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Unusually Tight Ion Pairing of the 1,4- and 2,3-Di-*tert*-butylbuta-1,3-diene Radical Anions with Alkali-Metal Cations: An ESR and ENDOR Study

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Abstract: Radical anions of several alkyl-substituted buta-1,3-dienes, **4**−**9**, and of 1,4-di-*tert*-butylcyclohexa-1,3-diene (**11**) were characterized by their hyperfine data with the use of ESR and ENDOR spectroscopy. Some of these radical anions, which are protected by bulky alkyl substitutents, could be generated by reaction of the corresponding neutral compounds with a potassium, rubidium, or cesium mirror in 1,2-dimethoxyethane (DME) and, mostly, tetrahydrofuran (THF). In particular, the radical anions of 1,4- and 2,3-di-*tert*-butylbuta-1,3-dienes (**6** and **7**, respectively) prepared by this method proved to be fairly persistent, and their ESR and ENDOR spectra were thoroughly studied in a wide temperature range. Characteristic of the hyperfine patterns of $\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$ are very large coupling constants of the alkali-metal nuclei in the counterion: $a(^{39}\mathrm{K}) = 0.12-0.15$, $a(^{85}\mathrm{Rb}) = 0.40-0.84$, $a(^{87}\mathrm{Rb}) = 1.4-2.8$, and $a(^{133}\mathrm{Cs}) = 0.70-2.6$ mT. Values of this size, unusual for counterions of hydrocarbon radical anions, point to a tight or contact ion pairing of $\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$ with the alkali-metal cations M^+ (M = K, Rb, Cs). Whereas for $\mathbf{6}^{\bullet-}/M^+$ in DME and THF only such tight ion pairs were observed, their coexistence with loose or solvent-separated ion pairs was noticed for $\mathbf{7}^{\bullet-}/K^+$ in DME at very low temperatures. Apart from the large hyperfine splittings due to the alkali-metal nuclei, a striking feature of the tight ion pairs $\mathbf{7}^{\bullet-}/M^+$ is the coupling constant of two protons in the 1,4-positions; its absolute value (ca. 0.4 mT) is much smaller than that (ca. 0.7 mT) of the corresponding protons in the radical anions of buta-1,3-dienes. Assignment of this reduced value to the *endo*-protons is compatible with the ESR and ENDOR spectra of $\mathbf{7}\text{-}d_2^{\bullet-}/M^+$ dideuterated in the 1-position. The structures of $\mathbf{6}^{\bullet-}/M^+$ and $\mathbf{7}^{\bullet-}/M^+$ were discussed with the aid of theoretical calculations. Undoubtfully, the planar *trans*-conformation with the bulky 1,4-*tert*-butyl substituents in the sterically unhindered *exo*-positions is generally favored for $\mathbf{6}^{\bullet-}/M^+$. The counterion M^+ should be situated on the 2-fold axis above or below the molecular plane of $\mathbf{6}^{\bullet-}$. In $\mathbf{7}^{\bullet-}$, the steric overcrowding by the 2,3-*tert*-butyl substituents is relieved by a strong twist about the C(2)−C(3) bond; loose and tight ion pairs $\mathbf{7}^{\bullet-}/M^+$ may have different conformations. For the tight ion pairs $\mathbf{7}^{\bullet-}/M^+$, a conformation should be preferred in which the counterion M^+ is situated on the 2-fold axis with the two *tert*-butyl substituents "on the other side" of the molecule. The close contact of the alkali-metal cation M^+ with either $\mathbf{6}^{\bullet-}$ or $\mathbf{7}^{\bullet-}$ must be promoted by the spatial arrangement of these substituents.

