Crystal Structure of 1,3-Dimethylimidazole-2(3*H*)-thione ($C_5H_8N_2S$)

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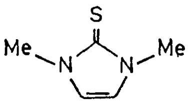
The structure of the title compound has been established by *X*-ray crystallography from diffractometer data. Crystals are orthorhombic, space group either *Bmmb* or $Bm2_1b$, $Z = 4$, with cell dimensions: $a = 8{\cdot}475 \pm 0{\cdot}002$, $b = 6{\cdot}826 \pm 0{\cdot}003$, $c = 11{\cdot}206 \pm 0{\cdot}005$ Å.

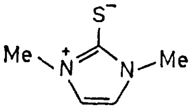
In space group *Bmmb*, 195 observable reflections were refined to *R* 0·028. The molecule has *mm* symmetry. The C–S distance and bond lengths within the five membered ring clearly indicate that (Ib) is the major contributor to the resonance hybrid (Ic). The planar molecules are stacked along the *b* axis with a perpendicular separation of 3·413 Å. All intermolecular distances appear to be van der Waals separations. The model was investigated for the effects of thermal motion on bond lengths. The corrections were of the order of the estimated standard deviations for the corresponding bonds.

In space group $Bm2_1b$ refinement stops at *R* 0·027. The molecule has *m* (pseudo-*m*) symmetry and differs only very slightly from the previous model. There are small changes in thermal parameters (particularly for hydrogen) and the methyl group is twisted very slightly so as not to lie symmetrically above, below, and in the plane formed by the heavy atoms. The ring hydrogens also deviate slightly from this plane.

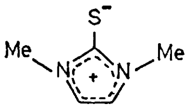
THE compound 1,3-dimethylimidazole-2(3*H*)-thione (I) was found to have an unusually high m.p. (181—182 °C) compared with its 1-ethyl-3-methyl homologue (51 °C). We have therefore carried out an *X*-ray structural analysis to determine whether the compound had a non-polar structure (Ia) or a polar structure (Ib) and (Ic).



(Ia)



(Ib)



(Ic)

EXPERIMENTAL

The synthesis of both compounds has been described earlier.[1] All dimensions were measured on a General Electric single-crystal orienter using Cu-K_{α_1} and Cu-K_{α_2} [$\lambda = 1{\cdot}54050$ and $1{\cdot}54434$ Å; $\mu(\text{Cu-}K_\alpha) = 35$ cm^{-1}] peaks at room temperature. The errors quoted were estimated from the observed deviations of individual values from their mean.

Crystal Data.—$C_5H_8N_2S$, $M = 128{\cdot}1$, Orthorhombic, $a = 8{\cdot}475 \pm 0{\cdot}002$, $b = 6{\cdot}826 \pm 0{\cdot}003$, $c = 11{\cdot}206 \pm 0{\cdot}005$ Å, $D_m = 1{\cdot}29$, $Z = 4$, $D_c = 1{\cdot}31$.

Systematic absences: *hkl* when $h + l = 2n + 1$, $0kl$ when $l = 2n + 1$; $h0l$ when $h + l = 2n + 1$, $hk0$ when $h = 2n + 1$, $h00$ when $h = 2n + 1$, $0k0$ when $k = 2n + 1$, and $00l$ when $l = 2n + 1$ showed the possibility of two space groups. (*a*) The four molecules can occupy the special *mm* or 2/*m* positions of space group *Bmmb* [a non-standard setting of *Cmcm* (No. 63)] with equivalent positions: $\pm(x, y, z;\ \tfrac{1}{2} + x, y, \tfrac{1}{2} + z;\ \tfrac{1}{2} + x, \tfrac{1}{2} - y, \tfrac{1}{2} + z;\ x, \tfrac{1}{2} - y, z;\ x, \tfrac{1}{2} + y, \bar{z};\ \tfrac{1}{2} + x, \tfrac{1}{2} + y, \tfrac{1}{2} - z;\ \tfrac{1}{2} + x, y, \tfrac{1}{2} - z;\ x, \bar{y}, \bar{z})$. Since the molecule cannot have 2/*m* symmetry each molecule could only occupy four special *mm* positions at $(0, \tfrac{1}{4}, z;\ 0, \tfrac{3}{4}, z;\ \tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{2} + z;\ \tfrac{1}{2}, \tfrac{3}{4}, \tfrac{1}{2} - z)$. (*b*) Alternatively, the four molecules could occupy the special position of *m* symmetry in the space group $Bm2_1b$ [a non-standard setting of space group $Cmc2_1$ (No. 36)] with equivalent positions: $x, y, z;\ \bar{x}, y, z;\ x, \tfrac{1}{2} + y, \bar{z};\ \bar{x}, \tfrac{1}{2} + y, \bar{z};\ \tfrac{1}{2} + x, y, \tfrac{1}{2} + z;\ \tfrac{1}{2} - x, y, \tfrac{1}{2} + z;\ \tfrac{1}{2} + x, \tfrac{1}{2} + y, \tfrac{1}{2} - z;\ \tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$

