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212. ESR. Spectra and Structures of Radical Anions in the Dibenzo[*a, e*]cyclooctene Series

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Summary. ESR. studies are reported for the radical anions of 5,6-didehydro- and 5,6,11,12-tetrahydro-dibenzo[*a, e*]cyclooctene (III and IV, resp.), in addition to that of dibenzo[*a, e*]cyclooctene (II) itself, the spectrum of which has been reexamined. Comparison of the proton and ¹³C coupling constants for II · [−], III · [−] and IV · [−] indicates that the three radical anions do not differ greatly in their electronic and molecular structures. This statement implies that II · [−] should also be substantially planar, *i. e.*, the tub-shaped eight-membered ring in II is expected to flatten on passing from the neutral molecule to its radical anion. Support for postulating such a change in geometry, analogous to that encountered with the parent cyclooctatetraene (I), is provided by INDO calculations.

Introduction. – Although, to our knowledge, the geometry of dibenzo[*a, e*]cyclooctene (*sym*-dibenzocyclooctatetraene; II) has not yet been determined, it is generally assumed [1] [2] that the eight-membered ring in II possesses the tub-like shape resembling the parent cyclooctatetraene (I) [3]. In other words, there should exist a considerable twist about the essential single bonds (4a–5, 6–6a, 10a–11 and 12–12a) between the benzene and ethylene π -systems in II. As for II · [−], one may expect that the eight-membered ring in this radical anion will exhibit less tendency than I · [−] to ‘aromatize’ by adopting a planar arrangement of the carbon centres. This point has given rise to some controversy in the past. Whereas Carrington *et al.* [4] successfully treated II · [−] as consisting of four weakly coupled π -systems, Katz *et al.* [2] put forward some powerful arguments in favour of a substantial π -electron delocalization over the eight-membered ring in this radical anion. The two views advocated in [4]

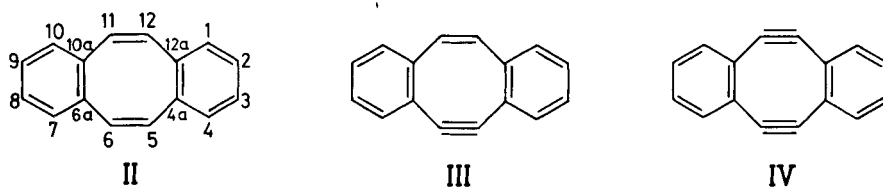
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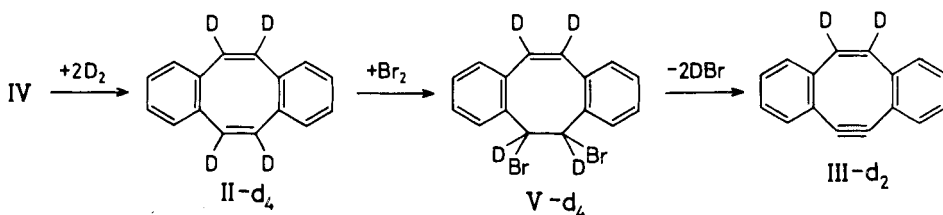
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and [2] presuppose a different geometry of $\text{II} \cdot^-$: a non-planar and a nearly planar one, respectively.

Recently, two derivatives of II, 5,6-didehydro-dibenzo[*a,e*]-cyclooctene (*sym*-dibenzo-1,3,5-cyclooctatrien-7-yne; III) and 5,6,11,12-tetradehydro-dibenzo[*a,e*]-cyclooctene (*sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne; IV) were synthesized [5] and the eight-membered ring of the latter compound (IV) has been shown to be planar in the crystalline state [6]. The present paper reports the ESR. data for the radical anions $\text{III} \cdot^-$ and $\text{IV} \cdot^-$ and compares them with those for $\text{II} \cdot^-$, obtained under the same conditions. Furthermore, in order to confirm the assignment made for the proton coupling constants, the radical anions produced from the 5,6,11,12-tetradeterio- and 11,12-dideuterio-derivatives of II and III, respectively, have also been investigated. Finally, we have performed a number of MO calculations on $\text{II} \cdot^-$, $\text{III} \cdot^-$ and $\text{IV} \cdot^-$ which - combined with the experimental ESR. data - enable us to draw some conclusions with respect to the structure of these radicals anions.



Experimental Part. - Dibenzo[*a,e*]cyclooctene (II) was prepared according to the procedure of Rabideau *et al.* [7]. The syntheses of 5,6-didehydro-dibenzo[*a,e*]cyclooctene (III) and 5,6,11,12-tetradehydro-dibenzo[*a,e*]cyclooctene (IV) were described in a previous paper [5]. 5,6,11,12-Tetradeterio-dibenzo[*a,e*]cyclooctene (II- d_4) resulted from treatment of IV with 2 molar equivalents of deuterium gas in hexadeuterioacetone over a platinum catalyst at *ca.* 0°. Bromination of II- d_4 in carbon tetrachloride under UV. irradiation yielded the 5,6-dibromo-adduct (V- d_4) which was converted with potassium *tert.*-butoxide in tetrahydrofuran into 11,12-dideuterio-5,6-dehydro-dibenzo[*a,e*]cyclooctene (III- d_2).



