Journal of Chemical Crystallography, Vol. 31, Nos. 9–10, October 2001 (© 2002)

Synthesis and structural study of 1-(*N*,*N*-diethylamino)-2,2-bis(2-nitrophenylthio)ethene

John H. Aupers,(1) **Janet M.S. Skakle,**(1)* **James L. Wardell,**(2) **and Solange M.S.V. Wardell**(3)

Received April 4, 2001

The synthesis, variable temperature NMR spectra, and crystal structures of two crystalline forms, **2a** and **2b**, of the enamine 1-(*N*,*N*-diethylamino)-2,2-bis(2-nitrophenylthio)ethene have been obtained. Both forms crystallize in the monoclinic space group $P2_1/a$. The two phases have similar molecular structures but possess different intermolecular C—H···O hydrogen bonding interactions. Both forms exhibit disorder within the NEt_2 fragment at 298 K: sufficient disorder persisted with **2a** (orange needles) down to 100 K to make the geometric parameters pertaining to the enamine fragment unreliable. The disorder was effectively eliminated on cooling **2b** down (red colored blocks) to 150 K. Cell dimensions for the **2a**-phase are at 100 K: $a = 11.1030(4)$ Å, $b = 15.1325(7)$ Å, $c = 12.4504(7)$ Å, $\beta = 114.606(3)^\circ$, while for the **2b**-phase at 150 K, $a = 15.5206(4)$ Å, $b = 7.6958(2)$ Å, $c = 15.7137(3)$ Å, $\beta = 92.580(7)^\circ$. The C—N bond length in the β-form at 150 K of 1.335(3) Å indicates considerable double bond character: the rotational barrier of the C—N bond in $CDCl_3$ was calculated to be 52.4 kJ mol^{-1}.

KEY WORDS: Enamine; ketene dithioacetals; rotational barrier; push–pull compounds.

Introduction

Electron delocalization has been studied in various push–pull alkenes, including compounds, $(RS)_2C{=}CXY$, having electron donating RS groups, e.g., MeS, and electron accepting X,Y groups, e.g., MeCO, MeOCO, NC, and O_2N.[1] Both spectroscopy, especially NMR spectroscopy, for solution studies on rotational barriers and X-ray crystallography for solid-state structures have been used to provide information on the electron delocalisation about the double bond. For push–pull alkenes, with electron acceptor sulfido units and electron donating amino groups, $(RS)_2C{=}CHNR'_2$, there is scant information in the literature: a single paper refers to the restricted rotation about the C—N bond in 1-(*N*,*N*-diethylamino)-2,2-bis(trichloromethylthio)ethene, $(Cl_3CS)_2C{=}CHNEt_2$ (**1**) as determined by ^1H NMR spectroscopy.[2] In order to further investigate such enamines or aminoketene dithioketals, 1-(*N*,*N*-diethylamino)-2,2-bis(2-nitrophenylthio)ethene (**2**) has been synthesized and its solution behavior and crystal structure determined.

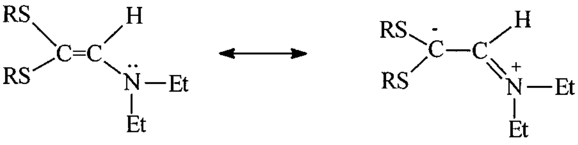
---

(1) Department of Chemistry, University of Aberdeen, Old Aberdeen AB24 3UE, Scotland.

(2) Departamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil.

(3) Departamento de Química Orgânica, Instituto de Química, Universidade Federal Fluminense, 24020-150 Niterói, RJ, Brazil.

* To whom correspondence should be addressed. E-mail: j.skakle@abdn.ac.uk.



1: R = Cl_3CS; **2**: R = 2-$O_2NC_6H_4S$.

Experimental

Melting points were measured using a Kofler hot-stage microscope and are uncorrected. NMR spectra were obtained on Bruker 250 MHz and Bruker 400 MHz instruments. Diffractometer data were obtained with an Enraf Nonius KappaCCD diffractometer by the EPSRC service, based at the University of Southampton, England.

Synthesis of 2

Method 1. A mixture of 2-$O_2NC_6H_4SH$ (3.10 g, 20 mmol), *N*-bromosuccinimide (3.76 g, 20 mmol) and Et_3N (2 ml) in CCl_4 (50 mL) was refluxed for 1 h. The mixture was cooled, filtered to remove $Et_3NH^+Cl^-$ and the filtrate rotary evaporated to leave a solid residue. Crystallization of the residue from EtOH initially gave *N*-(2-nitrophenylthio)succinimide.[3] Repeated recrystallizations of the mother liquors from EtOH eventually gave **2**, as orange needles (**a**-form), suitable for X-ray crytstallography, in yields of 8–12%, based on 2-$O_2NC_6H_4SH$; m.p. 195–197°C.

Anal. Calc. for $C_{18}H_{19}N_3O_4S_2$: C, 53.3; H, 4.7; N, 10.4. Found: C, 53.5, H, 4.7, N, 10.2%.

