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Dipole Moments of Guaiacol Derivatives

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The molar polarizations and dipole moments of eugenol, dehydrodi-*iso*eugenol, 2,6-dimethoxyphenol, vanillin and *o*-vanillin have been determined in benzene and dioxan solution. It is found impossible to distinguish by means of dipole moment data between a stiff configuration containing an OH...OCH_3-chelate and a structure with "freely" rotating substituents. The rearrangements observed in the ultraviolet spectrum of guaiacol, when changing from an inert solvent (*cyclo*hexane) to dioxan, however, indicate a loss of planarity of the molecule when going from intramolecular to intermolecular hydrogen bond formation in accordance with previous infra-red spectroscopic investigations. A marked intermolecular interaction between *o*-vanillin and dioxan is noted.

It has been observed that the association between solute and solvent due to hydrogen bonds brings about an increase of the dipole moment of the associated molecules which is higher than the pure vectorial addition of the moments of the isolated molecules [1–3]. The observed dipole moment increment grows usually with the increase of the hydrogen bond strength. An exception is made by guaiacol, which shows the same moment in inert solvent (benzene) as in hydrogen acceptor solvent (dioxan). This effect was explained by Curran [4] as being caused by the OH...OCH_3 chelate, which should hinder the formation of the intermolecular hydrogen bond between the phenolic hydroxyl group and the oxygen atom of dioxan. This explanation, however, is contradicted by spectroscopic evidence, which indicates that guaiacol, like phenol, forms intermolecular hydrogen bonds with proton acceptor solvents [5–7]. Furthermore a series of investigations seems to indicate that the chelate in question is very weak in nature [7–9]. Actually, Fischer and Zengin [10] concluded from measurements of relaxation times that the hydroxyl group in eugenol is completely free to rotate also in such inert solvents as carbon tetrachloride. However, in the light of investigated infra-red spectra this assumption does not seem to be justified [7].

Full clarity regarding the interpretation of the dipole data of guaiacol appears to be obtainable only by determining the dipole moments of a series of guaiacylic and related compounds in inert and proton acceptor solvents. In order to achieve this end the measurements in benzene and dioxan solutions of the dipole moments of a series of compounds related to guaiacol are reported in the present paper.

EXPERIMENTAL

The dielectric constants required in the dipole moment determinations, were measured by the heterodyne-beat method at 500 kc using an apparatus described elsewhere [11]. The cylindrical measurement cell used in the investigation was made of Pyrex glass and was of the type described by le Fevre [12]. Its volume was 50 ml and its variable capacity about 25.5 pF.

The refractivities used in the calculations of the dipole moments were partially taken from the relevant literature and partially determined experimentally using an Abbe refractometer. The molar polarization at infinite dilution was calculated by the methods developed by Halverstadt and Kumler [13] and Smith and Cleverdon [14], from the dielectric increment and the variation of the specific volume with concentration.

The dipole moments were calculated employing the usual formula

$$\mu = 0.01281\sqrt{(P_{2\infty} - [R])\,T} \quad D \qquad (1)$$

Table 1. Weight fractions, dielectric constants and specific volumes of benzene solutions at 25°C. w_2 denotes weight fraction of solute, v_2 specific volume of solution, $\alpha = \frac{\partial \varepsilon}{\partial w_2}$ and $\beta = \frac{\partial v_2}{\partial w_2}$ at infinite dilution. ε is dielectric constant of solution.

	w_2	ε	v_2	α	β
Benzene	1.00000	2.2726	1.14670		
Guaiacol	0.01638	2.360	1.1420	+5.294	−0.2620
	0.02836	2.424	1.1386		
	0.04584	2.522	1.1347		
Eugenol	0.01522	2.336	1.1428	+4.096	−0.2162
	0.02647	2.383	1.1415		
	0.04116	2.446	1.1374		
Dehydrodi*iso*-eugenol	0.004703	2.286	1.1445	+3.041	−0.483
	0.008014	2.298	1.1427		
	0.01290	2.312	1.1416		
2,6-Dimethoxy-phenol	0.009678	2.317	1.1427	+4.545	−0.3375
	0.009842	2.314	1.1438		
	0.01523	2.342	1.1407		
	0.02491	2.374	1.1386		
	0.02735	2.396	1.1371		
	0.03379	2.428	1.1356		
Vanillin	0.01118	2.336	...	+5.365	−0.4150
	0.01329	2.350	1.1410		
	0.01866	2.384	1.1391		
	0.02251	2.408	...		
	0.03397	2.491	...		
	0.02673	...	1.1356		
	0.02792	...	1.1348		
o-Vanillin	0.005961	2.334	1.1441	+10.00	−0.465
	0.008308	2.356	1.1426		
	0.01147	2.388	1.1410		
	0.01345	2.403	1.1408		
	0.01743	2.446	1.1389		
	0.01963	2.471	...		

