

THE CONFORMATION AND NMR OF CONJUGATED DIIMINES

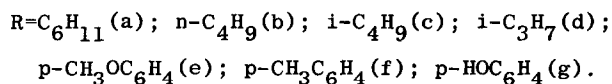
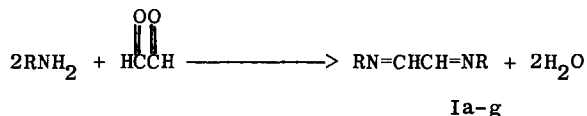
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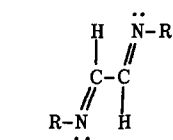
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In a recent communication, Nelson and Atkins (1) have reported on the NMR spectra of aliphatic azomethines in which "five-bond" coupling and geometrical isomerization played an important role in the interpretation of the data. Karabatsos and Lande have published an extensive paper describing the conformation of aliphatic imines in which "4-bond coupling" between the aldimine proton and N-alkyl proton and similar "5-bond" in ketimines was observed (2). At this point, we wish to report our findings with conjugated diimines of known conformation.

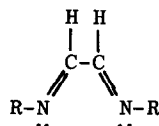
The diimines studied were prepared by the reaction of 40% aqueous glyoxal with the appropriate primary amine (3):



Inspection of molecular models of the possible conformations (Ia-g) indicates that the anti-s-trans-anti and anti-s-cis-anti configurations should be most favored.



anti-s-trans-anti



anti-s-cis-anti

Recent studies by Hine and Yeh (4), and Karabatsos and Lande (2) on the geometry of imines confirms the greater stability of the anti-configuration; and the position of the resonance line in the NMR spectrum for the aldimine protons in

compounds Ia-g (Table I and II) coincides with that observed for mono-imines.

PARTIAL NMR SPECTRA OF ALIPHATIC CONJUGATED DIIMINES

| Compound <sup>a</sup> | $\text{CHN=}$ | $\text{-N=CH-}$ |
|-----------------------|---------------|-----------------|
| Ia                    | 3.20, m       | 7.93, s         |
| Ib                    | 3.50, tr      | 7.78, s         |
| Ic                    | 3.30, d       | 7.77, s         |
| Id                    | 3.50, sept    | 7.97, s         |

<sup>a</sup> $\text{CDCl}_3$ , 60  $\text{MH}_z$ , in ppm from internal TMS. The remaining portions of the spectra appear with normal shifts and multiplicities.

TABLE II

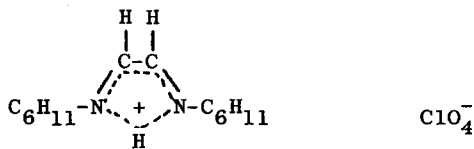
NMR SPECTRA OF AROMATIC CONJUGATED DIIMINES<sup>a</sup>

| Compound                    | R                          | $\text{R-C}_6\text{H}_4$ | $\text{-N=CH-}$ |
|-----------------------------|----------------------------|--------------------------|-----------------|
| Ie                          | 3.82, s ( $\text{OCH}_3$ ) | 7.13, m                  | 8.42, s         |
| If                          | 2.37, s ( $\text{CH}_3$ )  | 7.70, m                  | 8.38, s         |
| I <sub>g</sub> <sup>b</sup> | 9.75, s (OH)               | 7.18, m                  | 8.40, s         |

<sup>a</sup> $\text{CDCl}_3$ , 60  $\text{MH}_z$ , in ppm from internal TMS

<sup>b</sup> $\text{DMSO-d}_6$

Corroboration for the anti-conformation in the diimines is found in their behavior with mineral acids, i.e., they are monobasic when titrated with 0.1 N perchloric acid in acetic acid. For example, 1.00-1.15 equivalents of acid are consumed per mole of diimine and for the particular case of Ia, a diimine hydroperchlorate, II, can be readily isolated. Structure II is proposed to be a planar, resonance-stabilized, five membered ring containing the diimine linkage and an additional proton.

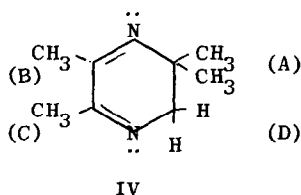
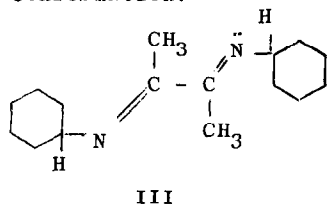


II

This structure is allowed only if the conformation about the imine groups is anti-, since a syn-conformation would preclude rotation because of the severe steric interaction of the alkyl groups attached to nitrogen. Further support for the structure of II is available from its NMR spectrum in which no additional coupling of the cyclohexylmethine or aldimine protons is observed, thereby eliminating a tautomeric equilibrium.

Unlike aliphatic imines (2) the NMR spectra of compounds Ia-g shows both the lack of splitting of the aldimine protons and lack of additional coupling of the proton on the saturated carbon (for aliphatic diimines) adjacent to nitrogen due to syn-anti isomerization, or "4-bond coupling". Reducing the temperature of the NMR probe to  $-40^{\circ}$  ( $100 \text{ MHz}_2$ ) caused no change in the spectra of Ia or Ie. From these results we conclude that only the anti-conformer is present and that no temperature-dependent syn-anti isomerization or "4-bond" coupling exists in these compounds.

Our interest in the aforementioned (1,2) observations of "5-bond" coupling in azomethines suggested the preparation of N,N'-bis(cyclohexyl)-butylene-2,3-diimine, III (5), which by analogy to compounds Ia-g exists in an anti-anti conformation. We were particularly interested in a comparison of III with 2,3,5,5-tetramethyl-5,6-dihydropyrazine, IV (6), a diimine which must exist in the syn-syn conformation.



The NMR Spectrum of III shows the methyl protons as a single, sharp line at 2.03 ppm with a half-height width of less than 0.3 cps. This observation demonstrates the lack of "five-bond" coupling between the methyl protons and the cyclohexylmethine proton.

The NMR spectrum of IV is more complicated and shows the following peaks: Protons A and B appear as singlets at 1.07 ppm and 1.82 ppm, respectively.

The C protons appear as a triplet at 1.88 ppm,  $J = 1.85$  cps; and the D protons are a quartet at 3.33 ppm,  $J = 1.85$  cps. For this particular compound we observe a clear case of "five-bond" coupling between protons C and D.

The conformational requirements leading to "five-bond" coupling through unsaturated systems have been discussed previously (2,7).

The lack of "four-or five-bond" coupling in the anti-anti compounds and the observation of such coupling in the syn-syn compound (IV) implies that the conformation of the imine groups and thus the geometry of nitrogen's lone pair makes the major contribution to the observed spectrum.

Further studies are presently in progress to verify the above conclusions.

#### Acknowledgement

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#### Bibliography

- (1) D. A. Nelson and R. L. Atkins, Tetrahedron Letters, No. 51, 5197 (1967)
- (2) G. J. Karabatsos and S. S. Lande, Tetrahedron, 24, 3907 (1968), and references therein.
- (3) The experimental details of this reaction will appear in the future.
- (4) J. Hine and C. Y. Yeh, J. Am. Chem. Soc., 85 2669 (1963).
- (5) J. F. Carson, J. Am. Chem. Soc., 75, 4300 (1953).
- (6) We are indebted to Dr. D. R. Arnold, Union Carbide Research Institute, Tarrytown, N. Y., for the NMR spectrum of this compound, the preparative details of which will appear, among others, in the near future.
- (7) G. J. Karabatsos and F. M. Vane, J. Am. Chem. Soc., 85, 3886 (1963); and references therein.