Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Conformational preferences in 2-nitrophenylthiolates: interplay between intra- and intermolecular forces; structures of (*E*)-1-(4-methyl-2-nitrobenzenethiolato)-2-phenylethene, *S*-(2-nitrophenyl)-benzenecarbothiolate and 1-(2-nitrophenylthio)-2,5-pyrrolidinedione

John N. Low,[a] Emily J. Storey,[a] Mary McCarron,[a] James L. Wardell,[b] George Ferguson[c]† and Christopher Glidewell[c]*

[a]Department of Applied Physics and Electronic and Mechanical Engineering, University of Dundee, Dundee DD1 4HN, Scotland, [b]Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland, and [c]School of Chemistry, University of St Andrews, St Andrews KY16 9ST, Scotland

† On leave from Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Correspondence e-mail: cg@st-andrews.ac.uk

Received 12 May 1999
Accepted 1 July 1999

In (*E*)-1-(4-methyl-2-nitrobenzenethiolato)-2-phenylethene, $C_{15}H_{13}NO_2S$ (1) (orthorhombic *Pbca*), the nitro group is almost coplanar with the adjacent aryl ring, but the dihedral angles between the nitro-aryl and styryl fragments is ~121°. The molecules are linked by paired C—H···O hydrogen bonds in a chain of rings. In *S*-(2-nitrophenyl)benzenecarbothiolate, $C_{13}H_9NO_3S$ (2) (monoclinic $P2_1/a$), the nitro group is rotated by 33.0 (2)° out of the plane of the adjacent aryl ring and the thiobenzoate group is strongly twisted away from the plane of the disubstituted aryl ring. The molecules of (2) are linked into chains by C—H···O hydrogen bonds, and each chain is linked to two neighbouring chains by means of aromatic $\pi\cdots\pi$ stacking interactions. In 1-(2-nitrophenylthio)-2,5-pyrrolidinedione, $C_{10}H_8N_2O_4S$ (3) (monoclinic $P2_1/a$), the nitro group is again almost coplanar with the adjacent aryl ring, but the pyrrolidinedione unit is almost orthogonal to the $O_2NC_6H_4SN$ plane. There are three types of C—H···O hydrogen bond in the structure, and these link the molecules into a two-dimensional net. The conformations of these molecules have been investigated by SCF calculations and two energy minima have been identified for each: the molecules of (1) and (3) adopt conformations in their crystals which are close to those at the overall energy minima calculated for isolated molecules, while molecules of (2) adopt a conformation in the crystal close to that calculated for the local energy minimum. Comparisons are made with the structures of some related compounds and it is concluded that, while the nature of the two conformational minima is determined by intramolecular forces, the choice between them is determined primarily by intermolecular forces.

1. Introduction

In nitrobenzene the molecules are highly polar, with significant negative charge on the O atoms, and in the minimum-energy conformation the atoms are coplanar (Høg *et al.*, 1971; Domenicano *et al.*, 1990; Boese *et al.*, 1992). Hence, when an electropositive atom *X* is placed *ortho* to the nitro group, it is to be expected that there will be an attractive electrostatic interaction between *X* and the neighbouring O atom. For example, when *X* is S, it is commonly observed that the shortest intramolecular S···O distance is significantly shorter than the sum of the van der Waals radii (Aupers *et al.*, 1999; Kucsman *et al.*, 1984; Kucsman & Kapovits, 1985).

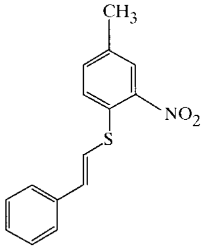
On the other hand, it has been convincingly demonstrated (Domenicano *et al.*, 1990) that the mesomeric interaction

Table 1
Experimental details.

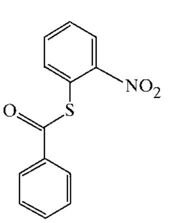
	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{15}H_{13}NO_2S$	$C_{13}H_9NO_3S$	$C_{10}H_8N_2O_4S$
Chemical formula weight	271.32	259.27	252.24
Cell setting	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/a$	$P2_1/a$
a (Å)	21.595 (3)	7.51 (5)	7.918 (5)
b (Å)	14.518 (2)	21.16 (5)	13.132 (5)
c (Å)	7.9530 (7)	7.66 (5)	10.983 (5)
β (°)	90	92.043 (10)	110.7 (3)
V (Å^3)	2493.4 (5)	1216 (12)	1068.5 (9)
Z	8	4	4
D_x (Mg m^{-3})	1.446	1.417	1.568
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25
θ range (°)	9.40–16.53	9.64–16.89	8.06–18.61
μ (mm^{-1})	0.256	0.265	0.307
Temperature (K)	293 (1)	294 (1)	294 (1)
Crystal form	Plate	Block	Needle
Crystal size (mm)	0.42 × 0.29 × 0.08	0.42 × 0.24 × 0.24	0.42 × 0.15 × 0.11
Crystal colour	Colourless	Yellow	Yellow
Data collection			
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\theta/2\theta$ scans	$\theta/2\theta$ scans	$\theta/2\theta$ scans
Absorption correction	Gaussian	Gaussian	Gaussian
$T_{\min}$	0.9351	0.8876	0.9510
$T_{\max}$	0.9820	0.9571	0.9702
No. of measured reflections	2877	2418	2733
No. of independent reflections	2877	2251	2452
No. of observed reflections	1237	1348	1649
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.000	0.009	0.008
$\theta_{\max}$ (°)	27.43	25.60	27.42
Range of h, k, l	$-28 \rightarrow h \rightarrow 0$ $0 \rightarrow k \rightarrow 18$ $0 \rightarrow l \rightarrow 10$	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 25$ $0 \rightarrow l \rightarrow 9$	$-10 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 17$ $0 \rightarrow l \rightarrow 14$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 120 min	Every 180 min	Every 180 min
Intensity decay (%)	0.1	0	0
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0655	0.0441	0.0352
$wR(F^2)$	0.1441	0.1522	0.1215
S	0.910	0.917	0.858
No. of reflections used in refinement	2877	2251	2452
No. of parameters used	173	163	154
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0972P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.000	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.274	0.301	0.256
$\Delta\rho_{\min}$ (e Å^{-3})	−0.270	−0.280	−0.244
Extinction method	None	None	None
Source of atomic scattering factors	*International Tables for Crystallography* (1991, Vol. C)	*International Tables for Crystallography* (1991, Vol. C)	*International Tables for Crystallography* (1991, Vol. C)
Computer programs			
Data collection	*CAD*-4 (Enraf–Nonius, 1992)	*CAD-4-PC Software* (Enraf–Nonius, 1992)	*CAD-4-PC Software* (Enraf–Nonius, 1992)
Cell refinement	*SET*4, *CELDIM* (Enraf–Nonius, 1992)	*SET*4, *CELDIM* in *CAD-4-PC Software* (Enraf–Nonius, 1992)	*SET*4, *CELDIM* in *CAD-4-PC Software* (Enraf–Nonius, 1992)
Data reduction	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)	*DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989)
Structure solution	*SHELXS*97 (Sheldrick, 199)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997)	*NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*NRCVAX*96, *SHELXL*97, *WordPerfect* macro *PREP*8 (Ferguson, 1998)	*NRCVAX*96, *SHELXL*97, *WordPerfect* macro *PREP*8 (Ferguson, 1998)	*NRCVAX*96, *SHELXL*97, *WordPerfect* macro *PREP*8 (Ferguson, 1998)

between the nitro group and the aryl ring is rather small in nitrobenzene, so that the C—N bond is to all intents and purposes a single bond with a correspondingly small barrier to rotation (Høg *et al.*, 1971; Carreira & Townes, 1977; Domenicano *et al.*, 1990). Hence, in the solid state quite modest intermolecular interactions could, if sufficiently specific, perturb the nitro-aryl moiety from its planar conformation.

