FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

REDAKTÖR — TOIMITTAJA

Gösta Brunow

INNEHÅLL — SISÄLTÖ

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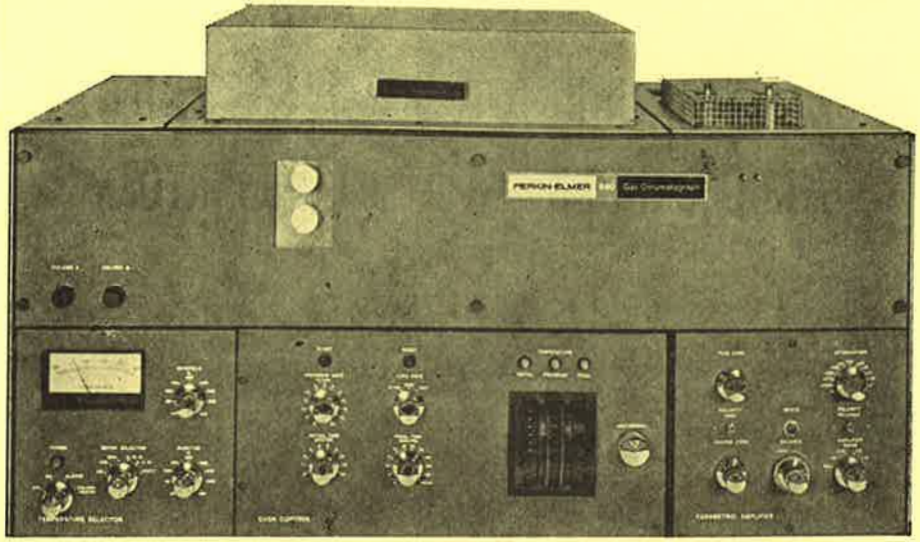

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CONTENTS

Evaluation of Solubility Parameters of Polymers

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The miscibility of two liquids, liquid-polymer and polymer-polymer depends on the free energy involved in the process. This can be represented by the familiar free energy equation.

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

The significance of this equation is to predict whether a given process will take place or not. If ΔG has a negative value, the process will occur. As is well known, increasing the temperature will favor solution. When a polymer goes into solution, the polymeric chains uncoil and are separated from one another. This gives rise to increased ΔS. Hence, T and ΔS favor negative free energy values. Apparently, whether the two systems would be miscible, depends on ΔH value.

According to Hildebrand [27] the heat of mixing, ΔH, of two components is defined as

$$\Delta H_M = V_M \cdot v_1 \cdot v_2 \left[\left(\frac{E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{E_2}{V_2} \right)^{\frac{1}{2}} \right] \tag{2}$$

where V_M = the total volume of the mixture
v_1 and v_2 = volume fractions of components 1 and 2.
V_1 and V_2 = molar volumes of components 1 and 2.
E_1 and E_2 = the energy of vaporization of components 1 and 2.

Since cohesive energy density (c.e.d.) is the energy of vaporization per cm^3, and it is customary to use the $(c.e.d.)^{\frac{1}{2}}$, known as solubility parameter denoted by δ, a rearrangement of Eq (2) gives

$$\frac{\Delta H}{V_M \cdot V_1 \cdot V_2} = (\delta_1 - \delta_2)^2 \tag{3}$$

and as a working definition of Hildebrand's solubility parameter

$$\delta = \left(\frac{-E}{V} \right)^{\frac{1}{2}} \tag{4}$$

Calculation of the solubility parameter: The solubility parameters of solvents, δ_s, are readily calculated from the heats of vaporization,[27,41] thermal coefficients, relation of pressures to temperatures, van der Waals gas constants, critical pressures,[29] surface tensions,[29] or structural formulas.[30] The solubility parameters of polymers, δ_p, cannot be determined directly, because most polymers cannot be vaporized. They can be determined indirectly from the δ_s of a solvent in which the polymer mixes

- in all proportions
- without heat effect
- without volume change
- without reaction or any special association.

The solubility parameter of a solvent mixture is related to equation [10]

$$\delta_{mix} = \frac{x_1 V_1 \delta_1 + x_2 V_2 \delta_2}{x_1 V_1 + x_2 V_2} \tag{5}$$

where x_1 and x_2 = the mole fractions of components 1 and 2.

Gee [22] suggested that equilibrium swelling measurements can be used to estimate the solubility parameter of the polymer. Neglecting the entropy of elastic deformation, he showed that maximum swelling occurs in a solvent having the same δ as the polymer. For swelling equilibrium state the Flory-Rehner equation [18] may be written as

$$RT \left\{ \log \frac{Q}{Q+1} + \frac{1}{Q+1} + \frac{\chi}{(Q+1)^2} - \frac{V}{V_c} \left(\frac{1}{Q+1} \right)^{1/3} \right\} \tag{6}$$

where Q = the swelling coefficient (volume of liquid imbined per unit volume of the polymer)
χ = the interaction parameter.

Using Scatchard-Hildebrand equation,

$$\Delta H_1^m = \frac{KV}{RT} (\delta - \delta_p)^2 V_p^2 \tag{7}$$

and assuming K to be constant, Gee [21] showed that Q is a function of $V^{\frac{1}{2}} (\delta - \delta_p)$. He also showed that Q versus $V(\delta - \delta_p)$ curve is Gaussian and

$$Q = Q_{max} \cdot \exp \{ -KV (\delta - \delta_p)^2 \} \tag{8}$$

Hence a plot of $\left(\frac{1}{V} \log \frac{Q_{max}}{Q} \right)^{\frac{1}{2}}$ versus δ of the liquids gives a

straight line having the intercept equal to δ_p. Although Gee was largely successful in determining δ_p for a number of rubber compounds, it was obvious that swelling coefficients of aromatic liquids were much higher than what would be expected from their cohesive energy densities. Subsequently Boyer and Spencer [6] calculated V_c by measuring Q in a liquid of known χ. χ being a free-energy term, is usually written as the sum of χ_s and χ_H,

$$\chi = \chi_s + \frac{KV}{RT}(\delta - \delta_p)^2 \tag{9}$$

Bristow and Watson [8] have determined the constants in the last term of Eq (6) by stress strain measurement and calculated χ values of a number of rubber compounds in about twenty different liquids.

