144. The Radical Anions of 1,2-Diphenylcyclohexene and Structurally Related Compounds. Conformational ESR and ENDOR Studies

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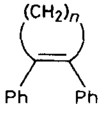
ESR, ENDOR, and TRIPLE resonance studies have been performed on the radical anions of 1,2-diphenylcyclohex-1-ene (**4**), 1,2-di(perdeuteriophenyl)cyclohex-1-ene ((D_{10})**4**), the *trans*-configurated 3,4-diphenyl-8-oxabicyclo[4.3.0]non-3-ene (**5**) and its 2,2,5,5-tetradeuterio derivative (D_4)**5**, and 2,3-diphenyl-8,9,10-trinorborn-2-ene (**6**). The spectra of **4**$^{\cdot-}$ exhibit strong temperature dependence along with a specific broadening of ESR hyperfine lines and proton ENDOR signals. The coupling constant, which bears the main responsibility for these features, is that of the β-protons in the *quasi*-equatorial positions of the cyclohexene ring, and the experimental findings are readily rationalized in terms of relatively modest conformational changes without invoking the inversion of the half-chair form. The hyperfine data for the β-protons in **5**$^{\cdot-}$ closely resemble the corresponding low-temperature values for **4**$^{\cdot-}$. However, the 'unusual' features observed for **4**$^{\cdot-}$ are absent in the ESR and ENDOR spectra of **5**$^{\cdot-}$, because the half-chair conformation of the cyclohexene ring in **5**$^{\cdot-}$ is deprived of its flexibility. Although the boat form of this ring in **6**$^{\cdot-}$ is also rigid, the spectra of **6**$^{\cdot-}$ are temperature-dependent, due to an interconversion between two propeller-like conformations of the phenyl groups. The pertinent energy barrier is 30 ± 5 kJ·mol^{-1}. An analogous interconversion presumably takes place in **4**$^{\cdot-}$ and **5**$^{\cdot-}$ as well, but, unlike **6**$^{\cdot-}$, it is not amenable to experimental study.

Introduction. – 1,2-Diphenylcyclohex-1-ene (**4**) is the fourth representative of correspondingly substituted cycloalkenes which can be considered as 'non-isomerizable' (Z)-stilbenes. The radical anions, **1**$^{\cdot-}$, **2**$^{\cdot-}$, and **3**$^{\cdot-}$, of the first three compounds in the series, namely the 1,2-diphenyl derivatives of cyclopropene, cyclobutene, and cyclopentene, have been characterized by their hyperfine data a number of years ago [1]. A report on the analogous data for **4**$^{\cdot-}$ has been delayed, because some unusual spectral features of this radical anion required a careful study of their temperature dependence as well as a complementary investigation of suitable reference species.



1 $n = 1$
2 $n = 2$
3 $n = 3$
4 $n = 4$

Here, we describe the ESR and ENDOR spectra of **4**$^{\cdot-}$ and (D_{10})**4**$^{\cdot-}$ which is the radical anion of 1,2-di(perdeuteriophenyl)cyclohex-1-ene. Also dealt with are the structurally related radical anions of the *trans*-configurated 3,4-diphenyl-8-oxabicyclo[4.3.0]non-3-ene (**5**) and its 2,2,5,5-tetradeuterio derivative ((D_4)**5**), in addition to that of 2,3-diphenyl-8,9,10-trinorborn-2-ene (2,3-diphenylbicyclo[2.2.1]hept-2-ene; **6**).

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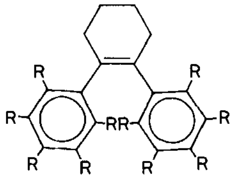
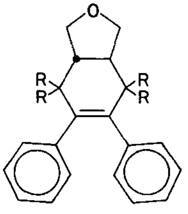
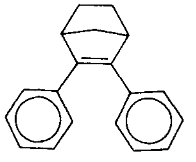


4 R=H
(D$_{10}$)**4** R=D



5 R=H
(D$_4$)**5** R=D



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Experimental. – *Source of Compounds.* 1,2-Diphenylcyclohex-1-ene (**4**) was prepared from 2-phenylcyclohexanone according to the procedure described by *Tomboulian* [2]. The synthesis of (D$_{10}$)**4** started from cyclohexene oxide *(Aldrich)* which, upon reaction with (D$_5$)PhLi and (successively) H_2O, yielded 2-(perdeuteriophenyl)cyclohexanol [3]. Oxidation by CrO_3 led to the corresponding ketone which was also treated with (D$_5$)PhLi and H_2O to give 1,2-di(perdeuteriophenyl)cyclohexanol [2]. The final product (D$_{10}$)**4** was obtained by reaction of this alcohol with $SOCl_2$ in the presence of pyridine. Isotopic purity of (D$_{10}$)**4** was better than 95% (by ^{1}H-NMR).

The synthesis of the diphenyloxabicyclononene **5** started from diphenylethyne which reacted with the conjugate base of $(CH_3)_2SO$ to yield 2,3-diphenyl-1,3-butadiene. This compound underwent a *Diels-Alder* addition with diethyl fumarate, and the diethyl 1,2-diphenylcyclohex-1-ene-4,5-dicarboxylate thus obtained was reduced with $LiAlH_4$ to the corresponding diol. Cyclization of the diol led to **5** as the final product. The deuterio derivative (D$_4$)**5** was prepared by a fully analogous procedure starting from diphenylethyne and the conjugate acid of $(CD_3)_2SO$. A more detailed description of the syntheses of **5** and (D$_4$)**5** will be published elsewhere [4].

