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Studies on Components in Wood

6. Isolation and Mass Spectrometric Identification of Monoenoic Fatty Acids in Norway Spruce (*Picea abies*)

Rainer Ekman and Göran Pensar

The Institute of Wood Chemistry and Cellulose Technology. Abo Akademi, Abo, Finland

Abstract

The monoenoic long chain fatty acids from an extract of spruce wood were identified by gas chromatography on capillary columns in combination with mass spectrometry. The acids investigated were isolated as methyl esters on silver nitrate impregnated thin-layer plates. Hydrogenation gave both straight and branched chain saturated esters. Even and odd numbered esters from C₁₄ to C₂₀ were found. Trimethylsilyloxy (TMSO) derivatives of the monoenoic fatty acid esters were used for determining the double bond position by gas chromatography-mass spectrometry. The analysis gave evidence of positional isomers. Unsaturation was found predominantly in position 9 with the exception of the monoenoic esters C₁₅ and C₂₀. The most abundant member was methyl octadecenoate (91,5 %), followed by the anteiso branched methyl 16-methyl-octadecenoate (3,8 %).

Introduction

Several groups of workers have studied the distribution of fatty acids in wood extractives by gas chromatography.¹⁻⁵ At present, little is known about the detailed composition of the fatty acids, and especially the isomeric monounsaturated fatty acids, in wood. The object of this work was to contribute new information on isomeric unsaturated fatty acids in the course of our studies on wood extractives. It is well known that mass spectrometric analysis of unsaturated fatty acids is complicated because positional isomers usually give almost identical mass spectra. Several workers have applied mass spectrometry to the analysis of derivatives of hydroxylated fatty acids.⁶⁻⁸

The analysis of trimethylsilyloxy (TMSO) derivatives of the monoenoic esters has proved to be a valuable method for the determination of the double bond positions.⁹⁻¹⁰

The TMSO derivatives of straight chain and methyl branched monoenes with the same number of carbon atoms were found to give very similar mass spectra. Saturation of the monoenes by catalytic hydrogenation followed by gas chromatography — mass spectrometry gave mass spectra which could be compared with the corresponding spectra of saturated fatty acids investigated in a previous work.¹¹ In this way the branched chain acids could be easily identified.

Experimental

Material. A 75-year old spruce (*P. abies* (L) Karst.), grown in Houtskär in the southwestern archipelago of Finland, was felled in April, 1972. A cross section of the trunk was taken at the level of two meters and, after chipping, the wood sample was air-dried and ground to wood meal of 20 mesh particle size.

The isolation and analysis of the monoenoic acids were carried out according to the simplified scheme given in Fig. 1.

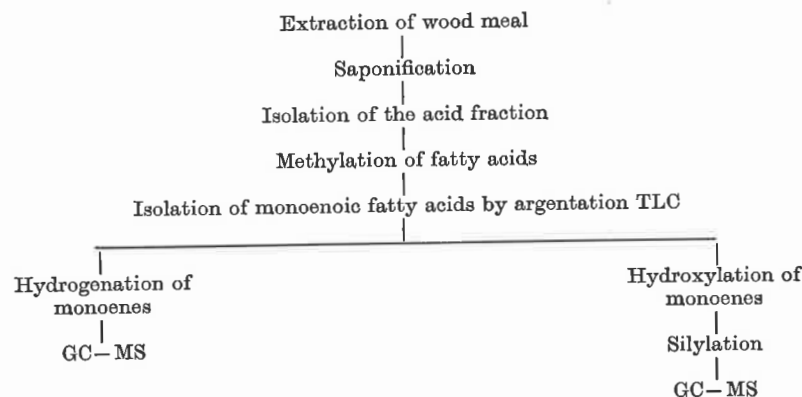


Fig. 1. Different steps in the isolation and analysis of monoenoic fatty acids in a spruce extract.

Extraction, saponification and isolation of the acid fraction.

The wood meal was extracted in a Soxhlet apparatus with dichloromethane for three hours. The solvent was removed by gentle heating at a reduced pressure under nitrogen. The residue was saponified for three hours with 0.4 N potassium hydroxide solution in ethanol-water (10:1 v/v) at a temperature of 75°C. The solution, containing the potassium salts of resin and fatty acids together with unsaponifiable compounds, was diluted with water to obtain a water-ethanol mixture of 50:50 v/v. The unsaponifiable matter in this mixture was removed by solvent-solvent extraction with petroleum ether (bp. 30–40°). The remaining aqueous solution was analysed by thin-layer chromatography on micro plates (7.5 × 2.5 cm) using silicic acid as adsorbent in order to confirm that no unsaponifiable compounds were present after the extraction. The resin and fatty acid salts were then converted to free acids by adding 1.5-N hydrochloric acid. The acids were extracted into petroleum ether and the solvent was evaporated.

Methylation of the fatty acids. The residue was dissolved in a solution of concentrated hydrochloric acid in methanol (5:100 v/v) in order to methylate only the fatty acids. The mixture was boiled for two minutes on a steam bath. Water was added, and the mixture was treated with diethyl ether to extract the fatty acid methyl esters and the resin acids from the aqueous mixture. An extraction of this ether phase with a sodium carbonate solution removed the resin acids from the ether solution. Thus, the remaining ether solution contained all the fatty acids extracted from the wood sample. This fraction was analyzed by gas chromatography. The thin-layer analyses of the different steps of the procedure are illustrated in Fig. 2.

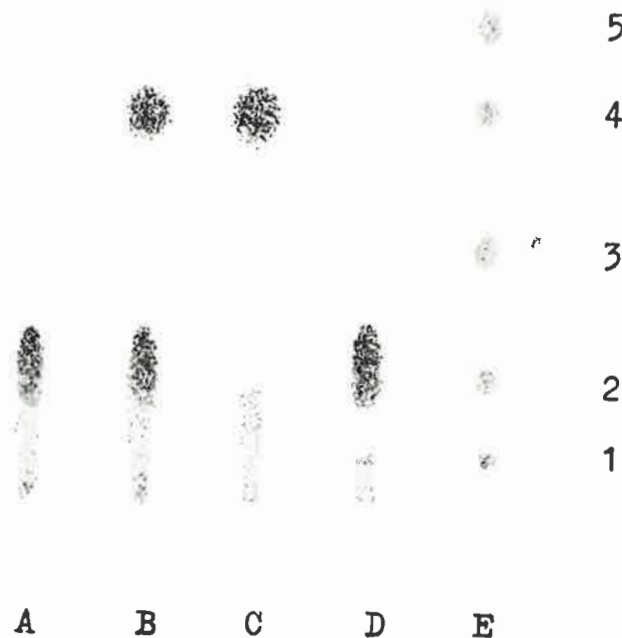


Fig. 2. Thin-layer chromatography of different fractions during the methylation of fatty acids in a mixture with resin acids. Solvent system: petroleum ether:diethyl ether:acetic acid (85:15:1 v/v).

- A. Resin and fatty acids in petroleum ether after saponification and extraction
- B. Fatty acid esters and resin acids after two minutes of boiling in hydrochloric acid - methanol
- C. Extracted fatty acid esters in diethyl ether
- D. Resin acids in the sodium carbonate solution
- E. Reference mixture; 1. Sterols, 2. Free acids, 3. Triglycerides, 4. Methyl esters, 5. Sterol esters.

Isolation of the monoenoic fatty acid esters. The monoenoic esters were separated by silver ion thin-layer chromatography. The thin-layer plates with silicic acid as adsorbent were sprayed with a solution of 15 % silver nitrate in 28-30 % ammonium hydroxide. The impregnated plates were air-dried and activated at 110°C for half an hour. The sample of total fatty acid methyl

esters was applied as a thin line onto the plate and developed with a solvent mixture of petroleum ether:diethyl ether (90:10 v/v) at room temperature. After moving to the top edge of the plate, the solvent mixture was allowed to evaporate and the plate was sprayed with a solution of 0.2 % dichlorofluorescein in 96 % ethanol. The lines on the plate were visualized under ultraviolet light. A reference mixture containing the methyl esters of 18:0, 9-18:1, 9,12-18:2 and 5,9,12-18:3 was used for locating the lines.* The zone containing the monoenes was scraped off the plate, extracted with benzene and studied by gas chromatography.

Hydrogenation. The hydrogenation of the monoenoic esters was performed by leading hydrogen into the benzene solution of the esters with a suspension of platinum oxide as catalyst. The reaction was complete within one hour, as confirmed by gas chromatography.