The phenomenon of solution viscosity of polymers is quite akin to that of swelling. In a good solvent the molecular chains get extended, giving rise to a retractive force similar to one encountered in swelling process. Hence both equilibrium configuration of the molecular chain and solution viscosity, like swelling, depend on the balance between the free-energy-change due to mixing and that due to elastic deformation. The analogy between swelling coefficients and intrinsic viscosity numbers was first pointed out by Gee. Later on Frith [19] using statistical mechanics, deduced a relation

$$\frac{\eta_{sp}}{C} = \left[\eta\right] - \frac{KV}{RT}(\delta - \delta_p)^2 C \tag{10}$$

which showed that whereas $[\eta]$ is independent of solvent, the slope of η_{sp}/C against C increases with increase in solvent capacity. This was contradicted by Spurlin et al [44] who found that for flexible polymers, $[\eta]$ increases and the slope decreases with solvent capacity. Subsequently Flory and Fox [17] deduced the equation

$$\tfrac{1}{2} - \chi = \frac{V[\eta]}{2\,C_M^1\,KM}\left\{\left(\frac{[\eta]}{[\eta]_\Theta}\right)^{2/3} - 1\right\} \tag{11}$$

where C_M^1 = a constant characteristic of a particular polymer sample.

$[\eta]_\Theta$ = the intrinsic viscosity in Θ solvent.

The fundamental Eq (11) is applicable to homogeneous polymer samples only. Since Q and $[\eta]$ both depend on similar parameters, it is logical to think, that, like Q, $[\eta]$ is a Gaussian function of $V^{\frac{1}{2}}(\delta - \delta_p)$ and

$$[\eta] = \eta_{max} \cdot \exp\{V(\delta - \delta_p)^2\} \tag{12}$$

Small [43] has found a set of additive constants, which allow the calculation of $(EV)^{\frac{1}{2}}$. These are called molar-attraction

constants, and are denoted by the symbol F. Then $\sum F$ summed over the groups present gives the value of $(EV)^{\frac{1}{2}}$ for one mole of the substance concerned; the molar cohesive energy E, cohesive energy density c.e.d. and solubility parameter are then given by

$$E = \frac{(\sum F)^2}{V};\ \text{c.e.d.} = \left(\frac{\sum F}{V}\right)^2;\ \delta = \frac{\sum F}{V} \tag{13}$$

This method cannot be used for compounds such as hydroxyl compounds, amines, amides, and carboxylic acids, in which hydrogen bonding occurs.

Polar systems: In Hildebrands treatment of his "regular" solutions the solubility parameter is a measure of only the cohesive forces between like molecules. By extending the heat of mixing approach from a regular solution to one where more than pure dispersion forces are operative, the square of the difference of the solubility parameters now becomes a measure of all the interactions between unlike molecules. The implicit assumption in this derivation, however, is that a "regular" solution exists only where positive deviations from Raoults law are possible. Therefore to account for all polar interactions and negative deviations from Raoults law the basic equation must be modified. Hildebrands theory can be modified to account for the orientation forces neglecting induction forces [5]

$$\Delta H_M = V_s A_{12}(n_1 + x n_2)\, v_1\, V_2 \tag{14}$$

where A_{12} = the interchange energy density

V_s = the solvent molar volume

The Flory interaction parameter may be written

$$\chi = \chi_s + \frac{V_1}{RT} A_{12} \tag{15}$$

The interchange energy density, A_{12}, is given by

$$A_{12} = (C_{11} + C_{22} - 2C_{12}) \tag{16}$$

where C_{12} characterizes the intermolecular forces acting between molecules 1 and 2. For the pure components, C_{11} and C_{22} are the cohesive energy densities of components 1 and 2:

$$C_{11} = \frac{\Delta E_1^V}{V_1} = \lambda_1^2 + \tau_1^2$$

$$C_{22} = \frac{\Delta E_2^V}{V_2} = \lambda_2^2 + \tau_2^2 \tag{17}$$

Splitting the energy of vaporization of a polar fluid into nonpolar and polar parts permits the following definition of solubility parameters to be made.

Nonpolar solubility parameter $\lambda_i = \left(\frac{\Delta E^V_{i\,(np)}}{V_i}\right)^{1/2}$ (18)

Polar solubility parameter $\tau_i = \left(\frac{\Delta E^V_{i\,(p)}}{V_i}\right)^{1/2}$ (19)

where $\Delta E^V_i(np)$ and $\Delta E^V_i(p)$ are the nonpolar and the polar contributions to the energy of vaporization

$$\Delta E^V_{i\,(total)} = \Delta E^V_{i\,(np)} + \Delta E^V_{i\,(p)} \quad (20)$$

Since the polar term can be related to the dipolmoment and the dipolmoment can be in turn related to the dielectric constant, it is proposed that the dielectric constant could be used as a measure of the polar term in the modified Hildebrand equation. *Dielectric constants:* The central problem in the Kirkwood [31] treatment was the recognition of the effects due to the orientation restraints on near neighbours by a given permanent dipole

$$\frac{4\pi\,Ng\,\mu\bar{\mu}d}{9kTM} = \left(\frac{(\varepsilon-1)(2\varepsilon+1)}{9\varepsilon} - \frac{\varepsilon\infty - 1}{\varepsilon\infty + 2}\right) \quad (21)$$

where μ is the dipole moment and $\bar{\mu}$ is the sum of the molecular dipole and the moment induced as a result of hindered rotation in the spherical region surrounding the molecule. The product $\mu\bar{\mu}$ may be replaced by $g\mu$,[2] where g is a correlation parameter. The limiting form of the Kirkwood Eq (21) assuming $\frac{\varepsilon\infty - 1}{\varepsilon\infty + 2}$ is smale, can be written as $\frac{(\varepsilon-1)(2\varepsilon+1)}{9\varepsilon}$ and when ε is much greater than unity, the limiting form is $2/g\ \varepsilon = 0.22\varepsilon$.

