DIPOLE MOMENTS OF STERICALLY HINDERED p-HYDROXYSTYRYLPYRIDINES

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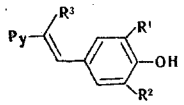
On the basis of measurements of dipole moments and a comparison of the results obtained with those calculated by a vectorial additive scheme, the structure of a series of sterically hindered p-hydroxystyrylpyridines have been determined.

The physicochemical and biological properties of sterically hindered p-hydroxystyrylpyridines depend on the nature of the ortho substituent in the phenol ring and the substituent in the ethylene bridge [1, 2]. The reason for such a dependence could be a change in the planarity or the geometric configuration of the styrylpyridines investigated, which contain voluminous substituents. To determine the structure of these compounds, we have determined experimentally (μ_{exp}) and have calculated by a vectorial scheme (μ_{calc}) the values of the dipole moments of 2,6-di-tert-butylphenol (I) and some substituted p-hydroxystyrylpyridines (II-VI).



II-VI

II–IV, VI Py=pyridin-4-yl; $R^1=R^2=t\text{-}C_4H_9$; V Py=pyridin-2-yl; $R^1=t\text{-}C_4H_9$; $R^2=CH_3$
II, V $R^3=H$; III $R^3=CH_3$; IV $R^3=C_6H_5$; VI $R^3=p\text{-}O_2NC_6H_4$

In the vectorial calculation of dipole moments, we assumed that the phenyl ring of the 2,6-di-tert-butylphenyl group was located in the plane of the figure; the angles between the bonds of the vinyl group, the plane of which coincides with the plane of the figure, was 120° and the y axis was directed through carbon atoms 1 and 4 of the 2,6-di-tert-butylphenol ring. The components of the dipole moments of the individual fragments of the molecule, calculated by the method given by Eda and Ito [3] are: pyridine, $\mu_x = 0.65$ D; $\mu_y = +2.14$ D (from the ring); nitrobenzene, $\mu_x = 0.98$ D; $\mu_y = +3.90$ D (from the ring). The dipole moment of fragment *a* (Fig. 1) was determined by comparing the components of the dipole moments of the styrylpyridines calculated for the 4-substituted derivatives [4]: $\mu_x = 0.50$ D, $\mu_y = -2.70$ D (from the ring), and the component of the dipole moment of pyridine is $\mu_x = \pm 0.15$ D, $\mu_y = -0.56$ D; the moment of the OH group is 1.55 D [3] and is directed perpendicularly to the plane of the figure, that of the tert-butyl group is 0.44 D and that of the methyl group 0.40 D, as in benzene derivatives [5].

Using the values of the components of the dipole moments of the individual fragments of the molecule obtained and also the angles of the vinyl group that were adopted, we have calculated [6] the dipole moments of the compounds under investigation. It is convenient to consider the calculation of the dipole moments for the cases of compounds (III) and (V), which are shown in Fig. 1. For compound (III) calculation of the trans and cis forms leads to values of 3.98 and 2.92 D, respectively (pyridine ring perpendicular to the plane of the figure). Since the experimental value of the dipole moment is 3.40 D, it may be assumed that in solution a mixture of cis and trans forms exists with some predominance of the less polar cis form. On the other hand it is extremely likely that the donor effect of the methyl group changes the direction of the dipole

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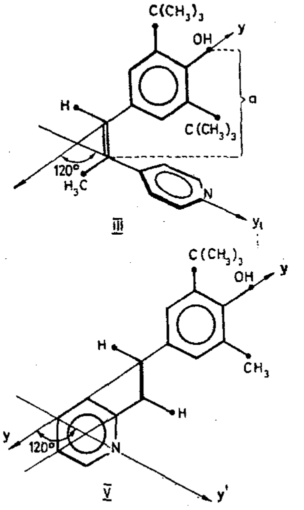

Fig. 1. Scheme of calculation of the dipole moments of compounds (III) and (V).

moment μ_y of fragment *a* to the opposite direction. In this case, the calculated dipole moment for the cis form will be 3.34 D, which is in good agreement with the experimentally determined value of this magnitude.