Introduction

The fact that ions of opposite charges tend to pair is of great importance for the course of organic reactions in solution.[1] Clear evidence for such an ion pairing is provided by hyperfine splittings from paramagnetic nuclei of alkali-metal cations associated with organic radical anions in ethereal solvents. Consequently, ESR spectroscopy represents a method of choice for the studies of ion pairs.[2,3a] Since the first observation of a ^{23}Na-hyperfine splitting in the ESR spectrum of naphthalene reduced to its radical anion with sodium in tetrahydrofuran (THF) or 2-methyltetrahydrofuran (MTHF),[4] a large number of papers describing similar findings appeared. The largest coupling constants of alkali-metal nuclei in counterions of organic radical anions were reported therein for cations attached in a chelate-like fashion to the lone electron pairs of the oxygen atoms in the radical anion. In this respect, alkali-metal cations associated with the radical anion of *o*-dimesitoylbenzene in 1,2-dimethoxyethane (DME) and THF served as a paradigm.[5] With DME at room temperature, the ^{7}Li-, ^{23}Na-, ^{39}K-, ^{85}Rb-, ^{87}Rb-, and ^{133}Cs-coupling constants (absolute values) amounted there to 0.375,[5] 0.695,[5] 0.133,[5] 0.491,[6] 1.66,[6] and 1.02 mT,[5] respectively; such ion pairs are denoted "tight" or "contact" ones. On

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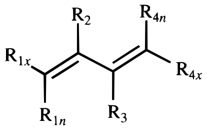
the other hand, ion pairs of alkali-metal cations associated with radical anions of hydrocarbons are generally considered as “loose” or “solvent-separated” ones, because the molecules of the ethereal solvent successfully compete with the radical anion for the positively charged counterion. Accordingly, the hyperfine splittings from alkali-metal nuclei are in these ion pairs smaller by 1−2 orders of magnitude than the values given above in the case of the *o*-dimesitoylbenzene radical anion.[7] Typically for the ion pairs of the naphthalene radical anion in DME at room temperature, the ^{7}Li-, ^{23}Na-, ^{39}K-, ^{85}Rb-, ^{87}Rb-, and ^{133}Cs-coupling constants (absolute values) amounted to <0.01, <0.0405, <0.01, 0.0095, 0.0316, and 0.1071 mT, respectively.[10]

In addition to ESR spectroscopy, the ENDOR technique was successfully applied to studies on ion pairing of some very persistent organic radical anions with alkali-metal cations,[6,11a,12,13] in which case the relative signs of the coupling constants of protons and metal nuclei could be determined by general-TRIPLE resonance.[11b] Absolute signs of these values are accessible by NMR spectroscopy which was also used for such studies,[14] although the high concentration of the radical anion salts required by this method led to some deviations from the corresponding results obtained by ESR and ENDOR spectroscopy.

For a given radical anion, the strength of the association with the counterion depends on several factors, such as the solvating power of the ether, the temperature, and the radius of the cation. The ion pairing tightens and the coupling constant of an alkali-metal nucleus increases with the decreasing solvating power of the ether in the order DME, THF, and MTHF, and also on raising the temperature which reduces this power.[2,3a] The dependence on the radius of the cation is less clear. For tight ion pairs of radical anions containing heteroatoms, the association tends to weaken with the increasing radius of the cation, in the order Li^{+}, Na^{+}, K^{+}, Rb^{+}, and Cs^{+}, because the contact of the counterion with the lone electron pairs of the heteroatom diminishes in the same order. On the other hand, for loose ion pairs of radical anions without heteroatoms, an opposite sequence seems to prevail, as the solvation of the counterion decreases with the increasing radius of the cation.

