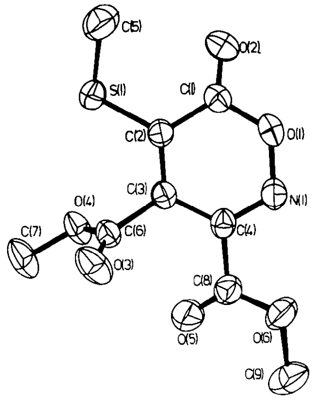

Fig. 1. *ORTEP*-Darstellung (Johnson, 1965) der Molekülstruktur von (4) mit Numerierungsschema. Die thermischen Schwingungs-ellipsoide entsprechen 50% Wahrscheinlichkeit.

Differenz-Fourier-Analyse enthielt keine Peaks grösser als 0,34 e Å^{-3}.

Diskussion. In Tabelle 1 sind die Atomkoordinaten der Nichtwasserstoffatome von (4) zusammengestellt. Die Bindungslängen und Bindungswinkel bieten die Tabellen 2 und 3, während das Numerierungsschema aus Fig. 1 ersichtlich ist.*

Diese Arbeit wurde dankenswerterweise durch den Fonds der Chemischen Industrie unterstützt. Herrn Dr C. Krüger, Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, danken wir für die Benutzung des Diffraktometers und der Rechenprogramme, und Herrn Dr D. J. Brauer, Universität/Gesamthochschule Wuppertal, gilt unser Dank für die Einweisung in die Methode.

* Die Liste der Strukturfaktoren und die Tabelle der thermischen Parameter wurden bei der British Library Lending Division (Supplementary Publication No. SUP 36355: 14 pp.) hinterlegt. Kopien sind erhältlich durch: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1982). B**38**, 682–685

The Structure of Azobenzene *N*-(Benzothiazol-2-yl)-imide [3-(2-Benzothiazolyl)-1,2-diphenyltriazenium Hydroxide, Inner Salt]

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(*Received* 10 *June* 1981; *accepted* 3 *August* 1981)

Abstract. $C_{19}H_{14}N_4S$, triclinic, $P\bar{1}$, $a = 11.699$ (1), $b = 8.170$ (1), $c = 10.388$ (1) Å, $\alpha = 106.13$ (1), $\beta = 108.16$ (1), $\gamma = 106.76$ (1)°, $Z = 2$, $D_c = 1.33$ Mg m^{-3}, $\bar{\mu}$(Cu $K\alpha$) = 0.174 mm^{-1}. The structure was solved by the heavy-atom method using diffractometer data and refined by a full-matrix least-squares method to $R = 0.044$ for 1817 significant reflections. The compound formed by the addition reaction of benzyne to dehydrodithizone [(2,3-diphenyl-1,2,3,4-tetraazolan-5-ylio)sulphide] is dipolar.

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Introduction. Dehydrodithizone (I) undergoes addition reactions with many types of olefins and acetylenes (Rajagopalan & Penev, 1971). In the case of the

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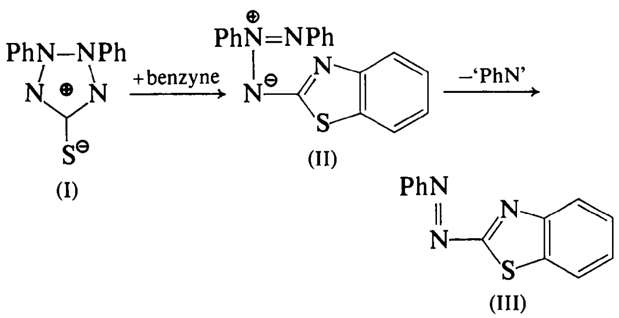
reaction with benzyne conducted at 423 K, the product benzothiazole-2-azobenzene (III) was thought to be formed from the intermediate 3-(2-benzothiazolyl)-1,2-diphenyltriazenium hydroxide, inner salt, (II) by formal loss of phenylnitrene (Boyd, Norris, Lindley & Mahmoud, 1977; Potts, Elliott, Titus, Al-Hilal, Lindley, Boyd & Norris, 1981). Under milder reaction conditions (boiling tetrahydrofuran at *ca* 343 K) the postulated dipolar product is obtained as a stable orange-red solid. The single-crystal structure analysis of (II) is reported herein.