^1H NMR (400.13 MHz, $CDCl_3$, 300 K): δ 1.16 (6H, t, $J = 7.2$ Hz, Me), 3.40 (4H, q, $J = 7.2$ Hz, CH_2), 7.18–7.23 (2H, m, aryl-H), 7.24 (1H, s, C═CH), 7.58 (2H, tt, $J = 1.4$, ca. 7.5, ca. 7.5, aryl-H), 7.65 (2H, ddd, $J = 1.4$, 6.2, 8.2 Hz, aryl-H), 8.15 (1H, dd, $J = 1.4$, 8.2 Hz, aryl-H_3), 8.18 (1H, dd, $J = 1.4$, 8.2 Hz, aryl-H_3).

^1H NMR (250 MHz, CD_3COCD_3, 298 K): δ 1.12 (6H, t, $J = 7.0$ Hz, Me), 3.46 (4H, q, $J = 7.0$ Hz, CH_2), 7.40 (1H, dt, aryl-H), 7.42 (1H, dt, aryl-H), 7.51 (1H, s, C═CH), 7.70 (2H, dd, aryl-H), 7.84 (2H, t.br, aryl-H), 8.21 (1H, dd, aryl-H_3), 8.23 (1H, dd, aryl-H_3) [all *J* for aryl-H ca. 1.2 and 7.4 Hz].

^{13}C NMR (63.3 MHz, $CDCl_3$, 300 K): δ 159.1, 146.0, 141.7, 140.1, 135.0, 134.7, 128.8, 128.4, 126.9, 126.6, 126.2, 125.9, 47.3, 14.9.

Method 2. A reaction mixture of 2-$O_2NC_6H_4SCl$ (1.90 g, 10 mmol), L-cysteine (1.25 g, 10 mmol), and Et_3N (2 mL) in CH_2Cl_2 (50 mL) was refluxed for 3 h. The mixture was cooled, filtered to remove $(2\text{-}O_2NC_6H_4S)_2$, and the filtrate rotary evaporated. The residue was taken up in CCl_4, filtered, and the filtrate evaporated. The residue was fractionally recrystallized from EtOH to give more disulfide and orange **2a**: yield of **2a** was 14.5%.

A similar reaction using homocysteine led to the isolation of **2b** in a similar yield, m.p. 194–196°C.

Anal. Calc. for $C_{18}H_{19}N_3O_4S_2$: C, 53.3; H, 4.7; N, 10.4. Found: C, 53.4, H, 4.6, N, 10.3%. The NMR spectra in solution were identical with those of **2a**.

Crystallography

Data were collected on an Enraf Nonius KappaCCD diffractometer, by the EPSRC service at Southampton. Structures of **2a** and **2b** were solved by direct methods with SHELXS-97[4] and refined using SHELXL-97.[5] Hydrogen atoms were placed in geometrical positions and refined with a riding model. Crystal data and structure refinement details are listed in Table 1. Final atom coordinates and equivalent isotropic parameters are listed in Tables 2 and 3 for atomic coordinates, bond angles and lengths, torsional angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre: deposition nos – 156041 (**2a**) and 156042 (**2b**).

Results and discussion

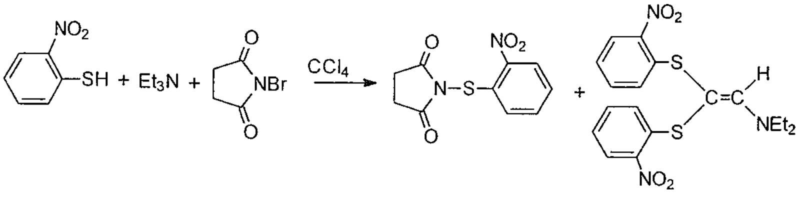
Synthesis

Compound **1** had been prepared[2] by Senning and Kelly from the reaction of Cl_3CSCl with NEt_3: however, a similar reaction between 2-$O_2NC_6H_4SCl$ and NEt_3 in CH_2Cl_2 was reported by them not to provide **2**. Compound **2** has

