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Mesoionic Compounds. 4.* Structure of 1,4,5-Triphenyl-1,2,4-triazolium-3-thiolate

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(*Received* 27 *July* 1992; *accepted* 1 *December* 1992)

Abstract. $C_{20}H_{15}N_3S$, $M_r = 329.43$, monoclinic, $P2_1/c$, $a = 11.745\ (4)$, $b = 7.600\ (4)$, $c = 21.929\ (6)$ Å, $\beta = 118.36\ (4)°$, $V = 1722.4\ (1.0)$ Å^3, $Z = 4$, $D_x = 1.270$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.8$ cm^{-1}, $F(000) = 688$, $T = 297$ K, $R = 0.038$ for 1372 reflections. The mesoionic compound has a nearly planar pentatomic heterocyclic ring and an exocyclic C—S$^-$ bond.

Introduction. The title compound (*B*) is a rearrangement product of 4,5-diphenyl-1,3,4-thiadiazolium-2-phenylaminide (*A*), in which the S atom of (*A*) becomes the exocyclic S atom of (*B*). Alternatively, (*B*) may be obtained directly from

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[*] Part 3: Cheung, Echevarria, Galembeck, Maciel, Miller, Rumjanek & Simas (1992).

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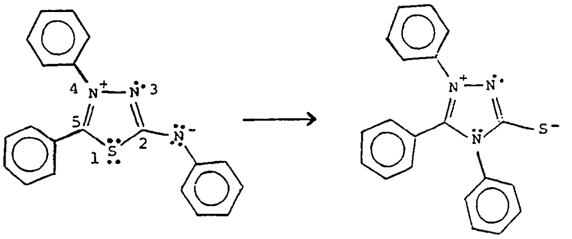
0108-2701/93/061092-03$06.00

open-chain precursors (Maciel, Echevarria, Rumjanek, Montanari & Miller, 1992). Both are mesoionic compounds for which we now give a new definition. Mesoionic compounds are poly-heteroatom five-membered ring betaines, stabilized by electron delocalization and with dipole moments not less than 5 D (1 D = 3.33564×10^{-30} C m), in which electrons and a positive charge are delocalized over a part of the ring and attached groups, and in which electrons and a negative charge, formally on an α-atom (normally a heteroatom), are delocalized over the remaining part of the ring.



(*A*) (*B*)

Experimental. Recrystallization from chloroform yielded pale yellow prism-like crystals. Crystal 0.15 × 0.15 × 0.07 mm. Enraf–Nonius CAD-4 diffractometer, with graphite monochromated Mo $K\alpha$ radiation and scintillation counter. Cell parameters by least squares from setting angles of 25 reflections ($9.8 < 2\theta < 13.8°$) measured on the diffractometer. The intensities of 4591 reflections ($2\theta_{\max} = 44°$) in the range $-12 \leq h \leq 12$, $0 \leq k \leq 8$, $-20 \leq l \leq 20$, were measured using ω–2θ scans, with ω-scan angle $(1.00 + 0.344\tan\theta)°$ and at 0.97 to 5.49° min^{-1}, extended 25% on each side for background measurement. Three standard reflections measured every 2 h showed no decay. Systematic absences indicated space group $P2_1/c$ which was confirmed by the structure solution. The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied. Averaging of equivalent reflections gave 2299 reflections; $R_{\text{int}} = 0.025$ for observed reflections [$I > 3\sigma(I)$] and 0.040 for all reflections. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least squares using the *SDP* program package (Enraf–Nonius, 1985) on a MicroVAX II computer with atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). H atoms in calculated positions were not refined. Convergence for 217 parameters by least squares with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.045F_o^2)^2]$, for $F_o^2 > \sigma^2(F_o^2)$, and $w = -2.0$ for all other reflections, was reached at $R = 0.039$, $wR = 0.041$ and $S = 1.024$ for 1372 reflections with $|F_o| > 2\sigma(|F_o|)$. $(\Delta/\sigma)_{\max} = 0.01$. A final difference Fourier map was featureless, with maximum positive and negative peaks of 0.13 and -0.14 e Å^{-3}, respectively.

Discussion. An *ORTEP*II drawing (Johnson, 1976) of the molecule with the atomic numbering scheme is shown in Fig. 1. The atomic parameters of C, N, O and S atoms are listed in Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. The pentatomic heterocyclic ring is nearly planar ($\chi^2 = 11$). The C(2)—S$^-$ bond length of 1.681 (2) Å is intermediate between the double-bond length of 1.645 Å (Bocelli & Rizzoli, 1989) and the single-bond length of 1.737 Å in 5-benzoylthio-1,2,3,4-thiatriazole (Perman & Gleason, 1991). The bond lengths C(2)—N(3) 1.328 (3), C(5)—N(1) 1.346 (2) and C(5)—N(4) 1.323 (4) Å suggest that these bonds have some double-bond character as they are comparable to the C—N bond length of 1.347 Å in 4,5,6,7-tetrahydro-1,3-benzimidazole-2-thione, which also has a C—S bond length of 1.690 Å (Kitano, Ishitani, Sato, Imamura & Ashida, 1991), and the C—N bond length of 1.352 Å in 5,5-dimethyl-4-(2-methylallyl)-2-tolyl-1,2,4-triazolidine-3-thione, with C—S bond length of 1.677 Å (Schulze, Richter & Faure, 1988). The C(2)—N(1)

