The Rotational Barrier in 2-Chloro-4-dimethylamino-1,3,5-triazanaphthalene

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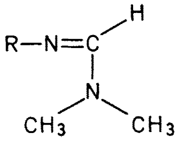
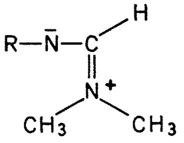
Summary N.m.r. studies indicate a barrier to the rotation of the dimethylamino-group in 2-chloro-4-dimethylamino-1,3,5-triazanaphthalene (III); no such barrier could be observed in the analogous 2-chloro-4-dimethylaminoquinazoline (IV).

IN suitably substituted formamidines (*N'*-aryl- and *N'*-t-butyl-*NN*-dimethylformamidines) (I), there exists[1,2] a rotational barrier which makes the two *N*-methyl groups nonequivalent, and which is ascribed to the contribution of a zwitterion of type (II).



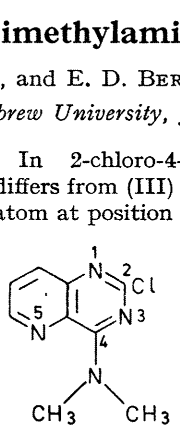
(I)



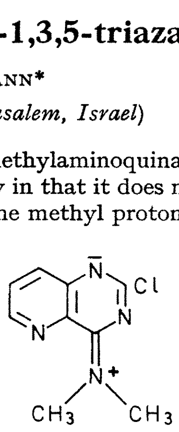
(II)

In a study of derivatives of the 1,3,5-triazanaphthalene system, we have observed a similar phenomenon in compounds such as 2-chloro-4-dimethylamino-1,3,5-triazanaphthalene (III)† which contains an amidine system anchored in a ring, and for which a resonance structure such as (IIIa) is possible. The two methyl groups give rise at room temperature to a broad n.m.r. singlet‡ (4 Hz) at δ 3·66 p.p.m. (in $CDCl_3$), which broadens further with decreasing temperature and splits into two singlet peaks (Δν 36 Hz). The coalescence temperature is −10·5°. The free energy of activation, determined directly from the coalescence parameters, is 14·0 kcal/mole.

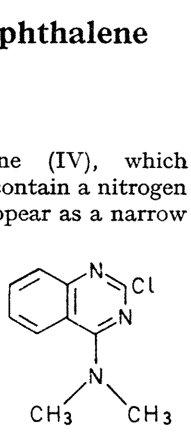
In 2-chloro-4-dimethylaminoquinazoline (IV), which differs from (III) only in that it does not contain a nitrogen atom at position 5, the methyl protons appear as a narrow singlet (1 Hz at 3·43 p.p.m., $CDCl_3$ solution), which does not broaden down to −50° and in deuterioacetone even not at −100°. The free energy of activation must be smaller than 8 kcal/mole (assuming that in this case, too, Δν = 36 Hz).



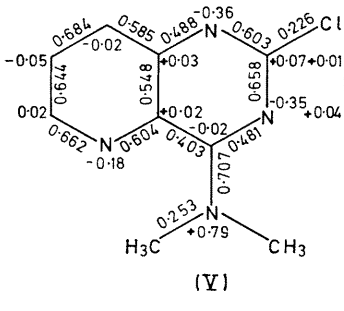
(III)



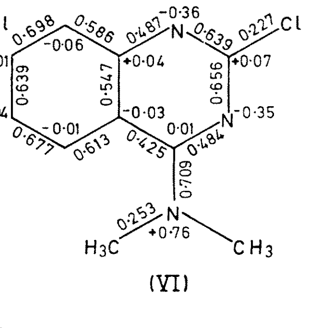
(IIIa)



(IV)



(V)



(VI)

It is thus clear that the nitrogen atom in the 5-position

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† Syntheses: Aqueous-alcoholic dimethylamine replaces only the 4-chlorine atom in 2,4-dichloro-1,3,5-triazanaphthalene[5] leading to (III), pale yellow needles of m.p. 115—116°, from petroleum. Analogously, (IV) was prepared from 2,4-dichloroquinazoline;[6] yellow crystals, m.p. 104–106°, from cyclohexane. The compound shows a yellow-green fluorescence.

‡ The spectra were determined at 60 MHz with a Varian T56-60 instrument.

of (III) has a strong influence on the tendency to form the zwitterionic system (IIIa).

Hückel-type calculations (in which the planarity of the π-system is implicit) were performed with the parameters of Pullman and his co-workers.[3,4] The resultant molecular diagrams (V, VI) fail to differentiate between the two systems: the C-4–N linkages in both molecules have a bond order of about 0·71; obviously there exist determining factors which are not taken into account in these calculations. We conclude that (III) is planar, while the proton at C-5 interferes with planarity.[7,8]

Similar observations have been made with analogues of (III) and (IV); they will be reported in a forthcoming paper.

(*Received, June 5th,* 1970; *Com.* 865.)

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