Chemistry

1963

SovietRxiv

Abstract

Full Text

Chemistry

A. L. Buchachenko, E. N. Gur' yanova, L. A. Kalashnikova, M. B. Neiman

Dipole Moments of a Radical and a Molecule: Diphenyl Nitroxide and Diphenylhydroxylamine

(Presented by Academician V. N. Kondrat' ev, 1 VIII 1962)

Determining the dipole moments of radicals and comparing them with the dipole moments of the corresponding molecules is of considerable interest in connection with the study of the behavior of the unpaired electron in radicals. The information thereby obtained on the distribution of charge density in the radical is conveniently correlated with the distribution of the spin density of the unpaired electron, which can be obtained by the method of electron paramagnetic resonance (e.p.r.). Up to now, the dipole moments of radicals had not been determined, with the exception of diphenylpicrylhydrazyl and the corresponding hydrazine (^{1}); in that case a substantial difference was found between the dipole moments of the molecule and the radical. However, it is very difficult to analyze this difference because of the complex structure of the particles.

We determined the dipole moments (d.m.) of the diphenyl nitroxide radical (I, see Table 1) and of the corresponding molecule—diphenylhydroxylamine (II). The substances were synthesized by the method described by Wieland (^{2}). The d.m. values were determined by the beat method in benzene at 25°. For each substance, the dielectric constants and densities of 5–6 solutions of different concentrations were determined in the range from 0 to 0.4 mole % for I and to 0.8 mole % for II. The results are given in Table 1. Here P_∞ is the molar polarization at infinite dilution; R_D is the molar refraction for the sodium D line, calculated by an additive scheme; μ is the dipole moment determined from the formula $\mu = 0.22\sqrt{P_\infty - R_D}$. Extrapolation of the experimental data to infinite dilution was carried out by the Hedestrand method.

Table 1

	Name of substance	$T_{\text{m.p.}}$, °C	P_∞	R_D	$\mu \cdot 10^{18}$
I	Diphenyl nitroxide, $Ph_2N{-}O\cdot$	64	240.8	55.8	3.0
II	Diphenylhydroxylamine, $Ph_2N{-}OH$	60	91.8	56.9	1.3

From the data on the d.m. of di- and trisubstituted amines it may be concluded that the contribution of the Ph_2N group to the d.m. of diphenylhydroxylamine is $\sim 0.7D$. If, as an extreme case, one assumes a planar configuration of the bonds at the nitrogen atom, an HON angle equal to $\sim 105^\circ$, and $\mu_{\text{OH}} \simeq 1.5D$, then the vector scheme gives a value of $\sim 1.0D$ for the d.m. of the N–O bond. In reality, the true value of this quantity is still smaller owing to deviations from the planar structure of the Ph_2NO group in the molecule.

If it is assumed that the contribution of the Ph_2N group to the dipole moment of the planar radical remains the same as in the molecule, then μ_{NO} in the radical proves to be equal to $\sim 2.3D$. Such a difference cannot be explained either by the possibility of association of molecules through intermolecular hydrogen bonds, or by a possible inaccuracy in the determination of R_D for the radical. It should be noted that the additive scheme is apparently insufficient as applied to radicals, since it does not take into account the possible exaltation of refraction. However, a direct determination of R_D in this case is difficult because of absorption at the wavelength of the sodium D-line.

The reason for the difference in the dipole moments should be sought in the features of the electronic structure of the particles. The increase in the dipole moment of the N—O bond in the radical as compared with the molecule can be explained by the interaction of the unpaired electron, which appears as a result of the removal of a hydrogen atom, with the lone pair of nitrogen. In this case oxygen supplies its partially occupied p-orbital for one of the electrons of this pair, as a result of which an excess negative charge appears on oxygen and a positive charge on nitrogen. At the same time, spin density of the unpaired electron appears on nitrogen. This picture is in qualitative agreement with the direction of the N $\rightarrow$ O dipole moment, and also with data on the distribution of the spin density of the unpaired p-electron in the radical, obtained by the EPR method,[3] ($\sim 30\%$ spin density on the oxygen atom, $\sim 40\%$ on nitrogen, and $\sim 30\%$ in the benzene rings). However, a more rigorous correlation of these data is possible only on the basis of theoretical calculations of the spin and charge electron densities in the radical.

Institute of Chemical Physics
Academy of Sciences of the USSR

Physicochemical Institute
named after L. Ya. Karpov

Received
1 VIII 1962

REFERENCES

[1] J. Turkevich, P. F. Oesper, C. P. Smith, J. Am. Chem. Soc., **64**, 1179 (1942).
[2] H. Wieland, Ber., **1**, 494 (1912).
[3] Y. Deguchi, Bull. Chem. Soc. Japan, **34**, 910 (1961).

Note: Figure translations are in progress. See original paper for figures.