The samples of II- d_4 and III- d_2 prepared in this way contained considerable amounts of less deuteriated material. As shown by the mass spectra and confirmed by ESR. spectroscopy of the corresponding radical anions, the 'isotopic impurities' consisted mainly of 5,6,11-trideuterio-dibenzo[*a,e*]cyclooctene (II- d_3 ; *ca.* 25 %) and 11-deuterio-5,6-didehydro-dibenzo[*a,e*]cyclooctene; (III- d_1 ; *ca.* 20%), respectively.

The radical anions $\text{II} \cdot^-$, $\text{II-d}_4 \cdot^-$, $\text{III} \cdot^-$, $\text{III-d}_2 \cdot^-$ and $\text{IV} \cdot^-$ were produced from the neutral hydrocarbons by reaction with potassium in 1,2-dimethoxyethane (DME) at -80°. In addition, the undeuteriated compounds II, III and IV were reduced in 2-methyltetrahydrofuran (MTHF), but the ESR. spectra of the radical anions could be observed only in the case of $\text{III} \cdot^-$ and $\text{IV} \cdot^-$ (see Results).

Below -40° the radical anions were relatively stable in DME solution, but decayed readily at higher temperatures. In most cases, the decay led to secondary radical anions which exhibited well-defined ESR. spectra. However, the structure of the species giving rise to these spectra could not be elucidated with certainty.

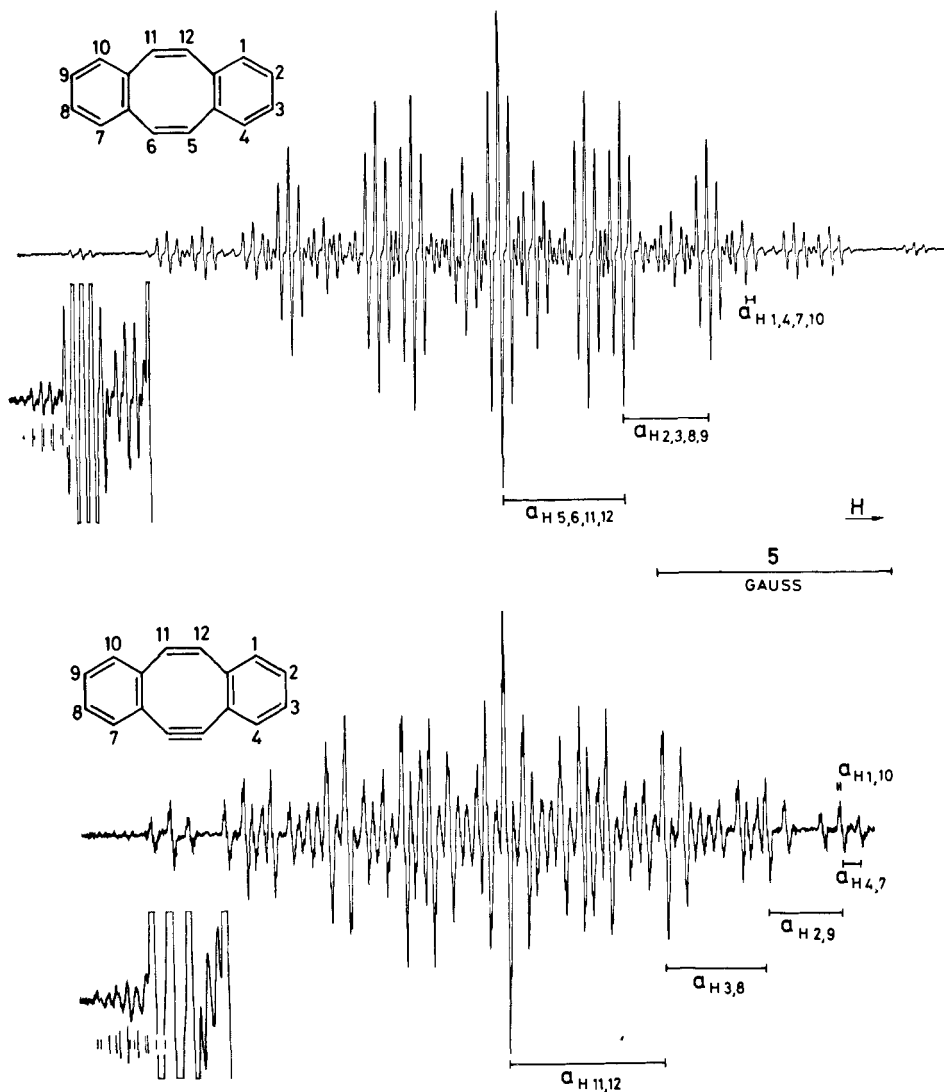


Fig. 1. ESR. spectra of the radical anions $II \cdot \ominus$ (top) and $III \cdot \ominus$ (bottom). Solvent: DME; counter-ion: K^{\oplus} ; temp.: -80° . The ^{13}C satellite lines at the amplified low-field end of the spectra are simulated by a stick diagram

