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135. The Radical Anion of *trans*-10b,10c-Dihydropyrene

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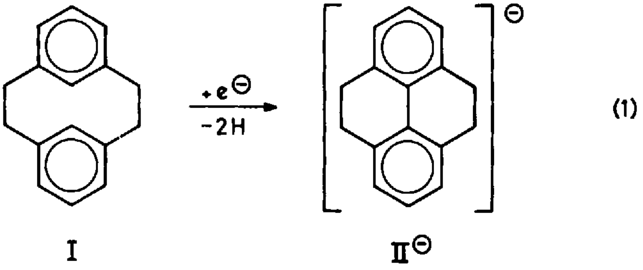
(2. IV. 75)

Summary. The radical anion of *trans*-10b,10c-dihydropyrene (V), which is formed upon reduction of the isomeric [2.2]metacyclophane-1,9-diene (III) with solvated electrons, has been identified by its ESR.-spectrum. The large coupling constant (19.1 Gauss), due to the two equivalent β-protons in the alkyl bridge, gives evidence of an important hyperfine interaction between the σ-MO's of the C(sp^3)-H bonds and the singly occupied π-MO of the fourteen-membered perimeter. This finding supports the assumption that the unexpected energy sequence of the lowest antibonding perimeter MO's in the dihydropyrene V and its 10b,10c-dimethyl derivative (VI) is determined by hyperconjugation rather than by the inductive effect of the alkyl bridge.

When the solution of V$^\ominus$ in 1,2-dimethoxyethane (DME) is brought in contact with an alkali metal mirror, an immediate conversion of V$^\ominus$ into the radical anion of pyrene (IV) occurs. The anion IV$^\ominus$ also results from reduction of [2.2.2](1,3,5)cyclophane-1,9,17-triene (VIII) with potassium in DME, whereas the radical anions of 4,5,9,10-tetrahydropyrene (II) and its 2,7-dimethyl-derivative (IX) are obtained by corresponding reactions of [2.2]metacyclophane (I) and [2.2.2](1,3,5)cyclophane (VII), respectively.

It has been reported several years ago [1] that reaction of *anti*-[2.2]metacyclophane (I) with potassium in 1,2-dimethoxyethane (DME) yields the radical anion of 4,5,9,10-tetrahydropyrene (II), whereby two hydrogen atoms are lost (*Scheme* 1). Neither the primary radical anion nor any other intermediate paramagnetic species has been thus far detected by ESR.-spectroscopy.

Scheme 1



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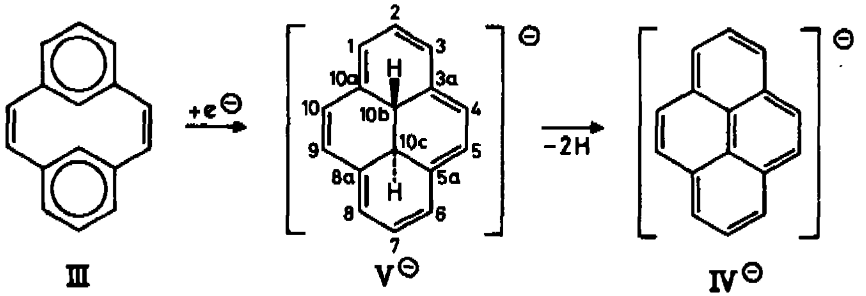
More recently, we have found that an analogous reduction procedure applied to *anti*-[2.2]metacyclophane-1,9-diene (III) leads to the radical anion of pyrene (IV) as a final product (*Scheme 2*). However, in this case, it has been possible to observe the ESR.-spectrum of an intermediate species which is identified as the hitherto unknown radical anion of *trans*-10b,10c-dihydropyrene (V). Interestingly, the neutral compound V itself, a bridged [14]annulene, has not yet been isolated in pure form, but could be generated by UV.-irradiation of the diene III in cyclohexane solution, where it gradually converts into pyrene (IV) [2].

Scheme 2



In the present paper we describe the ESR.-spectrum of $V^{\ominus}$ and link the results with those previously obtained [3] for the radical anion of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (VI).