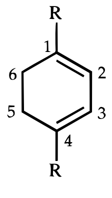
Furthermore, stronger association with the counterion should be favored by the smallness of a π-system in the radical anion. This is because (i) the lower electron affinity of a small π-system is expected to ease a partial retrotransfer of spin and charge to the counterion and (ii) the higher degree of localization of the negative charge in such a system should strengthen the association of the cation with the radical anion. To our knowledge, the radical anion of ethene, a two-center π-system, has not yet been generated in solution. That of buta-1,3-diene (**1**), with two conjugated π-bonds, was produced by electrolytic reduction of **1** at a Pt-wire cathode in liquid ammonia at 195 K;[15] this procedure also worked for 2-methylbuta-1,3-diene (isoprene, **2**), 2,3-dimethylbuta-1,3-diene (**3**), and cyclohexa-1,3-diene (**10**).[16] Moreover, the radical anions of **1** and **3**, as well as that of 1,1,4,4-tetramethylbuta-1,3-diene (**4**) were generated from their neutral precursors in a similar electrolytic cell at the same temperature but with THF replacing liquid ammonia as the solvent.[17] In these experiments, a tetraalkylammonium cation served as the counterion, the nuclei of which did not give rise to additional hyperfine splittings in the ESR spectra.

In general, reaction of buta-1,3-diene and its derivatives with an alkali-metal mirror in an ethereal solvent fails to yield a persistent radical anion, because of rapid polymerization to rubber-like products.[18] This process can, however, be hindered by bulky alkyl substituents. Here, we describe the ESR and ENDOR spectra of the radical anions of 1,4-di-*tert*-butylbuta-1,3-diene (**6**) and 2,3-di-*tert*-butylbuta-1,3-diene (**7**), including the 1,1-dideuterio derivative (**7**-d_2) of the latter compound. These radical anions were obtained by reaction of **6**, **7**, and **7**-d_2 with a potassium, rubidium, or cesium mirror in DME and, mostly, THF at 195 K, and their spectra revealed the presence of hyperfine splittings from the ^{39}K, ^{85}Rb, ^{87}Rb, and ^{133}Cs nuclei which equal or even exceed the values found for the tight ion pairs of the *o*-dimesitoylbenzene radical anion. Also reported are the results for reduction experiments on further alkyl



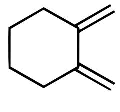
x = *exo*
n = *endo*

	R$_{1x}$	R$_{1n}$	R$_2$	R$_3$	R$_{4x}$	R$_{4n}$
1	H	H	H	H	H	H
2	H	H	Me	H	H	H
3	H	H	Me	Me	H	H
4	Me	Me	H	H	Me	Me
5	H	H	*i*Pr	*i*Pr	H	H
6	*t*Bu	H	H	H	*t*Bu	H
7	H	H	*t*Bu	*t*Bu	H	H
7-d_2	D	D	*t*Bu	*t*Bu	H	H
8	H	*t*Bu	*t*Bu	H	H	H
9	*t*Bu	H	H	*t*Bu	H	H



10 R = H

11 R = *t*Bu



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[7] Such a statement seems to hold generally for radical anions of hydrocarbons in DME or THF as the solvent and particularly for the radical anion of 1,5,8,12- tetra-*tert*-butyl-6,7,13,14-tetradehydro[14]annulene.[8] Only changing to diethyl ether, a solvent of very low solvating power for alkali-metal cations, large hyperfine splittings were observed for the ^{39}K and ^{133}Cs nuclei of the counterions in the ESR spectra of this radical anion.[9] Presumably the counterion is situated there on the 4-fold axis of the π-system, where it closely contacts the radical anion.

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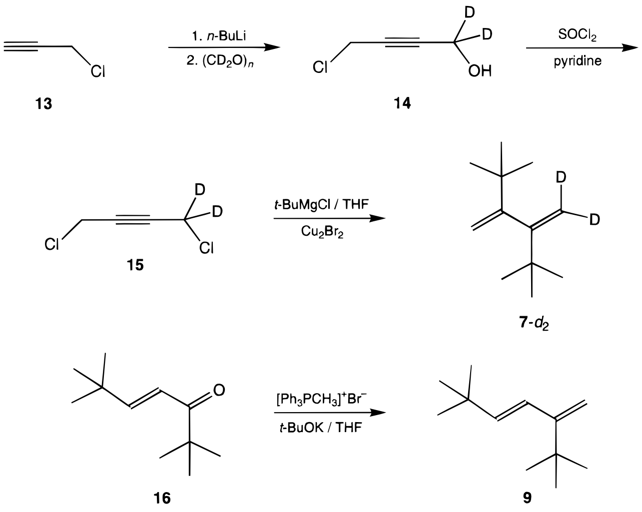
Scheme 1