Table 2. Weight fractions, dielectric constants and specific volumes of dioxan solutions at 25°C.

	w_2	ε	v_2	α	β
Dioxan	1.00000	2.214	0.97272		
Eugenol	0.01297	2.275	0.9724	+4.790	−0.0254
	0.02266	2.321	0.9719		
	0.03545	2.384	0.9722		
Dehydrodi*iso*-eugenol	0.002970	2.223	0.9725	+3.348	−0.1388
	0.008350	2.242	0.9723		
	0.01314	2.259	0.9709		
2,6-Dimethoxyphenol	0.01122	2.269	0.9714	+4.903	−0.1246
	0.02044	2.314	0.9713		
	0.02972	2.353	0.9690		
Vanillin	0.009672	2.307	0.9714	+9.625	−0.1820
	0.01988	2.406	0.9686		
	0.02862	2.484	0.9679		
o-Vanillin	0.007409	2.319	0.9710	+14.13	−0.0760
	0.01165	2.382	0.9706		
	0.01967	2.502	0.9698		

Table 3. Molar polarizations and dipole moments.

Substance	Solvent	$P_{2\infty}$	$[R]$	μ	$\Delta\mu$	Author
Methanol *	Benzene	—	—	1.66	+0.25	2
	Dioxan	—	—	1.91		2
Phenol *	Benzene	—	—	1.53	+0.25	2
	Dioxan **	—	—	1.78		2
Anisol *	Benzene	—	—	1.31	+0.03	2
	Dioxan	—	—	1.34		2
Guaiacol	Benzene	156.6	34.6	2.44	±0.0	Present
	Benzene	155.2		2.41		4
	Dioxan	155.0		2.41		4
Eugenol	Benzene	172.2	48.3	2.46	+0.05	Present
	Dioxan	177.0		2.51		»
Dehydrodi*iso*-eugenol	Benzene	251.6	92.8	2.79	+0.09	»
	Dioxan	261.9		2.88		»
2,6-Dimethoxyphenol	Benzene	169.2	41.4	2.50	−0.07	»
	Dioxan	161.9		2.43		»
Vanillin	Benzene	208.9	40.5	2.87	+0.52	»
	Dioxan	275.3		3.39		»
o-Vanillin	Benzene	317.7	41.2	3.67	+0.47	»
	Dioxan	392.2		4.14		»
Salicylaldehyde	Benzene	—	—	2.88	+0.11	4
	Dioxan	—	—	2.99		4
p-Hydroxybenzaldehyde	Dioxan	—	—	4.19		17

* For the sake of conformity, the dipole data of methanol, phenol and anisol are taken from one and the same publication although also other data are available, cf. *e.g.* Ref.[1].

** On dilution with heptane 1.86 *D* [2].

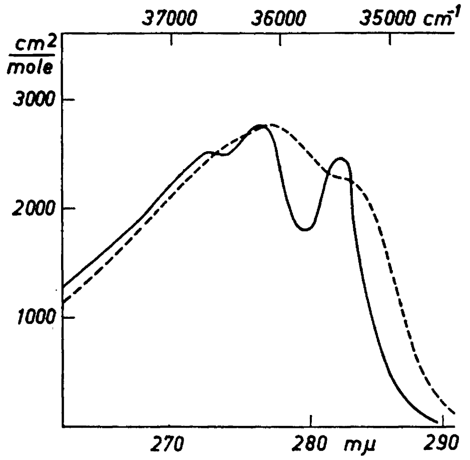


Fig. 1. Ultraviolet absorption spectrum of guaiacol at 20°C. Solvents: *Cyclo*hexane ———, dioxan -------.

No correction was made for the influence of the atomic refraction, *cf.* Ref.[15].

The ultraviolet spectra investigated were determined with a Beckmann spectrophotometer Model DU equipped with a thermostat, which was adjusted to 20.0°C.

Reagents. The investigated phenols were purified as previously described [7]. *Pro analysi* benzene (Merck AG) was distilled twice and stored over sodium. Dioxan was purified using the method given by Hess and Frahm [16] and stored over sodium. The *cyclo*hexane used was of "spectrograde" purity (Eastman Kodak).