Hydroxylation and silylation. The TMSO derivatives of the monounsaturated fatty acid methyl esters were prepared by hydroxylation of the olefinic bond by oxidation with OsO₄ and subsequent reduction of the osmate with Na₂SO₃ according to McCloskey and McClelland⁶. The dihydroxy fatty acid esters were then converted to the corresponding TMSO derivatives by treatment with a pyridine-hexamethyldisilazane solution and catalytic amounts of trimethylchlorosilane. The mixture was then analysed by gas chromatography - mass spectrometry.

Gas chromatography - mass spectrometry. An LKB-9000 instrument was used for the mass spectrometric investigations. The gas chromatograph was equipped with a capillary column having an ID of 0.5 mm and coated with butane-1,4-diol succinate (BDS). This 50m long steel column was used for the separation of the methyl esters. The column temperature was held at 190°C, the injection port at 220°C, and the helium carrier gas flow through the column was 2 ml/min.

The TMSO derivatives were analyzed with a 50m long capillary steel column (ID=0.5 mm) coated with liquid methyl silicone OV-101. The column temperature was held at 225°C and injection port at 240°C. The carrier gas flow rate was 2 ml/min.

All analyses were made with a molecule separator temperature of 240°C and an ion source temperature of 270°C. The ionizing potential was 70 eV and the ionizing current 60 μA.

Results and Discussion

A gas chromatographic record on the total content of the methylated fatty acids isolated from the spruce extract is shown in Fig. 3.

The positions of the straight chain saturated and monoenoic esters are given in the figure, while esters with more than 21 carbon atoms in the chain are omitted because all the monoenoic esters found in the extract fall within the range C₁₂-C₂₁.

* The following abbreviated nomenclature, according to R.T. Holman,¹² is used in this work. For groups of fatty acids or derivatives having a common number of carbon atoms but varying in the number or position of double bonds, the fractions are referred to in the usual manner, C₁₆, C₁₈ etc. The examples 18:1 and 9-18:1 denote, besides the number of carbon atoms, the number of double bonds and the number+position of double bonds respectively. The notations *i* and *ai* are used for iso- and anteiso-branched fatty acids.

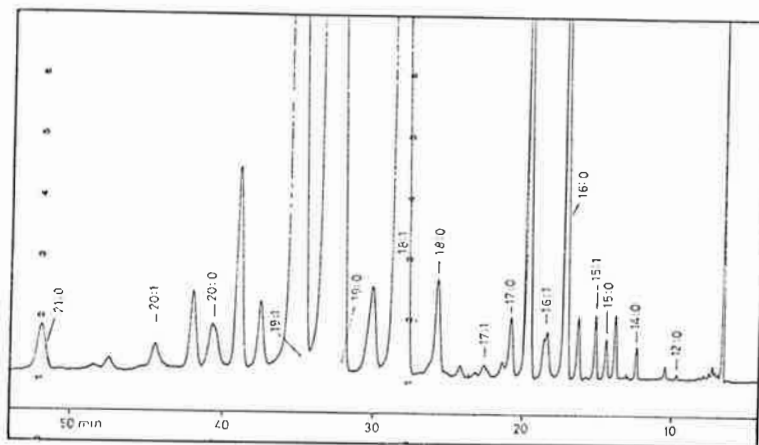


Fig. 3. Gas chromatographic separation of total fatty acid methyl esters from a spruce extract. Conditions: Gas chromatograph — mass spectrometer LKB-9000 equipped with a 50m long capillary column (ID=0.5 mm) coated with butane-1,4-diol succinate. Column temperature 190°C, injection port 220°C and helium carrier gas flow 2 ml/min.

Fig. 4 shows a gas chromatogram of the isolated saturated fatty acids 12:0–21:0. This fraction was investigated in an earlier work using packed columns.¹¹ Because of the superior resolution of the capillary column, two additional branched chain acids, 16:0i and 18:0i, were identified in this work. Thus the number of saturated fatty acids found in a spruce extract is now 30.

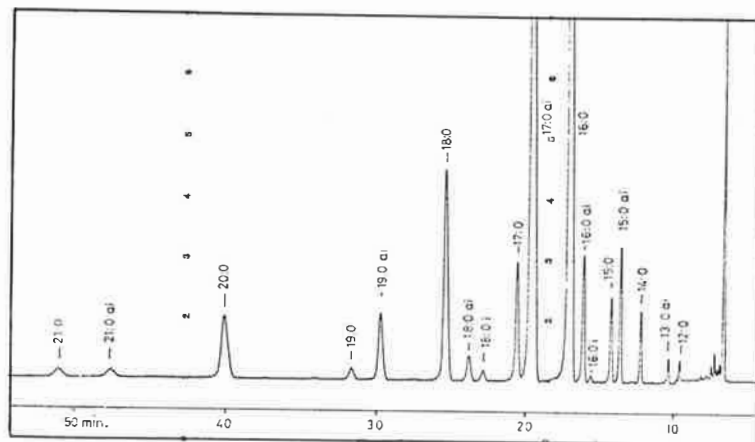


Fig. 4. Gas chromatographic separation of saturated fatty acid methyl esters from a spruce extract. Conditions as in Fig. 3.

The gas chromatographic separation of the catalytically hydrogenated monoenoic fatty acid methyl esters is shown in Fig. 5. These hydrogenated esters were identified from retention times and mass spectra. Straight chain acids, C₁₄–C₂₀, together with monomethyl-substituted acids were represented in the fraction.

It is obvious, even in the case of monoenoic fatty acids, that those with an odd number of carbon atoms are more frequently accompanied by considerable amounts of anteiso branched isomers than are the even numbered acids. The same tendency was found in the distribution of the saturated acids. The only exception to this rule seems to be the acid 15:1. Only one iso branched monoene, 18:1i, was found.

The distribution of monoenoic fatty acids present in a spruce extract is given in Table 1. The relative amounts are calculated from the chromatographic record in Fig. 5 and must be considered tentative because the composition of an extract from wood depends, within certain limits, on the structural characteristics of the tree providing the sample.⁵ The monoenoic fatty acid fraction represents about 20 % of the total fatty acid content.

The gas chromatographic record in Fig. 6 illustrates the separation of the monounsaturated fatty acid methyl esters. The peaks in the figure are asymmetric because the positional isomers are only partially resolved.

The mass spectra of positional isomers differ only slightly from each other and therefore an analysis of the unsaturated methyl esters is very difficult. We found that anteiso branched monoenoic fatty acid methyl esters gave mass spectra showing more

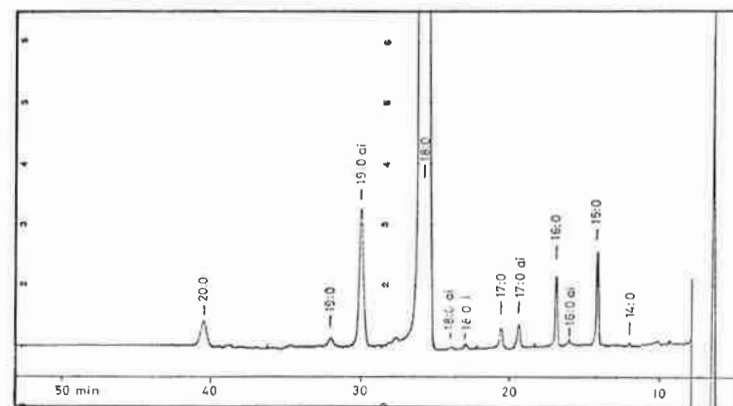


Fig. 5. Gas chromatographic separation of catalytically hydrogenated monoenoic fatty acid methyl esters from a spruce extract. Conditions as in Fig. 3.

Table 1. Distribution of monounsaturated fatty acids from a spruce extract.

