Crystal Structure of 1-Ethyl-3-methylbenzimidazole-2-thione

Şebnem Kandil İNGEÇ*1†, Hüseyin SOYLU*1, Hasan KÜÇÜKBAY*2, Filiz ERCAN*3 and Mehmet AKKURT*4

*1 *Gazi University, Gazi Education Faculty, Physics Department, 06500 Besevler, Ankara, Turkey*
*2 *Inönü University, Faculty of Sciences, Department of Chemistry, 44069 Malatya, Turkey*
*3 *Hacettepe University, Department of Engineering Physics, Beytepe, 06532 Ankara, Turkey*
*4 *Erciyes University, Arts and Sciences Faculty, Physics Department, 38039 Kayseri, Turkey*

Electron-rich olefins, especially tetraaminoethylenes, are strong reducing agents and react with sulfur to give cyclic thiourea derivatives in high yield. Cyclic thioureas (*e.g.*, imidazolidine-2-thione) are of considerable importance as ligands in transition metal chemistry. There are extensive studies about cyclic thiourea, particularly those having imidazole moiety, and X-ray crystal structures of this type of cyclic ureas had been published. However, there is no example of an X-ray crystal structure study for the cyclic thiourea having benzimidazole moiety. To a solution of bis(1-ethyl-3-methylbenzimidazolidine-2-ylidine) (1 g; 3.12 mmol) in toluene (30 cm^3) is sulfur (0.2 g; 6.25 mmol) was added and the mixture was refluxed for 3 h. Then all the volatiles were driven off and the residue was solved in EtOH (15 cm^3). After the solution was cooled to –30°C, white crystals of the title compound were obtained: 1.02 g; 85% m.p.=54 – 55°C. All reactions were performed under an argon or dinitrogen atmosphere with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. ^1H and ^{13}C NMR spectra were recorded.

The aim of this study was to elucidate the crystal structure of cyclic thiourea having benzimidazole moiety. Table 1 shows the crystal and experimental data. The final coordinates and equivalent thermal parameters for non-hydrogen atoms are given in Table 2, selected bond

Table 1 Crystal and experimental data

Formula: $C_{10}H_{12}N_2S$	
Formula weight=192.28	
Crystal system: tetragonal	
Space group: $P4_2/n$	Z=8
a=15.0380(10)Å	α=90.00°
b=15.0380(10)Å	β=90.00°
c=9.2640(10)Å	γ=90.00°
V=2095.0(3)Å^3	
D_x=1.219 g/cm^3	
μ(Mo K$_\alpha$)=0.265 mm^{-1}	
T=293(2)K	
Light yellow	
F(0 0 0)=816	
Crystal size=0.25×0.35×0.40 mm	
Radiation=Mo K$_\alpha$	
R=0.0478	
wR=0.1373	
No. of reflections used=1501	
No. of parameters=121	
Goodness-of-fit: 1.179	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Refinement: full matrix least-squares (SHELXL-97)	
Program system: CAD-4 EXPRESS software	
Structure determination: SHELXS-97	
Treatment of hydrogen atoms: geometric calculation	

† To whom correspondence should be addressed.

Table 2 Final coordinates and equivalent anisotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	U_{eq}/Å^2
S1	0.10218(9)	0.32493(9)	0.16588(14)	0.1117(7)
N1	0.15655(19)	0.19971(19)	-0.0258(3)	0.0821(9)
N2	0.0926(2)	0.3139(2)	-0.1280(4)	0.0853(10)
C1	0.1171(2)	0.2785(2)	0.0016(4)	0.0814(11)
C2	0.1571(2)	0.1844(3)	-0.1749(4)	0.0823(11)
C3	0.1882(3)	0.1143(3)	-0.2575(5)	0.1009(13)
C4	0.1776(4)	0.1220(4)	-0.4067(6)	0.1209(18)
C5	0.1375(4)	0.1943(5)	-0.4678(6)	0.1286(19)
C6	0.1060(3)	0.2623(4)	-0.3866(5)	0.1102(15).
C7	0.1164(2)	0.2572(3)	-0.2384(4)	0.0844(10)
C8	0.1931(3)	0.1407(3)	0.0846(5)	0.1049(14)
C9	0.1253(4)	0.0774(3)	0.1427(6)	0.1234(17)
C10	0.0504(3)	0.4000(3)	-0.1457(6)	0.1162(16)

$U_{eq}=(1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

Table 3 Selected bond distances (Å) and angles (°)