Preliminary unit-cell dimensions and space-group information for the orange-red crystals were obtained from precession photographs. Refined cell parameters were obtained by least-squares refinement of the angular positions of the Cu $K\alpha_1$ components (λ = 1·5405 Å) of 20 reflections measured on a Hilger & Watts Y290 four-circle automated diffractometer. Intensity data were also collected on this instrument using Ni-filtered Cu radiation and the $\omega/2\theta$ step scanning technique. The scan width was 0·90° (45 steps of 0·02° at 1 s per step) plus a dispersion correction, and stationary background counts were taken either side of the peak for one tenth of the total scan time. Gradual variations in the experimental conditions were monitored by measuring three reference reflections after every 50 reflections and the intensity sums of the reference reflections were used to scale the observed intensities by interpolation between groups of references.

Intensity data were collected for the $\pm h,k,\pm l$ reflections over the range $1 \leq \theta \leq 70°$ and in addition for the $\pm h,-k,\pm l$ reflections over the range $1 \leq \theta \leq 45°$. Averaging of the symmetry-related reflections gave 2682 independent reflections of which 1817 were significant by the criterion $I \geq 3\sigma(I)$. Allowance for absorption was made experimentally using the method of North, Phillips & Mathews (1968).

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares technique using only the significant reflections and initially with all atoms treated isotropically. H atoms, observable as diffuse maxima in a difference Fourier synthesis, were placed in calculated positions assuming a C—H bond length of 1·0 Å, but no attempt was made to refine their positional or thermal parameters. Refinement with all non-H atoms treated anisotropically yielded final residuals of $R = 0·044$ and R' [$= (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$] = 0·051. Weights were assigned to the observed structure factors throughout the refinement according to the scheme $w = 0·002$ if $|F_o| < 60·0$ otherwise $w = [1 - \exp(-20·0 \sin^2\theta/\lambda^2)]/(60·0 + |F_o| + 3 \times 10^{-5}|F_o|^2)$. An analysis of this weighting scheme in terms of batches of increasing $\sin\theta/\lambda$ and $|F_o|$ showed constancy in the values of $\sum w\Delta^2$.

Structure-factor calculations for the 'unobserved' reflections after the final refinement cycle showed no outstanding discrepancies and a difference Fourier synthesis computed at this stage confirmed the correctness of the refinement. Throughout the structure-factor calculations the atomic scattering factors listed by Hanson, Herman, Lea & Skillman (1964) were used and computations were performed on the IBM 360 computer at University College, London, Computing Centre and on the CDC 6600 computer at the University of London Computing Centre.

The final atomic coordinates of the non-H atoms are listed in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36311 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters for the non-hydrogen atoms with e.s.d.'s in parentheses*

$B_{eq} = 8\pi^2 U_{eq} = (U_1U_2U_3)^{1/3}$.

	x	y	z	B_{eq} (Å^2)
S(1)	0·4000 (1)	0·6360 (1)	0·7001 (1)	3·55 (8)
C(2)	0·3414 (3)	0·3905 (4)	0·6117 (3)	3·5 (2)
N(3)	0·2285 (3)	0·3081 (4)	0·4958 (3)	3·9 (2)
C(4)	0·1816 (3)	0·4366 (4)	0·4678 (3)	3·8 (2)
C(5)	0·2626 (3)	0·6234 (4)	0·5665 (4)	3·9 (2)
C(6)	0·2276 (4)	0·7688 (5)	0·5515 (4)	5·1 (2)
C(7)	0·1103 (4)	0·7253 (6)	0·4388 (4)	5·8 (2)
C(8)	0·0286 (4)	0·5399 (6)	0·3385 (4)	5·5 (2)
C(9)	0·0620 (3)	0·3955 (5)	0·3516 (4)	4·7 (2)
N(10)	0·4059 (2)	0·2836 (4)	0·6511 (3)	3·8 (2)
N(11)	0·5196 (2)	0·3687 (3)	0·7675 (3)	3·7 (2)
N(12)	0·5649 (2)	0·5427 (4)	0·8574 (3)	3·9 (2)
C(111)	0·5839 (3)	0·2459 (4)	0·7958 (4)	3·6 (2)
C(112)	0·6120 (3)	0·1470 (4)	0·6875 (4)	4·2 (2)
C(113)	0·6759 (3)	0·0343 (5)	0·7173 (5)	4·8 (2)
C(114)	0·7092 (3)	0·0209 (5)	0·8523 (5)	5·1 (2)
C(115)	0·6790 (4)	0·1206 (5)	0·9587 (4)	5·4 (2)
C(116)	0·6158 (3)	0·2341 (5)	0·9313 (4)	4·6 (2)
C(121)	0·7003 (3)	0·6344 (4)	0·9575 (3)	3·6 (2)
C(122)	0·7304 (3)	0·7558 (5)	1·0988 (4)	4·3 (2)
C(123)	0·8605 (3)	0·8651 (5)	1·1985 (4)	4·7 (2)
C(124)	0·9604 (3)	0·8601 (5)	1·1577 (4)	4·6 (2)
C(125)	0·9302 (3)	0·7402 (5)	1·0165 (4)	4·8 (2)
C(126)	0·8007 (3)	0·6274 (5)	0·9164 (4)	4·3 (2)

