As can be seen from the figure the molecule adopts the *E* configuration in which the bulkier phenyl and *o*-nitroanilino groups lie on opposite sides of the C—N double bond. This is almost certainly a consequence of steric effects and emphasizes the size aspect of the particular substituents at C(9), *e.g.* whenever these differ in steric bulk (and in the absence of any intramolecular hydrogen-bonding dictates to the contrary), it seems that the *Z* isomer is normally formed. This immediately precludes any hydrogen-bonding interactions between R^4 and H(7). Such investigations will need to be performed for compounds with $R^3 = R^4 =$ Ph.

Least-squares planes show that the two phenyl rings intersect at an angle of 3·2 (1)°. The *o*-nitro group intersects the hydrazine ring at an angle of 7·7 (1)°. This relatively small angle is similar to that found in (II) and therefore must be part of the general dimer geometry. In other phenylhydrazine structures the angle of rotation of attached nitro groups can be up to 15°.

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Refinement of the Structure of *N*-Phenyl-*N'*-sulfinylhydrazine, $C_6H_6N_2OS$, at 120 (1) K with Neutron Data

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Abstract. $M_r = 154·19$, monoclinic, $P2_1/a$, $a = 10·451$ (10), $b = 15·561$ (18), $c = 8·346$ (10) Å, $\beta = 95·44$ (4)°, $V = 1351·2$ Å^3, $Z = 8$, $D_x = 1·516$ Mg m^{-3}, $R = 0·056$, $R_w = 0·055$, 1789 unique reflections, sin $\theta/\lambda \leq 0·56$ Å^{-1}. The asymmetric unit contains two identical molecules which form a dimer. They are linked by two (N)—H···O=(S) hydrogen bonds. The hydrogen bonds are bifurcated, forming a five-membered chelate ring with the intramolecular branch. The intermolecular H···O distances are 1·99 (1) and 1·95 (1) Å, respectively; the intramolecular H···O distances are 2·380 (8) Å.

Introduction. This work is part of a series of structural investigations of a compound class containing formal S^{IV}=N bond systems (Gieren, Lamm, Haddon & Kaplan, 1979; Gieren & Dederer, 1980; Dederer & Gieren, 1979). A better characterization of the S—N bonding is possible with a charge density analysis. For this purpose we undertook as a first step a neutron diffraction experiment to determine unbiased (by bonding effects) atomic positional and thermal parameters of the title compound. An advantage is the fact that the crystal structure contains two chemically identical molecules, which are crystallographically independent. An internal check of the results is provided in this way.

Experimental. Crystal obtained from ethanolic solution, dimensions 2·78 × 2·71 × 1·00 mm. Diffractometer D10 at the Institut Laue–Langevin (Grenoble), vertically focusing Cu monochromator (200, $\lambda = 1·262$ Å), maximum flux at the sample $6·8 \times 10^6$ n cm^{-2} s^{-1}. Lattice parameters and orientation from the

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observed Eulerian angles of 8 reflections. $\theta/2\theta$ step-scan technique. Integrated intensities calculated with the *COLLEGE V DATAREDUCTION SYSTEM* 'minimal $\sigma(I)/I$' method (Lehmann & Larsen, 1974; Lehmann, 1975). 1478 of the unique reflections had intensities $I \geq 2\sigma_I$. Three standard reflections measured after every 50 reflections: standard deviations of their intensity distributions 2·3, 0·9 and 1·7%. After data collection, the transmission of the sample was measured. The absorption coefficient was calculated to 1·48 ± 0·03 cm^{-1}. As the main contribution to absorption comes from the incoherent scattering of the H the observed total cross section of $(41\cdot7 \pm 0\cdot9) \times 10^{-24}$ cm^2 is quite reasonable at this wavelength (1·262 Å). An absorption correction by analytical integration was applied with a local (ILL) version (*ABSCO2*) of the original *ABSCOR* program of the XRAY72/74 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972/74). The exactly determined distances of the six main boundary planes of the crystal [(±100), (0±10), (00±1)] and the measured absorption coefficient were used. The transmission factors varied between 0·862 and 0·707. The mosaic spread of the sample was determined by analysis of reflection profiles to 34 ± 12′. No extinction correction was therefore applied. Refinement started with the positional parameters from the room-temperature X-ray study (Dederer, 1978), minimizing $\sum w(|\Delta F|)^2$ (*ORFLS*, XRAY67, Stewart, 1967). Appropriate weights $w = [\sigma^2(F_o) + (2\times10^{-2})|F_o| + (2\times10^{-4})|F_o|^2]^{-1}$ estimated by plotting $w(|\Delta F|)^2$ *versus* $|F_o|$. No significant dependence on $|F_o|$ present with this weighting scheme. At the end of refinement $(\Delta/\sigma)_{\max} = 0\cdot4$ ($R = 0\cdot056$, $R_w = 0\cdot055$, GOF = 1·08, 289 variables). Scattering lengths used: $b(\mathrm{O}) = 0\cdot575$, $b(\mathrm{N}) = 0\cdot940$, $b(\mathrm{C}) = 0\cdot663$, $b(\mathrm{S}) = 0\cdot285$ and $b(\mathrm{H}) = -0\cdot372$ (all $\times 10^{-12}$ cm) (*International Tables for X-ray Crystallography*, 1974). Correlation coefficients between positional parameters of the two molecules of the asymmetric unit are smaller than 0·25.

