silver & Houlton, 1994). In an effort to examine the effects of positional substitution, we have determined the structures of two isomeric nitro-*N*-(*p*-methoxybenzylidene)anilines, namely the *m*-nitro derivative, (I), and the *p*-nitro derivative, (II).



The entire molecule of (I) (Fig. 1) is essentially planar [r.m.s. deviation 0.071 (3) Å for non-H atoms]. The dihedral angle between the two aromatic rings is 7.5 (7)°. However, this apparently small twist represents the balance of two moderate but opposite C—N and C—C torsions (Table 5).

The crystal structure of (II) contains two symmetry-inequivalent molecules with quite different conformations. Molecule *A* (top of Fig. 2) is almost planar [r.m.s. deviation 0.113 (1) Å for non-H atoms] with a dihedral angle of 16.5 (2)° between the rings, this twist being almost entirely accounted for by the moderate C—N torsion of 14.7 (2)°. Molecule *B* (bottom of Fig. 2) is much

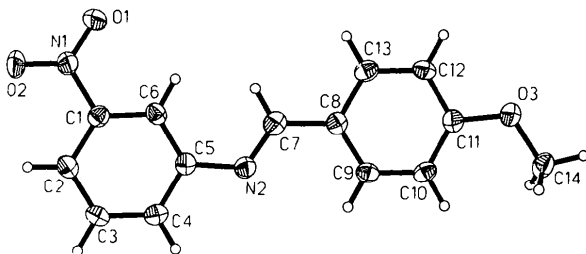


Fig. 1. The molecular structure of (I) with atom labels and 50% probability ellipsoids for non-H atoms.

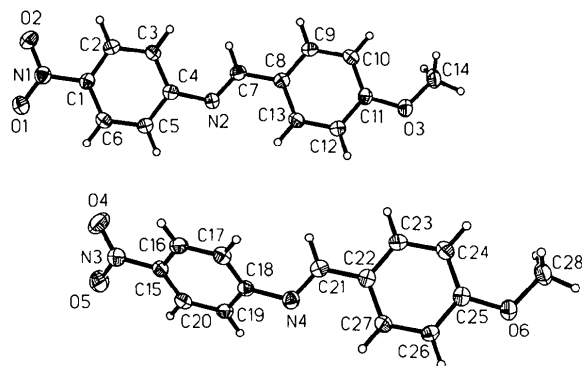


Fig. 2. The structure of both independent molecules of (II) with atom labels and 50% probability ellipsoids for non-H atoms.

more twisted, with an r.m.s. deviation of  $0.287(2) \text{ \AA}$  from the mean plane of the non-H atoms and an inter-ring dihedral angle of  $47.5(2)^\circ$ , largely because of to a  $40.6(2)^\circ$  C—N torsion. There are, however, no significant differences between the bond lengths of the *A* and *B* molecules of (II) and those of (I). In all three molecules, the nitro and methoxy substituents are twisted slightly out of the planes of their respective rings (Table 5).

The packing of (I) is in stacks of precisely parallel molecules along the short *b* axis (Fig. 3), the translational symmetry requiring that all molecules in a stack

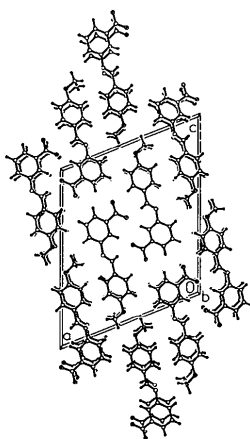


Fig. 3. The packing of (I) seen along the *b* axis.

are identical in orientation as well as form. There are no particularly short contacts between stacks. The molecules are tilted by  $26.3(2)^\circ$  relative to the (010) plane so that the perpendicular spacing between adjacent molecules in a stack is reduced to  $3.490(2) \text{ \AA}$  and adjacent molecules are offset from an exact overlap in a direction perpendicular to the main molecular axis.

Molecules of (II) also form stacks. Each stack is composed of molecules of one type (*A* or *B*), and the *A* stacks and *B* stacks are arranged in alternating rows (Fig. 4). Within each stack adjacent molecules are oriented head-to-tail, in contrast to the head-to-head stacking in (I). Stacks of type *B* are generated by screw axes and have the central C—N=C—C units approximately eclipsed; the perpendicular spacing between stacked rings is  $3.277(2) \text{ \AA}$ . Stacks of type *A* are generated by inversion centres and adjacent molecules are stepped relative to one another, with no eclipsing of rings or central bridge units, though many chemically different bonds do lie directly in line when viewed normal to the mean plane of the molecule; perpendicular distances between the molecular mean planes are alternately  $3.319(2)$  and  $3.446(2) \text{ \AA}$ . In (II), as in (I), there are no particularly short contacts between the stacks.

