Mesoionic Compounds. 1. Structure of 5-Methyl-2-piperidino-1,3-dithiolium-4-thiolate

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Abstract. $C_9H_{13}NS_3$, $M_r = 231.39$, triclinic, $P\bar{1}$, $a = 6.783$ (1), $b = 7.617$ (2), $c = 11.725$ (1) Å, $\alpha = 82.61$ (1), $\beta = 74.31$ (1), $\gamma = 66.06$ (2)°, $V = 533.0$ (2) Å^3, $Z = 2$, $D_x = 1.442$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 6.2$ cm^{-1}, $F(000) = 244$, $T = 295$ K, $R = 0.034$ for 1127 reflections with $|F_o| > 3\sigma(|F_o|)$. This mesoionic compound has, in the pentatomic ring system, two short C—S bonds [1.717 (3) and 1.715 (4) Å] which are comparable to the C—S$^-$ (thiolate) bond of 1.714 (4) Å, and two longer C—S bonds [1.777 (3) and 1.745 (3) Å].

Introduction. The concept of mesoionic compounds has developed gradually, undergoing a number of changes over the years. A reasonably well accepted current description is that mesoionic compounds are a class of heteroaromatic betaines, characterized by possessing a pentatomic heterocyclic system with a sextet of π electrons associated with the heterocycle and which also supports a formal positive charge. This is counter-balanced by a formal negative charge on the α atom of a side chain.

The extent of delocalization of the positive charge within and, indeed, outside the pentatomic heterocycle and the degree of aromaticity or level of aromatic stabilization energy have not yet been sufficiently studied and clarified. There is, nevertheless, ample evidence to support the separation of charge and the existence of positive charge associated with the pentatomic heterocycle.

Bearing in mind the mode of aromaticity of pentatomic heteroaromatic compounds, we consider it appropriate to represent mesoionic compounds generally as shown in (1) below.

(1)
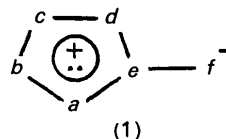
The inclusion of an electron pair, as well as positive charge within the circle representing an aromatic sextet, refers to the contribution of a pair of electrons to the aromtic sextet by one of the heteroatoms.

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It is worth stressing at this point that the side chain f is not necessarily monatomic and where this is so the possibility of delocalization of the negative charge may arise. The extent to which the bond to f has an order greater than unity has been considered in various systems, noting that a degree of double-bond character implies some reduction in polarity and in aromatic character.

Experimental. Orange crystal of dimensions $0.05 \times 0.1 \times 0.15$ 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 ($10 < 2\theta < 13°$) measured on the diffractometer. The intensities of 3732 reflections ($2\theta_{max} = 50°$), in the range $-8 \le h \le 8$, $-9 \le k \le 9$, $-13 \le l \le 13$ were measured using ω–2θ scans, ω-scan angle $(0.60 + 0.344\tan\theta)°$ at 0.87–$5.49°$ min^{-1}, extended 25% on each side for background measurement. Three standard reflections measured every 2 h showed no decay. Wilson statistics indicated a centrosymmetric space group; the structure solution confirmed $P\bar{1}$. The intensity data were corrected for Lorentz and polarization effects. After equivalent reflections had been averaged, the 3732 measured data gave 1866 independent reflections, of which 1127 with $I > 1.5\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2)$ ($S = $ scan, B_1 and $B_2 = $ background counts), were considered observed. $R_{int} = 0.022$ for observed reflections and 0.041 for all reflections. The structure was solved with the fragment N—CS$_2$ as input using *DIRDIF* (Beurskens *et al.*, 1984), which gave all non-H atoms, and refined by full-matrix least squares with atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV), using the *SDP* programs (Enraf–Nonius, 1985) on a MicroVAXII computer. The H atoms in calculated positions were not refined. Convergence for 118 variables by least squares with $w = 4F_o^2/[\sigma^2(F_o)^2 + (0.03F_o^2)^2]$ was reached at $R = 0.034$, $wR = 0.039$ and $S = 1.172$ for the 1127 reflections with $|F_o| > 3\sigma(|F_o|)$. $(\Delta/\sigma)_{max} = 0.05$. A final difference Fourier map was featureless, with maximum positive and negative peaks of 0.38
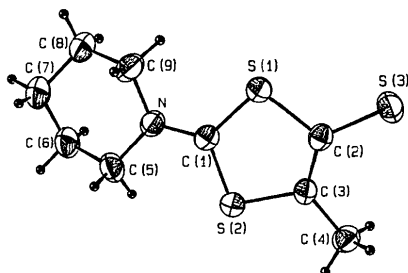

Fig. 1. *ORTEP* drawing of the molecule with numbering of atoms.