Intensity data were measured using a block crysyal of dimensions $0{\cdot}01 \times 0{\cdot}01 \times 0{\cdot}01$ cm. All *hkl* total intensities (T_c) were measured for $0° < 2\theta \leqslant 120°$ on the automated diffractometer described previously[2] by the moving-crystal–moving-counter 2θ scan method over a range of 3·66° at 2°-min^{-1}. Stationary-crystal–stationary-counter background counts of 40 s (B_1 and B_2) were made at 1·83° before and after the computed 2θ setting for the reflection. The integrated intensity of the reflection (I) was calculated as $I = T_c - 1{\cdot}83/1{\cdot}33\ (B_1 + B_2)$. Structure factors were obtained by application of the usual Lorentz and polarization corrections. Equivalent reflections were averaged. 195 reflections having a net count $> 1{\cdot}5\sigma$ [$\sigma^2 = T_c + 1{\cdot}83/1{\cdot}33\ (B_1 + B_2)$] were considered to be statistically significant, and were used in the subsequent refinement. The intensities were not corrected for absorption.

Solution and Refinement.—The *z* co-ordinate of the sulphur atom was found by solution of a three-dimensional Patterson synthesis using the Harker line $x = 0$, $y = \tfrac{1}{2}$. Carbon and nitrogen atoms were positioned by the usual Fourier and least-squares procedures. An isotropic full-matrix least-squares structure-factor calculation using scattering factors taken from ref. 3 terminated at *R* 0·116. At this stage hydrogen co-ordinates were predicted assuming tetrahedral and trigonal geometries around C(3) and C(2). Full-matrix anisotropic refinement for non-hydrogen atoms and isotropic refinement for hydrogen yielded a final conventional *R* value of 0·028 and weighted factor *R'* 0·031. During the last cycle of refinement shifts for all parameters were $< 0{\cdot}2\sigma$. A weighting scheme giving similar average values of $w\Delta^2$ for increasing ranges of *F* was chosen such that for reflections $> 18\sqrt{w} = 18/F_o$, for reflections $< 12\sqrt{w} = F_o/12$ and for reflections between 12 and 18, $w = 1$. Of the 85 reflections with $< 1{\cdot}5\sigma$, only 3 gave $F_c > F_t$ [$F_t = \sqrt{(1{\cdot}5\sigma \times Lp)}$]. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20280 (3 pp., 1 microfiche).*

The reflection (020) was omitted from least-squares calculations because it appeared to suffer from extinction. Reflections (200), (111), (101) were also excluded because

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* See note about supplementary publications in Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 11 (items less than 10 pp. will be supplied as full size copies).

[1] G. B. Ansell, D. M. Forkey, and D. W. Moore, *Chem. Comm.*, 1970, 56.

[2] G. B. Ansell, *J. Chem. Soc.* (*B*), 1969, 730.

[3] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham.

their backgrounds were asymmetric. Atomic positions with estimated standard deviations are given in Table 1, bond lengths and angles in Figure 1, temperature factor values in Table 2 and thermal amplitudes and vibration directions in Table 3.

Refinement of the Structure on the Basis of Space Group $Bm2_1b$.—This refinement was initiated with atomic co-ordinates based on those found in the *Bmmb* refinement, the same weighing scheme and the addition of a hydrogen atom, no longer generated by the symmetry of the *Bmmb* space-group, at (0·3158, 0·1400, 0·3425). The refinement quickly reached R 0·027 and R' 0·029. Although this R value is lower than that for the *Bmmb* refinement it should be noted that 55 parameters were varied for $Bm2_1b$ as compared with 36 for *Bmmb* and that successive refinements, although giving identical R and R' values, were giving shifts of the order of magnitude of the estimated standard deviation for the parameter. Atomic co-ordinates are listed in Table 1, thermal parameters in Table 2, and thermal elipsoid data in Table 3, all listed below the corresponding values for the *Bmmb* refinement.