derivatives of **1** and structurally related dienes, such as **4**, 2,3-diisopropylbuta-1,3-diene (**5**), 1,2-di-*tert*-butylbuta-1,3-diene (**8**), and 1,3-di-*tert*-butylbuta-1,3-diene (**9**), along with 1,4-di-*tert*-butylcyclohexa-1,3-diene (**11**) and 1,2-dimethylenecyclohexane (**12**).

Results

Syntheses. Whereas most of the dienes used in the present work were either commercially available (**4**) or prepared according to methods described in the literature (**5**,[19] **6**,[20] **7**,[19] **8**,[21] **11**[22]), two of them, **7**-d_2 and **9**, had to be synthesized for the present studies as indicated in Scheme 1.

In the synthesis of **7**-d_2, propargyl chloride (**13**) was metalated with *n*-butyllithium and, subsequently, reacted with perdeuterioformaldehyde to give the deuterated propargyl alcohol **14** (53% yield). Chlorination of the latter with thionyl chloride yielded the dichloride **15** (85%), which provided **7**-d_2 (60%) on treatment with *tert*-butylmagnesium chloride in the presence of cuprous bromide.[19]

For the preparation of **9**, the known α,β-unsaturated ketone (**16**)[23] was subjected to a Wittig olefination (83%). The structures of the compounds presented in Scheme 1 were determined by the usual spectroscopic tools (see the Experimental Section).

Generation of Radical Anions. The two methods applied in the present work to the reduction of **4**−**9**, **11**, and **12** were both the "chemical" and the electrolytic ones. The chemical procedure implied the standard reaction with an alkali-metal mirror in DME and THF at 195 K. The electrolytic reduction was carried out on a helical Au/Hg cathode in a cylindrical cell with a Pt-wire anode along its axis at ca. 200 K;[24] THF and *n*-Bu_4NBF_4 served as the solvent and the supporting salt, respectively. In our hands, the chemical procedure was successful in generating the radical anions of **4**, **6**−**8**, and **11**, albeit not with lithium or sodium which had an insufficient reducing power for these compounds of low electron affinity. Of no avail proved the addition of an excess of LiCl or $NaBPh_4$ salt, which aimed at introducing Li^+ or Na^+ as the counterion into the solution of the radical anion obtained by reaction with a potassium mirror in DME. Electrolytic generation of radical anions worked with **5** and **9**, but failed when KO*t*Bu replaced *n*-Bu_4NBF_4 as the supporting salt. Thus, except for **4**, the radical anion of which was also produced electrolytically in a previous work,[17] only one of the two methods met with success for a given compound. It is noteworthy that **6**$^{\bullet-}$ and **7**$^{\bullet-}$ were considerably more persistent than the remaining radical anions of the alkyl-substituted buta-1,3-dienes generated with an alkali-metal mirror in the present work.

