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Crystal structures of (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)sulfide and the corresponding disulfane

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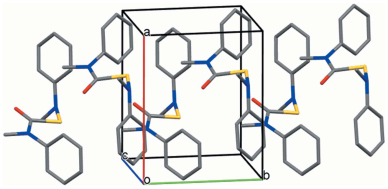
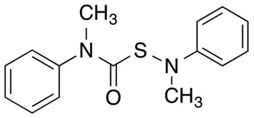


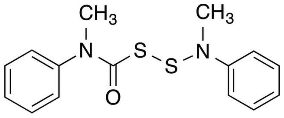
The title compounds, (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)sulfide, $C_{15}H_{16}N_2OS$, (I), and (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)disulfane, $C_{15}H_{16}N_2OS_2$, (II), are stable derivatives of (chlorocarbonyl)sulfenyl chloride and (chlorocarbonyl)disulfanyl chloride, respectively. The torsion angle about the S—S bond in (II) is −92.62 (6)°, which is close to the theoretical value of 90°. In the crystal of (II), non-classical intermolecular C—H⋯O hydrogen bonds form centrosymmetric cyclic dimers [graph set $R_2^2(10)$], while inter-dimer C—H⋯S interactions generate chains extending along the *b* axis.

1. Chemical context

As part of a multifaceted program in synthetic and mechanistic organosulfur chemistry (Barany *et al.*, 1983; Barany & Mott, 1984; Schroll & Barany, 1986; Schrader *et al.*, 2011, and references cited therein), we frequently encounter challenging-to-characterize compounds with one or more reactive acid chloride and/or sulfenyl chloride moieties. These are converted to the corresponding stable carbamoyl and/or sulfenamide derivatives, which are often crystalline, through their reliable, rapid, and high-yield reactions with *N*-methylaniline.



(I)



(II)

The present paper reports the structures of two such derivatives, *i.e.* (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)sulfide (I) and (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)disulfane (II), as determined by X-ray crystallography. The title compounds are derived respectively from (chlorocarbonyl)sulfenyl chloride and (chlorocarbonyl)disulfanyl chloride, which are noxious, distillable liquids. They are the first two members of a general family of compounds with the structure Ph(Me)N(C═O)S_nN(Me)Ph, in which the higher members (n = 3–6) were found, but not isolated in crystalline form, as components in the reactions of *in situ* generated (2-propoxydichloromethyl)(chlorocarbonyl)polysulfanes with *N*-methylaniline (Schroll & Barany, 1986).

2. Structural commentary

The title compounds differ by the number of sulfur atoms: one in (I) (Fig. 1) *versus* two in (II) (Fig. 2), and by the resulting

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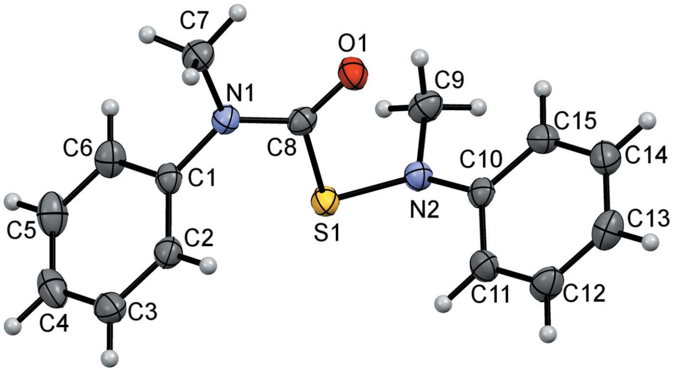


Figure 1
The molecular conformation of compound (I), showing 50% probability displacement ellipsoids with all non-H atoms labeled and numbered.

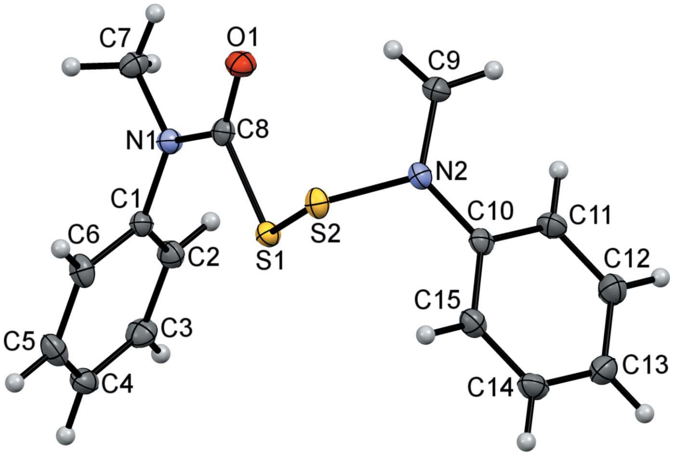


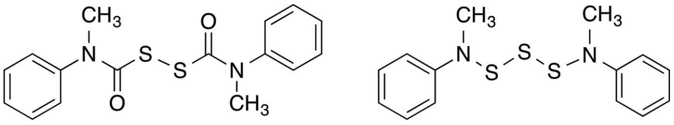
Figure 2
The molecular conformation of compound (II), showing 50% probability displacement ellipsoids with all non-hydrogen atoms labeled and numbered.