Results. – An immediate formation of the pyrene (IV) radical anion from [2.2]-metacyclophane-1,9-diene (III)[3] can be prevented if a direct exposure of the 1,2-dimethoxyethane (DME) solution to the surface of potassium is avoided. The pertinent procedure has been described in detail elsewhere [4]. It implies reduction of III in two separate steps: 1) generation of solvated electrons ($e^{\ominus}_{\text{solv.}}$) in DME, and 2) reaction of III with $e^{\ominus}_{\text{solv.}}$. Both steps have to be carried out at low temperature (–80°C). The ESR.-spectrum obtained thereupon is shown in Fig. 1. Its intensity decreases only slowly at –80° (half-life of ca. 20 min), without new signals appearing. However, when one allows the solution to contact briefly the alkali metal mirror, the spectrum of Fig. 1 is rapidly replaced by that of $IV^{\ominus}$. Along with this change, the colour of the solution turns from brown-red to blue-green.

The hyperfine structure displayed by the spectrum of Fig. 1 is readily analyzed in terms of two large coupling constants, 19.10 ± 0.05 and 5.48 ± 0.03 Gauss[4], due to pairs of equivalent protons, and two smaller ones, 0.86 ± 0.01 and 0.51 ± 0.01 Gauss, due to sets of four equivalent protons. A derivative curve computed with the use of these values is reproduced in Fig. 1, below the experimental spectrum. The simulation also accounts for a second order hyperfine term which arises from the largest coupling constant (19.1 Gauss). This term shifts the whole spectrum by 0.05 Gauss to lower field and splits the lines of the central group by 0.10 Gauss [5]. However, since such a splitting has not been resolved in the experimental spectrum, its effect consists in the broadening of the pertinent lines which therefore appear to be less than twice as

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[3] The compound III was prepared according to the synthetic method specified in [2].

[4] 1 Gauss = 10^{-4} Tesla.