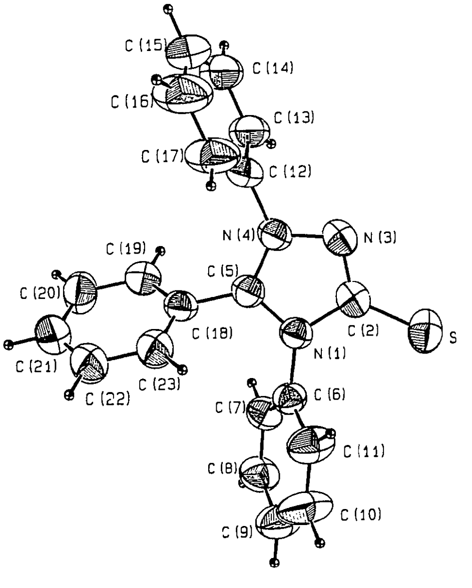


Fig. 1. *ORTEP*II drawing of the title molecule with the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and geometry, torsion angles and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55820 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1022]

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	0.10872 (8)	0.2262 (1)	0.09123 (4)	5.86 (2)
N(1)	0.0178 (2)	0.2547 (3)	−0.04969 (9)	3.94 (5)
N(3)	−0.1300 (2)	0.2801 (3)	−0.01463 (9)	4.56 (6)
N(4)	−0.1840 (2)	0.2927 (3)	−0.0857 (1)	4.16 (6)
C(2)	−0.0043 (2)	0.2550 (4)	0.0083 (1)	4.17 (7)
C(5)	−0.0965 (2)	0.2768 (4)	−0.1071 (1)	3.97 (7)
C(6)	0.1425 (2)	0.2517 (4)	−0.0472 (1)	3.96 (7)
C(7)	0.1850 (2)	0.4007 (4)	−0.0657 (1)	4.62 (8)
C(8)	0.3058 (2)	0.3998 (5)	−0.0624 (1)	5.65 (9)
C(9)	0.3822 (3)	0.2531 (5)	−0.0406 (2)	6.6 (1)
C(10)	0.3374 (3)	0.1057 (5)	−0.0218 (2)	7.9 (1)
C(11)	0.2171 (3)	0.1040 (5)	−0.0249 (2)	6.11 (9)
C(12)	−0.3226 (2)	0.3094 (4)	−0.1267 (1)	4.89 (8)
C(13)	−0.3805 (2)	0.4591 (5)	−0.1215 (1)	5.55 (9)
C(14)	−0.5145 (3)	0.4736 (5)	−0.1606 (2)	7.0 (1)
C(15)	−0.5843 (3)	0.3352 (6)	−0.2023 (2)	8.1 (1)
C(16)	−0.5222 (3)	0.1869 (7)	−0.2056 (2)	10.3 (1)
C(17)	−0.3904 (3)	0.1708 (6)	−0.1667 (2)	7.7 (1)
C(18)	−0.1193 (2)	0.2797 (4)	−0.1788 (1)	3.98 (7)
C(19)	−0.1817 (3)	0.4199 (5)	−0.2215 (1)	5.10 (8)
C(20)	−0.2028 (3)	0.4208 (5)	−0.2896 (1)	5.95 (9)
C(21)	−0.1613 (3)	0.2808 (5)	−0.3139 (1)	5.75 (9)
C(22)	−0.1002 (3)	0.1408 (5)	−0.2717 (1)	6.13 (9)
C(23)	−0.0787 (3)	0.1387 (5)	−0.2035 (1)	5.32 (8)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

S—C(2)	1.681 (2)	C(14)—C(15)	1.379 (5)
N(1)—C(2)	1.413 (4)	C(15)—C(16)	1.364 (6)
N(1)—C(5)	1.346 (2)	C(16)—C(17)	1.373 (5)
N(1)—C(6)	1.439 (3)	C(18)—C(19)	1.377 (4)
N(3)—N(4)	1.379 (3)	C(18)—C(23)	1.384 (5)
N(3)—C(2)	1.328 (3)	C(19)—C(20)	1.392 (4)
N(4)—C(5)	1.323 (4)	C(20)—C(21)	1.379 (5)
N(4)—C(12)	1.443 (3)	C(21)—C(22)	1.369 (4)
C(5)—C(18)	1.465 (4)	C(22)—C(23)	1.392 (4)
C(6)—C(7)	1.374 (4)	C(10)—C(11)	1.382 (5)
C(6)—C(11)	1.365 (4)	C(12)—C(13)	1.357 (5)
C(7)—C(8)	1.386 (4)	C(12)—C(17)	1.360 (5)
C(8)—C(9)	1.367 (5)	C(13)—C(14)	1.393 (4)
C(9)—C(10)	1.381 (6)		