A sample of 2,3-diphenyl-8,9,10-trinorborn-2-ene (**6**) [5] was kindly provided by Professor *G. Kaupp*.

Generation and Study of the Radical Anions. These were produced from the corresponding neutral compounds by reduction with K metal in 1,2-dimethoxyethane (DME). In some experiments, a small quantity of THF was admixed to DME, in order to prevent freezing of the soln. below 193 K. All radical anions were sufficiently persistent to be investigated at temp. ranging up to 293 K. The ESR spectra were taken on a *Varian-E9* instrument, while a *Bruker-ESP-300* spectrometer system served for the ENDOR and TRIPLE measurements.

Results. – *1,2-Diphenylcyclohex-1-ene* (**4**). *Fig. 1a* shows a highly resolved ESR spectrum of $4^{\cdot-}$ at 233 K (g = 2.0026 ± 0.001). It has a total width of 3.84 mT to which the main contributor is a large two-proton coupling constant of *ca.* 1.0 mT. Upon enhancement of the modulation amplitude, this width increases further by 0.72 mT to 4.56 mT, as is demonstrated by the spectrum in *Fig. 1b*. A clue to the analysis of both ESR spectra is provided by the ENDOR technique. The pertinent proton ENDOR spectra of $4^{\cdot-}$ at 193 and 263 K are reproduced in *Fig. 2a* and *2b*, respectively. The signal labelled β_{ax} at the highest frequency is clearly associated with the large coupling constant ($a_{H\beta(ax)}$) of 1.0 mT; it is slightly displaced to lower frequencies on going from 193 to 263 K. The positions of the remaining signals are essentially temperature-independent, with the striking exception of the pair denoted β_{eq}. The conspicuously broad signals belonging to this pair move from 20.3 to 19.3 and from 8.8 to 9.8 MHz, when the temperature is raised from 193 to 263 K, a shift corresponding to a decrease from 0.41 to 0.34 mT in the associated coupling constant $a_{H\beta(eq)}$.

The proton hyperfine data determined from the positions of the ENDOR signals are given in *Table 1* for several selected temperatures. Computer simulation using these data reveals that, in order to fit the highly resolved ESR spectrum of $4^{\cdot-}$ *(Fig. 1a)*, the two-proton coupling constant $a_{H\beta(eq)}$ should be omitted. By contrast, this value must be accounted for in the simulation of the overmodulated spectrum *(Fig. 1b)* which owes its enlarged total width just to inclusion of $a_{H\beta(eq)}$.

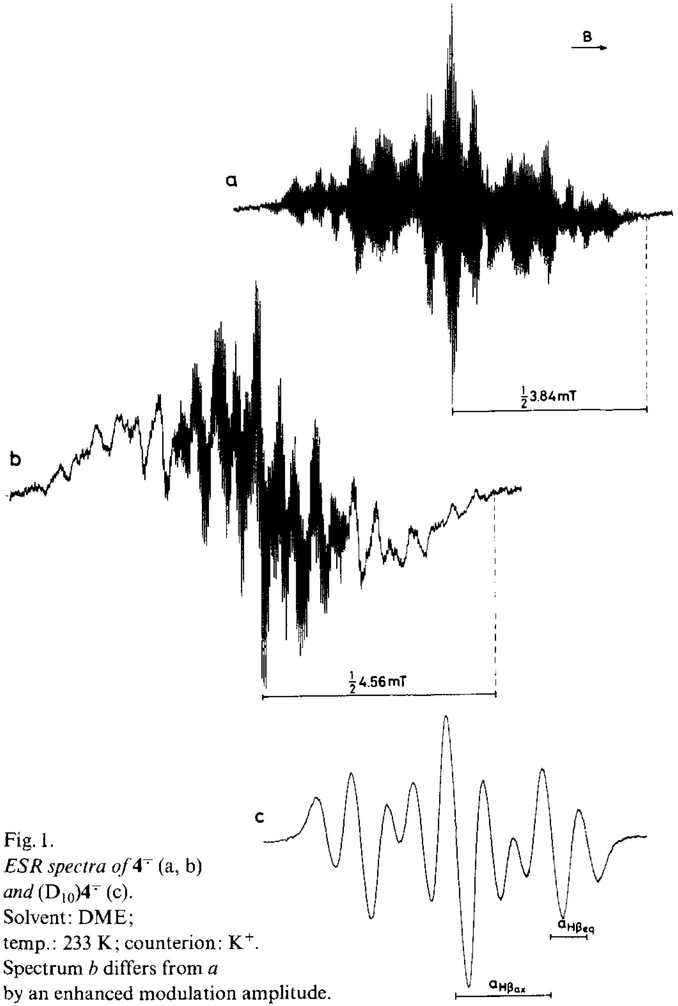

Fig. 1.
ESR spectra of **4**$^{\bar{\cdot}}$ (a, b)
and (D_{10})**4**$^{\bar{\cdot}}$ (c).
Solvent: DME;
temp.: 233 K; counterion: K^+.
Spectrum *b* differs from *a*
by an enhanced modulation amplitude.

