

The Crystal and Molecular Structures of 5-Phenyl-1,2,3,4-thiaziazole and its 3-Oxide and 3-Ethyl Derivatives

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The structures of I: 5-phenyl-1,2,3,4-thiaziazole, II: 5-phenyl-(1,2,3,4-thiaziazolio)-3-oxide, and III: 3-ethyl-5-phenyl-1,2,3,4-thiaziazolium tetrafluoroborate have been determined by X-ray methods using 1617, 1502 and 1514 reflections, respectively, collected on a counter diffractometer. Data for the first two compounds were collected at -165°C and for the third compound at 19°C . The crystal data are as follows:

I: Monoclinic, space group $P2_1/c$, $a = 9.806(2)$ Å; $b = 7.184(1)$ Å; $c = 11.204(2)$ Å; $\beta = 115.85^{\circ}(1)$; $Z = 4$

II: Monoclinic, space group $P2_1/c$, $a = 7.591(4)$ Å; $b = 13.337(6)$ Å; $c = 14.667(7)$ Å; $\beta = 96.65^{\circ}(4)$; $Z = 8$

III: Orthorhombic, space group $Pbca$, $a = 19.551(4)$ Å; $b = 19.755(4)$ Å; $c = 13.187(2)$ Å; $Z = 16$.

The structures were refined to conventional R -factors of 0.035 (I), 0.072 (II) and 0.091 (III). The standard deviations in bond lengths and angles involving only nonhydrogen atoms are: 0.002 Å and 0.1° (I), 0.005–0.009 Å and 0.3 – 0.6° (II), and 0.014–0.040 Å and 0.7 – 2.0° (III) excluding the tetrafluoroborate groups.

The thiaziazole rings are planar and the planes of the benzene rings are tilted 18.0° (I), 13.9° (II.A), 3.6° (II.B), 15.5° (III.A), and 11.5° (III.B), respectively, to the planes of the thiaziazole rings.

The chemistry of the heteroaromatic 1,2,3,4-thiaziazoles has attracted considerable interest during the last decades,^{1,2} and both their physical and chemical properties have been investigated. On the basis of a series of theoretical calculations a set of structural parameters has been suggested for the parent ring.²

Several structural studies of thiaziazoles have been reported (see, e.g., Refs. 3–8), and structural models of 1,2,3-, 1,2,5- and 1,3,4-thiaziazoles and/or derivatives thereof have

been derived. However, no structural investigations of the thiaziazoles have been reported. An X-ray diffraction study of 5-phenyl-1,2,3,4-thiaziazole (I) was therefore carried out in order to establish a structural model of this heteroaromatic ring.

Since a confirmation of the oxidation⁹ and alkylation¹⁰ sites of the thiaziazole ring was wanted, the structures of 5-phenyl-(1,2,3,4-thiaziazolio)-3-oxide (II) and 3-ethyl-5-phenyl-1,2,3,4-thiaziazolium tetrafluoroborate (III) have also been studied in the present investigation.

EXPERIMENTAL, STRUCTURE DETERMINATION AND REFINEMENTS

Space groups were determined by film methods. A computer-controlled Syntex PI four-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation, and in the cases of low-temperature work equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope), was utilized in the determination of unit cell parameters and the collection of intensity data. Unit cell parameters and their standard deviations were determined by a least-squares treatment of the angular coordinates of fifteen symmetry-independent reflections with 2θ -values between 32 – 45° (I), 25 – 40° (II) and 18 – 26° (III). The temperatures at crystal site were -165°C (I), -165°C (II) and 19°C (III).

The computer programs utilized are part of a local assembly and are described in Refs. 11 and 12. Atomic scattering factors used were those of Doyle and Turner¹³ for S, F, O, N, C, and B, and of Stewart *et al.*¹⁴ for H.

The crystals used were plates of approximate dimensions $0.4 \times 0.2 \times 0.05$ mm (I), $0.4 \times 0.2 \times 0.15$ mm (II) and $0.3 \times 0.2 \times 0.05$ mm (III). Three-dimensional intensity data were recorded

utilizing the $\omega-2\theta$ scanning mode with scan speed variable between $2-8^\circ \text{ min}^{-1}$ (I and II) and $3-8^\circ \text{ min}^{-1}$ (III), depending on the intensity of the reflection. Background counting time was equal to $0.35 \times$ scan time on each side of the reflections. The intensity variations of three standard reflections which were re-measured after every hundred reflections were random for all data-sets collected. Accordingly no corrections were applied to the intensity data for these variations.