Table 1. Crystal Data and Structure Refinement

	2a	**2b**
CCDC deposit no.	CCDC-1003/6074	CCDC-1003/6075
Empirical formula	$C_{18}H_{19}N_3O_4S_2$	$C_{18}H_{19}N_3O_4S_2$
Formula weight	405.48	405.48
T, K	100(2)	150(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/a$	$P2_1/a$
Unit cell dimensions		
a, Å	11.1030(4)	15.5206(4)
b, Å	15.1325(7)	7.6958(2)
c, Å	12.4504(7)	15.7137(3)
β, deg	114.606(3)	92.580(7)
Volume, $Å^3$	1901.92(15)	1875.00(8)
Z	4	4
Calculated density, Mg m^{-3}	1.416	1.436
Absorption coefficient, mm^{-1}	0.310	0.314
$F(100)$	848	848
Crystal color	Orange	Red
Crystal size, mm	0.30 × 0.20 × 0.20	0.22 × 0.16 × 0.16
Theta range for data collection, deg	2.25–27.49	1.30–27.80
Index range	$-14 \leq h \leq 13, -19 \leq k \leq 18, -15 \leq l \leq 16$	$-20 \leq h \leq 20, -9 \leq k \leq 9, -20 \leq l \leq 20$
Reflections collected/unique	14254/4261 [$R_{\text{int}} = 0.0741$]	17144/4287 [$R_{\text{int}} = 0.0529$]
Completeness to 2θ	27.49; 97.2%	27.80; 96.5%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.946 and 0.783	0.9515 and 0.9341
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	4261/0/246	4287/0/246
Goodness of fit on F^2	1.102	1.047
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0911$, $wR2 = 0.2291$	$R1 = 0.0427$, $wR2 = 0.1096$
R indices (all data)	$R1 = 0.1113$, $wR2 = 0.2414$	$R1 = 0.0635$, $wR2 = 0.1216$
Largest diff. peak and hole, e. $Å^{-3}$	1.175 and −0.833	0.635 and −0.308

now been isolated, albeit as minor products from two types of reactions. It has been isolated in ca. 10% yield from a reaction mixture consisting of N-bromosuccinimide (NBS), 2-nitrobenzenethiol and NEt_3 in CCl_4: fractional crystallization and chromatography were used to separate **2** from other products, including the major one, the simple substitution product, N-(2-nitrophenylthio)succinimide (**3**)[3] (reaction 1). Compound **2** has also been isolated from reaction mixtures consisting of $2\text{-}O_2NC_6H_4SCl$, NEt_3, and unprotected mercapto-aminoacids, e.g., L-cysteine and homocysteine, in CH_2Cl_2 (reaction 2). Again compound **2** was a minor product, ca. 15%, the major isolated product being the disulfide $(2\text{-}O_2NC_6H_4S)_2$.



2

(1)

Table 2. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **2a** at 100 K

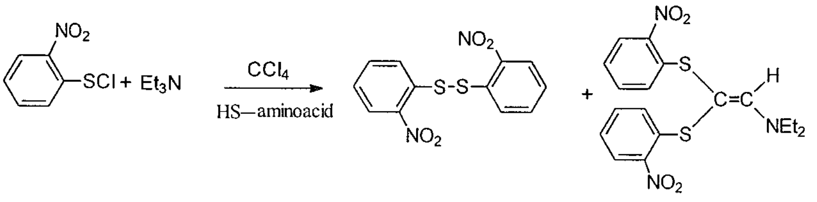
Atom	*x*	*y*	*z*	U_{eq}[a]
S(1)	6512(1)	675(1)	3364(1)	32(1)
C(1)	5160(4)	1413(3)	2743(4)	29(1)
C(2)	4077(4)	1199(3)	1675(4)	35(1)
C(3)	2983(5)	1744(4)	1184(5)	44(1)
C(4)	2916(6)	2530(4)	1746(6)	50(1)
C(5)	3950(6)	2764(3)	2777(5)	45(1)
C(6)	5060(5)	2215(3)	3257(4)	36(1)
N(1)	6104(5)	2487(3)	4393(4)	48(1)
O(1)	5958(5)	3207(3)	4806(4)	72(1)
O(2)	7051(4)	1985(3)	4897(3)	50(1)
S(2)	6788(1)	92(1)	1179(1)	33(1)
C(7)	8521(4)	−43(3)	2006(4)	29(1)
C(8)	9039(4)	−416(3)	3123(4)	31(1)
C(9)	10382(4)	−506(3)	3791(4)	34(1)
C(10)	11282(4)	−208(4)	3351(4)	39(1)
C(11)	10817(5)	172(4)	2253(4)	39(1)
C(12)	9455(4)	250(3)	1588(4)	32(1)
N(2)	9038(4)	647(3)	429(4)	38(1)
O(3)	9837(4)	1061(3)	191(3)	50(1)
O(4)	7875(3)	530(3)	−284(3)	45(1)
C(13)	6181(4)	−133(3)	2259(4)	33(1)
C(14)	5566(5)	−941(4)	2075(6)	47(1)
N(3)	4887(5)	−1360(3)	2566(5)	53(1)
C(15)	4711(6)	−962(5)	3591(7)	64(2)
C(16)	5868(8)	−1187(5)	4766(7)	76(2)
C(17)	4523(7)	−2278(4)	2357(10)	89(3)
C(18)	2983(7)	−2412(5)	1986(8)	78(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Atomic Coordinates (10^4) and Equivalent Isotropic Displacement Parameters (10^3 Å^2) for **2b** at 150 K