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

Note that when S is not numbered, it is S1 for compound (I) and S2 for compound (II). To specify certain torsion angles, the last atom in the linear structure differs between the two compounds, so *X* is used in place of an atom label.

	(I)	(II)
N1—C8	1.351 (3)	1.357 (2)
S—N2	1.678 (2)	1.666 (1)
S1—C8	1.824 (2)	1.827 (1)
S1—S2	–	2.0625 (5)
C9—N2—S	115.90 (14)	116.23 (8)
C10—N2—S	118.74 (12)	118.86 (8)
C10—N2—C9	118.37 (17)	118.17 (11)
C1—N1—C8—S1	3.3 (2)	9.16 (15)
N1—C8—S1—*X*	172.19 (14)	−165.53 (8)
C8—S1—S2—N2	–	−92.62 (6)
C10—N2—S—*X*	77.3 (2)	−72.86 (10)

relative orientations of the Ph(Me)N(C═O)S and N(Me)Ph moieties. Otherwise, they share similar bond lengths and angles across all analogous bonds (Table 1). Furthermore, the molecular parameters are all within expected ranges. The S—S bond of (II) is 2.0625 (5) Å, which is comparable to the bond length in elemental sulfur, S_8 (2.07 Å), but slightly longer than the 2.03 Å found for bis(*N*-methyl-*N*-phenylcarbamoyl)disulfane ($[Ph(Me)N(C{=}O)S]_2$) (III) (Schroll *et al.*, 2012). In compound (III) (Fig. 3), the slight shortening of the S—S bond was attributed to a partial double-bond character imparted by the adjacent carbonyl groups. Because (II) is essentially (III) minus one carbonyl group, it is not surprising for the S—S bond length in (II) to be closer to that in S_8. The torsion angle about the S—S bond in (II) is −92.62 (6)°, which is comparable to the theoretical optimum of 90° (Pauling, 1949; Torrico-Vallejos *et al.*, 2010).



(III) (IV)

Figure 3
Structures of selected comparison compounds, bis(*N*-methyl-*N*-phenylcarbamoyl)disulfane, (III), and bis(*N*-methyl-*N*-phenylamino)trisulfane, (IV)

3. Supramolecular features

The unit cell of (I) contains two molecules related by a twofold screw axis (Fig. 4). There are no intermolecular contacts in the crystal structure of (I). In the crystal of (II) non-classical intermolecular C7—H···O1 hydrogen bonds (Table 2) form centrosymmetric cyclic dimers [graph set $R_2^2(10)$]. Chains of molecules extending along the *b* axis result from inter-dimer C2—H···S1 interactions (Fig. 5).

4. Database survey

A search for similar structures in the Cambridge Structural Database (CSD; Version 5.36, update of November 2014; Groom & Allen, 2014) gave bis(*N*-methyl-*N*-phenylcarbamoyl)disulfane (III), published previously from our research (Schroll *et al.*, 2012), as well as two similar bis(carbamoyl)disulfanes (Bereman *et al.*, 1983; Li *et al.*, 2006). Structures containing a similar sulfenamide moiety were absent from the

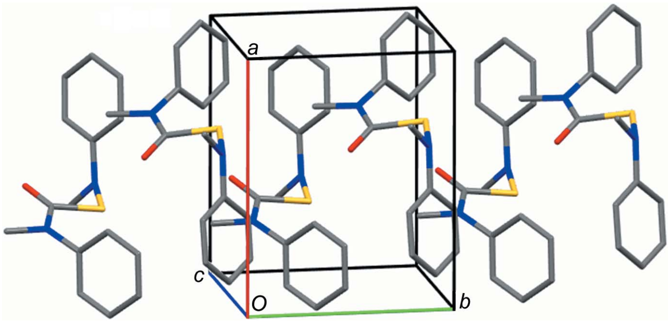


Figure 4
Crystal packing of (I). H atoms are not shown.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2A⋯S1^{i}	0.95	2.84	3.766 (1)	165
C7—H7B⋯O1^{ii}	0.98	2.60	3.532 (2)	160

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y, -z$.

CSD, although two structures reported N—S bonds connected to 'imido' [(RC═O)$_2$N] moieties (Farrell *et al.*, 2002; Ul-Haque & Behforouz, 1976). A very recent report from our research describes bis(N-methyl-N-phenylamino)trisulfane (IV) (Fig. 3) (Barany *et al.*, 2015), an N-methylanilide which contains two 'sulfenamide' ends [whereas (III) contains two 'carbamoyl' ends]. Not surprisingly, many geometric parameters of (III) and (IV) superimpose onto the corresponding portions of (I) and (II). For example, the sulfenamide N2—S bond lengths of (I) [1.6784 (15) Å] and (II) [1.6660 (11) Å] are close to that of (IV) [average N—S bond length of 1.657 Å] and the carbamoyl N1—C8 and S1—C8 bond lengths of (I) [1.351 (3) and 1.824 (2) Å, respectively] and (II) [1.357 (2) and 1.827 (1) Å, respectively] are similar to that of (III) [1.345 (3) and 1.825 (2) Å, respectively]. In addition, the torsion angles about the N1—C8 bond of (I) [3.3 (2)°] and (II) [9.16 (15)°] are similar to that of (III) [−6.4 (3)°] and the torsion angle about the N2—S bond in (I) [77.3 (2)°] and (II) [−72.86 (10)] are similar but slightly smaller than that of (IV) (average angle 80.3°).