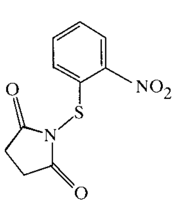
Here we report the molecular and crystal structures of three nitro-aryl derivatives of general type 2-$O_2NC_6H_4SR$, (*E*)-1-(4-methyl-2-nitrobenzenethiolato)-2-phenylethene, $C_{15}H_{13}NO_2S$ (1), *S*-(2-nitrophenyl)benzenecarbothiolate, $C_{13}H_9NO_3S$ (2), and 1-(2-nitrophenylthio)-2,5-pyrrolidinedione, $C_{10}H_8N_2O_4S$ (3), which illustrate the subtle interactions between inter- and intramolecular interactions in these systems.



(1)



(2)



(3)

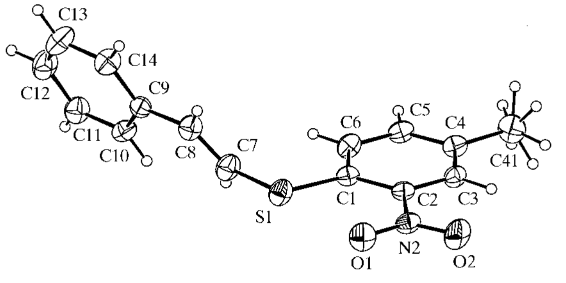


Figure 1
The asymmetric unit of (1), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

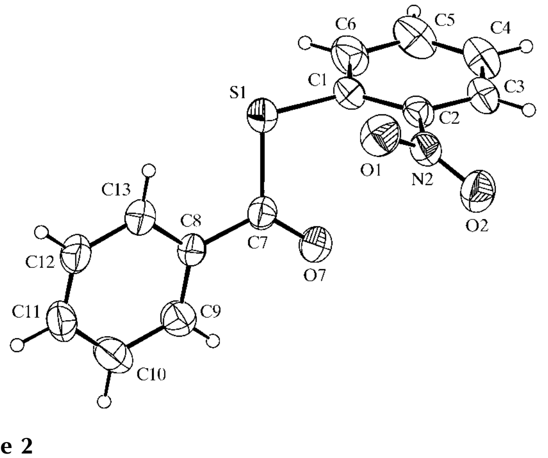


Figure 2
The asymmetric unit of (2), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

2. Experimental

2.1. Synthesis

Compound (1) was prepared as previously described (Wardell, 1975). Compounds (2) and (3) were prepared by the reaction of 2-$O_2NC_6H_4SH$ with either benzoyl chloride, for (2), or *N*-bromosuccinimide, for (3), in CCl_4 solution in the presence of Et_3N as base. Analyses: (2) found C 60.4, H 3.4, N 5.4%; $C_{13}H_9NO_3S$ requires C 60.2, H 3.5, N 5.4%; (3) found C 47.5, H 3.4, N 11.3; $C_{10}H_8N_2O_4S$ requires C 47.6, H 3.2, N 11.1%. Melting points: (1) 131–133°C [lit. (Wardell, 1975) 130–132°C]; (2) 45–47°C [lit. (Morgenstein *et al.*, 1969) 47–49°C]; (3) 223–225°C [lit. (Furukawa *et al.*, 1972) 210°C]. For each compound, crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in EtOH.

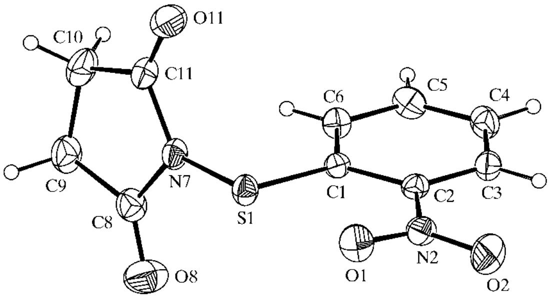


Figure 3
The asymmetric unit of (3), showing the atom-labelling scheme. Atoms are depicted as in Fig. 1.

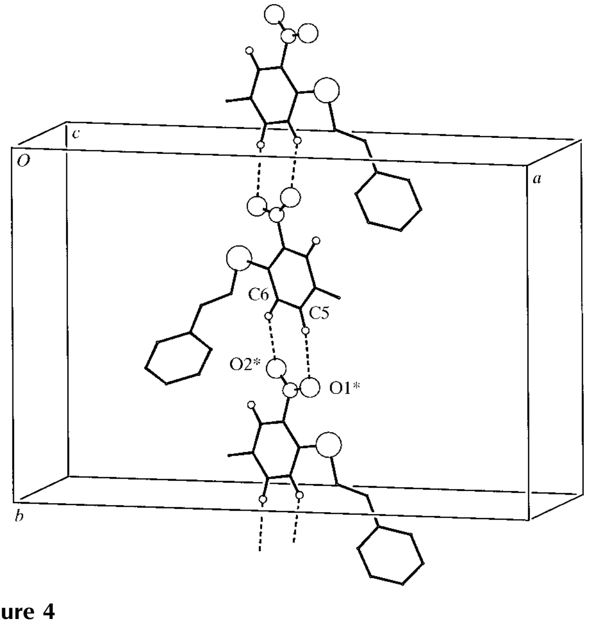


Figure 4
Part of the crystal structure of (1), showing the *C*(6) [$R_2^2(7)$] chain of rings running parallel to [010]. For the sake of clarity, H atoms in the methyl and PhCH=CH groups are omitted. Acceptor atoms marked with an asterisk and donor atoms are in molecules related by the 2_1 screw axis along ($\frac{1}{2}$, *y*, $\frac{1}{4}$).