Results. – Fig. 1 shows the ESR. spectra of the radical anions $II \cdot \ominus$ and $III \cdot \ominus$ in DME, at -80° , with K^{\oplus} as the counter-ion. The spectrum of $IV \cdot \ominus$, taken under the same conditions, is displayed at the top of Fig. 2. Table 1 lists the coupling constants ($a_{H\mu}$) of the protons in the three radical anions. The $a_{H\mu}$ values for $III \cdot \ominus$ have been confirmed by ENDOR studies⁴), in particular the smallest one (0.04

⁴) The ENDOR spectrum of $III \cdot \ominus$ was taken at -90° of the same solution as the ESR. spectrum. The apparatus used was *Varian-E 1700-ENDOR* system attached to an E-9 spectrometer.

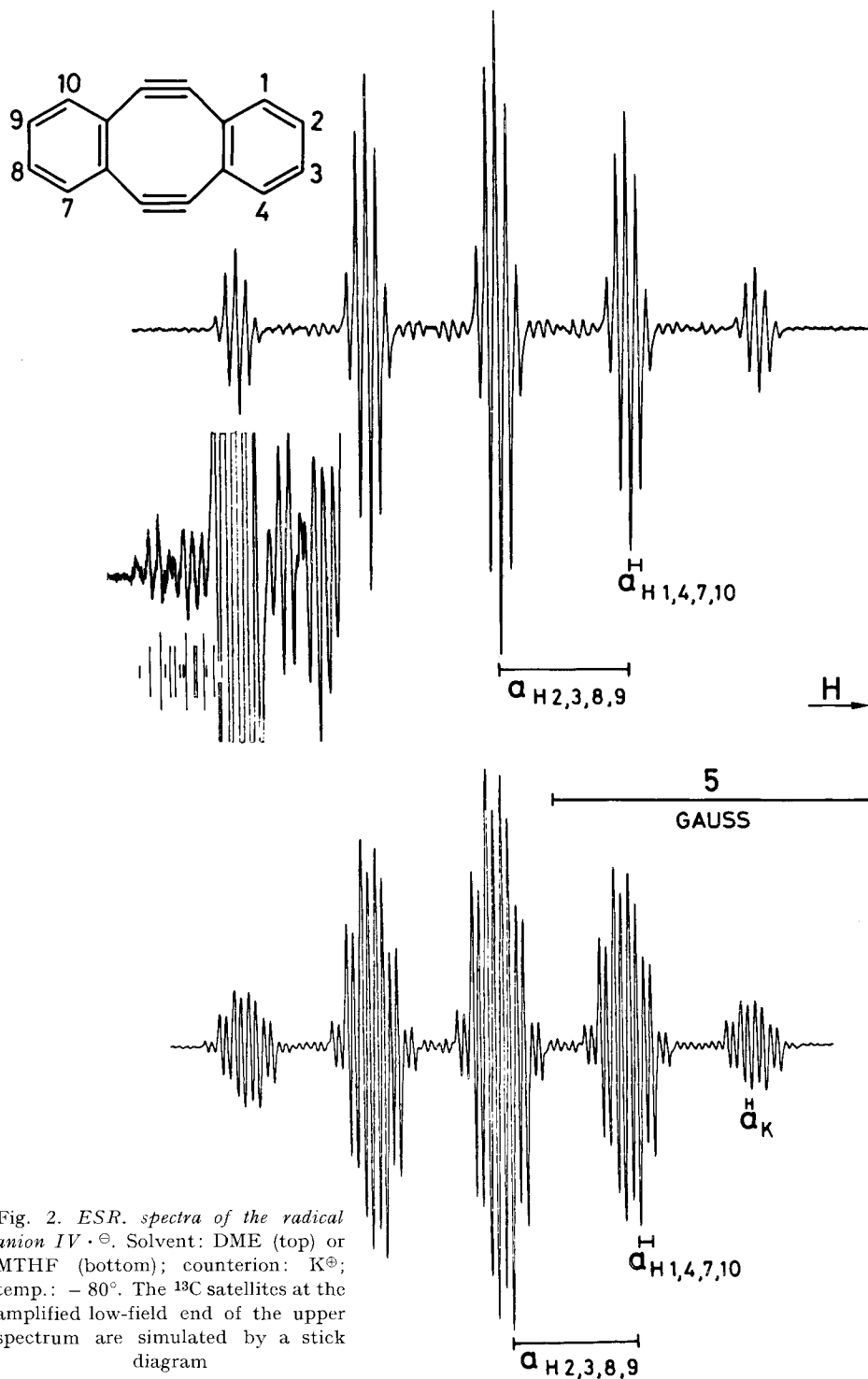


Fig. 2. ESR. spectra of the radical anion $IV \cdot^-$. Solvent: DME (top) or MTHF (bottom); counterion: K^+ ; temp.: -80° . The ^{13}C satellites at the amplified low-field end of the upper spectrum are simulated by a stick diagram