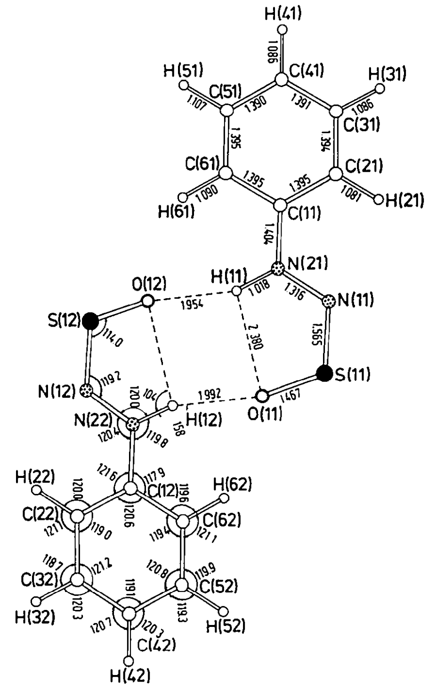

Fig. 1. Bond lengths (Å) and angles (°), averaged over the two molecules of the asymmetric unit. The mean e.s.d.'s of the bond lengths and angles (not including S and H) are 0·005 Å and 0·3° respectively. For bonds including S and H atoms the means are 0·008 Å and 0·5°.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors*