2.2. Data collection, structure solution and refinement

Details of cell data, data collection and refinement are summarized in Table 1 (Enraf–Nonius, 1992; Gabe *et al.*, 1989; Ferguson, 1998; Sheldrick, 1997; Spek, 1998). The space groups *Pbca* for (1) and $P2_1/a$ for both (2) and (3) were uniquely determined from the systematic absences. The structures were all solved by direct methods using *NRCVAX* (Gabe *et al.*, 1989), and refined with all data on F^2 using *SHELXL*97 (Sheldrick, 1997). A weighting scheme based upon $P = (F_o^2 + 2F_c^2)/3$ was employed in order to reduce statistical bias (Wilson, 1976). All H atoms were located from difference maps, and all were included in the refinements as riding atoms. The methyl H atoms in (1) were disordered and were modelled using two sets of sites, offset by a 60° rotation about the exocyclic C—C bond and each with 0.50 occupancy. The diagrams were prepared with the aid of *PLATON* (Spek, 1998). Figs. 1–3 show the molecular structures of (1)–(3) and Figs. 4–10 show aspects of the crystal structures. Figs. 11 and 13 were drawn using coordinates retrieved from the Cambridge Structural Database (Allen & Kennard, 1993); Figs. 12 and 14 were drawn using coordinates given by Aupers *et al.* (1999). Selected molecular dimensions are presented in Tables 2 and 3, calculated net charges in Table 4, and details of the hydrogen bonding in Tables 5 and 6.

Figure 5
Part of the crystal structure of (2), showing $C(7)$ parallel to [100]. For the sake of clarity, H atoms in the PhC(O)S group are omitted. The acceptor atom O7 marked with an asterisk is in the molecule at $(\frac{1}{2} + x, \frac{1}{2} - y, z)$.

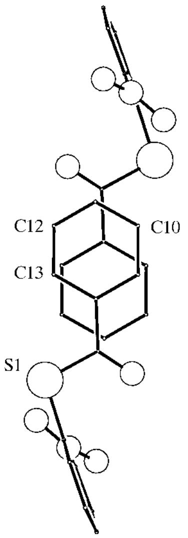


Figure 6
Part of the crystal structure of (2), showing the $\pi\cdots\pi$ stacking interaction between two molecules related by a centre of inversion. For the sake of clarity, all H atoms are omitted.

2.3. Molecular modelling

Computations of molecular geometry and energy were made using the AM1 method (Dewar *et al.*, 1985), as implemented in *MOPAC* version 6 (Stewart, 1990). Each stationary point was characterized by calculation of the force-constant

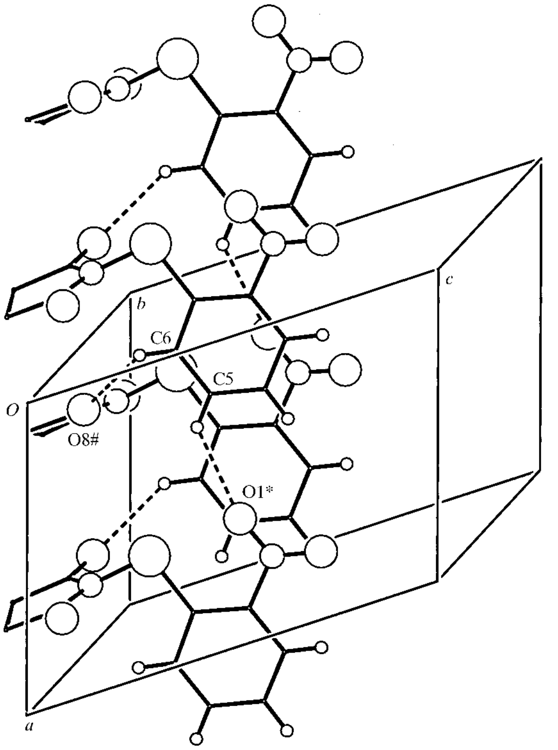


Figure 7
Part of the crystal structure of (3), showing the two $C(7)$ motifs forming a ladder of $R_4^4(26)$ rings parallel to [100]. For the sake of clarity, H atoms in the pyrrolidinedione group are omitted. Atoms marked with an asterisk or hash symbol are in molecules at $(1 + x, y, z)$ and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$, respectively.

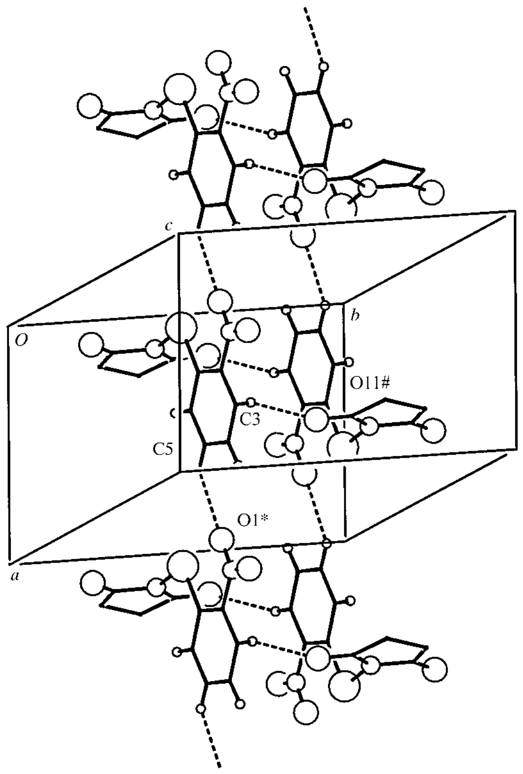


Figure 8
Part of the crystal structure of (3), showing the centrosymmetric $R_2^2(16)$ and $R_4^4(26)$ rings. For the sake of clarity, H atoms in the pyrrolidinedione group are omitted. Atoms marked with an asterisk or hash symbol are in molecules at $(1 + x, y, z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

matrix. Selected conformational data are given in Table 3 and calculated net charges in Table 4.[1]

3. Results and discussion

3.1. Molecular structures of (1)–(3)

3.1.1. Molecular conformations. In crystals of (1)–(3) the molecules all lie in general positions and hence have no symmetry imposed upon them. All adopt conformations of C_1 symmetry, and hence all the molecules are chiral. Since, however, each compound crystallizes in a centric space group, equal numbers of each enantiomer are present in the solid state.

In the molecules of (1) (Fig. 1 and Table 3) the nitro group is virtually coplanar with its neighbouring aryl ring, and the styryl fragment comprising the aryl ring C9–C14 and the adjacent C7═C8 double bond is also almost planar. However, the dihedral angle C1—S1—C7—C8 of −121.0 (4)° means that the nitro-aryl and styryl fragments are by no means coplanar: moreover, this twist around the S1—C7 bond, which is the origin of the molecular chirality, means that the two faces of the nitro-aryl ring are no longer equivalent.

By contrast with (1), in the molecules of compound (2) (Fig. 2 and Table 3) the nitro group is rotated away from the plane of the adjacent aryl ring by 33.0 (2)°. The thiobenzoate fragment PhC(O)S—C is, however, virtually planar, having the nitro-aryl substituent in the *cisoid* conformation usual for esters of type *R*COO*R*′. This thio-ester fragment is not coplanar with the disubstituted aryl ring, as indicated by the torsional angle C2—C1—S1—C7 of −66.9 (3)°. Thus, while the major twist in (1) is around the S1—C7 bond, in (2) it occurs around the S1—C1 bond, when it is accompanied by a disrotatory twist about the C2—N2 bond (Fig. 2).