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

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

	x	y	z	B_{eq}
S(1)	0.2012 (1)	0.2293 (1)	0.49984 (8)	2.98 (2)
S(2)	−0.2076 (1)	0.2809 (1)	0.44452 (8)	2.87 (2)
S(3)	0.0528 (2)	0.1649 (1)	0.75827 (8)	3.76 (2)
N	0.1514 (4)	0.2777 (4)	0.2774 (2)	2.87 (7)
C(1)	0.0612 (5)	0.2645 (4)	0.3917 (3)	2.57 (8)
C(2)	−0.0121 (5)	0.2138 (5)	0.6231 (3)	2.73 (8)
C(3)	−0.2034 (5)	0.2406 (5)	0.5940 (3)	2.65 (8)
C(4)	−0.4087 (5)	0.2348 (5)	0.6791 (3)	3.44 (9)
C(5)	0.0122 (6)	0.3246 (5)	0.1911 (3)	3.5 (1)
C(6)	0.1499 (6)	0.2414 (6)	0.0708 (3)	4.1 (1)
C(7)	0.3504 (6)	0.2971 (6)	0.0292 (3)	4.7 (1)
C(8)	0.4944 (6)	0.2213 (6)	0.1183 (3)	4.2 (1)
C(9)	0.3652 (6)	0.3023 (6)	0.2401 (3)	3.9 (1)

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

S(1)—C(1)	1.715 (4)	N—C(9)	1.480 (5)
S(1)—C(2)	1.777 (3)	C(2)—C(3)	1.360 (5)
S(2)—C(1)	1.717 (3)	C(3)—C(4)	1.492 (5)
S(2)—C(3)	1.745 (3)	C(5)—C(6)	1.516 (5)
S(3)—C(2)	1.714 (4)	C(6)—C(7)	1.525 (7)
N—C(1)	1.323 (4)	C(7)—C(8)	1.523 (7)
N—C(5)	1.481 (5)	C(8)—C(9)	1.517 (5)

C(1)—S(1)—C(2)	97.7 (2)	S(3)—C(2)—C(3)	129.9 (3)
C(1)—S(2)—C(3)	97.0 (2)	S(2)—C(3)—C(2)	117.5 (2)
C(1)—N—C(5)	119.4 (3)	S(2)—C(3)—C(4)	117.3 (3)
C(1)—N—C(9)	119.4 (3)	C(2)—C(3)—C(4)	125.3 (3)
C(5)—N—C(9)	118.7 (3)	N—C(5)—C(6)	111.4 (3)
S(1)—C(1)—S(2)	114.1 (2)	C(5)—C(6)—C(7)	110.8 (4)
S(1)—C(1)—N	123.2 (3)	C(6)—C(7)—C(8)	109.4 (3)
S(2)—C(1)—N	122.7 (3)	C(7)—C(8)—C(9)	111.2 (3)
S(1)—C(2)—S(3)	116.4 (2)	N—C(9)—C(8)	111.4 (4)
S(1)—C(2)—C(3)	113.7 (3)		

C(9)—N—C(1)—S(1)	−12.6 (4)	N—C(5)—C(6)—C(7)	−51.5 (4)
C(9)—N—C(1)—S(2)	167.5 (3)	C(5)—C(6)—C(7)—C(8)	59.7 (4)
C(1)—N—C(5)—C(6)	−152.1 (3)	C(6)—C(7)—C(8)—C(9)	−59.4 (4)
C(1)—N—C(9)—C(8)	152.7 (3)	C(7)—C(8)—C(9)—N	50.8 (4)
C(5)—N—C(9)—C(8)	−45.1 (4)		

and 0.21 e Å^{-3} respectively. There are no intermolecular distances less than 3.5 Å.