Component	% of the monoene fraction	Component	% of the monoene fraction
14:1	<0.1	18:1i	<0.1
15:1	1.3	18:1ai	<0.1
16:1ai	<0.1	18:1	91.5
16:1	1.1	19:1ai	3.8
17:1ai	0.5	19:1	0.3
17:1	0.4	20:1	1.0

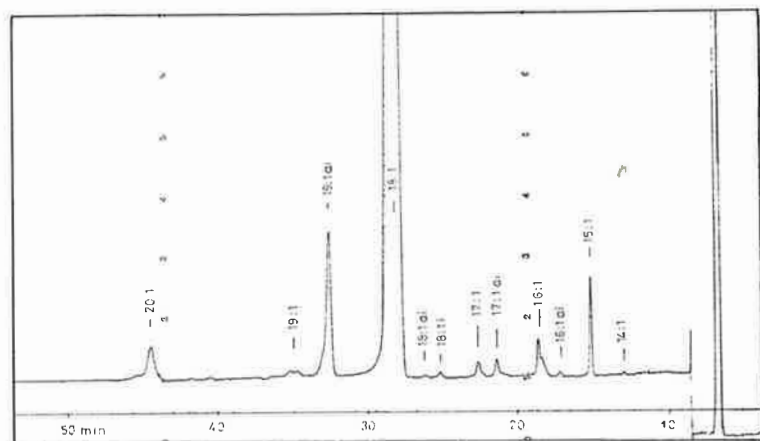


Fig. 6. Gas chromatographic separation of monoenoic fatty acid methyl esters from a spruce extract. Conditions as in Fig. 3.

abundant peaks at m/e M-29 (molecular ion — ethyl group) than the spectra of corresponding normal chain esters. This is also true in the case of saturated anteiso esters.¹³

The hydroxylation of the monoenes followed by silylation results in TMSO derivatives well suited for double bond determination.^{9,10} Fig. 7 shows the gas chromatographic separation of the TMSO derivatives of the monoenoic fatty acid methyl esters from a spruce extract.

As can be seen from Fig. 7, the components are incompletely resolved, but repeated mass spectrometric scannings at different points on the peaks make identification of the derivatives of the monoenoic esters possible.

The mass spectrum of the TMSO derivative of the methyl ester 9-18:1 is shown in Fig. 8 where typical fragment ions are denoted according to the work of Capella and Zorzut.⁹

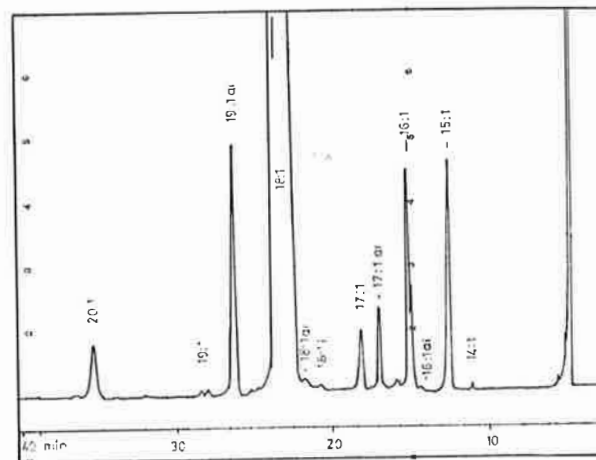


Fig. 7. Gas chromatographic separation of the TMSO derivatives of the monoenoic fatty acid methyl esters from a spruce extract. Conditions: Gas chromatograph — mass spectrometer LKB-9000 equipped with a 50m long capillary column (ID=0.5mm) coated with liquid silicone OV-101. Column temperature 225°C, injection port 240°C and helium carrier gas flow 2 ml/min.

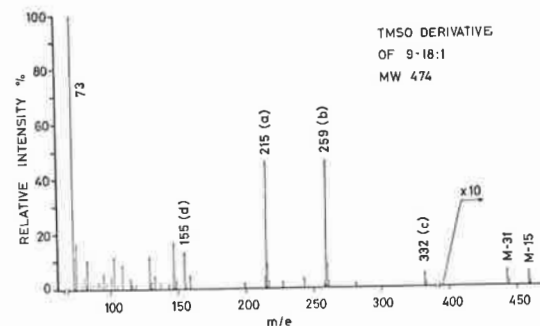
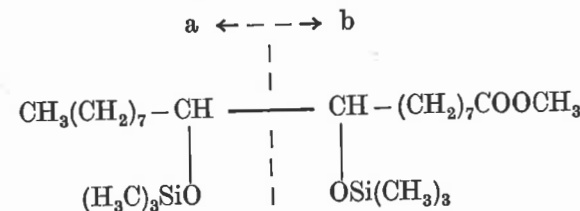


Fig. 8. Mass spectrum of the TMSO derivative of 9-18:1 methyl ester.

The carbon-carbon bond between the TMSO groups is easily broken, and two peaks, a and b, with approximately the same intensities are principally formed as follows:



The base peak is at m/e 73 ($(\text{CH}_3)_3\text{Si}^+$), and some other characteristic fragments make a reliable identification possible. The formation of the ions b, c and d is believed to follow the mechanism given in Fig. 9.

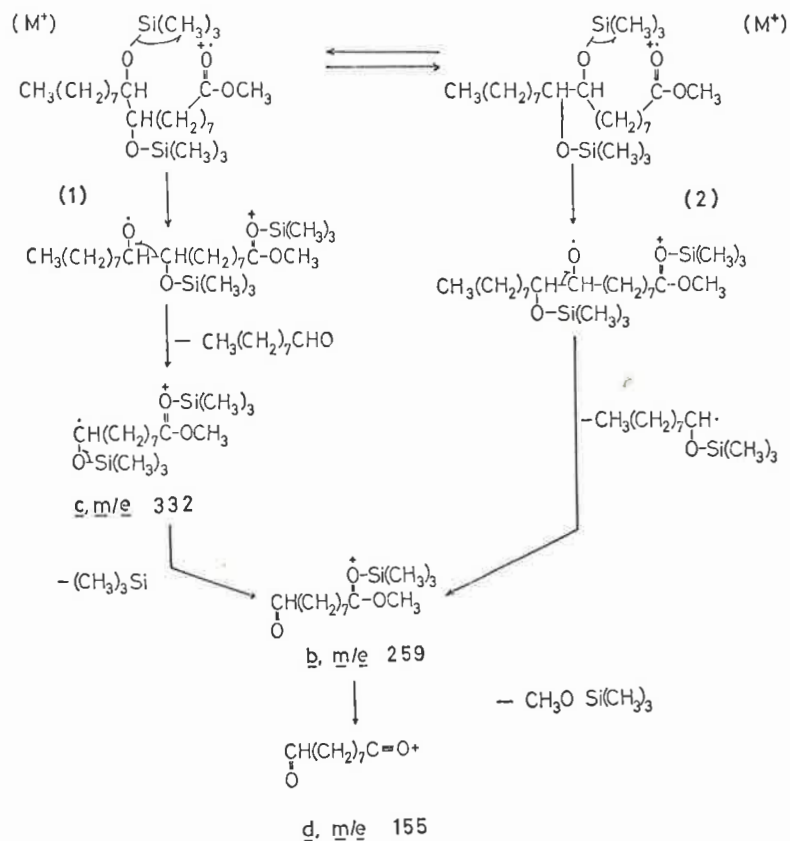


Fig. 9. Formation of ions b, c and d, proposed by Capella and Zorzut.⁹

The mass spectra of the anteiso branched TMSO derivatives differ very little from the corresponding straight chain derivatives. Fig. 10 shows as an example the mass spectra of the TMSO derivatives of 9-17:1 and 9-17:1ai methyl esters.

The spectra in Fig. 10 differ from each other in two main respects. In the spectrum of 9-17:1ai, the peak a at m/e 201 is of lower intensity whereas the peak at m/e 111 is of higher intensity than the corresponding peaks in the spectrum of the straight chain derivative. The fragment m/e 111 is probably formed by cleavage of trimethylsilanol ($(\text{H}_3\text{C})_3\text{SiOH}$, mass = 90) from the ion a at m/e 201.

The mass spectrum given in Fig. 11 demonstrates how gas chromatographically unresolved components can be identified from a spectrum representing a three-component mixture. The number indexed characteristic peaks are due to the presence of the TMSO derivatives of the methyl esters 9-16:1 (1), 7-16:1 (2) and 6-16:1 (3).

