

Diisopropylammonium 2-[(2,4-dinitrophenyl)sulfanylaminocarbonyl]-benzoate

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The structure of title compound, $C_6H_{16}N^+ \cdot C_{14}H_8N_3O_7S^-$, comprises discrete ions which are interconnected by N—H \cdots O⁻ and N—H⁺ \cdots O⁻ hydrogen bonds, leading to a neutral one-dimensional network along [100]. These hydrogen bonds appear to complement the Coulombic interaction and help to stabilize the structure further.

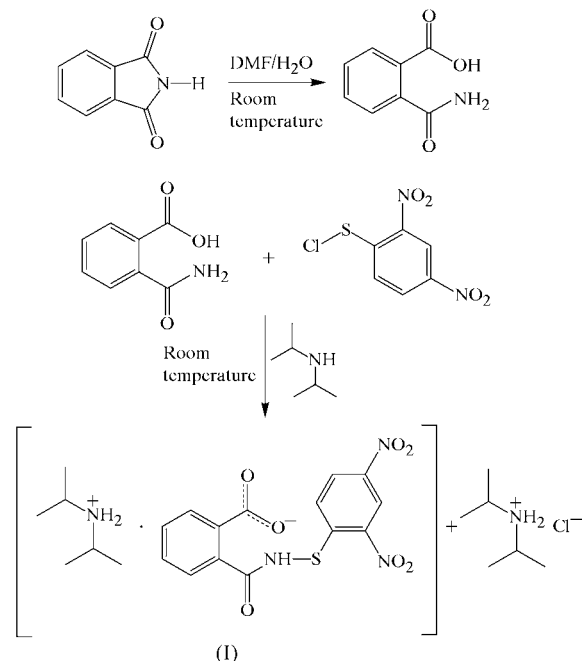
Comment

Sulfenamides are important compounds with versatile industrial applications (Kuhle, 1973). Bond polarization in sulfenamide derivatives, resulting from the difference in electronegativity between S and N, activates the S—N bond for attack by both nucleophiles and electrophiles, and appears to be the factor primarily responsible for the chemistry of these compounds. The title compound, (I), is the result of the condensation reaction of 2,4-dinitrophenylsulfenyl chloride and 2-carbamoylbenzoic acid. As part of our work involving the study of the synthesis and structural characterization of divalent-sulfur compounds (Brito *et al.*, 2004, 2005; Brito, López-Rodríguez, Cárdenas & Vargas, 2006; Brito, López-Rodríguez, Vargas & León, 2006), we report here the molecular and supramolecular structure of (I). To our knowledge (Cambridge Structural Database, Version 5.27; Allen, 2002), this is the first reported structure of an ionic sulfenamide.

The structure of compound (I) comprises discrete ions (Fig. 1 and Table 1). The cation in (I) has approximate C_2 symmetry and the molecular dimensions are within normal ranges (Allen *et al.*, 1987), with mean $Csp^3-Csp^3 = 1.508$ (4) Å and mean $Csp^3-N = 1.504$ (3) Å.

The benzene rings are slightly distorted and the nitro groups are slightly twisted with respect to the ring to which they are bonded (Table 1). The C—S and N—S bond distances [1.760 (2) and 1.6885 (18) Å, respectively] are normal for this

type of compound [literature values are in the ranges C—S = 1.763–1.791 Å and S—N = 1.679–1.695 Å (Mahmoudkhani & Vargas-Baca, 2003; Glidewell *et al.*, 2003; Lee *et al.*, 1995; Zhang *et al.*, 2005; Bao *et al.*, 2003)]. The S—N distance is shorter than the normal S—N single-bond length (1.74 Å; Pauling, 1960), but is normal for this type of structure as a result of the π character of the S—N bond.



