

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1134). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Amino-4-nitrobenzothiazole

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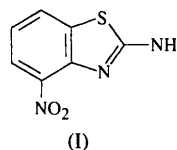
Abstract

The crystal structure of the title compound, C₇H₅N₃O₂S, consists of centrosymmetric dimers, the principal intradimer interaction being two pairs of three-centre hydrogen bonds involving the amino group, the ring N atom and one O atom of the nitro group. The structure is compared with those of three unsubstituted 2-aminobenzothiazoles reported earlier. The molecule exists as a resonance hybrid of two tautomers, one neutral and the other dipolar. There is some indication that π density localized in the N_{amino}—C—N_{ring} portion of the molecule is in part transferred to the nitro group, but this should be confirmed by other techniques.

Comment

As part of our study of the relationship between molecular and electronic structures and absorption properties of benzothiazole derivatives, we prepared a series of 2-aminobenzothiazoles having a nitro group in various positions on the benzene ring. These compounds can be described as polarized molecules having electron-releasing (amino) and electron-accepting (nitro) groups bonded to the unsaturated framework, with an absorption in the near-ultraviolet and visible region due to delocalization

of π electrons. Indeed, these derivatives were found to exhibit pronounced colour changes depending on the position of the nitro group, which makes their utilization as organic dyes a possibility. Thus, it is of interest to examine the extent of conjugation in these molecules by combined use of theoretical and experimental methods. We report here on the crystal structure of the 4-nitro isomer, (I).



As shown in Fig. 1 the molecule is nearly planar. The six C atoms [C(4)–C(9)] of the benzene ring are essentially exactly coplanar (r.m.s. deviation 0.0017 Å); atoms C(2) and N(3) lie in the benzene plane [deviations 0.002 (1) and 0.000 (1) Å, respectively], while atom S(1) deviates by 0.008 (1) Å from this plane. As for the ring substituents, atom N(2) is displaced by 0.014 (1) Å on the same side as atom S(1) and the N(4) atom of the nitro group is displaced by 0.014 (1) Å in the opposite direction. The N(2) atom is sp^2 hybridized, as evidenced by the sum of the valence angles around this atom [359 (1)°], with the lone-pair electrons available for π bonding [torsion angle N(3)—C(2)—N(2)—H(1) 6 (1)°]. The nitro group at C(4) is rotated by 10.6 (2)° from the mean plane of the benzene ring.

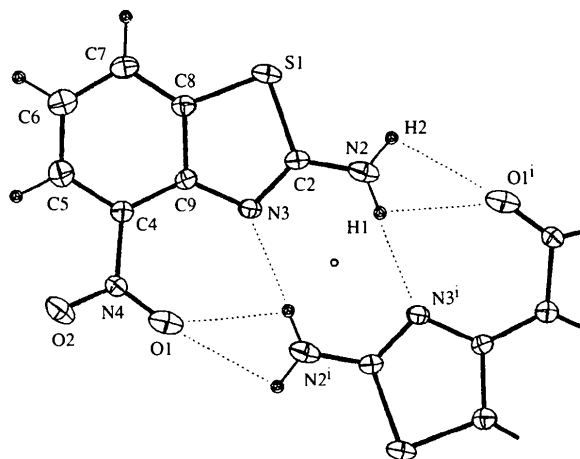


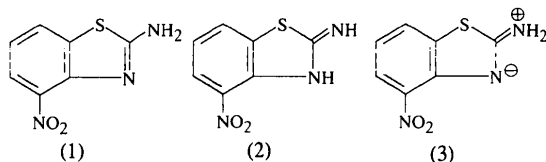
Fig. 1. ORTEP (Johnson, 1971) drawing of the title compound showing the atom-numbering scheme. Displacement ellipsoids are shown at 50% probability levels. Part of the symmetry-related molecule is shown to illustrate the hydrogen bonding. [Symmetry code: (i) $-x, 1-y, 1-z$.]

The two C—S distances [1.754 (1) and 1.726 (1) Å] in the thiazole ring have values intermediate between those reported for a C_{sp³}—S single (1.81 Å) and a double bond (1.61 Å) (Khan, Taylor, Lehn & Dietrich, 1988), but are longer than the C—S bond in thio-

phene (1.714 Å) (Bak, Christensen, Hansen-Nygaard & Rastrap-Anderson, 1961). Thus, the shortening of the C—S bonds might be attributed to the difference between the sp^2 and sp^3 C atoms rather than to the partial double-bond character of the C—S bonds. The large difference (0.028 Å) between the two C—S bond lengths and an acute value for the C—S—C valence angle [88.91 (6)°] are commonly observed in substituted thiazole compounds (Jain, 1987; Laurent, Durant & Evrard, 1981).