Paruta [39] suggested that there exists an emphirical relationship between the dielectric constant and the solubility parameter. In general the solvents, which associate primarily through hydrogen bonding give the best correlation between reported δ and their respective ε, ($\delta = 0.22\ \varepsilon + 7{,}5$).

For dielectric constants below 10 but greater than 3, the modified solubility parameter for pure solvents and solvent mixtures are presented as follows

$$Sp = 7.5 + \left(0.2 - \frac{0.25}{\varepsilon - 0.1}\right)\varepsilon \quad (22)$$

$$Sp_{12} = 7.5 + \left(0.2 - \frac{0.25}{\varepsilon - 0.1}\right)\varepsilon_{12} \quad (23)$$

For nonpolar solvents, the modified solubility parameter for pure solvents and solvent mixtures are defined as follows

$$Sp = 7.5 + 0.03\ \varepsilon \quad (24)$$

$$Sp_{12} = 7.5 + 0.03\ \varepsilon_{12} \quad (25)$$

Hydrogen bonding. For practical purposes, solvents are divided into three classes according to their hydrogen bonding capacity [10]: poorly, moderately and strongly hydrogen bonded. The quantitative values of Gordy's [23] infrared shift were included, although it was pointed out that this was not a true measure of the hydrogen bond strength. This idea was developed by Lieberman [32] who arbitrarily assigned values of 0—0,6, 0,7—1,3 and 1,4—2,0 to solvents which belonged to the poorly, moderately and strongly bonded groups. By plotting the square of the hydrogen bonding capacities as ordinates against δ values as abscissas, he was able to prepare maps which graphically showed the solubility characteristics of typical polymers.

A careful extension of Lieberman's calculations was given by Dyck and Hoyer.[13] They proposed a new set based on polystyren as the polymer.

Nygard attempted to evaluate the hydrogen bond factor by solving for the attraction constant for hydroxyl in Small's Eq (13).

Gardon [20] has given an extensive discussion of the influence of various kinds of intermolecular forces on solubility parameter.

Crowley et al [11] reported a three-dimensional approach to solubility based on dipole moment, hydrogen bonding and solubility parameter values for solvents. Three-dimensional models were constructed that described the solubility of some polymers. Further Crowley et al presented a method by which three-dimensional models are reduced to 2-dimensional solubility maps.

A three-dimensional solubility parameter system based on the homomorph concept has been developed by Hansen.[25] The basis of the system is the assumption that the total cohesive energy ΔE can be divided into contributions from dispersion forces, ΔE_d, polar forces, ΔE_p, and hydrogen bonding forces, ΔE_h. Thus

$$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h \quad (26)$$

or

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (27)$$

According to Eq (27), the solubility parameter of a given solvent can be considered a vector with components δ_d, δ_p and δ_h. Each solvent can be located in a three dimensional system as a fixed point with co-ordinates agreeing with Eq (27) as demonstrated in Figure 1.

The whole treatment of the solubility parameter is semi-empirical; no real theory has been developed. The best empirical rule to remember is still "like dissolves like".

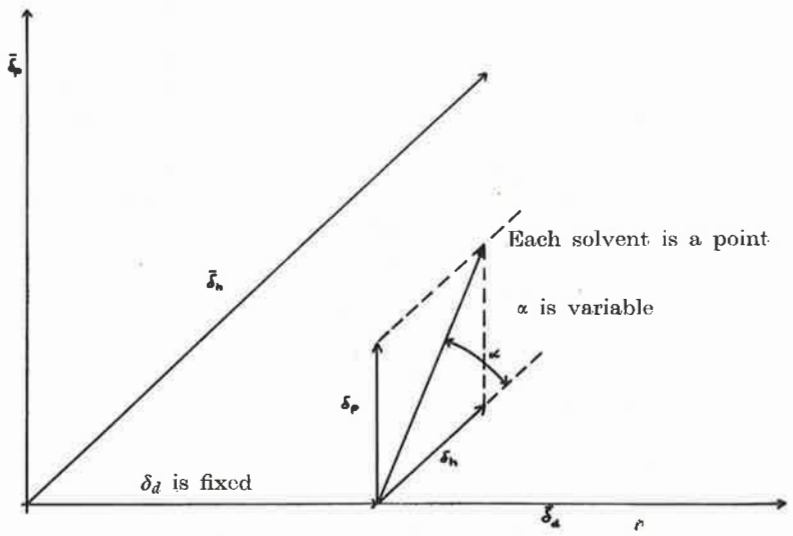

Figure 1. The experimental method of locating solvents as points in the solubility parameter plotting technique.[25]

Applications

Solubility data on some polymers have been reported.

Addition polymers of unsaturated esters: poly(methylmethacrylate),[28, 35, 2, 5, 25] poly(t-butyl methacrylate),[28, 35] poly(ethylmethacrylate),[28, 35] poly (n-propylmethacrylate),[28] poly(isobornyl methacrylate),[28] poly(ethoxyethyl methacrylate),[35] poly(methylacrylate),[28, 37] poly(ethyl acrylate),[28, 35, 37] poly(propyl acrylate),[37] poly (n-butyl acrylate)[28, 35, 37] poly(vinyl acetate).[25, 5, 28]

Hydrocarbon polymers: polyethylene,[26, 40 2, 5] polystyrene,[14, 7, 8, 26, 45, 36, 33, 42] polyisobutylene,[26, 42, 10, 8, 5, 25, 16] polyisoprene,[43, 36, 33, 21, 22] polybutadiene,[4, 5, 25, 42] natural rubber [3, 42, 33, 21, 34, 22]

Halogen-containing polymers: polytetrafluoroethylene,[43] polychlorotrifluoroethylene,[24, 9] poly(vinylchloride),[8, 10, 26, 12, 25, 33] poly(vinylidene chloride),[10] chlorinated rubber,[10] polychloroprene,[43, 21, 22, 8] poly(vinylbromide).[15, 43]

Nitrile-containing polymers: polyacrylonitrile,[43, 46] polymethacrylonitrile.[43]

Cellulose derivatives: cellulose dinitrate,[43, 33] cellulose nitrate,[10, 11, 38] cellulose acetate,[43, 33] cellulose acetate butyrate [11].

