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Investigations on the Reactivity of Lignin and Lignin Models Using the LCAO-MO Method (Hückel Method)

J. Johan Lindberg and *Henrik Tylli*

Institute of Technology, Department of Chemistry, Otaniemi and Department of Chemistry, University of Helsinki (Helsingfors), Finland

The electrophilic aromatic substitution, cleavage of ether linkages, polarographic reduction and formation of extended aromatic structures and free radicals in lignins and their models have been discussed in terms of experimental data and of the electronic parameters calculated by the aid of the simple LCAO-MO method (Hückel method).

The structure and reactivity of lignin and its model compounds have been the subject of numerous experimental investigations. Nevertheless, so far we know, very little theoretical work has been done to correlate these experimental results with quantum mechanical evidence. It is a well known fact that quantum mechanical methods are capable of elucidating reactivity problems concerning delocalized π-electrons in aromatic systems. The aim of the present investigation is therefore to throw light on these questions with respect to lignin and its model compounds and to study the possibility of theoretical predictions using the simple LCAO-MO method (Hückel method) and related perturbation treatments.

Method of Investigation. The calculation by the Hückel method of the electronic parameters needed in the characterization of the reacting molecules, i.e. π-electron charge density q_r, aromatic bond order p_{rs}, free valence F_r and localization energy E_{loc} was performed in the usual manner, cf. e.g.[1,8]

The discussion of the reactivity was carried on where possible in terms of the Wheland π-electron localization approximation.[2] The electronic parameters needed for the treatment, i.e. the localization energies E_{loc} were arrived at from the values of the unreacted molecules by the perturbation methods described by Coulson and Longuet-Higgins [3] and Dewar.[4] Thus, the change in π-electron energy was deduced from the series expansion:

$$\Delta E\pi = 2\sum p_{rs}\Delta\beta_{rs} + q_r\Delta\alpha_r + \tfrac{1}{2}\,\pi_{rr}(\Delta\alpha_r)^2 + \ldots \tag{1}$$

If the change in coulomb integral $\Delta\alpha_r$ can be neglected and $\Delta\beta_{rs}$ is a small quantity the formula (1) is reduced to:

$$\Delta E\pi \simeq 2(\sqrt{3}-F_r)\Delta\beta_{rs} \tag{2}$$

$\Delta\beta_{rs}$ and $\Delta\alpha_r$ denote the changes in resonance and coulomb integrals on the reacting center when going from the initial molecule to the intermediate. π_{rr} is the atom-atom polarizability which was calculated by the approximate method of McWeeny,[5] cf. also Ref.[6]

In molecules containing non-carbon or hetero-atoms in the conjugated system the magnitude of the electronic parameters p_{rs}, q_r, F_r is sensitive to the choice of the adjustable empirical parameters for the hetero-atoms in the secular equation, i.e. the values of the resonance integral β and the coulomb integral α. It seemed therefore necessary to compare the results of calculations using several different sets of parameter values with results of more elaborate treatments for the same molecules in those few cases where it was possible to do so. In Table 1 such a comparison is made for phenol and catechol using the results of the extensive SCF-LCAO-MO computations of Forsén and Alm [7] as a point of reference. The following equations connect the coulomb integral α_X of the hetero-atom X and the resonance integral β_{XC} of the bond XC to the corresponding standard values α and β for benzene and a C—C bond in benzene itself:

$$\alpha_X = \alpha + h_X\beta, \qquad \beta_{XC} = k_{XC}\beta \tag{3}$$

Table 1. π-electron charge densities q_r obtained by the simple LCAO-MO method using various sets of $h_{\ddot{o}}$ and k_{CO} parameters for hydroxyl oxygen and CO-bond and by the extensive SCF-LCAO-MO method.[7] The atoms are numbered as in structure I.

				q_r		
Atom r in:	$h_{\ddot{o}}$	1 [1]	1 [1]	2	2	SCF [2]
Phenol	k_{CO}	0.5	1	0.7	0.9	LCAO-MO
1		0.981	0.938	0.965	0.944	0.982
2		1.025	1.089	1.031	1.050	1.029
3		0.999	0.997	0.998	0.997	0.992
4		1.020	1.072	1.023	1.037	1.015
7		1.950	1.820		1.924	1.962
Catechol						
1		1.004	0.999		0.987	1.019
3		1.025	1.101		1.050	1.028
4		1.019	1.066		1.033	1.009
7		1.952	1.834		1.928	1.944

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[1] Data taken from Ref.[8]

[2] Data taken from Ref.[7] They are based on an ionization energy of -10.50 eV for oxygen and a β_{CO} parameter value of -1.70 eV which gives almost perfect agreement with experimental electron impact data for phenol.

A comparison of the data in Table 1 indicates that in general moderate variations of the parameter values for α and especially β alters only the absolute magnitude of q_r but does not change the order of relative magnitudes between the different atoms. Furthermore, they seem to be in rough accordance with the results of the SCF-calculations of Forsén and Alm. The same trends were also observed for the other electronic parameters, cf. also [23b]. Therefore, remembering the approximate nature of the treatment and that only relative magnitudes of the electronic indices are of importance we selected for study the parameters $h_{\ddot{o}} = 2$ and $k_{CO} = 0.9$ for the hydroxyl oxygen and ether oxygen. They have been extensively used with success by Polansky [9] and Pullman [10] and their co-workers. In accordance with these authors the carbonyl oxygen was treated using the values $h_{\ddot{o}} = 1.2$ and $k_{C=O} = 2$. The ether oxygen and phenolic oxygen were considered to contribute two electrons, the other atoms one electron to the π-electron system.

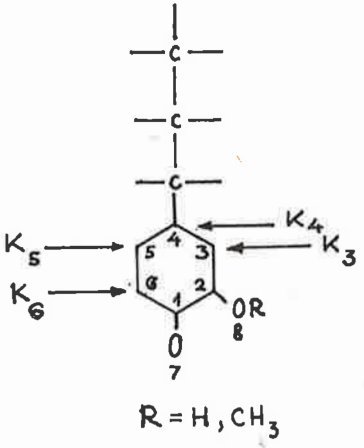
The influence of the methyl group on the aromatic system was included as an inductive effect operating through the parameter $h_C = -0.15$ on the neighbour carbon atom of the π-electron system. In the case of the methoxyl group the effect was considered by taking $h_{\ddot{o}} = 1.65$. Strong intra-molecular hydrogen bond effects of the type $C{=}O\cdots HO$ were considered in some cases by taking the $h_{\ddot{o}}$-value of the hydroxyl oxygen to 1.8 and that of the carbonyl oxygen to $h_{\ddot{o}} = 1.4$ (cf. also the discussion in Ref.[10,11]). Furthermore, overlap and any possible non-coplanarity of the aromatic system were neglected.

To improve the results obtained by the Hückel method when applied to systems containing hetero-atoms it has been recommended to introduce somewhat of SCF-nature into the method by employing calculations, e.g. of the iterative type described by Bergson,[12] the ω-method of Streitwieser[1] or other general improvements.[1,13] However, with the parameter values used and at the present stage of our investigation nothing essentially new seemed to be obtainable by such an additional mathematical labour. Thus, the improvements of the above mentioned type were omitted.

