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ELECTRIC DIPOLE MOMENT OF 2,4-DI-t-BUTYL-6-METHYL-N-THIOSULFINYLANILINE

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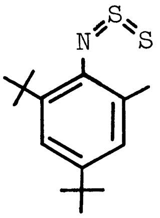
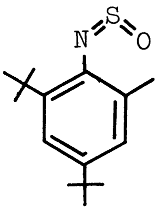
Electric dipole moments of the title compound and the corresponding sulfinyl and bromo compounds have been determined to be 1.51, 2.05, and 1.63 D respectively. From estimated bond moments of S=S (2.60 D) and N=S (0.55 D), charge separation of the N=S=S group has been found to be about half that of the N=S=O group.

Thiosulfinylamino compounds (R-N=S=S) exhibit interesting reactivities,[1] whereas their physical properties have scarcely been known. 2,4-Di-t-butyl-6-methyl-N-thiosulfinylaniline (1)[1b] is chosen for investigation of the physical properties of this novel functional group, because 1 is a stable crystalline compound whose molecular structure has been determined by X-ray crystallographic analysis and its thiosulfinylamino group does not suffer from a pronounced electronic perturbation as in the case of p-dimethylamino-N-thiosulfinylaniline prepared by Barton and Robson.[1a] We report here measurement of the dipole moment of 1 and estimation of the charge distribution in the thiosulfinylamino group.



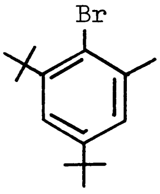
1.51 D

1



2.05 D

2



1.63 D

3

Dipole moments of 1, 2, and 3 were determined by measuring the dielectric constants in dilute benzene solutions at 25 °C and the values obtained are shown above.[2] As the dipole moment of 2,4-di-t-butyl-6-methylbromobenzene (3) (1.63 D) is nearly equal to the group moment of -Br (1.54 D),[3] contribution of 2,4-di-t-butyl-6-methylphenyl group to the C-Br bond can be neglected. Moreover, since the experimental value for the N-sulfinyl derivative 2 (2.05 D) is approximately the same as that of N-sulfinylaniline (1.9-2.0 D),[4] the dipole moment of the N-thiosulfinylaniline 1 (1.51 D) is reasonably assumed to be due to the group moment of thiosulfinylamino group.

Using the reported method in which the lone pair bond moments on the nitrogen and sulfur atoms have been taken into account,[5)] we estimated the bond moments of S=S and N=S bonds to be 2.60 and 0.55 D, respectively.[6)] From these values as well as the reported bond moments of S=O (3.4 D) and S=N (0.4 D) bonds of a sulfinylamino group (-N=S=O)[5)] and crystallographic data for thiosulfinylamino (-N=S=S)[7)] and sulfinylamino (-N=S=O)[8)] groups, we can estimate that the ratio of negative charge on the sulfur (II) of the N=S=S group to that on the nitrogen (δ_S-/δ_N-) is 3.8, and the corresponding ratio (δ_O-/δ_N-) in the N=S=O group is 8.7. Thus, charge separation in the thiosulfinylamino group is about half that in the sulfinylamino group. Furthermore, the large bond moment of the S=S bond (2.60 D) should be noted, because it presumably suggests that the S=S bond is of considerable coordination bond nature.

References and Notes

1) a) D.H.R. Barton and M.J. Robson, J. Chem. Soc., Perkin Trans. 1, 1974, 1245;
b) Y. Inagaki, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1974, 4575;
c) Idem., ibid., 1977, 293.

2) Molecular polarization was determined with the method of Halverstadt and Kumler[9)] in benzene at 25 °C. Electronic polarization was equated to molecular refractivity calculated on the basis of the additive property of atomic refractivity. Atomic polarization was assumed to be 5% of electronic polarization.

3) T. Shimozawa, "Yudenritsu no Kaishaku," Kyoritsu Shuppan, Tokyo (1967).

4) K.A. Jensen and N. Hofman Bang, Justus Liebigs Ann. Chem., 548, 95 (1941);
L. Jannelli, U. Lamanna, and H. Lumbroso, Bull. Soc. Chim. Fr., 1966, 3626;
G. Kresze and H. Smalla, Chem. Ber., 92, 1024 (1959).

5) H.F. van Woerden and S.H. Biji-Vilieger, Recl. Trav. Chim. Pays-Bas, 93, 85 (1974).

6) As the value of the dipole moment of N-sulfinylaniline (Ph-N=S=O) (1.95 D) is 95.1% of that of 2 (2.05 D), we employed the value 1.44 D (95.1% of the value of 1, 1.51 D) as the dipole moment of N-thiosulfinylaniline (Ph-N=S=S). X-Ray analysis revealed that the N-thiosulfinylaniline 1 has a Z-configuration in a crystalline state.[7)] The compound 1 is reasonably assumed to keep a Z-configuration in solution as well, because the IR spectrum in solution is identical with that in KBr disk, and also the NMR spectrum showed only one species over a temperature range of -102～+70 °C.

7) F. Iwasaki, R. Okazaki, and N. Inamoto, Abstracts of 10th Symposium on Structural Organic Chemistry (Oct. 1977, Matsuyama, Japan) 1S18; S=S and S=N bond lengths determined for 1 are 1.901 and 1.543 Å, respectively.

8) F. Iwasaki, Abstracts of Annual Meeting of the Crystallographic Society of Japan (1977, Tokyo) 2C1; S=O and S=N bond lengths determined for 2,4,6-tri-t-butyl-N-sulfinylaniline are 1.441 and 1.479 Å, respectively.

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

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