As noted above, the main structural features that are of special interest here are bond lengths within the conjugated part of the molecule. We have established, by use of the Cambridge Structural Database (Allen *et al.*, 1979), that no nitro-group-containing benzothiazole derivative has so far been studied structurally, but the database does contain three entries for 2-aminobenzothiazole: two structures of 2-aminobenzothiazole [hereafter (II)] in two different crystal environments and one structure of *N*-methyl-2-aminobenzothiazole [hereafter (III)]. Our results are thus directly comparable with those obtained previously for compounds (II) and (III).

In the present derivative, (I), the C(2)—N(2) and C(2)—N(3) bond lengths of 1.315 (2) and 1.312 (2) Å, respectively, are intermediate between pure single and double bonds (Kettmann & Csöllei, 1989; Kettmann, Csöllei & Ječný, 1992) and are equal to within 2σ , a feature indicating complete π -electron delocalization. It has been suggested (Chan, Ma & Mak, 1977) that compound (II) occurs in tautomeric form (1) or (2) (or as a mixture of both; see scheme below), but this was not confirmed by later structure determinations of compounds (II) and (III).



Similarly, in the present derivative, two H atoms were found in the $\Delta\rho$ map bonded to N(2), *i.e.* no proton transfer has occurred from atom N(2) to N(3) as required by the formula (2). This, along with the equivalency of the C(2)—N(2) and C(2)—N(3) bonds implies that the neutral form (1) and the zwitterionic form (3) are approximately equal contributors to the electronic structure of the molecule.

In compounds (II) and (III), the two C—N bonds are differentiated, the mean values for the longer (C—N_{amino}) and the shorter (C—N_{ring}) bonds being 1.336 and 1.294 Å, respectively. This indicates that introduction of the nitro group at position 4 of the ring enhances the contribution of form (3). Another effect of the NO₂ group is seen in the N(3)—C(9) bond length, which is on average 0.022 Å shorter in compound (I)

than in (II) and (III). There is, therefore, an indication that π density concentrated in the N(2)—C(2)—N(3) portion is transferred, at least in part, to the nitro group. Unfortunately, this cannot be confirmed by geometry at the acceptor side due to the relative insensitivity of the C_{aryl}—NO₂ bond length to the degree of conjugation. Although a correlation between the C—N bond length and the phenyl-ring–nitro-group torsion angle (φ) has been established (Cromer, Coburn, Ryan & Wasserman, 1986), the bond length varies in a narrow range from 1.425 (for $\varphi = 0$) to 1.460 Å (for $\varphi = 90^\circ$); the N—O bond lengths of the nitro group are even less sensitive to φ . In addition, many exceptions to the correlation are known (*e.g.* Jones, Edwards & Kirby, 1986; Banerjee & Brown, 1985), the title compound (I) representing one of these exceptions. Therefore, as a complement to the present results, quantum-chemical calculations are awaited in order to estimate (σ and π) charge densities and the resulting polarization of the molecule.

The crystal packing is dominated by two pairs of bifurcated (three-centre) hydrogen bonds acting across a centre of symmetry to form dimers. These hydrogen bonds are shown in Fig. 1 and the distances and angles are given in Table 3. The dimers are packed by van der Waals forces.

Experimental

2-Amino-4-nitrobenzothiazole was prepared by cyclization of 2-nitrophenylthiourea, which was obtained by the reaction of 2-nitrophenyl isothiocyanate with ammonia. The compound was recrystallized from ethanol by slow evaporation of the solvent. The density D_m was measured by flotation in cyclohexane/CHBr₃.

Crystal data

C₇H₅N₃O₂S

$M_r = 195.2$

Monoclinic

$P2_1/n$

$a = 10.622$ (3) Å

$b = 5.459$ (2) Å

$c = 13.708$ (4) Å

$\beta = 104.40$ (2)°

$V = 769.9$ (8) Å³

$Z = 4$

$D_x = 1.684$ Mg m⁻³

$D_m = 1.68$ (1) Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 7-17^\circ$

$\mu = 0.37$ mm⁻¹

$T = 293$ K

Prism

$0.50 \times 0.35 \times 0.32$ mm

Brownish yellow

Data collection

Syntex $P2_1$ diffractometer

$\theta/2\theta$ scans

Absorption correction:

none

1985 measured reflections

1777 independent reflections

1263 observed reflections

$[I > 2\sigma(I)]$

$R_{int} = 0.022$

$\theta_{max} = 27.5^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 7$

$l = -17 \rightarrow 17$

2 standard reflections

monitored every 100 reflections

intensity decay: 3%

Refinement

Refinement on F
 $R = 0.037$
 $wR = 0.042$
 $S = 1.34$
 1263 reflections
 138 parameters
 All H-atom parameters
 refined
 $w = 1$ for $|F_o| < 30$ and
 $w = 30/|F_o|$ for $|F_o| \geq 30$