The computations were carried out with an IBM 1620 computer using a program which gave in addition to the eigen values and eigen vectors also the charge density-bond order matrix. The numerical results of these calculations are collected in Appendix I. Additional information regarding the results of the computations may be delivered on request.

Results and Discussion. Owing to the informative nature of the investigation which has been announced by two preliminary communications[14,15] only some few selected types of reactions have been chosen for study: a) electrophilic aromatic substitution. b) cleavage of ether linkages. c) polarographic reduction of aldehydic groups. d) formation of extended aromatic systems and of free radicals in lignins.

a) *Electrophilic Aromatic Substitution.* A typical aromatic nucleus in lignin (formula I) is known to undergo with considerable ease a variety of eletrophilic substitution reactions, such as halogenation, nitration, mercuration and reaction with acidified formaldehyde and acid catalyzed self-condensation. Not only are the sites 3,5 and 6 reactive but also the side chain attached to the position 4 may be displaced by the electrophile.[16–19]

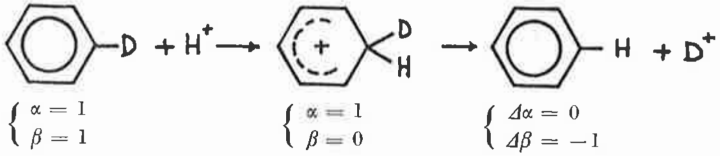


I

From the protodedeuteration work on lignin model compounds in 57 % and 36 % perchloric acid of Sarkanen and co-workers[19] we know that the aromatic substitution rate in general increases in the order: $k_3 < k_5$ and $k_6 < k_4$ and in 4-methylguaiacol (p-creosol) in the order: $k_6 < k_3 < k_5$, where the subscripts refer to the numbered positions in structure I. It is of interest to compare these results with theoretical predictions made, using the Hückel method and related perturbation treatments.

It is generally postulated[21] that the protodedeuteration reaction of benzene proceeds over the formation of a σ-complex intermediate of the type given in the following reaction scheme:

(4)



From the point of view of quantum chemistry such a reaction sequence can favourably be treated by the Wheland localization procedure.[2] The reacting carbon atom ($\alpha = 1$, $\beta = 1$) of the π-electron center is calculated as being converted to a saturated atom ($\alpha = 1$, $\beta = 0$) in the formation of the intermediate with localization of an electron pair. The localization energy E_{loc} which is roughly given by Eq. 1 and 2 can be regarded as a measure of the π-electron energy change between the aromatic molecule and the σ-complex intermediate formed during the substitution reaction. If all σ-bond changes are treated as being effectively constant in this transformation, a correlation can be anticipated between the calculated localization energies and experimental rate data (cf. also the discussion in Ref.[20] for the weaknesses in the assumptions made).

In Fig. 1 the logarithms of the protodedeuteration rates of Sarkanen and co-workers for guaiacol in 57 % perchloric acid are plotted against the localization energy E_{loc} calculated by the aid of Eq. 1 for the corresponding positions in the aromatic nucleus. The linear correlation between these two sets of values is evident as also between charge densities or free valences (cf. Tables 3 and 5) and reaction rates. However, the order of the points is the reverse one to that expected from the theoretical evaluation of the quantum mechanical results. The same inverted trend is also noted when the corresponding data of phenol, anisol and veratrol are compared (cf. Fig. 2) using the more crude approximation of Eq. 2.

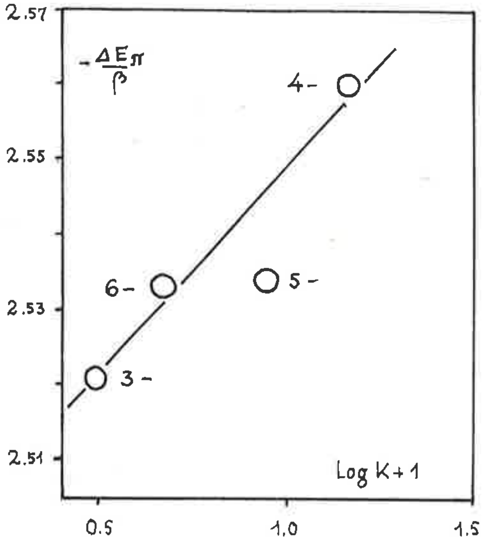


Fig. 1. Plot of the localization energies ΔE_{π} -versus the logarithm of the reaction rate for the protodedeuteration of guaiacol in 57 % perchloric acid. ΔE_{π} is calculated using Eq. 1.

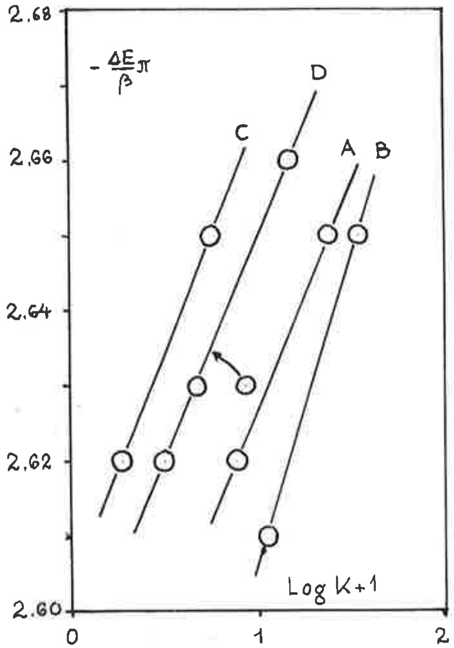


Fig. 2. Plot of the localization energies ΔE_{π} versus the logarithm of the reaction rate for the protodedeuteration of phenol (A), anisol (B), veratrol (C) and guaiacol (D) in 57 % perchloric acid. ΔE_{π} is calculated using Eq. 2. The upper points refer to p-positions.

It is a well known fact that the distribution of the *ortho-para* ratio in electrophilic aromatic substitution is strongly dependent on the steric and reaction conditions (cf. e.g. the nitration of anisol referred in [23a]) Thus, Andersen[22] found that when guaiacol is nitrated with surplus nitrous acid in acetone-ether at 0°C 60 % 6-nitroguaiacol and 40 % 4-nitroguaiacol (cf. formula I) was obtained. Therefore, theoretical results of the type discussed above must always be used with caution, cf. also the discussion in Ref.[23b] In the present case, however, the neglected inclusion of electrostatic interaction with substituent dipoles in the calculations may play a role.[1]

b) *Cleavage of Ether Linkages.* It is a well known fact that lignins undergo a variety of base-catalyzed hydrolysis reactions. Thus e.g. the treatment of lignins with alkali metals and metal amides in liquid ammonia, catalytic hydrogenation in the presence of alkali and hydrogenation by primary alcohols and alkali [24] involve ether cleavage.

