

1.456 (4), 1.417 (4) and 1.373 (4) Å respectively, are in agreement with this formulation. The phenyl rings at N(11) and N(12) are inclined to the plane defined by N(10), N(12) and C(111) by 54.8 (5) and 122.3 (8)° respectively.

The S(1)—N(12) separation, 2.560 (4) Å, is identical to that found in 3-(4,5-dimethoxycarbonyl-2-benzothiazolyl)-1,2-diphenyltriazenium hydroxide, inner salt, (Boyd *et al.*, 1977), and indicates weak interaction between these two atoms leading to further resonance stabilization in the molecule.

There are no intermolecular separations significantly less than the sum of the corresponding van der Waals radii.

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5-Nitroso-4-phenethylbenzo[*b*]thiophene

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Abstract. C₁₆H₁₃NOS, *M_r* = 267.35, monoclinic, *C*2/*c*, *a* = 17.313 (7), *b* = 10.09 (1), *c* = 15.463 (4) Å, β = 103.12 (3)°, *U* = 2631 Å³, *Z* = 8, *D_c* = 1.35 Mg m⁻³, Mo *Kα* radiation (λ = 0.71069 Å), μ = 0.2296 mm⁻¹, 940 independent reflections, *R* = 0.039. The asymmetric unit contains one molecule of a nitroso monomer; bond lengths: C—NO 1.419 (5), CN—O 1.213 (5) Å.

Introduction. In the solid state *C*-nitroso systems occur commonly as colourless dimeric azodioxides C—N(O)=N(O)—C, in special cases as oximes (nitrosophenols) or furoxans (*o*-dinitrosobenzenes) and rarely as characteristically coloured nitroso monomers in which the colour is attributed (Ha & Wild, 1974) to a transition from a nitroso σ lone-pair orbital to a low-lying nitroso π* orbital. Talberg (1979*a*) noted that structures of nitroso monomers reported prior to his own investigations involved some weak intramolecular (Johnson & Paul, 1969; Ferguson, Fritchie, Robertson & Sim, 1961; Cameron & Prout, 1969) or intermolecular (Webster, 1956) bond (or interaction) to the nitroso group. Talberg identified a class of nitrosoaryls forming stable green crystalline monomers characterized by the presence of activated protons and went

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on to show in an elegant series of papers (Rømming & Talberg, 1973; Talberg, 1975, 1976, 1977*a,b,c*, 1978, 1979*b*) that these compounds do not exhibit any weak secondary bonding to the nitroso group. The title compound (I) and 2-methyl-6-nitroso-7-phenethyl-1,3-benzothiazole (II), described in the following paper (Prout & Miao, 1982), do not fit comfortably into Talberg's class of compounds and are said to be monomeric (Bartoli, Leardini, Medici & Rosini, 1978).

The compound was supplied by G. Bartoli. A small pale-yellow plate (0.1 × 0.2 × 0.3 mm) recrystallized from ethanol was mounted on an Enraf–Nonius CAD-4F diffractometer. With Mo *Kα* radiation from a graphite monochromator, the unit-cell dimensions and orientation matrix were obtained by least squares from the setting angles of 25 reflections. The intensities of reflections with θ < 25° were measured in the ω/2θ scan mode, with a variable scan rate and ω-scan angle of (1 + 0.35 tan θ)°. 940 reflections with *I* > 2σ(*I*) were corrected for Lorentz and polarization effects (but not for absorption) and used in subsequent calculations. The structure was solved by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1979) from 152 reflections with 1.228 < *E* < 3.917. The *E* map corresponding to the best figure of merit gave the positions of all non-hydrogen atoms. The structure was refined by full-matrix least squares first with isotropic then anisotropic temperature factors. H atoms were located from a difference map calculated at

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$R = 0.067$. In the refinement, the bond lengths and angles involving H atoms were constrained (Waser, 1963; Rollett, 1969) to conventional values with e.s.d.'s of 0.03 Å for bond lengths and 2° for bond angles. In addition, the difference in mean-square displacement along the bond direction of the two atoms forming each bond involving H atoms was constrained to be zero with an e.s.d. of 0.01 Å. The refinement converged at $R = 0.039$, $R_w = 0.041$ using a three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) with coefficients 14.0, 18.7 and 6.6. All calculations were performed with *CRYSTALS* (Carruthers & Watkin, 1980). Final atomic parameters are given in Table 1.*