Table 1. Proton coupling constants $a_{H\mu}$ (in Gauss = 10^{-4} Tesla)^{a)} for the radical anions $II \cdot \ominus$, $III \cdot \ominus$ and $IV \cdot \ominus$

Position μ	$II \cdot \ominus$		$III \cdot \ominus$		$IV \cdot \ominus$	
	DME		DME	MTHF	DME	MTHF
1, 10 } 4, 7 }	0.22 ^{b)}	0.04 } 0.40 } 0.22 ^{c)}	0.06 } 0.43 } 0.25 ^{c)}		0.16	0.23
2, 9 } 3, 8 }	1.84 ^{b)}	1.59 } 2.17 } 1.88 ^{c)}	1.55 } 2.13 } 1.84 ^{c)}		2.04	1.99
5, 6 } 11, 12 }	2.60 ^{b) d)}	- 3.36 ^{d)}	- 3.42 ^{d)}		-	-

a) Experimental error: $\pm 1\%$.

b) These values are in essential agreement with those reported previously by other authors [2] [4] and obtained under different conditions and less good resolution.

c) Average values.

d) Replaced by $a_{D\mu} = 0.1535 a_{H\mu}$ for the radical anions of the deuteriated derivatives.

Gauss⁵⁾) which appears as a partially resolved splitting in the ESR. spectrum (Fig. 1). The assignment made in Table 1 – wherever not determined by deuterium substitution – is based on the internal consistency of the data and on the results of MO calculations (see Discussion).

Fig. 3 presents the ESR. spectra of the radical anions produced from the deuteriated samples of II and III. As indicated in the Experimental Part, the two samples were mixtures containing 5,6,11,12- d_4 and 5,6,11- d_3 derivatives of II, and, respectively, 11,12- d_2 and 11- d_1 derivatives of III. Also reproduced in Fig. 3 are the computer simulated derivative curves which were calculated with the concentration ratios $II-d_4 \cdot \ominus / II-d_3 \cdot \ominus = 3:1$ and $III-d_2 \cdot \ominus / III-d_1 \cdot \ominus = 4:1$. The simulations made use of the proton coupling constants given for $II \cdot \ominus$ and $III \cdot \ominus$ in Table 1, with the exception of the largest $a_{H\mu}$ values, 2.60 and 3.36 Gauss, respectively, which were replaced by $a_{D\mu} = 0.1535 a_{H\mu}$ for the deuteriated positions μ .

Upon amplification, satellite lines due to the ^{13}C isotopes in natural abundance could readily be identified, in particular at the wings of the spectra (Figs. 1 and 2). Their tentative analysis yielded the ^{13}C coupling constants listed below (a_C values in Gauss).

$$II \cdot \ominus: a'_C(4) = 1.8 \pm 0.1; a''_C(4) = 1.4 \pm 0.1;$$

$$III \cdot \ominus: a'_C(2) = 2.4 \pm 0.1; a''_C(2) \approx a'''_C(2) = 1.9 \pm 0.1; a''''_C(2) = 1.5 \pm 0.1;$$

$$IV \cdot \ominus: a'_C(4) = 2.4 \pm 0.1; a''_C(4) = 1.6 \pm 0.1; a'''_C(4) = 1.1 \pm 0.1.$$

The numbers in parentheses are those of equivalent carbon sites in which – according to the relative intensities of the satellite lines – the pertinent ^{13}C isotope should occur.

The fact that the observed values are of similar magnitude (1.0 to 2.5 Gauss), renders their assignment difficult. Since they do not account for all sets of equivalent

⁵⁾ 1 Gauss = 10^{-4} Tesla.