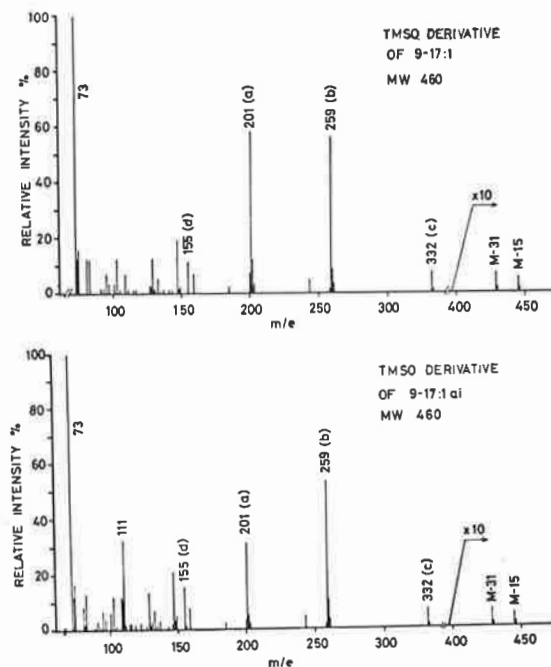


Fig. 10. Mass spectra of the TMSO derivatives of 9-17:1 and 9-17:1ai methyl esters.

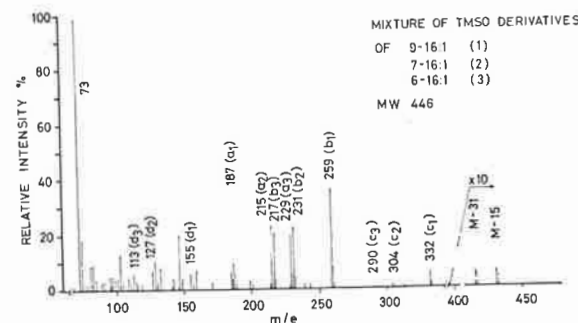


Fig. 11. Mass spectrum of a mixture of the TMSO derivatives of 9-16:1 (1), 7-16:1 (2) and 6-16:1 (3) methyl esters.

The positional isomers of different monoenoic fatty acids found in a spruce extract are listed in Table 2.

Table 2. Monoenoic fatty acid isomers in a spruce extract. The major components are marked by a line.

Acid	Isomers
14:1	?
15:1	<u>5-15:1</u> , 6-15:1 (T)
16:1ai	<u>9-16:1ai</u>
16:1	<u>6-16:1</u> , 7-16:1, 8-16:1 (T), <u>9-16:1</u> , 10-16:1 (T), 11-16:1
17:1ai	6-17:1ai, 7-17:1ai, <u>9-17:1ai</u>
17:1	6-17:1 (T), 7-17:1, 8-17:1, <u>9-17:1</u> , 11-17:1 (T)
18:1i	<u>9-18:1i</u>
18:1ai	<u>9-18:1ai</u>
18:1	<u>9-18:1</u> , 11-18:1
19:1ai	<u>9-19:1ai</u> , 11-19:1ai
19:1	<u>9-19:1</u> , 11-19:1
20:1	<u>9-20:1</u> , <u>11-20:1</u> , 13-20:1

(T)=trace amount

Straight chain monoenoic acids represent 95.6 % of the fraction, with 18:1 as the dominant member (91.5 %). The amount of anteiso branched monoenes is 4.4 %, the major component being 19:1ai (3.8 %). Less than 0.1 % of the monoenoic fraction consists of the iso branched 18:1i.

Branched chain monoenoic fatty acids have rarely been found in lipids of natural origin. Reports on the identification of branched monoenoic fatty acids in wood extracts have not been published.

Because of incomplete separation of the positional isomers as TMSO derivatives, no accurate quantitative estimations will be given. Unsaturation in position 9 is dominating in the monoenes 16:1ai-19:1. The acid 15:1 is almost entirely represented by the 5-15:1 isomer with trace amounts of 6-15:1. About 2/3 of the amount of the 16:1 isomers consist of 9-16:1. Isomers of the acids 18:1-20:1 seem to be predominately distributed between the 9- and 11-unsaturated members. Thus, approximately 90 % of 18:1 is represented by 9-18:1 and 10 % by 11-18:1. The contribution of 9-19:1ai to 19:1ai is more than 90 %, the re-

maining amount being 11-19:1ai. The 19:1 member consists of approximately equal amounts of the 9- and 11-unsaturated monoenes, whereas about 3/4 of 20:1 is represented by 11-20:1.

The low concentrations of the branched chain acids 16:1ai, 18:1i and 18:1ai allowed identification only of the dominating 9-isomers.

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On the Temperature Dependence of the Hyperfine Coupling Constants in the Cation Radical of 4,4'-dimethoxybiphenyl

Henrik Tylli

Department of Chemistry, University of Helsinki. E. Hesperiankatu 4, SF-00100 Helsinki 10, Finland.

Abstract

The temperature dependence of the hyperfine coupling constant of the *ortho* protons in the cation radical of 4,4'-dimethoxybiphenyl has been calculated for a series of the Mathieu parameter s , using the eigenvalues of the torsional oscillator. The value 4.18 kJ/mole was obtained for the torsional barrier about the central C—C bond, and the frequency of the torsional fundamental was predicted to be 20 cm⁻¹, by fitting the coupling constants observed at different temperatures to the calculated ones. The barrier value obtained is discussed in relation to recent experimental and theoretical results.

Introduction

There has been a number of electron resonance studies in which the conformation of molecules is correlated with the magnitudes of the experimental hyperfine coupling constants.¹⁻⁴ Several studies have also been published in which the temperature dependence of the coupling constants has been measured and the data analyzed in terms of restricted internal motion.⁵⁻¹⁴ In the following the temperature dependence of the hyperfine coupling constant of the *ortho* protons in the cation radical of 4,4'-dimethoxybiphenyl is treated in more detail.

The electron resonance spectrum of the cation radical of 4,4'-dimethoxybiphenyl has been investigated at different temperatures between -60°C and 70°C in two different solvent systems.^{15,16} At -20°C and below the spectrum could be assigned by assuming *cis-trans* isomerism,¹⁵ while at room temperature and above the spectrum could be completely assigned without this effect.¹⁶ However, the intensity ratios between the hyperfine components of the spectrum recorded at 8°C could not be completely accounted for if free rotation about the central C—C bond was assumed. This means that at 25°C and above one

observes the fast exchange region, but for temperatures lower than about 10°C one gradually reaches the region of intermediate exchange rates.

The hyperfine coupling constant of the protons *ortho* to the central C—C bond shows variations with the temperature. The value of this coupling constant increases with the temperature, while the coupling constants of the *meta* protons and of the protons in the methoxy groups are effectively independent of the temperature.¹⁶ The temperature dependence of the *ortho* coupling constants is evidently due to the fact that the barrier to internal rotation about the central C—C bond is increasingly overcome at higher temperatures. The temperature dependence is not attributed to the change of the properties of the solvent with temperature, because such a change should affect all the coupling constants in the same way.

Angle Dependence of the *Ortho* Hydrogen Hyperfine Coupling Constants.

The dependence of the *ortho* hydrogen hyperfine coupling constants on the angle of torsion about the central C—C bond cannot be concluded from experimental results. Therefore, in the present study this angular dependence has been calculated using the INDO method. The calculations were performed as described previously.¹⁶ In order to save computer time the INDO calculations were performed with only two values of the torsional angle for the *cis* and *trans* conformations of the molecule, namely for the planar conformation and for the one with the torsional angle 19°. The results of these calculations are shown in figure 1. It is seen that the average of the *ortho* proton coupling constants is larger in the planar conformation than in the nonplanar one. In the following it is therefore assumed that the angular dependence of the *ortho* coupling constant can be written as:¹⁷

$$a_H(\alpha) = B_0 + B_2 \cos^2 \alpha$$

where α is the torsional angle about the central C—C bond, and B_0 and B_2 are constants.