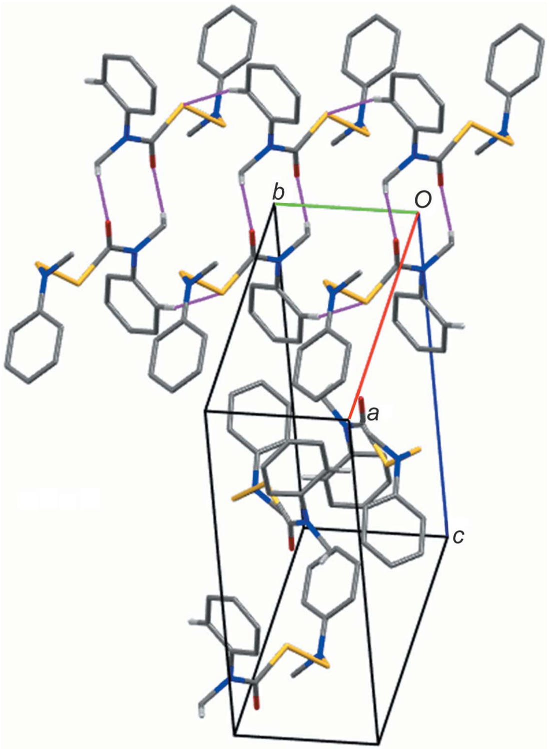


Figure 5
Crystal packing of (II). Only H atoms involved in intermolecular C2—H⋯S1 and C7—H⋯O1═C8 non-classical hydrogen bonds are shown.

5. Synthesis and crystallization

The title compound (I) was prepared on scales of up to 0.1 mol by addition of a 0.5 M solution of (chlorocarbonyl)sulfenyl chloride in CHCl$_3$ to an equal volume of a 2 M solution of N-methylaniline in CHCl$_3$ at 273 K, followed by stirring for 30 min at 298 K (Barany *et al.*, 1983). Workup by washing with equal volumes of 1 N aqueous HCl (3×) and brine (once), drying (MgSO$_4$), filtering, and concentrating *in vacuo* gave the product as an oil (nominally quantitative), and recrystallization from hot hexanes (30 mL g^{-1}) gave a white solid (typically 65–80% recovery), m.p. 338–340 K, which was stable for several decades when stored under ambient conditions. ^{1}H NMR (300 MHz; CDCl$_3$): δ 7.43–7.48 (m, 3H), 7.37 (dd, J = 1.9, 7.9 Hz, 2H), 7.23–7.29 (m, 2H), 7.12 (dd, J = 1.0, 8.8 Hz, 2H), 6.86 (t, J = 7.2 Hz, 1H), 3.41 (s, 3H), 3.31 (s, 3H). X-ray quality crystals were obtained by dissolving (I) (100 mg) in minimal CHCl$_3$ (200 µL) and then adding hexane (2 mL), followed by slow evaporation of the solvent at 298 K over two days.

To prepare compound (II), a solution of (chlorocarbonyl)-disulfanyl chloride (Schroll & Barany, 1986) (814 mg, 5.0 mmol) in CH$_2$Cl$_2$ (15 mL) was added over 10 min to a stirred solution of N-methylaniline (2.2 mL, 20 mmol) in CH$_2$Cl$_2$ (11 mL) at 273 K. The homogeneous reaction mixture was allowed to warm to 298 K, stirred an additional 30 min, and standard extractive workup [compare to procedure above for (I)] gave the product as a brown oil (1.44 g, 94% crude yield). The crude product was purified by flash column chromatography, eluting with hexane–ethyl acetate (8:1), to provide a yellow oil (1.37 g), which after storing under hexanes at 253 K overnight produced the title product as an off-white solid (757 mg, 2.5 mmol, 50%), m.p. 326–327 K (lit. 325–327 K; Barany & Mott, 1984). ^{1}H NMR (300 MHz; CDCl$_3$): δ 7.36–7.41 (m, 3H), 7.2–7.3 (m, 6H), 6.9–7.0 (m, 1H), 3.40 (s, 3H), 3.37 (s, 3H). X-ray quality crystals were prepared by dissolving (II) (23 mg) in CH$_2$Cl$_2$ (100 µL) and then adding heptane (200 µL), followed by slow evaporation of the solvent at 278 K over 11 days.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms were included at calculated positions [C—H(aromatic) = 0.95 Å or C—H(methyl) = 0.98 Å] and treated as riding, with $U_{\rm iso}$H = 1.2$U_{\rm eq}$C(aromatic) or 1.5$U_{\rm eq}$C(methyl). With (I), although of no importance in this achiral molecule, the Flack absolute structure factor (Parsons *et al.*, 2013) was determined as 0.05 (3) for 1450 Friedel pairs.