Investigations of the PMR and IR spectra of this compound confirmed this conclusion. Thus, it has been established [7] that in the IR spectra of trans isomers of various substituted ethylenes there are two characteristic bands in the 1330 and 965 cm^{-1} region which are absent from the spectra of the cis isomers. Unfortunately, the cis isomers do not have such characteristic bands, which makes it difficult to identify them directly by IR spectroscopy. We have also found in the IR spectra of all the compounds apart from (III) bands characteristic for the trans isomers, while in the spectrum of compound (III) these bands were absent or were extremely weak. However, in the PMR spectrum of this compound we detected two types of signals of hydrogen atoms of the ethylene group – in the 6.75 ppm region, which is characteristic for cis structures, and in the 7.65 ppm region, which is characteristic of trans isomers [8]. The intensity of the signals at about 6.75 ppm was approximately twice that of the signals in the 7.65 ppm region. Thus, on the basis of a study of the dipole moments and IR and PMR spectra it may be considered that compound (III) is a mixture of the cis and trans forms with a considerable predominance of the cis structure.

The dipole moment of compound (V) (Fig. 1) was found mathematically from the components of the dipole moment of α-substituted pyridine calculated by Eda and Ito's method [3] ($\mu_x = \pm\ 2.00$ D, $\mu_y = 0.94$ D, from the ring) and the values of the dipole moments adopted for the individual fragments (see above). The trans form in which the pyridin-2-yl ring is located in the plane of the figure (rotation by 180° about the C–C bond does not change the magnitude of the dipole moment) leads to satisfactory agreement with experiment. Calculation gives a value of the dipole moment of compound (V) of 2.65 D, while experiment gives 2.58 D. Depending on the orientation of the μ_x vector of the pyridin-2-yl ring relative to μ_z (OH), calculation for the cis form leads to values of 3.91 D (in the same direction), 1.70 D (in the opposite direction), and 3.02 D (pyridin-2-yl ring in the plane of the figure).

If the pyridin-2-yl ring is arranged perpendicular to the plane of the figure, then with $\mu_z(\mathrm{OH}) = \pm 1.55$D and μ_x (pyridin-2-yl) $= \pm 2.00$ D for the trans form we obtain the two values of the dipole moment of 3.55 and 0.45 D (the moments μ_x and μ_z in the same or opposite directions, respectively). Assuming that these forms exist in solution in equal amounts, from the formula $\mu^2 = \frac{1}{2}(3.55)^2 + \frac{1}{2}(0.45)^2$ we obtain $\mu_{\mathrm{calc}} =$ 2.53 D, which also agrees satisfactorily with the experimental moment of 2.58 D. It is clear that with such an approach to the calculation of the dipole moments of compound (V) (and the other compounds considered) it would be necessary to take into account the presence in the solution of other possible nonplanar conformations of the molecule. However, it is obvious that this cannot be done without special supplementary information.

The results of the determinations and calculations of the dipole moments of the p-hydroxystyrylpyridines investigated are given in Table 1. In the last column, this also shows the position of the pyridine ring relative to the 2,6-di-tert-butylphenol group. It can be seen from the results given that, in complete agreement with the results that we obtained previously [8] by IR and PMR spectroscopy, the sterically hindered p-hydroxystyrylpyridines studied have predominantly the trans configuration, with the exception of compounds (III) and (VI). According to PMR spectra [9], in inert solvents, 2,6-di-tert-butylphenol exists in the monomeric form. We have found that the dielectric constant ($\varepsilon_{1,2}$) of solutions of 2,6-di-tert-butylphenol in benzene depend linearly on the concentration, which also shows the absence of association. It might be assumed that in solutions of the compounds investigated, which contain a phenyl residue and a pyridine ring, acid–base interaction takes place. However, the linear dependence of $\varepsilon_{1,2}$ of solutions of the sterically hindered phenols in benzene on their concentration that we have established shows the practical absence of any interaction of the nitrogen heteroatom of the pyridine ring and the hydroxy group of the phenol because of the steric inaccessibility of the latter.

