

Polysulfonylamines. CXLV.¹ N-Diethylcarbamoyl-*o*-benzenedisulfonylimide, a urea with non-planar geometry at nitrogen and an amide single bond

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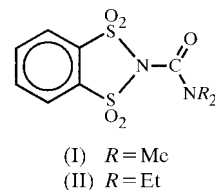
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The prominent features in the molecular structure of the title compound (alternative name: 2-diethylcarbamoyl-1,1,3,3-tetraoxo-1,3,2-benzodithiazole), C₁₁H₁₄N₂O₅S₂, arise in the urea moiety S₂N—C(O)—N'C₂: the sum of the angles at N is 332.3 (1)°, the N—C(O)—N'C₂ unit is planar, and distances N—C(O) = 1.494 (3) Å, N'—C(O) = 1.325 (2) Å and C—O = 1.215 (2) Å. The molecules are associated *via* five C—H···O hydrogen bonds to form layers parallel to the *yz* plane. This compound and its dimethyl homologue, which were synthesized by treating the silver salt of *o*-benzenedisulfonimide with carbamoyl chlorides, are prone to rapid hydrolysis at the weak N—C(O) bond. For both molecules, the rotational barrier about the partial N'—C(O) double bond is *ca* 50 kJ mol⁻¹ at 250 K (from dynamic ¹H NMR experiments).

Comment

The syntheses of the cyclic 1,1-disulfonylureas (I) and (II) (see Scheme), and the structure elucidation of (II) form part of a programme aimed at derivatives of *o*-benzenedisulfonimide, HN(SO₂)₂C₆H₄ (HZ), including metal complexes of the *N*-deprotonated species Z⁻ (*e.g.* Moers *et al.*, 2001*b*; Jones *et al.*, 1997) and covalently *N*-substituted molecules X—Z (Pröhl *et al.*, 1999; Hamann *et al.*, 1998; Jones *et al.*, 1995). The novel ureas, obtained by treating AgZ with the appropriate carbamoyl chlorides in acetonitrile, are moisture sensitive and readily hydrolyse to give the respective ammonium salts, [R₂NH₂]⁺Z⁻, and carbon dioxide. Crystals of (II) could be mounted in inert oil despite their sensitivity, but compound (I) proved impossible to mount because it is not wetted by the oil or by its own mother liquor (acetonitrile). Compound (II) and its acyclic congener (MeSO₂)₂N—C(O)—NMe₂ [(III);

Dalluhn *et al.*, 2001] appear to be the first crystallographically authenticated 1,1-disulfonylureas. No entry for any urea displaying an (SO₂)₂N—C(O) group was found in the April 2001 release of the Cambridge Structural Database (Allen & Kennard, 1993).



The molecular structure of (II) with the atomic labelling scheme is shown in Fig. 1 and Table 1 summarizes important bond lengths, bond angles and torsion angles. The most notable features are the degree of pyramidity of the ring N atom (N1), despite its being part of a urea moiety, and the astoundingly elongated amide N1—C1 bond.

In the bicyclic moiety, which possesses approximate mirror symmetry, the bond lengths and angles are as expected. The six-membered carbocycle and the two S atoms are coplanar (r.m.s. deviation of the eight atoms is 0.0045 Å). The five-membered heterocycle adopts an envelope conformation, with N1 lying 0.619 (2) Å out of the plane of the other eight ring atoms. The sulfonyl O atoms are located above or below the S11/N1/S12 plane, with O11 and O13 occupying equatorial positions [torsion angles: O11—S11—C11—C12 133.61 (16)° and O12—S11—C11—C12 -90.21 (16)°]. The greater part of the urea grouping, as defined by the ring N1 atom, the carbonyl C1—O1 function and the C21—N2—C22 fragment, is typically planar, with C1 and N2 deviating by only 0.001 (2) and -0.002 (2) Å from the respective planes formed by their three bonded neighbours; the corresponding torsion angles are included in Table 1.