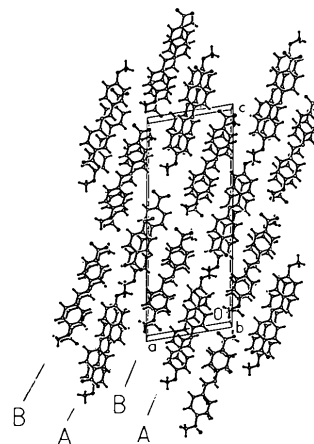


Fig. 4. The packing of (II) seen along the *b* axis, showing the alternating rows of stacked *A* and *B* molecules.

These results demonstrate further the ability of the crystal packing to stabilize preferentially conformations different from that expected for the isolated molecule, including the observation of two quite different conformations for the same molecule in one crystal structure. Parallel stacking of aromatic rings appears to be a particularly important factor.

### Experimental

(I) was prepared by dissolving *p*-methoxybenzaldehyde (1 g, 73 mmol) in dry ethanol (100 ml) containing a molecular sieve, and adding a slight molar excess of *m*-nitroaniline (1.22 g,

88 mmol). The solution was refluxed for 12 h, after which the solvent volume was reduced to about 20 ml and stored at 277 K. The resultant precipitate was filtered off, washed with cold ethanol and dried in air. Compound (II) was prepared analogously from *p*-nitroaniline. Crystals suitable for X-ray diffraction were obtained by recrystallization from acetone for (I) and chloroform for (II). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub> solution): δ 3.87 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.52 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 8.40 p.p.m. (s, 1H) for (I); δ 3.88 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.9 Hz, 2H), 8.33 p.p.m. (s, 1H) for (II).

**Compound (I)***Crystal data*C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>*M<sub>r</sub>* = 256.26

Monoclinic

*P*2<sub>1</sub>/*n**a* = 16.535 (5) Å*b* = 3.8939 (10) Å*c* = 19.890 (5) Å

β = 111.870 (8)°

*V* = 1188.5 (6) Å<sup>3</sup>*Z* = 4*D<sub>x</sub>* = 1.432 Mg m<sup>-3</sup>*D<sub>m</sub>* not measured*Data collection*

Siemens SMART CCD diffractometer

ω rotation with narrow frames

Absorption correction: none

5775 measured reflections

2091 independent reflections

*Refinement*Refinement on *F*<sup>2</sup>*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0715*wR*(*F*<sup>2</sup>) = 0.1765*S* = 1.221

2091 reflections

174 parameters

H atoms riding (see text)

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + 4.9505*P*]where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3(Δ/σ)<sub>max</sub> < 0.001Δρ<sub>max</sub> = 0.302 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.263 e Å<sup>-3</sup>

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 2510

reflections

θ = 2.65–28.04°

μ = 0.103 mm<sup>-1</sup>*T* = 160 (2) K

Triangular plate

0.56 × 0.48 × 0.06 mm

Pale yellow

1571 observed reflections

[*I* > 2σ(*I*)]*R*<sub>int</sub> = 0.0448θ<sub>max</sub> = 25.00°*h* = -17 → 20*k* = -5 → 5*l* = -26 → 18

Extinction correction:

*SHELXTL* (Sheldrick, 1994)

Extinction coefficient:

0.0068 (11)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

C3	0.8024 (3)	0.9201 (12)	0.6298 (2)	0.0305 (11)
C4	0.7826 (3)	0.8632 (12)	0.5564 (2)	0.0308 (11)
C5	0.7011 (3)	0.9552 (12)	0.5051 (2)	0.0263 (10)
C6	0.6396 (3)	1.0994 (12)	0.5287 (2)	0.0276 (10)
N2	0.6874 (2)	0.8850 (10)	0.43142 (19)	0.0286 (9)
C7	0.6235 (3)	1.0265 (12)	0.3817 (2)	0.0296 (10)
C8	0.6045 (3)	0.9668 (11)	0.3048 (2)	0.0261 (10)
C9	0.6610 (3)	0.7897 (12)	0.2801 (2)	0.0263 (10)
C10	0.6443 (3)	0.7504 (12)	0.2073 (2)	0.0270 (10)
C11	0.5674 (3)	0.8792 (12)	0.1569 (2)	0.0267 (10)
C12	0.5088 (3)	1.0535 (12)	0.1800 (2)	0.0272 (10)
C13	0.5268 (3)	1.0991 (12)	0.2530 (2)	0.0280 (10)
O3	0.54291 (19)	0.8528 (9)	0.08336 (15)	0.0325 (8)
C14	0.6031 (3)	0.6950 (13)	0.0567 (2)	0.0361 (12)