Acknowledgements

We thank Barbara L. Goldenberg for outstanding assistance in the preparation of this manuscript and Dominique Chavatte-Kallender, Phillip T. Goldblatt, David A. Halsrud, Kenneth P. Morris, and Andrew W. Mott for preparing (I) and (II) over the years.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{15}H_{16}N_2OS$	$C_{15}H_{16}N_2OS_2$
M_r	272.36	304.42
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$
Temperature (K)	173	123
a, b, c (Å)	9.0682 (7), 6.8402 (5), 11.4686 (9)	16.0414 (17), 5.5023 (6), 17.2986 (19)
β (°)	103.349 (1)	105.564 (1)
V (Å^3)	692.16 (9)	1470.9 (3)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.23	0.36
Crystal size (mm)	0.40 × 0.35 × 0.12	0.41 × 0.18 × 0.12
Data collection		
Diffractometer	Bruker SMART APEXII	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2002)	Multi-scan (*SADABS*; Bruker, 2002)
T_{min}, T_{max}	0.687, 0.746	0.699, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8061, 3145, 2961	16044, 3355, 3033
R_{int}	0.022	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.648	0.649
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.067, 1.05	0.028, 0.070, 1.06
No. of reflections	3145	3355
No. of parameters	174	183
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.15	0.32, −0.22
Absolute structure	Flack x determined using 1285 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)	–
Absolute structure parameter	0.05 (3)	–

Computer programs: *APEX2* and *SAINT* (Bruker, 2002), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2008).

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supporting information

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Crystal structures of (*N*-methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)sulfide and the corresponding disulfane

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) (*N*-Methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)sulfide

Crystal data

$C_{15}H_{16}N_2OS$
$M_r = 272.36$
Monoclinic, $P2_1$
$a = 9.0682\ (7)$ Å
$b = 6.8402\ (5)$ Å
$c = 11.4686\ (9)$ Å
$\beta = 103.349\ (1)°$
$V = 692.16\ (9)$ Å^3
$Z = 2$
$F(000) = 288$
$D_x = 1.307$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2915 reflections
$\theta = 2.3–27.4°$
$\mu = 0.23$ mm^{-1}
$T = 173$ K
Plate, colourless
0.40 × 0.35 × 0.12 mm

Data collection

Bruker SMART APEXII diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2002)
$T_{min} = 0.687$, $T_{max} = 0.746$
8061 measured reflections
3145 independent reflections
2961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 27.4°$, $\theta_{min} = 1.8°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.067$
$S = 1.05$
3145 reflections
174 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.1164P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Absolute structure: Flack x determined using 1285 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.05 (3)