The most striking aspects of the structure of (II) arise at the disulfonylated N1 centre. First, the sum of the angles at this atom is 332.3 (1)°, which correlates with a distance of 0.5054 (17) Å between N1 and the plane defined by C1, S11 and S12. Secondly, in order to reduce steric hindrance, the

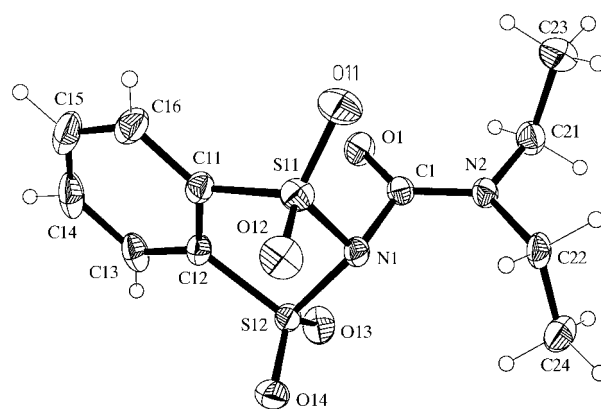


Figure 1

The molecule of compound (II) in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

¹ Part CXLIV: Moers, Blaschette & Jones (2001*a*).

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Et₂N—C(O) moiety is rotated about N1—C1 in such a way that O1—C1 and N2—C1 adopt an asymmetrically staggered orientation relative to the N—S bonds (the torsion angles are given in Table 1). Thirdly, the N1—C1 amide bond has a length of 1.494 (3) Å and must accordingly be regarded as a covalent single bond devoid of electron delocalization *via* $p\pi-p\pi$ bonding. It is even longer than the Nsp²—Csp³ bonds in the Et₂N group and exceeds by 0.13 Å the mean Nsp²—Csp² distance in tetrasubstituted ureas, and by 0.03 Å the mean Nsp³—Csp³ distance in tertiary aliphatic amines (Allen *et al.*, 1987). Consistent with the established interdependence of C—N and C—O bond lengths in ureas (Blessing, 1983), the adjacent N2—C1 and O1—C1 bonds are shortened to 1.325 (2) and 1.215 (2) Å, respectively, thus closely approaching the low end of the range associated with related distances in urea molecules (Allen *et al.*, 1987). It should be emphasized that the abnormal electronic properties of (II) are not exclusively induced by N1 being part of a five-membered heterocycle; a similar geometry has been detected for the acyclic urea (III), where the sum of angles at the disulfonylated N atom amounts to 351.3 (1)° and the (SO₂)₂N—C(O) bond length is 1.486 (3) Å (Dalluhn *et al.*, 2001). The great tendency of the compounds to hydrolyse reflects a high degree of electrophilic activation of the carbonyl C atom that can be traced back to the low order of the (SO₂)₂N—C(O) bond.

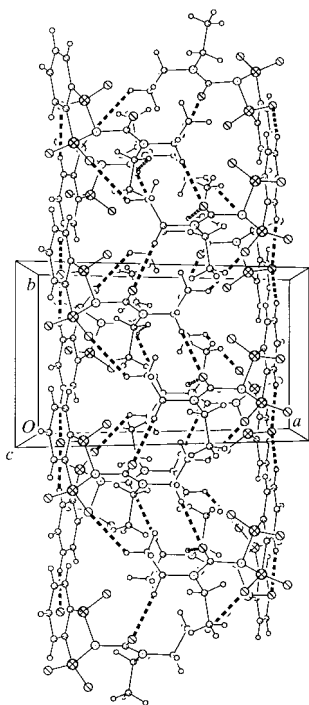


Figure 2

Packing diagram of compound (II) viewed parallel to the *z* axis. Atoms are identified as follows: circles with crosses represent S and dotted circles N. circles with diagonal lines O, circles with slight shading C and small open circles H. Hydrogen bonds are indicated by thick dashed lines. Normalized H···O distances (C—H = 1.08 Å, *cf.* Table 2) are H13···O12ⁱ 2.55, H15···O12ⁱⁱ 2.51, H21B···O1ⁱⁱⁱ 2.38, H22B···O1^{iv} 2.46, H23A···O13^v 2.52 and H14···O14^{vi} 2.51 Å.