The estimated standard deviations were taken as the square root of the total count with an addition of 2% of the net intensity for experimental uncertainties. The intensities were corrected for Lorentz and polarization effects.

The phase problems were solved by the MULTAN¹² program package, and the structure models were refined by full-matrix least-squares refinements. The final atomic parameters for nonhydrogen atoms are listed in Table

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations for non-hydrogen atoms. The temperature factor is given by $\exp\{-2\pi^2[u_{11}(a^*h)^2 + u_{22}(b^*k)^2 + u_{33}(c^*l)^2 + u_{12}(a^*b^*hk) + u_{13}(a^*c^*hl) + u_{23}(b^*c^*kl)]\}$.

Atom	\bar{x}	\bar{y}	\bar{z}	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Compound I									
N1	.2912(8)	.3983(8)	.0227(8)	.0133(2)	.0308(2)	.0158(2)	-.0026(3)	.0034(3)	-.0045(3)
N2	.4138(1)	.0182(4)	.0133(5)	.0133(5)	.0307(8)	.0203(7)	.0011(5)	.0076(5)	.0014(6)
N3	.3424(1)	.3502(2)	.7200(1)	.0156(6)	.0338(8)	.0269(7)	-.0001(5)	.0111(5)	-.0003(5)
N4	.1809(1)	.3536(2)	.6772(1)	.0152(6)	.0304(8)	.0102(5)	.0018(4)	.0011(4)	.0005(4)
C5	.1424(1)	.3729(2)	.7712(1)	.0119(5)	.0182(7)	.0155(5)	-.0004(4)	.0042(4)	.0002(4)
C7	.0179(1)	.3745(2)	.7442(1)	.0124(5)	.0157(7)	.0143(5)	-.0001(4)	.0057(4)	.0001(4)
C8	-.0625(1)	.3455(2)	.6458(1)	.0109(5)	.0283(7)	.0148(5)	.0017(5)	.0006(4)	.0000(5)
C9	-.2163(2)	.3475(2)	.6165(1)	.0191(6)	.0273(8)	.0241(7)	.0000(5)	.0141(5)	.0004(5)
C10	-.3253(1)	.3779(2)	.6071(1)	.0153(5)	.0242(8)	.0273(7)	.0017(5)	.0107(5)	.0003(5)
C11	-.2003(1)	.4092(2)	.5063(1)	.0134(5)	.0277(7)	.0202(6)	.0018(5)	.0058(4)	.0005(5)
C12	-.1266(1)	.4082(2)	.6148(1)	.0137(5)	.0248(7)	.0157(5)	.0012(5)	.0059(4)	.0000(5)
Compound II									
N1A	.4647(2)	.2050(8)	.2349(1)	.0313(8)	.0116(6)	.0101(7)	-.0005(4)	.0094(4)	.0005(4)
N2A	.4442(8)	.3237(3)	.2661(3)	.0324(26)	.0149(19)	.0173(19)	.0016(10)	.0096(17)	.0004(16)
N3A	.5233(7)	.3606(3)	.2195(3)	.0246(22)	.0139(20)	.0129(17)	.0011(10)	.0034(15)	.0012(15)
N4A	.5835(7)	.3361(3)	.1801(3)	.0227(23)	.0100(17)	.0165(19)	-.0022(15)	.0044(16)	.0003(14)
C5A	.5833(3)	.2366(3)	.1467(3)	.0199(23)	.0110(20)	.0126(18)	-.0018(15)	.0021(15)	.0008(15)
O6A	.5307(7)	.4739(3)	.2191(3)	.0309(25)	.0099(16)	.0241(18)	.0016(16)	.0095(16)	-.0002(15)
C7A	.6492(8)	.1667(4)	.0842(3)	.0251(27)	.0122(19)	.0139(20)	-.0003(17)	.0030(17)	-.0000(16)
C8A	.7897(8)	.1591(4)	.0819(3)	.0269(26)	.0143(20)	.0106(21)	-.0019(18)	.0054(16)	-.0002(17)
C9A	.7219(8)	.1305(4)	-.0525(4)	.0343(31)	.0176(23)	.0100(21)	.0017(21)	.0101(20)	.0001(19)
C10A	.7745(10)	.0208(5)	-.0354(4)	.0351(33)	.0168(25)	.0239(25)	.0031(21)	.0044(22)	.0005(20)
C11A	.7183(11)	-.0042(4)	.0472(4)	.0422(36)	.0114(19)	.0244(26)	.0021(20)	.0004(17)	-.0005(16)
C12A	.6525(9)	.0842(4)	.1803(3)	.0302(32)	.0107(19)	.0171(21)	.0013(18)	.0054(19)	.0000(16)
N1B	-.6335(2)	.0238(8)	.7309(1)	.0302(8)	.0113(6)	.0108(7)	.0024(4)	.0102(4)	.0001(4)
N2B	.1595(8)	.3237(3)	.2661(3)	.0246(22)	.0134(19)	.0086(17)	.0003(10)	.0003(15)	.0000(16)
N3B	.0519(7)	-.1500(3)	.7151(3)	.0257(26)	.0141(20)	.0169(18)	-.0017(16)	.0017(17)	.0002(15)
N4B	.1331(8)	-.1941(3)	.6471(3)	.0309(26)	.0131(18)	.0154(18)	-.0005(17)	.0024(17)	-.0002(14)
