

EXISTENCE OF ALTERNATIVE TAUTOMERS OF  
HETEROCYCLIC HYDRAZINE DERIVATIVES IN  
THE CRYSTALLINE STATE

D. J. Le Count and A. T. Greer

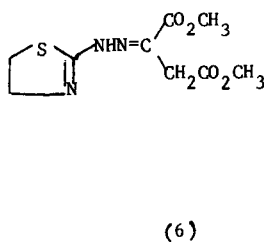
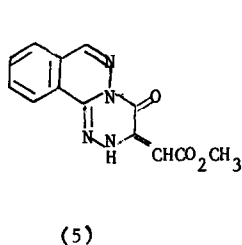
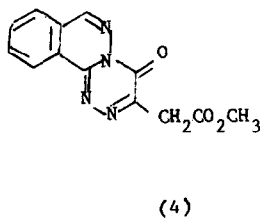
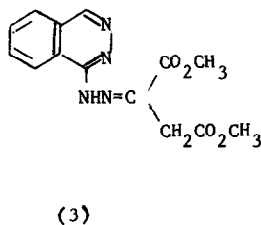
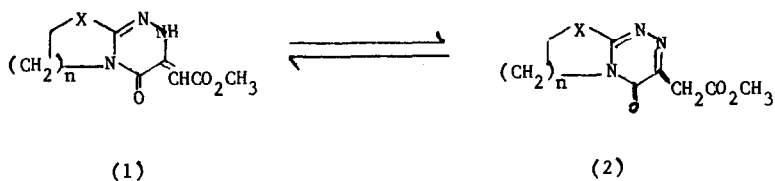
Imperial Chemical Industries Limited, Pharmaceuticals Division,  
Alderley Park, Macclesfield, Cheshire SK10 4TG

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In a recent publication Wamhoff<sup>1</sup> described the preparation of the triazinones (1, X=CH<sub>2</sub>, n=1-4). In chloroform solution the compounds were in equilibrium with the endocyclic tautomers (2, X=CH<sub>2</sub>, n=1-4) although the enamine form (1, X=CH<sub>2</sub>, n=1-4) existed in the solid state. We wish to report two similar cases where both tautomers may be isolated crystalline.

When the hydrazone (3), prepared from 1-hydrazinophthalazine and dimethyl acetylenedicarboxylate, is fused or heated in water the triazinone (4) is isolated. The i.r. spectrum (nujol) showed carbonyl bands at 1738cm<sup>-1</sup> and 1690cm<sup>-1</sup>. If, however, the cyclisation is carried out in methanol in the presence of triethylamine the exocyclic tautomer (5) is precipitated. The i.r. spectrum (nujol) showed carbonyl bands at 1712cm<sup>-1</sup> and 1650cm<sup>-1</sup> and N-H stretching at 3250cm<sup>-1</sup>. The tautomer (5) is converted into (4) on warming in dimethylsulphoxide and the n.m.r. spectra of the two compounds in d<sub>6</sub>DMSO are identical (CH<sub>2</sub> τ 5.95; CH<sub>3</sub> τ 6.27).

The hydrazone (6) behaves similarly. On stirring (6) in cold methanol containing triethylamine the triazinone (1, X=S, n=1) is precipitated. The i.r. spectrum (nujol) shows carbonyl bands at 1695cm<sup>-1</sup> and 1655cm<sup>-1</sup> and N-H stretching at 3150 cm<sup>-1</sup>. The product is sufficiently stable to be recovered unchanged from cold chloroform on addition of light petrol but on warming it is converted into the endocyclic tautomer (2, X=S, n=1) (ν c=O nujol 1735cm<sup>-1</sup> and 1680cm<sup>-1</sup>). As before the n.m.r. spectra of the two tautomers in d<sub>6</sub>DMSO are identical, showing two multiplets at τ 5.62 and τ 6.50 (thiazoline ring protons) τ 6.23 (CH<sub>2</sub>) and τ 6.38 (CH<sub>3</sub>).



Heterocyclic tautomers have been isolated previously in the solid state<sup>2</sup> but as far as we are aware only one case involving  $C=C \rightarrow C=N$  tautomerism has been reported.<sup>3</sup>

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