Crystal and Molecular Structure of the Addition Product of *N*-Thiocarbamoylpiperidine and Dimethyl Acetylenedicarboxylate

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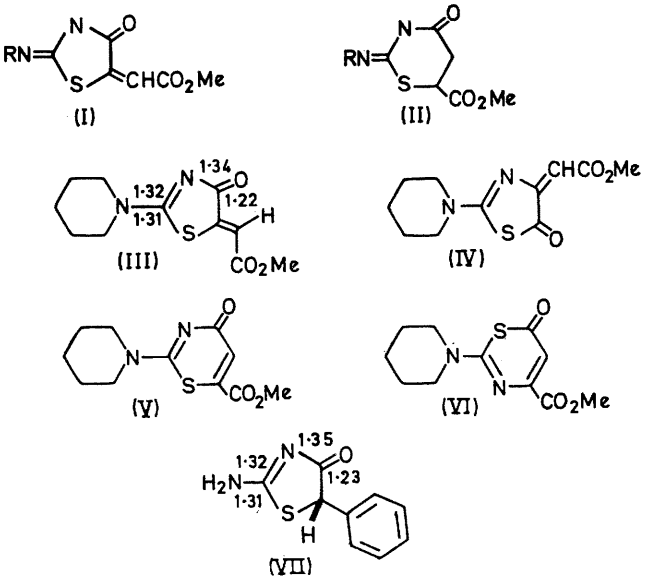
Summary The addition product of *N*-thiocarbamoylpiperidine and dimethyl acetylenedicarboxylate has been shown by *X*-ray structure analysis to be 5-methoxycarbonylmethylene-2-piperidino-Δ^2-1,3-thiazol-4-one (III)

THE structures of the products obtained by the addition of thioureas to dimethyl acetylenedicarboxylate have been the subject of considerable speculation. Early studies[1] suggested that they possessed the thiazolin-4-one (I) type of structure, but in later publications[2] they were considered to be 1,3-thiazines (II), although this latter assignment has recently been refuted.[3] We have synthesised several such compounds, and on the basis of preliminary spectroscopic investigations rejected (II) as a possible formulation, but could not unambiguously assign more definite structures. This problem has now been resolved in one case by an *X*-ray analysis of the most suitably crystalline of our compounds, formed by the addition of *N*-thiocarbamoyl-piperidine to dimethyl acetylenedicarboxylate. The interaction of this bidentate nucleophile and the acetylenic ester can plausibly generate six isomeric products, (V), (VI) and the geometrical isomers of (III) and (IV). The crystal structure analysis of the single product of this reaction shows conclusively that it is 5-methoxycarbonylmethylene-2-piperidino-Δ^2-1,3-thiazol-4-one (III), with the stereochemistry shown.



Compound (III) $C_{11}H_{14}N_2O_3S$, is monoclinic, space group $P2_1/c$, a = 10·25, b = 16·51, c = 7·85 Å, β = 114·9°, Z = 4. The structure was solved by Patterson and Fourier methods using *ca.* 1600 independent reflexions from

the reciprocal-lattice nets *hk*0—6 recorded by Weissenberg photographic techniques. Preliminary refinement of the structure by full-matrix least-squares calculations gives *R* 0·13.

The structure of a similar molecule, 2-imino-5-phenyl-1,3-thiazolidin-4-one (VII) has recently been reported,[4] and on the bases both of molecular dimensions and the positions of located hydrogen atoms, it has been demonstrated that this molecule possesses a zwitterionic structure. The dimensions of our molecule (III),† while calculated at an early stage of the refinement, show a close similarity to the bond lengths of (VII) which would suggest that the two molecules possess closely related electron-density distributions.

We thank Professor R. A. Raphael, F.R.S., whose interest has stimulated much of this research, and the Carnegie Trust for the Universities of Scotland for a post-graduate award (to N.J.H.).

(*Received, June 3rd,* 1970; *Com.* 864.)

† Average e.s.d. 0·02 Å.

[1] L. K. Mushkalo and G. Y. Yangol, *Ukrain. khim. Zhur.*, 1955, **21**, 732. (*Chem. Abs.*, 1956, **50**, 16751a); J. B. Hendrickson, R. Rees, and J. F. Templeton, *J. Amer. Chem. Soc.*, 1964, **86**, 107; Y. Iwanami, H. Saaki, and H. Sakata, *J. Chem. Soc. Japan*, 1964, **85**, 704.
[2] J. W. Lown and J. C. N. Ma, *Canad. J. Chem.* 1967, **45**, 939; E. Winterfeldte and J. M. Nelke, *Chem. Ber.*, 1967, **100**, 3671; Y. Kishida and A. Terada, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 1351.
[3] E. N. Cain and R. N. Warrener, *Austral. J. Chem.*, 1970, **23**, 51.
[4] L. A. Plastas and J. M. Stewart, *Chem. Comm.*, 1969, 811.