Special details

Geometry. All e.s.d.'s are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.32124 (5)	0.41906 (8)	0.67886 (4)	0.02848 (13)
O1	0.41605 (17)	0.0518 (2)	0.71103 (13)	0.0314 (3)
N1	0.2797 (2)	0.1212 (3)	0.52292 (15)	0.0265 (4)
N2	0.39549 (17)	0.4094 (3)	0.82703 (13)	0.0264 (3)
C1	0.2020 (2)	0.2644 (3)	0.43921 (17)	0.0248 (4)
C2	0.2834 (2)	0.3936 (4)	0.38553 (17)	0.0289 (5)
H2A	0.3910	0.3938	0.4080	0.035*
C3	0.2080 (3)	0.5227 (3)	0.2990 (2)	0.0352 (5)
H3A	0.2637	0.6114	0.2619	0.042*
C4	0.0517 (3)	0.5218 (4)	0.2669 (2)	0.0383 (6)
H4A	−0.0001	0.6109	0.2079	0.046*
C5	−0.0302 (2)	0.3922 (4)	0.31988 (19)	0.0391 (6)
H5A	−0.1378	0.3926	0.2972	0.047*
C6	0.0446 (2)	0.2620 (4)	0.40601 (19)	0.0317 (5)
H6A	−0.0112	0.1719	0.4420	0.038*
C7	0.2839 (2)	−0.0795 (4)	0.47987 (18)	0.0317 (4)
H7A	0.3168	−0.1675	0.5483	0.048*
H7B	0.3553	−0.0877	0.4276	0.048*
H7C	0.1826	−0.1176	0.4348	0.048*
C8	0.3469 (2)	0.1659 (3)	0.63758 (18)	0.0247 (4)
C9	0.3038 (3)	0.3084 (4)	0.8984 (2)	0.0330 (5)
H9A	0.3380	0.3467	0.9827	0.050*
H9B	0.3151	0.1668	0.8911	0.050*
H9C	0.1970	0.3443	0.8691	0.050*
C10	0.5557 (2)	0.4074 (4)	0.86869 (15)	0.0248 (4)
C11	0.6441 (3)	0.5337 (4)	0.81829 (18)	0.0317 (5)
H11A	0.5971	0.6177	0.7545	0.038*
C12	0.8000 (3)	0.5379 (4)	0.8604 (2)	0.0364 (5)
H12A	0.8592	0.6238	0.8248	0.044*
C13	0.8703 (2)	0.4179 (5)	0.95412 (18)	0.0363 (5)
H13A	0.9774	0.4200	0.9825	0.044*
C14	0.7824 (3)	0.2954 (4)	1.0056 (2)	0.0357 (5)
H14A	0.8297	0.2139	1.0706	0.043*
C15	0.6264 (3)	0.2891 (3)	0.9641 (2)	0.0306 (5)
H15A	0.5676	0.2041	1.0008	0.037*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0321 (2)	0.0234 (2)	0.0263 (2)	0.0027 (2)	−0.00070 (17)	−0.0012 (2)
O1	0.0339 (8)	0.0284 (8)	0.0284 (8)	0.0061 (6)	0.0002 (6)	0.0003 (7)
N1	0.0291 (9)	0.0245 (9)	0.0240 (8)	−0.0005 (7)	0.0019 (7)	−0.0019 (7)
N2	0.0278 (8)	0.0279 (8)	0.0232 (7)	−0.0030 (9)	0.0053 (6)	−0.0007 (9)
C1	0.0266 (10)	0.0259 (10)	0.0207 (10)	0.0016 (8)	0.0031 (8)	−0.0037 (8)
C2	0.0283 (10)	0.0291 (13)	0.0273 (9)	−0.0012 (9)	0.0021 (8)	−0.0029 (9)
C3	0.0461 (13)	0.0285 (12)	0.0294 (11)	−0.0029 (10)	0.0054 (10)	−0.0002 (9)
C4	0.0475 (14)	0.0365 (13)	0.0268 (11)	0.0149 (11)	−0.0002 (10)	0.0002 (10)
C5	0.0275 (10)	0.0534 (17)	0.0340 (11)	0.0107 (12)	0.0024 (8)	−0.0059 (12)
C6	0.0253 (10)	0.0419 (13)	0.0285 (11)	0.0011 (9)	0.0075 (8)	−0.0026 (9)
C7	0.0364 (10)	0.0276 (9)	0.0309 (10)	0.0006 (12)	0.0073 (8)	−0.0040 (12)
C8	0.0222 (9)	0.0231 (10)	0.0287 (10)	−0.0003 (8)	0.0059 (8)	−0.0021 (8)
C9	0.0323 (11)	0.0330 (12)	0.0355 (12)	−0.0054 (10)	0.0115 (9)	−0.0031 (10)
C10	0.0292 (9)	0.0252 (9)	0.0197 (8)	−0.0028 (10)	0.0049 (7)	−0.0053 (9)
C11	0.0363 (11)	0.0364 (12)	0.0218 (10)	−0.0061 (10)	0.0055 (9)	0.0016 (9)
C12	0.0351 (12)	0.0457 (14)	0.0302 (11)	−0.0135 (11)	0.0115 (10)	−0.0034 (10)
C13	0.0286 (10)	0.0442 (12)	0.0348 (10)	−0.0034 (13)	0.0045 (8)	−0.0094 (14)
C14	0.0363 (12)	0.0343 (11)	0.0322 (12)	0.0010 (10)	−0.0007 (9)	0.0006 (10)
C15	0.0345 (11)	0.0261 (10)	0.0307 (11)	−0.0027 (10)	0.0069 (9)	0.0017 (9)

Geometric parameters (Å, º)

S1—N2	1.6784 (15)	C6—H6A	0.9500
S1—C8	1.824 (2)	C7—H7A	0.9800
O1—C8	1.212 (3)	C7—H7B	0.9800
N1—C8	1.351 (3)	C7—H7C	0.9800
N1—C1	1.437 (3)	C9—H9A	0.9800
N1—C7	1.462 (3)	C9—H9B	0.9800
N2—C10	1.421 (2)	C9—H9C	0.9800
N2—C9	1.467 (3)	C10—C11	1.392 (3)
C1—C2	1.383 (3)	C10—C15	1.393 (3)
C1—C6	1.390 (3)	C11—C12	1.385 (3)
C2—C3	1.385 (3)	C11—H11A	0.9500
C2—H2A	0.9500	C12—C13	1.385 (4)
C3—C4	1.380 (3)	C12—H12A	0.9500
C3—H3A	0.9500	C13—C14	1.379 (4)
C4—C5	1.384 (4)	C13—H13A	0.9500
C4—H4A	0.9500	C14—C15	1.385 (3)
C5—C6	1.386 (3)	C14—H14A	0.9500
C5—H5A	0.9500	C15—H15A	0.9500
N2—S1—C8	100.36 (10)	H7A—C7—H7C	109.5
C8—N1—C1	122.48 (18)	H7B—C7—H7C	109.5
C8—N1—C7	120.04 (17)	O1—C8—N1	125.12 (19)
C1—N1—C7	117.48 (16)	O1—C8—S1	120.52 (16)