Already Hibbert and co-workers [25] found that the hydrolysis of phenyl-β-d-xylosides by 5 % sodium hydroxide at 60°C takes place in the following order of decreasing rate: α-hydroxypropiosyringone-β-d-xyloside > acetovanillone-β-d-xyloside > α-hydroxypropiovanillone-β-d-xyloside ≫ guaiacol-β-d-xyloside > phenol-β-d-xyloside which is also the approximate order of decreasing acidity of the phenolic hydroxyl group in the corresponding free phenolic compound. In contrast to the phenyl-sugar ethers, aryl-alkyl ethers are fairly stable under alkaline conditions. Thus, Sarkanen and coworkers [26] reported that the methoxyl group of guaiacol is more slowly cleaved than that of veratrol in 5 % sodium hydroxide at 190°C and only those aromatic ethers which contain strong electron attracting substituents on their rings are more easily hydrolysed.

The base catalyzed cleavage of aromatic alkyl-ethers may occur by two different reaction mechanisms, one involving a S_N2 displacement on the phenyl ring and the other a S_N2 displacement on the alkyl carbon adjacent to the oxygen atom:

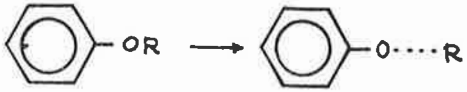
(5a) $\mathrm{Ar{-}O{-}R + B{:}^{-} \rightleftharpoons Ar{-}O \cdots R \cdots B \rightleftharpoons Ar\bar{O}{:} + RB}$

(5b)

Both mechanisms are known to occur in the methyl cleavage. Usually, however, two or more strongly electron attracting substituents on the phenyl ring are required for mechanism (5b) to operate.[27] In the case of hydrolysis of aromatic methoxyl groups by aqueous alkali the same products are obtained by both mechanisms and could only be distinguished by a study based on the use of the O^{18} isotope. According to Sarkanen[26] it is most likely that mechanism (5a) is dominant in the reaction of lignin and its model compounds which are generally devoid of strong electron attracting substituents.

From the point of view of the quantum mechanical calculations the actual steps in the cleavage reactions seem to be the following ones:

(6)



$$\left\{\begin{array}{l}\alpha\ddot{o} = 1.65\\ \beta co = 0.9\end{array}\right. \qquad \left\{\begin{array}{l}\alpha\ddot{o} = 2.00\\ \beta co = 0.9\end{array}\right. \qquad \left\{\begin{array}{l}\varDelta\alpha\ddot{o} = +\,0.35\\ \varDelta\beta co = \,0\end{array}\right.$$

(7)

$$\left\{\begin{array}{l}\alpha = 1\\ \beta = 1\end{array}\right. \qquad \left\{\begin{array}{l}\alpha = 1\\ \beta = 0\end{array}\right. \qquad \left\{\begin{array}{l}\varDelta\alpha = 0\\ \varDelta\beta = -1\end{array}\right.$$

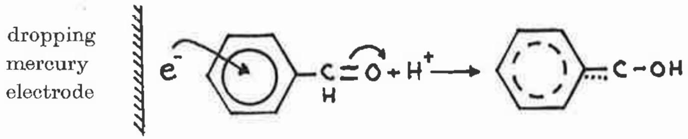
An approximate value for the change in π-electron energy and π-electron energy of activation $\varDelta\ E_\pi{}^{\ddagger}$ should be obtained by substituting the α- and β-values of reactions (6) and (7) in Eq. 1 and taking in consideration only the first order terms. Thus, $\varDelta E_\pi{}^{\ddagger}$ would either be a function of q_O, the charge density of the reacting oxygen atom of reaction (6) or of the sum of the bond orders p_{CC} of the reacting carbon atom in reaction (7). An inspection of the data in Appendix I for anisol, veratrol, guaiacol, 4-methyl guaiacol and vanillin indicates that no certain predictions can be made by the crude methods described above.

However, using the molecular orbital theorems of Dewar[28] regarding the charge displacements caused by electromeric substituents, it can be predicted that the methyl ether group of vanillin should be more easily cleaved than that of guaiacol which is in accordance with experimental evidence. Furthermore it is of interest to note that Chalvet, Daudel and Peradejordi[28a] using the extensive Pariser, Parr and Pople method of calculation were able to show a good correlation between difference in π-electron energy and the basic strength in quinoline derivatives.

c) *Polarographic Reduction.* The polarographic reduction on the dropping mercury electrode of lignins and some of their model compounds have been studied by Kanda and Kawakami.[29] They found that alkali lignins and sulphate lignins show, except for catalytic waves in $CoCl_2$-solution, extended indistinct catodic wayes in usual buffer solutions. The latter waves are probably caused by the carbonyl groups and double bonds present in the lignin structure. Furthermore, one of the present authors[14] found that the polarographic half-wave reduction potential of the aldehydic group in lignin model compounds may roughly be correlated with other reactivity data, such as e.g. protodedeuteration.

The polarographic reduction of aldehydes and ketones has been analyzed both experimentally and using the Hückel method and other methods by several authors from various points of views, cf. e.g. the references cited in[2] and.[31] It seems evident that in acid and weakly alkaline solution the reversible and potential determining step can be formulated as follows:

(8)



$$\left\{\begin{array}{l}\alpha = 1.2\\ \beta = 2.0\end{array}\right. \qquad \left\{\begin{array}{l}\varDelta\alpha = +0.8\\ \varDelta\beta = -1.1\end{array}\right. \qquad \left\{\begin{array}{l}\alpha = 2.0\\ \beta = 0.9\end{array}\right.$$

Using Eq. 1 and the coulomb and resonance integral values of reaction (8) we find that the reactivity of the rate determining step and its change in π-electron energy $\varDelta\ E_\pi$ can roughly be expressed by the relation:

$$\varDelta\ E_\pi = 2\ p_{rs}\ \varDelta\beta_{rs} + q_r\varDelta\alpha_r \tag{9}$$

In Table 2 some half-wave potential data for formylphenols in 0.1 N NH_4Cl solution are collected together with $\varDelta\ E_\pi$-values calculated from Eq. (9) and the data in Appendix I. A purely theoretical prediction of substituent effects is still impossible.[46,23b,28] However a comparison of the present data shows that with the parameter values used in reaction (8) the results obtained are in rough accordance with expectations, cf. also.[47] Thus one can see that the influence of the hydrogen bond formed between the carbonyl group and the hydroxyl group in 6-formyl guaiacols is considerable, whereas the influence of the methyl group in *para*-position to the hydroxyl group is very small. The free valence index (Table 5) F_r of the 3-position is changed from 0.437 to 0.428 on H-bond chelate formation.

d) *Formation of Extended Aromatic Systems and Radicals.* From the work of Falkehag,[32] cf. also[33] and Turunen[34] it is known that dehydrodiconiferylalcohol, dihydrodehydrodiisoeugenol and Björkman lignin which have been subjected to kraft cooking or

Table 2. Polarographic half-wave reduction potentials $E_{1/2}$ and delocalization energies ΔE_π for formylguaiacols.