S1	C1		1.689(4)	N2	C7		1.379(5)
N1	C1		1.349(5)	N2	C10		1.451(5)
N1	C2		1.401(5)	C7	C6		1.384(6)
N1	C8		1.462(5)	C3	C4		1.397(8)
C2	C3		1.384(5)	C8	C9		1.495(8)
C2	C7		1.385(5)	C6	C5		1.355(8)
N2	C1		1.364(5)	C5	C4		1.366(8)
C1	N1	C2	109.4(3)	N1	C1	S1	126.3(3)
C1	N1	C8	124.5(3)	N2	C1	S1	126.5(3)
C2	N1	C8	126.0(3)	N2	C7	C6	132.2(4)
C3	C2	C7	121.1(4)	N2	C7	C2	106.8(3)
C3	C2	N1	132.2(4)	C6	C7	C2	121.0(4)
C7	C2	N1	106.6(3)	C2	C3	C4	116.4(5)
C1	N2	C7	109.9(3)	N1	C8	C9	112.4(4)
C1	N2	C10	124.5(4)	C5	C6	C7	118.0(5)
C7	N2	C10	125.6(4)	C6	C5	C4	121.7(5)
N1	C1	N2	107.2(3)	C5	C4	C3	121.8(5)

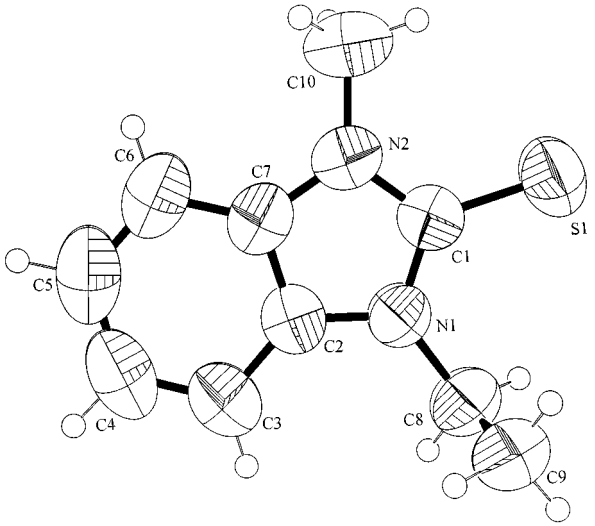

Fig. 1 The molecular structure of the title compound with the atom numbering scheme.

distances and angles in Table 3. Figure 1 represents the molecular structure of the title compound. The bond lengths and angles are similar to those found in *cis*-1,1′-dimethyl-3,3′-diphenyl-2,2′-biimidazolidinylidene[5] and in 4,5,6,7-tetrahydro-1,3-benzimidazole-2-thione.[1] All atoms except C9 and C10 are coplanar (r.m.s. deviation 0.005 Å). C9 atom lies below 1.372(8)Å. Torsion angles for C1–N1–C8–C9 and C2–N1–C8–C9 are 88.0(5) and –92.3(5)°, respectively. C10 atom lies above 0.042(6)Å. In other similar structures the five-membered imidazole ring and the six-membered ring are not in the same plane. The five-membered ring is generally planar. Phenyl ring atoms have a distorted half-chair conformation in 4,5,6,7-tetrahydro-1,3-benzimidazole-2-thione.[1] The bond length of S1–C1 is 1.694(4)Å. In similar studies, this length has been reported to be 1.685(3)Å in a 1:1 adduct of 4,6-dimethylpyrimidine-2(1*H*)-thione and thiourea[2] and 1.690(3)Å in 4,5,6,7-tetrahydro-1,3-benzimidazole-2-thione.[1] In our structure, C1–N2 bond length [1.361(5)Å] is longer than C1–N1 bond length [1.346(5)Å], although the bond lengths of C1–N1 and C1–N2 are about the same in the other similar structures.

The authors wish to acknowledge the purchase of the CAD4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey

References

1. Y. Kitano, A. Ishitani, H. Sato, S. Imamura and T. Ashida, *Acta Crystallogr*., **C47**, 1269 (1991).
2. S. Seth and H. Sur, *Acta Crystallogr*., **C51**, 487 (1995).
3. G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany (1997).
4. G. M. Sheldrick, SHELXS-97. Program for the Solution of Crystal Structures. Univ. of Göttingen, Germany (1997).
5. D. Ülkü, M. N. Tahir, B. Çetinkaya and I. Özdemir, *Acta Crystallogr*., **C53**, 240 (1997).

(Received December 28, 1998)
(Accepted May 31, 1999)