¹H and ¹³C NMR data for (I) and (II) show that rotation around the N2—C1 amide multiple bond is not hindered in solution at ambient temperature. On cooling, decoalescence of the alkyl ¹H signals starts at 250 K and is completed at 230 K. Using the conventional Eyring equation, a rotational barrier of $\Delta G_c^\ddagger \simeq 50$ kJ mol⁻¹ at *T*_c = 250 K was obtained for both molecules. In contrast to these results, the Me₂N group in (III) gave rise to distinct ¹H and ¹³C NMR signals at room temperature, the barrier to rotation amounting to $\Delta G_c^\ddagger \simeq 80$ kJ mol⁻¹ at *T*_c = 380 K (Dalluhn *et al.*, 2001). The high values of the activation parameters and the large discrepancy between the acyclic and cyclic cases probably stem from intramolecular steric hindrance, which, according to simulation experiments on rigid-rotator models, is more pronounced in (III) than in the cyclic urea (II). In any case, it should be borne in mind that the currently known rotational barriers about C—N bonds in ureas are generally lower than 50 kJ mol⁻¹ [see, for example, Wawer & Koleva (1995), and references therein].

The packing of (II) involves six C—H···O interactions that may reasonably be classified as hydrogen bonds (Table 2). The first five of these link the molecules to form thick layers parallel to the *yz* plane (Fig. 2), with one layer per *x*-axis repeat distance. The end faces of the layers are formed by the six-membered rings, which are linked by bifurcated C13—H13···O12···H15—C15 hydrogen-bond systems. Prominent in the centre of the layers are short C21—H21B···O1 interactions. The layers are linked by the sixth hydrogen bond, *i.e.* C14—H14···O14.

Experimental

The silver salt, AgZ, used to synthesize compounds (I) and (II) was prepared and dehydrated as described elsewhere (Blaschette *et al.*, 1993). Compounds (I) and (II) are moisture sensitive and are best handled within glove-bags or within a dry box. For the preparation of compound (I), dimethylcarbamoyl chloride (1.07 g, 10.0 mmol) was dissolved in anhydrous acetonitrile (20 ml) and the solution added dropwise to a stirred solution of AgZ (3.26 g, 10.0 mmol) in the same solvent (50 ml). After stirring for 48 h at room temperature in the dark, AgCl was removed by filtration and washed with dichloromethane (30 ml). The combined liquid phases were evaporated to dryness under reduced pressure and the crude product was recrystallized from dichloromethane/petroleum ether (3:1) [yield 72% (2.1 g), m.p. 415 K]. ¹H NMR (CD₂Cl₂, 200 MHz, 300 K, p.p.m.): δ 3.14 (*s*, 6H, Me₂N), 7.85–7.98 (4H, C_{ar}H); ¹H NMR (CD₂Cl₂, 200 MHz, 230 K, p.p.m.): δ 3.00 (*s*, 3H, MeN), 3.22 (*s*, 3H, MeN), 7.90–8.05 (4H, C_{ar}H); ¹³C NMR (CD₂Cl₂, 50 MHz, 300 K, p.p.m.): δ 38.47 (Me₂N), 122.73, 135.42, 138.88 (all C_{ar}), 147.94 (CO). For the preparation of compound (II), the same procedure was employed as for (I), but using diethylcarbamoyl chloride (1.36 g, 10.0 mmol) and AgZ (3.26 g, 10.0 mmol) [yield 91% (2.9 g), m.p. 458 K]. ¹H NMR (CD₂Cl₂, 200 MHz, 300 K, p.p.m.): δ 1.24 [*t*, 6H, 2 × Me, ³*J*(H—H) = 7.2 Hz], 3.51 [*q*, 4H, 2 × CH₂, ³*J*(H—H) = 7.2 Hz], 7.87–8.01 (4H, C_{ar}H); ¹H NMR (CD₂Cl₂, 200 MHz, 230 K, p.p.m.): δ 1.05–1.32 (*t* + *t*, 2 × Me, spectral resolution poor), 3.34 [*q*, 2H, CH₂, ³*J*(H—H) = 6.8 Hz], 3.57 [*q*, 2H, CH₂, ³*J*(H—H) = 7.0 Hz], 7.90–8.10 (4H, C_{ar}H); ¹³C NMR (CDCl₃, 50 MHz, 300 K, p.p.m.): δ 13.43 (2 × Me), 44.04