The conformation of (3) (Fig. 3 and Table 3) shows some similarity with that of (1). Again the nitro group is almost coplanar with the adjacent aryl ring, and again the non-planarity arises from rotation about the S1—N7 bond, analogous to the S1—C7 bond in (1) (Figs. 1 and 3). In compounds containing an open-chain C_2NSC fragment, in which the N and S atoms are three- and two-coordinate, respectively, the C—N—S—C torsional angles show that the lone pairs on N and S are mutually orthogonal, or nearly so, regardless of whether the N coordination is planar [as in (3)] or pyramidal (Sato *et al.*, 1975; Moss & Jacobson, 1981; Iwasaki & Masuko, 1986; Ruostesuo *et al.*, 1989; Rodríguez *et al.*, 1992;

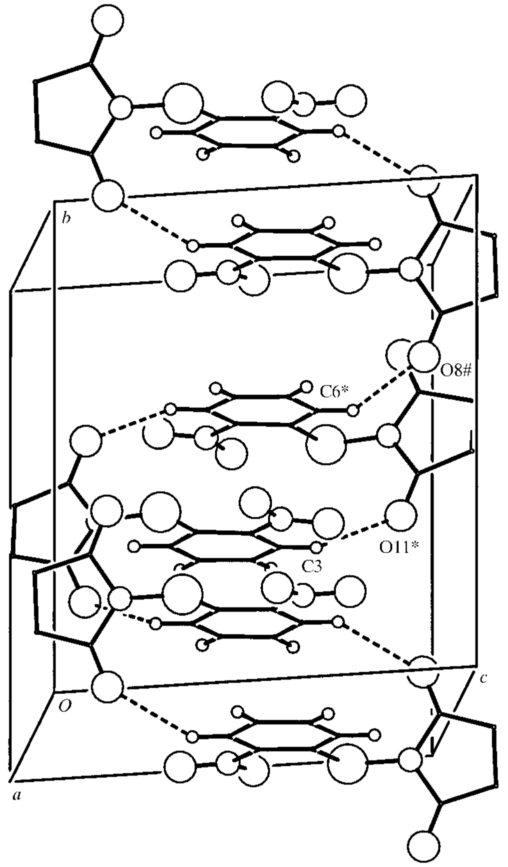


Figure 9
Part of the crystal structure of (3), showing the $C_2^2(15)$ chain parallel to [010]. For the sake of clarity, H atoms in the pyrrolidinedione group are omitted. Atoms marked with an asterisk or hash symbol are in molecules at $(1 - x, 1 - y, 1 - z)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, z)$, respectively.

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference NA0092). Services for accessing these data are described at the back of the journal.

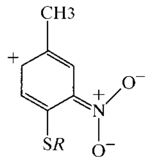
Table 2
Selected bond lengths and angles (Å, °).

	(1)	(2)	(3)
C1—C2	1.353 (4)	1.392 (5)	1.401 (3)
C2—C3	1.374 (5)	1.374 (5)	1.383 (5)
C3—C4	1.310 (4)	1.370 (9)	1.379 (4)
C4—C5	1.331 (5)	1.381 (6)	1.372 (3)
C5—C6	1.369 (5)	1.380 (5)	1.376 (5)
C6—C1	1.315 (4)	1.387 (9)	1.394 (3)
C1—S1	1.761 (4)	1.767 (5)	1.766 (6)
C2—N2	1.383 (4)	1.476 (9)	1.452 (3)
N2—O1	1.217 (4)	1.213 (4)	1.222 (5)
N2—O2	1.189 (4)	1.229 (4)	1.214 (3)
S1—*X*7†	1.667 (4)	1.788 (12)	1.701 (2)
C1—C2—C3	125.3 (3)	122.1 (4)	123.0 (3)
C2—C1—C6	111.6 (3)	116.6 (3)	116.0 (3)
O1—N2—O2	126.3 (3)	122.9 (4)	123.2 (3)
C1—S1—*X*7†	104.0 (2)	100.8 (1)	99.7 (2)

† *X*7 = C7 in (1) and (2), and N7 in (3).

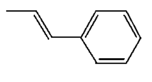
Sudha *et al.*, 1996; Jones *et al.*, 1996; Aupers *et al.*, 1999). The heterocyclic ring in (3) is slightly non-planar, doubtless as a consequence of the perfectly eclipsed C—H bonds which would occur in a strictly planar pyrrolidinedione ring.

3.1.2. Molecular dimensions. In all three compounds the internal angles of the nitro-aryl ring show significant deviations from 120° (Table 2). For (2) and (3) the observed values of the C—C—C angles are reasonably consistent with those predicted from the additive use of substituent constants (Domenicano & Murray-Rust, 1979), but in (1) the deviations are far bigger than can reasonably be accommodated using such a model. For example, the internal C—C—C angles *ipso* to S and to NO_2 in (1) are 111.6 (3) and 125.3 (3)°, respectively, while the angle C3—C4—C5 (*para* to S and *meta* to NO_2) is 113.6 (3)°. These extreme values are associated with significant bond fixation within this ring, where the C3—C4 and C1—C6 distances are very much shorter than the remainder (Table 2), and with a C2—N2 distance of only 1.383 (4) Å: the mean value of the C(aryl)—NO_2 bond length is 1.468 Å, with upper and lower quartile values of 1.476 and 1.460 Å, respectively (Allen *et al.*, 1987). By contrast, in (2) and (3) the C—C distances in the nitro aryl rings are reasonably uniform and the exocyclic C—N distances, 1.476 (9) and 1.452 (3) Å, respectively, are normal. In addition, the angle O—N—O is significantly larger in (1) than in either (2) or (3). These data indicate that in (1) the canonical form (1*a*) (Boese *et al.*, 1992) is more significant than the corresponding forms in (2) and (3).



(1*a*)

R=



The other covalent bond lengths are all typical of their types (Allen *et al.*, 1987). In particular, the S—N bond length in (3), 1.701 (2) Å, is close to the mean value, 1.710 Å, for systems *X*—S—NX_2 containing planar N, but is far shorter than the corresponding value, 1.765 Å, with pyramidal N: the sum of the bond angles at N7 in (3) is 359.4 (3)°.

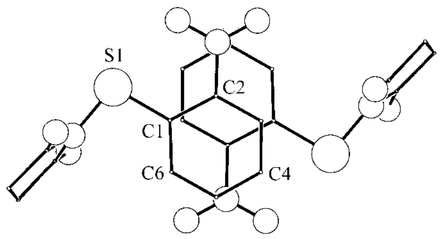


Figure 10
Part of the crystal structure of (3), showing the $\pi\cdots\pi$ stacking interaction within the $R_2^2(16)$ motif. Atoms are depicted as in Fig. 6.