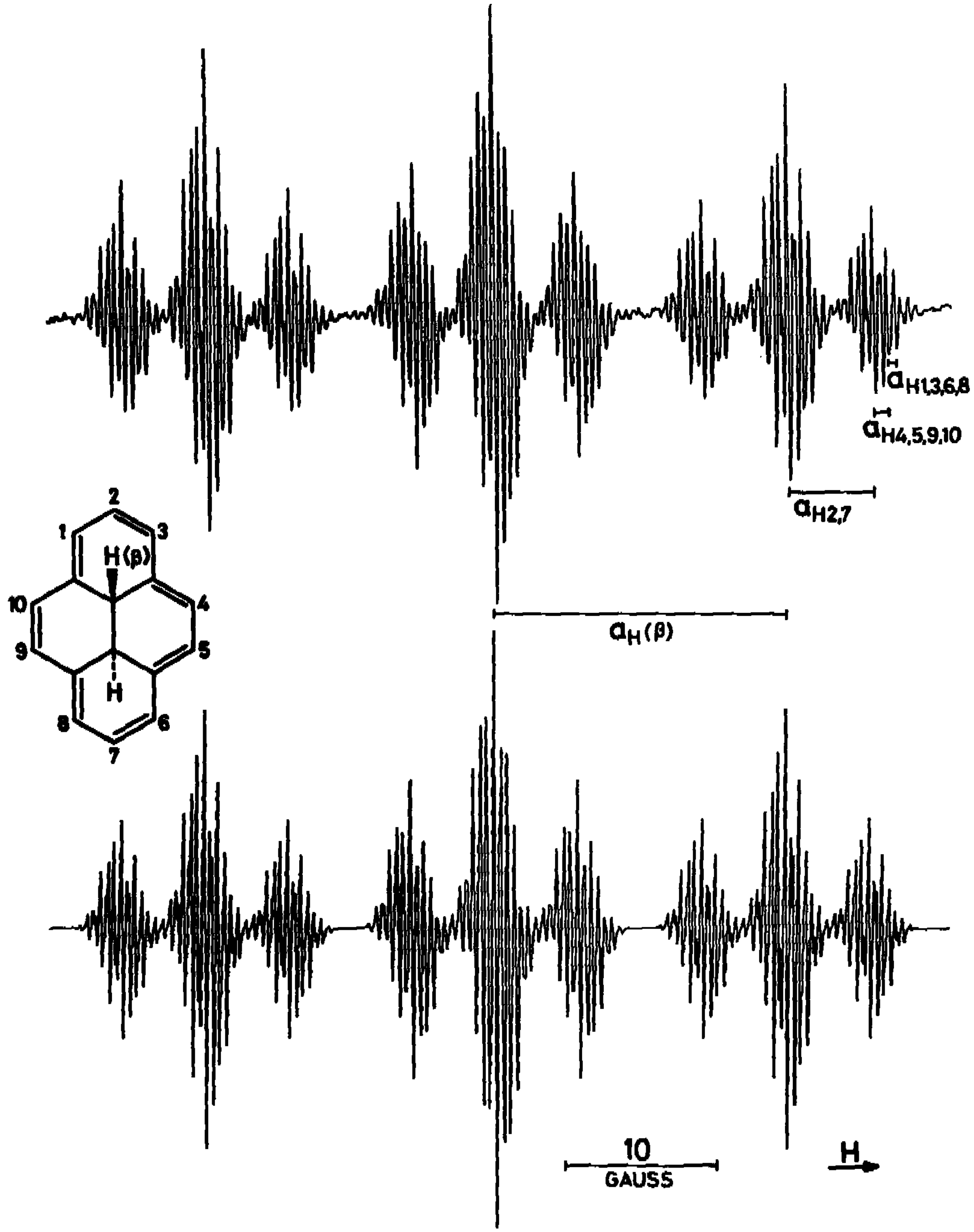


Fig. 1. *ESR.-spectra of the radical anion V*$^{\ominus}$

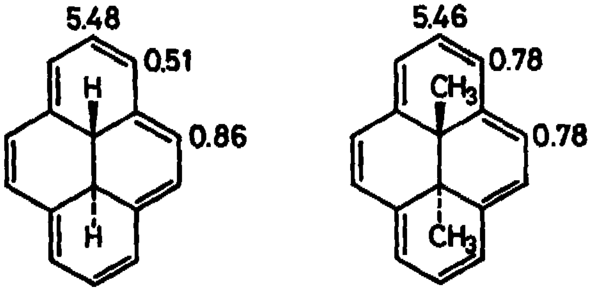
Top: Experimental spectrum. Solvent: DME; counter-ion: $K^{\oplus}$; temp.: −80°.

Bottom: Computer simulated spectrum. Coupling constants as given in the text; line-shape: Lorentzian; line-width: 0.12 Gauss.

intense as those of the two outer groups. (This effect is superimposed on a real decrease in intensity caused by a radical decay during the recording of the spectrum.)

The proton hyperfine data by themselves leave no doubt that the spectrum stems from the radical anion of *trans*-10b,10c-dihydropyrene (V). The assignment of the largest value of 19.1 Gauss to the two equivalent β-protons[5]) in positions 10b and 10c of the alkyl bridge is straightforward, since hyperfine splitting of this magnitude cannot arise from α-protons[5]) in an extended π-system. On the other hand, such coupling constants are encountered with β-protons of methylene and methine groups linking two π-centers of high spin population, provided that the pertinent LCAO coefficients for the singly occupied MO have the same sign [6] [7] (see Discussion). The second largest value of 5.48 Gauss is thus left for the two equivalent α-protons in positions 2 and 7. The remaining smaller coupling constants of 0.86 and 0.51 Gauss are assigned to the sets of four equivalent α-protons in positions 4,5,9,10 and 1,3,6,8, respectively; however, a reverse assignment cannot be excluded.

The statement that the spectrum of Fig. 1 must be ascribed to the radical anion of *trans*-10b,10c-dihydropyrene (V) is further corroborated by a comparison of the α-proton coupling constants for $V^{\ominus}$ with the corresponding values previously reported for the more stable 10b,10c-dimethyl-derivative $VI^{\ominus}$ [3]. It is evident (Fig. 2) that



$V^{\ominus}$ $VI^{\ominus}$

Fig. 2. *Coupling constants of the α-protons* (in Gauss = 10^{-4} Tesla) *in the radical anions $V^{\ominus}$ and $VI^{\ominus}$*

the two sets of data are either equal within experimental error (for positions 2 and 7) or they have the same magnitude (for the remaining positions of the fourteen-membered ring).

Finally, the above mentioned finding [2] that *trans*-10b,10c-dihydropyrene (V) is formed by UV.-irradiation of [2.2]metacyclophane-1,9-diene (III) nicely ties in with our conclusion, since it is to be expected that molecules in an excited state should undergo similar reactions as the corresponding radical ions.