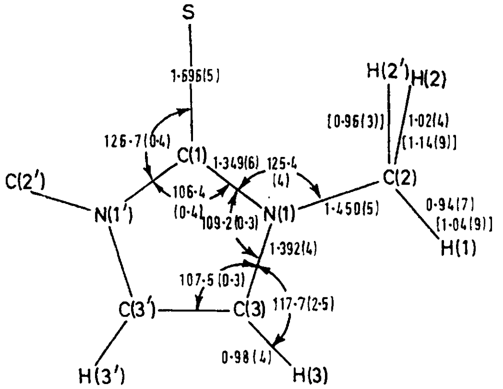

FIGURE 1 Bond lengths and angles (with estimated errors) within the molecule for *Bmmb* refinement. For the $Bm2_1b$ refinement, bond lengths vary by amounts smaller than the estimated standard deviations for *Bmmb* except for those shown in square brackets. For S and C(1) the standard deviation for the atom was taken as $\sigma(z)$, for C(2), C(3), N(1), H(1), and H(3) the root-mean-square of $\sigma(x)$ and $\sigma(z)$ and for H(2) the root-mean-square of $\sigma(x)$, $\sigma(y)$, $\sigma(z)$

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$),* with estimated standard deviations in parentheses (Å $\times$ 10^4)

	x	y	z
S	0(0)	2500(0)	2161(16)
	0(0)	2500(0)	2162(17)
C(1)	0(0)	2500(0)	3674(55)
	0(0)	2429(324)	3671(64)
C(2)	2905(41)	2500(0)	3996(46)
	2906(50)	2328(348)	3994(52)
C(3)	782(43)	2500(0)	5577(33)
	782(50)	2399(228)	5578(38)
N(1)	1276(27)	2500(0)	4393(27)
	1275(29)	2382(159)	4391(30)
H(1)	3685(813)	2500(0)	4594(606)
	3674(628)	3078(660)	4561(496)
H(2)	3158(322)	3616(333)	3425(548)
	2991(933)	3510(968)	3268(781)
H(3)	1595(416)	2500(0)	6195(420)
	1601(383)	2693(721)	6208(413)
H(2′)	Obtained by symmetry operations on H(2)		
	3220(702)	1172(839)	3569(784)

* Upper line, space group *Bmmb*; lower line, space group $Bm2_1b$.

TABLE 2

Final thermal parameters with their estimated standard deviations in parentheses; upper line *Bmmb*, lower line $Bm2_1b$

(*a*) Anisotropic * ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	127(2)	310(4)	46(1)	0(0)	0(0)	0(0)
	125(2)	299(6)	46(1)	0(0)	0(0)	5(12)
C(1)	127(9)	171(13)	57(4)	0(0)	0(0)	0(0)
	128(9)	206(21)	60(5)	0(0)	0(0)	70(25)
C(2)	113(6)	356(14)	95(5)	0(0)	−11(5)	0(0)
	108(6)	329(27)	93(5)	−5(33)	−14(5)	−5(32)
C(3)	170(6)	240(9)	54(3)	0(0)	9(4)	0(0)
	169(6)	236(14)	52(3)	18(25)	−8(4)	6(19)
N(1)	102(4)	186(7)	62(2)	0(0)	−7(3)	0(0)
	101(4)	181(10)	61(2)	−12(21)	−66(3)	2(19)

(*b*) Isotropic † ($\times 10^2$) $B/10^2$ Å^2

H(1)	943(229)
	333(181)
H(2)	481(85)
	237(280)
[H(2′]	436(174)
H(3)	202(87)
	113(98)

* In the form: $\exp -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$. † In the form: $\exp\{-B\,(\sin^2/\theta\lambda^2)\}$.

TABLE 3

Thermal elipsoid data *

Atom	R.m.s. amplitude (Å)	Direction angles (deg. relative to cell axes) a	b	c
S(1)	0·171	90·0	90·0	0·0
	(0·172)	(90·0)	(92·9)	(2·9)
	0·215	0·0	90·0	90·0
	(0·214)	(0·0)	(90·0)	(90·0)
	0·270	90·0	0·0	90·0
	(0·266)	(90·0)	(2·9)	(87·1)
C(1)	0·191	90·0	90·0	0·0
	(0·125)	(90·0)	(129·5)	(39·5)
	0·201	90·0	0·0	90·0
	(0·216)	(0·0)	(90·0)	(90·0)
	0·215	0·0	90·0	90·0
	(0·266)	(90·0)	(39·5)	(50·5)
C(2)	0·199	14·7	90·0	75·3
	(0·192)	(17·5)	(88·6)	(72·5)
	0·249	104·7	90·0	14·7
	(0·248)	(107·1)	(97·8)	(18·9)
	0·290	90·0	0·0	90·0
	(0·279)	(93·6)	(7·9)	(83·0)
C(3)	0·183	81·3	90·0	8·7
	(0·180)	(81·2)	(97·2)	(11·4)
	0·238	90·0	10·0	90·0
	(0·230)	(118·8)	(31·1)	(79·3)
	0·250	8·7	90·0	98·7
	(0·255)	(30·4)	(59·9)	(94·0)
N(1)	0·187	35·9	90·0	54·1
	(0·184)	(32·4)	(72·1)	(63·9)
	0·204	125·9	90·0	35·9
	(0·198)	(105·9)	(117·2)	(32·2)
	0·209	90·0	0·0	90·0
	(0·213)	(117·4)	(33·4)	(72·4)

* Upper line, *Bmmb*; lower line, in parentheses, $Bm2_1b$.