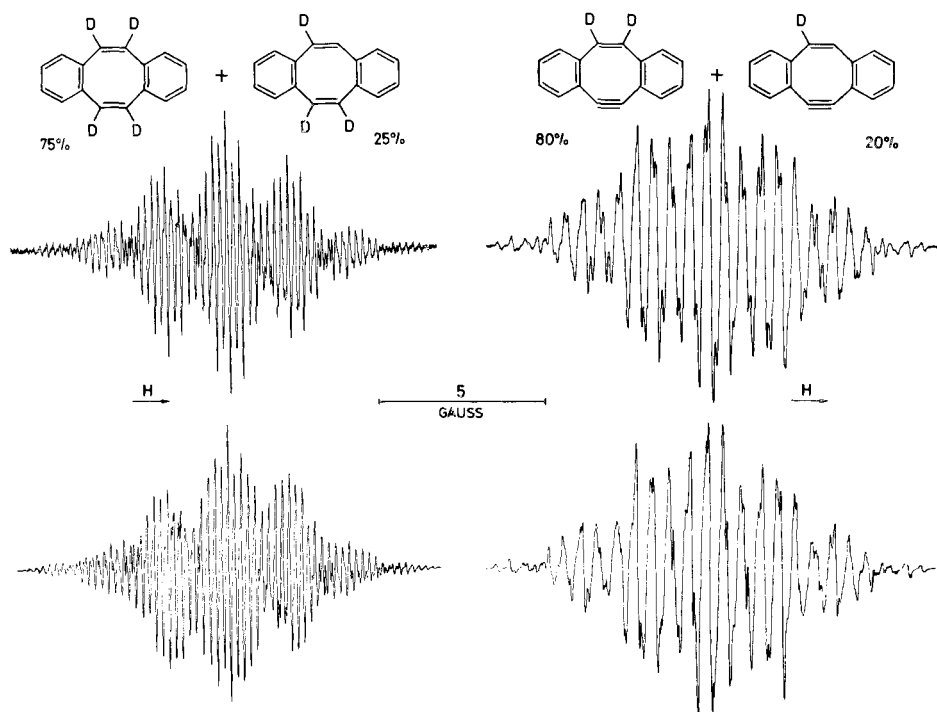


Fig. 3. ESR. spectra of the radical anions $II-d_4 \cdot \ominus / II-d_3 \cdot \ominus$ (left) and $III-d_2 \cdot \ominus / III-d_1 \cdot \ominus$ (right). Top: Experimental spectra. Solvent: DME; counter-ion: K^\oplus ; temp.: -80° . Bottom: Computer-simulated spectra. Coupling constants $a_{H\mu}$ and $a_{D\mu}$ as indicated in Table 1 and the text. Lineshape: Lorentzian. Line-width: 0.06 Gauss

carbon sites in the radical anions, it must be assumed that the missing ^{13}C coupling constants are smaller than 1 Gauss and, consequently, the corresponding satellite lines are masked by the main spectrum.

As mentioned in the Experimental Part, the compounds II, III and IV were also reacted with potassium in MTHF, a solvent which is known to promote the association between a radical anion and its counter-ion to a much larger extent than DME [8]. Unexpectedly, no ESR. spectrum could be observed when II was reduced under these conditions. Such a finding prompted us to use MTHF as the solvent for the reduction of parent cyclooctatetraene (I), but no ESR. signals were detected in this case either⁶⁾. On the other hand, ESR. spectra of the radical anions $III \cdot \ominus$ and $IV \cdot \ominus$ are readily observable, when the respective compounds are reduced with potassium in MTHF. These spectra differ strikingly from those taken with the solvent DME, as illustrated for $IV \cdot \ominus$ in Fig. 2. Their most conspicuous feature is the occurrence of an additional hyperfine splitting due to the ^{39}K nucleus of the counter-ion. The pertinent coupling constant (a_K) amounts to 0.11 ± 0.01 Gauss for both $III \cdot \ominus$ and $IV \cdot \ominus$ at -80° ; it increases slightly with rise in temperature. Furthermore, on going from DME to MTHF, there are also some minor, but significant changes in the coupling constants $a_{H\mu}$. These changes can be gathered from Table 1.

⁶⁾ Although the radical anion of cyclooctatetraene (I) has been the subject of numerous investigations [9], no ESR. data are reported for $I \cdot \ominus$ prepared by reduction of I with potassium in MTHF. Presumably other workers were also unable to observe an ESR. spectrum of $I \cdot \ominus$ produced in this way.

Discussion. – *HMO models.* Table 2 lists the proton coupling constants ($a_{H\mu}$) obtained for $II \cdot^{\ominus}$, $III \cdot^{\ominus}$ and $IV \cdot^{\ominus}$ with the aid of the *McConnell* [10] equation

$$a_{H\mu} = Q \rho_{\mu}$$

where $Q = -25.7$ Gauss is the total extension of the ESR. spectrum of the cyclooctatetraene radical anion ($I \cdot^{\ominus}$) [11], and the π -spin populations ρ_{μ} at the carbon centres μ are values computed by means of two HMO models (A and B) combined with the *McLachlan* [12] procedure ($\lambda = 1.0$). The HMO models made use of the parameter 0.75β for the four essential single bonds (4a–5, 6–6a, 10a–11 and 12–12a), as suggested by *Katz et al.* [2] for such bonds in $II \cdot^{\ominus}$. Furthermore, the parameter 1.5β , which proved to be adequate in the case of dehydro[n]annulenes [13], was adopted for the triple bonds in $III \cdot^{\ominus}$ and $IV \cdot^{\ominus}$. Besides these parameters, common to both models A and B, two additional ones, 0.2β and 0.1β , were introduced in model B. As illustrated by the diagrams in Fig. 4, such auxiliary parameters should account for the