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

C5—N2	1.424 (5)	C7—C8	1.462 (6)
N2—C7	1.272 (6)		
C7—N2—C5	119.0 (4)	N2—C7—C8	122.5 (4)
O2—N1—C1—C6	-174.6 (5)	C5—N2—C7—C8	-179.6 (4)
O1—N1—C1—C6	4.9 (6)	N2—C7—C8—C9	-9.0 (7)
O2—N1—C1—C2	5.0 (7)	N2—C7—C8—C13	172.4 (4)
O1—N1—C1—C2	-175.5 (4)	C10—C11—O3—C14	-3.2 (7)
C6—C5—N2—C7	16.3 (7)	C12—C11—O3—C14	176.3 (4)
C4—C5—N2—C7	-165.0 (4)		

**Compound (II)***Crystal data*C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>*M<sub>r</sub>* = 256.26

Monoclinic

*P*2<sub>1</sub>/*n**a* = 11.4508 (10) Å*b* = 7.3793 (7) Å*c* = 29.047 (3) Å

β = 99.642 (2)°

*V* = 2419.8 (4) Å<sup>3</sup>*Z* = 8*D<sub>x</sub>* = 1.407 Mg m<sup>-3</sup>*D<sub>m</sub>* not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 6209

reflections

θ = 2.85–27.97°

μ = 0.101 mm<sup>-1</sup>*T* = 160 (2) K

Block

0.40 × 0.28 × 0.20 mm

Yellow

*Data collection*

Siemens SMART CCD diffractometer

ω rotation with narrow frames

Absorption correction: none

12225 measured reflections

4260 independent reflections

*Refinement*Refinement on *F*<sup>2</sup>*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.0386*wR*(*F*<sup>2</sup>) = 0.1061*S* = 1.063

4260 reflections

346 parameters

H atoms riding (see text)

*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.0487*P*)<sup>2</sup> + 0.7611*P*]where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3(Δ/σ)<sub>max</sub> < 0.001

3314 observed reflections

[*I* > 2σ(*I*)]*R*<sub>int</sub> = 0.0345θ<sub>max</sub> = 25.00°*h* = -12 → 15*k* = -9 → 9*l* = -31 → 36Δρ<sub>max</sub> = 0.231 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.200 e Å<sup>-3</sup>

Extinction correction:

*SHELXTL* (Sheldrick, 1994)

Extinction coefficient:

0.0027 (4)