C5B	.0906(8)	-.0075(4)	.6479(3)	.0192(23)	.0155(22)	.0145(19)	.0000(16)	.0047(16)	-.0002(15)
C6B	.0608(8)	-.2415(3)	.7273(3)	.0439(28)	.0109(16)	.0223(18)	.0011(16)	.0071(17)	.0004(14)
C7B	.3647(8)	.4119(3)	.4784(3)	.0191(24)	.0115(15)	.0141(17)	.0004(16)	.0015(16)	.0000(16)
C8B	.0573(8)	.0384(3)	.5142(3)	.0248(25)	.0104(15)	.0179(20)	.0012(17)	.0039(17)	-.0002(16)
C9B	.3100(8)	.0909(4)	.4566(3)	.0279(26)	.0170(22)	.0146(20)	-.0009(19)	.0000(17)	.0000(17)
C10B	.2040(8)	.2002(4)	.4564(4)	.0251(27)	.0157(23)	.0100(20)	-.0025(18)	.0041(18)	.0001(17)
C11B	.1682(9)	.3262(3)	.5243(4)	.0314(29)	.0102(19)	.0206(22)	-.0000(18)	.0059(20)	.0001(16)
C12B	.1105(9)	.1681(4)	.6076(3)	.0360(28)	.0103(19)	.0167(21)	.0004(16)	.0053(18)	-.0001(16)
Compound III									
N1A	.3392(2)	.3322(2)	.4481(3)	.104(3)	.061(2)	.078(2)	-.014(2)	.016(2)	-.002(2)
N2A	.2991(6)	.3285(7)	.5491(10)	.094(7)	.074(7)	.063(7)	-.014(6)	-.013(7)	-.006(7)
N3A	.2978(6)	.3009(8)	.5976(9)	.071(7)	.083(9)	.072(7)	-.005(7)	-.001(6)	.002(7)
N4A	.3362(8)	.4309(9)	.5636(8)	.074(6)	.063(6)	.060(6)	-.007(6)	.000(6)	-.002(5)
C7A	.4115(6)	.4541(6)	.4283(10)	.057(7)	.065(6)	.064(6)	.009(6)	.011(6)	.000(6)
C8A	.4166(7)	.5226(6)	.4498(11)	.072(8)	.059(6)	.065(6)	.008(7)	.001(6)	.009(7)
C9A	.4636(9)	.5601(7)	.3873(14)	.093(9)	.060(7)	.102(11)	-.009(8)	.007(11)	.017(8)
N1B	.3221(2)	.4153(2)	.1407(3)	.098(3)	.080(2)	.075(2)	.006(2)	.000(2)	-.012(2)
N2B	.3948(6)	.4193(6)	.0901(10)	.085(8)	.081(8)	.083(8)	.011(8)	.000(6)	.000(8)
N3B	.3902(6)	.3919(7)	.0897(10)	.064(8)	.081(7)	.074(8)	-.002(7)	.000(6)	.001(7)
N4B	.3329(8)	.3503(6)	-.0111(8)	.088(10)	.080(7)	.061(8)	.028(7)	.020(7)	-.004(6)
C5B	.2875(7)	.3627(6)	.0596(10)	.080(9)	.061(6)	.063(6)	.005(6)	.014(6)	.012(6)
C7B	.2179(8)	.3356(6)	.0632(12)	.098(11)	.064(7)	.080(10)	.012(8)	.000(9)	-.000(8)
C8B	.1931(10)	.3044(9)	-.0218(14)	.100(14)	.102(11)	.100(12)	.021(11)	-.016(12)	.003(9)
C9B	.1251(13)	.2776(13)	-.0206(21)	.107(16)	.100(13)	.139(20)	-.014(11)	-.030(16)	.000(11)
C10B	.0839(12)	.2640(12)	.0606(21)	.081(14)	.110(14)	.171(26)	-.003(11)	.030(20)	.001(11)
C11B	.0924(13)	.3149(12)	.1478(22)	.107(17)	.105(19)	.159(19)	.011(14)	.050(17)	.010(16)
C12B	.1784(9)	.3434(7)	.1483(14)	.071(10)	.080(9)	.101(10)	.004(6)	.025(9)	.014(8)
C13B	.4468(10)	.3718(13)	-.0610(14)	.084(12)	.108(16)	.093(10)	.016(11)	.030(10)	.007(12)
C14B	.5099(12)	.3309(10)	-.0254(21)	.105(16)	.123(15)	.105(21)	.010(11)	.074(15)	.030(14)
B15A	.4203(3)	.2302(8)	.1905(19)	.099(16)	.065(10)	.075(10)	.018(8)	-.001(8)	-.001(8)
B16A	.4126(6)	.1742(5)	.1955(10)	.165(8)	.094(6)	.101(8)	-.008(7)	.000(7)	.000(7)
B17A	.3735(16)	.2744(7)	.2284(15)	.343(29)	.131(8)	.200(14)	.062(12)	.040(14)	-.027(8)
B18A	.4644(19)	.2547(17)	.2758(20)	.372(35)	.307(24)	.216(18)	-.194(28)	.148(22)	.053(17)
B19A	.4399(18)	.2595(13)	.1054(15)	.246(14)	.235(16)	.150(11)	-.009(13)	.003(12)	.051(11)
B15B	.1013(20)	.4614(30)	.3878(18)	.308(61)	.332(73)	.069(14)	.276(64)	.005(24)	.005(25)
B16B	.4000(7)	.4000(11)	.3474(12)	.133(7)	.206(18)	.178(11)	.060(19)	-.036(8)	.079(11)
B17B	.1918(8)	.4662(15)	.4877(9)	.176(11)	.340(20)	.097(7)	.062(13)	.005(7)	.000(11)
B18B	.1716(34)	.3947(9)	.3922(20)	.589(65)	.140(16)	.223(19)	-.001(20)	.032(31)	.024(11)
B19B	.2427(8)	.4571(12)	.3329(9)	.168(9)	.305(10)	.122(7)	.094(11)	.024(7)	-.013(9)