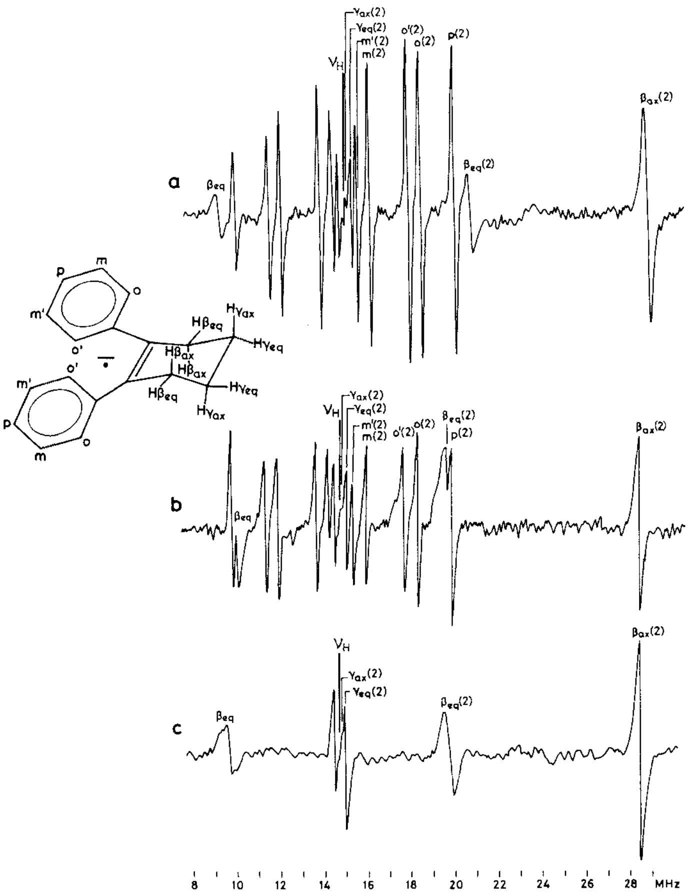

Fig. 2. *Proton ENDOR spectra of* **4**$^{\bar{\cdot}}$ (a, b) *and* (D_{10})**4**$^{\bar{\cdot}}$ (c). Solvent: DME; temp.: 193 (*a*), 263 (*b*), and 233 K (*c*); counterion: K^+. The numbers in parentheses refer to those of equivalent protons.

Table 1. *Proton Coupling Constants, a_H [mT]*[a]*), for* $\mathbf{4}^{\cdot-}$ *and* $\mathbf{5}^{\cdot-}$

	T[K]	o	o'	m	m'	p	β_{ax}	β_{eq}	γ_{ax}	γ_{eq}	δ
$\mathbf{4}^{\cdot-}$	173	−0.250(2)[b])	−0.209(2)	+0.082(2)	+0.041(2)	−0.361(2)	+1.003(2)	+0.429(2)	0.005(2)[c])	−0.020(2)	–
	193	−0.249	−0.209	+0.082	+0.041	−0.360	+0.997	+0.410	0.005	−0.020	
	213	−0.249	−0.208	+0.082	+0.042	−0.359	+0.988	+0.382	0.005	−0.020	
	233	−0.248	−0.207	+0.082	+0.042	−0.358	+0.980	+0.359[d])	[e])	−0.019	
	263	−0.246	−0.207	+0.082	+0.042	−0.360	+0.974	+0.338[d])	[e])	−0.018	
	293	−0.246	−0.207	+0.081	+0.042	−0.361	+0.968[d])	+0.322	[e])	−0.018	
$\mathbf{5}^{\cdot-}$	173	−0.251(2)	−0.212(2)	+0.083(2)	+0.045(2)	−0.356(2)	+0.998(2)	+0.440(2)	0.005(2)[c])	–	[f])
	213	−0.250	−0.212	+0.083	+0.045	−0.357	+0.996	+0.438	0.005		
	263	−0.248	−0.211	+0.084	+0.047	−0.357	+0.984	+0.436	[e])		
	293	−0.248	−0.210	+0.083	+0.046	−0.357	+0.980	+0.436	[e])		

[a]) Experimental error [mT]: ±0.001 for $|a_H| < 0.1$ and 0.002 for $|a_H| > 0.1$.
[b]) The numbers in parentheses refer to those of equivalent protons.
[c]) Sign undetermined.
[d]) From the ESR and ENDOR spectra of $(D_{10})\mathbf{4}^{\cdot-}$ (*cf.* text).
[e]) Could not be exactly measured for $T > 213$ K.
[f]) *Cf. Footnote 3.*

The notation applied to the protons in $\mathbf{4}^{\cdot-}$ is indicated by the molecular formula depicted in *Fig. 2*. Herein, β_{ax} and β_{eq} refer to the *quasi*-axial and *quasi*-equatorial positions of the protons in the two CH_2 groups which are adjacent to the central double bond in the half-chair conformation of the cyclohexene ring. Likewise, according to the conventional nomenclature of ESR spectroscopy[2]), the protons in the *quasi*-axial and *quasi*-equatorial positions of the two remaining CH_2 groups are denoted γ_{ax} and γ_{eq}. The protons attached to the two Ph groups (α protons) are designated o and o' at the *ortho*-, m and m' at the *meta*-, and p at the *para*-positions, whereby the presence and the absence of the 'dash' refer to the inward and outward locations, respectively. Assignments of the coupling constants to individual pairs of equivalent protons in $\mathbf{4}^{\cdot-}$ are based on comparison with the hyperfine data for structurally related radical anions of **1**, **2**, **3** [1], and (*Z*)-stilbene [7]. The signs of these coupling constants (*Table 1*) have been determined by the general TRIPLE resonance technique [8] with $a_{H(p)}$, $a_{H(o)}$, and $a_{H(o')}$ being taken as negative.