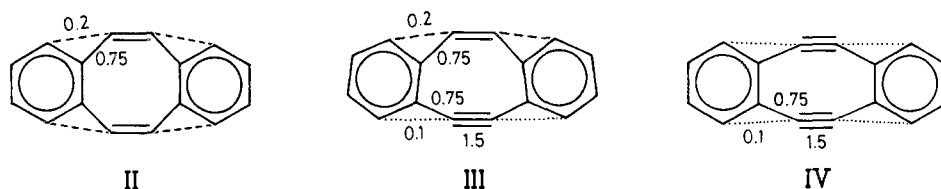


Fig. 4. Special bond parameters (in β) used in the HMO model B of *II*, *III* and *IV*

relatively short C–C interatomic distances of the formally non-bonded π -centres in the eight- and six-membered rings (4–5, 6–7, 10–11 and 12–1). It is interesting to note that the correlation between the calculated $a_{H\mu}$ values (Table 2) and their experimental counterparts (Table 1) is notably improved for $II \cdot^{\ominus}$ and $III \cdot^{\ominus}$ when model A is modified in this way to yield model B.

Table 2. Proton coupling constants $a_{H\mu}$ (in Gauss = 10^{-4} Tesla) calculated by means of HMO – McLachlan procedure for the radical anions $II \cdot^{\ominus}$, $III \cdot^{\ominus}$ and $IV \cdot^{\ominus}$

Position μ	$II \cdot^{\ominus}$		$III \cdot^{\ominus}$		$IV \cdot^{\ominus}$	
	A	B	A	B	A	B
1, 10	+0.04	+0.04	-0.50	+0.04	+0.38	+0.39
4, 7			+0.60	+0.33		
2, 9	-1.45	-1.79	-0.58	-1.69	-1.83	-2.14
3, 8			-2.05	-2.04		
5, 6	-3.15	-2.93	-	-	-	-
11, 12			-4.70	-3.78	-	-

Although the HMO-*McLachlan* calculations nicely reproduce the observed proton coupling constants and thus can serve as a basis for an assignment of the latter, they fail to provide information of the geometry of the radical anions. As noted previously in the case of $II \cdot^{\ominus}$ [2], this deficiency of the HMO models is due to

relative lack of sensitivity of the resulting π -spin populations ρ_μ to variations in the parameters of the essential single bonds, such variations being the conventional way to simulate the twist about the four bonds in question.

Indirect evidence for planarity of $II \cdot^\ominus$, $III \cdot^\ominus$ and $IV \cdot^\ominus$. Since, according to HMO models, the LUMO (lowest unoccupied MO) of II, III and IV is bonding with respect to the four linkages 4a–5, 6–6a, 10a–11 and 12–12a, the trend towards planar geometry must be enhanced on passing from the neutral compounds to their radical anions. Consequently, planarity of the eight-membered ring should be taken for granted in the case of $IV \cdot^\ominus$ where this ring has been shown to be substantially planar in the corresponding neutral molecule [6]. Moreover, our finding that not only the protons but also the ^{13}C nuclei have comparable coupling constants in all three radical anions argues against drastic differences in the planarity of the π -systems under consideration. This finding implies that $III \cdot^\ominus$ and, in particular, $II \cdot^\ominus$ should also be planar. In other words, dibenzo[*a,e*]cyclooctene (II) is expected to exhibit a behaviour analogous to that of the parent cyclooctatetraene (I) by having its eight-membered ring flattened upon one- or two-electron reduction, a point of view advocated by *Katz et al.* [2] and based on polarographic studies of II, as well as on the $^1\text{H-NMR}$ spectrum of $II^{2\ominus}$.

A similar behaviour of I and II is also apparent in the reaction of the two hydrocarbons with potassium in MTHF. The failure of both compounds to yield the ESR. spectra of their radical anions in this solvent (see Results) suggests that II, like the parent compound I [14], has a marked tendency to pass directly into its dianion [2]. Since the association with the cations K^\oplus stabilizes the dianions more strongly than the radical anions, such a tendency should be reinforced by ion pairing and thus be still more pronounced with MTHF than with DME as solvent. Accordingly the equilibria $2 I \cdot^\ominus \rightleftharpoons I + I^{2\ominus}$ and $2 II \cdot^\ominus \rightleftharpoons II + II^{2\ominus}$ must be shifted in MTHF even further to the right than in DME, and, as a result, no measurable concentrations of $I \cdot^\ominus$ and $II \cdot^\ominus$ are present in the former solvent.

Last but not least, a planar geometry of $II \cdot^\ominus$ is supported by a comparison of the hyperfine data for this radical anion with the result of INDO calculations described below.