Discussion. – *Conversion of the radical anion of trans-10b,10c-dihydropyrene (V) into that of pyrene (IV).* As pointed out in the Results, one fails to detect $V^{\ominus}$ in the reduction of III (*Scheme 2*) when the DMF solution is directly exposed to the potassium mirror. This observation strongly suggests that the elimination of two hydrogen atoms from $V^{\ominus}$ to yield $IV^{\ominus}$ is catalysed by the surface of alkali metal. It is noteworthy that a similar role has been attributed to the sodium mirror in the reduction

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[5]) In ESR.-spectroscopy, protons separated from a π-electron centre by 0, 1, 2 ... sp^3-hybridized carbon atoms are denoted α, β, γ ... .

of N-methyl-1,6-imino[10]annulene [8]. In this reaction not only the NCH_3 bridge is lost, but also a 1,2-hydrogen shift occurs, leading to the radical anion of azulene (instead of naphthalene) as a final product.

Hyperconjugation in trans-10b,10c-dihydropyrenes. The prominent feature in the spectrum of Fig. 1 is the large hyperfine splitting from the two equivalent β-protons in $V^{\ominus}$. It indicates an efficient hyperconjugative interaction between the σ-MO's of the C(10b,c)-H(β) bonds[6]) and the singly occupied π-MO of the fourteen-membered perimeter. The importance of an analogous interaction between the σ-MO's of the C(10b,c)-C(methyl) bonds and the singly occupied π-MO has already been realized in former work [3] on the radical anion of *trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (VI), even though direct ESR.-spectroscopic evidence was missing in that case, because of the absence of β-protons. The necessity to invoke hyperconjugation in $VI^{\ominus}$ has emerged from the correlation of the α-proton coupling constants (Fig. 2) with the LCAO-coefficients of the lowest antibonding perimeter MO's[7])

$$\begin{aligned}\psi_S = {} & 0.084\,(\varphi_1 + \varphi_3 + \varphi_6 + \varphi_8) - 0.378\,(\varphi_2 + \varphi_7) \\ & - 0.236\,(\varphi_4 + \varphi_5 + \varphi_9 + \varphi_{10}) + 0.340\,(\varphi_{3a} + \varphi_{5a} + \varphi_{8a} + \varphi_{10a})\end{aligned}$$

and

$$\begin{aligned}\psi_A = {} & 0.368\,(\varphi_1 - \varphi_3 + \varphi_6 - \varphi_8) + 0.296\,(\varphi_4 - \varphi_5 + \varphi_9 - \varphi_{10}) \\ & + 0.164\,(\varphi_{3a} - \varphi_{5a} + \varphi_{8a} - \varphi_{10a})\,.\end{aligned}$$

Obviously, the π-MO which accomodates the unpaired electron in VI°, as well as in $V^{\ominus}$, is *symmetric* (ψ_S) with respect to the mirror plane (m) perpendicular to the mean plane of the fourteen-membered ring and passing through the carbon atoms 2 and 7 (Fig. 3, left).

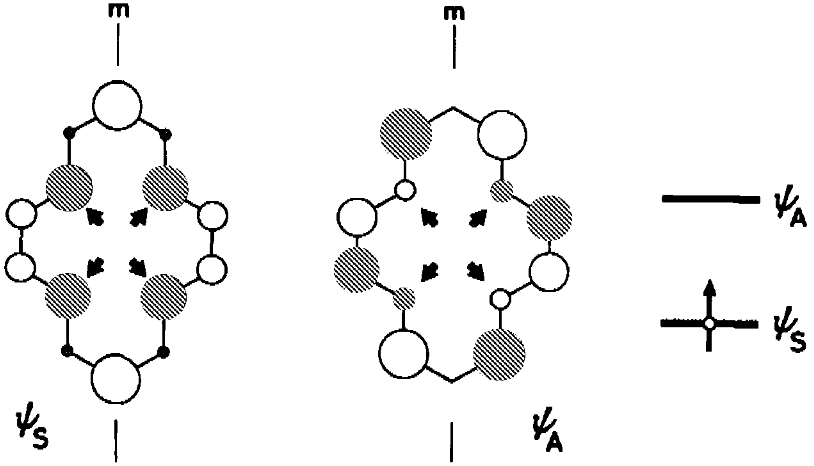

Fig. 3. Left: *The lowest antibonding MO's ψ_S and ψ_A of the fourteen-membered perimeter.* The radii of the circles are proportional to the absolute values of the LCAO-coefficients. Blank and filled areas symbolize different signs. The centres, which are bridged in V and VI, have been marked by arrows. The letter m denotes the trace of the mirror plane used for the classification of ψ_S and ψ_A
Right: *Energy sequence of ψ_S and ψ_A and its occupancy in the radical anions $V^{\ominus}$ and $VI^{\ominus}$*

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[6]) C(10b,c) stands for one of the two sp^3-hybridized carbon atoms (10b or 10c) in the alkyl bridge.

