Instrumental Achievements

— X-Ray Analysis —

Crystal Structure of 1-(4-Nitrobenzyl)-4-thiocarbamoyl-5-cyano-2-imidazolethione Monohydrate

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The imidazolethione and its derivatives are known to be synthetically and biologically useful compounds.

The C(1)=S(1) distance of 1.684(8) Å is shorter than the single bond distance of 1.81 Å and longer than the C=S double bond distance of 1.61 Å. This appears to be generally representative of C-S bonding in molecules containing the grouping (N-(C=S)-X) where X=N or CH.^{1,2} The shortening of the two adjacent C(1)-N(1) and C(1)-N(2) bonds confirms the existence of some partial double-bonded character (C-N: 1.36(1), 1.36(1) Å). This indicates that structures (a) and (b) contribute to the resonance hybrid. The shortening of the other two C(2)-N(1) and C(3)-N(2) bonds and the lengthening of a C(2)=C(3) bond confirms another contribution of structure (c) and (d) to the resonance hybrid (C-N: 1.39(1), 1.38(1) Å, C=C: 1.38(1) Å). Additional evidence

Fig. 1 View of the molecules. Thermal ellipsoids are at the 50% probability.

Scheme 1

Fig. 2 The packing in the cell.

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Table 1 Crystal data and experimental conditions

Formula: $C_{12}H_5N_5O_2S_2 \cdot H_2O$
Formula weight=337.4
Color and crystal habit: orange, plate
Crystal system: orthorhombic
Space group: $P2_12_12_1$ $Z=4$
$a=12.720(2)$ Å
$b=5.016(2)$ Å
$c=23.270(3)$ Å
$V=1484.8(5)$ Å ³
$D_x=1.498$ g/cm ³
$D_m=1.476$ g/cm ³
$R=0.085$
Range of measurement: $2\theta < 60^\circ$ (Mo K_α)
No. of reflections used=1347
Measurement: Rigaku AFC-III
Program system: HBLIS IV (by Ashida)
Structure determination: MULTAN78
Refinement: block-diagonal least squares method

Table 2 Final atomic coordinate ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2$), with e.s.d.'s in parentheses

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
S(1)	7653(2)	1275(5)	1975(1)	3.86(8)
S(2)	9070(2)	-8102(5)	145(1)	4.5(1)
O(1)	2083(4)	-7518(17)	1598(3)	5.5(3)
O(2)	3223(5)	-9313(16)	2144(3)	5.1(3)
N(1)	7181(4)	-1574(13)	1012(3)	3.2(3)
N(2)	8716(4)	-2482(14)	1353(3)	3.2(3)
N(3)	6700(6)	-4852(24)	-260(3)	6.0(5)
N(4)	10294(5)	-6039(18)	931(4)	5.3(4)
N(5)	2967(5)	-7697(17)	1803(3)	4.2(3)
OW	10677(5)	-2142(19)	1933(3)	6.5(4)
C(1)	7856(6)	-924(16)	1442(3)	3.1(3)
C(2)	7624(5)	-3489(17)	661(3)	3.1(3)
C(3)	8603(5)	-4092(16)	873(3)	2.7(3)
C(4)	7132(6)	-4345(20)	144(4)	4.0(4)
C(5)	9375(6)	-6039(18)	671(3)	3.2(3)
C(6)	6109(5)	-482(17)	949(3)	3.2(3)
C(7)	5278(5)	-2334(17)	1185(3)	2.9(3)
C(8)	5475(5)	-3980(20)	1642(4)	3.5(4)
C(9)	4731(6)	-5736(18)	1863(3)	3.4(4)
C(10)	3750(5)	-5721(18)	1590(3)	2.8(3)
C(11)	3503(6)	-4103(21)	1157(4)	3.8(4)
C(12)	4261(6)	-2328(22)	948(4)	4.0(4)

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* (a_i \cdot a_j).$$

for the contribution of the structure (c) and (d) is seen in the shortening of C(2)–C(4) (1.43(1) Å) and lengthening of C(4)–N(3) (1.13(2) Å) and C(5)–S(2) (1.653(9) Å) and also in the non-linearity of the C–CN group (175(1)°). Thus four structures (a), (b), (c) and (d) contribute to

Table 3 Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

S1	-C1	1.684(8)	C1	-N1	-C3	111.9(6)	
S2	-C5	1.653(9)	O1	-N5	-O2	124.6(9)	
O1	-N5	1.23(1)	O1	-N5	-C10	115.8(8)	
O2	-N5	1.18(1)	O2	-N5	-C10	119.6(8)	
N1	-C1	1.36(1)	S1	-C1	-N1	127.2(6)	
N1	-C2	1.38(1)	S1	-C1	-N2	127.7(6)	
N1	-C6	1.48(1)	N1	-C1	-N2	105.0(6)	
N2	-C1	1.36(1)	N1	-C2	-C3	108.0(7)	
N2	-C3	1.39(1)	N1	-C2	-C4	122.1(7)	
N3	-C4	1.13(2)	C3	-C2	-C4	129.7(8)	
N4	-C5	1.32(1)	N2	-C3	-C2	104.9(6)	
N5	-C10	1.49(1)	N2	-C3	-C5	125.3(7)	
C2	-C3	1.38(1)	C2	-C3	-C5	129.7(7)	
C2	-C4	1.43(1)	N3	-C4	-C2	175(1)	
C3	-C5	1.47(1)	S2	-C5	-N4	123.5(7)	
C6	-C7	1.51(1)	S2	-C5	-C3	119.9(6)	
C7	-C8	1.37(1)	N4	-C5	-C3	116.6(7)	
C7	-C12	1.41(1)	N1	-C6	-C7	112.6(6)	
C8	-C9	1.39(1)	C6	-C7	-C8	121.6(7)	
C9	-C10	1.41(1)	C6	-C7	-C12	120.0(8)	
C10	-C11	1.34(1)	C8	-C7	-C12	118.4(8)	
C11	-C12	1.40(2)	C7	-C8	-C9	122.9(8)	
			C8	-C9	-C10	115.8(8)	
			N5	-C10	-C9	116.2(7)	
C1	-N1	-C2	110.2(6)	N5	-C10	-C11	119.9(8)
C1	-N1	-C6	124.6(6)	C9	-C10	-C11	123.9(8)
C2	-N1	-C6	125.1(6)	C10	-C11	-C12	119.1(9)
				C7	-C12	-C11	119.8(9)

the resonance hybrid. Especially for the contribution of (c) and (d) structures, imidazole ring and cyano or carbamoyl group are conjugated with each other, suggesting that this imidazole ring has higher aromaticity than that of a normal imidazole ring.

The crystal structure is stabilized by three hydrogen bonds. They are N(2)–H...OW, 2.84(2) Å, 168(2)°; N(4)–H...OW, 3.08(3) Å, 177(2)°; N(4)–H...O(1), 2.86(3) Å, 106(2)°. The molecules are stacked along the *b* axis.

References

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