Atomic scattering factors

from *International Tables for Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (I)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N1	0.5973 (2)	1.3155 (11)	0.62649 (19)	0.0304 (9)
O1	0.5242 (2)	1.3724 (11)	0.58159 (17)	0.0439 (10)
O2	0.6184 (2)	1.3895 (12)	0.69040 (17)	0.0525 (11)
C1	0.6618 (3)	1.1552 (12)	0.6019 (2)	0.0264 (10)
C2	0.7425 (3)	1.0697 (12)	0.6539 (2)	0.0297 (11)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for (II)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
O1	0.74678 (11)	0.59374 (19)	-0.14399 (4)	0.0418 (3)
O2	0.56733 (11)	0.65672 (18)	-0.17618 (4)	0.0399 (3)
N1	0.64361 (12)	0.63512 (19)	-0.14161 (5)	0.0308 (3)
C1	0.61159 (14)	0.6607 (2)	-0.09542 (5)	0.0261 (4)
C2	0.49467 (14)	0.6950 (2)	-0.09207 (6)	0.0288 (4)
C3	0.46390 (14)	0.7211 (2)	-0.04872 (6)	0.0292 (4)
C4	0.54996 (13)	0.7181 (2)	-0.00839 (6)	0.0255 (4)
C5	0.66725 (14)	0.6825 (2)	-0.01292 (6)	0.0305 (4)
C6	0.69862 (14)	0.6534 (2)	-0.05622 (6)	0.0316 (4)
N2	0.52740 (11)	0.74359 (19)	0.03741 (5)	0.0277 (3)
C7	0.42926 (14)	0.8109 (2)	0.04449 (6)	0.0277 (4)
C8	0.40201 (13)	0.8332 (2)	0.09130 (5)	0.0249 (4)
C9	0.29548 (14)	0.9109 (2)	0.09839 (6)	0.0276 (4)
C10	0.27126 (14)	0.9390 (2)	0.14307 (6)	0.0278 (4)
C11	0.35394 (14)	0.8886 (2)	0.18143 (6)	0.0255 (4)
C12	0.45998 (14)	0.8062 (2)	0.17486 (6)	0.0297 (4)
C13	0.48267 (13)	0.7799 (2)	0.13055 (6)	0.0276 (4)
O3	0.34108 (10)	0.91301 (16)	0.22686 (4)	0.0330 (3)
C14	0.24133 (16)	1.0169 (3)	0.23568 (6)	0.0382 (4)
O4	0.84749 (12)	0.1158 (2)	0.02056 (4)	0.0562 (4)
O5	1.02618 (11)	0.1903 (2)	0.05005 (4)	0.0470 (4)
N3	0.92548 (13)	0.1453 (2)	0.05406 (5)	0.0353 (4)
C15	0.89666 (14)	0.1275 (2)	0.10102 (6)	0.0273 (4)
C16	0.79105 (14)	0.0450 (2)	0.10647 (6)	0.0283 (4)
C17	0.76200 (14)	0.0360 (2)	0.15061 (6)	0.0266 (4)
C18	0.83706 (14)	0.1084 (2)	0.18894 (6)	0.0248 (4)
C19	0.94510 (13)	0.1845 (2)	0.18268 (6)	0.0260 (4)
C20	0.97475 (13)	0.1956 (2)	0.13858 (6)	0.0267 (4)
N4	0.81133 (11)	0.10037 (18)	0.23477 (5)	0.0272 (3)
C21	0.70560 (14)	0.1318 (2)	0.24128 (6)	0.0265 (4)
C22	0.67146 (13)	0.1189 (2)	0.28723 (6)	0.0248 (4)
C23	0.55873 (14)	0.1722 (2)	0.29386 (6)	0.0278 (4)
C24	0.52589 (14)	0.1679 (2)	0.33768 (6)	0.0282 (4)
C25	0.60768 (14)	0.1113 (2)	0.37574 (6)	0.0257 (4)
C26	0.72032 (14)	0.0557 (2)	0.36969 (6)	0.0259 (4)
C27	0.75158 (14)	0.0583 (2)	0.32607 (6)	0.0250 (4)
O6	0.58700 (10)	0.10211 (17)	0.42072 (4)	0.0339 (3)
C28	0.47538 (15)	0.1672 (3)	0.42980 (6)	0.0389 (4)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II)

C4—N2	1.410 (2)	C18—N4	1.412 (2)
N2—C7	1.277 (2)	N4—C21	1.278 (2)
C7—C8	1.454 (2)	C21—C22	1.455 (2)
C7—N2—C4	120.63 (14)	C21—N4—C18	118.97 (14)
N2—C7—C8	121.83 (15)	N4—C21—C22	122.05 (15)
O2—N1—C1—C2	4.8 (2)	O5—N3—C15—C20	12.7 (2)
O1—N1—C1—C2	-175.66 (15)	O4—N3—C15—C20	-166.78 (16)
O2—N1—C1—C6	-174.08 (15)	O5—N3—C15—C16	-168.10 (16)
O1—N1—C1—C6	5.5 (2)	O4—N3—C15—C16	12.4 (2)
C5—C4—N2—C7	166.24 (16)	C17—C18—N4—C21	-42.2 (2)
C3—C4—N2—C7	-15.6 (2)	C19—C18—N4—C21	141.01 (16)
C4—N2—C7—C8	177.95 (14)	C18—N4—C21—C22	177.50 (14)
N2—C7—C8—C9	178.50 (16)	N4—C21—C22—C23	173.34 (15)
N2—C7—C8—C13	-0.5 (2)	N4—C21—C22—C27	-4.7 (2)
C10—C11—O3—C14	-7.6 (2)	C24—C25—O6—C28	-4.4 (2)
C12—C11—O3—C14	172.34 (15)	C26—C25—O6—C28	176.44 (15)

Table 5. Comparison of geometry ( $\text{\AA}$ ,  $^\circ$ ) for the three molecules

The dihedral angle is between the two  $C_6$ -ring mean planes. Each torsion angle  $\tau$  is the mean of the appropriate values ( $\pm 180^\circ$  if required). The values for (IIA) and (IIB) are all inverted for comparison with (I), equivalent to selecting the enantiomorphic molecules.

