The Molecular Structure of 1,3-Dimethyl-2(3*H*)-imidazolethione ($C_5H_8N_2S$)

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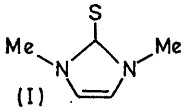
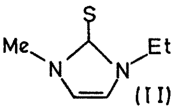
Summary The crystal structure of the heterocyclic molecule 1,3-dimethyl-2(3*H*)-imidazolethione and its ¹H n.m.r. spectrum have been interpreted as showing partial double-bond character in the N–C–N system, but no aromaticity.

AN investigation of the molecular structure of 1,3-dimethyl-2(3*H*)-imidazolethione, (I), was undertaken when it was

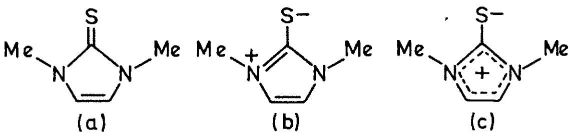


(I)



(II)

found that the compound had an unusually high melting point (181—182°) compared with its 1-methyl-3-ethyl homologue, (II) (51°). Both compounds were synthesized from *N*-methylimidazole by conversion into the appropriate dialkylimidazolium iodide and treatment with sulphur in methanolic K_2CO_3. An *X*-ray structure determination was undertaken to decide which of the three structures (a), (b), or (c) (Figure 1) best described the molecule.



(a) (b) (c)

FIGURE 1

Crystals suitable for *X*-ray investigation were grown from water: orthorhombic, *a* 8·475 Å, *b* 6·826 Å, *c* 11·306 Å, $Z = 4$, $D_m = 1{\cdot}29$ g.cm.$^{-3}$ Systematic absences show the space group to be *Bmmb* with each molecule having *mm* symmetry.

X-Ray data were collected with a diffractometer using Cu-K_α radiation and a scintillation counter. The structure was solved using Patterson and Fourier methods. The full-matrix structure-factor refinement (anisotropic for C, N, and S and fixed isotropic for H) using 153 statistically significant reflections with $2\theta < 120°$ and varying 31 parameters gave $R = 0{\cdot}031$.

Bond lengths and angles given in Figure 2 clearly indicate that structure (b) is the major contributor to the resonance hybrid. Absence of significant lengthening of the olefinic double bond, or shortening of the adjacent C–N bonds demonstrates the failure to form the delocalized aromatic bond system which might be expected for this molecule. However, the lengthening of the C=S bond and shortening of the two adjacent C–N bonds confirms the existence of some partial double-bond character. The C=S distance of 1·695 Å is shorter than the single bond value[1] of 1·81 Å and greater than the C=S value of 1·61 Å.[2,3] This appears to be generally representative of C–S bonding in molecules containing the grouping (>N–CS–X<)[4–7] where X = N or CH. Here the C–S distance varies from 1·64 to 1·71 Å, depending on substituents and the possibility of such resonance forms as (b).

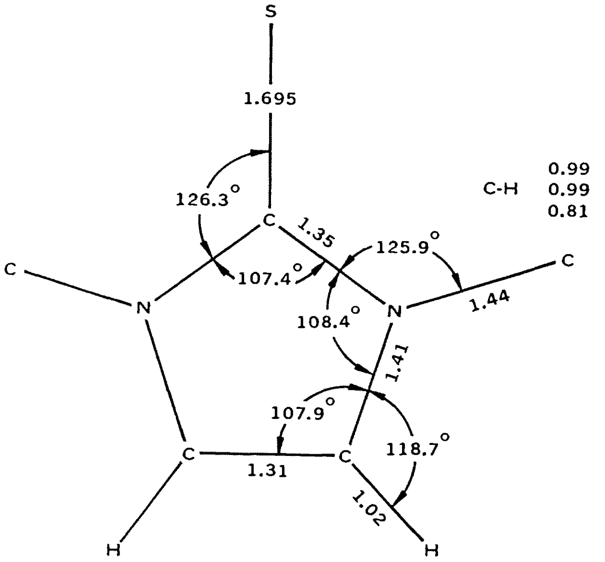


FIGURE 2. *Bond lengths and angles*: σ = 0·02 Å *for* C–S, 0·03 Å *for* C–N, C–C *and* 0·07 Å *for* C–H.

The 60 MHz ^{1}H n.m.r. spectrum of (I) shows only the expected two single signals, intensity ratio 1 : 3, at τ 3·25 and 6·42. These values are not significantly different from the shifts observed for the closely related 1-methylimidazole;[8] *N*-methyl shift τ 6·33, two olefinic protons 3·14 and 2·95.

To confirm the olefinic nature of the ring protons, the n.m.r. spectrum of (II) was investigated in several solvents. Using [$^2H_8$]toluene it was possible to obtain a sufficient chemical shift separation between H_4 and H_5 to observe a spin-coupled AB quartet, J = 2·2 Hz. This value is within the range 1·5—3·0 Hz generally found for substituted imidazoles.

It now appears that the high melting point of (I) as compared to (II) is a consequence of the more favourable symmetry of the crystal lattice (Figure 3) which permits stronger dipolar interaction between molecules in adjacent layers and a relatively dense packing of the molecules.

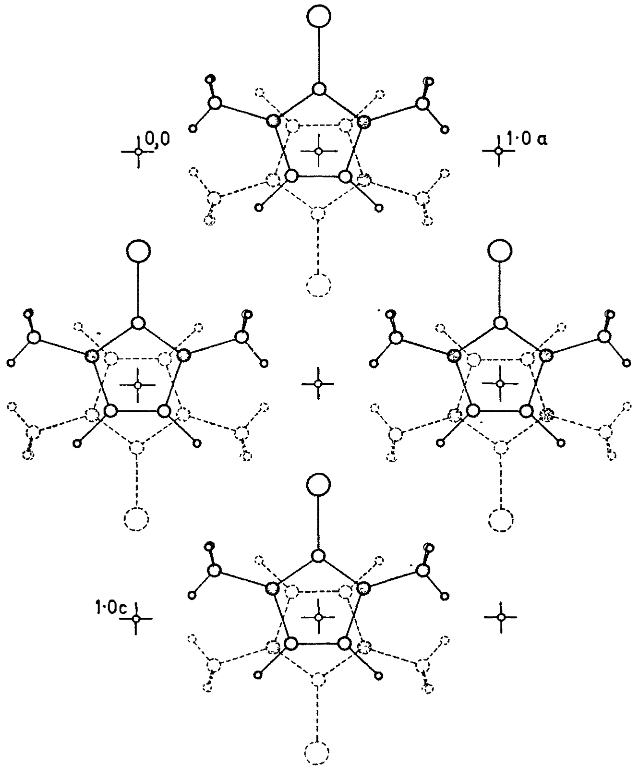


FIGURE 3. *Packing of molecules in the crystal lattice.*

(———) *Represents molecules at* b = 0·25.
(- - - - -) ,, ,, *at* b = − 0·25.

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