Model for the Temperature Dependence

The torsional oscillations which the biphenyl molecular performs about the central C—C bond can be treated quantitatively if the energy levels of the torsional oscillator are known. Since the transitions between the torsional energy levels occur much faster than the Larmor frequency of the unpaired electron, the observed hyperfine splitting can be written:

$$a_H(T) = \frac{\sum_{i=0}^{\infty} g_i \langle i | a_H(\alpha) | i \rangle e^{-\frac{E_i}{kT}}}{\sum_{i=0}^{\infty} g_i e^{-\frac{E_i}{kT}}}$$

where g_i is the degeneracy, and E_i the energy of the i :th torsional state and $\langle i | a_H(\alpha) | i \rangle$ is the expectation value of $a_H(\alpha)$ in that state in the representation which diagonalizes the torsional Hamiltonian. If the expression for $a_H(\alpha)$ is introduced it is seen that the above expression essentially sums the expectation values of $\cos^2\alpha$ for all torsional states i , properly weighted according to their populations. According to this model the observed coupling constant is temperature dependent in the presence of a substantial barrier. It is possible to determine the torsional barrier by fitting the above expression to the observed

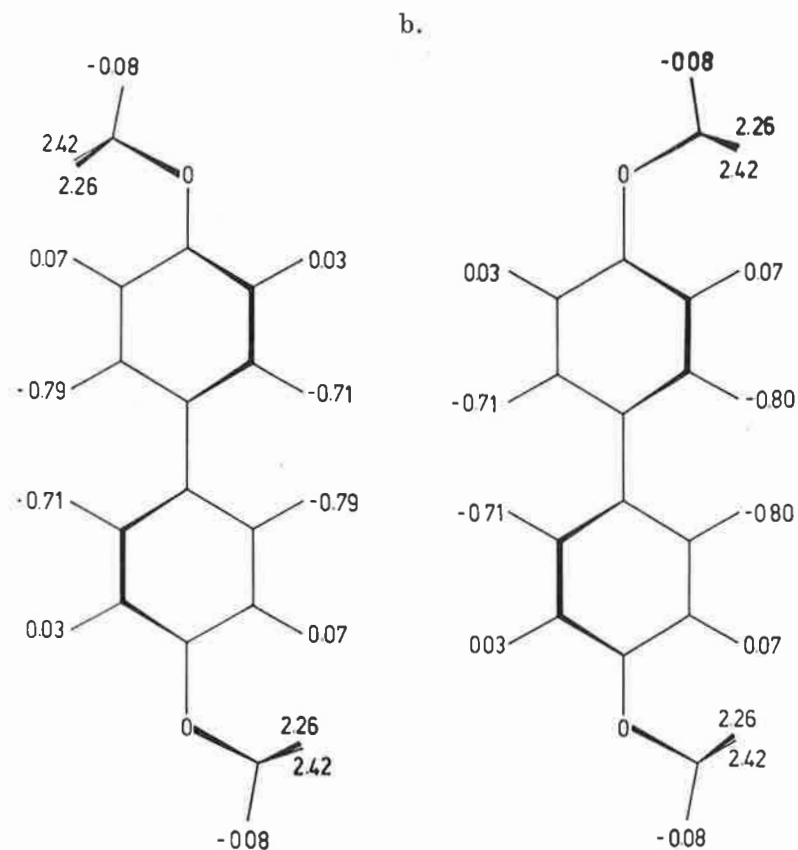
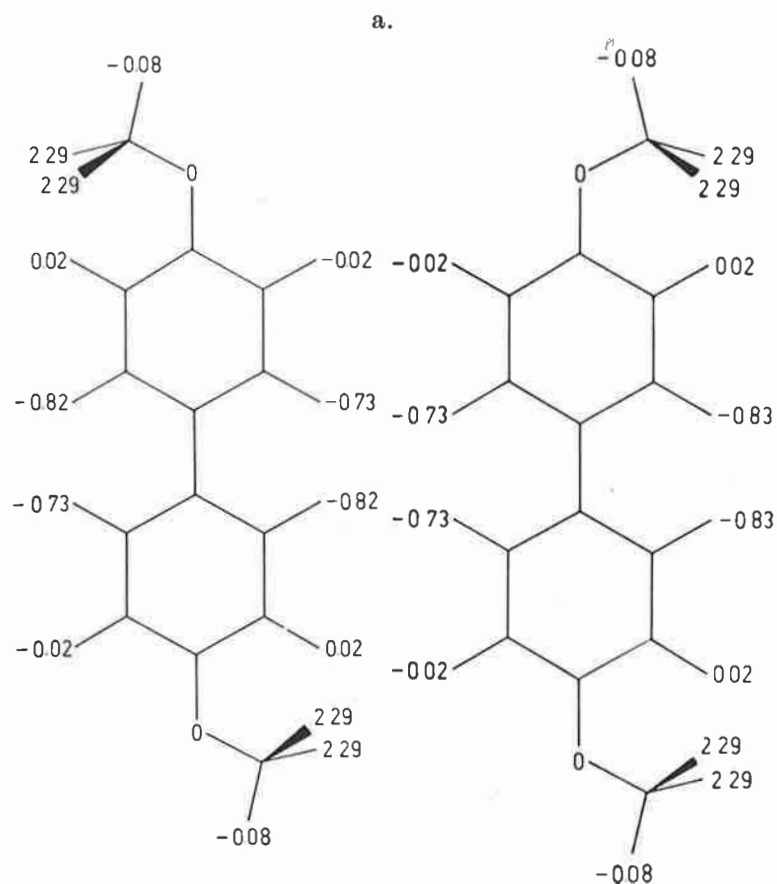


Figure 1. The calculated proton hyperfine coupling constants in the cation radical of 4,4'-dimethoxybiphenyl. INDO with annihilation, $\langle S^2 \rangle = 0.750$. a. The planar *cis* and *trans* conformations. b. The *cis* and *trans* conformations with the interplanar angle 19° .

temperature dependence.¹³ The value of the constant B_0 was assumed to be negligible,¹³ whereas the constant B_2 was adjusted to give agreement with the experimental coupling constant at 8°C . In order to apply the equation for $a_H(T)$ to the present problem the energy levels of the torsional oscillator must be known.

Method

The computations made in the present study are based upon a model chosen to represent the 4,4'-dimethoxybiphenyl molecule.

First, solution of the torsional wave equation for the model implies that the potential energy for the internal motion can be expressed adequately by a Fourier series in terms of the angle of internal rotation α :¹⁹

$$2V = \sum_{N=1}^{\infty} V_N(1 - \cos N\alpha)$$

As applied to the present case of an essentially two-fold barrier this yields the expression:

$$V(\alpha) = \frac{V_2}{2}(1 - \cos 2\alpha) + \frac{V_4}{4}(1 - \cos 4\alpha)$$

where V_2 represents the height of the two-fold barrier and V_4 the height of the four-fold one. It is assumed, that for the present purpose the contribution of V_4 can be neglected, although Kurland and Wise²⁰ from their NMR study of biphenyl and 4,4'-disubstituted biphenyls reported four-fold barrier values of about 10 % of the two-fold barrier. Substitution of this potential into the Schrödinger equation leads to the torsional wave equation²¹⁻²³:

$$-\frac{\hbar^2}{2I} \frac{d^2\psi}{d\alpha^2} + \frac{V_2}{2}(1 - \cos 2\alpha) \psi = E\psi$$

Making the substitution:

$$b_{v\sigma} = \frac{2IE_{v\sigma}}{\hbar^2} \quad \text{and} \quad s = \frac{2IV_2}{\hbar^2}$$

the Mathieu equation is obtained in the form²⁴⁻³⁴:

$$\frac{d^2\psi}{d\alpha^2} + (b_{v\sigma} - s \cos^2\alpha) \psi = 0$$

Above I stands for the reduced moment of inertia of the top, s is a dimensionless parameter and $b_{v\sigma}$ are the characteristic values of the Mathieu equation. For a fixed value of s there exists a countably infinite sequence of characteristic values. The Mathieu equation has previously been applied to problems in electron resonance spectroscopy by Fessenden,¹¹ by Freed,³⁵ and by Bauld et al.³⁶

Second, some further approximations have to be introduced in order to calculate the reduced moment of inertia of the top. The model molecule will therefore be taken to consist of two rigid anisole molecules bonded *para* to each other. The only internal degree of freedom allowed in this semirigid model is

therefore the torsional oscillations of the two anisole fragments relative to each other. The torsional oscillations of the methoxy and methyl groups about their C—O axes were not taken into account. As the frequency of the torsional oscillations about the central C—C bond in the neutral biphenyl molecule is estimated to be of the order of magnitude of 60 cm^{-1} ³⁷⁻³⁹ (compare *Discussion* in the present paper), and for the torsional modes of OCH₃ and CH₃ $108-115 \text{ cm}^{-1}$ and 216 cm^{-1} respectively (compare references cited in 16), this approximation is not likely to introduce any large errors. In a normal coordinate treatment this means that those force constants which are not associated with the C—C torsional mode are increased to infinity thereby making the molecule rigid. Because of the initial lack of resonance between the torsional mode about the coannular C—C bond and the other fundamentals, the hindered rotation will not be materially affected.