The assignments are confirmed by the ESR and ENDOR studies of $(D_{10})\mathbf{4}^{\cdot-}$, as far as the distinction between the Ph (α) and CH_2 protons (β and γ) is concerned. Due to unresolved splittings from the Ph deuterons, the ESR spectra of $(D_{10})\mathbf{4}^{\cdot-}$ exhibit extremely broad hyperfine components (*Fig. 1c*), so that the specific broadening of the lines involving $a_{H\beta(eq)}$ does not come into play. In fact, $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$ are the only coupling constants which can be determined therefrom. Expectedly, the signals attributed to the α-protons are missing in the corresponding ENDOR spectra (*Fig. 2c*). The temperature dependence of $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$, as found by the ESR and ENDOR studies of $(D_{10})\mathbf{4}^{\cdot-}$, is in good agreement with the results of the analogous investigations of $\mathbf{4}^{\cdot-}$. Actually, some of the values given for these coupling constants in *Table 1* have been derived from the spectra of $(D_{10})\mathbf{4}^{\cdot-}$ rather than from those of its undeuterated counterpart, because the simplicity of the former relative to the latter facilitated the measurements of $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$. In

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[2]) In the ESR nomenclature, protons separated by 0,1,2,3,...sp^3-hybridized C-atoms from a π-centre are called $\alpha,\beta,\gamma,\delta,\ldots$, respectively [6].

particular, difficulties caused by $|a_{H\beta(eq)}|$ becoming almost equal to $|a_{H(p)}|$ in the temperature range around 233 K were avoided, when $a_{H(p)}$ was replaced by $a_{D(p)}$.

3,4-Diphenyl-8-oxabicyclo[4.3.0]non-3-ene (**5**). The ESR spectrum of **5**$^{\cdot-}$ ($g = 2.0027 \pm 0.0001$), shown in *Fig. 3a*, has been analyzed with the use of the proton-coupling constants determined from the positions of the ENDOR signals *(Fig. 3b)*. The close structural relationship between **4**$^{\cdot-}$ and **5**$^{\cdot-}$ is faithfully reflected in their ENDOR spectra, which are almost congruent at low temperatures. All the signals occurring in the ENDOR spectrum of **4**$^{\cdot-}$ *(Fig. 2a)* are also found for **5**$^{\cdot-}$ *(Fig. 3b)*, with the exception of those arising from the γ_{eq}-protons which have been eliminated by the $-CH_2OCH_2-$ group bridging two adjacent C-atoms of the cyclohexene ring[3]). Notwithstanding this similarity, the spectra of the two radical anions differ in that no 'unusual' features are observed for **5**$^{\cdot-}$. Thus, contrary to **4**$^{\cdot-}$, specific broadening does not appear in the spectra of **5**$^{\cdot-}$ for either the ESR hyperfine lines *(Fig. 3a)* or the ENDOR signals associated with $a_{H\beta(eq)}$ *(Fig. 3b)*. Moreover, again in contrast to **4**$^{\cdot-}$, this coupling constant is nearly temperature-independent for **5**$^{\cdot-}$, as is evident from *Table 1* containing the hyperfine data of the protons in **5**$^{\cdot-}$, along with the corresponding values for **4**$^{\cdot-}$. Assignments of $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$ are confirmed by ESR and ENDOR studies of (D$_4$)**5**$^{\cdot-}$ in which the four CH_2 β-protons have been replaced by deuterons. Signs of the coupling constants stem from the general TRIPLE spectra of **5**$^{\cdot-}$ with $a_{H(p)}$, $a_{H(o)}$, and $a_{H(o')}$ assumed to be negative.

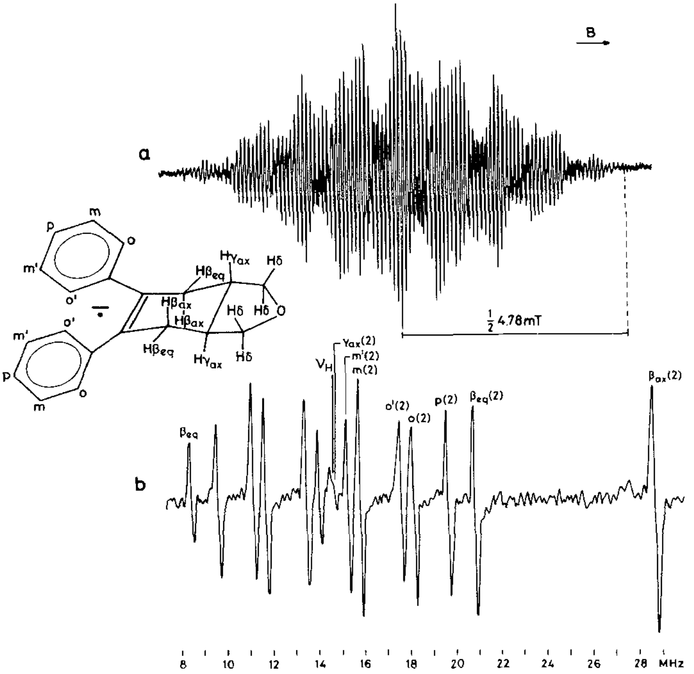

Fig. 3. *ESR* (a) *and proton ENDOR* (b) *spectra of* **5**$^{\cdot-}$. Solvent: DME; temp.: 213 K; counterion: K$^+$. The numbers in parentheses refer to those of equivalent protons.

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[3]) The four CH_2 δ-protons in the bridging $-CH_2OCH_2-$ group of **5**$^{\cdot-}$ (*cf.* molecular formula in *Fig. 3*) have vanishingly small coupling constants and do not give rise to measurable hyperfine splittings and ENDOR signals.