Discussion. An *ORTEP* drawing (Johnson, 1976) of the molecule with atomic numbering scheme is shown in Fig. 1. The atomic parameters of C, N, S atoms are listed in Table 1.* Bond lengths and bond angles and selected torsion angles are given in Table 2. The C(2)—C(3) bond of 1.360 (5) Å is comparable to the C=C bond of 1.362 (25) Å in thiophenes (Allen, Kennard, Watson, Brammer, Orpen &

Taylor, 1987). The S(3)—C(2) bond of 1·714 (4) Å is longer than the C=S bond of 1·683 (1) Å in the substituted thione 4-phenylthiazole-2(3*H*)-thione (Nalini & Desiraju, 1989), and is comparable to the S(1)—C(1) and S(2)—C(1) bonds of 1·715 (4) and 1·717 (3) Å respectively, but is significantly shorter than the S(1)—C(2) and S(2)—C(3) bonds of 1·777 (3) and 1·745 (3) Å respectively. The short S(3)—C(2) bond can be viewed as a single bond with the S atom carrying a negative charge so that C(2) is positive relative to S(3). The comparable and short S(1)—C(1) and S(2)—C(1) bonds can be viewed as a positive charge in the pentatomic ring close to C(1), so that C(1) is positive relative to the S(1) and S(2) atoms. The pentatomic ring system is nearly planar and the torsion angles involving the ring system are close to 0 and 180°. All the features of the pentatomic heterocyclic system in this compound agree very well with those in 2-morpholino-5-propyl-1,3-dithiolium-4-thiolate (Cheung, Galembeck, Miller, de Oliveira, Pereira & Simas, 1992). The C(1)—N bridging distance between the two ring systems is 1·323 (4) Å. The piperidyl ring has a chair conformation with N and C(7) deviating −0·500 (3) and

0·708 (4) Å respectively from the plane through C(5), C(6), C(8) and C(9). The two C_{sp^3}—N_{sp^3} bonds are 1·481 (5) and 1·480 (5) Å. The two C_{sp^3}—C_{sp^3} bonds [1·525 (7) and 1·523 (7) Å] farther away from the N atom are longer than the other two [1·516 (5) and 1·517 (5) Å] although the differences are not significant. All six bond angles are close to 109·5°.

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Stereochemical Studies. 124.* Structures of (I) *cis-* and (II) *trans*-Decahydroquinazoline-2-spiro-1'-cyclohexan-4-one

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Abstract. $C_{13}H_{22}N_2O$, $M_r = 222·32$. The title compound has two conformations, *cis* (I) and *trans* (II). Compound (I): monoclinic, $P2_1/c$, $a = 10·859$ (2), $b = 10·745$ (3), $c = 10·975$ (2) Å, $\beta = 101·13$ (3)°, $V = 1256·5$ (3) Å^3, $Z = 4$, $D_x = 1·175$ Mg m^{-3}, m.p. 428–429 K, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 0·070$ mm^{-1}, $F(000) = 488$, $T = 293$ K, final $R = 0·058$ for 1735 reflections with $I > 2·5\sigma(I)$. Compound (II): triclinic, $P\bar{1}$, $a = 11·836$ (1), $b = 9·879$ (1), $c = 5·726$ (2) Å, $\alpha = 101·23$ (1), $\beta = 103·08$ (1), $\gamma = 94·02$ (1)°, $V =$ 635·1 (1) Å^3, $Z = 2$, $D_x = 1·162$ Mg m^{-3}, m.p. = 471–472 K, $\lambda(\text{Cu } K\alpha) = 1·54178$ Å, $\mu = 0·505$ mm^{-1}, $F(000) = 244$, $T = 293$ K, final $R = 0·044$ for 1792 reflections with $I > 1·5\sigma(I)$. The molecules in the two compounds have the expected bond lengths and angles and form dimers connected through N—H⋯O hydrogen bonds with the following lengths and angles: N3⋯O11 = 2·868 (3), H3⋯O11 = 2·056 (32) Å, ∠N3—H3⋯O11 = 165·0 (31)° in compound (I), and 2·861 (2), 1·979 (24) Å, 173·3 (21)°, respectively, in compound (II). The conformation of the pyrimidine ring is $^1H_6$ in both compounds.