Condensation polymers: poly(ethylene terephthalate),[43] nylon-6,6,[10] nylon-8,[10] polyurethan.[34]

Polysiloxanes: polydimethylsiloxane.[10, 34, 47]

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An Extended Hückel Calculation of the Torsional Barrier in Anisole

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Abstract

Using the Extended Hückel Theory the electronic energy for anisole with different torsional angles for the methoxy group has been calculated. The minimum energy is found with the methoxy group 75° out of plane and the corresponding torsional barrier 7,9 kcal/mole. Some evidence for the existence of a double potential exists. The variation of overlap population, net charge and hybridization with the torsional angle, and the validity of the $\sigma-\pi$ separation for the nonplanar conformations is discussed.

Introduction

In connection with the analysis of ESR-spectra of methoxy-substituted benzenes and biphenyls, the orientation of the methoxy group is important. In the study: "Oxidation of Methoxybenzenes" Zweig and coworkers [1] proposed the existence of cis and trans rotamers in 1,4-dimethoxybenzene. In a more recent study Forbes and Sullivan [2] have shown that the ESR-spectrum of 1,4-dimethoxybenzene could be fully assigned if the presence of the cis and trans rotamers was supposed. The aim of the present calculation is to find out if the planar or nonplanar conformation is the most stable.

The Method [3]

The molecular orbitals are constructed as linear combinations of unhybridized valence shell atomic orbitals:

$$\psi_i = \sum_j c_{ij} \Phi_j$$

Using the variation method the total energy is minimized and a set of Hückel equations is obtained:

$$\sum_{j=1}^{n} [H_{ij} - ES_{ij}] c_{ij} = 0 \quad ; \quad i = 1,2,\ldots,n$$

where as usual:

$$S_{ij} = \langle \Phi_i | \Phi_j \rangle$$

and

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$$

All the overlap integrals are retained in this approximation and calculated according to Mulliken et al.[4] The exchange integrals H_{ij} are found using the familiar Wolfsberg—Helmholtz approximation [5]:

$$H_{ij} = 0.5K\,(H_{ii} + H_{jj})\,S_{ij}$$

The value of K used was 1.75 (see ref. 3 for a discussion). The Coulomb integrals H_{ii} were approximated as the valence state ionization potentials for the particular atomic orbital under consideration [6]:

Hydrogen	$H_{ii}(1s) = -13.6$ eV
Carbon	$H_{ii}(2s) = -21.4$ »
	$H_{ii}(2p) = -11.4$ »
Oxygen	$H_{ii}(2s) = -35.3$ »
	$H_{ii}(2p) = -17.5$ »

The values of the Slater orbital exponents were taken to 1.000 for H, 1.625 for C and 2.275 for O. The geometry assumed for anisole is shown in fig. 1. The value 121° for the COC angle and the lengths of the C—O and O—CH_3 bonds were taken from x-ray data for 1,4-dimethoxybenzene in the crystalline state.[8] In the present calculation only the angle between the plane of the ring and the plane containing the O—CH_3 group was varied. Only one fixed orientation was given to the methyl group (fig. 1).

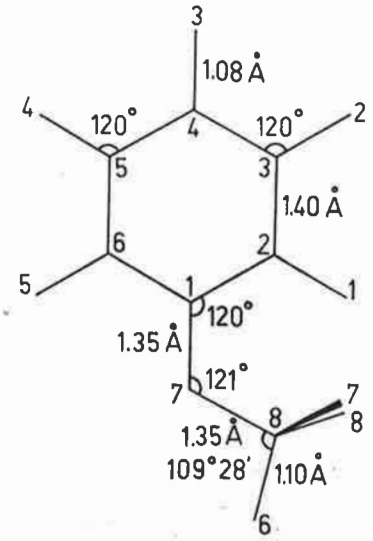

Fig. 1.

The calculations were performed on an IBM 7094 computer at NEUCC, Copenhagen using the original EHT program written by R. Hoffmann [8] and distributed by the QCPE organization.[9]

Results

The electronic energy of the molecule as a function of the torsional angle is summarized in table 1 and fig. 2.

Table 1.

Energy	0°	15°	45°	60°	75°	90°
eV	−777.238	−777.309	−777.449	−777.514	−777.581	−777.571
kcal/mole	−17930.89	−17932.51	−17935.74	−17937.25	−17938.79	−17938.57

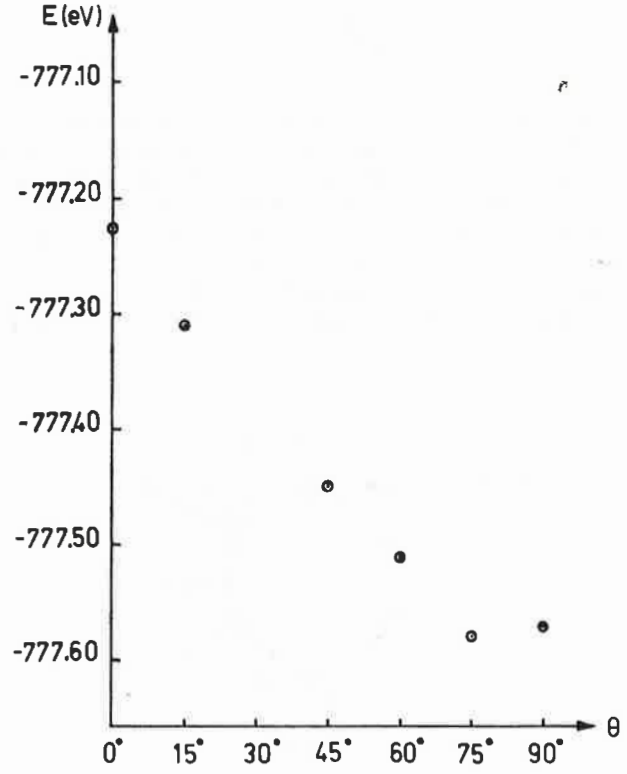

Fig. 2.