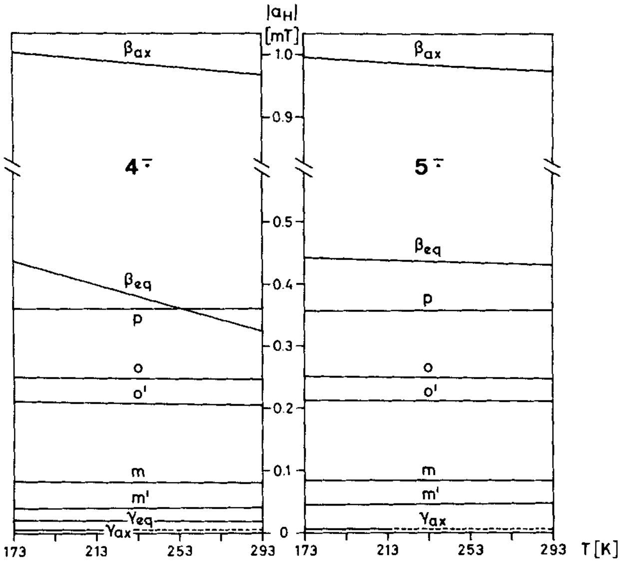

Fig. 4. *Regression of the proton-coupling constants* (absolute values $|a_H|$) *on the temperature (T) for* **4**$^{\cdot-}$ *and* **5**$^{\cdot-}$

The different temperature dependence of $a_{H_{\beta(eq)}}$ in the spectra of **4**$^{\cdot-}$ and **5**$^{\cdot-}$ is illustrated in *Fig. 4* which displays such a dependence for all proton-coupling constants characterizing the two radical anions.

2,3-Diphenyl-8,9,10-trinorborn-2-ene (**6**). The ESR spectra of **6**$^{\cdot-}$ (g = 2.0026 ± 0.0001; total width 2.6 mT) are poorly resolved, due to a large number of overlapping hyperfine

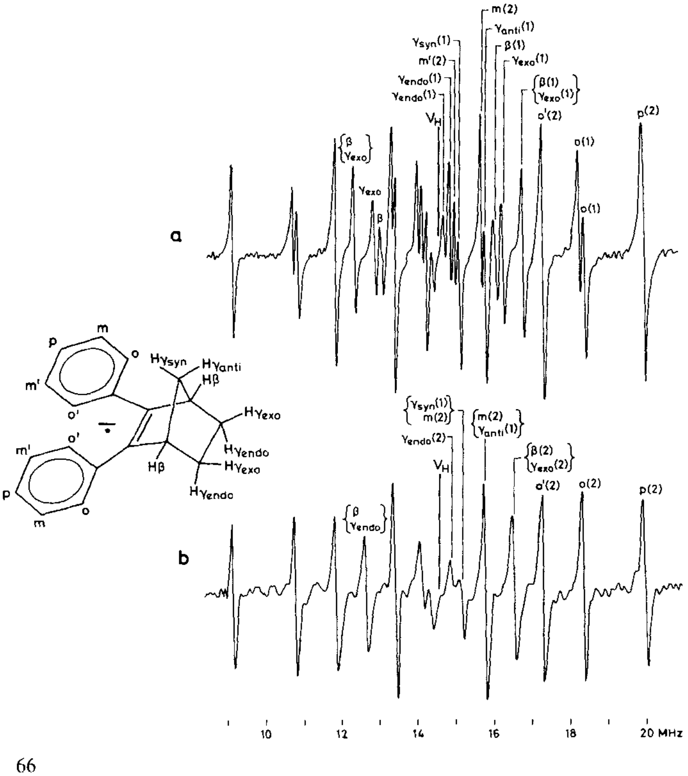

Fig. 5. *Proton ENDOR spectra of* **6**$^{\cdot-}$. Solvent: DME; temp.: 193 (*a*) and 273 K (*b*); counterion: K^+. The numbers in parentheses refer to those of equivalent protons.

lines. More information is provided by the corresponding ENDOR spectra, such as the one taken at 193 K *(Fig. 5a)*. The signals in this spectrum mostly arise from single (non-equivalent) protons and some of them broadened, when the temperature is raised. The phenomenon is particularly conspicuous for the signals denoted β and γ_{exo} in the frequency ranges 16–17 and 12–13 MHz; these signals are broadened beyond detection at 233 K (coalescence). Further increase in the temperature leads to the appearance of new signals at intermediate frequencies (16.5 and 12.6 MHz), as demonstrated by the ENDOR spectrum of **6**$^{\cdot-}$ at 273 K *(Fig. 5b)*. The *Arrhenius* activation energy for the phenomenon, which gives rise to these spectral changes, has been estimated as 30 ± 5 kJ mol^{-1}.

Table 2. *Proton Coupling Constants, a_H [mT]* [a]*), for* **6**$^{\cdot-}$

T [K]	o	o'	m	m'	p	β	γ_{syn}	γ_{anti}	γ_{endo}	γ_{exo}
193	−0.277(1)[b])	−0.195(2)	+0.082(2)	+0.030(2)	−0.388(2)	+0.159(1)	−0.038(1)	−0.089(1)	−0.024(1)	+0.159(1)
	−0.266(1)					+0.109(1)			−0.011(1)	+0.121(1)
273	−0.271(2)	−0.195(2)	+0.086(2)	+0.034(2)	−0.388(2)	+0.139(2)	−0.034(1)	−0.086(1)	−0.020(2)	+0.139(2)

[a]) Experimental error [mT]: ±0.001 for $|a_H| < 0.1$ and ±0.002 for $|a_H| > 0.1$.

[b]) The numbers in parentheses refer to those of equivalent protons.