C10—N2—C9	118.37 (17)	N1—C8—S1	114.34 (15)
C10—N2—S1	118.74 (12)	N2—C9—H9A	109.5
C9—N2—S1	115.90 (14)	N2—C9—H9B	109.5
C2—C1—C6	120.34 (19)	H9A—C9—H9B	109.5
C2—C1—N1	120.23 (18)	N2—C9—H9C	109.5
C6—C1—N1	119.25 (19)	H9A—C9—H9C	109.5
C1—C2—C3	120.05 (19)	H9B—C9—H9C	109.5
C1—C2—H2A	120.0	C11—C10—C15	118.84 (18)
C3—C2—H2A	120.0	C11—C10—N2	119.8 (2)
C4—C3—C2	119.7 (2)	C15—C10—N2	121.28 (19)
C4—C3—H3A	120.2	C12—C11—C10	120.5 (2)
C2—C3—H3A	120.2	C12—C11—H11A	119.8
C3—C4—C5	120.5 (2)	C10—C11—H11A	119.8
C3—C4—H4A	119.7	C11—C12—C13	120.6 (2)
C5—C4—H4A	119.7	C11—C12—H12A	119.7
C4—C5—C6	120.1 (2)	C13—C12—H12A	119.7
C4—C5—H5A	120.0	C14—C13—C12	118.91 (19)
C6—C5—H5A	120.0	C14—C13—H13A	120.5
C5—C6—C1	119.4 (2)	C12—C13—H13A	120.5
C5—C6—H6A	120.3	C13—C14—C15	121.1 (2)
C1—C6—H6A	120.3	C13—C14—H14A	119.4
N1—C7—H7A	109.5	C15—C14—H14A	119.4
N1—C7—H7B	109.5	C14—C15—C10	120.0 (2)
H7A—C7—H7B	109.5	C14—C15—H15A	120.0
N1—C7—H7C	109.5	C10—C15—H15A	120.0

C8—S1—N2—C10	77.3 (2)	C1—N1—C8—S1	3.3 (2)
C8—S1—N2—C9	−73.05 (18)	C7—N1—C8—S1	−176.52 (14)
C8—N1—C1—C2	78.2 (3)	N2—S1—C8—O1	−6.02 (19)
C7—N1—C1—C2	−101.9 (2)	N2—S1—C8—N1	172.19 (14)
C8—N1—C1—C6	−106.6 (2)	C9—N2—C10—C11	−166.6 (2)
C7—N1—C1—C6	73.2 (2)	S1—N2—C10—C11	43.8 (3)
C6—C1—C2—C3	0.6 (3)	C9—N2—C10—C15	9.7 (3)
N1—C1—C2—C3	175.69 (19)	S1—N2—C10—C15	−139.90 (19)
C1—C2—C3—C4	0.1 (3)	C15—C10—C11—C12	1.6 (3)
C2—C3—C4—C5	−0.4 (3)	N2—C10—C11—C12	178.0 (2)
C3—C4—C5—C6	0.0 (4)	C10—C11—C12—C13	−0.6 (4)
C4—C5—C6—C1	0.6 (3)	C11—C12—C13—C14	−0.6 (4)
C2—C1—C6—C5	−0.9 (3)	C12—C13—C14—C15	0.8 (4)
N1—C1—C6—C5	−176.1 (2)	C13—C14—C15—C10	0.2 (4)
C1—N1—C8—O1	−178.6 (2)	C11—C10—C15—C14	−1.4 (3)
C7—N1—C8—O1	1.6 (3)	N2—C10—C15—C14	−177.7 (2)

(II) (*N*-Methyl-*N*-phenylamino)(*N*-methyl-*N*-phenylcarbamoyl)disulfane

Crystal data

$C_{15}H_{16}N_2OS_2$	$F(000) = 640$
$M_r = 304.42$	$D_x = 1.375$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 16.0414$ (17) Å	Cell parameters from 2950 reflections
$b = 5.5023$ (6) Å	$\theta = 3.1$–$27.5°$
$c = 17.2986$ (19) Å	$\mu = 0.36$ mm^{-1}
$\beta = 105.564$ (1)°	$T = 123$ K
$V = 1470.9$ (3) Å^3	Block, colorless
$Z = 4$	0.41 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer	3355 independent reflections
Radiation source: sealed tube	3033 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.024$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$\theta_{max} = 27.5°$, $\theta_{min} = 1.3°$
$T_{min} = 0.699$, $T_{max} = 0.746$	$h = -20 \rightarrow 20$
16044 measured reflections	$k = -7 \rightarrow 7$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.7728P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
3355 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
183 parameters	
0 restraints	

Special details

Geometry. All e.s.d.'s are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.24264 (2)	0.27366 (6)	0.12829 (2)	0.01720 (9)
S2	0.27516 (2)	0.52421 (6)	0.05260 (2)	0.01821 (9)
O1	0.15803 (6)	0.07736 (18)	−0.01294 (5)	0.0215 (2)
N1	0.12052 (7)	−0.0673 (2)	0.09646 (6)	0.0173 (2)
N2	0.36329 (7)	0.4255 (2)	0.02877 (6)	0.0184 (2)
C1	0.12310 (8)	−0.0405 (2)	0.18005 (7)	0.0160 (2)
C2	0.16345 (8)	−0.2156 (2)	0.23508 (8)	0.0199 (3)
H2A	0.1907	−0.3512	0.2182	0.024*
C3	0.16379 (9)	−0.1914 (3)	0.31517 (8)	0.0232 (3)
H3A	0.1907	−0.3119	0.3530	0.028*

