Tetrahedron Letters No.11, pp. 1285-1286, 1968. Pergamon Press. Printed in Great Britain.

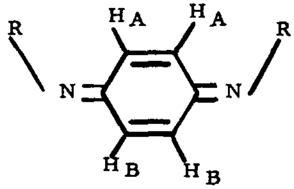
ISOMERIZATION ABOUT THE C=N DOUBLE BOND OF QUINONEDIIMINES

R. W. Layer and C. J. Carman

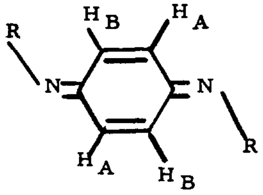
The B. F. Goodrich Company Research Center, Brecksville, Ohio

(Received in USA 10 November 1967)

Isomerization about the C=N bond of imines has been the subject of interest for many years (1). Recently, it has been shown by NMR that syn and anti isomers of certain imines can be detected in solution (2). We wish to report that p-benzoquinonediimines also form a mixture of syn and anti isomers in solution. We have detected these isomers for N, N'-di-(2, 6-diethylphenyl)-p-benzoquinonediimine, m. p. 75-6°. This diimine was obtained from a PbO_2 oxidation of the corresponding amine. The protons of interest for this molecule are those on the quinone nucleus. The isomers of this molecule can be represented as follows:



I



II

If the molecule exists as the syn isomer I, only two kinds of quinoidal protons are possible H_A and H_B. Thus the quinoidal proton spectrum of I should be two peaks of equal area. For the anti isomer II, a typical AB pattern of four peaks is expected.

The NMR spectrum of the diimine was obtained in both perchloroethylene and decane at 31° using a Varian A-60 spectrometer. The NMR spectrum of the quinoidal protons of this diimine shows six peaks. The two peaks at 7. 03 and 6. 10 ppm (relative to hexamethyldisiloxane as an internal standard) are attributed to the syn isomer I. The other four peaks are due to the two AB doublets of the anti isomer II. One AB doublet is centered at 6. 81 ppm and the other doublet is at 6.33 ppm (J_{AB} = 10.5 H_z). The integrated areas show equal amounts of these two isomers to be present. All six peaks coalesced to a single peak at 6.56 ppm. at about 125°. This represents about a 20 kcal./mole energy barrier to isomerization (3). This is within the energy barrier range of 13 to 27 kcal./mole observed for the isomerizations about the C=N bonds of acyclic imines (2).

The NMR spectrum of N, N'-diphenyl-p-benzoquinonediimine-N, N'-dioxide (4) proved to be very interesting. In $CDCl_3$ at 31° the quinoidal protons exist as one peak at 7.32 ppm and the aromatic protons as another peak at 7.46 ppm with peak areas of four to ten respectively. Below -40° the spectrum shows the presence of both the syn and anti isomers. An energy barrier of about 12 kcal./mole was found from the coalescence temperature. The interconversion of syn and anti isomers is significant because a "lateral shift mechanism" of isomerization (2) is not possible for this molecule. Thus its isomerization must proceed through a rotational path.

Our data supports a rotational mechanism (1) for the isomerization of imines even though the energy of activation for isomerization is low (2).

It should also be mentioned that besides syn - anti isomerization restricted rotation about the aryl to nitrogen single bond was also noted in the case of N, N'-di-(2, 6-diethylphenyl)-p-benzoquinonediimine. The kinetics of this process will be reported elsewhere.

REFERENCES

1. R. W. Layer, Chem. Rev., **63**, 489 (1963).
2. D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, J. Amer. Chem. Soc., **88**, 2775 (1966).
3. H. S. Gutowsky, D. W. McCall and C. P. Slichter, J. Chem. Phys. **21**, 279 (1953).
4. C. J. Pedersen, J. Amer. Chem. Soc., **79**, 2295 (1957).