C(2)—N(1)—C(5)	108.2 (2)	C(9)—C(10)—C(11)	121.2 (3)
C(2)—N(1)—C(6)	125.8 (2)	C(6)—C(11)—C(10)	118.5 (3)
C(5)—N(1)—C(6)	125.6 (2)	N(4)—C(12)—C(13)	118.9 (2)
N(4)—N(3)—C(2)	105.6 (2)	N(4)—C(12)—C(17)	118.3 (3)
N(3)—N(4)—C(5)	112.1 (2)	C(13)—C(12)—C(17)	122.8 (2)
N(3)—N(4)—C(12)	191.2 (1)	C(12)—C(13)—C(14)	118.6 (3)
C(5)—N(4)—C(12)	128.6 (3)	C(13)—C(14)—C(15)	119.3 (3)
S—C(2)—N(1)	125.8 (2)	C(14)—C(15)—C(16)	120.1 (3)
S—C(2)—N(3)	126.4 (2)	C(15)—C(16)—C(17)	121.0 (4)
N(1)—C(2)—N(3)	107.9 (2)	C(12)—C(17)—C(16)	118.2 (4)
N(1)—C(5)—N(4)	106.2 (2)	C(5)—C(18)—C(19)	120.6 (3)
N(1)—C(5)—C(18)	126.8 (3)	C(5)—C(18)—C(23)	119.2 (2)
N(4)—C(5)—C(18)	127.1 (2)	C(19)—C(18)—C(23)	120.3 (3)
N(1)—C(6)—C(7)	118.9 (2)	C(18)—C(19)—C(20)	119.9 (4)
N(1)—C(6)—C(11)	119.7 (3)	C(19)—C(20)—C(21)	119.7 (3)
C(7)—C(6)—C(11)	121.5 (3)	C(20)—C(21)—C(22)	120.4 (3)
C(6)—C(7)—C(8)	119.2 (3)	C(21)—C(22)—C(23)	120.3 (3)
C(7)—C(8)—C(9)	120.6 (3)	C(18)—C(23)—C(22)	119.4 (3)
C(8)—C(9)—C(10)	119.2 (3)		

C(2)—N(1)—C(6)—C(7)	−108.9 (3)	C(5)—N(4)—C(12)—C(13)	−116.8 (3)
C(2)—N(1)—C(6)—C(11)	69.3 (4)	C(5)—N(4)—C(12)—C(17)	65.9 (4)
C(5)—N(1)—C(6)—C(7)	63.4 (4)	N(1)—C(5)—C(18)—C(19)	−125.5 (3)
C(5)—N(1)—C(6)—C(11)	−118.4 (3)	N(1)—C(5)—C(18)—C(23)	55.3 (4)
N(3)—N(4)—C(12)—C(13)	67.6 (4)	N(4)—C(5)—C(18)—C(19)	55.6 (4)
N(3)—N(4)—C(12)—C(17)	−109.7 (3)	N(4)—C(5)—C(18)—C(23)	−123.6 (3)

bond length of 1.413 (4) Å is significantly longer but still less than the mean single-bond value of 1.478 Å for the above triazole compound.

The N(3)—N(4) length of 1.379 (3) Å is slightly shorter than the single-bond value of 1.401 Å (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), and the value of 1.393 (4) Å in the hydrochloride of 5-(4-methoxyphenyl)-4-phenyl-1,3,4-thiadiazolium-2-phenylaminide (Cheung, Echevarria, Galembeck, Maciel, Miller, Rumjanek & Simas, 1992). The fact that the C(2)—N(1) and N(3)—N(4) bond lengths are closer to the single-bond length supports the view, implicit in our definition of mesoionic compounds, that the conjugation in the pentatomic ring is not uniform, but is separated into two conjugated systems, one involving the atoms N(1), C(5) and N(4), and the other involving N(3), C(2) and S$^-$. This conjugation is likely to weaken the exocyclic bonds to the phenyl C atoms. Thus, the N(1)—C(6) length of 1.439 (3) Å and the N(4)—C(12) bond of 1.443 (3) Å are significantly longer than the value of 1.417 Å in the above triazole compound, and the C(5)—C(18) value of 1.465 (4) Å is comparable to other inter-ring C(sp^2)—C(sp^2) bonds. The dihedral angles formed by the least-squares planes of the triazole ring and the three phenyl rings are 66.6 (1)° for the ring C(6) – C(11), 112.8 (1)° for C(12) – C(17) and 55.5 (3)° for C(18) – C(23). N(3) is 2.40 Å from the H atom bonded to C(11) at $-x$, $-y$, $-z$, and 2.67 Å from the H atom bonded to C(7) at $-x$, $1-y$, $-z$; there is no other non-H to H atom intermolecular distance less than 2.91 Å. The shortest intermolecular distance involving non-H atoms is 3.24 Å for N(3) to C(7) at $-x$, $1-y$, $-z$.

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