C4	0.12493 (9)	0.0083 (3)	0.33984 (8)	0.0227 (3)
H4A	0.1266	0.0268	0.3948	0.027*
C5	0.08363 (9)	0.1808 (3)	0.28448 (8)	0.0239 (3)
H5A	0.0565	0.3166	0.3015	0.029*
C6	0.08171 (8)	0.1558 (2)	0.20413 (8)	0.0209 (3)
H6A	0.0523	0.2721	0.1659	0.025*
C7	0.06129 (8)	−0.2499 (2)	0.05015 (8)	0.0204 (3)
H7A	0.0626	−0.2431	−0.0061	0.031*
H7B	0.0024	−0.2168	0.0537	0.031*
H7C	0.0792	−0.4118	0.0719	0.031*
C8	0.16585 (8)	0.0771 (2)	0.05874 (7)	0.0163 (2)
C9	0.34991 (9)	0.2336 (3)	−0.03205 (8)	0.0233 (3)
H9A	0.3968	0.2384	−0.0585	0.035*
H9B	0.2943	0.2589	−0.0720	0.035*
H9C	0.3497	0.0750	−0.0063	0.035*
C10	0.44464 (8)	0.4352 (2)	0.08806 (7)	0.0168 (2)
C11	0.50700 (9)	0.2568 (2)	0.09139 (8)	0.0219 (3)
H11A	0.4951	0.1250	0.0546	0.026*
C12	0.58679 (9)	0.2706 (3)	0.14843 (9)	0.0256 (3)
H12A	0.6291	0.1485	0.1500	0.031*
C13	0.60500 (9)	0.4600 (3)	0.20266 (8)	0.0242 (3)
H13A	0.6594	0.4686	0.2416	0.029*
C14	0.54283 (9)	0.6379 (3)	0.19970 (8)	0.0228 (3)
H14A	0.5548	0.7683	0.2371	0.027*
C15	0.46357 (9)	0.6273 (2)	0.14279 (8)	0.0202 (3)
H15A	0.4219	0.7512	0.1410	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01726 (16)	0.01986 (16)	0.01529 (15)	−0.00238 (11)	0.00576 (12)	−0.00051 (11)
S2	0.01769 (16)	0.01601 (16)	0.02234 (16)	0.00171 (11)	0.00784 (12)	0.00252 (12)
O1	0.0234 (5)	0.0262 (5)	0.0148 (4)	−0.0021 (4)	0.0049 (4)	0.0012 (4)
N1	0.0179 (5)	0.0187 (5)	0.0158 (5)	−0.0033 (4)	0.0055 (4)	−0.0012 (4)
N2	0.0170 (5)	0.0226 (6)	0.0175 (5)	−0.0012 (4)	0.0079 (4)	−0.0021 (4)
C1	0.0150 (6)	0.0183 (6)	0.0159 (6)	−0.0029 (5)	0.0063 (4)	−0.0013 (5)
C2	0.0203 (6)	0.0192 (6)	0.0208 (6)	0.0021 (5)	0.0066 (5)	−0.0011 (5)
C3	0.0234 (7)	0.0254 (7)	0.0192 (6)	0.0008 (5)	0.0030 (5)	0.0033 (5)
C4	0.0231 (7)	0.0293 (7)	0.0177 (6)	−0.0064 (5)	0.0088 (5)	−0.0050 (5)
C5	0.0269 (7)	0.0203 (7)	0.0299 (7)	−0.0006 (5)	0.0168 (6)	−0.0042 (5)
C6	0.0211 (6)	0.0193 (6)	0.0251 (7)	0.0025 (5)	0.0110 (5)	0.0037 (5)
C7	0.0197 (6)	0.0204 (6)	0.0198 (6)	−0.0034 (5)	0.0031 (5)	−0.0009 (5)
C8	0.0144 (6)	0.0161 (6)	0.0181 (6)	0.0020 (5)	0.0039 (5)	0.0013 (5)
C9	0.0211 (6)	0.0322 (8)	0.0173 (6)	−0.0031 (5)	0.0064 (5)	−0.0068 (5)
C10	0.0177 (6)	0.0185 (6)	0.0165 (6)	−0.0035 (5)	0.0087 (5)	0.0004 (5)
C11	0.0235 (7)	0.0204 (7)	0.0225 (6)	−0.0008 (5)	0.0074 (5)	−0.0064 (5)
C12	0.0212 (7)	0.0255 (7)	0.0295 (7)	0.0026 (5)	0.0056 (6)	−0.0049 (6)
C13	0.0198 (6)	0.0292 (7)	0.0228 (7)	−0.0040 (5)	0.0042 (5)	−0.0027 (6)

C14	0.0264 (7)	0.0220 (7)	0.0218 (6)	−0.0060 (5)	0.0098 (5)	−0.0069 (5)
C15	0.0226 (6)	0.0177 (6)	0.0230 (6)	−0.0014 (5)	0.0106 (5)	−0.0023 (5)

Geometric parameters (Å, º)