$(B_{\mathrm{eq}} = \frac{1}{3}\sum_i B_{ii})$

	x	y	z	B_{eq}(Å^2)
S(11)	0·4370 (10)	0·0874 (7)	0·6208 (13)	1·5 (4)
O(11)	0·5725 (5)	0·0684 (4)	0·6091 (6)	1·6 (2)
N(11)	0·3693 (3)	0·0244 (2)	0·7338 (4)	1·5 (1)
N(21)	0·4367 (4)	−0·0382 (2)	0·8080 (4)	1·4 (2)
C(11)	0·3782 (4)	−0·0958 (3)	0·9068 (5)	1·2 (2)
C(21)	0·2456 (5)	−0·0945 (4)	0·9183 (6)	1·5 (2)
C(31)	0·1918 (5)	−0·1538 (3)	1·0173 (5)	1·7 (2)
C(41)	0·2677 (4)	−0·2143 (3)	1·1038 (6)	1·6 (2)
C(51)	0·3993 (5)	−0·2154 (3)	1·0907 (6)	1·6 (2)
C(61)	0·4554 (5)	−0·1569 (3)	0·9920 (6)	1·5 (2)
H(11)	0·5332 (10)	−0·0429 (6)	0·7951 (11)	2·2 (4)
H(21)	0·1871 (9)	−0·0485 (8)	0·8488 (13)	2·8 (5)
H(31)	0·0892 (10)	−0·1514 (8)	1·0257 (13)	3·4 (5)
H(41)	0·2250 (10)	−0·2604 (8)	1·1823 (14)	3·3 (5)
H(51)	0·4601 (10)	−0·2626 (8)	1·1617 (14)	3·4 (5)
H(61)	0·5584 (10)	−0·1586 (7)	0·9795 (13)	2·9 (5)
S(12)	0·1546 (10)	0·0839 (7)	0·1295 (13)	1·4 (4)
O(12)	0·2930 (5)	0·0905 (4)	0·1823 (7)	1·8 (2)
N(12)	0·0835 (3)	0·0136 (2)	0·2192 (4)	1·6 (1)
N(22)	0·1495 (4)	−0·0341 (2)	0·3267 (4)	1·4 (1)
C(12)	0·0876 (4)	−0·0979 (3)	0·4115 (5)	1·0 (2)
C(22)	−0·0455 (4)	−0·1071 (3)	0·3944 (6)	1·3 (2)
C(32)	−0·1008 (5)	−0·1711 (3)	0·4824 (6)	1·6 (2)
C(42)	−0·0259 (4)	−0·2246 (3)	0·5869 (6)	1·5 (2)
C(52)	0·1067 (4)	−0·2141 (3)	0·6025 (6)	1·5 (2)
C(62)	0·1643 (5)	−0·1506 (3)	0·5156 (5)	1·4 (2)
H(12)	0·2462 (10)	−0·0300 (6)	0·3412 (11)	2·2 (4)
H(22)	−0·1050 (9)	−0·0647 (7)	0·3152 (13)	3·0 (5)
H(32)	−0·2048 (9)	−0·1790 (7)	0·4687 (14)	3·2 (5)
H(42)	−0·0698 (11)	−0·2732 (9)	0·6554 (13)	3·4 (5)
H(52)	0·1667 (9)	−0·2557 (7)	0·6866 (13)	3·1 (5)
H(62)	0·2681 (9)	−0·1423 (7)	0·5264 (14)	3·1 (5)

Discussion. Final positional parameters are given in Table 1.* The bond lengths and angles given in Fig. 1 are averaged over the two molecules of the asymmetric unit, because they are not different at the 5% level of significance (*t*-test). A half-normal probability plot (Abrahams & Keve, 1971) of the differences in the

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* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles of the individual molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38950 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond lengths shows a good fit to a straight line (correlation 0·989, intercept 10^{-3}) with a slope of 0·88, indicating that the parameter standard deviations are satisfactorily estimated. Compared with the bond lengths from the room-temperature X-ray structure study (Gieren & Dederer, 1977) the distances in the neutron study at 120 K are larger than the corresponding X-ray values, with one exception. The S—O bond is 0·007 (8) Å shorter. This could be explained by the presence of O lone-pair electrons. A similar effect, where the O shifts more into its lone-pair region than into a C—O bond has been reported by Coppens & Vos (1971). The largest differences compared to the X-ray study occur in the *X*—H distances, which are on average 0·13 (2) Å longer in the present study. This is the usual asphericity shift of the H atom in the conventional X-ray refinement (Coppens, 1974). The N—H distance [1·018 (8) Å] is 0·15 (4) Å longer than the corresponding X-ray value and seems to be typical for the case of an N—H···O hydrogen bond, where the N is sp^2 hybridized (Lehmann, Verbist, Hamilton & Koetzle, 1973). Compared to other hydrogen bonds of the same type (reviewed by Olovsson & Jönsson, 1976) the H···O distances of the present work indicate medium to strong intermolecular hydrogen bonding, and a weak intramolecular bond.

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Structure of Trimethyl 4,5,6-Trichloro-1,2,3-benzenetricarboxylate, $C_{12}H_9Cl_3O_6$

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Abstract. $M_r = 355·56$, monoclinic, $P2_1/c$, $a = 13·649$ (6), $b = 5·819$ (2), $c = 19·667$ (8) Å, $\beta = 109·09$ (2)°, $V = 1476$ (1) Å^3, $Z = 4$, $D_x = 1·600$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 5·978$ mm^{-1}, $F(000) = 720$, room temperature. Final $R = 0·059$ for 2103 observed reflections. The molecular structure is strongly influenced by the three vicinal methoxycarbonyl groups as well by three vicinal Cl atoms attached to the benzene ring. The central ester group is twisted 34·9 (1)° out of the best plane through the benzene ring. The other two groups are twisted 68·7 (1) and 66·6 (1)° out of this plane. The average

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