–Formylguaiacol	pco	qo	ΔE_π [3]	$-E_{1/2}$ [2]
3–	0.8976	1.3282	−0.9121	—
4–	0.9001	1.3241	−0.9209	1.41
5–	0.8990	1.3257	−0.9172	1.40
6– [1]	0.8989	1.3264	−0.9165	
6–	0.8878	1.3632	−0.8626	1.31
4-methyl-6-formyl guaiacol [1]	0.8990	1.3264	−0.9167	1.30

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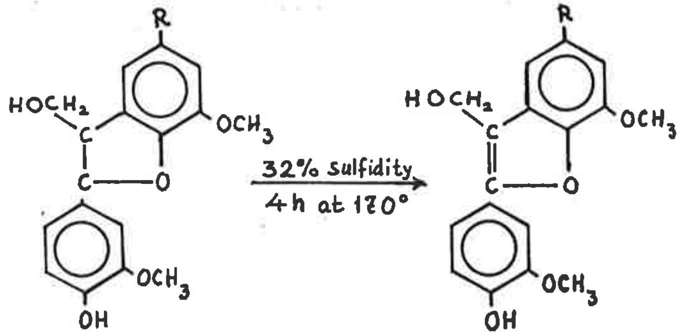
[1] Hydrogen bond chelate effect of the type OH · · · O=C not included in the HMO-calculation.

[2] The data taken from Ref.[14] except for the last one.[30]

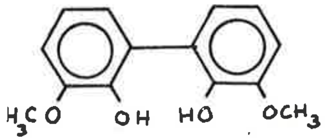
[3] Units of β.

other alkaline digestions under pressure at 250°C yield stilbenic derivatives e.g. according to the scheme:

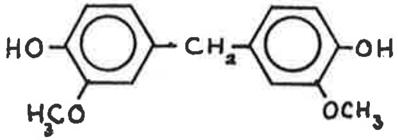
(10)



In addition the formation or the presence of biphenyl (II) and diguaiacylmethane (III) structures in the lignin polymer seems to be quite likely [35–37]:



II

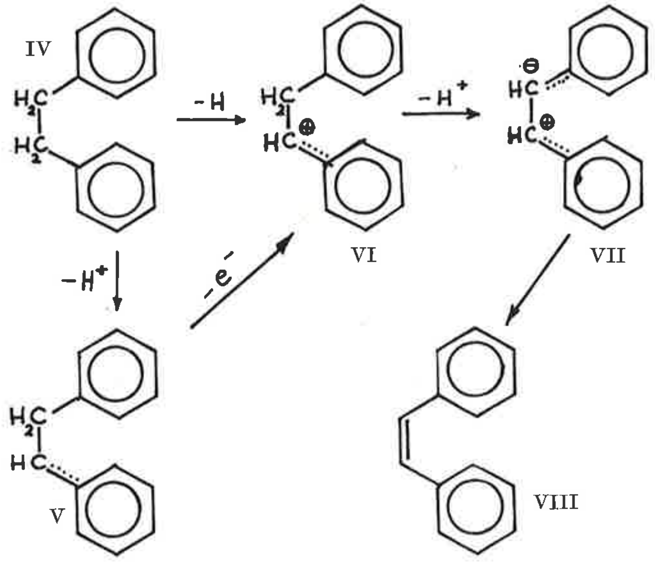


III

Thus, in lignins subjected to treatments with alkaline solutions at elevated temperatures condensation and elimination reactions seem to take place and to produce more extended aromatic systems. The experimental evidence for these reactions is still very scanty [35,37] and it would therefore be of interest to study the energetic conditions for them from quantum mechanical

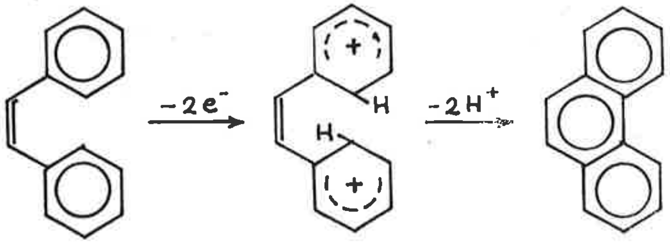
point of view. In order to elucidate these questions we selected the following reactions and reaction sequences for study. To reduce the mathematical labour involved the problems have been reduced to a comparison of corresponding isoconjugate hydrocarbons without equivalents for methoxyl and hydroxyl groups. The numbers under the structures give the β-resonance integral part of the total π-electron energy obtained from Ref.[8,38]

(11)



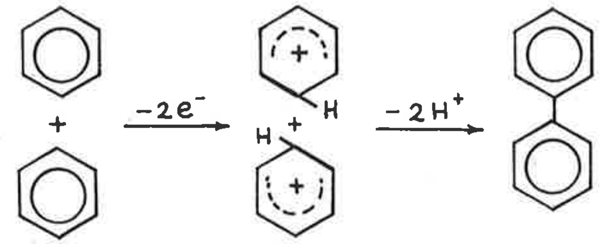
IV: 16.00β, IV → VI: $\Delta E_\pi = +0.72\beta$
V: 16.72β,
VI: 16.72β, VI → VII: $\Delta E_\pi = +0.72\beta$
VII: 17.44β, VII → VIII: $\Delta E_\pi = +1.44\beta$
VIII: 18.88β,
Total change $\Delta E_\pi = +\ 2.88\beta$.

(12)



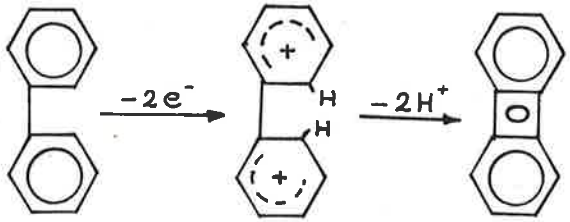
VIII: (cis-form) $\Delta E_\pi = -4.29\beta$, IX: $14.59{,}\beta$ X: $19{,}45\beta$,
18.88β,

(13)



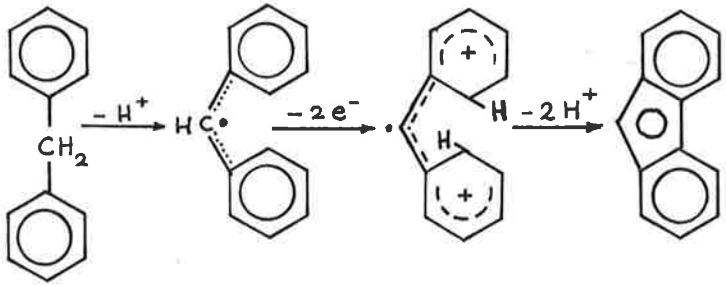
XI: 16.00β, $\Delta E_{\pi} = -5.07\beta$, XII: 10.93β, XIII: 16.38β,

(14)



XIII: 16.38β, $\Delta E_{\pi} = -4.33\beta$, XIV: 12.05β, XV: 16.51β,

(15)



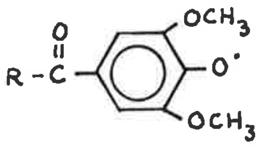
XVI: 16.00β, XVII: 17.30β, $\Delta E_{\pi} = -4.11\beta$, XVIII: 13.19β, XIX: 17.54β.
XVI → XVII: $\Delta E_{\pi} = +1.30\beta$.