INDO calculations. Our computational procedure closely followed that developed by *Pople & Beveridge* [15]. Fig. 5 indicates the geometry of the carbon skeleton in the eight-membered ring of those radical anions for which the calculations were performed: $II \cdot^\ominus$, with this ring being either planar or tub-shaped like cyclooctatetraene [3], and $IV \cdot^\ominus$ [6]. The benzene rings were taken throughout as regular hexagons

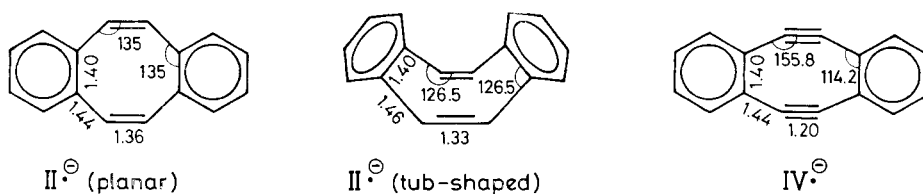


Fig. 5. C–C bond lengths (in Å) and C–C–C bond angles (in degrees) used for the eight-membered ring in the INDO calculations of $II \cdot^\ominus$ and $IV \cdot^\ominus$

having a lateral length of 1.40 Å. All C–H bonds lay in the same plane as the two adjacent C–C linkages and halved the C–C–C angles; their length was 1.09 Å. The coupling constants $a_{H\mu}$ computed by means of the INDO procedure for these geometries of $\text{II} \cdot \ominus$ and $\text{IV} \cdot \ominus$ are given in Table 3. Contrary to the corresponding values resulting from the HMO models (Table 2), they are very sensitive to deviations

Table 3. Proton coupling constants $a_{H\mu}$ (in Gauss = 10^{-4} Tesla) calculated by the INDO procedure

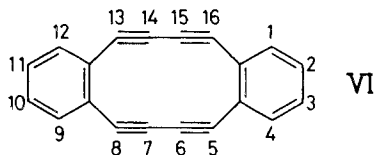
Position μ	$\text{II} \cdot \ominus$		$\text{IV} \cdot \ominus$
	planar	tub-shaped	
1, 4, 7, 10	+0.04	+0.68	+0.42
2, 3, 8, 9	-1.39	-1.23	-1.79
5, 6, 11, 12	-2.58	-0.30	-

of the eight-membered ring from planarity. Such a statement is justified by a comparison of the coupling constants $a_{H\mu}$ obtained for the 'planar' and 'tub-shaped' radical anion $\text{II} \cdot \ominus$. In particular the $|a_{H5,6,11,12}|$ values are predicted to decrease dramatically when the twist angle about the four essential single bonds is enlarged from 0° ($\text{II} \cdot \ominus$ planar) to 57° ($\text{II} \cdot \ominus$ tub-shaped). Concomitantly, the agreement with the observed proton coupling constants (Table 1) becomes increasingly poorer. The same holds with respect to the coupling constants of the ^{13}C nuclei in the eight-membered ring of $\text{II} \cdot \ominus$: upon enlargement of the pertinent twist angle to 57° the computed values increase up to 4–5 Gauss, far beyond the observed upper limit of 1.8 Gauss (see Results). It is also noteworthy that, according to the INDO procedure, the planar radical anion $\text{II} \cdot \ominus$ should be 0.46 eV more stable than the tub-shaped one.

The proton coupling constants, which result from the INDO calculations for the radical anion $\text{IV} \cdot \ominus$ having the planar geometry of the neutral molecule [6], deserve only little comments. They are in general accord with both the HMO theoretical (Table 2) and experimental values (Table 1).

Conclusions. The studies of $\text{II} \cdot \ominus$, $\text{III} \cdot \ominus$ and $\text{IV} \cdot \ominus$ point to similar electronic and molecular structures of the three radical anions. They strongly suggest that not only $\text{IV} \cdot \ominus$, but also $\text{II} \cdot \ominus$ and $\text{III} \cdot \ominus$ are substantially planar.

Appendix. – An ESR. spectrum similar to that of $\text{IV} \cdot \ominus$ (Fig. 2) is observed for the radical anion of 5,6,7,8,13,14,15,16-octadehydro-dibenzo[*a,g*]cyclododecene (VI) which was synthesized according to the procedure described in the literature [16].



The spectrum of $\text{VI} \cdot \ominus$, shown in Fig. 6, is readily analysed in terms of the coupling constants $a_{H\mu} = 1.55 \pm 0.01$ and 0.21 ± 0.01 Gauss. Their assignment to the sets of four equivalent protons at the positions $\mu = 2, 3, 10, 11$ and $1, 4, 9, 12$, resp., is based on HMO models, which made use