Atom	*x*	*y*	*z*	U_{eq}[a]
S(1)	295(1)	3471(1)	2295(1)	30(1)
S(2)	−590(1)	418(1)	3054(1)	30(1)
C(1)	−321(1)	3422(2)	1315(1)	28(1)
C(2)	−482(1)	1846(2)	889(1)	32(1)
C(3)	−964(2)	1772(3)	125(6)	40(1)
C(4)	−1317(2)	3260(3)	−240(1)	44(1)
C(5)	−1181(1)	4829(3)	160(1)	40(1)
C(6)	−685(1)	4899(2)	925(1)	32(1)
N(1)	−544(1)	6611(2)	1300(1)	41(1)
O(1)	−1003(1)	7813(2)	1051(1)	60(1)
O(2)	34(1)	6777(2)	1853(1)	48(1)
C(7)	−583(1)	1449(2)	4076(1)	28(1)
C(8)	175(1)	2097(2)	4458(1)	34(1)
C(9)	186(2)	2919(3)	5247(1)	44(1)
C(10)	−557(2)	3158(3)	5681(1)	50(1)
C(11)	−1312(2)	2548(3)	5321(1)	47(1)
C(12)	−1317(1)	1687(3)	4534(1)	35(1)
N(2)	−2134(1)	1014(3)	4190(1)	46(1)
O(3)	−2785(1)	1730(3)	4414(1)	78(1)
O(4)	−2129(1)	−242(2)	3704(1)	49(1)
C(13)	331(1)	1277(2)	2608(1)	30(1)
C(14)	1003(1)	170(2)	2561(1)	31(1)
N(3)	1728(1)	232(2)	2136(1)	38(1)
C(15)	1917(1)	1582(3)	1490(1)	42(1)
C(16)	2416(2)	3104(3)	1852(2)	56(1)
C(17)	2377(1)	−1118(3)	2324(2)	42(1)
C(18)	3050(2)	−647(3)	3007(2)	54(1)

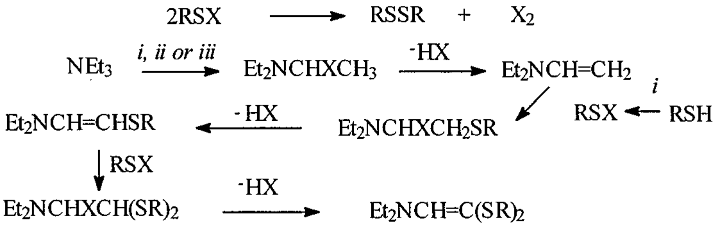
[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.



2

(2)

The intermediacy of $Et_2NCH{=}CH_2$ is considered in all the formations of **1** and **2**: Senning and Kelly[2] confirmed that **1** could be obtained from $Et_2NCH{=}CH_2$ and Cl_3CSCl. They suggested that the formation of $Et_2NCH{=}CH_2$ from Et_3N arose by an α-halogenation/elimination sequence, with the sulfenyl chloride, Cl_3CSCl, as the halogenation source (see Scheme 1). The formation of $Et_2NCH{=}CH_2$ from NEt_3, in the presence of NBS has been reported in the literature.[6] An additional role for NBS in reaction 1 is considered to be in the halogenation of $2\text{-}O_2NC_6H_4SH$ to $2\text{-}O_2NC_6H_4SBr$: this reaction has also been documented.[7] The precise role of



Scheme 1. R = Cl_3C (**1**); 2-$O_2NC_6H_4$ (**2**). Reagents: *i*: NBS; *ii*: RSX: *iii*: X_2

a mercapto-aminoacid in reaction 2 remains unknown: however, a role as a disproportionation agent of 2-$O_2NC_6H_4SCl$ to (2-$O_2NC_6H_4S)_2$ and Cl_2 would account for the subsequent reactions. Once formed, $Et_2NCH{=}CH_2$ would react via the the addition/elimination sequences shown in Scheme 1.

Variable NMR spectral study in solution

In the ^1H NMR 400 MHz spectrum at ambient temperature in $CDCl_3$, the two 2-nitrophenylthio units in **2** are distinct, whereas the Et groups in the NEt_2 group are equivalent, appearing as a triplet [$\delta = 3.44$ ppm, $J = 7.2$ Hz] and quartet [$\delta = 1.20$ ppm, $J = 7.2$ Hz]. At 253 K, the CH_2 absorptions appear as a broad unresolved peak at ca. 3.42 ppm, which at 248 K splits into two broad absorptions at 3.24 and 3.59 ppm, peak separation $\Delta\nu$ of 83.3 Hz. No further changes in the signal for the CH_2 group result on lowering the temperature to 233 K. The rotational barrier at the C—N bond in **2** was calculated[8] to be 52.4 kJ mol^{-1}, using Eq. 3, with the coalescence temperature T_c of 250 K.

$$\Delta G^{\neq}(\text{kJ mol}^{-1}) = 4.184 \times 4.57 \times 10^{-3}(T_c) \times[9.97 + \log(T_c/\Delta\nu)] \quad (3)$$