* Lists of structure factors and anisotropic thermal parameters for the non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36353 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$) and isotropic temperature factors ($\times 10^4$, for H $\times 10^3$) (equivalent values for heavy atoms, mean e.s.d. 0.004 Å²)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$, where U_1 , U_2 , U_3 are the mean-square displacements (Å²) along the principal axes of the thermal ellipsoid.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U (Å ²)
S(1)	4421.1 (8)	2919 (1)	6324.2 (9)	573
C(2)	4188 (3)	2037 (6)	5354 (3)	560
C(3)	4676 (3)	2262 (5)	4823 (3)	529
C(4)	5283 (2)	3174 (4)	5195 (3)	413
C(5)	5890 (3)	3676 (5)	4829 (3)	452
C(6)	6394 (3)	4564 (5)	5339 (3)	429
C(7)	6313 (3)	5004 (5)	6165 (3)	476
C(8)	5728 (3)	4543 (5)	6520 (3)	502
C(9)	5210 (3)	3629 (4)	6027 (3)	413
N(10)	7010 (3)	5027 (5)	4948 (3)	635
O(11)	7439 (2)	5841 (4)	5395 (3)	728
C(12)	5970 (3)	3189 (5)	3906 (3)	562
C(13)	6467 (3)	1953 (6)	4023 (3)	730
C(14)	6552 (3)	1394 (5)	3131 (3)	528
C(15)	6118 (3)	327 (6)	2753 (4)	652
C(16)	6242 (4)	-244 (6)	1994 (4)	729
C(17)	6774 (4)	235 (7)	1589 (4)	672
C(18)	7192 (3)	1306 (7)	1922 (4)	676
C(19)	7087 (3)	1904 (7)	2697 (4)	669
H(161)	5917 (24)	-983 (41)	1730 (22)	53 (10)
H(181)	7584 (23)	1655 (33)	1637 (22)	50 (10)
H(191)	7407 (26)	2680 (42)	2939 (23)	67 (10)
H(171)	6905 (23)	-251 (32)	1086 (26)	51 (10)
H(151)	5732 (24)	-86 (35)	3051 (20)	51 (10)
H(131)	7011 (15)	2167 (14)	4398 (12)	88 (11)
H(132)	6217 (11)	1281 (20)	4333 (11)	88 (11)
H(121)	5443 (15)	2993 (13)	3536 (11)	51 (9)
H(122)	6230 (10)	3886 (20)	3616 (10)	49 (10)
H(71)	6718 (18)	5600 (39)	6513 (16)	23 (9)
H(81)	5671 (19)	4800 (38)	7115 (21)	44 (9)
H(31)	4604 (15)	1859 (36)	4226 (19)	28 (9)
H(21)	3721 (20)	1488 (42)	5192 (16)	44 (9)

Table 2. Bond distances (Å) and interbond angles (°)

S(1)—C(2)	1.712 (5)	N(10)—O(11)	1.213 (5)
C(2)—C(3)	1.326 (6)	C(5)—C(12)	1.545 (6)
C(3)—C(4)	1.417 (6)	C(12)—C(13)	1.503 (7)
C(4)—C(5)	1.398 (6)	C(13)—C(14)	1.529 (7)
C(5)—C(6)	1.369 (6)	C(14)—C(15)	1.365 (7)
C(6)—C(7)	1.389 (6)	C(15)—C(16)	1.366 (7)
C(7)—C(8)	1.340 (6)	C(16)—C(17)	1.319 (7)
C(8)—C(9)	1.388 (6)	C(17)—C(18)	1.337 (8)
C(9)—C(4)	1.397 (6)	C(18)—C(19)	1.390 (8)
C(9)—S(1)	1.696 (4)	C(19)—C(14)	1.362 (6)
C(6)—N(10)	1.419 (5)		
C(2)—S(1)—C(9)	91.5 (3)	S(1)—C(9)—C(4)	110.9 (4)
S(1)—C(2)—C(3)	113.4 (4)	S(1)—C(9)—C(8)	126.3 (4)
C(2)—C(3)—C(4)	112.2 (5)	C(4)—C(9)—C(8)	122.8 (4)
C(3)—C(4)—C(5)	128.8 (5)	C(5)—C(12)—C(13)	108.8 (4)
C(3)—C(4)—C(9)	112.0 (4)	C(12)—C(13)—C(14)	111.6 (4)
C(5)—C(4)—C(9)	119.2 (5)	C(13)—C(14)—C(15)	121.4 (5)
C(4)—C(5)—C(6)	116.3 (5)	C(13)—C(14)—C(19)	121.4 (5)
C(4)—C(5)—C(12)	119.5 (5)	C(15)—C(14)—C(19)	117.2 (5)
C(6)—C(5)—C(12)	124.1 (5)	C(14)—C(15)—C(16)	121.5 (6)
C(5)—C(6)—C(7)	123.7 (5)	C(15)—C(16)—C(17)	121.0 (6)
C(5)—C(6)—N(10)	114.4 (5)	C(16)—C(17)—C(18)	119.3 (6)
C(7)—C(6)—N(10)	121.9 (5)	C(17)—C(18)—C(19)	121.2 (6)
C(6)—C(7)—C(8)	120.6 (5)	C(18)—C(19)—C(14)	119.8 (6)
C(7)—C(8)—C(9)	117.4 (5)	C(6)—N(10)—O(11)	113.8 (5)