In the scheme (11) the reaction mechanism put forward by Gierer and Norén [39] for the formation of stilbenic derivatives from dehydrodiconiferylalcohols has been written in a form suitable for the present analysis, i.e. two isolated benzene rings form benzyl cations and anions which unite to stilbene. In scheme (12) the further way which parallells the photochemical work of Srinivasan and Powers and others [40] has been followed. In the schemes (13)—(15) the similar reactions for the formation of diphenyl, biphenylene and dibenz-cyclopentadienyl have been given.

Assuming that the difference in π-electron energy between the molecule for and after the electron withdrawal can be taken as a measure for the energy barrier for the formation reaction the great energy difference between reactions (11) and (12) is evident (high negative ΔE_{π}-values in the sense given correspond to a high barrier). Thus, already this difference, not to speak of the conformation energy needed [40,41] for the transformation *trans*-stilbene → *cis*-stilbene, would explain why one obtains stilbene and not phenanthrene as the main product of the additional aromaticitation.

It is also of interest to compare the reactions (12) to (15) with oneother. From the ΔE_{π}-data it would be expected that the formation of radical XVII or dibenz-cyclopentadienyl would be more likely than the formation of phenanthrene and biphenylene if the starting products are available in a suitable conformation. The presence and formation of biphenyl bonds in lignins have been reported by several authors [35,37] as mentioned above and it seems therefore that this bond would be formed with especial ease possibly for conformational reasons.

From several EPR-investigations on lignin materials [42] it is known that lignins and especially those isolated by alkaline digestions of wood contain large amounts of stable radicals. The nature of these radicals is, except for those belonging to the syringyl group (XX) and (XXI), still unknown.[43]



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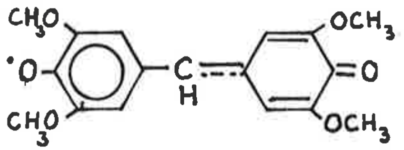

XXI

From the point of view of quantum chemistry according to the molecular orbital theorems of Dewar [44] all types of electromeric substituents and also heteroatoms increase the stability of free radicals. Thus as known from experimental investigations [45] the radical (XXI) is much more stable than those obtained from anisol and vanillin. The long time stability of lignin radicals could therefore partly be explicable in terms of extensive substitution although also other effects seem to operate. Regarding the nature of the radicals present in the lignin structure those of quinone methide type (analogous to (V)) and of diguaiacylmethane type (XVII) in addition to the syringyl radicals seem not unlikely.

Conclusions. In the discussion above some of the various possibilities for the use of simple quantum chemical perturbation methods in connection with the Hückel treatment for the investigation of the properties of lignins have been elucidated. Although, there is very little "apriori flavor" inherent in the results obtained above and the influence of the heteroatoms is not completely mastered, it seems evident that the mentioned methods are usable in treating various reactivity problems for similar and nearly related compounds and in studying aromaticitation. In a later report which is under preparation the present view will be extended to other types of reactions and to more elaborate quantum chemical methods.

Acknowledgement. The authors are indebted to the National Research Council for Sciences and the Finnish Society of Science for financial aid. Furthermore we express our gratitude to the Mathematical Institute of the University of Helsinki for placing their computer at our disposal, to Mr. V. Nummi, M.Sc. for help with the computer program and to Docent J. Murto and Mr. G. Brunow, Phil.lic. for elucidating discussions.

Appendix I.

Table 3. π-electron energies E_π and excess π-electron charge densities $(1\text{-}q_r)$.[5]

		$1\text{-}q_r$									
	E_π	r = 1	2	3	4	5	6	7	8	−C=[2]	=O[4]
Phenol	$8\alpha + 12.250\,\beta$	+0.056	−0.050	+0.003	−0.037	+0.003	−0.050	+0.076	—	—	—
Anisol	$8\alpha + 11.580\,\beta$	+0.057	−0.057	+0.003	−0.043	+0.003	−0.057	+0.094	—	—	—
Catechol	$10\alpha + 16.486\,\beta$	+0.013	+0.013	−0.050	−0.033	−0.033	−0.050	+0.072	+0.072	—	—
Veratrol	$10\alpha + 15.142\,\beta$	+0.009	+0.009	−0.058	−0.039	−0.039	−0.058	+0.088	+0.088	—	—
Guaiacol	$10\alpha + 15.814\,\beta$	+0.007	+0.015	−0.058	−0.033	−0.039	−0.051	+0.071	+0.088	—	—
4-Methylguaiacol	$10\alpha + 15.664\,\beta$	−0.007	+0.016	−0.081	+0.027	−0.063	−0.049	+0.068	+0.089	—	—
6-Methylguaiacol	$10\alpha + 15.661\,\beta$	−0.016	+0.015	−0.071	−0.032	−0.062	+0.010	+0.068	+0.088	—	—
3-Formylguaiacol	$12\alpha + 21.525\,\beta$	+0.007	+0.049	−0.077	−0.004	−0.039	−0.028	+0.071	+0.099	+0.252	−0.328
4-Formylguaiacol	$12\alpha + 21.518\,\beta$	+0.034	+0.014	−0.029	−0.055	−0.006	−0.051	+0.076	+0.088	+0.253	−0.324
5-Formylguaiacol	$12\alpha + 21.520\,\beta$	+0.007	+0.041	−0.057	+0.006	−0.020	−0.071	+0.077	+0.108	+0.253	−0.326
6-Formylguaiacol[1]	$12\alpha + 21.380\,\beta$	+0.039	+0.014	−0.039	−0.035	−0.014	−0.073	+0.107	+0.089	+0.284	−0.363
6-Formylguaiacol[2]	$12\alpha + 21.585\,\beta$	+0.033	+0.027	−0.048	−0.032	−0.020	−0.071	+0.077	+0.108	+0.253	−0.326
4-Methyl-6-formyl guaiacol[2]	$12\alpha + 21.682\,\beta$	+0.056	+0.013	−0.013	−0.093	+0.015	−0.072	+0.080	+0.088	+0.253	−0.326
6-Methyl-4-formyl guaiacol	$12\alpha + 21.680\,\beta$	+0.056	+0.014	−0.016	−0.056	+0.018	−0.011	+0.079	+0.088	+0.253	−0.324

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[1] With H-bond C=H...HO included.

[2] Without H-bond.

[3] C in >C=O.

[4] O in >C=O.

[5] The atoms are numbered as in structure I.