The minimum electronic energy occurs with the methoxy group about 75° out of plane and the two torsional barriers found are 7.9 kcal/mole and 0.2 kcal/mole (fig. 2.) This is in good agreement

with vibrational spectral data of Delorme [10] who assigned an absorption at 113 cm^{-1} to the $O—CH_3$ torsional vibration and with the more detailed study of Owen and Hester [11] who obtained 108 cm^{-1} for the torsional frequency and 6.02 kcal/mole for the torsional barrier. Both of these assignments are supported by Inelastic Neutron Scattering (INS) data of Janik and cowerkers.[12] For p-azoxyanisole in the nematic phase at 125°C they obtained the value 150 cm^{-1} for the torsional frequency.

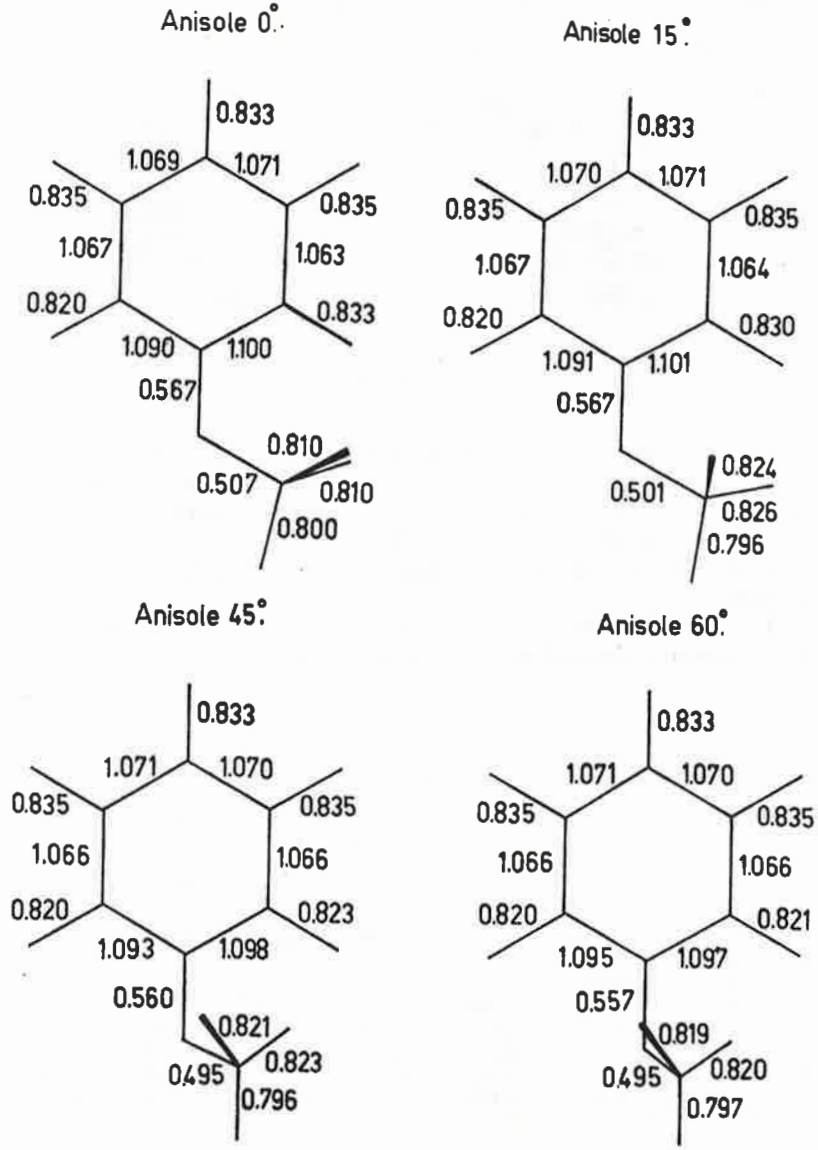

Fig. 3.

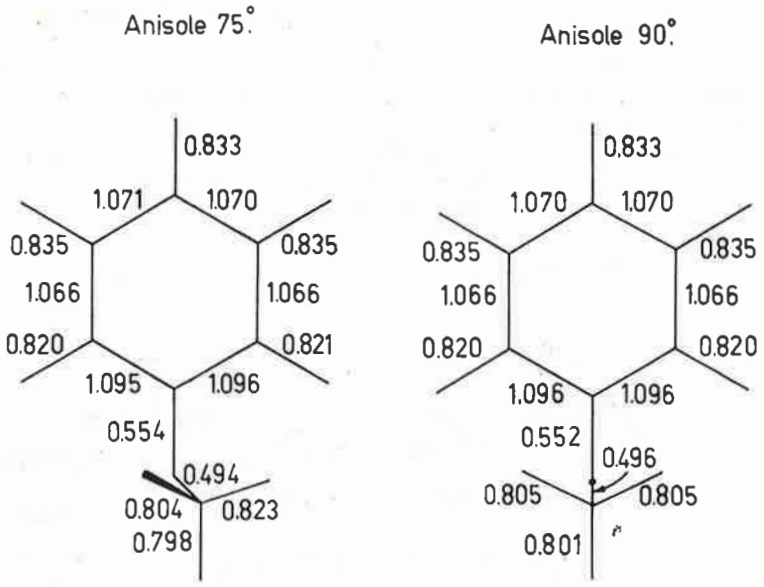

Fig: 3. (Continued)

The variation of the overlap population with the angle of torsion is shown in fig. 3. It is seen that the variation is biggest in the C_1-C_2 and C_1-C_6 bonds and among the carbon-hydrogen overlap populations in the C_8-H_7, C_8-H_8 and C_2-H_1 bonds. Considerable variation is also found in C_1-O and C_8-O overlap populations.

The net charges on hydrogen and carbon-oxygen are listed for different torsional angles in tables 2 and 3.

Table 2.