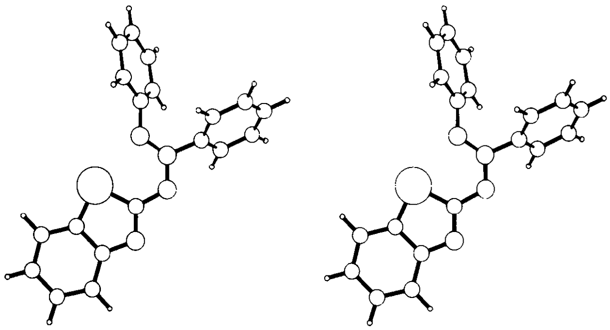


Fig. 1. A stereodrawing of the molecule.

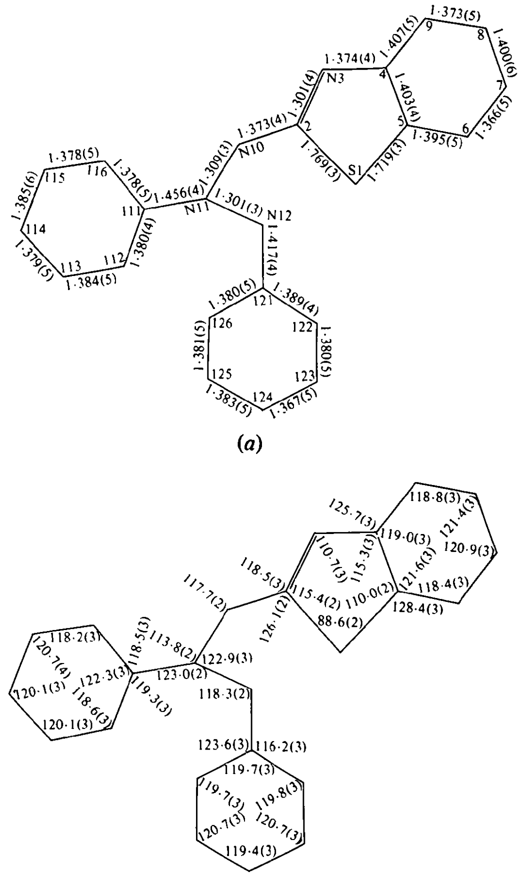


Fig. 2. A schematic drawing of the molecule showing (*a*) the atom labelling and intramolecular bond lengths (Å) and (*b*) angles (°), and their associated e.s.d.'s.

Table 2. *Molecular geometry*

Least-squares planes defined by atomic positions and distances of atoms (Å) from these planes; X, Y, and Z refer to orthogonal coordinates obtained by the transformation

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a\sin\beta\sin\gamma^* & 0 & 0 \\ -a\sin\beta\cos\gamma^* & b\sin\alpha & 0 \\ a\cos\beta & b\cos\alpha & c \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Plane (i): S(1), C(2), N(3), C(4) and C(5)

$$0{\cdot}4827X - 0{\cdot}1061Y - 0{\cdot}8693Z = -2{\cdot}1692$$

[S(1) −0·01 (1), C(2) 0·01 (1), N(3) 0·00 (1), C(4) −0·01 (1), C(5) 0·01 (1), C(6) 0·01 (1), C(7) −0·02 (1), C(8) −0·03 (1), C(9) −0·03 (1), N(10) 0·08 (1), N(11) 0·10 (1), N(12) −0·13 (1)]