[7]) The MO's ψ_S and ψ_A were denoted ψ_{a+} and ψ_{a-} in [3] and [9].

The degeneracy of the two perimeter MO's has thus been removed in such a way that ψ_S is *lower* in energy than its antisymmetric counterpart ψ_A (Fig. 3, right). This result was rather unexpected, because it did not comply with the experience that the energy sequence in alkyl substituted π-perimeters is governed by an inductive effect of the alkyl groups [10] [11a]. Since such an effect is electron-repelling, it should destabilize ψ_S more strongly than ψ_A (*cf.* the squares of LCAO-coefficients at the bridged carbon centers 3a, 5a, 8a and 10a). In order to account for the discrepancy between prediction (ψ_S *above* ψ_A) and experiment (ψ_S *below* ψ_A) it has been suggested [3] [9] that the energy ordering of ψ_S and ψ_A is determined by a hyperconjugative effect rather than by an inductive one. For reason of symmetry, the hyperconjugation considered above can affect only the MO ψ_S which should be *lowered* in energy (relative to ψ_A) by interaction with the antibonding σ-MO's (*cf.* Fig. 36 of [9]).

Hyperconjugative interaction in VI$^{\ominus}$ is promoted by the geometry of the molecule, since – according to molecular models and in line with an X-ray crystallographic analysis [12] – the C(10b,c)-C(methyl) bonds are almost parallel to the $2p_z$-axes at the bridged carbon centers. Moreover, hyperconjugation should be particularly important for ψ_S, as the LCAO coefficients c_{S_μ} and $c_{S_{\mu'}}$ at two such centers μ and μ', which are linked by an sp^3-hybridized carbon atom 10b or 10c, have large magnitude and the same sign (μ = 3a and μ' = 10a or μ = 5a und μ' = 8a). Both arguments put forward in favour of this effect in VI$^{\ominus}$, also apply to V$^{\ominus}$ where the C(10b,c)-C(methyl)-are replaced by the C(10b,c)-H(β) bonds. The dihedral angle θ between the latter bonds and the $2p_z$-axes at the nearest bridged centers μ and μ' (Fig. 4) can here be estimated from the β-proton coupling constant, $a_H(\beta)$ = 19.1 Gauss, by means of the formula [6]

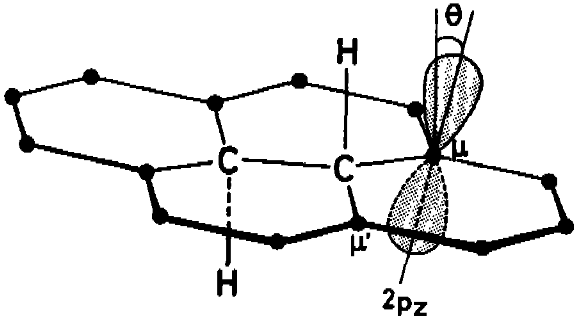

Fig. 4. *Molecular model of V indicating the dihedral angle θ*

$$a_H(\beta) = B(c_{S_\mu} + c_{S_{\mu'}})^2\cos^2\theta.$$

Taking B = 44.8 Gauss, a value appropriate for a radical anion[8]) and setting $c_{S_\mu} = c_{S_{\mu'}} = 0.340$, one obtains an angle $\theta = 16.6°$. Such an estimate meets the expectation that the C(10b,c)-H(β) bonds should be almost parallel to the $2p_z$-axes at the centres μ and μ'.