Nr	Q(H)					
	0°	15°	45°	60°	75°	90°
1	+ 0,131	+ 0,130	+ 0,123	+ 0,119	+ 0,116	+ 0,115
2	+ 0,107	+ 0,107	+ 0,107	+ 0,107	+ 0,107	+ 0,107
3	+ 0,106	+ 0,106	+ 0,106	+ 0,106	+ 0,106	+ 0,106
4	+ 0,108	+ 0,108	+ 0,108	+ 0,108	+ 0,107	+ 0,107
5	+ 0,114	+ 0,114	+ 0,114	+ 0,114	+ 0,114	+ 0,115
6	+ 0,105	+ 0,108	+ 0,108	+ 0,108	+ 0,108	+ 0,107
7	+ 0,112	+ 0,119	+ 0,117	+ 0,115	+ 0,104	+ 0,106
8	+ 0,112	+ 0,129	+ 0,128	+ 0,122	+ 0,119	+ 0,106

Table 3.

Nr	Q(X)					
	0°	15°	45°	60°	75°	90°
1	+ 0,632	+ 0,632	+ 0,636	+ 0,637	+ 0,638	+ 0,639
2	− 0,204	− 0,202	− 0,188	− 0,181	− 0,178	− 0,177
3	− 0,098	− 0,098	− 0,098	− 0,098	− 0,098	− 0,098
4	− 0,147	− 0,147	− 0,145	− 0,145	− 0,144	− 0,144
5	− 0,099	− 0,099	− 0,098	− 0,098	− 0,098	− 0,098
6	− 0,176	− 0,177	− 0,177	− 0,177	− 0,177	− 0,177
7(O)	− 1,013	− 1,019	− 1,029	− 1,031	− 1,035	− 1,032
8	+ 0,209	+ 0,188	+ 0,189	+ 0,195	+ 0,210	+ 0,218

Only the carbon atoms 1 and 8 which are directly bonded to oxygen are positively charged, the charge on C_1 being remarkably high. Also the negative charge on the oxygen atom is found to be very high. This overemphasis of charge migration is a well known feature of EHT and related approximations.[13] The variations with angle are in general small. The biggest differences in Q(H) are found in positions 1,6,7 and 8 and in Q(C) in positions 2 and 8. The effective electron configuration for oxygen and C_8 could be written:

$$1s_O^{2.00}\ 2s_O^{1.73}\ 2p_O^{5.30}$$

$$1s_C^{2.00}\ 2s_C^{1.08}\ 2p_C^{2.70}$$

and this shows no significant variation with the torsional angle. The effective electron configuration on C_8 corresponds very nearly to a sp^3 hybridization.

No attempts has been done to calculate the σ and π charges separately. The reason for this is that only the planar conformation has pure π orbitals. For the cases where the methoxy group is not in the ring plane a rather heavy $\sigma-\pi$ mixing occurs. As an example of this the highest filled molecular orbitals for the torsional angles 0° and 45° are listed in table 4.

Table 4.

			0°	45°
		Nr	−12.525 eV	−12.507 eV
	1s	1	0.0	0.1028
	1s	2	0.0	− 0.0837
	1s	3	0.0	− 0.0112
H	1s	4	0.0	0.0874
	1s	5	0.0	− 0.0814
	1s	6	0.0	0.0339
	1s	7	− 0.0487	0.0500
	1s	8	0.0487	− 0.0854

Table 4 (Continued)

			0°	45°
	2s	1	0.0	0.0039
	2s	2	0.0	— 0.0116
	2s	3	0.0	0.0077
X	2s	4	0.0	0.0045
	2s	5	0.0	— 0.0093
	2s	6	0.0	0.0173
	2s	7(O)	0.0	0.0049
	2s	8	0.0	— 0.0200
	$2p_x$	1	0.0	— 0.1568
	$2p_x$	2	0.0	0.1577
	$2p_x$	3	0.0	— 0.1125
X	$2p_x$	4	0.0	0.1315
	$2p_x$	5	0.0	— 0.1012
	$2p_x$	6	0.0	0.1342
	$2p_x$	7(O)	0.0	0.1303
	$2p_x$	8	0.0	— 0.0680
	$2p_y$	1	0.0	— 0.0098
	$2p_y$	2	0.0	0.0050
	$2p_y$	3	0.0	0.0211
X	$2p_y$	4	0.0	— 0.0159
	$2p_y$	5	0.0	0.0031
	$2p_y$	6	0.0	— 0.0411
	$2p_y$	7(O)	0.0	— 0.0048
	$2p_y$	8	0.0	— 0.0532
	$2p_z$	1	— 0.4811	0.4391
	$2p_z$	2	— 0.3111	0.3130
	$2p_z$	3	0.2426	— 0.1803
X	$2p_z$	4	0.5205	— 0.4690
	$2p_z$	5	0.1998	— 0.2142
	$2p_z$	6	— 0.3468	0.2854
	$2p_z$	7(O)	0.2460	— 0.2129
	$2p_z$	8	— 0.0137	0.0368

Conclusion

From EHT calculations one might conclude, that the most stable conformation of anisole is a nonplanar one, the equilibrium angle beeing 75°. By comparison of theoretical and experimental molar Kerr constants, Aroney et al [14] obtained the value 18° for the out of plane angle. This is apparently a time average value and cannot directly be compared with the equilibrium torsional angle. Experimental evidence however exist which speaks for the existence of cis-trans rotamers for 1,4-dimethoxybenzene [2] and for m-fluoroanisole.[11] It seems likely that a more elaborate approximation, which includes the interelectronic repulsion, should lower the equilibrium angle and give a higher value for the second torsional barrier. The possibility for nonplanar cis-trans conformations would then exist.

Acknowledgements

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Reactivity and Quantum Mechanics of Lignin*

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Introduction. The structure and reactivity of lignins and their models have been the subject of numerous experimental investigations, but to our knowledge only half a dozen papers have appeared concerning the correlation of experimental data with quantum chemical theory. The aim of the present paper is therefore briefly to discuss the present status of lignin quantum chemistry.