DISCUSSION

The experimental data and the results of the investigation are found in Tables 1—3 and Fig. 1. An examination of Table 3, especially the column giving $\Delta\mu$-values, *i.e.* differences between dipole moments in dioxan and benzene solution, shows that the investigated substances, roughly taken, can be divided into three groups:

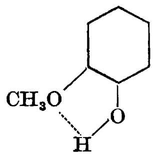
a) Substances with free hydroxyl groups (phenol, methanol), showing a moderate increase in dipole moment (about 0.3 *D*) when forming hydrogen bonds with dioxan.

b) Substances forming chelates of the type OH...OCH_3 (guaiacol, eugenol, 2,6-dimethoxyphenol and dehydrodi*iso*eugenol), having almost identical moments in benzene and dioxan solution.

c) Vanillin and *o*-vanillin, having substantially higher dipole moments in dioxan than in benzene solution (about 0.5 *D*). A small increase in the dipole moment is also shown by salicylaldehyde (0.11 *D*), which forms a strong chelate of the same type as *o*-vanillin, *i.e.* CHO...HO [8].

Below, some of the experimental results will be discussed in closer detail. Taking guaiacol as an example it is found, that in the same manner as in phenol [2], there is a marked rearrangement of the ultraviolet spectrum of guaiacol, when going from an inert solvent (*cyclo*hexane) to dioxan (*cf.* Fig. 1). Thus, counting from the band maxima there seems to be a "red shift" of the bands in the 280 mμ region of about 200—300 cm^{-1}. Furthermore a marked deletion of spectral fine structure is observed. According to Merkel[18] such phenomena could be accounted for by an increase of the significance of polar valence structures and a decrease of the planarity of the whole molecule. In the case under review it would mean that the planar, stiff chelate structure is replaced by a less symmetric guaiacol-dioxan complex, where the positive and negative charge centers of the hydroxyl group are more separated. This interpretation is also in conformity with previous infra-red spectroscopic investigations on guaiacylic compounds and their deuterated derivatives [7,19].

According to the calculations made by Curran[4] a stiff *cis*-configuration of guaiacol (I) should cause a dipole moment of 2.45 *D*, while in the same



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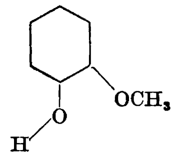

II

conditions a stiff *trans*configuration (II) should cause a moment of only 0.8 *D* in benzene and 0.9 *D* in dioxan solution. In the light of the previously discussed spectroscopic results it can be stated, that although in benzene solution a stiff *cis*-configuration can be taken for granted, it is not as likely, that a stiff structure would at all be present in dioxan solution. Using known dipole data for phenol and anisol (*cf.* Table 3) simple vector rules[20] give a moment of about 2.5 *D* for a guaiacol molecule with "freely" rotating substituents. Thus, in this case, a selection between the different possibilities must be made by other means than dipole data.

The ionization constants in water, p*K* (and thus also the hydrogen bond formation capacity of the hydroxyl group[7]), of phenol, guaiacol, 2,6-dimethoxyphenol and eugenol (and probably also of dehydrodi*iso*eugenol) are nearly equal and about 10, *cf.* Refs. [21], [22], whereas the p*K*-values of vanillin and *o*-vanillin are considerably lower, *i.e.* 7.4 and 7.9, respectively[23]. Bearing in mind the introductory discussion it would be expected that the difference between dipole moment in dioxan and benzene solution, $\Delta\mu$, should be much higher in the latter two substances than in the former ones. It is of interest to note that this is indeed the case (*cf.* Table 3).

On the other hand, the small $\Delta\mu$-value of salicylaldehyde, *i.e.* $+ 0.11$ *D*, is worth noting. In *p*-hydroxybenzaldehyde the $\Delta\mu$-effect must be very high as indicated by the strong dipole moment in dioxan solution, *i.e.* 4.19 *D*. The great difference in behaviour between the two isomers must principally be attributed to the influence of the CHO...HO chelate in salicylaldehyde. This chelating effect seems to be of greater strength than the corresponding one in *o*-vanillin, *cf.* Refs. [21], [24], where a more marked intermolecular interaction is noted.

Summing up the results it can be concluded that it is impossible to distinguish between a stiff *cis*-structure and a structure with "freely" rotating substituents in guaiacylic compounds by means of dipole moment studies.

The absence of increase of dipole moment in guaiacylic compounds of very weak acidity (p*K* 10) when an intermolecular hydrogen bond is formed with a proton acceptor solvent must apparently, at least partly, be ascribed to charge rearrangements when the weak OH...OCH_3 chelate is broken.

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