The C—O bond distances in the carboxylate group are nearly equal and lie midway between the usual single and double C—O bond lengths found in a carboxylate fragment, as a consequence of the virtually complete electron delocalization. These lengths also compare favourably with those reported [1.2593 (16)–1.259 (2) Å] by Parvez *et al.* (2004), as a representative example. In the anion, the C6/S1/N3 plane

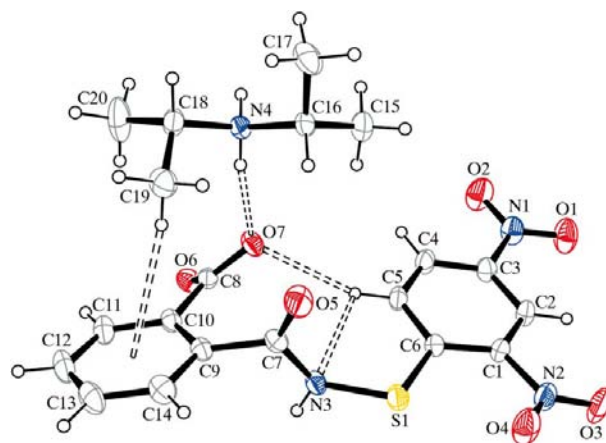


Figure 1
The structure of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. The dashed lines denote the hydrogen-bonding interactions and the C—H \cdots π interaction (centroid of the C9–C14 ring) within the asymmetric unit.

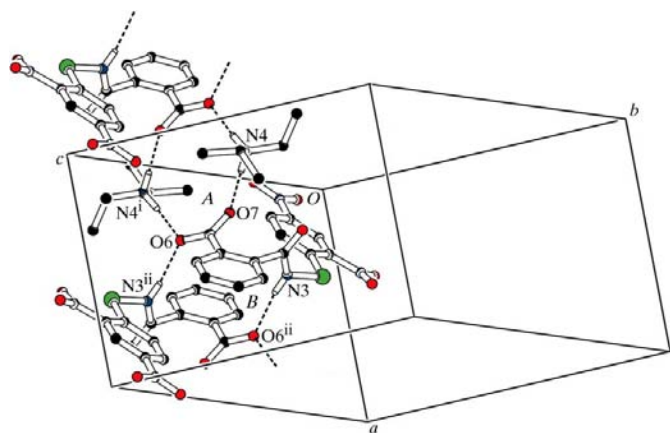


Figure 2

A view of the one-dimensional supramolecular aggregate, showing the formation of $R_4^4(12)$ and $R_2^2(14)$ rings (labelled *A* and *B*, respectively). H atoms not involved in the N—H...O interactions have been omitted. [Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $1 - x, -y, 1 - z$.]

makes a dihedral angle of $88.4(8)^\circ$ with the H3/N3/C7 plane, in good agreement with the value of 90.0° for the torsional ground state of this type of species. The conformation of the anion is stabilized by two intramolecular hydrogen bonds involving atom C5 as a donor, *viz.* C5—H5...N3 and C5—H5...O7 (Fig. 1). The crystal packing also shows a weak intramolecular C—H... π interaction between pairs of cations and anions (Fig. 1 and Table 2).

Two cations in (I) bridge two anions through $N^+—H...O^-$ hydrogen bonds (Table 2). Ammonium atom N4 forms hydrogen bonds to a different carboxylate O atom in each of two adjacent anions, to form a centrosymmetric macro-ring at $(0, 0, \frac{1}{2})$ characterized by the $R_4^4(12)$ motif (labelled *A* in Fig. 2) (Bernstein *et al.*, 1995). Pairs of anions are then connected *via* hydrogen bonds involving atom N3 as the donor in one anion and atom O6 of the carboxylate group of the other anion as the acceptor, thereby generating an $R_2^2(14)$ centrosymmetric ring (labelled *B* in Fig. 2) at $(\frac{1}{2}, 0, \frac{1}{2})$. These two types of rings combine alternately in an ...*ABAB*... fashion to form a one-dimensional supramolecular aggregate (Fig. 2).