$(\Delta/\sigma)_{\max} = 0.02$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)
$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
S(1)	0.32808 (3)	0.16666 (7)	0.58959 (3)	3.06 (1)
C(2)	0.17734 (11)	0.3144 (2)	0.54967 (9)	2.54 (3)
N(2)	0.14971 (10)	0.4988 (2)	0.60255 (8)	3.36 (3)
N(3)	0.09820 (9)	0.2257 (2)	0.46822 (8)	2.46 (2)
C(4)	0.10550 (11)	-0.1133 (2)	0.34737 (9)	2.62 (3)
C(5)	0.17726 (14)	-0.3044 (3)	0.32142 (10)	3.26 (4)
C(6)	0.30004 (14)	-0.3546 (3)	0.37847 (11)	3.44 (4)
C(7)	0.35356 (12)	-0.2166 (3)	0.46304 (10)	3.07 (3)
C(8)	0.28241 (12)	-0.0288 (3)	0.48793 (9)	2.67 (3)
C(9)	0.15492 (11)	0.0325 (2)	0.43211 (9)	2.33 (3)
N(4)	-0.02310 (10)	-0.0702 (2)	0.28228 (8)	2.90 (3)
O(1)	-0.09683 (9)	0.0703 (2)	0.30805 (8)	4.11 (3)
O(2)	-0.05270 (10)	-0.1783 (2)	0.20156 (7)	4.37 (3)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

S(1)—C(2)	1.754 (1)	C(5)—C(6)	1.371 (2)
S(1)—C(8)	1.726 (1)	C(6)—C(7)	1.381 (2)
C(2)—N(2)	1.315 (2)	C(7)—C(8)	1.366 (2)
C(2)—N(3)	1.312 (2)	C(8)—C(9)	1.420 (2)
N(3)—C(9)	1.367 (2)	C(4)—N(4)	1.453 (2)
C(4)—C(9)	1.398 (2)	N(4)—O(1)	1.210 (2)
C(4)—C(5)	1.389 (2)	N(4)—O(2)	1.224 (2)
C(2)—S(1)—C(8)	88.91 (6)	C(6)—C(7)—C(8)	118.77 (13)
S(1)—C(2)—N(2)	119.42 (10)	C(7)—C(8)—S(1)	127.12 (10)
S(1)—C(2)—N(3)	115.95 (9)	C(7)—C(8)—C(9)	123.72 (12)
N(2)—C(2)—N(3)	124.60 (12)	S(1)—C(8)—C(9)	109.16 (9)
C(2)—N(3)—C(9)	110.25 (10)	C(8)—C(9)—N(3)	115.72 (11)
C(5)—C(4)—C(9)	121.57 (12)	C(8)—C(9)—C(4)	115.10 (11)
C(5)—C(4)—N(4)	117.13 (11)	N(3)—C(9)—C(4)	129.18 (11)
C(9)—C(4)—N(4)	121.30 (11)	C(4)—N(4)—O(1)	120.08 (11)
C(4)—C(5)—C(6)	120.57 (13)	C(4)—N(4)—O(2)	117.91 (11)
C(5)—C(6)—C(7)	120.27 (13)	O(1)—N(4)—O(2)	122.00 (12)

Table 3. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N(2)—H1N2 $\cdots$ O(1 ⁱ)	0.85 (2)	2.40 (2)	2.774 (2)	107 (1)
N(2)—H2N2 $\cdots$ O(1 ⁱ)	0.84 (2)	2.49 (2)	2.774 (2)	100 (1)
N(2)—H1N2 $\cdots$ N(3 ⁱ)	0.85 (2)	2.12 (2)	2.978 (2)	178 (2)

Symmetry code: (i) $-x, 1-y, 1-z$.

Data collection: Syntex P2₁ software. Cell refinement: Syntex P2₁ software. Data reduction: XP21 (Pavelčík, 1987). Program(s) used to solve structure: MULTAN80 (Main *et al.*, 1980). Program(s) used to refine structure: NRC Crystallographic Programs (Ahmed & Singh, 1973). Molecular graphics: ORTEPII (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: CF1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tarapacol 15-Acetate, a New Diterpenoid from *Grindelia tarapacana* Phil.

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Abstract

In the title compound, 15-acetoxy-14(*S*)-hydroxy-13-*epi*-manoyl oxide {IUPAC systematic name: 2-(dodecahydro-3,4a,7,7,10a-pentamethyl-1*H*-naphtho[2,1-*b*]pyran-3-yl)-2-hydroxyethyl acetate}, C₂₂H₃₈O₄, rings *A* and *B* have chair conformations. Ring *C* adopts a boat con-