The reduced moment of inertia of the top can now be calculated according to the formula given by Pitzer and Gwinn:⁴⁰

$$I_m = I_m^o \left[1 - I_m^o \left(\frac{\lambda_{mA}^2}{I_A} + \frac{\lambda_{mB}^2}{I_B} + \frac{\lambda_{mC}^2}{I_C} \right) \right]$$

Here I_m' denotes the reduced moment of inertia of the m :th top, I_m^o the moment of inertia of the top itself with respect to the top axis, and $\lambda_{m\alpha}$ is the direction cosine between the axis of the m :th top and one of the principal moments of inertia, I_A , I_B or I_C . The above formula holds exactly for a single attached top. The principal moments of inertia for the top and the whole molecule were calculated with the aid of the computer program CART, originally written by Schachtschneider.⁴¹

Tabulations of the characteristic values of the Mathieu equation exist, but not for the large value of the parameter s needed in the present study. One therefore has to solve the Mathieu equation numerically. Only the periodic solutions are considered. This implies that the coupling between the internal motion and the overall rotation is neglected, although the conditions for their separability are not met in the present case^{29,42-45}.

Computational Details

The calculations of the characteristic values of the Mathieu equation were performed with the aid of the computer program MATHIEU, kindly put to the author's disposal by prof. Bauld.³⁶ The program was slightly modified for the two-fold barrier case. The program is essentially based upon a computational procedure given in the literature.^{33,34} Good trial solutions are extremely helpful in order to obtain convergence to the right

characteristic values. The trial solutions were obtained with the aid of the asymptotic expressions given by Ince,^{24,46,47} and independently by Goldstein.^{25,48} The asymptotic expressions used give satisfactory trial solutions only when $v \leq 10$ in the present case.⁴⁹ Care must also be taken to ensure that the trial solution is not separated from the desired characteristic value by a pole.³³ A pole occurs between each characteristic value. If one exists between the first approximation and the desired root, the continued fraction converges to the adjacent root. To obtain the actual solutions of the Mathieu equation, we have to solve equations involving continued fractions.^{33,43,45} This was done iteratively, and the convergence of the iteration was improved by use of the Newton-Raphson method, suggested by Swalen.^{33,45} Eighteen terms were retained in the continued fractions, and the convergence criterion for the characteristic value iteration was taken to be $0.3 \cdot 10^{-10}$. Thus, the lowest characteristic values are accurate to seven decimal places. The convergence is usually rapid. However, the convergence becomes worse as we go to larger values of the internal energy (larger values of the parameter s). The performance of the program was checked for accuracy against characteristic values obtained by other workers.^{25,26,32,45,49,50}

Results and Discussion

The Mathieu equation characteristic values were calculated for a series of s -values in order to fit the calculated temperature dependent coupling constants to the values observed for the *ortho* hydrogens at different temperatures. The corresponding eigenvalues of the torsional wave equation in the two-fold barrier case are obtained according to the relation.¹⁹

$$E_{v\sigma} = Fb_{v\sigma} \text{ where } F = \frac{\hbar^2}{2I}$$

is the internal rotation constant. Substitution of these eigenvalues in the Boltzmann expression gives the desired weight factors. The summation was extended only over torsional states with the energy $E_{v\sigma} \leq V_2$. For $E_{v\sigma} > V_2$ the internal motion fairly rapidly goes over into an essentially free rotation. These states can therefore hardly contribute to the temperature dependence of the coupling constants. The calculated coupling constants are given for each s -value together with the experimental coupling constants in *table 1*. Agreement with the coupling constants measured at different temperatures¹⁶ is obtained for $s=1159.16$. Assuming that no other effects contribute to the observed temperature dependence of the *ortho*

proton coupling constants, the torsional barrier can now be calculated from this s -value to be 4.18 kJ/mole (1.00 kcal/mole). Using this barrier value, and the value 0.3011 cm^{-1} for F the frequency of the fundamental torsional transition can be calculated to be 20 cm^{-1} . No unambiguous results from vibrational spectroscopy seem to exist for this torsional transition.

Table 1. The experimental hyperfine coupling constants of the *ortho* protons in 4,4'-dimethoxybiphenyl cation radical at different temperatures, compared with the calculated coupling constants for different values of the parameter s .

	$s=208.65$	$s=231.83$	$s=289.79$	$s=579.58$	$s=1159.16$	Experimental
T (°C)	$a_H(T)$	$a_H(T)$	$a_H(T)$	$a_H(T)$	$a_H(T)$	a_H
8°	1.670	1.670	1.670	1.670	1.670	1.67
25°	1.675	1.675	1.677	1.682	1.685	1.68
50°	1.682	1.683	1.686	1.698	1.705	1.70
70°	1.686	1.687	1.693	1.710	1.718	1.72

There are two torsional barriers in biphenyl, corresponding to the interplanar angles $\alpha = 0^\circ$ and $\alpha = 90^\circ$. According to the results of NMR studies also the larger of these barriers is small.^{20,51} On the other hand, analysis of the results of phosphorescence and quenching experiments under the assumption that the triplet state of biphenyl is planar, yielded a barrier value of 16.7 kJ/mole (4 kcal/mole) for the rotation through $\alpha = 0^\circ$.⁵² Also molecular orbital calculations using various semiempirical methods give barrier estimates of about 8 to 20 kJ/mole (2 to 5 kcal/mole), (see references cited in 16). Which of the two torsional barriers is the larger one seems to be rather uncertain, as judged from the results of the semiempirical calculations. However, according to electron diffraction results of Almenningen and Bastiansen,⁵³ the probability of deviation from the equilibrium form to the planar form seems to be larger than the probability of deviation towards the orthogonal form.

The rather low barrier value obtained in the present study of the temperature dependence of the *ortho* proton coupling constants is in agreement with the fact that the electron resonance spectrum of the 4,4'-dimethoxybiphenyl cation radical in sulfuric acid already at room temperature can be completely interpreted without the additional assumption of *cis-trans* isomerism.¹⁶ It is also in accord with the NMR results of Kurland and Wise,²⁰ and by Mayo and Goldstein.⁵¹ The results of Kurland and Wise²⁰ also show that the measured barrier is largely dependent of the solvent used.

Two additional facts may be pointed out. First, the bond order of the coannular bond is smaller in the cation radical than in the neutral biphenyl molecule. Second, from the point of view of the electron resonance results it is sufficient if the smaller of the two torsional barriers is surmounted, thus causing rapid interconversion between the *cis* and *trans* conformations.

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Studies on the Anion Radical Formation from Symmetrically Di- and Tetramethoxy Substituted Biphenyls

Henrik Tylli

Department of Chemistry, University of Helsinki. E. Hesperiankatu 4, SF-00100 Helsinki 10, Finland.

Abstract

The alkali metal reduction of 2,2'-dimethoxybiphenyl, 4,4'-dimethoxybiphenyl and 2,4,2',4'-tetramethoxybiphenyl has been studied in different solvents. Reductive cleavage of the methoxy groups was observed and the electron resonance spectrum of the biphenyl anion radical was obtained. Only with 4,4'-dimethoxybiphenyl the parent compound anion radical was obtained. The electron resonance spectrum of the 4,4'-dimethoxybiphenyl anion radical was analyzed with the coupling constants $a_{ortho}=2.98$ G, $a_{meta}=2.80$ G, and $a_{OCH_3}=0.25$ G. The assignment given was based on INDO MO calculations.

Introduction

The electron resonance spectrum of the cation radical of 4,4'-dimethoxybiphenyl has been studied previously in different solvents at temperatures ranging from -60° to 70°C .^{1,2} It can be concluded from these studies that the electron resonance spectrum of 4,4'-dimethoxybiphenyl cation radical is well understood throughout this temperature region. At lower temperatures *cis-trans* isomerism must be assumed in order to account for the observed electron resonance spectra.¹ However, at room temperature and above the spectrum can be analyzed without this effect.²

Recently the electron resonance spectrum of the anion radical of 3,3'-dimethoxybiphenyl has also been analyzed assuming *cis-trans* isomerism with respect to the central C—C bond³. In view of this it seemed to be a matter of further interest to study the anion radicals of other symmetrically di- and tetramethoxy substituted biphenyls, especially with regard to the hindered reorientation about the coannular bond. In the present paper these complementary studies are reported.