Table 2. Fractional atomic coordinates and thermal parameters for hydrogen atoms (see text).

Atom	x	y	z	B
Compound I				
HCB	008(2)	.322(2)	.933(2)	1.7(3)
HC9	-.246(2)	.323(3)	.887(2)	2.5(4)
HC10	-.431(2)	.377(2)	.667(2)	2.0(4)
HC11	-.354(2)	.434(2)	.496(2)	2.0(4)
HC12	-.095(2)	.431(2)	.548(2)	2.2(4)
Compound II				
HC8A	.718	.273	.012	
HC9A	.810	.154	-.116	
HC10A	.827	-.021	-.077	
HC11A	.719	-.076	.063	
HC12A	.616	.041	.165	
HC8B	.293	-.040	.511	
HC9B	.386	.074	.402	
HC10B	.302	.249	.409	
HC11B	.135	.304	.529	
HC12B	.046	.189	.639	
Compound III				
HC8A	.386	.544	.491	
HC9A	.469	.610	.404	
HC10A	.538	.559	.277	
HC11A	.526	.446	.240	
HC12A	.450	.373	.336	
H1C13A	.260	.444	.706	
H2C13A	.284	.370	.749	
H1C14A	.168	.381	.755	
H2C14A	.190	.321	.676	
H3C14A	.166	.395	.633	
HC8B	.222	.300	-.084	
HC9B	.107	.255	-.083	
HC10B	.036	.265	.069	
HC11B	.084	.317	.210	
HC12B	.196	.368	.208	
H1C13B	.435	.394	-.125	
H2C13B	.450	.322	-.072	
H1C14B	.545	.387	-.077	
H2C14B	.522	.373	.040	
H3C14B	.506	.446	-.013	

1 and those for hydrogen atoms in Table 2. Standard deviations in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell parameters.

Compound I. Reflections with 2θ -values larger than 45° which had integrated counts of less than 8 cps determined in a $2s$ scan over the peak, were not measured. Of the 1975 reflections measured ($2\theta_{\max} = 60^\circ$), 1617 had intensities larger than twice their standard devia-

tions. These were regarded as "observed" reflections, and the remaining were excluded from further calculations.