Table 2 gives the proton-coupling constants for **6**$^{\cdot-}$ at 193 and 273 K with their relative signs determined by the general TRIPLE technique at 193 K. Assignments to the α-protons in the Ph groups have been achieved by comparison with the corresponding hyperfine data for **4**$^{\cdot-}$ and **5**$^{\cdot-}$ *(Table 1)*, while those to the β- and γ-protons are based on the results of an INDO calculation [9] for the hitherto unknown radical anion of norbornene. The subscripts *syn-anti* and *endo-exo* serve to distinguish the two γ-protons at a CH_2 C-atom in the methano- and ethano-bridging group, respectively (see molecular formula in *Fig. 5*).

Discussion. – *Conformational Flexibility of the Cyclohexene Ring.* The coupling constants of the β-protons in **4**$^{\cdot-}$ and **5**$^{\cdot-}$ ($a_{H\beta(ax)} \approx 1.0$ and $a_{H\beta(eq)} \approx 0.4$ mT) strikingly differ from the corresponding value for **6**$^{\cdot-}$ ($a_{H\beta} < 0.2$ mT). Rationalization of these findings is straightforward. Whereas in both **4**$^{\cdot-}$ and **5**$^{\cdot-}$ the cyclohexene ring adopts a half-chair conformation, it is forced into a boat form by the rigid norbornene framework of **6**$^{\cdot-}$. A further important finding is that, despite the common conformation, the unusual features observed in the spectra of **4**$^{\cdot-}$ are absent in those of **5**$^{\cdot-}$. This finding reflects the differing conformational flexibilities of the cyclohexene ring in the two radical anions. Contrary to **4**$^{\cdot-}$, in which the half-chair form is endowed with such flexibility, this conformation becomes rigid in **5**$^{\cdot-}$ due to the bridging of two adjacent C-atoms by a *trans*-configurated $-CH_2OCH_2-$ group.

The dependence of the β-proton-coupling constant on conformation is usually expressed by the so called $\cos^2\theta$ relationship where θ is the dihedral angle between the C–Hβ bond and the $2p_z$-axis at the neighbouring π-centre [10]. Prior to applying this relationship to the β-protons in the conformationally flexible cyclohexene ring of **4**$^{\cdot-}$, it is essential to note that an interchange of the *quasi*-axial and *quasi*-equatorial positions is *not* observed for the β-protons of **4**$^{\cdot-}$ in the temperature range of investigation (173–293 K). Therefore, the unusual features in the ESR and ENDOR spectra of **4**$^{\cdot-}$ *cannot arise from an inversion of the half-chair conformation.* This result is rather surprising in view of the relatively low activation energy (23 kJ mol^{-1}) determined for such an inversion in cyclo hexene (^{1}H-NMR [11]) and the (cyclohex-2-enyl)methyl radical (ESR [12]). Obviously the barrier to inversion must be considerably raised in $\mathbf{4}^{\overline{\cdot}}$ by the substitution of the cyclohexene ring with two Ph groups. It will be shown below, how the experimental findings for the β-protons in $\mathbf{4}^{\overline{\cdot}}$ are rationalized in terms of the $\cos^2\theta$ relationship without invoking an inversion of the half-chair conformation.

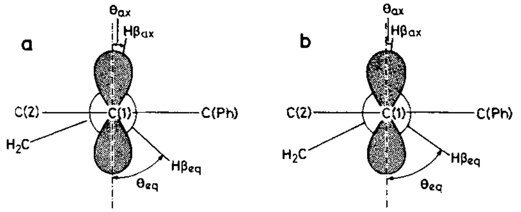

Fig. 6. Newman *projections showing the dihedral angles* θ_{ax} and θ_{eq} *in the* $C(1)-CH_2\beta$ *fragment of* $\mathbf{4}^{\overline{\cdot}}$ *at 173* (a) *and 293 K* (b)

The relevant *Eqns. 1–3* relate the temperature-dependent coupling constants $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$ to the dihedral angles θ_{ax} and θ_{eq} *(Fig. 6)* which themselves are a function of the temperature (T).

$$a_{H\beta(ax)}(T) = B\rho_{1,2}(T)\,\langle\cos^2\theta_{ax}(T)\rangle \tag{1}$$

$$a_{H\beta(eq)}(T) = B\rho_{1,2}(T)\,\langle\cos^2\theta_{eq}(T)\rangle \tag{2}$$

$$180° - \{\theta_{ax}(T) + \theta_{eq}(T)\} = 120° \tag{3}$$

Therein, B is a proportionality factor having the value of +4.0 to +4.5 mT for radical anions[4]), and $\rho_{1,2}$ represents the π-spin population at a C-atom (1 or 2) in the central double bond. Whereas B should be essentially independent of temperature, such a dependence may, to some extent, exist for $\rho_{1,2}$. This is because the π-spin distribution in $\mathbf{4}^{\overline{\cdot}}$ is influenced by the twist angle (ϕ) about the linkages of the Ph groups to the central double bond (see next section), and the angle ϕ, in turn, is likely to be sensitive to variations in temperature.

