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

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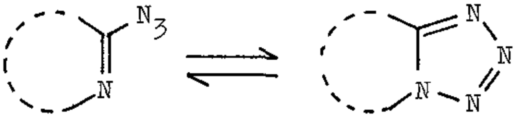
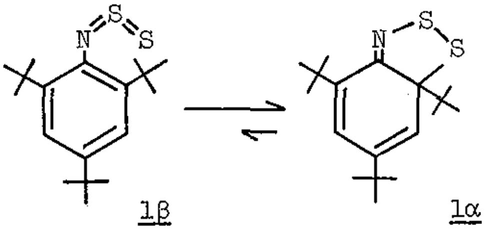
Electric dipole moment of 2,4,6-tri-t-butyl-7,8,9-dithiazabicyclo[4.3.0]nona-2,4,9-triene (1α) was estimated to be about 3.0 D by measuring the dielectric constants of dilute benzene solutions of the equilibrium mixture of 1α and 2,4,6-tri-t-butyl-N-thiosulfinylaniline (1β) with a known molar ratio.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

Both inter-[1] and intra-molecular[2] 1,3-dipolar cycloadditions 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 intramolecualr 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 (1α) in solid state, while in solution an equilibrium between 1α and 1β is established with the former being a major component.[5]



1β

1α

As part of study to clarify the factors affecting the equilibrium, we calculated the electric dipole moment of 1α 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 1α (99.999 cm^3) and 1β (102.644 cm^3) calculated from atomic refractivity are nearly equal, they were assumed to be the same, 100 cm^3. 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 $\underline{1\alpha}$ and $\underline{1\beta}$ respectively and K is the equilibrium constant [$\underline{1\alpha}$]/[$\underline{1\beta}$], 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 $\underline{1\alpha}$ is much larger than that of $\underline{1\beta}$. This fact is in keeping with the observation by NMR spectroscopy that the more polar is a solvent, the larger is population of $\underline{1\alpha}$.[8]

Inspite 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 $\underline{1}$ appears very similar to that of the azide-tetrazole equilibrium.

REFERENCES

1 R. Huisgen, Angew. Chem., 1963, 75, 604; R. Huisgen, R. Grashey, and J. Sauer, 'The Chemistry of Alkenes', ed. by S. Patai, Interscience Publishers, New York, 1964, p. 806.

2 J. Elguero, Bull. Soc. Chim. Fr., 1971, 1925; H. Reimlinger, Chem. Ber., 1970, 103, 1900.

3 For reviews, see R.N. Butler, Chem. Ind. (London), 1971, 371; M. Tišler, Synthesis, 1973, 123; R.N. Butler, Adv. Het. Chem., 1977, 21, 323.

4 J. Elguero, R. Faure, J.P. Galy, and E.J. Vincent, Bull. Soc. Chim. Belg., 1975, 84, 1189; M. Rull and J. Vilarrasa, Tetrahedron Lett., 1976, 4175; L.A. Burke, J. Elguero, G. Leroy, and M. Sana, J. Am. Chem. Soc., 1976, 98, 1685; A. Könnecke, R. Dörre, E. Kleinpeter, and E. Lippmann, Tetrahedron Lett., 1978, 1311.

5 Y. Inagaki, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1974, 4575.

6 I.F. Halverstadt and W.D. Kumler, J. Am. Chem. Soc., 1942, 64, 2988.

7 Y. Inagaki, R. Okazaki, N. Inamoto, and T. Shimozawa, Chem. Lett., in press.

8 Y. Inagaki, R. Okazaki, N. Inamoto, K. Yamada, and H. Kawazura, unpublished results.

9 A.L. McClellan, 'Tables of Experimental Dipole Moment', W.H. Freeman and Co., San Francisco, 1963.

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