The structure model was refined to a conventional R of 0.07. At this point hydrogen atoms were included, and anisotropic thermal parameters were introduced for nonhydrogen atoms. Refinement of all positional and thermal parameters converged to a conventional R of 0.033 and a weighted R_w of 0.035.

In order to reduce the influence of the asphericity of the valence electrons all reflections with $\sin \theta/\lambda < 0.5$ were excluded from the final refinement¹⁵ (leaving 935 F_o 's). Refinement of all parameters involving nonhydrogen atoms resulted in a weighted R_w of 0.032, a conventional R of 0.035 and an R_t for the total dataset of 0.036. The standard deviation of an observation of unit weight, $(\sum W \Delta F^2 / (m-s))^{1/2}$, was 1.18.

The r.m.s. difference between the observed U_{ij} 's and those calculated from the "rigid body" model¹⁶ is 0.0007 \AA^2 , which indicates that the molecule may be regarded as a rigid body. The atomic positions were accordingly corrected for the librational motion. The eigenvalues of T are 0.13, 0.12 and 0.11 \AA^2 , and the r.m.s. librational amplitudes are 4.3, 2.1 and 1.7° .

Compound II. The unit cell volume found indicated eight formula units in the unit cell, i.e. two molecules in the asymmetric unit (space group $P2_1/c$); these will be denoted A and B, respectively.

Unfortunately, the crystal used in the first recording of intensity data cracked during the collection. This data-set (low-angle data, $2\theta_{\max} = 45^\circ$) was later used in the structure determination (987 reflections above 3σ level). A new data-set consisting of all reflections with 2θ -values between 42.5 and 60° which had integrated counts of more than 7 cps, determined in a $2s$ scan, were collected. Of the 1831 reflections measured, 1502 had intensities larger than 2.5 times their standard deviations. These were regarded as "observed" reflections, and the remaining were excluded from further calculations.

Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms yielded, after inclusion of the hydrogen atoms in calculated positions with a common isotropic temperature factor of 2.0 \AA^2 , a conventional R of 0.09, using the low-angle data-set.

Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, using the high-angle data-set, converged to an R of 0.072 and a weighted R_w of 0.080. The standard deviation of an observation of unit weight was 2.51.

The r.m.s. difference between the observed U_{ij} 's and those calculated from the "rigid-body" model¹⁶ is 0.0012 \AA^2 for molecule A and 0.0014 \AA^2 for molecule B, which indicate that both molecules may be regarded as rigid

Table 3. Molecular parameters with estimated standard deviations.