DISCUSSION

The Structure Based on Space Group Bmmb.—The compound consists of planar molecules (*mm* symmetry) stacked along the *b* axis with a perpendicular separation of 3·413 Å (half the *b* axis). Within the molecule the C–S distance of 1·696 Å is shorter than the single-bond value of 1·81 Å[3] and greater than the C=S value of 1·61 Å.[4,5] It is representative of C–S bonding in a selection of molecules containing the grouping -N–CS–X- where X = N or C.[6-13]

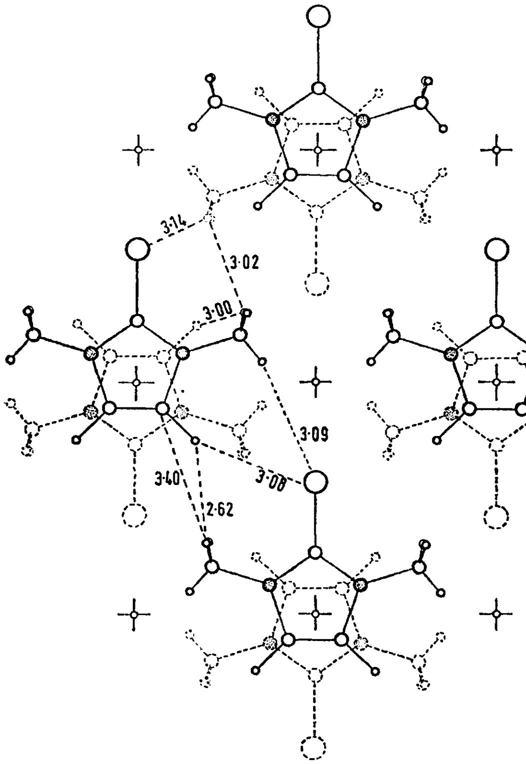

FIGURE 2 The packing of the molecules as viewed down the *b* axis; closest intermolecular contacts are shown (*Bmmb* refinement)

The identical adjacent C–N bonds are of 1·349 Å. A rigorous analysis of thermal motion[14] within the molecule shows that a correction of +0·007 may be necessary, bringing it up to 1·356 Å. Both the corrected and uncorrected values are very close to the value of 1·352 Å given as representative of partial double bonding in nitrogen heterocyclic systems.[3] The bond between C(3) and C(3′) is 1·325 Å (1·333 Å when corrected for thermal motion) and is clearly olefinic in nature. This and n.m.r.[1,15] evidence indicates that structure (Ib) is the major contributor to the resonance hybrid (Ic). The C(3)–N(1) value, 1·392 Å shows some shortening from the single-bond value due to the presence of the adjacent olefinc and partial double-bonds. The shortest intermolecular distances appear to be van der Waals separations and are shown in Figure 2.

The Structure Based on Space Group, $Bm2_1b$.—As a symmetry requirement the molecule has *m* symmetry perpendicular to the plane of the five-membered ring and passing through S and C(1). A pseudo-mirror-plane is still found passing through the eight heavy atoms of equation $-0{\cdot}000x - 1{\cdot}000y - 0{\cdot}0202z + 1{\cdot}726 = 0$ and deviations of the heavy atoms are $\leqslant 0{\cdot}046$ Å from it. The methyl hydrogens deviate −0·478, −0·743, and 0·845 Å from this plane as compared with 0·000 and ±0·762 Å in the *Bmmb* refinement. This indicates a little twisting and distortion of the methyl group. H(3) deviates 0·253 Å from this plane as compared with 0·000 Å in the *mm* description.

The bond lengths in this refinement are all almost identical to those found for *Bmmb* and lie within the estimated standard deviations quoted. The only small differences between these two descriptions of the structure seem to revolve around C–H bond lengths, hydrogen thermal parameters, and the orientation of the methyl and ring hydrogens. All the essential intra- and inter-molecular features of the compound are as discussed previously.

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[1/729 *Received*, 10*th May*, 1971]

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