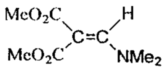
This value is close to the reported value[2] for **1** of 58.5 kJ mol^{-1}: these values are also similar to those found for $(MeO_2C)_2C{=}CH{-}NMe_2$ (**3**)[9] and 6-(*N*,*N*-dimethylamino)-pentafulvene (**4**)[10] but intermediate between values for (2-benzothiazolyl)$_2C{=}CHNMe_2$ (**5**)[11] and 5-diaminomethylene-2,2-dimethyl-1,3-dioxane-4,6-dione (**6**)[12] (see Table 4). The two 2-nitrobenzenethiolato groups have distinct sets of absorptions throughout the temperature range 233–373 K, in DMSO-d_6, as indicated by the number of carbon signals in the ^{13}C NMR spectra: the slight changes in the aryl region of the ^1H NMR spectra which arise on changing the

Table 4. Bond Lengths (Å), Rotational Barriers ΔG^*_{rot} (kJ mol^{-1}) for C═C and C—N Bonds, and NMR Coalescence Temperatures T_c (K) for Selected Enamines

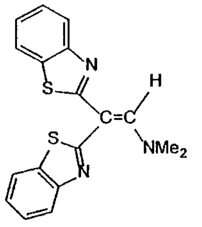
Compound	*d*(C═C)	ΔG^*_{rot}(C═C)/solvent[a]	*d*(C—N)	ΔG^*_{rot}(C═N)/solvent[a]
3	1.380(5)[7]	65.2/CH_2Cl_2[23] (292)	1.337(4)[7]	55.6/CH_2Cl_2[23] (264)
4	1.367[10]	70.2/$Cl_2CDCDCl_2$[10] (—)	1.334[10]	36.4/CS_2[10] (—)
6	1.387(4)[11]	53.5/CD_2Cl_2[11] (280)	1.307(4)[11]	90.5/DMSO-d_6[11] (435)
5	1.387(4)[9]	92.3/Me_2SO[24] (421)	1.331(4)[9]	56.4/$CDCl_3$:C_6F_6[24] (254)
2[a]	1.352(3)	(—)/Me_2SO (<373)	1.335(3)	52.4/$CDCl_3$ (248)
1				58.5/$CDCl_3$[2]

[a] The values in parentheses indicate T_c (K).

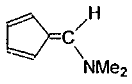
[b] This study: **2b** at 150 K.



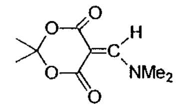
3



4



5



6

temperature merely reflect rotation changes about the C—S bonds. As the two nitrophenylthio groups maintain different NMR signals up to 100°C in DMSO-d_6, the energy barrier for rotation about the C═C bond in **2** is clearly high: generally higher energy barriers[13] are found for C═C in $(RS)_2C{=}CXY$ than in either $(R_2N)_2C{=}CXY$ or $(RS)(R_2N)C{=}CXY$.

Solid-state structure

Two crystalline phases of **2** (**a** and **b**) have been isolated and their structures determined by X-ray crystallography. The two phases have very similar molecular structures (see Fig. 1), but each possesses different intermolecular C—H$\cdots$O hydrogen bonding interactions. Orange-colored needles, **2a**, were obtained from the NBS reaction, reaction 1, and also from the reaction mixture containing L-cysteine, reaction 2: red-colored blocks, **2b**, were also isolated from EtOH solution from the reaction mixture containing homocysteine, reaction 2. Selected geometric parameters are listed in Table 5. Both forms exhibited disorder within the NEt$_2$ fragment at ambient temperature: sufficient disorder persisted with **2a** down to 100 K to make the geometric parameters pertaining to the C(14)—C(13)—N(3) fragment unreliable. The disorder was effectively eliminated on cooling **2b** down to 150 K: the geometric data for **2b** at 150 K show clear evidence for delocalization in the C(14)—C(13)—N(3) fragment (see Table 5). The C(13)—C(14) bond length at 1.352(3) Å is slightly longer than an isolated C═C bond length,[14] 1.326 Å: on the other hand, the C(14)—N(3) bond length of 1.335(3) Å is much shorter than a N—C(sp^2) single bond length [1.452(2) Å][15] and is closer to a N═C(sp^2) bond length of 1.279Å.[14] The C—N bond lengths in the enamines listed in the Cambridge Crystallographic Database cover a range of values, with the majority being between 1.30 and 1.34 Å.[16] The planar geometry about N(3) allows for strong overlap of the lone pair

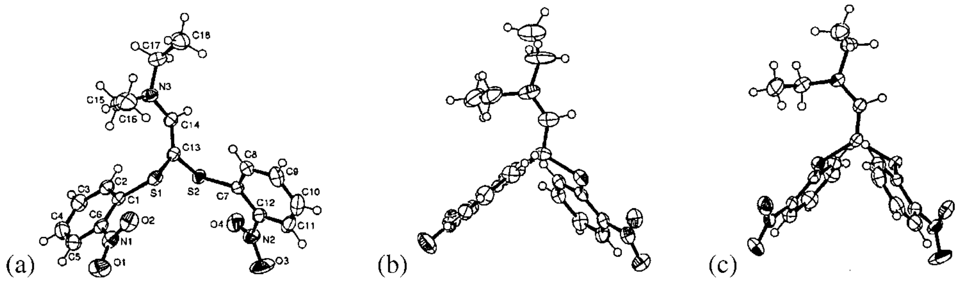


Fig. 1. General atom numbering system for **2** is illustrated in (a): specific atom arrangements for **2a** at 100 K and **2b** and 150 K are shown in (b) and (c), respectively.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **2a** at 100 K and **2b** at 150 K