	I	II.A	II.B	III.A	III.B			
<i>Bond lengths</i> (Å). The values listed in the second column for compound I and II are the corrected lengths.								
S1-N2	1.677(2)	1.680	1.661(5)	1.664	1.662(5)	1.664	1.644(14)	1.618(13)
S1-C5	1.698(2)	1.702	1.717(6)	1.721	1.714(6)	1.718	1.700(14)	1.713(14)
N2-N3	1.283(2)	1.287	1.308(8)	1.312	1.313(8)	1.317	1.225(17)	1.261(17)
N3-N4	1.358(2)	1.359	1.383(7)	1.385	1.375(7)	1.375	1.320(16)	1.311(18)
N4-C5	1.326(2)	1.329	1.314(6)	1.317	1.315(7)	1.318	1.309(16)	1.306(18)
C5-C7	1.465(2)	1.467	1.455(7)	1.457	1.469(7)	1.470	1.456(19)	1.463(21)
C7-C8	1.403(2)	1.407	1.408(7)	1.411	1.383(8)	1.386	1.381(19)	1.370(24)
C8-C9	1.396(2)	1.397	1.381(8)	1.382	1.400(8)	1.400	1.370(22)	1.429(32)
C9-C10	1.393(2)	1.397	1.395(9)	1.397	1.401(8)	1.404	1.357(24)	1.406(40)
C10-C11	1.398(2)	1.402	1.407(10)	1.410	1.386(9)	1.389	1.327(26)	1.343(39)
C11-C12	1.398(2)	1.399	1.390(8)	1.391	1.394(8)	1.394	1.394(26)	1.412(33)
C7-C12	1.396(2)	1.399	1.406(7)	1.409	1.405(7)	1.408	1.378(21)	1.369(24)
N3-O6			1.252(7)	1.254	1.238(7)	1.240		
N3-C13							1.472(21)	1.449(22)
C13-C14							1.441(40)	1.417(36)
B15-F16							1.302(21)	1.227(28)
B15-F17							1.348(32)	1.337(38)
B15-F18							1.281(26)	1.333(70)
B15-F19							1.318(26)	1.404(44)
<i>Bond angles</i> (°)								
N2-S1-C5	90.6(1)		91.9(3)		91.8(3)		91.2(7)	91.4(7)
S1-N2-N3	111.0(1)		108.5(4)		108.8(4)		108.3(10)	109.4(10)
N2-N3-N4	116.0(1)		118.9(5)		118.2(5)		121.6(11)	119.5(12)
N3-N4-C5	111.1(1)		108.2(5)		109.0(5)		108.6(11)	110.1(12)
S1-C5-N4	111.2(1)		112.5(4)		112.2(4)		110.1(9)	109.4(11)
S1-C5-C7	125.7(1)		123.4(4)		124.1(4)		126.3(10)	124.3(12)
N4-C5-C7	123.1(1)		124.1(5)		123.6(5)		123.7(12)	126.3(14)
C5-C7-C8	121.1(1)		120.4(5)		119.8(5)		120.5(13)	117.5(16)
C5-C7-C12	118.8(1)		119.7(5)		118.7(5)		118.5(11)	121.1(15)
C8-C7-C12	120.1(1)		119.9(5)		121.4(5)		120.9(12)	121.4(16)
C7-C8-C9	119.6(1)		120.2(5)		119.2(5)		118.9(14)	119.0(19)
C8-C9-C10	120.5(1)		120.2(6)		119.8(6)		120.3(13)	120.8(21)
C9-C10-C11	119.8(1)		120.0(6)		120.4(6)		120.9(16)	116.5(19)
C10-C11-C12	120.2(1)		120.2(6)		120.3(6)		121.4(16)	124.6(22)
C7-C11-C12	119.8(1)		119.6(6)		118.8(5)		117.5(14)	117.5(19)
N4-N3-O6			118.9(5)		120.0(6)			
N2-N3-O6			122.2(5)		121.8(5)			
N2-N3-C13							121.9(13)	124.2(14)
N4-N3-C13							116.3(13)	116.3(15)
N3-C13-C4							113.7(15)	113.8(18)
F16-B15-F17							109.7(18)	118.9(25)
F16-B15-F18							113.6(18)	122.2(67)
F16-B15-F19							108.8(19)	112.2(23)
F17-B15-F18							94.0(28)	92.8(24)
F17-B15-F19							103.9(18)	112.4(41)
F18-B15-F19							124.4(19)	94.8(31)
<i>Dihedral angles</i> (°) The angles are positive in a right-hand screw								
N3-N4-C5-C7	178.9(2)	179.5(5)		177.8(5)		-178.9(10)		-178.9(11)
N2-S1-C5-C7	-179.0(2)	179.3(5)		177.4(5)		179.0(10)		-179.5(10)
S1-C5-C7-C8	-18.2(2)	165.7(5)		-176.3(5)		165.6(10)		169.0(11)
S1-C5-C7-C12	160.9(1)	-14.4(8)		1.3(8)		-16.8(14)		-9.6(16)
N4-N3-C13-C14						134.3(21)		-168.5(16)
N2-N3-C13-C14						-40.7(24)		11.4(25)

bodies. The atomic positions were accordingly corrected for the librational motion. The eigenvalues of T are 0.14, 0.12 and 0.10 Å² for both molecules, and the r.m.s. librational amplitudes are 4.1, 2.0 and 1.5° for molecule A, and 4.3, 1.3 and 1.3° for molecule B.

Compound III. The unit cell volume found indicated sixteen formula units in the unit cell, i.e. two molecules in the asymmetric unit (space group $Pbca$); these will be denoted A and B, respectively.

Three-dimensional intensity data at -165 °C were recorded using scan speed variable between 6 and 8° min⁻¹. A check showed that the intensity data only had monoclinic symmetry, and, further, the systematic absences were those corresponding to the space group $P2_1/c$. This may indicate a phase transition. This data-set was later used in the structure determination while a new data-set was collected. Of the 5995 reflections measured ($2\theta_{\max} = 55^\circ$) 2763 had intensities larger than twice their standard deviations. These were regarded as observed.

A new data-set was collected at 19 °C consisting only of reflections with an integrated count larger than 9 cps determined in a 2s scan. Of the 1805 reflections measured ($2\theta_{\max} = 55^\circ$) 1514 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections, and the remaining were excluded from further calculations.