With the use of the experimental data for $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$ *(Table 1), Eqns. 1–3* can be solved for any temperature T in the range of investigation, thus yielding the relevant values of θ_{ax}, θ_{eq}, and $\rho_{1,2}$. Taking

$$a_{H\beta(ax)}(173) = +1.003;\ a_{H\beta(eq)}(173) = +0.429\ \text{mT}$$

and

$$a_{H\beta(ax)}(293) = +0.968;\ a_{H\beta(eq)}(293) = +0.322\ \text{mT},$$

which are the β-proton-coupling constants determined for $\mathbf{4}^{\overline{\cdot}}$ at the lowest (T = 173 K) and the highest temperature (T = 293 K), one obtains

$$\theta_{ax}(173) = 10°;\ \theta_{eq}(173) = 50°;\ B\rho_{1,2}(173) = +1.03\ \text{mT}$$

and

$$\theta_{ax}(293) = 5°;\ \theta_{eq}(293) = 55°;\ B\rho_{1,2}(293) = +0.98\ \text{mT}.$$

Depending on the choice of B (see above), $\rho_{1,2}(173) = +0.23$ to $+0.26$ and $\rho_{1,2}(293) = +0.22$ to $+0.25$.

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[4]) $|B| = 4$ mT was suggested by *Russell* [13]; $|B| = 4.5\ \text{mT} \approx 2 \times 2.24$ mT is derived from an ESR study on the radical anions of dimethyl-substituted naphthalenes [14].

This result means that shifts by only 5° in the dihedral angles θ_{ax} and θ_{eq}, along with a slight decrease in the π-spin population $\rho_{1,2}$, are sufficient to reproduce the experimentally found changes in $a_{H\beta(ax)}$ and $a_{H\beta(eq)}$ over a temperature rise of 120 K. The finding that the change is much more impressive for $a_{H\beta(eq)}$ than for $a_{H\beta(ax)}$ is mainly due to the shape of the $\cos^2\theta$ function which has the average slopes of -0.96 and -0.26 in the ranges pertaining to θ_{eq} ($50° < \theta < 55°$) and θ_{ax} ($5° < \theta < 10°$), respectively. Thus, $a_{H\beta(eq)}$ should be considerably more sensitive than $a_{H\beta(ax)}$ to variations in θ and therewith to conformational preferences of the cyclohexene ring. This sensitivity manifests itself not only in the pronounced temperature dependence of $a_{H\beta(eq)}$, but it is also responsible for the observed selective broadening of ESR hyperfine lines and proton ENDOR signals associated with this coupling constant. Evidently, variations in θ_{eq} caused by bending vibrations of the cyclohexene ring are too large to be averaged on the hyperfine time-scale, so that the coupling constant $a_{H\beta(eq)}$ is modulated and the incident ESR lines and ENDOR signals are broadened.

The values $\theta_{ax}(173) = 10°$, $\theta_{eq}(173) = 50°$, and $\rho_{1,2}(173) = +0.22$ to $+0.26$, derived for $\mathbf{4}^{\overline{\cdot}}$, should also hold for $\mathbf{5}^{\overline{\cdot}}$ in the whole temperature range of investigation, since the coupling constants of the β-protons in the rigid half-chair conformation of the cyclohexene ring in $\mathbf{5}^{\overline{\cdot}}$ strongly resemble the values $a_{H\beta(ax)}(173)$ and $a_{H\beta(eq)}(173)$ for $\mathbf{4}^{\overline{\cdot}}$ and do not markedly depend on temperature (*Table 1* and *Fig. 4*).

In the case of $\mathbf{6}^{\overline{\cdot}}$, only one equation analogous to *Eqn. 1* and *2* can be set up for the coupling constant $a_{H\beta}$, as only a single β-proton is attached to each bridgehead C-atom. Use of $a_{H\beta} = +0.139$ mT (*Table 2*) and $\rho_{1,2} \approx +0.25$ (see above) leads to a dihedral angle θ of nearly 70°, a result which is consistent with the rigid boat conformation of the cyclohexene ring in $\mathbf{6}^{\overline{\cdot}}$; in this conformation the β-protons are located close to the nodal plane of the central double bond.

Rotation of the Ph Groups. It has been found by an electron diffraction study of (Z)-stilbene in the gas phase [15] that this molecule possesses the C_2 symmetry and may be described as having a propeller-like conformation with the Ph groups twisted by an angle $\phi = 43°$ about their linkages to the C-atoms of the central double bond. The non-planar conformation of C_2 symmetry should also be adopted by the (Z)-stilbene-like π-systems of $\mathbf{4}^{\overline{\cdot}}$, $\mathbf{5}^{\overline{\cdot}}$, and $\mathbf{6}^{\overline{\cdot}}$ with the two-fold axis passing through the midpoint of the central double bond. Since this axis is shared by the alkene moieties of $\mathbf{4}^{\overline{\cdot}}$ and $\mathbf{5}^{\overline{\cdot}}$, in which the cyclohexene ring has the half-chair conformation, the overall symmetry of the two radical anions is C_2 as well. On the other hand, such a symmetry is reduced to C_1 in $\mathbf{6}^{\overline{\cdot}}$, because the two-fold axis of the (Z)-stilbene-like π-system is incompatible with the C_s symmetry of the norbornene moiety.