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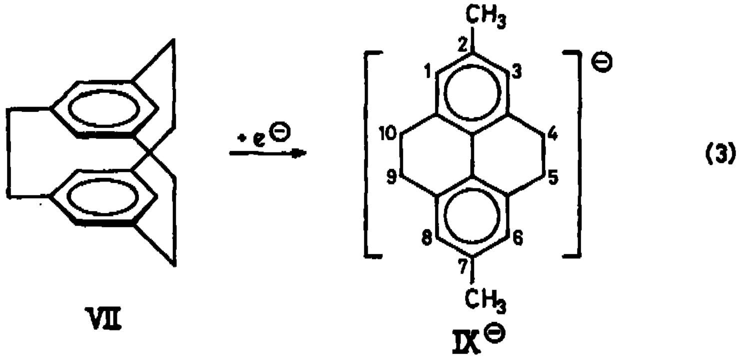
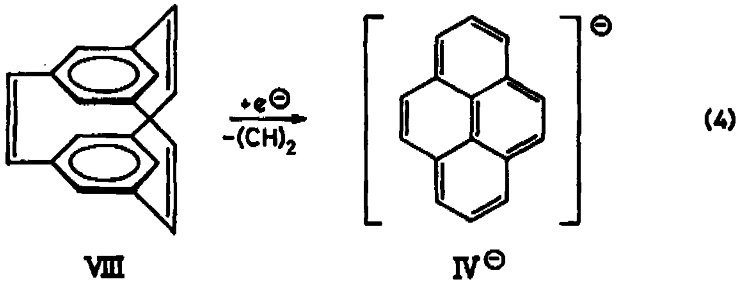
[8]) The value B = 2(22.4) Gauss results from the ESR.-study of the radical anions of dimethylnaphthalenes [11b] [13].

Appendix. – Related to the reduction of the metacyclophanes I and III with potassium in DME (*Schemes 1 and 2*) are the analogous reactions of [2.2.2](1,3,5)cyclophane (VII) and its 1,9,17-triene (VIII). In this case, as well, no primary radical anions ($VII^{\ominus}$ and $VIII^{\ominus}$) could be detected by ESR.-spectroscopy. The secondary products obtained upon reduction of VII and VIII are the radical anions of 2,7-dimethyl-4,5,9,10-tetrahydropyrene (IX) and pyrene (IV) respectively (*Schemes 3 and 4*).

Scheme 3



Scheme 4



Since – to our knowledge – ESR.-studies of $IX^{\ominus}$ have not yet been reported, the low temperature spectrum of this radical anion (–85°) is reproduced in Fig. 5, along with the computer simulated derivative curve. The coupling constants (in Gauss) used in the simulation are as follows: 6.41 ± 0.05 (six β-protons of the two methyl substituents in positions 2 and 7), 4.06 ± 0.03 and 0.89 ± 0.01 (four axial and four equatorial β-protons, respectively, of the two 4,5- and 9,10-dimethylene chains) and 0.44 ± 0.01 (four α-protons in positions 1,3,6 and 8). These values compare favourably with the corresponding data for the radical anion of 4,5,9,10-tetrahydropyrene (II) [14]. Also, as has been previously observed in ESR.-studies of $II^{\ominus}$, raising the temperature above –70° gives rise to alternating line-widths [15] in the spectrum of $IX^{\ominus}$. In both cases, this effect is due to the inversion of the 4,5- and 9,10-dimethylene chains and the concommitant interchange in the axial and equatorial positions of the β-protons.

