Tetrahedron Letters No. 40, pp 3695 - 3696, 1971. Pergamon Press. Printed in Great Britain.

THE MOLECULAR STRUCTURE OF 1,3-DIMETHYL-4-IMINO-5-OXO-2-THIONE-IMIDAZOLIDINE

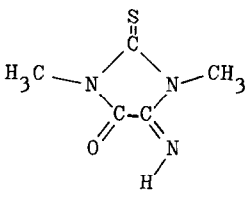
Takeshi Kinoshita, Sadao Sato and Chihiro Tamura

Central Research Laboratories, Sankyo Co., Ltd.

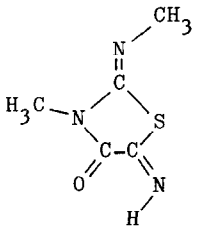
Hiromachi, Shinagawa-ku, Tokyo, Japan

(Received in Japan 14 July 1971; received in UK for publication 15 August 1971)

Reaction of methylaminoacetonitrile with methyl isocyanate in methanol gave a novel compound (I-a or b) for which the physico chemical data are: n.m.r., 10.10 (s, 1H), 3.37 (s, 3H), 3.23 (s, 3H) δ p.p.m. in DMSO; i.r., 3250 (N-H), 1755 (C=O), 1680 (C=N) cm^{-1} (nujol); u.v., λ max 309 mμ (ε=11400) in EtOH. Although intramolecular rearrangements by electron bombardment are often observed for sulfur containing compounds[1,2,3], the structure of this reaction product was successfully established as 1,3-dimethyl-4-imino-5-oxo-2-thione-imidazolidine (I-a) by these mass fragmentation analyses as shown in Fig. 1 and Table 1.



(I-a)



(I-b)

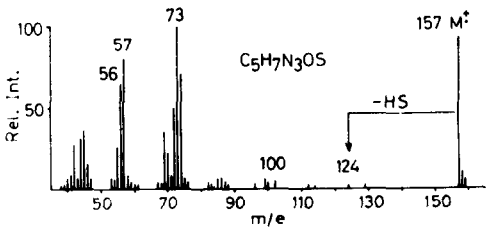


Fig. 1. Mass spectrum of (I).

In order to determine the crystal structure and demonstrate the stability of imino group in crystalline state, X-ray analysis has been carried out. Cell constants are : a = 4.48, b = 6.83, c = 23.61 Å, β = 91.0°, space group = $P2_1/c$, z = 4. Symbolic addition procedures

Table 1. High resolution mass of (I).

m/e	composition	M.W.obs.	M.W.calc.
157	$C_5H_7N_3OS$	157.030	157.031
102	$C_3H_6N_2S$	102.027	102.025
100	$C_3H_4N_2S$	100.008	100.010
73	C_2H_3NS	72.998	72.999
70	$C_3H_6N_2$	70.055	70.053
57	$C_2H_5N_2$	57.043	57.045
	C_2H_3NO	57.021	57.021
56	$C_2H_4N_2$	56.035	56.037

were applied for the phase determination. After determination of the molecular structure of (I), seven cycles of the full matrix least squares refinements were proceeded and the R-factor reached to 14.1% at this state. For a total of ten atoms, the deviation from its least squares plane is within 0.035 Å. The C=S bond distance, 1.624 Å is somewhat shorter than those reported on the similar molecules[4,5,6]. No intermolecular hydrogen bonding and significant short contacts are observed. Thus, the imino proton may be hydrogen bonded intramolecularly to the carbonyl group.

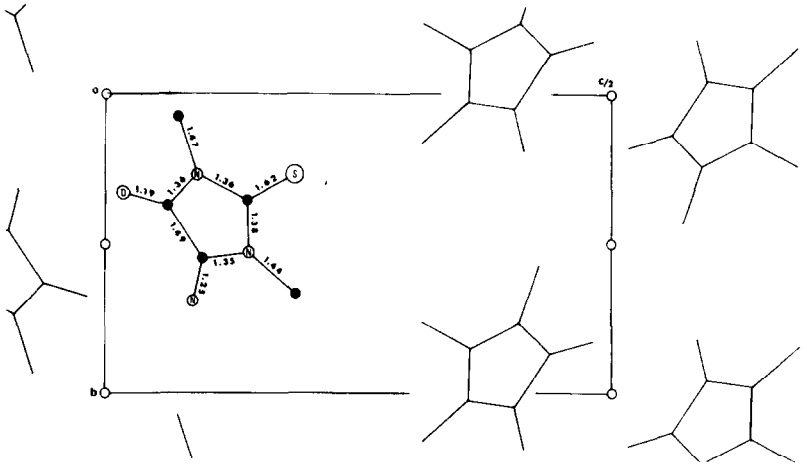


Fig. 2. Crystal and molecular structure of (I).

The reaction mechanism and the structural investigation are currently under progress.

References

1) S. O. Lawesson, L. Dalgaard and J. O. Madsen, Chem. Comm., 218 (1969).

2) A. Ohno, T. Koizumi, Y. Ohnishi and G. Tsuchihashi, Org. Mass Spectrum., 3, 261 (1970).

3) T. Kinoshita, S. Sato and C. Tamura, Abstracts of third international congress of heterocyclic chemistry (1971), in press.

4) I. L. Karle and J. Karle, Acta Cryst., 19, 92 (1965).

5) Y. Kushi and Q. Fernand, Chem. Comm., 1240 (1969).

6) G. B. Ansell, D. M. Forkey and D. W. Moore, Chem. Comm., 56 (1970).