The Quantum Mechanical Method. Lignin can be considered, as we know, as a three-dimensional polymer which is built up by enzymatic dehydrogenative polycondensation from three aromatic alcohols: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The occurrence of these so-called C_9-units will therefore give different lignins depending on the relative amounts of the three units. Already a brief glance on the resulting macromolecular net-work structure (see for instance ref. 16) shows that a complete quantum mechanical treatment – an *ab initio* calculation – of its properties taking in consideration all of its molecular orbitals is at present and probably for a considerable future an impossible task.

* Based on a lecture delivered at the International Wood Chemistry Symposium in Seattle August 31st—September 4th 1969.

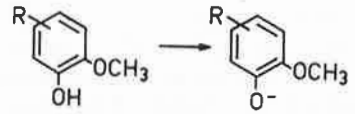
However, owing to the fact that the most important chemical properties of the lignin structure are confined to its π-electron system, the mathematical model can be considerably simplified and the problem thus amenable to a treatment with available calculating tools. The procedure is especially simple in those problems which in some way can be solved using the ground state of the molecule. Here already the simple semi-empirical Hückel-method (HMO) will work with success. However, in the case of the excited states of the molecules and of free radicals more advanced methods, such as for example the Pariser-Parr-Pople method or the CNDO-method should be consulted, although also simpler methods will give important information. Owing to the lack of space we cannot discuss here the mathematical details, but only the results with the aid of some selected examples.

Linear Free Energy Relations. A great lot of problems in lignin chemistry are related to the effect of various substituents, their positions in the aromatic structure and their relative reactivity. As an example we may mention the accessibility of the guaiacylic nucleus to electrophilic aromatic substitution. In experimental chemistry those properties are correlated with one another with the aid of the well known empirical Hammet equation which has been shown, also to work in the case of lignin models:[1]

$$\log k = \log k_0 + \varrho\sigma \qquad (1)$$

In the simple Hückel scheme the substituent effect (in Eq. 1 expressed by σ) can be managed by suitable choice of some adjustable parameters in the secular equation, i.e. the coulomb integral α and the resonance integral β for the noncarbon or heteroatoms in the molecular back-bone.[2] In the discussion below we shall adopt those Hückel parameters which have been developed partially by Polansky, Schuster and their co-workers[3] and by us and which seem to correlate especially well with Hammett's substituent constant σ.

Thus e.g. the pK of ionization of lignophenols:



$\alpha_O = 2 \longrightarrow 1.5$

$\beta_{CO} = 0.9 \longrightarrow 1$

correlates with the change in π-electron energy, ΔE_π, when going from the free phenol to the ion (Fig. 1) cf. also.[4]

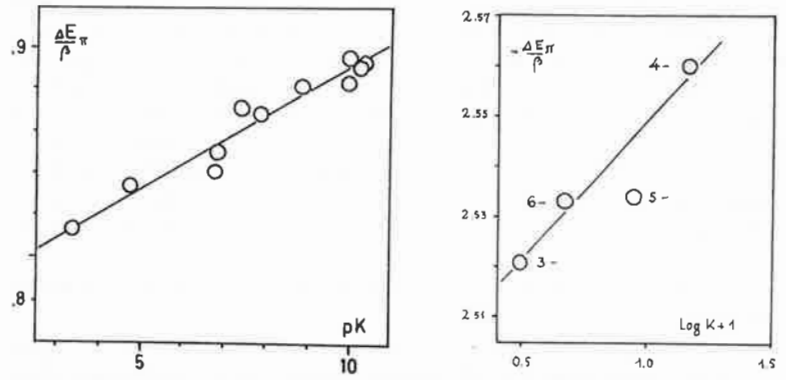
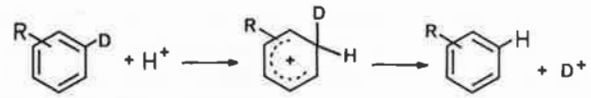


Fig. 1. Plot of the change in π-electron energy, ΔE_π when going from the free phenol to the ion versus pK of the phenol.

Fig. 2. Plot of the localization energies ΔE_π versus the logarithm of the reaction rate for the protodedeuteration of guaiacol in 57 % perchloric acid.[6]

From the above mentioned linearity the experimental order of hydrolysis of phenyl- β-d-xylosides reported by Hibbert and co-workers [5] can be deduced: α-hydroxypropiosyringone-β-d-xyloside (=R) > acetovanillone-R > α-hydroxypropiovanillone-R >> guaiacol-R > phenol-R. Likewise the protodedeuteration reactions of guaiacols studied by Sarkanen [6] may be mentioned. Using the reaction hypothesis:[7]



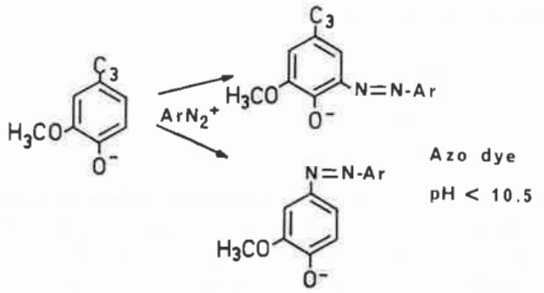
$\alpha = 1 \longrightarrow 1$

$\beta = 1 \longrightarrow 0$

the nearly linear plot of localization energy, ΔE_π, versus the logarithm of the reaction rate in 57 % perchloric acid may be obtained (Fig. 2). However, as in all investigations of this type, one must take care of the choice of reaction conditions. Thus e.g. the use of 36 % acid instead of the above gives not as good a correlation as the above mentioned one.

Another property which belongs to the same type of correlations is the acidity and reactivity of azo dyes formed by coupling

of lignins or their phenolic degradation products with diazonium salts:[8]



From Fig. 3 it can be seen that with the parameter values used a linear correlation is obtained between Hammett's σ-constant and the general reactivity on the nitrogen atom, described by the charge density q_7. The polarographic investigations of Kozeny and Velich [9] and the investigations of Chipalkatti and co-workers [10] on the colour persistence of azodyes (lower part of Fig. 3) show further that these properties can be interrelated and managed by quantum chemical calculations.