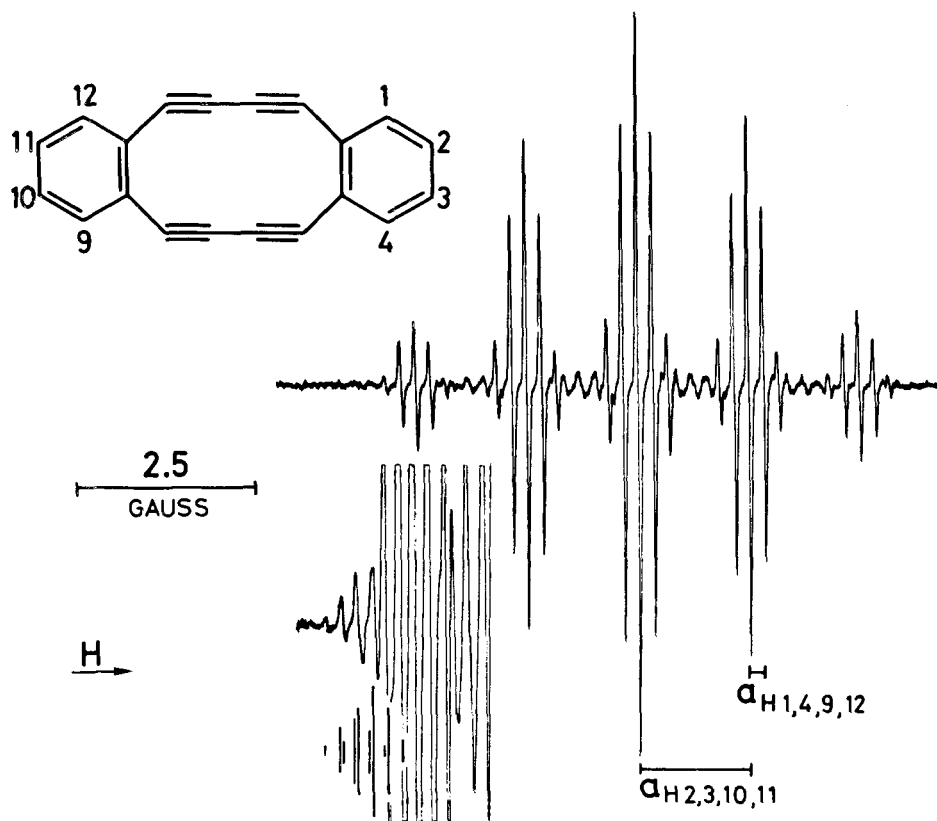


Fig. 6. ESR. spectrum of the radical anion $VI \cdot ^-$. Solvent: DME; counter-ion: K^+ ; temp.: -80° . The ¹³C satellites at the amplified low-field end of the spectrum are simulated by a stick diagram

of bond parameters analogous to those employed for $IV \cdot ^-$. Also displayed in Fig. 6 is the amplified low-field end of the spectrum from which the following ¹³C coupling constants are obtained: $a_C^I(4) = 1.6 \pm 0.1$; $a_C^II(4) \approx a_C^III(4) = 1.1 \pm 0.1$ Gauss.

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213. Homoisoflavanone. IV.¹⁾ Neue Inhaltsstoffe der Eucomin-Reihe von *Eucomis bicolor*

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Homoisoflavanones. IV. New constituents of the Eucomin Series of *Eucomis bicolor*. – *Summary.* Four new homoisoflavanones, (*E*)-7-O-methyl-eucomin (**2a**), (–)-7-O-methyl-eucomol (**5**), (+)-3,9-dihydro-eucomin (**7a**) and 7-O-methyl-3,9-dihydro-eucomin (**8**), were isolated from the bulbs of *Eucomis bicolor* BAK. (*Liliaceae*). Their structures were determined by spectral data and synthesis. These compounds occur exclusively in the waxy material between the bulb leaves. Furthermore it was shown that only (*Z*)-eucomin (**1b**) is genuine, (*E*)-eucomin (**1a**) being an artefact. It is likely that **2a** is also not genuine. A new method for a selective 7-O-methylation is described.

1. Einleitung. – Seit der Isolierung und Strukturaufklärung von (*E*)-Eucomin (**1a**) und Eucomol (**4**), den ersten Vertretern der Homoisoflavanone aus den Zwiebeln von *Eucomis bicolor* BAK. (*Liliaceae*) durch *Böhler & Tamm* [2] im Jahre 1967, ist nur noch über das Vorkommen von 7-O-Methyl-eucomol (**5**) in dieser Pflanze berichtet worden [3]. Weitere Verbindungen dieser Stoffklasse treten in dieser Spezies, im Gegensatz zu anderen Arten der Gattung *Eucomis* L'HÉRIT., in nur recht geringer Menge auf und lassen sich erst nach sorgfältiger Trennung der Rohextrakte gewinnen. Wir berichten im folgenden über die Isolierung und Konstitutionsermittlung dieser neuen Verbindungen.

2. Isolierung. – Bei der Suche nach verbesserten Methoden zur chromatographischen Trennung von Homoisoflavanonen prüften wir auch Polyamid als Adsorbens. Unter Verwendung lipophiler Fließmittelsysteme, wie z.B. Petroläther/Benzol/Butanon/Methanol im Verhältnis 10:8:1:1 [4]²⁾ konnten wir beobachten, dass die Mutterlagen von natürlichem (*E*)-Eucomin (**1a**) zwei weitere, weniger polare Verbindungen enthielten. Die eine davon, gelb gefärbt wie **1a**, erwies sich als das (*Z*)-

¹⁾ Teil III: siehe [1].

²⁾ Erst kürzlich berichteten *Jay et al.* [5] ausführlich über diese vorteilhafte Methode.