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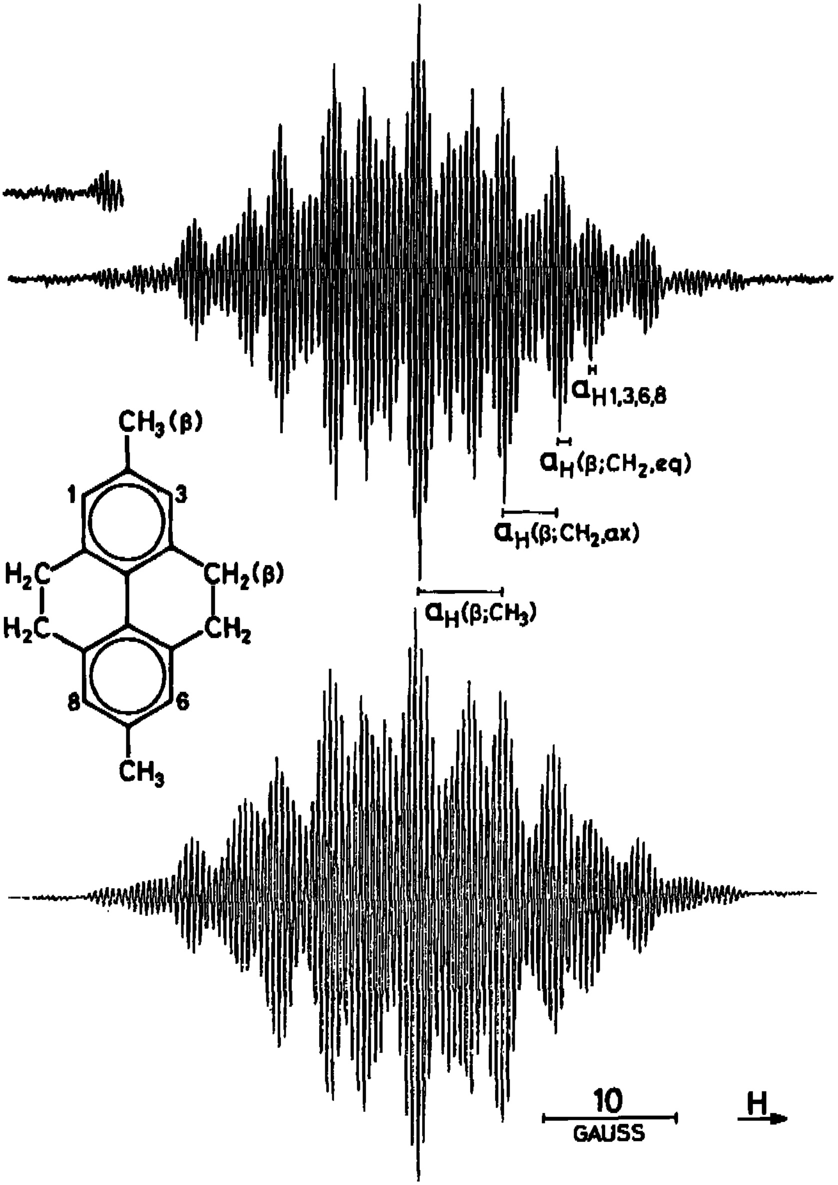

Fig. 5. *ESR.-spectra of the radical anion IX*$^{\ominus}$

Top: Experimental spectrum. Solvent: DME; counter-ion: K$^{\oplus}$; temp.: −85°.

Bottom: Computer simulated spectrum. Coupling constants as given in the text; line-shape: Lorentzian; line-width: 0.15 Gauss. ax = axial; eq = equatorial.

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136. Isolierung und Charakterisierung von nativer nuklearer Desoxyribonukleinsäure aus Tabakblättern

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(4. III. 75)

Summary. Tobacco nuclear DNA (nDNA) was isolated from tobacco leaf nuclei which were prepared according to our previously published procedure [8]. The nDNA was characterized by base analysis, absorption spectrophotometry, analytical CsCl density gradient equilibrium centrifugation and by its melting behaviour. The results show that the isolated tobacco nDNA is native, high molecular weight DNA, which is free of detectable amounts of chloroplast DNA, RNA, protein and polysaccharides. From its melting behaviour it was concluded that tobacco nDNA can be placed close to calf thymus DNA with respect to intramolecular heterogeneity. Experiments on the partial and complete denaturation of tobacco nDNA and its ability to renature are also reported.

Einleitung. – Die Untersuchung des genetischen Materials, der Desoxyribonukleinsäuren (DNS) höherer Pflanzen wird dadurch erschwert, dass die DNS sowohl im Zellkern (nukleare DNS) als auch in Mitochondrien und Chloroplasten vorkommt. Die Mitochondrien-DNS und die Chloroplasten-DNS unterscheiden sich oft, aber nicht immer von der nuklearen-DNS (nDNS). Dieser Befund und die Tatsache, dass in den meisten Fällen nur grob angereicherte Zellkernfraktionen (sog. «nuclear pellets») zur Gewinnung von nDNS zur Verfügung standen, mögen die Gründe sein, dass bisher über die Eigenschaften pflanzlicher nDNS relativ wenige und zum Teil recht widersprüchliche Untersuchungen vorliegen [1–7].

Wir haben kürzlich ein Verfahren zur Gewinnung einer reinen Kernfraktion aus Tabakblättern veröffentlicht [8]. Nachstehend beschreiben wir die Isolierung von reiner Tabak-nDNS sowie deren Charakterisierung.

Experimenteller Teil. – 1. *Isolierung und Reinigung der Tabak-nDNS.* Als Ausgangsmaterial für die Isolierung der nDNS dienten nach unserem Verfahren gewonnene Zellkerne aus jungen Tabakblättern [8]. Aus 10 g Blättern liessen sich etwa 4×10^8 Kerne isolieren, die einen DNS-Gehalt von *ca.* 4 mg aufwiesen. Die Kerne wurden entweder direkt weiterverarbeitet oder bis zur