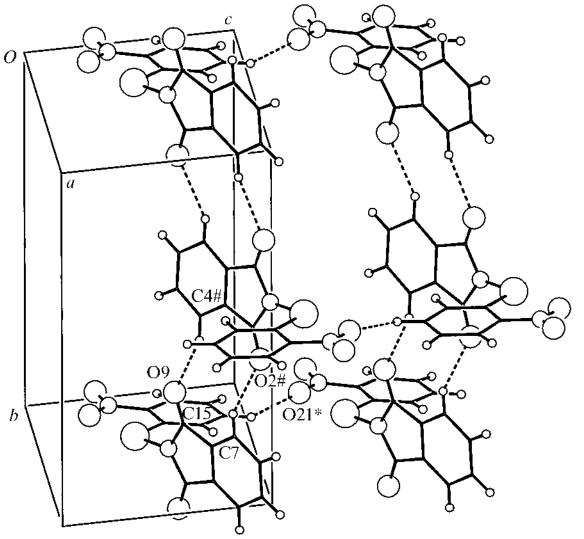


Figure 11
Part of the crystal structure of (phthalimido)$SC_6H_4NO_2$, showing the linking of the *C*(6) [$R_2^2(10)$] chain of rings into a (100) net built from $R_4^4(36)$ rings. Atoms marked with an asterisk or hash symbol are in molecules at (x, y, $1 + z$) and ($2 - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$), respectively.

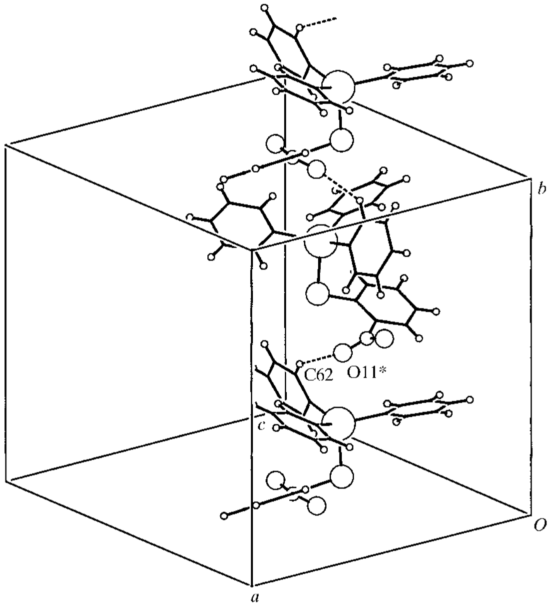


Figure 12
Part of the crystal structure of $O_2NC_6H_4SSnPh_3$ showing the *C*(9) chain parallel to [010]. The atom O11 marked with an asterisk is in the molecule at ($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$).

Table 3
Molecular conformations: comparison of observed and calculated dihedral angles (°).

	Compound (1)			Compound (2)			Compound (3)		
	Observed	Calculated (global)	Calculated (local)	Observed	Calculated (global)	Calculated (local)	Observed	Calculated (global)	Calculated (local)
C1—C2—N2—O1	0.8 (5)	172.3	99.0	−32.2 (4)	−3.0	−25.6	−4.6 (2)	−0.1	52.6
C1—C2—N2—O2	−178.5 (3)	−7.5	−78.7	148.6 (3)	177.0	151.8	175.2 (2)	179.9	−124.2
C2—C1—S1—*X*7†	−175.9 (3)	−168.2	47.9	−66.9 (3)	−175.0	−48.0	−177.4 (1)	−179.7	−2.7
C1—S1—*X*7†—C8	−121.0 (4)	−147.9	−168.5	−174.6 (2)	−179.8	−179.9	100.7 (2)	94.2	−94.1
S1—*X*7†—C8—C9	−172.9 (3)	−172.0	−178.3	159.2 (3)	155.1	147.8	171.7 (1)	169.6	−178.2
*X*7†—C8—C9—C10	3.7 (6)	−20.1	27.2	−179.4 (3)	−179.1	−179.8	6.5 (2)	1.6	3.0

† *X*7 = C7 in (1) and (2), and N7 in (3).

Table 4
Calculated atomic charges.

	(1)	(2)	(3)
q(N2)	+0.57	+0.57	+0.56
q(O1)	−0.36	−0.35	−0.36
q(O2)	−0.35	−0.36	−0.34
q(S1)	+0.52	+0.39	+0.62
q(*X*7)†	−0.43	+0.10	−0.34
q(O7)	–	−0.29	–

† *X*7 = C7 in (1) and (2), and N7 in (3).

Of the non-covalently bonded dimensions within the molecules, the most important are the S···O distances: these are generally found to be significantly less than the sum of the van der Waals radii, 3.3 Å (Bondi, 1964). Thus, in (1) and (3), where the nitro groups are almost coplanar with the adjacent aryl ring, the shortest intramolecular S···O distances are 2.490 (2) and 2.505 (2) Å, respectively, associated with C—S···O and N—S···O angles of 173.9 (2) and 175.8 (3)°, respectively. It may be noted here that the S···O distances in (3) which involve the O atoms of the pyrrolidinedione fragment are significantly longer, 3.031 (3) and 3.044 (3) Å, but still less than the van der Waals sum. By contrast, in (2), where the nitro group has rotated out of the plane of the adjacent aryl ring, the shortest intramolecular S···O distance involving the nitro group is 2.96 (2) Å, much longer than the corresponding distances in (1) and (3), although still much less than the van der Waals sum of 3.3 Å. Rotation of the nitro group about the C—N bond necessarily increases the shortest S···O distance.

3.2. Modelling the molecular structures of (1)–(3)

For each of (1)–(3), free optimization of the structures for isolated molecules, using the AM1 semi-empirical SCF method, led to a global minimum in which the nitro group was essentially coplanar with the adjacent aryl ring and where the torsional angle C2—C1—S1—*X* [*X* = C7 in (1) and (2); N7 in (3)] is close to 180° (Table 3). At these global minima the remainder of each molecule is not coplanar with the near-planar $O_2NC_6H_4SX$ fragment; Table 3 lists the key dihedral angles for both the experimental solid-state structures and the computed gas-phase structures. For (1) and (3) it is clear that the conformation observed in the crystal structures is close to the minimum energy conformation of the isolated molecules.

Common features in the calculated charge distributions for (1)–(3) are the very polar N—O bonds (Table 4), and the strongly positive S atoms: in (1) and (3), atoms C7 and N7, respectively, carry large negative charges, but C7 in the thioester (2) carries a positive charge. Any close contacts between S1 and the O atoms of the nitro group are therefore expected to be strongly attractive on electrostatic grounds, as are any close contacts in (2) between N2 and O7 or between C7 and O1. The purely electrostatic nature of these interactions is demonstrated by the negligibly small bond orders calculated for these atom pairs.

The near-orthogonality in (3) between the C1—S1—N7 and C8—N7—C11 planes, which persisted throughout all computations, must be ascribed to the mutually repulsive effect of the lone pairs on S and N normal to these two planes, which themselves seek to become orthogonal in order to minimize their mutual overlap and resonance integrals.

