Tetrahedron Letters No.44, pp. 3279-3284, 1964. Pergamon Press Ltd.
Printed in Great Britain.

A CASE OF HINDERED INVERSION OF TRIGONAL NITROGEN

by

W.N.Speckamp[**], U.K.Pandit and H.O.Huisman
Laboratory for Organic Chemistry,
University of Amsterdam, The Netherlands.

(Received 3 August 1964; in revised form 18 September 1964)

The rapid inversion of nonplanar trigonal nitrogen has so far prevented the resolution, into optically active isomers, of trisubstituted amines which are asymmetric only by virtue of the configuration at the nitrogen atom. With the aid of NMR spectroscopy, however, Bottini and Roberts1) were recently able to show the existence of a definite energy barrier in the inversion of certain three-membered cyclic imines. Since the structural characteristics of the transition state for the inversion process should strongly influence the rate of conformational isomerization, it may be anticipated that the introduction of substituents which would

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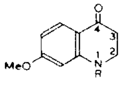
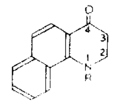
[*] This paper is to be regarded as the third paper in the Dihydroquinolone series.

[**] Abstracted in part from the forthcoming dissertation of W.N.Speckamp, University of Amsterdam, 1964.

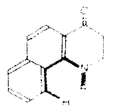
destabilize the transition state will also tend to inhibit the inversion phenomena. In suitably chosen systems this inhibition may attain a magnitude which could become sufficient to permit the recognition of conformational isomerism by appropiate physical methods. In this communication we wish to present evidence for the existence of hindered inversion of the nitrogen atom in certain substituted benzquinolone systems.



I R = H
IV R = (p)$MeC_6H_4SO_2$



II R = H
III R = (p)$MeC_6H_4SO_2$



V

The NMR spectrum of quinolone I (Fig.I) exhibits a recognizable pattern in which the four methylene hydrogens at positions 2 and 3 appear as a pair of triplets centered at 3,46 δ and 2.55 δ respectively. The benzquinolone II also shows a similar pair of triplets for the corresponding methylene protons though the signals are slightly displaced to the lower field region (Fig.2). However, in comparison to the spectrum of I the triplet due to the C_2 protons from II appears to be appreciably broadened in character. Such a broadening arises due to the non-equality of the two protons and may be attributed to a hinderance to the conformational change of the N-H bond. The fact that only one of the triplets - due to C_2 protons, is broadened is significant since it implies that the observed effect is not due to changes in the equilibrium between the two half-chair forms of the quinolone ring.

The restriction to the inversion of nitrogen in this system is not so unexpected since the planar transition state V for the inversion will involve steric interaction of the type which is well known for the ortho hydrogens in the biphenyl system and for the peri hydrogens of the phenanthrene molecule. Recently, Curtin (2) has shown that a similar interaction is responsible for conformational isomerism in certain 9,10-dihydroanthracene derivatives. From the foregoing discussion it is suggestive that the replacement of the proton on the nitrogen atom in II, by a bulkier substituent, should lead to an enhancement of the observed hinderance to inversion.

Examination of the NMR spectrum of III (Fig.3) in which the hydrogen is replaced by a bulky tosyl group shows that indeed the signal due to the corresponding C_2 hydrogens has collapsed to a broad hump in the region 5.8 δ - 4.4 δ. That the tosyl group in III is itself not responsible for any unexpected influence on the spectrum is demonstrated by reference to the spectrum of compound IV (Fig.4) in which the N-$\underline{CH_2}$-signal clearly exhibits a normal triplet pattern.

