The Conformation of Substituted 1,2,3,6-Tetrahydropyridazines

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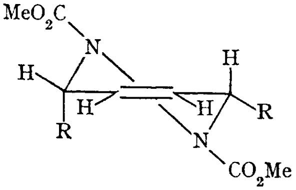
THIS Communication is prompted by the appearance[1] of a critique dealing with the analysis of the proton magnetic resonance spectrum obtained for the Diels–Alder adduct of dimethyl azodicarboxylate with *trans, trans*-1,4-diphenylbuta-1,3-diene (Ia). The present authors have given a detailed analysis of this spectrum[2] and have described the p.m.r. spectra of related 1,2,3,6-tetrahydropyridazines prepared by this reaction.[3] Spectral analysis of (Ia) and (Ib) accord with the *cis*-configuration shown for these structures.

In the case of (Ia) or (Ib), the p.m.r. spectrum is characterized by the appearance of two separate *O*-methyl signals. The diverse chemical shifts of these methyl groups were ascribed to the existence of a conformation of (I) whose rate of ring inversion is slow compared to that of the magnetic transition being analyzed.[3,4] In that event, two magnetically non-equivalent *O*-methyl groups would be present. Other spectral data of (I) can be accommodated on the same basis.



(I) a; R=Ph; b; R=Me

Bushweller[1] rejected this interpretation because the conformational stability it implies should give rise to two *O*-methyl signals of equal intensity. In an attempt to interpret the spectrum, Bushweller assumed a 1·5 : 1 ratio for these intensities and associated the difference with the existence of two nitrogen rotational conformations having unequal populations.

In order to resolve this dilemma we have examined the p.m.r. spectrum of (Ia) in great detail[5] and have measured the intensities at various r.f. fields. The Figure shows a typical spectrum while the Table records the ratios of intensities of the two *O*-methyl signals.

It is apparent that these data support our interpretation[3] because the two peaks have virtually identical intensities. We reject Bushweller's analysis since it is based on an erroneous estimate of these intensities.[6]

TABLE

Ratios of peak intensities of O-*methyl signals of* (Ia)

R.f. field	Ratios[a,b]
0·10	1·03 ± 0·02
0·16	1·02 ± 0·02
0·20	1·04 ± 0·01
0·30	1·05 ± 0·02

[a] Ratio of intensity of peak at 229·2 c./sec. to that at 206·6 c./sec.

[b] Confidence limit, 95%.

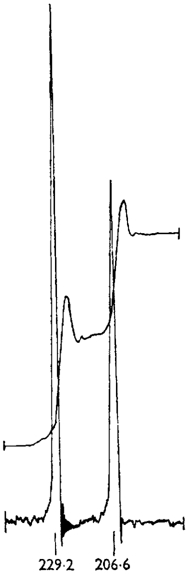


FIGURE *Proton magnetic resonance spectrum of* (Ia). *Data are given in c./sec. downfield from tetramethylsilane at* 35°.

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[1] C. H. Bushweller, *Chem. Comm.*, 1966, 80.

[2] Presented on March 25, 1965 at the third MIKI Meeting held in Chicago, Illinois.

[3] R. Daniels and K. A. Roseman, *Tetrahedron Letters*, 1966, 1335.

[4] J. C. Breliere and J. H. Lehn, *Chem. Comm.*, 1965, 426.

[5] The spectral data were obtained as described in reference 3.

[6] It is noteworthy that whilst all spectra show *peak heights* in a ratio 1·5:1 (see Fig.), the *integrated intensities* are always identical.