For each molecule a second local minimum was identified by systematic variation of the dihedral angles C2—C1—S1—*X* and C1—S1—*X*—C8 [*X* = C7 in (1) and (2); N7 in (3)], followed by full optimization once this minimum had been approximately located. In (1)–(3) these minima were 7.3, 8.2 and 6.9 kJ mol^{-1}, respectively, above the global minima with energy barriers above the global minima of 12.8, 13.4 and 15.9 kJ mol^{-1}, respectively. All of the rotations about the S1—C1 bonds are associated in the local minima with a disrotatory motion of the nitro group, about the C2—N2 bond and out of the C1—C6 plane. The barriers to rotation are all calculated to be small, less than 20 kJ mol^{-1}, and in (1) and (2) they are actually calculated to be smaller than the barrier calculated for nitrobenzene itself. While an enforced rotation about the C1—S1 bond always leads to a correlated rotation about the C2—N2 bond, the reverse is not so: driving the nitro group conformation from coplanar with the aryl ring to perpendicular effects only a modest perturbation of the conformation of the rest of the molecule, and no genuine energy minimum is located on this pathway. To this extent the orientation around the C1—S1 bond of the alkene, thio-ester or pyrrolidinedione units in (1)–(3) determines, or at least limits, the conformational possibilities for the nitro group. For (2), the observed conformation in the crystal is close to that computed for the local minimum (Table 3).

It may be noted here that the barriers calculated for a 90° rotation of the nitro group about the C—N bond are actually smaller for (1) and (2), and for $2\text{-}O_2NC_6H_4SCH_3$ than the

Table 5
Hydrogen-bond dimensions (Å, °).

Compound (1)					
C5···O1^{i}	3.362 (4)	H5···O1^{i}	2.52	C5—H5···O1^{i}	151
C6···O2^{i}	3.155 (4)	H6···O2^{i}	2.34	C6—H6···O2^{i}	146
Compound (2)					
C3···O7^{ii}	3.11 (2)	H3···O7^{ii}	2.51	C3—H3···O7^{ii}	123
Compound (3)					
a: C3···O11^{iii}	3.355 (3)	H3···O11^{iii}	2.54	C3—H3···O11^{iii}	147
b: C5···O1^{iv}	3.203 (4)	H5···O1^{iv}	2.50	C5—H5···O1^{iv}	132
c: C6···O8^{ii}	3.261 (3)	H6···O8^{ii}	2.52	C6—H6···O8^{ii}	137

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

barrier calculated for nitrobenzene itself, while that for (3) is only marginally larger than the nitrobenzene barrier. This suggests that the short S···O distances found at the global energy minima for molecules of this type do not themselves confer or imply any significant thermodynamic stabilization.

For such polar molecules as these [calculated dipole moments are (1) 2.95 D; (2) 5.39 D; (3) 4.78 D; *cf.* nitrobenzene calculated dipole moment 5.25 D, experimental 4.21 D], capable of forming fairly strong hydrogen bonds where the donor sites, but particularly the acceptor sites, carry large residual charges, it is improbable that the observed molecular conformations result exclusively from the influence of intramolecular forces. Instead, the observed conformations result from the subtle interplay of intra- and intermolecular forces.

3.3. Supramolecular structures of (1)–(3)

The nitro group is a well established acceptor of hydrogen bonds which occurs in a variety of supramolecular synthons (Desiraju, 1995). Its role as an acceptor in C—H···O hydrogen bonds is well exemplified in the structure of nitrobenzene itself (Boese *et al.*, 1992), where the molecules are linked into cyclic centrosymmetric dimers by paired C—H···O hydrogen bonds forming an $R_2^2(10)$ motif (Bernstein *et al.*, 1995). Similarly, C—H···O hydrogen bonds are observed in the structures of both the 1,2- and 1,3-isomers of dinitrobenzene (Herbstein & Kapon, 1990; Trotter & Williston, 1966), although not in the 1,4-isomer (Tonogaki *et al.*, 1993); in the structure of 1,3,5-trinitrobenzene (Choi & Abel, 1972); and in both the 2,2′- and 4,4′- isomers of dinitrobiphenyl (Sekine *et al.*, 1994; Boonstra, 1963). Hence, is it reasonable to expect the occurrence in (1)–(3) of C—H···O hydrogen bonds? In the event, (1) and (3) exhibit C—H···O hydrogen bonds utilizing the nitro-group O atoms as acceptors, while in (2) it is the O atom of the thio-ester group which acts as the acceptor.

Table 6
First- and second-level graph-set descriptors for (3).

Hydrogen bonds labelled *a, b, c* are defined in Table 5.

	a	*b*	*c*
a	$R_2^2(16)$	$R_4^4(26)$	$C_2^2(15)$
b	–	*C*(7)	$R_4^4(26)$
c	–	–	*C*(7)

3.3.1. Compound (1). In (1) the molecules are linked by C—H···O hydrogen bonds into a chain of rings (Bernstein *et al.*, 1995) running parallel to [010] (Fig. 4). The aromatic C5 and C6 atoms in the molecule at (x, y, z) act as donors to the O1 and O2 atoms, respectively, at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, while C5 and C6 at $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$ in turn are donors to O1 and O2 at (x, 1 + y, z). The interactions between C—H bonds polarized $C^{\delta-}$—$H^{\delta+}$ and N—O bonds strongly polarized $N^{\delta+}$—$O^{\delta-}$ give rise to C—H···O hydrogen bonds (Table 5) which are short, and presumably therefore strong, for their type (Desiraju, 1991), and propagation by means of the 2_1 screw axis along (0, y, $\frac{1}{4}$) gives a *C*(6) [$R_2^2(7)$] chain of rings: four such chains run through each unit cell. The chain-of-rings motif is constructed entirely from the nitrophenyl groups, with the PhCH=CH— units pendent from this chain in a stem-and-leaves motif (Ferguson *et al.*, 1998).

3.3.2. Compound (2). As in (1) the molecules of (2) are linked into chains by C—H···O hydrogen bonds (Fig. 5). However, it is the O7 atom of the thio-ester functionality which acts as the hydrogen-bond acceptor and, in (2), the nitro group plays no part in the hydrogen-bonding arrangement. Aromatic C3 in the molecule at (x, y, z) is a donor to O7 at $(\frac{1}{2}+x, \frac{1}{2}-y, z)$ while C3 at $(\frac{1}{2}+x, \frac{1}{2}-y, z)$ similarly acts as a donor to O7 at ($1+x, y, z$), so forming a markedly zigzag *C*(7) chain running parallel to [100] and generated by the glide plane at $y = \frac{1}{4}$. Two independent chains of this type run through each unit cell, and each chain is linked to two neighbouring chains by means of $\pi\cdots\pi$ stacking interactions to form a two-dimensional sheet.