Experimental

The methoxy substituted biphenyls were prepared from the appropriate iodo compounds through the usual Ullman reaction.⁴ The products were recrystallized from methanol and sublimed repeatedly at elevated temperature and 0.04 mm Hg until the melting points remained unchanged. The purity of the samples was checked by gas-liquid chromatography.

The anion radicals were generated by chemical reduction of the parent compounds with sodium or potassium metal in 1,2-dimethoxyethane or tetrahydrofuran solution, employing the conventional high vacuum technique.⁵ 1,2-dimethoxyethane was a Fluka Ag purum quality product, and tetrahydrofuran was a Merck Ag Uvasol gade product. The solvents were purified according to Paul, Lipkin and Weissman⁶, degassed several times on the vacuum line by a series of freeze-pump-thaw cycles, and stored over sodium-potassium alloy (2:1). The sample was contained in a quartz cell with 2 mm inner diameter, incorporated as a side arm in the sample tube.

The electron resonance spectra were recorded on Varian E3 or E6 spectrometers, operating in the X-band region with 100 kc modulation. Care was taken to avoid saturation, and the modulation was 70 mG. The sweep speed did not exceed 20 G/h. The low temperature measurements were made with the aid of the Varian variable temperature accessories.

The INDO MO calculations and the computer simulations of the one component electron resonance spectra were performed as described previously.² The simulations of the two component electron resonance spectra were done with the aid of the computer program ESSP2, originally written by B.S. Snowden Jr. and E.T. Strom, and distributed by the QCPE organization.⁷ The necessary modifications of the program were done by FK Erkki Vehkamäki at the University of Helsinki Computing Center.

Results and Discussion

Results from several electron resonance studies show that anion radicals can be generated from methoxy substituted aromatic compounds by alkali metal reduction of the parent compounds in aliphatic ether solvents.^{3,8-11} However, care must be taken to ensure that the spectrum studied is not a superposition of the spectra of two or several components, or even the spectrum of a new compound formed during the alkali metal reduction.

When aryl ethers are treated with alkali metals at elevated temperatures, metalation and cleavage of the ethers is ob-

served.¹²⁻¹⁴ Also under less extreme conditions, when aryl ethers are treated with alkali metals in aliphatic ether solvents at room temperature, cleavage and replacement with hydrogen, hydrogenation and coupling reactions occur.^{3,8,5-20} Reductive cleavage and replacement with hydrogen could be shown to occur also with the compounds studied in the present investigation.

The compounds studied in the present paper are 2,2'-dimethoxybiphenyl, 4,4'-dimethoxybiphenyl and 2,4,2',4'-tetramethoxybiphenyl. When these compounds were treated with potassium in 1,2-dimethoxyethane, complete demethoxylation occurred, and at room temperature rather pure electron resonance spectra of the anion radical of biphenyl²¹⁻²⁵ were observed, compare *figure 1*. The demethoxylation was further established by analysis of the contents in the sample tubes with gas-liquid chromatography and mass spectrometry. Brown, Burnham and Rogers have previously observed demethoxylation of *ortho*- and *para*-methoxybiphenyl when these compounds were reduced with potassium in tetrahydrofuran or dimethoxyethane.²⁰ Recently cleavage of the 4,4' methoxy groups has also been observed when 3,4,3',4'-teramethoxybiphenyl was reduced with alkali metal in dimethoxyethane or tetrahydrofuran, and the anion radical of 3,3'-dimethoxybiphenyl was formed.³



Figure 1. Electron resonance spectrum of the reaction mixture obtained when 4,4'-dimethoxybiphenyl was treated with potassium in dimethoxyethane. The spectrum of the biphenyl anion radical dominates.

In order to be able to prepare the anion radical of the parent compounds, the effect of the variation of solvent and alkali metal was also studied. The results are summarized in *table 1*. It is seen that only 4,4'-dimethoxybiphenyl did undergo one-electron reduction to form the desired parent compound anion radical. The study of the anion radical of 4,4'-dimethoxybiphenyl is reported in the next section.

Table 1. Summary of the results of the alkali metal reduction of methoxy substituted biphenyls in different solvents.

Parent compound	Solvent	Alkali metal	Paramagnetic product
2,2'-dimethoxybiphenyl	DME	K	Biphenyl anion radical ^a
»	THF	K	»
»	THF	Na	None
4,4'-dimethoxybiphenyl	DME	K	Biphenyl anion radical
»	DME	Na	and parent compound
»	THF	K	anion radical (see text).
»	THF	Na	None
»	THF:DME(1:1)	Na	Parent compound anion radical ^b
2,4,2',4'-tetramethoxybiphenyl	DME	K	Biphenyl anion radical ^c
»	THF	K	»
»	THF	Na	None

Abbreviations: DME = 1,2-dimethoxyethane, THF = tetrahydrofuran.

Analysis of the reaction mixtures, reaction time 7 days at room temperature:

- Parent compound, biphenyl and six additional compounds in trace amounts.
- Parent compound and one additional compound. The yield of the reaction product increased with time. A reaction time of 48 h gave the yield 24.8 % of the parent compound.
- Parent compound, biphenyl and thirteen additional compounds in trace amounts.

The Anion Radical of 4,4'-dimethoxybiphenyl

The electron resonance spectrum of the sample reduced with potassium in dimethoxyethane is shown in *figure 2*. It is clearly seen that the spectrum of at least one additional compound is mixed in. The equilibrium ratio between the concentrations of these radical anions was found to be temperature dependent. At -40°C the concentration of a second radical, presumably the anion radical of the parent compound 4,4'-dimethoxybiphenyl is considerably higher than at room temperature, but the spectrum of the biphenyl anion radical still dominates, *figure 3*. When the sample for a longer time has been subjected to the distilled potassium, the biphenyl anion radical spectrum dominates more and more.

Assignment of the electron resonance spectrum of the anion radical of 4,4'-dimethoxybiphenyl is not possible on the basis of the spectra shown in *figures 2* and *3*. Attempts were therefore made to generate the radical under milder conditions in order to avoid the cleavage reaction. Reduction with sodium metal in tetrahydrofuran did not give measureable concentrations of the desired radical ion. However, if the solvent was replaced by a



Figure 2. Electron resonance spectrum of the reaction mixture obtained when 4,4'-dimethoxybiphenyl was treated with potassium in dimethoxyethane. The spectrum was recorded immediately after the solution was placed into contact with the distilled potassium.



Figure 3. Electron resonance spectrum recorded at -40°C using the same sample as for the spectrum shown in figure 2. The temperature dependence is clearly seen.

mixture of tetrahydrofuran and dimethoxyethane (1:1 by volume), a solution with orange colour was obtained. At room temperature an electron resonance spectrum could be recorded only using a high microwave power level and overmodulating the signal, but at -88°C a spectrum with a rather satisfactory signal to noise ratio was obtained, figure 4. This spectrum was obtained from a sample which was placed in contact with the distilled sodium just before the spectrum was recorded. This, in addition to the low temperature employed, was believed to minimize the amount of the second compound formed during the reduction, (table I). Attempts were made to study also the

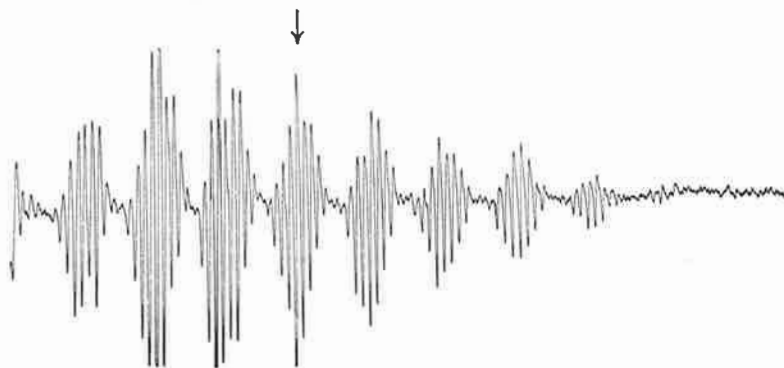


Figure 4. The electron resonance spectrum of the 4,4'-dimethoxybiphenyl anion radical obtained through reduction with sodium in a dimethoxyethane-tetrahydrofuran mixture at -88°C . (Center indicated by the arrow).

temperature dependence of the spectrum, but the rapid decay of the radical at higher temperatures prevented the study of the spectrum in a wider temperature range.

