

The Absolute Configuration of Isomeric *syn*- and *anti*-Formazans

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A STUDY of 3-methylthio-1,5-diphenylformazan (I, $R^1 = R^2 = \text{Ph}$, $R^3 = \text{SMe}$) has confirmed a previous observation¹ that the molecule adopts two of the four possible (I, II, III, IV) configurations in solution. These are presumably the *syn*-(I) and *anti*-(III) geometrical isomers about

the $>\text{C}=\text{N}-$ bond, with the azo-group having the preferred *trans*-configuration.

Configurational isomers with characteristic red and yellow colours have been identified^{2,3} for a number of formazans. Based on a study⁴ of the photochemistry of 1,3,5-triphenylformazan

(I, $R^1 = R^2 = R^3 = \text{Ph}$), in which all four configurational isomers were identified, the red isomer has been assigned structure (I) and the yellow isomer structure (III).

We have observed a band at $17,200 \text{ cm.}^{-1}$ in the reflectance spectrum of solid 3-methylthio-1,5-diphenylformazan, similar to the intense "red" absorption band at $17,800 \text{ cm.}^{-1}$ for a freshly prepared chloroform solution. A new band slowly appears in the solution spectrum at $23,700 \text{ cm.}^{-1}$ with a corresponding colour change from violet to yellow-brown.

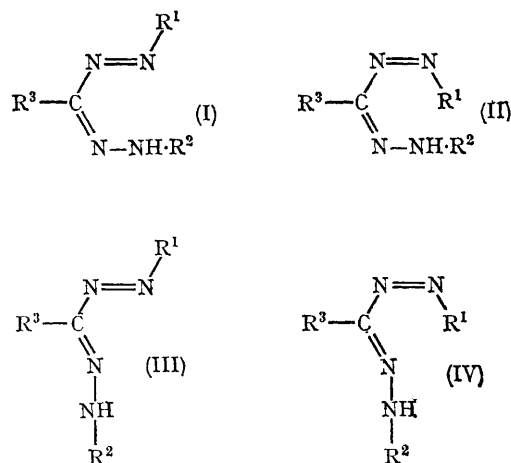
The 60 Mc./sec. proton n.m.r. spectrum of 3-methylthio-1,5-diphenylformazan in deuteriochloroform showed two singlets at 138 and 147 c./sec. attributable to the methyl protons and two smaller singlets at 570 and 617 c./sec. attributable to the NH proton. All four bands were concentration-independent in the range 0.02–0.2M. However, the intensity of the low-field singlet for both the methyl and the NH protons increased with time relative to that of the high-field singlet, with a corresponding colour change from violet to yellow-brown. Accompanying these changes was a broadening of the phenyl signals suggesting an increase in the coupling between the two phenyl groups.

In the infrared spectrum of the solid, no NH stretching vibration was observed. However, a fresh chloroform solution showed a band at 3334 cm.^{-1} which can be assigned as ν_{NH} . A subsidiary band at 3240 cm.^{-1} increased in intensity with time while the shorter-wavelength band decreased in intensity. There was again no observable shift in the position of either band over the same concentration range.

The shift in both the n.m.r. signal and the stretching vibration of the NH group to lower

energies suggests some type of inter- or intramolecular interaction. The absence of any dependence on the concentration of solute and the increased coupling between the phenyl protons would be expected for intramolecular hydrogen bonding. These results can be explained by a change from the *trans-anti*- to the *trans-syn*-isomer, implying that in the solid state, 3-methylthio-1,5-diphenylformazan has the *trans-anti*-configuration stabilised by intermolecular hydrogen bonding. This would explain the absence of an NH stretching vibration from the infrared absorption spectrum of the solid.

If one extends these observations to other cases of configurational isomerism in formazans, the yellow isomer would have the *trans-syn*-configuration and not the *trans-anti*-configuration as previously supposed.



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³ H. Irving, F. B. Gill, and (in part) W. R. Cross, *J. Chem. Soc.*, 1960, 2087.

⁴ R. Kuhn and H. M. Weitz, *Chem. Ber.*, 1953, **86**, 1199.