	(I)	(IIA)	(IIB)
C=N	1.272 (6)	1.277 (2)	1.278 (2)
C—N	1.424 (5)	1.410 (2)	1.412 (2)
Dihedral angle	7.5 (7)	16.5 (2)	47.5 (2)

$\tau(\text{C—N})$	15.7 (6)	14.7 (2)	40.6 (2)
$\tau(\text{C—C})$	-8.3 (6)	1.0 (2)	5.7 (2)
$\tau(\text{C=N})$	-179.6 (4)	-178.0 (1)	-177.5 (1)
$\tau(\text{C—NO}_2)$	5.0 (6)	-5.1 (2)	-12.6 (2)
$\tau(\text{C—OMe})$	-3.5 (6)	7.6 (2)	3.9 (2)

Each data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was 4.94 cm and the detector, with an active area of  $6.25 \times 6.25$  cm, was offset by  $27^\circ$  in  $2\theta$ . Coverage of the unique set was complete. Some reflections with  $\theta > 25^\circ$  were recorded and used for cell refinement, but were not included in the refinement of the structure. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were placed geometrically and refined with a riding model including free rotation about O—C bonds, and with  $U_{iso}$  constrained to be 1.2 (1.5 for methyl groups) times  $U_{eq}$  of the carrier C atom. The crystals of (I) were relatively thin and of only moderate quality, giving weaker diffraction and rather high  $R$  values.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: local programs; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We thank EPSRC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1402). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Ahmet, M. T., Silver, J. & Houlton, A. (1994). *Acta Cryst.* **C50**, 1814–1818.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
- Bar, I. & Bernstein, J. (1984). *J. Am. Chem. Soc.* **88**, 243–248.
- Bar, I. & Bernstein, J. (1987). *Tetrahedron*, **43**, 1299–1305.
- Bernstein, J. (1972). *J. Chem. Soc. Perkin Trans. 2*, p. 946.
- Bernstein, J., Anderson, T. E. & Eckhardt, C. J. (1979). *J. Am. Chem. Soc.* **101**, 542–545.
- Bernstein, J., Engel, Y. M. & Hagler, A. T. (1981). *J. Chem. Phys.* **234**, 2346–2353.
- Bernstein, J. & Izak, I. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 429–434.
- Bryan, R. F. & Forcier, P. G. (1980). *Mol. Cryst. Liq. Cryst.* **60**, 133–151.
- Bürgi, H.-B. & Dunitz, J. D. (1970). *Helv. Chim. Acta*, **52**, 1747–1764.
- Gane, P. A. C. & Leadbetter, A. J. (1981). *Mol. Cryst. Liq. Cryst.* **78**, 183–200.
- Hagler, A. T. & Bernstein, J. (1978). *J. Am. Chem. Soc.* **100**, 6349–6354.
- Houlton, A., Jassim, N., Roberts, R. M. G., Silver, J., McArdle, P., Cunningham, D. & Higgins, T. (1992). *J. Chem. Soc. Dalton Trans.* pp. 2234–2241.
- Kurogoshi, S. & Hori, K. (1996). *Acta Cryst.* **C52**, 660–663.
- Leadbetter, A. J., Mazid, M. A., Kelly, B. A., Goodby, J. W. & Gray, G. W. (1979). *Phys. Rev. Lett.* **43**, 630–633.

- Sato, M., Nakano, T. & Mukaida, K. I. (1995). *Liq. Cryst.* **18**, 645–649.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART and SAINT Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tsunekawa, T., Gotoh, J., Mataka, H., Kondoh, T., Fukuda, S. & Iwamoto, M. (1990). *Nonlinear Opt. Prop. Org. Mater.* **3**, 272–284.
- Zamir, S., Bernstein, J., Ioffe, A., Brunvoll, J., Kolonits, M. & Hargittai, I. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 895–900.