1,4-Di-*tert*-butylbuta-1,3-diene (6). Reaction of **6** with a potassium mirror in DME and THF led to a well-resolved ESR spectrum of **6**$^{\bullet-}$ which exhibited an unusually large hyperfine splitting from the ^{39}K nucleus ($I = {}^3/_2$) of the counterion, in addition to those from the two pairs of α-protons in the 1,4- and 2,3-positions and from the 18 γ-protons in the two 1,4-*tert*-butyl substituents.[25] The pertinent coupling constants are $a(^{39}\mathrm{K})$, $a(\mathrm{H}_n\text{-}1,4)$, a(H-2,3), and a(H-*t*Bu), with the subscript n specifying the α-protons in the 1,4-positions as *endo*. (This specification is reasonable, considering the preference of the bulky 1,4-*tert*-butyl substituents for an *exo* conformation; see the Discussion.) The ESR studies were carried out in the range 190−280 K, and the ^{1}H- and ^{39}K-coupling constants could also be determined from the corresponding ENDOR signals, preferably at lower temperatures. An ESR and a ^{1}H/^{39}K-ENDOR spectrum of the ion pair **6**$^{\bullet-}$/K^+ are shown in Figure 1.

Ion pairs **6**$^{\bullet-}$/Rb^+ and **6**$^{\bullet-}$/Cs^+ were likewise formed upon reaction of **6** with a rubidium or cesium mirror in DME and THF. The resolution of the ESR spectra, observed in the same temperature range as those of **6**$^{\bullet-}$/K^+, was less good, so that the small coupling constant a(H-*t*Bu) remained masked by the line width of ca. 0.1 mT. Prominent features of these spectra were the surprisingly large hyperfine splittings from the ^{85}Rb ($I = {}^5/_2$), ^{87}Rb ($I = {}^3/_2$), and ^{133}Cs ($I = {}^7/_2$) nuclei of the counterions. For **6**$^{\bullet-}$/Rb^+, a mixture of the two isotopic species was produced, in which the ratios $[^{85}\mathrm{Rb}]:[^{87}\mathrm{Rb}] = 2.59$ of the concentrations and $|a(^{85}\mathrm{Rb})|:|a(^{87}\mathrm{Rb})| = 0.295$ of the coupling constants agreed with the natural abundance and magnetic moments of the two nuclei. ESR spectra of **6**$^{\bullet-}$/Rb^+ and **6**$^{\bullet-}$/Cs^+ are presented in Figure 2. The quality of the corresponding ^{1}H-ENDOR spectra deteriorated with the increased size of the counterion. While the ENDOR technique applied to **6**$^{\bullet-}$/Rb^+ allowed the $|a(\mathrm{H}\text{-}t\mathrm{Bu})|$ value not available from the ESR spectrum to be determined, it did not provide this information for **6**$^{\bullet-}$/Cs^+. The ENDOR signals from the ^{85}Rb and ^{133}Cs nuclei could be observed, but those from the less abundant ^{87}Rb isotope escaped detection.

The ion pairs **6**$^{\bullet-}$/M^+ (M = K, Rb, Cs) in DME and THF must be classified as tight or contact ones, on account of the large coupling constants of the alkali-metal nuclei. Table 1 lists the hyperfine data for all three ion pairs in both solvents and at several temperatures. Assignments of the coupling constants $a(\mathrm{H}_n\text{-}1,4)$ and a(H-2,3) to α-protons in the individual positions is straightforward, considering the well-known LCAO coefficients of the LUMO of buta-1,3-diene[26] and the results of the previous ESR studies.[15−17] The negative sign of these coupling

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Table 1. Coupling Constants of Protons and Alkali-Metal Nuclei (mT) and *g* Factors for Ion Pairs of the 1,4-Di-*tert*-butylbuta-1,3-diene Radical Anion ($\mathbf{6}^{\bullet-}$) with K$^+$, Rb$^+$, and Cs$^+$

