

A Splitting of Aryl Proton Signals in the N.m.r. Spectra of N-Alkyl-N-Arylamides

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THE *N*-methyl protons of *NN*-dimethylamides,¹ *N*-alkyl-*N*-methylamides,^{2,3} and *N*-aryl-*N*-methylamides⁴ resonate in the n.m.r. spectra as two distinct signals. The relative intensities of the two signals depend upon the proportion of rotational isomer with the *N*-methyl group oriented either *cis* or *trans* with respect to the amide oxygen atom. The signals from *N*-formyl^{2,3} and *N*-acetyl^{2,4} protons are also observed as two distinct resonances in amides which possess a magnetically anisotropic group (*e.g.*, aryl) capable of producing differential shielding in the two rotational isomers.

The *NN*-disubstituted amide (Ia), obtained by heating dicentrine in a mixture of acetic anhydride and pyridine at 100°, shows the expected splitting

of both *N*-methyl and *N*-acetyl proton signals. In addition, however, the spectrum (measured at 60 Mc./sec.) shows a splitting of the C-2 and C-10 aryl proton signals. The C-2 proton resonates as two distinct singlets, the relative intensities of which are in the same ratio as the *N*-methyl and *N*-acetyl proton signals. The expected AB doublet of the C-10 proton is similarly split into two doublets with the same relative intensities as the other pairs of signals. This splitting of the signals of the two aryl protons can be ascribed to differential shielding by the amide group in the *cis*- and *trans*-configurations. That the C-2 and C-10 protons are the only aryl protons affected can be explained by the close approach of the anisotropic amide group to these protons.

TABLE. Chemical shifts (δ) of split signals in spectra of phenanthrenes (Ia—d)

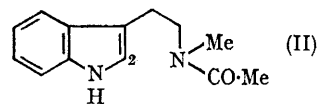
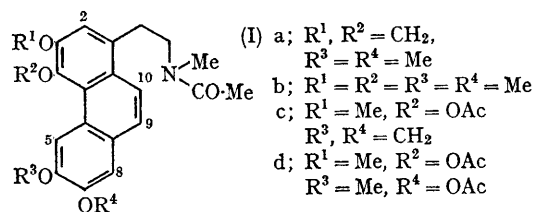
	C-2 Proton	C-10 Proton	NCH ₃	CO-CH ₃
(Ia)	6.91, 7.01	7.81, 7.56 ($J_{9,10}$ 9.3 c./sec.)	2.74, 2.91	1.78, 2.01
(Ib)	7.05, 7.17	7.90, 7.67 (")	2.82, 2.98	1.77, 2.08
(Ic)	7.05, 7.17	7.87, 7.61 (")	2.80, 2.98	1.82, 2.08
(Id)	7.12, 7.27	7.89, 7.67 (")	2.78, 2.98	1.80, 2.06

A shift to higher field of the *N*-methyl proton signal from the *trans*-isomer after dilution of the deuteriochloroform solution with benzene has been used to differentiate the *trans*- from the *cis*-isomer.⁵ The relative intensities of the *N*-methyl signals in the spectrum of (Ia) and the shift to higher field of the δ 2.74 peak after dilution with benzene indicate a *cis* : *trans*-ratio of 1:1.9 at 40°. At 100° the frequency of exchange between the *cis*- and *trans*-configurations is such that time-averaged signals are observed for all proton resonances in the spectrum which then closely resembles the spectrum of dicentrine methine.⁶

Chemical shifts of the corresponding split signals in the related phenanthrenes (Ib), (Ic), and (Id) derived from glaucine, domesticine, and isoboldine respectively, are shown in the Table.

Similar effects attributed to *cis*- and *trans*-rotational isomers are observed in the spectrum of *N*-acetyl-*N*-methyltryptamine (II) in which the signal from the C-2 proton, as well as those of the *N*-methyl and *N*-acetyl groups, is split. The split signal from the C-2 proton is most clearly seen after exchange with deuterium oxide which removes the coupling between the C-2 proton and

the indolic NH proton. At 100° a time-averaged spectrum is obtained which corresponds closely with the spectrum of *NN*-dimethyltryptamine; the signal from the C-2 proton appears as a doublet initially and as a sharp singlet after exchange with deuterium oxide.



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