*Acta Cryst.* (1996). **C52**, 2552–2554

### 6-(4-Methoxyphenyl)thieno[2,3-*d*][1,3]-dithiole-2-thione at 150 K

TURAN OZTURK AND JOHN D. WALLIS

*Chemical Laboratory, University of Kent, Canterbury CT2 7NH, England. E-mail: jdw@ukc.ac.uk*

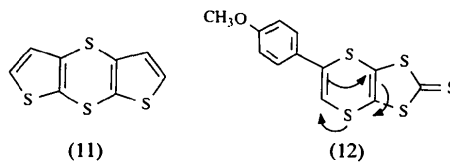
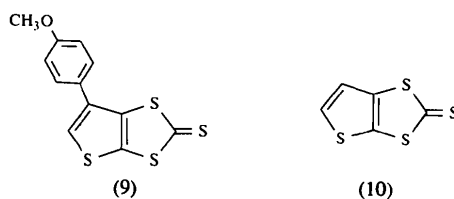
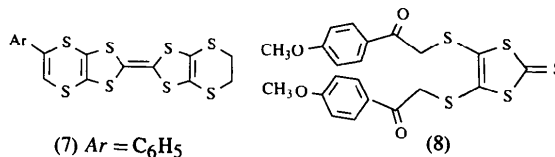
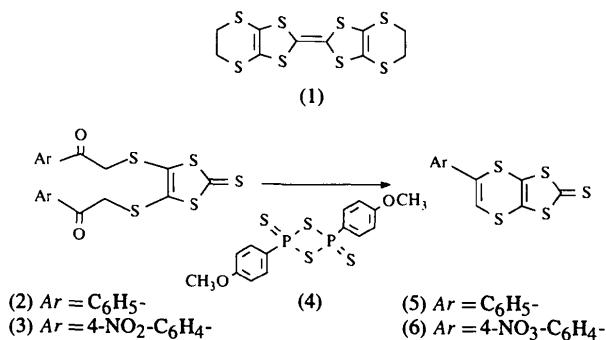
(Received 25 March 1996; accepted 23 April 1996)

#### Abstract

The structure determination at 150 K of 6-(4-methoxyphenyl)thieno[2,3-*d*][1,3]dithiole-2-thione, C<sub>12</sub>H<sub>8</sub>OS<sub>4</sub>, which was obtained from a novel rearrangement reaction, is the first measurement of this heterocyclic system. The bond lengths in the thiophene ring are not perturbed significantly by the fusion of the second ring; however, there is a degree of asymmetry in the bond lengths of the dithiole ring.

#### Comment

Since many radical cation salts of bis(ethylenedithio)tetrathiafulvalene, (1), show electrical conductivity, and in some cases superconductivity (Williams *et al.*, 1985), we have been exploring synthetic routes to new derivatives of (1) (Ozturk, Rice & Wallis, 1995). Recently, it was discovered that reactions of 4,5-bis(benzoylmethylthio)-1,3-dithiolethione, (2), and 4,5-bis(4-nitrobenzoylmethylthio)-1,3-dithiolethione, (3), with Lawesson's reagent, (4), provide an efficient route to the 1,3-dithiolo[1,4]dithiin-2-thiones (5) and (6) (Ozturk, 1996); the former has been converted subsequently to the tetrathiafulvalene derivative (7), a precursor for the preparation of organic metals. In contrast, reaction with Lawesson's reagent of the corresponding bis(4-methoxybenzoyl) derivative, (8), gave a material (58%) containing one less S atom than (5) or (6) according to chemical analysis and mass spectral data. To determine the structure of this substance unambiguously, the crystal structure was determined at 150 K.



The substance was identified as the thieno[2,3-*d*][1,3]dithiole derivative (9). The molecular structure is shown in Fig. 1. No structure determinations of molecules containing this heterocyclic system have been reported, indeed only the preparation of the unsubstituted thione, (10), has been recorded (Engler, Patel, Andersen, Schumaker & Fukushima, 1978; Santalo *et al.*, 1991). The fused heterocycle is almost planar; the best planes of the two five-membered rings lie at just 4.2(1)°. The bond lengths in the thiophene ring are very similar to those for an isolated thiophene ring (Allen *et al.*, 1987), showing the shortest bonds from C to S in the molecule [S4—C2 1.716(4), S4—C3 1.713(4) Å] and C—C bonds in the range 1.362(5)–1.433(5) Å. There is a marked asymmetry in the dithiole ring; the bonds to ring atom S1 are longer than those to ring atom S3 [S1—C1 1.751(4) and S1—C5 1.748(4) Å *cf.* S3—C1 1.737(4) and S3—C2 1.730(4) Å]. Similar general trends are found in the molecular structure of the dithieno[1,4]dithiin, (11) (Hiemstra & Kiers, 1979). The best plane through the substituted benzene ring lies at 30.0(1)° to the best plane through the heterocyclic system. The aryl substituent is prevented from attaining coplanarity with the heterocyclic system by two short