Table 4. Bond orders p_{rs}.

r-s=	1—2	2—3	3—4	4—5	5—6	1—6	1—7	2—8	C=C [4]	C=O [5]
Phenol	0.639	0.672	0.663	0.663	0.672	0.639	0.280	—	—	—
Anisol	0.633	0.674	0.662	0.662	0.674	0.633	0.312	—	—	—
Catechol	0.614	0.651	0.665	0.665	0.663	0.614	0.266	0.266	—	—
Veratrol	0.603	0.648	0.661	0.665	0.661	0.648	0.295	0.295	—	—
Guaiacol	0.609	0.645	0.663	0.665	0.661	0.653	0.265	0.296	—	—
4-Methylguaiacol	0.610	0.643	0.664	0.655	0.658	0.655	0.259	0.297	—	—
6-Methylguaiacol	0.613	0.642	0.665	0.662	0.663	0.653	0.256	0.296	—	—
3-Formylguaiacol	0.606	0.608	0.622	0.678	0.651	0.656	0.264	0.317	0.328	0.898
4-Formylguaiacol	0.602	0.656	0.624	0.627	0.673	0.645	0.277	0.297	0.321	0.900
5-Formylguaiacol	0.601	0.636	0.676	0.626	0.621	0.665	0.264	0.311	0.323	0.899
6-Formylguaiacol [1,3]	0.599	0.653	0.651	0.680	0.620	0.618	0.311	0.297	0.317	0.888
6-Formylguaiacol [2]	0.600	0.640	0.655	0.677	0.618	0.619	0.279	0.330	0.325	0.899
4-Methyl-6-formylguaiacol [2]	0.606	0.650	0.651	0.674	0.623	0.614	0.287	0.296	0.325	0.899
6-Methyl-4-formylguaiacol	0.598	0.659	0.621	0.631	0.668	0.642	0.285	0.296	0.321	0.900

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[1] With H-bond C=O · · · HO included.

[2] Without H-bond.

[3] p_{rs} of O · · · H in C=O · · · HO = 0.107.

[4] C in $>$ C=O.

[5] O in $>$C=O.

Table 5. Free valences F_r.

r=	1	2	3	4	5	6
Phenol	0.174	0.421	0.397	0.406	0.397	0.421
Anisol	0.155	0.426	0.396	0.408	0.396	0.426
Catechol	0.201	0.201	0.418	0.404	0.404	0.418
Veratrol	0.189	0.189	0.423	0.406	0.406	0.423
Guaiacol	0.206	0.182	0.424	0.404	0.407	0.418
4-Methylguaiacol	0.208	0.179	0.425	0.407	0.409	0.419
6-Methylguaiacol	0.210	0.181	0.425	0.405	0.407	0.416
3-Formylguaiacol	0.206	0.201	0.174	0.432	0.403	0.425
4-Formylguaiacol	0.208	0.177	0.452	0.160	0.432	0.414
5-Formylguaiacol	0.202	0.184	0.420	0.430	0.162	0.446
6-Formylguaiacol [1]	0.204	0.183	0.428	0.401	0.432	0.177
6-Formylguaiacol [2]	0.234	0.162	0.437	0.400	0.437	0.170
4-Methyl-6-formylguaiacol [2]	0.225	0.180	0.431	0.407	0.435	0.170
6-Methyl-4-formylguaiacol	0.207	0.179	0.452	0.159	0.433	0.422

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[1] With H-bond C=O...HO included.

[2] Without H-bond.

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Kurt Buch in memoriam

Finska kemistsamfundets hedersmedlem, och verksamme medlem, professor emeritus, fil.dr. Kurt Buch har avlidit i en ålder av 85 år.

Professor Buch föddes i Helsingfors den 9 maj 1881. Han blev student 1899, fil.kandidat fem år senare och fil.licentiat och doktor 1918. Följande år utnämndes han till talassolog vid havsforskningsinstitutet och därmed till chef för dess kemiska avdelning. Under sin tid vid institutet blev han docent vid Helsingfors Universitet. År 1934 blev Buch professor i kemi vid Åbo Akademi, och här stannade han till 1942, då han utnämndes till motsvarande svenskspråkiga tjänst vid Helsingfors Universitet, en befattning han innehade tills han som emeritus lämnade lärostolen år 1951. Åren 1942—44 var han även professor vid Tekniska Högskolan.

Den moderna fysikalisk-kemiska havsforskningen skapades av en handfull män i Europa och Amerika. En av dem var professor Buch. Troligen vaknade hans intresse för skeendet i haven när han arbetade som assistent vid vetenskapssocieteten underlydande finska hydrografisk-biologiska undersökningar åren 1910—17. Redan 1910 finner man i Finska Kemistsamfundets Meddelanden en publikation om egna bestämningar av vätejonkoncentrationen i havsvatten. Nämnda pH och kolsyran i hav och atmosfär intog en central ställning i professor Buch's forskning. Dessa komponenter behandlas ingående i den

1918 publicerade doktorsavhandlingen »Uber die Alkalinität, Wasserstoffionen-Konzentration, Kohlensäure und Kohlensäuretension in Wasser der Finnland umgebenden Meere». Studiet av kolsyrejämvikten i atmosfär och hav kompletterades sedermera genom forskningsresor i vattnen mellan Norge och Island samt mellan Petsamo och Spetsbergen åren 1932—36. År 1945 utkom, av krigen fem år försenat, hans stora arbete »Kolsyrejämvikten i Baltiska Havet», för vilket han belönades med Hallbergska priset.

Det var naturligt att professor Buchs forskningsresultat observerades i utlandet. Han inbjöds att arbeta vid Woods Hole's oceanografiska institut 1935 och han höll som inbjuden föredrag vid motsvarande institutioner i Seattle och Scripps i Kalifornien. År 1941 var han inbjuden att hålla föredrag vid havsforskningsinstituten i Hamburg, Kiel och Berlin.

Professor Buchs undersökningar begränsade sig inte till kolsyrejämvikten, utan han studerade även ingående näringssalternas, fosfor- och kväveföreningarnas, distribution och kretslopp i haven och deras betydelse för produktionen. Inför Internationella havsforskningskonseljen höll professor Buch flera föredrag och på inbjudan av konseljen deltog han i en arbetskommission för utvecklandet av kemiska metoder för bestämning av närsalter i havsvatten i Oslo 1928 och liknande internationella arbeten ledde han i Helsingfors 1931 och 1935.

Professor Buch hade ett sällsynt sinne för naturvetenskapernas dynamiska förändring och i sin pedagogiska verksamhet blev ungdomen redan från början satt på rätt spår, ty han gav som lärare i kemi och fysik även preliminär undervisning i kemi och fysik vid lärdomsskolor och vid Tekniska Läroverket i Helsingfors. Hans lärobok »Kemi» var många år i följd en värdefull tillgång vid undervisningen, emedan han omredigerade varje ny upplaga enligt tidens krav. Även landets försvarsfrågor intresserade professor Buch och han utgav bl.a. en bok om stridsgaser.

Inom Finska Kemistsamfundet var professor Buch en förgrundsgestalt och dess medlemmar var oftast det forum där han till först berättade om sina forskningsresultat. Inom Samfundets styrelse var professor Buch verksam i flera repriser: 1923—25 var han sekreterare och redaktör, 1926 och 1943 viceordförande och ordförande 1927 och 1944. I Samfundets styrelse kvarstod han till 1951 då han kallades till hedersledamot. Genom Samfundet var professor Buch verksam i tillkomsten av Acta Chemica Scandinavica, en milstolpe i det nordiska samarbetet på kemins område. Professor Buch kallades till ledamot av Finska Vetenskapssocieteten år 1933 och dess ordförande var han 1952.