Table 2 lists interatomic distances and interbond angles with e.s.d.'s calculated from the full variance-covariance matrix.

Discussion. The crystals contain isolated molecules of the title compound, confirming that it is a C-nitroso monomer (Fig. 1). The nitroso group does not take part in any weak bonding interactions. Its shortest intramolecular non-bonded contacts are N(10)···H(122) 2.48 and O(11)···H(71) 2.36 Å. The shortest intermolecular contact is 2.40 Å from O(11) to H(21) of a neighbouring molecule. None of these distances differ significantly from 2.4 Å, the sum of the van der Waals radii for H···N and H···O systems. Similar non-bonded distances are found in (II) (Prout & Miao,

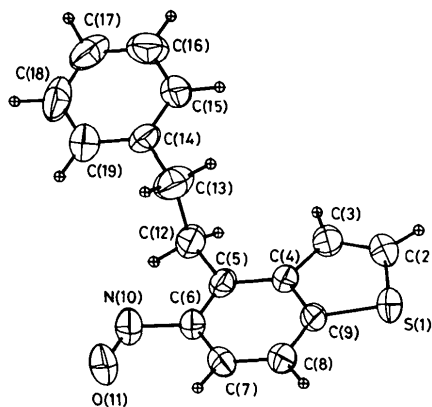


Fig. 1. A three-dimensional 50% probability thermal-ellipsoid plot (Davies, 1981) showing the atom numbering.

1982) so that neither compound falls into the group of C-nitroso compounds that exhibit weak intra- or intermolecular bonding.

The N(10)—O(11) bond in the nitroso group [1.213 (5) Å] is the shortest yet to be reported in a C-nitroso compound, just significantly shorter than that found in ethyl *trans-m*-nitrosocinnamate [1.229 (3) Å] (Talberg, 1978). The cinnamate, like (I), is a compound in which the nitroso group is not involved in 'extended mutual conjugation' (Talberg, 1978). The C(6)—N(10) bond, 1.419 (5) Å, is not as long as would be predicted from Talberg's (1979*a*) regression relationship between N—O and C—N bond lengths. The endocyclic angle at C(6), 123.7 (5)°, is greater than in the cinnamate, but in benzothiophene without substituents at C(6) (Pascard & Pascard-Billy, 1972) the endocyclic angle is already greater than 120°, so that the large angle probably represents the summation of the benzothiophene distortion and the effect of the nitroso substituent.

The dimensions of the rest of the molecule are unexceptional.

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2-Methyl-6-nitroso-7-phenethyl-1,3-benzothiazole

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Abstract. C₁₆H₁₄N₂OS, *M_r* = 282.37, monoclinic, *P*2₁/*c*, *a* = 9.355 (4), *b* = 7.403 (4), *c* = 20.665 (6) Å, β = 87.14 (3)°, *U* = 1429.4 Å³, *Z* = 4, *D_c* = 1.31 Mg m⁻³, Mo *K*α radiation (λ = 0.71069 Å), μ = 0.2219

mm⁻¹, 534 independent reflections, *R* = 0.043. The asymmetric unit contains one molecule of a nitroso monomer; bond lengths C—NO 1.41 (2), CN—O 1.23 (1) Å.

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Introduction. The structure was determined as part of a study of nitroso compounds [see Prout & Miao (1982), and references therein].