TABLE 1. Experimental Values of the Dipole Moments

Compound	$c\cdot10^4$, M	$\varepsilon_{1,2}$	α	$d_{1,2}$	β	P_{el}, cm^3	P_∞, cm^3	μ, D	
								μ_{eff}	μ_{calc}†
I	16,5523	2,2788	1,328	0,87359	−0,221	65,03	120,79	1,65	1,61
	10,7962	2,2770	1,315	0,87364	−0,289				
	6,79785	2,2758	1,294	0,87374	−0,286				
	3,85418	2,2749	1,255	0,87382	−0,267				
		$\varepsilon_1=2,2738$*	$\alpha_{av}=1,298$	$d_1=0,87391$*	$\beta_{av}=-0,266$				
II	3,38759	2,2790	7,533	0,87406	0,743	94,38	336,08	3,43	3,50- trans 2,90-cis
	4,14395	2,2804	7,645	0,87412	0,772				
	5,42033	2,2824	7,467	0,87421	0,781				
	6,63032	2,2844	7,431	0,87429	0,777				
		$\varepsilon_1=2,2732$	$\alpha_{av}=7,519$	$d_1=0,87384$	$\beta_{av}=0,768$				
III	2,14763	2,2760	7,171	0,87397	0,586	97,38	334,42	3,40	For explanation, see text
	3,01438	2,2775	7,299	0,87401	0,569				
	4,12628	2,2792	7,145	0,87407	0,582				
	5,21841	2,2809	7,084	0,87412	0,570				
		$\varepsilon_1=2,2725$	$\alpha_{av}=7,175$	$d_1=0,87386$	$\beta_{av}=0,577$				
IV	2,42605	2,2776	9,251	0,87385	0,160	119,91	435,35	3,93	3,80- trans 2,90-cis†
	3,04907	2,2789	9,237	0,87394	0,161				
	3,78641	2,2804	9,181	0,87405	0,163				
	5,38152	2,2838	9,240	0,87427	0,162				
	5,62633	2,2843	9,229	0,87431	0,163				
		$\varepsilon_1=2,2725$	$\alpha_{av}=9,228$	$d_1=0,87351$	$\beta_{av}=0,162$				
V	1,99678	2,2738	4,199	0,87377	0,535	81,08	217,10	2,58	For explanation, see text
	3,22730	2,2750	4,228	0,87383	0,603				
	4,06622	2,2758	4,222	0,87387	0,516				
		$\varepsilon_1=2,2719$	$\alpha_{av}=4,213$	$d_1=0,87368$	$\beta_{av}=0,551$				
VI	0,70644	2,2741	14,248	0,87372	−6,480	126,13	802,57	5,74	5,30-cis‡ 4,80- trans‡
	0,88333	2,2747	14,451	0,87380	−6,478				
	2,14892	2,2790	14,242	0,87381	−6,486				
		$\varepsilon_1=2,2718$	$\alpha_{av}=14,314$	$d_1=0,87385$	$\beta_{av}=-6,480$				

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* ε_1 and d_1 are the dielectric constant and density of benzene obtained by extrapolating $\varepsilon_{1,2}$ and $d_{1,2}$ of the solutions to zero concentration.

†The position of the pyridine ring relative to the 2,6-di-tert-butylphenol ring is shown.

‡Ring perpendicular to the plane of the figure.

EXPERIMENTAL

Compounds (II-VI) were synthesized by a published method [2]. Benzene of "cryoscopic" grade was purified as described by Osipov [10] and had bp 80.1°C (760 mm), d_4^{25} 0.8738, n_D^{25} 1.4979, ε^{25} 2.2725. The dielectric constants of the solutions were measured on an E-12-1 instrument with an oscillographic null indicator permitting the recording of a change of 0.005 of a relative capacity unit. The densities were determined pycnometrically. The electronic polarization (P_{el}) was taken as equal to the refraction, which was calculated from the sum of the refractions of the bonds [11] taking a refraction of 1.80 cm^3 for the O−H bonds as for an acid, and a refraction of 2.688 cm^3 for the C=C bond. The molecular polarization at infinite dilution (P_∞) was calculated by means of Hedestrand's equation [12]. The atomic polarization was not taken into account. The dipole moment was calculated from the equation $\mu = 0.221 \cdot \sqrt{P_\infty - P_{el}}$. All the measurements were performed at 25 ± 0.05°C. The errors in the determination of the dipole moments, evaluated by Le Fevre's method [13] did not exceed ±1-2% of the measured value.

The IR spectra were recorded on a UR-20 instrument in $CHCl_3$ solution and the PMR spectra were obtained on an INMC-60 instrument in acetonitrile and CCl_4 using tetramethylsilane as internal standard.

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