The hyperfine structure of the recorded spectrum is fairly well accounted for with the coupling constants $a_1 = 2.98$ G, four protons, $a_2 = 2.80$ G, four protons, and $a_3 = 0.25$ G, six protons. However, the agreement between the intensity ratios of the hyperfine lines in the experimental and computer simulated spectra is not completely satisfactory. The relatively high noise level and the high value of the time constant used (10 s), may account for part of the discrepancy. Previously Forbes and Sullivan¹ have observed *cis-trans* isomerism in their study of the cation radical of 4,4'-dimethoxybiphenyl at low temperatures. Invoking the same four-jump model²⁶ also in this case would improve the agreement between the experimental and calculated spectra especially for the outer groups of lines. The experimental foundation for doing this is in the present case at the moment a little scarce, however. Another possibility is to consider the recorded spectrum as the superposition of the spectra of two chemically different species (compare table I). The work is therefore continued in this field. Deuterated compounds are in preparation.

A tentative assignment of the coupling constants to hydrogens in specific positions may be done with the aid of INDO MO calculations.²⁷ After annihilation of the quartet state contaminant the hydrogen hyperfine coupling constants were calculated according to the formula:²⁸

$$a_{\text{H}} = 711.25 \rho_{\text{s}_H^{\text{s}_H}}$$

where $\rho_{\text{s}_H^{\text{s}_H}}$ is the s-orbital spin density of a particular hydrogen atom.

The geometry of the 4,4'-dimethoxybiphenyl molecule has been discussed previously in reference 2. The results of the calculations are shown in figure 5. It is seen that, contrary to the results obtained for the cation radical of the same compound,² the coupling constants are predicted to be the same in the *cis* and *trans* conformations in this case. The coupling constants calculated for the methoxy group hydrogens are only about one tenth of the values obtained for the cation radical. In the anion radical the spin density is therefore largely localized to the aromatic system, whereas in the cation radical even the methoxy substituents bear a considerable part of the spin density. As indicated by the calculations the largest coupling constant should be associated with the hydrogen atoms *ortho* to the central C-C bond in the anion radical. If we assume that the INDO approximation gives the correct succession among the coupling constants of the aromatic protons, it is seen that

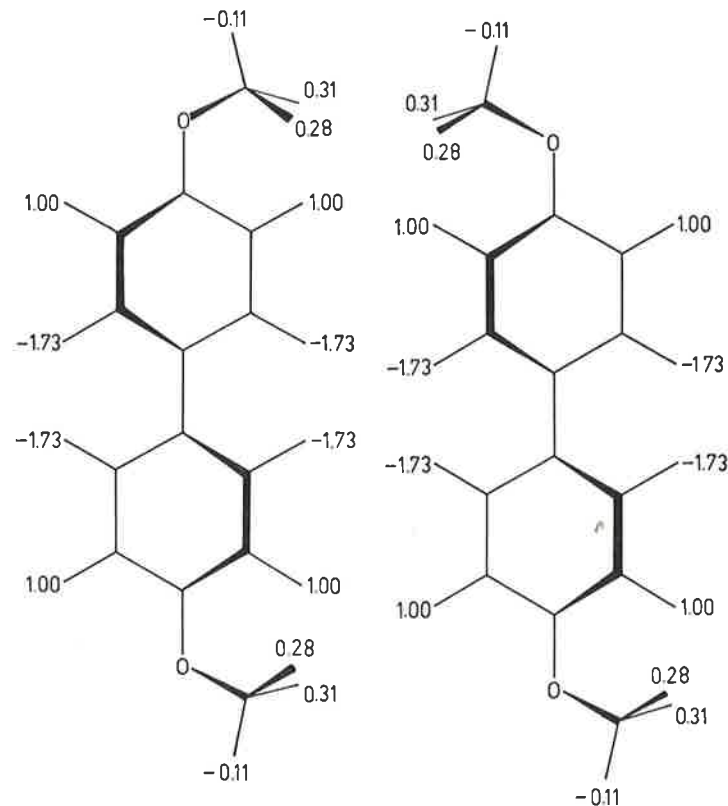


Figure 5. The calculated proton hyperfine coupling constants in the *cis* and *trans* conformations of the 4,4'-dimethoxybiphenyl anion radical, INDO with annihilation, $\langle S^2 \rangle = 0.750$.

the agreement with the experimental results is of the order of magnitude of 50 %. If the methoxy group hydrogen coupling constant is calculated as a simple average of the INDO results,² almost quantitative agreement with the experimental value is obtained. Good agreement for the methoxy hydrogen coupling constant was also obtained with the cation radical of 4,4'-dimethoxybiphenyl.²

Acknowledgements

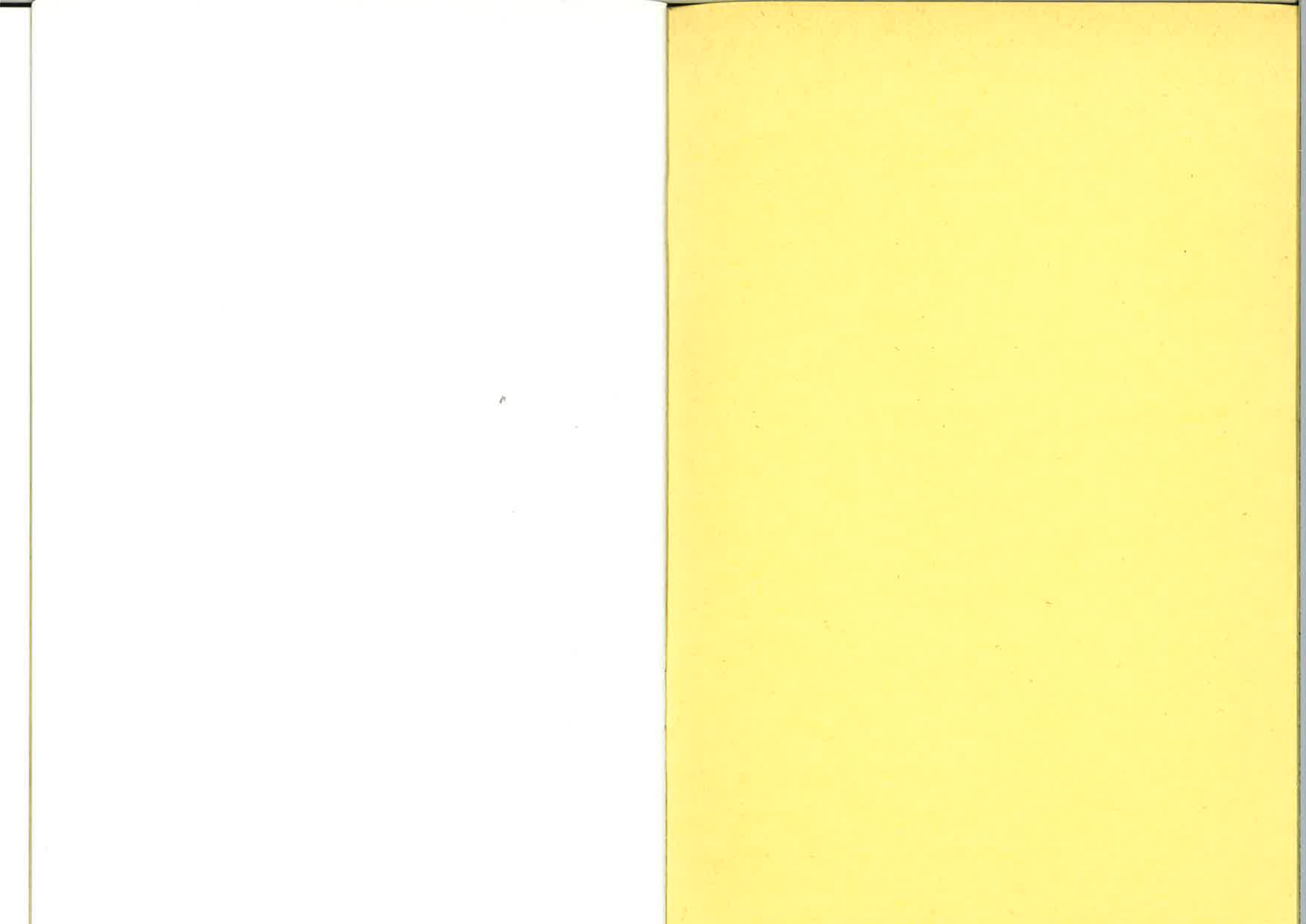
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