Novel Synthesis and *X*-Ray Crystal Structure Analysis of the 1,2,4-Thiadiazolo[4,5-*a*]benzimidazole Ring System

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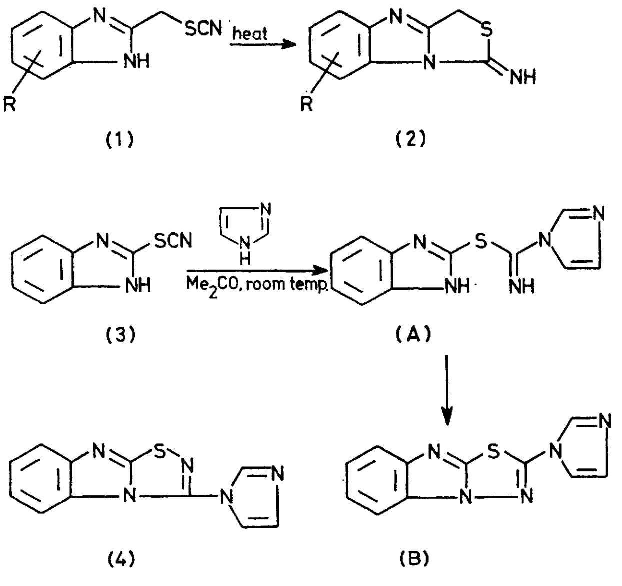
Summary Reaction of 2-thiocyanatobenzimidazoles and imidazole under mild conditions furnishes 1,2,4-thiadiazolo[4,5-*a*]benzimidazoles, the structure of which has been confirmed by *X*-ray analysis.

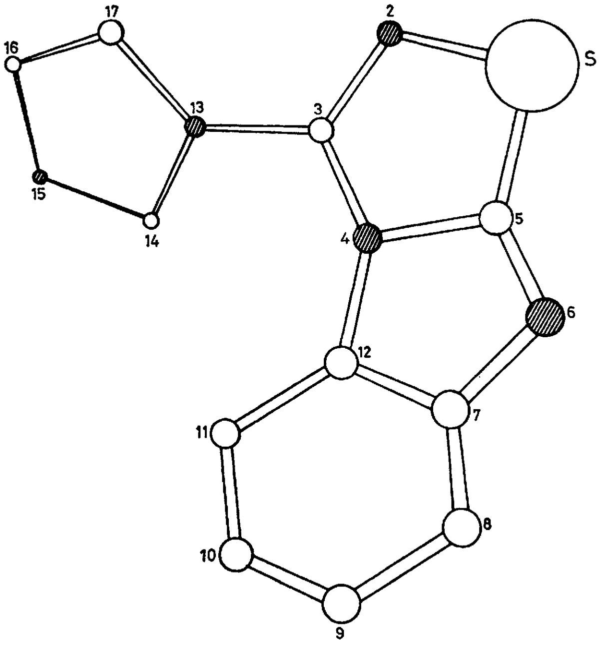
THE successful intramolecular cyclization of 2-thiocyanatomethylbenzimidazoles (**1**) to yield thiazolo[3,4-*a*]benzimidazoles (**2**)[1] by the reaction of the thiocyanato group with the imidazole ring NH prompted a further investigation of the reaction of 2-thiocyanatobenzimidazoles with imidazole. After a few hours at room temperature, an acetone solution (80 ml) of (**3**) (0·02 mol) and imidazole (0·02 mol) gave a crystalline product (*ca.* 30%), m.p. 213—214 °C (glyme),[†] the i.r. spectrum of which lacked the anticipated NH band at 3310 cm^{-1} and whose n.m.r. spectrum [$(CD_3)_2SO$, 60 MHz], τ 7·10—8·05 (6H, m, ArH) and 8·35—8·50 (1H, m, ArH), indicated the presence of aromatic protons only. These data excluded structure (**A**), and along with its mass spectrum [m/e 241 (M^+)] suggested instead an oxidation product, the tricyclic structure (**B**). $LiAlH_4$ reduction (2 h, room temp., Et_2O) of this product furnished 2-mercaptobenzimidazole and imidazole while Raney Ni degradation (10 h, reflux, EtOH) yielded benzimidazole. To confirm the assignment of structure (**B**), this product was subjected to single crystal *X*-ray diffraction analysis; however, Fourier and least-squares analysis ($R = 0{\cdot}08$) of 481 independent intensities measured diffractometrically (Cu-K_α) established (**4**),[‡] and not the expected structure (**B**), as the correct structure.



(**1**) (**2**)

(**3**) (**A**)

(**4**) (**B**)



FIGURE

Crystals grown from glyme were monoclinic with $a = 9{\cdot}222(4)$, $b = 3{\cdot}870(2)$, $c = 28{\cdot}48(2)$ Å, $\beta = 100{\cdot}4(2)°$, $D_m = 1{\cdot}558$ g cm^{-3}, and space group $P2_1/c$ with $Z = 4$.[§]

Chemical and geometrical considerations together with least-squares refinements of atom multiplicities served as the basis for distinguishing between carbon and nitrogen atoms (Figure). The dihedral angle between the least-

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[†] Satisfactory analytical data were obtained.

[‡] The 1,2,4-thiadiazolo[4,5-*a*]benzimidazole ring system was first reported in 1967 with the preparation of the 1,1-dioxide derivative: B. Stavnovnik and M. Tisler, *Arch. Pharm.*, 1967, **300**, 322.

[§] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

squares planes of the imidazole ring and the essentially flat fused tricyclic nucleus is 43°. The length of the N–S bond is 1·70(1) Å.

The generality of this reaction was shown by the 5-methyl, 5-chloro, and 5-nitro substituted analogues of (**3**) which gave the corresponding tricyclic products (**4**).

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[1] R. D. Haugwitz, B. V. Maurer, and V. L Narayanan, *Chem. Comm.*, **1971**, 1100; R. D. Haugwitz, B. V. Maurer, and V. L. Narayanan, *J. Org. Chem.*, **1971**, **39**, 1359.