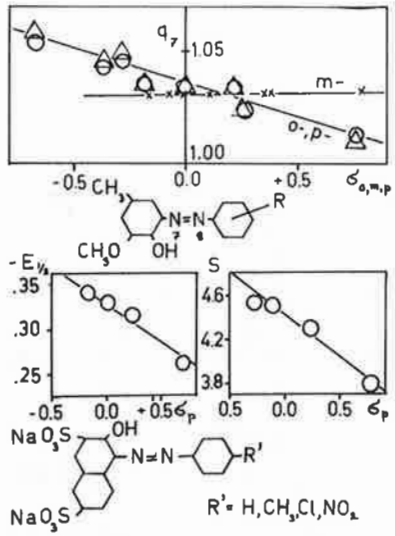
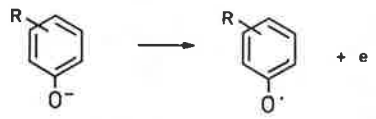


Fig. 3. Upper part: Plot of electron density q_7 on nitrogen versus Hammett's σ parameter. *Lower part: Left:* Polarographic half-wave reduction potential, $-E_{\frac{1}{2}}$ of the azodye (given under the plot) versus Hammett's σ-parameter.[9] *Right:* Colour persistence S of the azodye versus Hammett's σ-parameter.[10]

Free Radicals. It has been pointed out by Hush [11] and by Eyring with co-workers [12] and by Schuster [13] that a plot of Fieser's critical oxidation potential [14] (COP) of phenols against the

energy of the highest occupied molecular orbital, m_m, in the phenolate ion does give a straight line. The potential seems to be a measure of the reaction:



This reaction seems to be of importance when considering the radical reaction in the formation of the lignin molecule and also in the further reactions of phenolic fragments. The plot of COP versus m_m shows, as can be seen in Fig. 4, a straight line with some marked exceptions probably caused by the crudeness of the method used. Schuster points out that a much better correlation will be obtained with more sofisticated calculations.

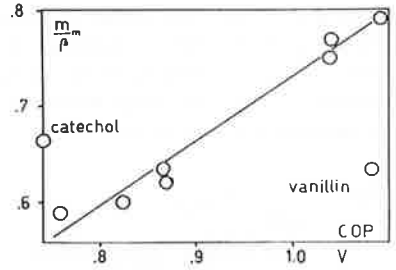


Fig. 4. Plot of critical oxydation potential, COP versus highest occupied molecular orbital, m_m of phenolate ions.[13]

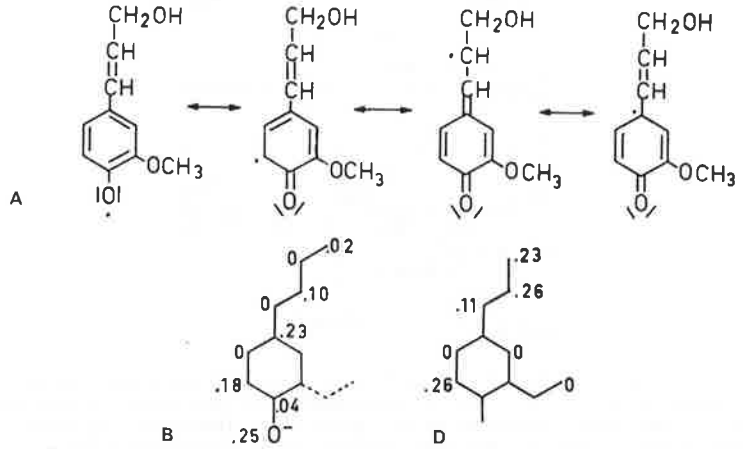


Fig. 5. A. Mesomeric forms of the radical formed from coniferyl alcohol ion by dehydrogenation.[16] B. Electron spin densities of the odd electron in coniferyl alcohol ion calculated by the Pariser-Parr-Pople method.[15] D. Experimentally determined electron spin densities of the odd electron in the cation radical of coniferyl alcohol.[18]

Mårtensson and Karlsson [15] investigated recently by the more elaborate Pariser-Parr-Pople-method the electron spin densities of the odd electron in the free radicals formed during the biosynthesis of lignin and showed that all the mesomeric forms predicted by the Freudenberg school [16] are consistent with theoretical predictions (Fig. 5). However small discrepancies are observed with regard to the charge distribution in the side chain, when the theoretical calculations are compared with the experimental evidence of electron spin densities.[18]

It is however, of interest to note that a crude picture of the odd-electron distribution in the lignin precursors may be reached also by comparison with the odd-electron distribution in the corresponding alternating hydrocarbon using the simple calculating rules developed by Coulson and Rushbrooke.[17]

Conclusions. The present brief review has shown only little of the wealth of possibilities for the use of quantum mechanics in lignin chemistry. In a lot of cases however, there is not very much of apriori flavour, but more a collection of our knowledge in a comprehensive form. Likewell, the theoretical methods seem to be of especial value when we try to compare various reaction models with one another or try to extend our knowledge to areas still not penetrated by experimentalists. Also they may be used to direct experimental research in the most profitable direction and to reject impossible working models.

Acknowledgement. The authors are indebted to the Finnish Society of Science for financial aid.

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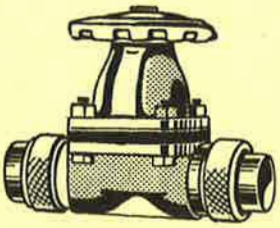
VALVES

SOLENOID



MANUAL

SOLENOID AIR ADMITTANCE

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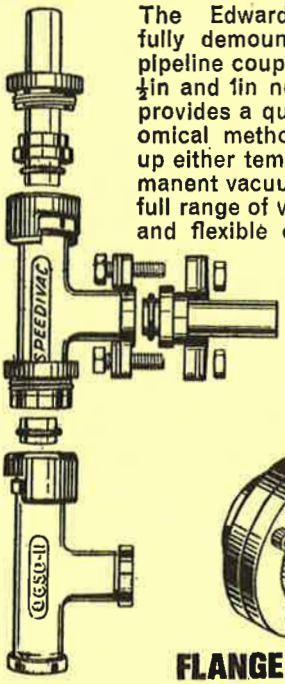

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