S1—C8	1.8273 (13)	C6—H6A	0.9500
S1—S2	2.0625 (5)	C7—H7A	0.9800
S2—N2	1.6660 (11)	C7—H7B	0.9800
O1—C8	1.2123 (15)	C7—H7C	0.9800
N1—C8	1.3569 (16)	C9—H9A	0.9800
N1—C1	1.4429 (15)	C9—H9B	0.9800
N1—C7	1.4646 (16)	C9—H9C	0.9800
N2—C10	1.4281 (16)	C10—C11	1.3917 (18)
N2—C9	1.4656 (16)	C10—C15	1.3967 (18)
C1—C2	1.3865 (18)	C11—C12	1.3929 (19)
C1—C6	1.3888 (18)	C11—H11A	0.9500
C2—C3	1.3905 (18)	C12—C13	1.3800 (19)
C2—H2A	0.9500	C12—H12A	0.9500
C3—C4	1.386 (2)	C13—C14	1.388 (2)
C3—H3A	0.9500	C13—H13A	0.9500
C4—C5	1.384 (2)	C14—C15	1.3847 (19)
C4—H4A	0.9500	C14—H14A	0.9500
C5—C6	1.3888 (18)	C15—H15A	0.9500
C5—H5A	0.9500		
C8—S1—S2	102.60 (4)	H7A—C7—H7C	109.5
N2—S2—S1	108.37 (4)	H7B—C7—H7C	109.5
C8—N1—C1	123.17 (10)	O1—C8—N1	124.80 (12)
C8—N1—C7	119.43 (10)	O1—C8—S1	122.64 (10)
C1—N1—C7	117.28 (10)	N1—C8—S1	112.55 (9)
C10—N2—C9	118.17 (11)	N2—C9—H9A	109.5
C10—N2—S2	118.86 (8)	N2—C9—H9B	109.5
C9—N2—S2	116.23 (8)	H9A—C9—H9B	109.5
C2—C1—C6	120.47 (11)	N2—C9—H9C	109.5
C2—C1—N1	119.97 (11)	H9A—C9—H9C	109.5
C6—C1—N1	119.51 (11)	H9B—C9—H9C	109.5
C1—C2—C3	119.60 (12)	C11—C10—C15	118.84 (12)
C1—C2—H2A	120.2	C11—C10—N2	120.77 (11)
C3—C2—H2A	120.2	C15—C10—N2	120.38 (12)
C4—C3—C2	120.05 (13)	C10—C11—C12	120.30 (12)
C4—C3—H3A	120.0	C10—C11—H11A	119.8
C2—C3—H3A	120.0	C12—C11—H11A	119.8
C5—C4—C3	120.12 (12)	C13—C12—C11	120.62 (13)
C5—C4—H4A	119.9	C13—C12—H12A	119.7
C3—C4—H4A	119.9	C11—C12—H12A	119.7
C4—C5—C6	120.16 (12)	C12—C13—C14	119.24 (13)
C4—C5—H5A	119.9	C12—C13—H13A	120.4
C6—C5—H5A	119.9	C14—C13—H13A	120.4

C1—C6—C5	119.55 (12)	C15—C14—C13	120.65 (12)
C1—C6—H6A	120.2	C15—C14—H14A	119.7
C5—C6—H6A	120.2	C13—C14—H14A	119.7
N1—C7—H7A	109.5	C14—C15—C10	120.34 (12)
N1—C7—H7B	109.5	C14—C15—H15A	119.8
H7A—C7—H7B	109.5	C10—C15—H15A	119.8
N1—C7—H7C	109.5		

S1—S2—N2—C10	−72.86 (10)	C7—N1—C8—S1	−175.04 (9)
S1—S2—N2—C9	77.90 (9)	C8—S1—S2—N2	−92.62 (6)
C8—N1—C1—C2	−110.35 (14)	S2—S1—C8—O1	15.13 (12)
C7—N1—C1—C2	73.77 (15)	S2—S1—C8—N1	−165.53 (8)
C8—N1—C1—C6	72.46 (16)	C9—N2—C10—C11	−4.59 (17)
C7—N1—C1—C6	−103.41 (14)	S2—N2—C10—C11	145.60 (11)
C6—C1—C2—C3	−1.25 (19)	C9—N2—C10—C15	174.12 (11)
N1—C1—C2—C3	−178.41 (12)	S2—N2—C10—C15	−35.69 (15)
C1—C2—C3—C4	−0.8 (2)	C15—C10—C11—C12	−0.02 (19)
C2—C3—C4—C5	1.8 (2)	N2—C10—C11—C12	178.70 (12)
C3—C4—C5—C6	−0.6 (2)	C10—C11—C12—C13	0.4 (2)
C2—C1—C6—C5	2.36 (19)	C11—C12—C13—C14	−0.2 (2)
N1—C1—C6—C5	179.54 (12)	C12—C13—C14—C15	−0.4 (2)
C4—C5—C6—C1	−1.4 (2)	C13—C14—C15—C10	0.8 (2)
C1—N1—C8—O1	−171.52 (12)	C11—C10—C15—C14	−0.56 (19)
C7—N1—C8—O1	4.27 (19)	N2—C10—C15—C14	−179.29 (11)
C1—N1—C8—S1	9.16 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···S1^{i}	0.95	2.84	3.766 (1)	165
C7—H7*B*···O1^{ii}	0.98	2.60	3.532 (2)	160

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*, −*z*.