The Indication of Coplanarity in 3-Phenylpyridazines by NMR

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The phenyl and pyridazine rings of 3-methoxy-6-phenylpyridazine (I) appear to be coplanar as indicated by the NMR spectrum of I (Table 1). The interpretation of the spectrum is confirmed by comparison with the spectra of 3-methoxy-6-p-tolylpyridazine (II) and 3-methoxy-4-methyl-6-phenylpyridazine (III), cf. Table 1. The two *ortho* hydrogen atoms of the
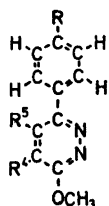
of the pyridazine ring is subject to nearly the same shift ($\Delta\delta$ = 0.72 ppm for compound II) by the phenyl group. The coupling constants of some of the protons may be derived from the spectrum of I and II (H^4 and H^5 of the pyridazine ring) and of III and IV (CH_3 of the pyridazine to H^4 or H^5). They are in accordance with values given elsewhere.[1]

The introduction of an alkyl group at position 5 in the pyridazine nucleus forces the two rings out of plane. The effect is illustrated by the NMR spectrum of 3-methoxy-5-methyl-6-phenylpyridazine (IV)

Table 1.[a]

Compound	Phenyl (*ortho*-hydrogen)	Phenyl (*meta* and *para*)	Pyridazine H^4	H^5	3-Methoxy	Methyl or t-butyl
I	7.87–8.09	7.30–7.51	6.92 [b]	7.66 [b]	4.16	—
II	7.80; 7.94	7.13; 7.27	6.91 [b]	7.63 [b]	4.15	2.36
III	7.82–8.02	7.30–7.45	—	7.47 [c]	4.17	2.22 [d]
IV	ca. 7.38 [e]		6.71 [c]	—	4.16	2.26 [d]
V	ca. 7.36 [f]		6.95	—	4.16	1.16
VI	7.86–8.13	7.35–7.56	—	7.62	4.24	1.42

[a] The spectra were taken on a Varian A-60 spectrometer at room temperature. The compounds (100 to 150 mg) were dissolved in deuterochloroform (500 μl) and the δ-values were partly measured from TMS (internal standard; methoxy, methyl and t-butyl) and partly from chloroform (internal standard, δ for $HCCl_3$ = 7.27; aromatic protons). [b] J_{45} = 9.6 cps. [c] Partially resolved quartets, J = 1.0 cps. [d] Doublet, J = 1.0 cps. [e] Half-width ca. 4 cps. [f] Half-width 1.5 cps.

In all instances the integral values were in accordance with the number of protons.

Fig. 1.　I R = R^4 = R^5 = H
　　　II R = CH_3; R^4 = R^5 = H
　　　III R^4 = CH_3; R = R^5 = H
　　　IV R^5 = CH_3; R = R^4 = H
　　　V R^5 = $(CH_3)_3C$; R = R^4 = H
　　　VI R^4 = $(CH_3)_3C$; R = R^5 = H

phenyl group are seen to be displaced (anisotropic effect of the pyridazine ring; $\Delta\delta$ = 0.67 ppm for compound II) towards lower field and, correspondingly, the H^5

in which the two sets of maxima ascribed to the 5 protons on the phenyl group collapse to a group of nearly fused peaks. The corresponding 5-t-butyl compound shows the same effect; in the latter case, however, the signals from the phenyl group are even less resolved and form one large peak (the half-width being reduced from 4 to 1.5 cps).

As expected, the introduction of a methyl group (III) or even a t-butyl group (VI) in the 4-position of the pyridazine nucleus does not inhibit the coplanarity of the two rings. This is indicated by the splitting of the phenyl protons and the shift of the 5-proton to δ = 7.62, cf. Table 1.

The compounds were prepared according to or in analogy with published methods.[2,3]

1. Tori, K., Ogata, M. and Kano, H. *Chem. Pharm. Bull. (Tokyo)* **11** (1963) 235.
2. Oppenheim, A. *Ber.* **34** (1901) 4227.
3. Crossland, I. and Rasmussen, L. K. *Acta Chem. Scand.* **19** (1965) 1652.