counterion	solvent	temp (K)	a(H$_n$-1,4)	a(H-2,3)	a(H-*t*Bu)			g^a
						a(^{39}K)		2.0028
K^{+b}	DME	200	−0.730	−0.242	+0.026	+0.126		
		220	−0.727	−0.242	+0.026	+0.130		
		250	−0.717	−0.241	+0.026	+0.135		
		270	−0.715	−0.240	+0.026	+0.136		
	THF	190	−0.734	−0.244	+0.026	+0.127		
		220	−0.723	−0.243	+0.025	+0.131		
		250	−0.711	−0.242	+0.025	+0.138		
		280	−0.701	−0.237	+0.025	+0.146		
						a(^{85}Rb)	a(^{87}Rb)	2.0036
Rb^{+b}	DME	200	−0.753	−0.242	+0.027	+0.405	+1.38	
		240	−0.740	−0.242	+0.026	+0.495	+1.67	
	THF	200	−0.746	−0.244	+0.025	+0.525	+1.78	
		240	−0.722	−0.237	+0.025	+0.567	+1.92	
		280	−0.713	−0.231	+0.025	+0.620	+2.11	
						a(^{133}Cs)		2.0056
Cs^{+c}	DME	200	−0.73	−0.24	<0.03	+0.70		
		240	−0.72	−0.23	<0.03	+0.80		
	THF	200	−0.76	−0.23	<0.03	+0.78		
		240	−0.74	−0.23	<0.03	+0.92		
		280	−0.73	−0.22	<0.03	+0.99		

[a] Experimental error ±0.0001. [b] Experimental error ±0.004 mT in a(H$_n$-1,4) and a(^{85}Rb), ±0.002 mT in a(H-2,3) and a(^{39}K), ±0.001 mT in a(H-*t*Bu), and ±0.01 mT in a(^{87}Rb). [c] Experimental error ±0.01 mT in a(H) and a(^{133}Cs).

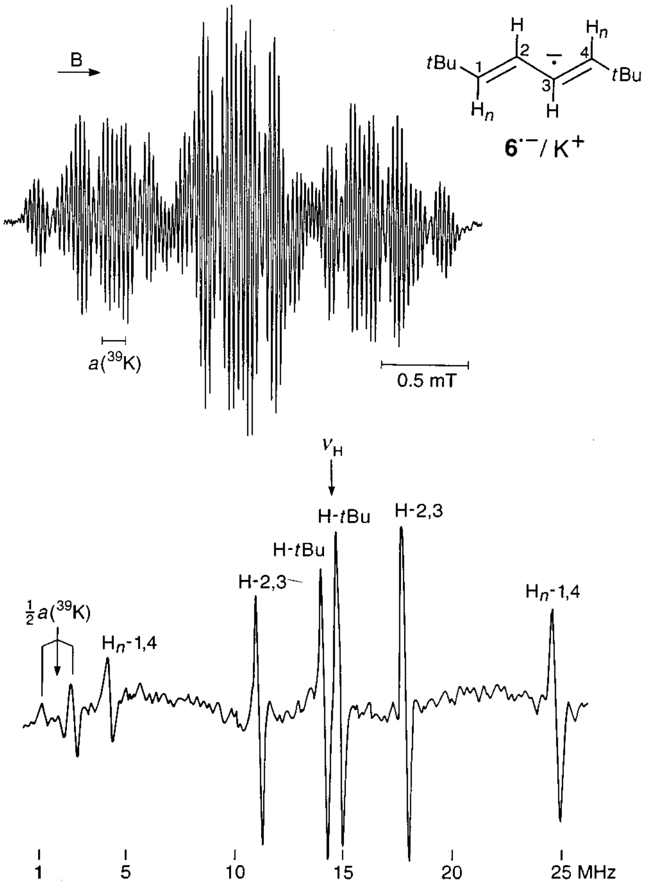

Figure 1. ESR (top) and ^{1}H/^{39}K-ENDOR spectrum (bottom) of $\mathbf{6}^{\bullet-}$/K$^+$. Solvent DME, temperature 200 K. For the structural formula, see the Discussion.