(2 × CH₂), 122.57, 134.64, 139.78 (all C_{ar}), 148.00 (CO). Satisfactory elemental analyses were obtained for both compounds. For (I), found: C 36.97, H 3.54, N 9.53, S 21.99%; calculated for C₉H₁₀N₂O₅S₂: C 37.23, H 3.47, N 9.65, S 22.09%; for (II), found: C 41.71, H 4.44, N 8.78, S 20.16%; calculated for C₁₁H₁₄N₂O₅S₂: C 41.50, H 4.43, N 8.80, S 20.14%. Crystals of (II) suitable for X-ray diffraction were grown at room temperature by vapour diffusion of petroleum ether into a dichloromethane solution of the compound.

Crystal data

C₁₁H₁₄N₂O₅S₂
M_r = 318.36
 Monoclinic, *P*₂₁/*c*
a = 14.393 (5) Å
b = 8.201 (2) Å
c = 12.606 (4) Å
 β = 113.17 (2)°
V = 1368.0 (7) Å³
Z = 4

D_x = 1.546 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 54 reflections
 θ = 10.0–11.5°
 μ = 0.41 mm⁻¹
T = 143 (2) K
 Prism, colourless
 0.6 × 0.5 × 0.4 mm

Data collection

Stoe Stadi-4 diffractometer
 ω/θ scans
 3327 measured reflections
 3148 independent reflections
 2663 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.059
 θ_{\max} = 27.6°

h = 0 → 18
k = -1 → 10
l = -16 → 15
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.040
wR(*F*²) = 0.109
S = 1.04
 3148 reflections
 183 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.9893P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—S11	1.7041 (18)	N2—C1	1.325 (2)
N1—S12	1.7048 (17)	N2—C21	1.469 (3)
N1—C1	1.494 (3)	N2—C22	1.471 (2)
O1—C1	1.215 (2)		
S11—N1—S12	107.72 (9)	O1—C1—N2	127.42 (19)
C1—N1—S11	111.24 (13)	C21—N2—C22	116.59 (16)
C1—N1—S12	113.36 (12)	C1—N2—C21	118.17 (17)
N2—C1—N1	112.45 (16)	C1—N2—C22	125.24 (17)
O1—C1—N1	120.13 (17)		
C21—N2—C1—N1	-178.70 (17)	S11—N1—C1—N2	111.08 (16)
C22—N2—C1—N1	1.6 (3)	S12—N1—C1—N2	-127.36 (15)
C21—N2—C1—O1	1.1 (3)	C1—N2—C21—C23	96.0 (2)
C22—N2—C1—O1	-178.6 (2)	C22—N2—C21—C23	-84.3 (2)
S11—N1—C1—O1	-68.8 (2)	C1—N2—C22—C24	92.0 (2)
S12—N1—C1—O1	52.8 (2)	C21—N2—C22—C24	-87.7 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...O12 ⁱ	0.95	2.67	3.602 (3)	166
C15—H15...O12 ⁱⁱ	0.95	2.41	3.313 (3)	159
C21—H21 <i>B</i> ...O1 ⁱⁱⁱ	0.99	2.46	3.353 (3)	150
C22—H22 <i>B</i> ...O1 ^{iv}	0.99	2.50	3.092 (2)	118
C23—H23 <i>A</i> ...O13 ^v	0.98	2.58	3.298 (3)	130
C14—H14...O14 ^{vi}	0.95	2.62	3.442 (3)	145

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (v) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

Methyl groups were refined as rigid groups allowed to rotate but not tip; the starting positions were obtained from difference syntheses. Other H atoms were refined using a riding model starting from calculated positions. The fixed C—H distances were 0.98 Å for methyl, 0.99 Å for methylene and 0.95 Å for aromatic H atoms.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1460). Services for accessing these data are described at the back of the journal.

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