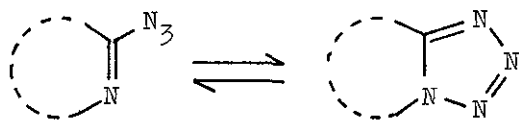


ELECTRIC DIPOLE MOMENT OF 5H-1,2,3-DITHIAZOLE
DERIVATIVE EQUILIBRATED WITH 2,4,6-TRI-t-
BUTYL-N-THIOSULFINYLANILINE

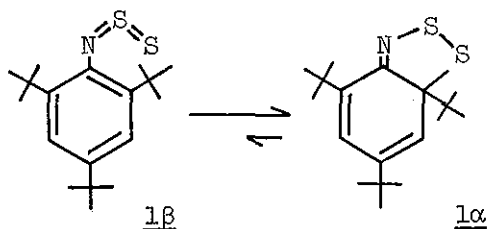
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Electric dipole moment of 2,4,6-tri-t-butyl-7,8,9-dithiaza-bicyclo[4.3.0]nona-2,4,9-triene (1a) was estimated to be about 3.0 D by measuring the dielectric constants of dilute benzene solutions of the equilibrium mixture of 1a and 2,4,6-tri-t-butyl-N-thiosulfinylaniline (1b) with a known molar ratio. This value is much larger than the estimated value of 1b (1.5 D).

Both inter-¹ and intra-molecular² 1,3-dipolar cyclo-additions are well established routes to various five-membered heterocycles. Of many examples of the latter reactions, most extensively studied is cyclization of an azido-azomethine into a tetrazole;³ the isomerization is usually reversible and the factors influencing the equilibrium have been a subject of some recent studies.⁴



Recently, we have found that a thiosulfinylamino group ($-N=S=S$) behaves like an azide group and undergoes intramolecular cyclization with "the double bond" of a benzene ring to give a novel heterocycle, 5H-1,2,3-dithiazole; the product (1) of the reaction between 2,4,6-tri-*t*-butylaniline and disulfur dichloride exists as a cyclized form (1 α) in solid state, while in solution an equilibrium between 1 α and 1 β is established with the former being a major component.⁵



As part of study to clarify the factors affecting the equilibrium, we calculated the electric dipole moment of 1 α by the following procedure and it was found to be about 3.0 D. Molecular polarization was determined by the method of Halverstadt and Kumler in benzene at 25 °C.⁶ Electronic polarization was equated to molecular refractivity and, since the molecular refractivities of 1 α (99.999 cm³) and 1 β (102.644 cm³) calculated from atomic refractivity are nearly equal, they were assumed to be the same, 100 cm³. Atomic polarization was

assumed to be 5% of electronic polarization. Apparent dipole moment (μ) thus obtained was 2.87 D. Since μ^2 can be expressed as in the following equation,

$$\mu^2 = \frac{\mu_\alpha^2 K + \mu_\beta^2}{K + 1}$$

where μ_α and μ_β are dipole moments of 1 α and 1 β respectively and K is the equilibrium constant [1 α]/[1 β], which was determined to be 11.3 at 25 °C by NMR spectrum in benzene- d_6 solution. μ_α is calculated to be 2.96 D assuming that μ_β is equal to the value of 2,4-di-*t*-butyl-6-methyl-N-thiosulfinylaniline (1.51 D).⁷

It is interesting that the dipole moment of 1 α is much larger than that of 1 β . This fact is in keeping with the observation by NMR spectroscopy that the more polar is a solvent, the larger is population of 1 α .⁸

In spite of extensive studies on the azide-tetrazole equilibrium, there seems no example in which dipole moments of the both components are measured. However, in the light of the reported values of phenyl azide (1.56 D)⁹ and benzotriazole (4.10 D),⁹ and the reported solvent effect on the azide-tetrazole equilibrium,⁴ the nature of the equilibrium observed for 1 appears very similar to that of the azide-tetrazole equilibrium.

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