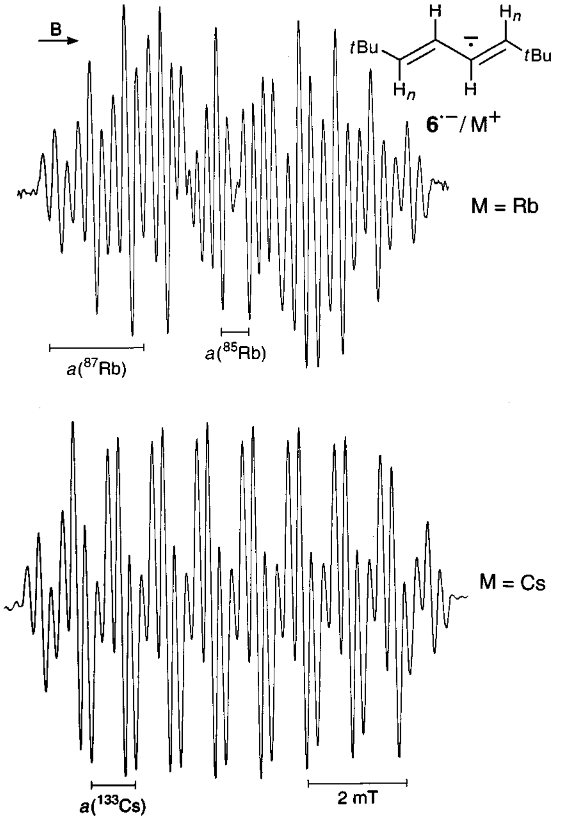

Figure 2. ESR spectra of $\mathbf{6}^{\bullet-}$/Rb$^+$ (top) and $\mathbf{6}^{\bullet-}$/Cs$^+$ (bottom). Solvent THF, temperature 240 K. For the structural formula, see the Discussion.

constants is required for α-protons by theory,[3b] and it is in line with the decrease in their absolute values at higher temperatures. According to the general-TRIPLE resonance experiments, carried out on the ENDOR signals of $\mathbf{6}^{\bullet-}$/K$^+$ (Figure 1), the sign of the coupling constants a(H-*t*Bu) and a(^{39}K) is opposite that of a(H$_n$-1,4) and a(H-2,3); i.e., it is positive. This sign complies with the pronounced increase in $|a(^{39}\mathrm{K})|$ upon raising the temperature,[2] and it must likewise be allotted to a(^{85}Rb), a(^{87}Rb), and a(^{133}Cs) which also exhibited such a behavior. The *g* factor of $\mathbf{6}^{\bullet-}$/M$^+$ (Table 1) increased with the growing size of the alkali-metal cation, but varied only within the experimental error of ±0.0001 on raising the temperature or changing from DME to THF.

2,3-Di-*tert*-butylbuta-1,3-diene (7). Reaction of **7** with a potassium mirror in DME generated $\mathbf{7}^{\bullet-}$, but it failed to this end in THF. The ESR spectrum observed at 195 K is shown at the center of Figure 3. Apart from a multiline pattern with