Two modes should be considered for the rotation of the Ph groups about their linkages to the central double bond. One of them is a conrotatory movement of these groups which pass through a *perpendicular* conformation (twist angle $\phi = 90°$). As depicted in *Fig. 7a*, the conformational interconversion A, resulting from such a movement, *not only reverses* the directions of twist of the Ph groups, *but also interchanges* the outward and inward positions ($o \rightleftarrows o'$ and $m \rightleftarrows m'$) within each group. Obviously, the energy barrier to the interconversion A in $\mathbf{4}^{\overline{\cdot}}$, $\mathbf{5}^{\overline{\cdot}}$, and $\mathbf{6}^{\overline{\cdot}}$ is too high to be perceived on the hyperfine time-scale, since for none of these radical anions could an exchange between the outward and inward positions of the Ph protons be observed below 293 K. The second mode is a conrotatory movement of the Ph groups, but in a direction opposite to that of

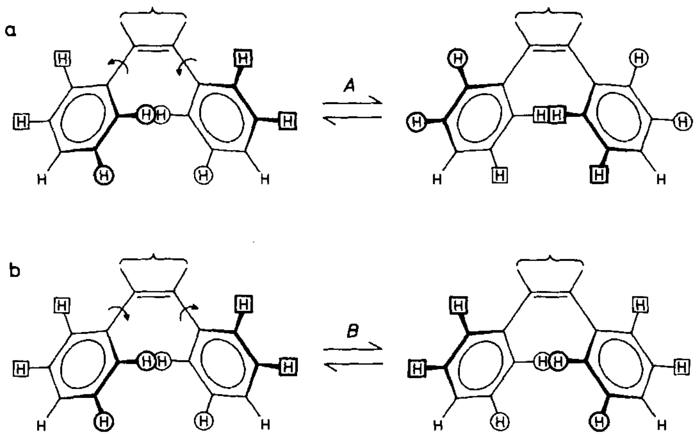

Fig. 7. *Conformational interconversions* A *and* B (*cf.* text) *of the Ph groups in* **4**$^{\cdot-}$, **5**$^{\cdot-}$, *and* **6**$^{\cdot-}$

the first one; thereby the two groups pass through a *planar* conformation ($\phi = 0°$). *Fig. 7b* demonstrates that the conformational interconversion *B* brought about by this movement *reverses only* the directions of twist of the Ph groups *without interchanging* the outward and inward positions within each group. Since the interconversion *B* does not change the C_2 symmetry of **4**$^{\cdot-}$ and **5**$^{\cdot-}$, it should hardly affect the ESR and ENDOR spectra of the two radical anions. For **6**$^{\cdot-}$, on the other hand, provided that the barrier to the interconversion *B* falls within an appropriate energy range, this movement must be amenable to an experimental study by raising the effective symmetry from C_1 to C_s.

Molecular models of **6**$^{\cdot-}$ in its 'frozen' C_1 conformation (with the twist angle $\phi \approx 43°$) clearly indicate which coupling constants should be markedly affected by deviations from the C_s symmetry. Accordingly, the long-range through-space interactions ought to impair the pairwise equivalence of the protons at the bridgehead C-atoms and in the ethano-bridging group of the norbornene moiety (β-, γ_{exo}-, and γ_{endo}-protons), in addition to those in the outward *ortho*-positions of the Ph group (*o*-protons). In fact, the two protons belonging to each of these four pairs exhibit different coupling constants below 213 K and become equivalent only above 263 K. The differences are particularly large for the β- and γ_{exo}-protons so that an activation energy of 30 ± 5 kJ mol^{-1} could be determined from the 'dynamic' behaviour of their ENDOR signals in the relevant temperature range (see *Results*). It is reasonable to identify this energy with the barrier to the conformational interconversion *B* which must thus be lower than that to the interconversion *A (Fig. 7)*. Moreover, it is tempting to use as an estimate of the analogous barrier in those structurally related radical anions, where the interconversion *B* is not amenable to experimental studies, *i.e.*, in **4**$^{\cdot-}$ and **5**$^{\cdot-}$, as well as in the easily isomerizable radical anion of (*Z*)-stilbene [7].

The lower energy barrier to the interconversion *B*, as compared with that to *A*, can be rationalized in terms of electronic factors having a greater impact on such a barrier than the steric ones. Steric interference is expected to hinder *B* more strongly than *A*, since *A* does not require a passing by of the H-atoms in the inward *ortho*-positions (*o'*) of the Ph groups, whereas this situation cannot be avoided in *B (Fig. 7)*. By contrast, changes in π-delocalization energy occurring in the interconversions are expected to favour *B* relative to *A*. As stated above, *A* implies a passage through a perpendicular conformation, in which the conjugation between the π-systems of the phenyl groups and the central double bond is disrupted. On the other hand, the corresponding transient conformation in *B* should be a planar one with a full conjugation between the individual π-systems.

Final Remark. A comment on the assignments of coupling constants to α-protons in the *ortho*-positions of the two Ph groups is here in place. For all radical anions containing the π-system of (*Z*)-stilbene, the four protons in these positions are only pairwise equivalent ([1] [7] and *Tables 1* and *2* in the present work). Typically, the coupling constants of the two pairs amount to –0.291 and –0.194 mT for the radical anion of (*Z*)-stilbene [1] (signs according to theory) and to –0.271 and –0.195 mT for $\mathbf{6}^{\overline{\cdot}}$ at 273 K. The (absolutely) larger value has generally been assigned to the pair of protons in the outward *ortho*-positions (*o* in the present notation), leaving the smaller one for that in the inward positions (*o'*). An argument underlying this assignment is that a sterical congestion should lead to a decrease in the absolute value of an α-proton coupling constant [16]. The finding that in the ENDOR spectra of $\mathbf{6}^{\overline{\cdot}}$ at low temperatures (*Fig. 5a*) the signals associated with –0.271 mT split into two (–0.277 and –0.263 mT), whereas those involving –0.195 mT do not, provides an indirect experimental support for the assignment in question. This assertion is justified, since, as noted in the preceding section, long-range through-space interactions in $\mathbf{6}^{\overline{\cdot}}$ are expected to affect the equivalence of the two Ph α-protons in the outward *o*-positions to a larger extent than that of their counterparts in the inward *o'*-positions.

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