The phase problem was solved using the low-temperature data-set and the space group $Pbca$. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms yielded a conventional R of 0.19. Attempts to refine anisotropic thermal parameters resulted in several negative U_{ij} 's.

Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms, using the room-temperature data-set, converged after inclusion of the hydrogen atoms in calculated positions with a common isotropic temperature factor of 7.0 Å², to a conventional R of 0.115 and a weighted R_w of 0.119. In the final refinement all structure factors with $\sin \theta/\lambda < 0.3$ were excluded (leaving 1018 F_o 's). Refinement of all parameters involving nonhydrogen atoms yielded a weighted R_w of 0.081, a conventional R of 0.091 and an R_i for the total data-set of 0.118. The standard deviation of an observation of unit weight was 2.00.

The thermal motion of the molecules or parts of them could not be described by the "rigid-body" model.¹⁶

CRYSTAL DATA

Compound I. 5-Phenyl-1,2,3,4-thiaziazole, C₇H₅N₃S, M = 163.2 amu, space group $P2_1/c$, $a = 9.806(2)$ Å, $b = 7.184(1)$ Å, $c = 11.204(2)$ Å,

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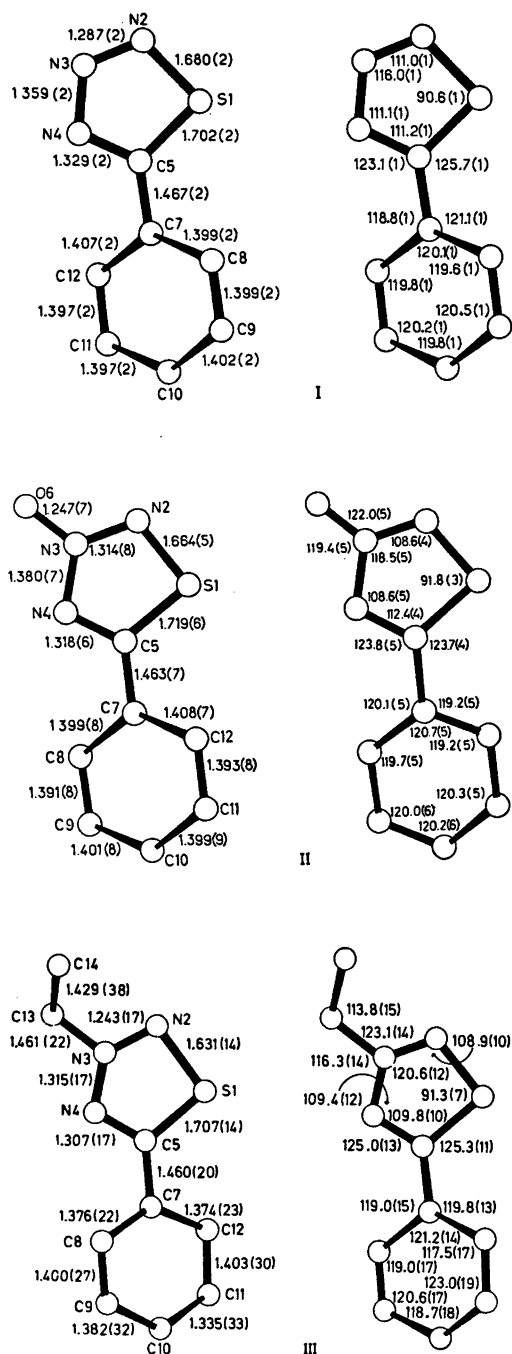


Fig. 1. Bond lengths (Å) (corrected for thermal libration effects for I and II), and bond angles (°) with estimated standard deviations. All parameters given for II and III including e.s.d.'s are mean values.

Table 4. Deviations from least-squares planes ($\text{\AA} \times 10^3$). The deviations for those atoms used to define the plane are given in italicized figures.