	2a	**2b**		**2a**	**2b**
Bond length					
S(1)—C(13)	1.761(5)	1.7584(19)	C(14)—N(3)	1.315(7)	1.335(3)
S(1)—C(1)	1.770(4)	1.777(2)	N(3)—C(17)	1.440(8)	1.467(3)
S(2)—C(13)	1.770(5)	1.7492(19)	N(3)—C(15)	1.495(9)	1.491(3)
S(2)—C(7)	1.776(4)	1.7914(19)	C(15)—C(16)	1.531(11)	1.502(3)
C(13)—C(14)	1.371(7)	1.352(3)	C(17)—C(18)	1.587(9)	1.509(3)
C(1)—C(2)	1.409(7)	1.403(3)	C(7)—C(8)	1.386(6)	1.389(3)
C(2)—C(3)	1.382(6)	1.386(3)	C(8)—C(9)	1.378(6)	1.391(3)
C(3)—C(4)	1.397(8)	1.383(3)	C(9)—C(10)	1.399(7)	1.378(4)
C(4)—C(5)	1.366(8)	1.373(3)	C(10)—C(11)	1.371(7)	1.361(4)
C(5)—C(6)	1.397(7)	1.398(3)	C(11)—C(12)	1.394(6)	1.402(4)
C(6)—C(1)	1.399(6)	1.398(3)	C(12)—C(7)	1.411(7)	1.387(3)
S1 · · · S2	2.9951(16)	2.9960(7)			
Bond angle					
C(13)—S(1)—C(1)	103.5(2)	103.36(9)	C(14)—C(13)—S(2)	111.4(4)	115.46(14)
C(13)—S(2)—C(7)	101.6(2)	102.66(9)	S(1)—C(13)—S(2)	116.0(2)	117.34(11)
C(14)—C(13)—S(1)	132.6(4)	127.19(15)	N(3)—C(14)—C(13)	133.9(6)	132.45(19)
C(1)—C(2)—C(3)	121.9(5)	121.79(18)	C(7)—C(8)—C(9)	122.6(4)	121.7(2)
C(2)—C(3)—C(4)	120.5(5)	120.89(19)	C(8)—C(9)—C(10)	120.1(4)	121.7(2)
C(3)—C(4)—C(5)	119.5(5)	119.2(2)	C(9)—C(10)—C(11)	119.5(4)	118.1(2)
C(4)—C(5)—C(6)	119.6(5)	119.66(19)	C(10)—C(11)—C(12)	119.5(5)	120.0(2)
C(5)—C(6)—C(1)	123.0(5)	122.80(18)	C(11)—C(12)—C(7)	122.5(4)	123.2(2)
C(6)—C(1)—C(2)	115.5(4)	115.65(17)	C(12)—C(7)—C(8)	115.9(4)	115.28(18)

(in a p orbital) on nitrogen with the π orbital of the alkene unit. The N(3)—C(14)—C(13) angle at 132.45(19)° shows considerable increase over that of a regular sp^2 angle. While there are many different types of enamines listed in the Cambridge Crystallographic Database,[16] no $(RS)_2C{=}CHNR_2$ species were included there before this study: Senning and Kelly[2] indicated in their publication in 1972 that the crystal structure of **1** was in press at that time, but it has yet not been published.

Noncovalently bonded interactions

Two conformational classes have been generally found for 2-nitrophenylthiolates, 2-$O_2NC_6H_4SX$.[3,17] In one, the nitro group is essentially coplanar with the attached aryl group with the α-atom of the group X also lying in this plane, trans to the nitro group: a result of this are short S · · · O separations well inside the sum of the van der Waals radii, 3.3 Å,[18] and with near linear X—S · · · O angles. This near-planar conformer is the global energy minimum.[3] In the other conformation, the nitro group is twisted out of the plane of the attached aryl group and at the same time the group X is also displaced from the phenyl–S plane: in this case, significant intermolecular interactions,[3,19] such as C—H · · · O hydrogen bonding, π–π stacking, and metal–O interaction, compensate for the energy cost of rotating the nitro group out of this plane. While some compounds exhibit only the S · · · O intramolecular interactions, e.g., 2-$O_2NC_6H_4SSC_6H_4$Y-4 (Y = Cl or Me),[20] or only the intermolecular hydrogen bonding interactions, e.g. 2-$O_2NC_6H_4SCOPh$[3]or 2-$O_2NC_6H_4SS(O)_2C_6H_4NO_2$-2,[20] others possess both, e.g. 2-O_2N-4-$MeC_6H_3SCH{=}CHPh$.[3] Both dimorphs of $(2\text{-}O_2NC_6H_4S)_2C{=}CHNEt_2$, **2**, also exhibit both short intramolecular S · · · O contacts and intermolecular hydrogen bonding