Plane (ii): C(4), C(5), C(6), C(7), C(8) and C(9)

$$0{\cdot}4689X - 0{\cdot}1072Y - 0{\cdot}8767Z = -2{\cdot}2250$$

[C(4) −0·001 (6), C(5) −0·002 (6), C(6) 0·006 (6), C(7) −0·007 (6), C(8) 0·004 (6), C(9) 0·004 (6), S(1) −0·045 (6), C(2) −0·016 (6), N(3) −0·008 (6)]

Plane (iii): N(10), C(111) and N(12)

$$0{\cdot}4861X + 0{\cdot}0515Y - 0{\cdot}8724Z = -2{\cdot}0289$$

[N(11) 0·043 (3), C(121) 0·377 (3), C(2) 0·104 (3), S(1) 0·350 (3)]

Plane (iv): C(111) to C(116) inclusive

$$0{\cdot}8852X + 0{\cdot}4433Y - 0{\cdot}1409Z = 4{\cdot}1219$$

[C(111) 0·004 (3), C(112) −0·004 (3), C(113) 0·001 (3), C(114) 0·001 (3), C(115) −0·001 (3), C(116) −0·001 (3), N(11) 0·032 (3)]

Plane (v): C(121) to C(126) inclusive

$$0{\cdot}0386X - 0{\cdot}8091Y + 0{\cdot}5864Z = 2{\cdot}3198$$

[C(121) 0·004 (9), C(122) −0·010 (9), C(123) 0·010 (9), C(124) −0·004 (9), C(125) −0·002 (9), C(126) 0·002 (9), N(12) −0·166 (9)]

Dihedral angles (°) between planes

Plane (*a*)	Plane (*b*)	
(i)	(ii)	0·9 (5)
(i)	(iii)	9·0 (5)
(iii)	(iv)	54·8 (6)
(iii)	(v)	122·3 (8)
(iv)	(v)	114·0 (8)

Discussion. Fig. 1 is a stereoscopic drawing of the molecule viewed perpendicular to the plane of the thiazole ring. Fig. 2 is a schematic drawing of the molecule showing the atom labelling and the intramolecular bond lengths and angles together with their corresponding e.s.d.'s. Further details of the molecular geometry are given in Table 2.

The overall configuration of the molecule is closely similar to that observed in 3-(4,5-dimethoxycarbonyl-2-benzothiazolyl)-1,2-diphenyltriazenium hydroxide, inner salt, (Boyd *et al.*, 1977). The considerable double-bond character of the N(10)—N(11) and N(11)—N(12) linkages, 1·309 (3) and 1·301 (3) Å respectively {*cf.* the N—N single-bond length of 1·403 (4) in, for example, 4-acetamido-3-[1-acetyl-2-(2,6-dichlorobenzylidene)hydrazino]-1,2,4-triazole (Werner, 1976)}, and the planarity at N(11) [N(11) lies only 0·043 (3) Å out of the plane through N(10), N(12) and C(111)] are consistent with a dipolar structure in which N(10) and N(11) have formal negative and positive charges respectively. The N(11)—C(111), N(12)—C(121), and N(10)—C(2) bond lengths, 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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Acta Cryst. (1982). B**38**, 685–687

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

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(*Received* 12 *June* 1981; *accepted* 12 *August* 1981)

Abstract. $C_{16}H_{13}NOS$, M_r = 267·35, monoclinic, $C2/c$, a = 17·313 (7), b = 10·09 (1), c = 15·463 (4) Å, β = 103·12 (3)°, U = 2631 Å^3, Z = 8, D_c = 1·35 Mg m^{-3}, Mo $K\alpha$ 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 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 $K\alpha$ 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 $\theta < 25°$ were measured in the $\omega/2\theta$ scan mode, with a variable scan rate and ω-scan angle of (1 + 0·35 tan θ)°. 940 reflections with $I > 2\sigma(I)$ 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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0567-7408/82/020685-03$01.00