The aryl ring C8–C13 in the thiobenzoate portion of the molecule at (x, y, z) forms a $\pi\cdots\pi$ stacking interaction with the corresponding ring of the molecule at $(1-x, 1-y, 1-z)$. The rings are necessarily parallel and the interplanar spacing is 3.65 (1) Å; the distance between the ring centroids is 3.85 (1) Å, so that the centroids are offset by 1.22 (1) Å. These dimensions are almost ideal for strong $\pi\cdots\pi$ stacking interactions (Hunter, 1994). The molecule at $(\frac{1}{2}+x, \frac{1}{2}-y, z)$, which is hydrogen-bonded to that at (x, y, z), similarly forms a $\pi\cdots\pi$ stacking interaction with the molecule at $(\frac{3}{2}-x, -\frac{1}{2}+y, 1-z)$, which forms part of the hydrogen-bonded chain generated by the glide plane at y = −0.25, and the molecule at $(1-x, 1-y, 1-z)$, which is $\pi\cdots\pi$ stacked with that at (x, y, z) forms part of the hydrogen-bonded chain generated by the glide plane at y = 0.75. In this manner a chain running parallel to [010] is generated, with links between adjacent molecules in this chain alternating between hydrogen bonds and $\pi\cdots\pi$ stacking interactions (Fig. 6).

3.3.3. Compound (3). There are three types of C—H···O hydrogen bond in (3) whose combined effect is to link the molecules into a two-dimensional network. The donors are three of the aromatic C atoms in the nitro-aryl group, and the acceptors are the two O atoms of the pyrrolidinedione fragment together with one of the O atoms of the nitro group.

Atom C5 at (x, y, z) acts as a donor to nitro-group O1 at ($1+x, y, z$), so generating a *C*(7) chain running parallel to the [100] direction (Fig. 7), with four such chains running through each unit cell. Atom C6 at (x, y, z) acts as hydrogen-bond donor to the pyrrolidinedione O8 atom at ($\frac{1}{2} + x, \frac{1}{2} - y, z$), with C6 at ($\frac{1}{2} + x, \frac{1}{2} - y, z$) in turn acting as donor to O8 at ($1 + x, y, z$). Thus, two of the $C(7)$ chains generated by translation are cross-linked by a spiral $C(7)$ motif generated by the glide plane (Fig. 7). These two types of hydrogen bond thus generate a ladder built from a single type of $R_4^4(26)$ ring (Fig. 7). The third type of C—H···O hydrogen bond links these ladders into a continuous two-dimensional net. Atom C3 at (x, y, z) acts as a donor to the other pyrrolidinedione O atom, O11, at ($1 - x, 1 - y, 1 - z$) and C3 at ($1 - x, 1 - y, 1 - z$) acts as a donor to O11 at (x, y, z), so generating an $R_2^2(16)$ motif centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) (Fig. 8). Between successive $R_2^2(16)$ rings centred at ($n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) ($n$ = zero or integer) there are $R_4^4(26)$ rings centred at ($n, \frac{1}{2}, \frac{1}{2}$) ($n$ = zero or integer; Fig. 8). In addition to these motifs it is possible to identify a $C_2^2(15)$ chain running parallel to the [010] direction (Fig. 9): all four symmetry-related molecules within the unit cell form part of this chain, so that only one such chain runs through each unit cell.

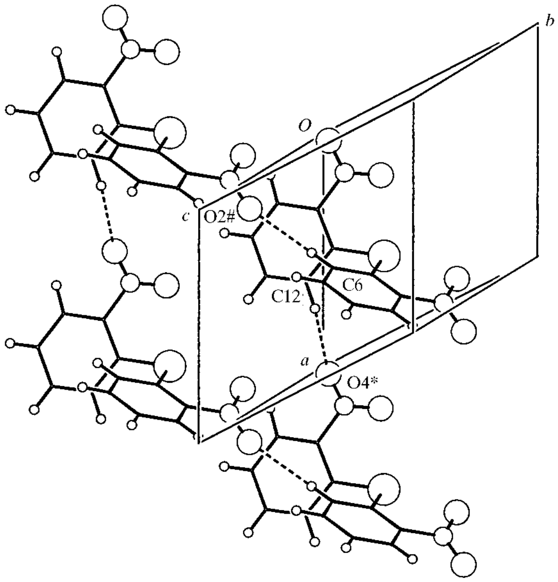


Figure 13
Part of the crystal structure of $(2\text{-}O_2NC_6H_4)_2S$, showing part of the (001) net built from $R_4^4(32)$ rings. Atoms marked with an asterisk or hash symbol are in molecules at ($1 + x, y, z$) and ($-1 + x, -1 + y, z$), respectively.

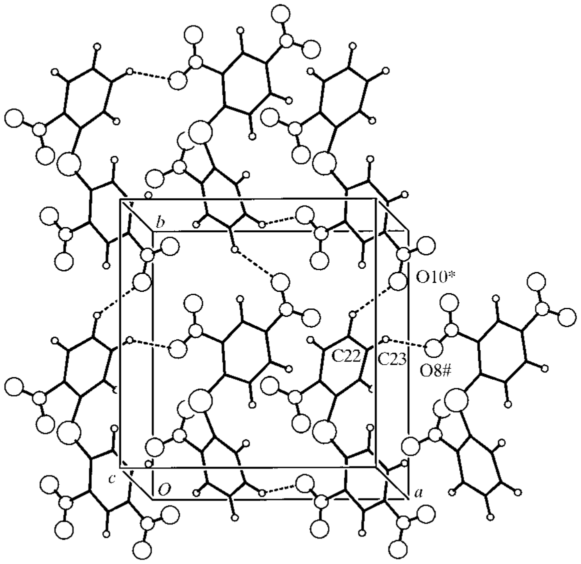


Figure 14
Part of the crystal structure of $(O_2N)_2C_6H_3SC_6H_4NO_2$, showing the (001) net built from $R_4^4(32)$ rings formed by the type 2 molecules. Atoms marked with an asterisk or hash symbol are in molecules at ($x, 1 + y, z$) and ($\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$), respectively.

Within the pairs of molecules forming the centrosymmetric $R_2^2(16)$ rings there are aryl $\pi \cdots \pi$ stacking interactions (Fig. 10): the planes of the parallel aryl rings are separated by 3.331 Å and their centroids are offset by 1.412 Å, effectively the radius of such a ring. The $C_2^2(15)$ chains can thus be envisaged as linking these $\pi \cdots \pi$ stacked $R_2^2(16)$ dimers by means of the 2_1 screw axis along ($\frac{1}{4}, y, \frac{1}{2}$) (Fig. 9).

3.4. Comparisons with related compounds

The findings described above (§§3.1–3.3) for (1)–(3) prompt re-evaluation of the conformational properties of closely related species, retrieved in many cases from the Cambridge Structural Database (Allen & Kennard, 1993). Both $2\text{-}O_2NC_6H_4SNMe_2$ (Ruostesuo *et al.*, 1989) and $2,4\text{-}(O_2N)_2C_6H_3SNMe_2$ (Aupers *et al.*, 1999) adopt conformations in the solid state which are identical, in the case of the mono-nitro compounds, and close to, in the case of the dinitro derivative, the global energy minimum; there are no intermolecular hydrogen bonds in either compound. *N*-(2-Nitrophenylthio)phthalimide (Iwasaki & Masuko, 1986) is a close analogue of (3), and the entire molecule is virtually planar except for the near-orthogonal phthalimido group, corresponding to the global minimum; nonetheless, there is extensive intermolecular hydrogen bonding involving both the phthalimido O atoms and one of the nitro-group O atoms, just as in (3). The molecules are linked by paired C—H···O hydrogen bonds, utilizing both O atoms of the phthalimido group as acceptors, into a $C(6)$ [$R_2^2(10)$] chain of rings running along [010], and these chains are linked by a third type of C—H···O hydrogen bond, with a nitro O atom as an acceptor, into sheets parallel to (100) and built from $R_4^4(36)$ rings (Fig. 11).