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. 2,4-Dinitrophenylsulfenyl chloride and phthalimide were purchased from Aldrich. The precursor compound, 2-carbamoylbenzoic acid, was prepared *in situ* by a hydrolysis reaction at room temperature of the phthalimide compound (see scheme). The title compound, (I), was prepared according to the method of Wunderly (1972). A methanol solution of 2,4-dinitrophenyl chloride (2.487 g, 0.010 mol) was added dropwise to a stirred solution of phthalimide (1.176 g, 0.008 mol) and diisopropylamine (1.13 ml, 0.008 mol) in dimethylformamide— H_2O (5:1 *v/v*) under a nitrogen atmosphere. Stirring was continued for 30 min at 298 K. The colourless crystals which formed were filtered off, washed with pentane and dried at room temperature. Colourless crystals suitable for single-crystal X-ray diffraction studies were obtained by slow evaporation of a solution of (I) in methanol [m.p.

423 K (decomposition)]. FT-IR (KBr pellet, cm^{-1}): $\nu(w, C—S)$ 735, $\nu(s, C=O)$ 1568, $\nu(s, N—H)$ 3106, $\nu(s, NO_2)$ 1521, $\nu(s, C—O)$ 1307, $\nu(m, S—N)$ 967, $\nu(s, C—H$ disubstitution, Ar) 830, $\nu(m, N—H$ amine) 2942.

Crystal data

$C_6H_{16}N^+ \cdot C_{14}H_8N_3O_7S^-$
 $M_r = 464.49$
 Monoclinic, $P2_1/n$
 $a = 9.4350(10) \text{ \AA}$
 $b = 18.098(8) \text{ \AA}$
 $c = 13.612(2) \text{ \AA}$
 $\beta = 102.485(9)^\circ$
 $V = 2269.3(11) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.36 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.19 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Prism, colourless
 $0.35 \times 0.23 \times 0.19 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer 12285 measured reflections
 φ scans, and ω scans with κ offsets 4866 independent reflections
 Absorption correction: multi-scan (SORTAV; Blessing, 1995) 4116 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.037$
 $\theta_{max} = 27^\circ$
 $T_{min} = 0.951, T_{max} = 0.963$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.166$
 $S = 1.17$
 4866 reflections
 307 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0801P)^2 + 0.6445P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.006$
 $\Delta\rho_{max} = 0.41 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.36 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

O5—C7	1.212 (3)	O7—C8	1.251 (2)
O6—C8	1.256 (3)	N3—C7	1.363 (3)
O3—N2—C1—C6	171.1 (2)	O1—N1—C3—C4	175.8 (2)

Table 2

Hydrogen-bond and short-contact geometry ($\text{\AA}, ^\circ$).

Cg1 is the centroid of the C9—C14 ring.

$D—H...A$	$D—H$	$H...A$	$D...A$	$D—H...A$
N3—H3...O6 ⁱ	0.82 (3)	1.96 (3)	2.770 (3)	170 (3)
N4—H4A...O7	0.85 (3)	1.96 (3)	2.810 (3)	171 (2)
N4—H4B...O6 ⁱⁱ	0.93 (3)	1.90 (3)	2.828 (3)	172 (2)
C5—H5...O7	0.93	2.37	3.253 (3)	160
C5—H5...N3	0.93	2.41	2.866 (3)	110
C19—H19A...Cg1	0.96	2.92	3.857 (3)	165

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

H atoms bonded to atoms N3 and N4 were located in difference density maps and refined with an isotropic model, giving N—H distances in the range 0.82 (3)–0.93 (3) \AA . H atoms bonded to C atoms were positioned geometrically and then allowed to ride on their parent atoms, with C—H distances of 0.94 \AA for aromatic H atoms, 0.96 \AA for methyl H atoms and 0.98 \AA for methylene H atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. 55 unique reflections with $\sin \theta/\lambda < 0.6$ were not included in the data set as they were either partially obscured by the beam stop or were eliminated during data reduction.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *MERCURY* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3028). Services for accessing these data are described at the back of the journal.

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