När professor Buch blev emeritus år 1951 kunde han se tillbaka på ett halvsekel utomordentligt forskningsarbete främst modern havsforskning till fromma. Dock var hans skapande förmåga ej till ända. Han inbjöds 1954 till Internationella meteorologiska institutet i Stockholm för att grunda en internationell organisation för regelbundna undersökningar rörande atmosfärens och nederbördens kemiska beståndsdelar, och åtta år framåt ledde han dessa arbeten i Finland med två värdefulla publikationer som resultat. Men även kolsyrejämvikten fortsatte att intressera honom och inflytandet av den ökade industriella förbränningen var föremål för hans tankeväckande slutsatser. I det stora verket »Handbuch der Pflanzenphysiologie» som utkom 1960 finns två längre artiklar av professor Buch.

Folke Koroleff

Finska Kemistsamfundets verksamhet

Protokoll fört vid Finska Kemistsamfundets jubileumsmöte på samfundets 75-årsdag den 3 oktober 1966 kl. 19 i Lilla Teaterns salong i Helsingfors. Ordet leddes av samfundets ordförande *Jacobus Sundman*. Närvarande var 75 personer.

§ 1. I sitt hälsningstal gav tekn.dr *Jacobus Sundman* en historisk översikt av samfundets verksamhet alltsedan dess konstituerande möte den 3 oktober 1891. Därefter meddelade han att samfundet beslutat kalla till nya hedersledamöter professorerna *Terje Enkvist*, *Arne Fredga*, *Anders Ringbom* och *Lars Gunnar Sillén*.

§ 2. De nya hedersledamöterna presenterades i korta anföranden, prof. *Fredga* av fil.dr *Tor Smedslund*, prof. *Sillén* av bitr. prof. *J. Johan Lindberg*, prof. *Enkvist* av fil.dr *Lars Andersen* och prof. *Ringbom* av prof. *Erkki Wänninen*.

§ 3. Professor *Lars Gunnar Sillén* höll sitt festföredrag HAV, LUFT OCH SEDIMENT, NU OCH I JORDENS URTID, vilket beledsagades av ljusbilder och ett sammandrag, av vilket föredragshållaren utdelade var sitt exemplar åt samtliga närvarande. Föredraget visade bl.a. belägg på att jorden och planeterna uppkommit av kalla fasta partiklar i ett ursprungligt stoftmoln kring solen. Det utmynnade i slutsatsen, att en okänd, troligen biokemisk process i havsytan måste vara orsaken till atmosfärens relativt höga andel av jordens totalkväve.

§ 4. I det andra festföredraget, 75 ÅR ANALYTISK KEMI visade professor *Anders Ringbom* hur forna tiders analyskonst genom bidrag från teoretisk kemi och tillkomsten av fysikaliska metoder övergått i exakt teknik. Föredraget gav även perspektiv på den analytiska kemins aktuella utvecklingstendenser.

§ 5. Större delen av deltagarna fortsatte mötet avnjutande restaurant Orfei håvor och FINSKA KEMISTSAMFUNDETS GLÄDJANDE MEDDELANDEN V.

Jacobus Sundman *Carl Enebäck*

Protokoll fört vid Finska Kemistsamfundets ordinarie möte den 14 november 1966 i Tekniska Föreningens lokal, Georgsg. 30, Helsingfors. Ordet leddes av ordf. *Jacobus Sundman* med sekr. *Eneböck* vid protokollet. Närvarande 25 medlemmar.

§ 1. Ordföranden hälsade de närvarande välkomna.

§ 2. Ordföranden meddelade, att styrelsen bifallit en ansökan av tekn.lic. *Göran Sundholm* om ett bidrag på mk 450,— ur Ständiga medlemmars fond för en studieresa till forskningscentra för elektrokemi i Sverige och Danmark.

§ 3. Till nya medlemmar av samfundet invaldes bitr. prof. *Herman Adlercreutz* på förslag av bitr. prof. *Lindberg* och docent *Saris*, fil.kand. *Helena Holmberg* och nat.kand. *Gunnel Sievers*, båda på förslag av bitr. prof. *Ellfolk* och doc. *Eneböck* samt fil.mag. *Nils Olof Sundblom* på förslag av doc. *Enari* och doc. *Eneböck*.

§ 4. Ordföranden meddelade att bergsrådet Alfthans pris av styrelsen höjts till mk 400,—, genom tillskott ur Ständiga medlemmars fond.

§ 5. Bitr. prof. *J. Johan Lindberg* höll ett föredrag benämnt »Korrosion». Med anledning av föredraget yttrade sig prof. *Terje Enkvist*, fil.lic. *Holger Sjöberg*, dipl.ing. *Runar Örnhjelm* och föredragshållaren.

§ 6. Nat.kand. *Gunnel Sievers* avgav en forskningsrapport: »Tunnskiktskromatografi av fria porfyriner». Med anledning av rapporten yttrade sig bitr. prof. *Jarl Gripenberg* och fil.dr *Veronica Sundman*.

§ 7. Efter mötet följde samkväm.

Jacobus Sundman *Carl Eneböck*

Protokoll fört vid Finska Kemistsamfundets årsmöte måndagen den 12 december 1966 i TFiF:s lokal. Ordet fördes av viceordförande, docent *N.-E. Saris* med sekreteraren, docent *C. Eneböck* vid protokollet. Närvarande 23 medlemmar.

§ 1. Förrättades val av styrelse för år 1967. I stället för fil.dr *K. Ekman*, docent *C. Eneböck* och dipl.ing. *E. Idman*, vilka anmält sin önskan att avgå, invaldes genom sluten omröstning fil.mag. *Karin Sandelin*, fil.dr *Veronica Sundman* och fil.kand. *Örn Wahlroos*, av vilka den sistnämnde utsågs till sekreterare. Till ordförande valdes docent *N.-E. Saris* och till viceordförande fil.dr *Kaj Forss*.

§ 2. Samfundets funktionärer återvaldes. Till revisorer valdes tekn. dr *Gösta Silén* och bitr. prof. *Jarl Gripenberg*, till revisorssuppleant docent *Charley Gustafsson*.

§ 3. Kassören presenterade budgetförslaget för år 1967, vilket godkändes. Årsavgiften bibehölls oförändrad, medan funktionärernas arvoden höjdes: sekreterarens till mk 575,—, arkivariens till mk 125,— och kassörs- och redaktörsarvodena vardera till mk 350,—.

§ 4. Till nya medlemmar av samfundet invaldes fil.kand. *Femi Odeyemi*, på förslag av bitr. prof. *Lindberg* och docent *Saris*, samt fil.kand. *Helena Aminoff*, på förslag av prof. *Enkvist* och bitr. prof. *Lindberg*.

§ 5. Mötesdagarna fastställdes till andra måndagen i de månader, då möte stadgeenligt skall hållas. Mötestiden beslöts framskjuten till kl. 19.30.