There are also several recently reported structures for related molecules which have conformations remote from that corresponding to the global energy minimum: in every case these conformations are associated with well developed intermolecular interactions, particularly the formation of C—H···O hydrogen bonds. Thus, in $2\text{-}O_2NC_6H_4SSnPh_3$ (Aupers *et al.*, 1999) the conformation is close to that of the local energy minimum, with the nitro group rotated out of the plane of the adjacent aryl ring by ~50°, associated with a C—C—S—Sn torsional angle of ~68°: the molecules are linked into $C(9)$ chains by means of C—H···O hydrogen bonds (Fig. 12). In both 2,2′-nitrodiphenyl sulfide (Kucsman *et al.*, 1984) and 2,2′,4-trinitrodiphenyl sulfide (Aupers *et al.*, 1999) only one of the nitro groups *ortho* to the S atom is approximately coplanar with its aryl ring. In the dinitro compound there are C—H···O hydrogen bonds, involving both nitro groups, which link the molecules into a two-dimensional net built from $R_4^4(32)$ rings (Fig. 13). The structure of the trinitro compound contains two molecules in the asymmetric unit and, in both, the nitro group acts as an acceptor of C—H···O hydrogen bonds; the interactions between molecules of type 2 again leads to the formation of a two-dimensional network built from Z-shaped $R_4^4(32)$ rings (Fig. 14).

3.5. The influence of intermolecular forces on the molecular conformations

As noted earlier (§3.2), the molecular conformations of (1) and (3) observed in the solid state are very close to those calculated for isolated molecules of these compounds at their global energy minima, whereas the observed conformation of (2) is similar to that calculated for the secondary conformational minimum. While the detailed conformations observed doubtless reflect minor perturbations from the minimum energy conformations of isolated molecules, it is striking that not only (1)–(3) but also the related compounds discussed in §3.4 adopt conformations in their crystals corresponding to one or other of the two energy minima. The choice of which of these two minima is actually adopted in any given case will be determined by the competing effects of the intramolecular energy difference between the minima and the intermolecular forces, particularly the hydrogen bonds, the aromatic $\pi\cdots\pi$ stacking interactions and the dipole–dipole interactions. It appears in general that whenever the observed molecular conformation for a compound of this type departs significantly from that associated with the global energy minimum for the isolated molecule, specific and directed intermolecular forces are responsible.

4. Conclusions

Compounds containing the 2-nitrobenzenethiolate fragment generally exhibit two well defined conformational minima. In the solid state both conformations are observed, and occurrences of the conformation associated with the secondary energy minimum are generally associated with specific and directed intermolecular forces, in particular C—H···O hydrogen bonds involving the O atoms of the nitro group as hydrogen-bond acceptors.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.

Aupers, J. H., Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Low, J. N. & Wardell, J. L. (1999). *Main Group Chem.* **3**, 23–42.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Boese, R., Bläser, D., Nussbaumer, M. & Krygowski, T. M. (1992). *Struct. Chem.* **3**, 363–368.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Boonstra, E. G. (1963). *Acta Cryst.* **16**, 816–823.

Carreira, L. A. & Townes, T. G. (1977). *J. Mol. Struct.* **41**, 1–9.

Choi, C. S. & Abel, J. E. (1972). *Acta Cryst.* B**28**, 193–201.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed Engl.* **34**, 2311–2327.

Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.

Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* pp. 2283–2286.

Domenicano, A., Schultz, G., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1990). *Struct. Chem.* **1**, 107–122.

Enraf–Nonius (1992). *CAD4-PC Software.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1998). *PREP8 – a WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL97 Programs.* University of Guelph, Canada.

Ferguson, G., Glidewell, C., Gregson, R. M. & Meehan, P. R. (1998). *Acta Cryst.* B**54**, 129–138.

Furukawa, M., Fujino, Y., Kojima, Y., Ono, M. & Hatashi, S. (1972). *Chem. Pharm. Bull.* **20**, 2024–2028.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Herbstein, F. H. & Kapon, M. (1990). *Acta Cryst.* B**46**, 567–572.

Høg, J. H., Nygaard, L. & Sørensen, G. O. (1971). *J. Mol. Struct.* **7**, 111–121.

Hunter, C. A. (1994). *Chem. Soc. Rev.* **23**, 101–109.

Iwasaki, F. & Masuko, Y. (1986). *Acta Cryst.* C**42**, 124–127.

Jones, P. G., Fischer, A. K., Muller, C., Pinchuk, V. A. & Schmutzler, R. (1996). *Acta Cryst.* C**52**, 2750–2752.

Kucsman, A. & Kapovits, I. (1985). *Organic Sulfur Compounds: Theoretical and Experimental Advances*, edited by F. Bernardi, I. G. Czizmadia & A. Mangini, pp. 191–245. Amsterdam: Elsevier.

Kucsman, A., Kapovits, I., Parkanyi, L., Argay, G. & Kalman, A. (1984). *J. Mol. Struct.* **125**, 331–347.

Morgenstein, J., Kunz, D. & Mayer, R. (1969). *Pharmazie*, **24**, 450–453.

Moss, L. E. & Jacobson, R. A. (1981). *Cryst. Struct. Commun.* **10**, 1545–1548.

Rodríguez, M. L., Brito, I., Diaz, C., González, G. & Manríquez, V. (1992). *J. Organomet. Chem.* **425**, 49–57.

Ruostesuo, P., Hakkinen, A.-M., Kivekas, R. & Sundberg, M. R. (1989). *J. Chem. Soc. Perkin Trans 2*, pp. 1397–1403.

Sato, S., Yosioka, T. & Tamura, C. (1975). *Acta Cryst.* B**31**, 1385–1392.

Sekine, A., Ohashi, Y., Yoshimura, K., Yagi, M. & Higuchi, J. (1994). *Acta Cryst.* C**50**, 1101–1104.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON. Molecular Geometry and Graphics Program.* Version of November 1998. University of Utrecht, The Netherlands.

Stewart, J. J. P. (1990). *MOPAC*6.0. *Quantum Chemistry Program Exchange*. Bloomington, Indiana, USA,

Sudha, L., Selvan, J. S., Subramanian, K., Steiner, T., Koellner, G., Srinivasan, N. & Ramdas, K. (1996). *Acta Cryst.* B**52**, 2047–2049.

Tonogaki, M., Kawata, T., Ohba, S., Iwata, Y. & Shibuya, I. (1993). *Acta Cryst.* B**49**, 1031–1039.

Trotter, J. & Williston, C. S. (1966). *Acta Cryst.* **21**, 285–288.

Wardell, J. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1786–1793.

Wilson, A. J. C. (1976). *Acta Cryst.* A**32**, 994–996.