Table 6. Nonbonded Covalent Interactions in **2**[a]

(a) S $\cdots$ O interactions			**2a** at 100 K	**2b** at 150 K
Angle between nitro [N(1)] plane and attached aryl plane			5.2(7)	15.71(16)
Angle between nitro [N(2)] plane and aryl plane			16.8(6)	26.38(16)
S(1) $\cdots$ O(2)			2.642(4)	2.6641(15)
C(13)-S(1) $\cdots$ O(2)			174.91(19)	172.95(7)
S(2) $\cdots$ O(4)			2.654(4)	2.6877(16)
C(13)-S(2) $\cdots$ (O4)			174.34(18)	168.35(7)
(b) Hydrogen bonds				
2b	d(D-H) (Å)	d(H $\cdots$ A) (Å)	d(D $\cdots$ A) (Å)	∠(DHA) (deg)
C(2)—H(2) $\cdots$ O(1)^1	0.95	2.58	3.220(2)	125.3
C(8)—H(8) $\cdots$ O(3)^2	0.95	2.57	3.296(3)	133.7
C(11)—H(11) $\cdots$ O(4)^3	0.95	2.53	3.381(3)	148.5
2a				
C(2)—H(2) $\cdots$ O(4)^4	0.95	2.71	3.379(6)	127.9
C(3)—H(3) $\cdots$ O(3)^5	0.95	2.70	3.348(6)	125.8
C(8)—H(8) $\cdots$ O(1)^6	0.95	2.68	3.314(6)	125.2

[a] Symmetry operations – 1: $x, y-1, z$; 2: $x+1/2, -y+1/2, z$; 3: $-x-1/2, y+1/2, -z+1$; 4: $-x+1, -y, -z$; 5: $x-1, y, z$; 6: $-x+3/2, y-1/2, -z+1$.

(see Table 6 and Fig. 2 and 3). All the nitro groups in **2** are twisted out of their attached phenyl planes by varying degrees [5.2(7) and 16.8(6)° in **2a**, and 15.71(16) and 28.6(16)° in **2b**] with the S $\cdots$ O separations between 2.642(4) and 2.6877(16) Å and O $\cdots$ S—C angles between 168.35(7) and 174.91(10)°. These parameters in **2b** can be compared with the near coplanar O_2N–aryl fragment, the S $\cdots$ O bond length of 2.490(2) Å, and the O $\cdots$ S—C angle of 173.99(2)° in 2-O_2N-4-$MeC_6H_3SCH{=}CHPh$.[17]

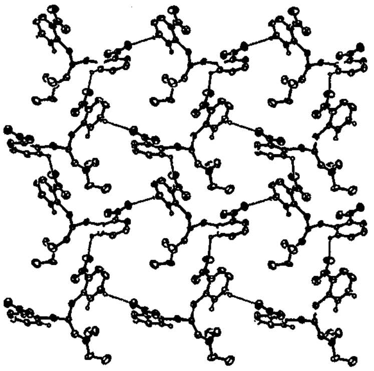


Fig. 2. Layers of **2a**, arising from hydrogen bonding interactions C2—H2 $\cdots$ O4 ($-x+1, -y, -z$), C3—H3 $\cdots$ O3 ($x+1, y, z$), and C8—H8 $\cdots$ O1 ($-x+3/2, y-0.5, -z+1$) shown normal to (001).

The H-bonding networks are distinct in the two polymorphs. Hydrogen bonding interactions, C2—H2 $\cdots$ O4 ($-x+1, -y, -z$), C3—H3 $\cdots$ O3 ($x+1, y, z$), and C8—H8 $\cdots$ O1 ($-x+3/2, y-0.5, -z+1$), in **2a** give rise to layers, normal to (001), as shown in Fig. 2(a): these layers are further linked into a 3D network. In **2b**, layers of molecules are formed normal to (001) from hydrogen bonding interactions, C2—H2 $\cdots$ O1 ($x, y-1, z$) and C8—H8 $\cdots$ O3 ($x+1/2, -y+1/2, z$), while layers, normal to (001), are produced from hydrogen bonding interactions C2—H2 $\cdots$ O1 ($x, y-1, z$) and C11—H11 $\cdots$ O4 ($-x-1/2, y+1/2, -z+1$) (see Fig. 3). These layers also combine to give a 3D array. The soft C—H $\cdots$ O(NO) hydrogen bonds in **2** fit well the currently accepted criteria for such bonds.[21,22]

Bond lengths and rotational barriers

Comparisons of C═C and C—N bond lengths in Table 1 show that no correlation exists between rotational barriers and bond orders.[9–12,23,24] This is expected as the barriers measure energy differences between ground state and transition states whereas bond order is a

