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Abstract

Full Text

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DIPOLE MOMENTS OF CERTAIN YLIDES AND DIPHENYLCYCLOPROPENONE

A quantum-mechanical treatment by the primitive method of molecular orbitals shows that in the C_5H_5 ring there is one vacant place for one electron on the bonding orbital, whereas in the C_3H_3 and C_7H_7 rings one electron is located on an antibonding orbital. Some confirmation of this is the fact that in C_5H_5 the upper occupied level lies 2.09 eV lower than in C_7H_7, since the ionization potentials are respectively 8.69 and 6.6 eV ([1]). In this connection, molecules containing cyclopropenyl and cyclopentadienyl rings may in some cases give rise to considerable polarity. This can be checked by measuring dipole moments. Thanks to the kindness of D. N. Kursanov, in whose laboratory compounds of this type are being studied, we had the opportunity to obtain three substances: pyridinium cyclopentadienylide (I), *N*-benzylpyridinium-γ-cyclopentadienylide (II), and diphenylcyclopropenone (III).

The dipole moments of these substances were measured at 25 and 20° by the heterodyne method in benzene. In addition, pyridinium cyclopentadienylide was also measured in dioxane. The first two substances are very poorly soluble in nonpolar solvents. In mole fractions their solubility is of the order of 10^{-4}–10^{-5}. Therefore the accuracy of the determination of the dipole moment is not high. An error of 1.5 D is not excluded. Poor solubility in benzene indicates the high polarity of these compounds. In view of the low solubility there was no need to extrapolate the polarization to infinite dilution.

Table 1

Formula / medium	f	ε	P	P	P	$\mu \cdot 10^{18}$
[structural formula: pyridinium cyclopentadienylide] in benzene	$8.1 \cdot 10^{-5}$	2.2776	3655	43	3612	13.2
The same	$7.6 \cdot 10^{-5}$	2.2773	3964	43	3921	13.7
in dioxane	$2.79 \cdot 10^{-4}$	2.999	4953	43	4910	15.4
in dioxane	$2.32 \cdot 10^{-4}$	2.297	6267	43	6224	17.4
$C_6H_5 \cdot CH_2 - \overset{+}{N}\langle$phenyl ring$\rangle -$ cyclopentadienyl$^-$	$1.96 \cdot 10^{-4}$	2.280	6663	43	6620	17.8
$C_6H_5 \cdot CH_2 - \overset{+}{N}\langle$phenyl ring$\rangle -$ cyclopentadienyl$^-$	$1.45 \cdot 10^{-4}$	2.2795	1764	43	1689	9.0
$C_6H_5 \cdot CH_2 - \overset{+}{N}\langle$phenyl ring$\rangle -$ cyclopentadienyl$^-$	$1.41 \cdot 10^{-4}$	2.2786	2271	43	2196	10.3

In Table 1 are given, in order, the formulas, mole fractions of the dissolved substance, dielectric constant of the solution, total polarization, electronic polarization calculated from bond refractions, orientational polarization, and dipole moment.

As average values one may take the quantities 13.5 ± 0.3, 16.9 ± 1.5, and 9.6 ± 0.7 D. As for diphenylcyclopropenone, its solubility in benzene is somewhat greater and in this case the dipole moment was determined in the usual way with subsequent calculation by Hedestrand. Table 2 gives the mole fractions, dielectric constant, solution densities, and the values α and β according to Hedestrand.

From the data of Table 2, the value obtained for the total polarization is 596.4.

With $P_{\text{el}} = 62$ cm^3, this gives 534.4 cm^3 for the orientational polarization and 5.08 D for the dipole moment.

Table 2

	f	ε	d	α	β	$\mu \cdot 10^{18}$
structural formula of diphenyl-cyclo-propenone, $C_6H_5{-}C_3O{-}C_6H_5$	$1.065 \cdot 10^{-3}$	2.312	0.8763	16.73		5.08
structural formula of diphenyl-cyclo-propenone, $C_6H_5{-}C_3O{-}C_6H_5$	$1.129 \cdot 10^{-3}$	2.314	0.8761	16.67	1.120	5.08
structural formula of diphenyl-cyclo-propenone, $C_6H_5{-}C_3O{-}C_6H_5$	$1.932 \cdot 10^{-3}$	2.344	0.8771	16.63	1.124	5.08

As is evident, the dipole moment of pyridiniumcyclopentadienylide is sufficiently large and, in magnitude, comparable with the moments of gaseous halides of alkali metals. It is close to the product of the elementary charge and the distance between the nitrogen and the center of the five-membered ring. This indicates that the five-membered ring is the carrier of a delocalized negative charge, and that the affinity of cyclopentadienyl for the electron is real.

(IV) structural formula: phenyl-$\overset{+}{\text{N}}$=cyclopentadienyl

(V) structural formula: $C_6H_5{-}CH_2{-}$N$-$phenyl$-$cyclopentadienyl

The molecule as a whole may be regarded as a dipolar ion. The large dipole also indicates that the state with the opposite direction of the moment, with

ordinary bonds in the five-membered ring (without charge) IV, does not play a noticeable role. The increase in the moment of this compound in dioxane is possibly caused by intermolecular interaction due to the positive charge on nitrogen and the negative end of the dipole on the ether oxygen of dioxane.

The dipole moment of *N*-benzylpyridinium-γ-cyclopentadienyl is somewhat smaller than that of pyridiniumcyclopentadienylide, despite the greater separation of charges. This is apparently connected with the fact that in this compound one can represent the electron distribution without large excess charges, as in molecules with low or medium polarity (V). It is possible that some role is played by conjugation of the phenyl ring with the CH_2 group, with displacement of the electron into the ortho and para positions and with the appearance of a moment in the opposite direction. But even when these circumstances are taken into account, the experimental value of the moment, about 10 D, indicates that in this molecule the affinity of the five-membered ring for the electron plays a noticeable role.

The dipole moment of diphenylcyclopropenone (5.08 D) is greater than that of ordinary ketones (2.8 D) and somewhat greater than that of tropone (4.3 D). But this moment is much smaller than in the first two molecules. Steric conditions reduce the stability of the C_3H_3 ring. If one takes into account the possibility of such a charge distribution in which the minus is located on oxygen and the positive charge in the ortho and para positions of the phenyl rings, then this should also lead to a significant increase of the dipole moment above 2.8 D. Thus it may be concluded that in this case the positively charged three-membered ring is represented only to a small extent.

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REFERENCES

1. A. G. Harrison, L. R. Honnen et al., *J. Am. Chem. Soc.*, **82**, No. 21, 5593 (1960).

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