Atom	Compound I		Compound II		II.B.1	II.B.2	Compound III			
	I.1	I.2	II.A.1	II.A.2			III.A.1	III.B.2	III.B.1	III.B.2
S1	<i>0</i>	422	-2	-351	<i>1</i>	-113	<i>6</i>	-273	-2	275
N2	-1	138	2	-145	3	-182	-23	-10	7	101
N3	<i>1</i>	-248	2	163	<i>4</i>	-131	22	335	-6	-155
N4	-1	-350	6	252	-3	-53	-7	361	<i>1</i>	-213
C5	<i>1</i>	-13	8	7	<i>1</i>	-28	-8	49	3	3
O6			24	394	12	-158				
C7	22	-8	-5	1	-51	6	-14	0	12	-4
C8	-330	3	-297	5	-124	2	-321	-11	225	-5
C9	-302	5	310	-3	-207	-3	-253	9	231	1
C10	70	8	-22	-3	-216	4	78	5	1	13
C11	441	2	286	9	-155	0	343	-16	-260	-24
C12	420	5	277	-8	-78	-5	340	14	-228	19
C13							-3	633	-33	-400
C14							-927	-280	-298	-580

$\beta = 115.85^\circ(1)$, $V = 710.3 \text{ \AA}^3$ ($t = -165^\circ\text{C}$), $Z = 4$, $D_{\text{calc}} = 1.525 \text{ g/cm}^3$, $F(000) = 336$.

Compound II. 5-Phenyl-(1,2,3,4-thiatriazolio)-3-oxide, $\text{C}_7\text{H}_5\text{N}_3\text{OS}$, $M = 179.2 \text{ amu}$, space group $P2_1/c$, $a = 7.591(4) \text{ \AA}$, $b = 13.337(6) \text{ \AA}$, $c = 14.667(7) \text{ \AA}$, $\beta = 96.65^\circ(4)$, $V = 1474.9 \text{ \AA}^3$ ($t = -165^\circ\text{C}$), $Z = 8$, $D_{\text{calc}} = 1.613 \text{ g/cm}^3$, $F(000) = 736$.

Compound III. 3-Ethyl-5-phenyl-1,2,3,4-thiatriazolium tetrafluoroborate, $\text{C}_9\text{H}_{10}\text{N}_3\text{S}^+\text{BF}_4^-$, $M = 279.0 \text{ amu}$, space group $Pbca$, $a = 19.551(4) \text{ \AA}$ [19.497(12) \AA], $b = 19.755(4) \text{ \AA}$ [19.221(8) \AA], $c = 13.187(2) \text{ \AA}$ [13.021(7) \AA], $V = 5092.9 \text{ \AA}^3$ ($t = 19^\circ\text{C}$), $Z = 16$, $D_{\text{calc}} = 1.455 \text{ g/cm}^3$, $F(000) = 2272$.

Numbers in brackets are cell dimensions at -165°C .

DISCUSSION

Bond lengths and bond angles are listed in Table 3. The numbering of the atoms is indicated in Fig. 1, where also the mean values of bond lengths and bond angles found for the two crystallographically nonequivalent molecules in II and III are given, together with the values obtained for I. The largest differences in equivalent bond lengths between the two molecules (A and B) in II and III, excluding the tetrafluoroborate groups, are about three times the mean estimated standard deviations. Some selected dihedral angles are given in Table 3 and deviations from planarity in Table 4.

The accuracy in the molecular parameters found for III is poor and this structure will not be discussed in detail.

The five-membered rings are planar and the bond lengths indicate a considerable resonance stabilization, as has also been found for the 1,2,5- and 1,3,4-thiadiazoles.^{3-5,17} However, there are two noteworthy changes in the parent thiatriazole ring (I) compared with the thiadiazoles. The S1-C5 bond is shortened by 0.02 \AA compared with 1,3,4-thiadiazole,^{4,5} and the S1-N2 bond is lengthened by 0.05 \AA compared with 1,2,5-thiadiazoles.^{3,17}

The angles between the benzene and thiatriazole rings are small [18.0° (I), 13.9° (II.A), 3.6° (II.B), 15.5° (III.A) and 11.5° (III.B)] and the C5-C7 bond lengths (1.46-1.47 \AA) indicate conjugation between the rings.

The N2-S7-C5 angle of 90.6° is between the N-S-N angle^{3,17} of 99.6° and the C-S-C angle^{4,5} of 86.4°, and is close to the N-S-C angle of 91.6° found in 2,4-dimethyl-3,5-di(phenylimino)-1,2,4-thiazolidine.¹⁸

The introduction of an oxygen atom at N3 in I, giving II, results in significant lengthenings of the N2-N3 and N3-N4 bonds, and an opening of the N2-N3-N4 angle by 2.5°. The angles S1-N2-N3 and N3-N4-C5 decrease by about 2.5°. Small changes in the other bond lengths are also indicated, implying charge redistributions over the whole ring.

The same angular changes as is found in II are also indicated in III.

For all these compounds the intermolecular forces in the crystals are of van der Waals type. The shortest intermolecular distances are mainly compatible with normal van der Waals contacts.

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