Confirmatory evidence for the phenomenon of the hindered inversion of nitrogen in III was obtained by a study of the temperature dependence of its NMR spectrum. Fig.5 shows the appropiate region of the NMR spectrum of III at 40°, 100° and 170°, in diphenyl ether. While at 40° the spectrum in diphenyl ether again exhibits a broad signal for the ethylene protons, this signal develops into a triplet at 100°

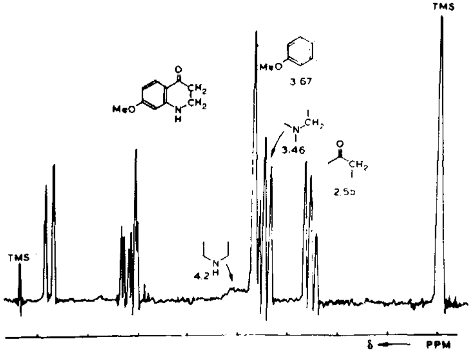


Fig.1

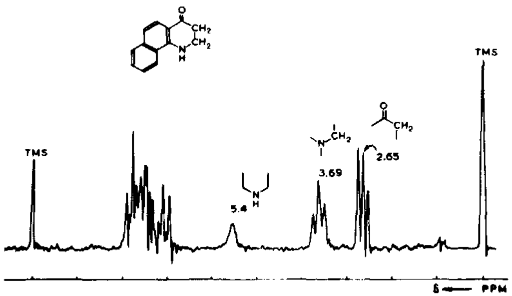


Fig.2

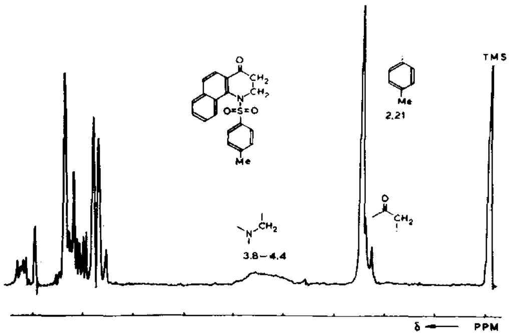


Fig.3

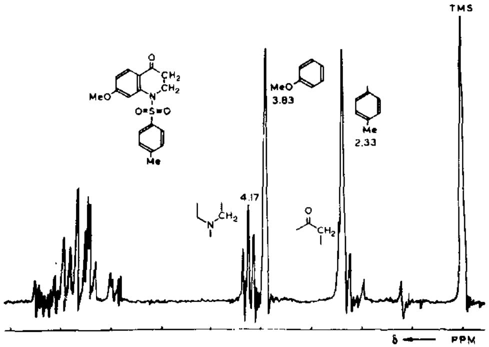
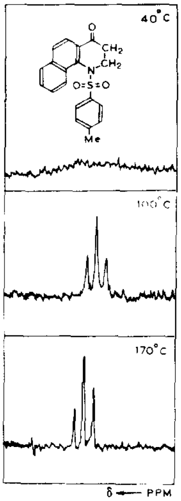


Fig.4

and is further sharpened in its structure at 170°. The observed changes in the spectrum are in accord with the expected behaviour of the system at higher temperatures where the inversion rate is sufficiently increased so as to eliminate the unequal shielding of the C_2 protons of the benzquinolone.

Fig.5



The phenomenon of restricted inversion of nitrogen has been observed in several other compounds incorporating the essential features of III and a detailed discussion of these systems will be presented elsewhere. Attempts to develop suitable derivatives which may permit the resolution of an asymmetric nitrogen are also in progress in this laboratory.

The spectra at 40°C were recorded on a Varian HR-60 spectrometer using a 10 % $CDCl_3$ solution, while the high temperature measurements were made on a Varian A-60 spectrometer using a diphenyl ether solution.

Acknowledgements

We are deeply indebted to Drs.P.K.Korver for the spectral measurements and for valuable discussion. We should also like to thank Drs.P.J.van der Haak of the Spectroscopic Division of this laboratory for helpful criticism.

Part of the present investigations have been carried out under the auspices of the Netherlands Foundation for Chemical Research (S.O.N.) and with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

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1) J.D.Roberts and A.T.Bottini, J.Am.Chem.Soc., 80, 5203 (1958)

2) D.Y.Curtin, C.G.Carlson and C.G.McCarty, Can.J.Chem., 42, 565 (1964).