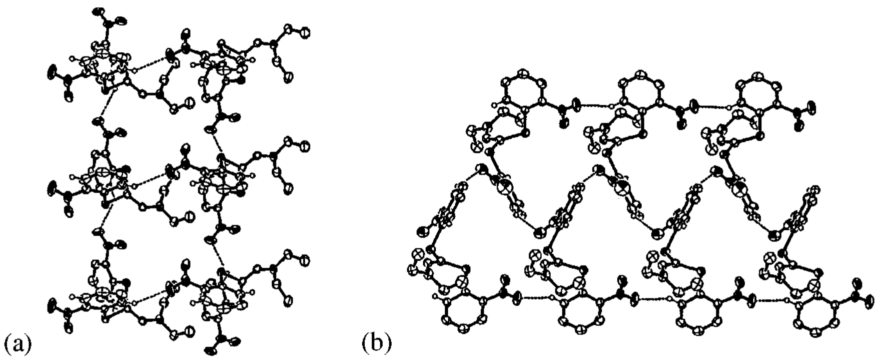


Fig. 3. (a) Layer of molecules of **2b**, arising from hydrogen bonding interactions, C2—H2 ⋯ O1 $(x, y-1, z)$ and C8—H8 ⋯ O3 $(x+1/2, -y+1/2, z)$, shown normal to (001). (b) Layer of molecules of **2b**, arising from hydrogen bonding interactions, C2—H2 ⋯ O1 $(x, y-1, z)$ and C11—H11 ⋯ O4 $(-x-1/2, y+1/2, -z+1)$, shown normal to (100).

function of the electron interactions in the ground state alone.

Acknowledgments

The authors thank the ERSRC X-Ray service at the University of Southampton for the data collections.

References

1. Sandström, J. *Topics in Stereochemistry* **1983**, *14,* 83; Kleinpeter, E.; Koch, A.; Taddei, F. *J. Mol. Struct*. **2001**, *535,* 257; Kleinpeter, E.; Thomas, S.; Uhlig, G.; Rudorf, W.D. *Magn. Reson. Chem*. **1993**, *31,* 714, and earlier references.
2. Senning, S.; Kelly, P. *Acta Chem. Scand*. **1972**, *26,* 2877.
3. Low, J.N.; Storey, E.J.; McCarron, M.; Wardell, J.L.; Ferguson, G.; Glidewell, C. *Acta Crystalloge., Sect. B* **2000**, *56,* 58.
4. Sheldrick, G.M. *Acta Crystallogr., Sect. A* **1990**, *46,* 467.
5. Sheldrick, G.M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.
6. Buckley, D.; Dunstan, S.; Henbest, H.B. *J. Chem. Soc.* **1957**, 4901.
7. Drabowicz, J.; Kielbasinski, D.; Mikolajczyk, M. In *The Chemistry of Sulphenic Acids and their Derivatives*; Patai, S., Ed.; Wiley: Chichester, 1990; Chap. 6.
8. Günther, H. *NMR Spectroscopy: An Introduction*; Wiley: Chichester, 1980; p 247.
9. Schmuehi, U.; Shanan-Atidi, H.; Horwitz, H.; Shvo, Y. *J. Chem. Soc., Perkin Trans. 2* **1973**, 657.
10. Ammon, H.L. *Acta Crystallogr., Sect. B* **1974**, *30,* 1731.
11. Abbotto, A.; Bradamante, S.; Capri, N.; Rzepe, H.; Williams, D. J.; White, A. *J. Org. Chem*. **1996**, *61,* 1770.
12. Blake, A.J.; McNab, H.; Monahan, L.C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 2003.
13. Sandstrom, J.; Wennerbeck, I. *Acta Chem. Scand., Sect. B* **1974**, *32,* 421.
14. Allen, F.H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
15. Ammon, Y.H.L.; Mazzocchi, P.H.; Regan, M.C.; Colicelli, E. *Acta Crystallogr., Sect. B* **1979**, *35,* 1722.
16. Allen, F.H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8,* 31.
17. Low, J.N.; Glidewell, C.; Wardell, J.L. *Acta Crystallogr., Sect. C* **2000**, *56,* 689.
18. Bondi, A.J. *Chem. Phys*. **1964,** *68,* 441.
19. Aupers, J.H.; Cox, P.J.; Doidge-Harrison, S.M.S.V.; Howie, R.A.; Low, J.N.; Wardell, J.L. *Main Group Chem*. **1999**, *3,* 23.
20. Low, J.N.; Glidewell, C.; Wardell, J.L. *Acta Crystallogr., Sect. B* **2000**, *56,* 893.
21. Desiraju, G.R.; *Angew. Chem., Int. Ed. Engl*. **1995**, *34,* 2311; *Acc. Chem. Res*., **1991**, *24,* 290; *Acc. Chem. Res*. **1996**, *29,* 4411.
22. Bernstein, J.; Davis, R.E.; Shimoni, L.; Chang, N.-L. *Angew. Chem., Int. Ed. Engl*. **1995**, *34,* 1555.
23. Shvo, Y.; Shanan-Atidi, H. *J. Am. Chem. Soc*. **1969**, *91,* 6683.
24. Downing, A.P.; Ollis, W.D.; Sutherland, I.O. *J. Chem. Soc. B* **1969**, 111.