§ 6. Ordförande meddelade att samfundets styrelse beslutat tilldela fil.kand. *Femi Odeyemi* bergsrådet Alfthans pris för år 1966 för uppsatsen »Comparative Kraft Cooks of Some Tropical Woods from Nigeria», vilken ingick i Finska Kemistsamfundets Meddelanden 75, N:o 2 (1966) ss. 33—45.

§ 7. T.f. professor *Erkki Wänninen* höll ett föredrag: »Några synpunkter på atomabsorptionsspektrofotometrin». Med anledning av föredraget yttrade sig bitr. prof. *Lindberg*, docent *Enari*, docent *Saris* samt föredragshållaren.

§ 8. Mötet avslutades med samkväm.

N.-E. Saris *Carl Eneböck*

Berättelse över Finska Kemistsamfundets verksamhet under år 1966

(avgiven vid samfundets möte den 13 februari 1967)

Samfundet sammanträdde stadgeenligt till sex ordinarie möten den 14 februari, den 14 mars, den 25 april, den 1 oktober, den 14 november och den 12 december, vid vilka i medeltal 31 medlemmar deltog. På samfundets 75-årsdag den 3 oktober hölls, förutom ett jämlikt § 3 i samfundets stadgar utlyst extraordinarie möte, även ett jubileumsmöte, vilket samlade 75 deltagare. En exkursion anordnades den 23 maj till Neste Oy:s oljeraffinaderi i Nådendal.

På programmet för de nämnda mötena har stått följande föredrag och meddelanden:

Fil.lic. *Gösta Brunow:* Aromatiska polykarbonsyror och deras separation på Sephadex-gel.
Fil.dr *Kurt Ekman:* Om impregneringen vid sulfatkok.
Fil.dr *G. R. Gummerus:* Eräiden ditiosemikarbatsonien stereoisomeriasta.
Bitr. prof. *J. Johan Lindberg:* Entropibegreppet i modern kemi och biokemi.
—»— Korrosion.
Prof. *Anders Ringbom:* 75 år analytisk kemi (jubileumsföredrag).
Docent *Nils-Erik Saris:* Om mekanismen för muskelkontraktion.
Nat.kand. *Gunnel Sievers:* Tunnskiktskromatografi av fria porfyriner.
Prof. *Lars Gunnar Sillén:* Hav, luft och sediment, nu och i jordens urtid (jubileumsföredrag).
Dipl.ing. *Bengt Stenlund:* Lignosulfonsyrors molekylvikter och molekylviktsfördelning.
T.f. prof. *Erkki Wänninen:* Några synpunkter på atomabsorptionsspektrofotometrin.

Under året har fyra nummer av Finska Kemistsamfundets Meddelanden med ett totalt sidoantal av 144 utkommit.

Vid årsmötet den 12 december tilldelades fil.kand. *Femi Odeyemi* bergsrådet Alfthans pris för sin uppsats »Comparative Kraft Cooks of Some Tropical Woods from Nigeria», vilken ingick i Finska Kemistsamfundets Meddelanden 75, N:o 2, 1966.

Bud har under året nått samfundet om att av dess medlemmar dipl.ing. *Edvard Degerholm*, dipl.ing. *Göran von Knorring*, fil.dr *Hanna Lappalainen*, dipl.ing. *B. Sundroos* och fil.mag. *Tor Wessman* avlidit.

I samband med 75-årshögtidligheterna kallades till hedersledamöter prof. *Terje Enkvist*, Helsingfors Universitet, prof. *Arne Fredga*, Uppsala Universitet, prof. *Anders Ringbom*, Åbo Akademi och prof. *Lars Gunnar Sillén*, Kungliga Tekniska Högskolan, Stockholm.

Elva medlemmar har avgått eller strukits ur förteckningen och sexton nya medlemmar har invalts, varigenom samfundets medlemsantal vid utgången av året var 391.

Styrelsen har sammanträtt 7 gånger. Dess sammansättning har varit:

Ordförande:	Tekn.dr *Jacobus Sundman*
Viceordförande:	Docent *Nils-Erik Saris*
Sekreterare:	Tekn.dr *Carl Eneböck*
Medlemmar:	Fil.dr *Kurt Ekman*
	Docent *Tor-Magnus Enari*
	Professor *Terje Enkvist*
	Fil.dr *Kaj Forss*
	Dipl.ing. *Edvard Idman*
	Bitr. prof. *J. Johan Lindberg*

Samfundets funktionärer har varit:

Kassör: Tekn.lic. *Göran Sundholm*
Arkivarie: Dipl.ing. *Nita Grönvik*
Redaktör: Docent *Tor-Magnus Enari*

Revisorer har varit tekn.dr *Gösta Silén* och fil.mag. *Karin Sandelin* med bitr. prof. *Jarl Gripenberg* och docent *Charley Gustafsson* som suppleanter.

Samfundets representanter i Centralrådet för Finlands Kemister har varit tekn.dr *Jacobus Sundman* och docent *Tor-Magnus Enari* med docent *Nils-Erik Saris* och docent *Carl Enebäck* som suppleanter. Revisor i Centralrådet har varit tekn.dr *Gösta Silén* med fil.dr *William Forsman* som suppleant.

Professor *Anders Ringbom* och bitr. professor *Jarl Gripenberg* har varit medlemmar av redaktionskommittén för Acta Chemica Scandinavica. Tekn.lic. *Göran Sundholm* har varit medlem i dess ekonomiutskott.

Jacobus Sundman
ordförande

Carl Enebäck
sekreterare

Notiser — Uutisia

Det 5. internationella symposiet över naturprodukternas kemi.

IUPAC anordnar den 8—13 juli 1968 i London ett internationellt symposium över naturprodukternas kemi. Vid symposiet hålles tio huvudföredrag av följande kända vetenskapsmän:

Dr. C. B. Anfinsen (U.S.A.)
Prof. D. Arigioni (Schweiz)
Prof. T. Goto (Japan)
Prof. H. H. Inhoffen (Tyskland)
Dr. B. Keil (Tscheckoslovakien)
Prof. H. B. Khorana (U.S.A.)
Prof. E. Lederer (Frankrike)
Prof. M. M. Shemyakin (Sovjetunionen)
Prof. G. Stork (U.S.A.)
Prof. R. B. Woodward (U.S.A.)

Utom huvudföredragen anordnas sektionsföredrag i följande fem grupper:

A. Fysikaliska metoder inklusive röntgenkristallografi.
B. Naturliga metallföreningar.
C. Biosynteser.
D. Proteiner och enzymsystem i relation till den organiska kemin.
E. Övriga biologiskt viktiga makromolekyler.

Sektionsföredragen bör anmälas senast den 1.2.1968. Ett cirkulär (nr. 2) med närmare uppgifter distribueras i december 1967 till dem som anmält sig. Det första cirkuläret kan erhållas från Centralrådet för Finland Kemister (postbox 10058, Helsingfors 10 eller tel. 642911/fil.mag. Christine Eriksson).