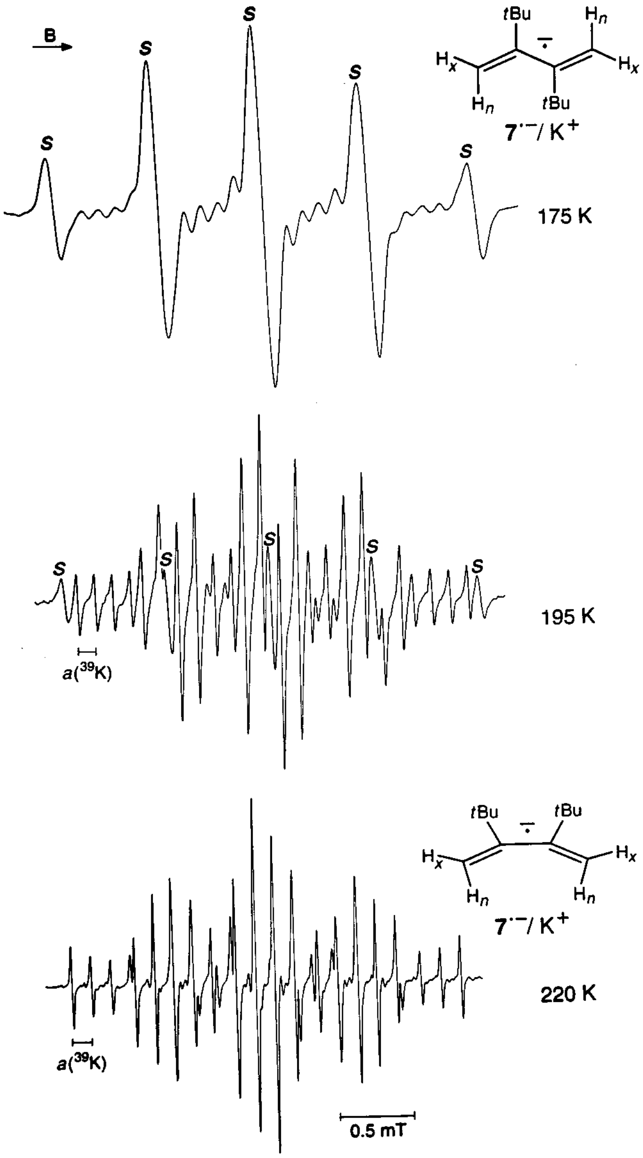

Figure 3. ESR spectra of **7**$^{\bullet-}$/K$^+$. Solvent DME, temperature as indicated. The lines due to the loose or solvent-separated ion pair are marked by ***s***. For the structural formulas, see the Discussion.

a ^{39}K-hyperfine splitting comparable to that observed for the ion pair **6**$^{\bullet-}$/K$^+$, it exhibited five broad equidistant lines marked ***s***. While these lines became overwhelmingly dominant upon undercooling the solution to 175 K (Figure 3, top), they disappeared when the temperature was raised to 220 K (Figure 3, bottom). Their binomial distribution of intensity qualifies them as arising from the four α-protons in both 1,4-*exo*-(*x*) and *endo*-(*n*) positions with $|a(\mathrm{H}_x\text{-}1,4)| \approx |a(\mathrm{H}_n\text{-}1,4)| = 0.71$ mT.[25] There were no observable splittings from the 18 γ-protons in the two 2,3-*tert*-butyl substituents nor from the ^{39}K nucleus of the counterion. The absence of a detectable ^{39}K-hyperfine splitting and the rapid decrease in intensity of the five lines ***s*** on raising the temperature justify their attribution to a loose or solvent-separated ion pair **7**$^{\bullet-}$/K$^+$. In contrast, the multiline spectrum, which exhibited a substantial ^{39}K-hyperfine splitting and which was the only one present at 220−260 K, is diagnostic of a tight or contact ion pair **7**$^{\bullet-}$/K$^+$. It is important to note that, for this ion pair, the set of four α-protons in the 1,4-positions with virtually the same coupling constant separated into two sets of two with strongly differing absolute values: one of them was reduced from ca. 0.7 mT, characteristic of such protons in the buta-1,3-diene radical anions, to ca. 0.4 mT. As indicated by the corresponding ESR spectra observed for the radical anion of 1,1-dideuterio-2,3-di-*tert*-butylbuta-1,3-diene (**7**-*d*$_2$) and described below, the *exo*- and *endo*-protons have now greatly different coupling constants. Following the arguments presented in the Discussion, the coupling constant with the reduced absolute value is assigned to the two *endo*-protons, $a(\mathrm{H}_n\text{-}1,4)$, leaving that with the "normal" value for the two *exo*-protons, $a(\mathrm{H}_x\text{-}1,4)$. The hyperfine splitting from the 18 γ-protons in the 2,3-*tert*-butyl substituents remained also unresolved in the ESR spectrum of the tight ion pair, i.e., $|a(\mathrm{H}\text{-}t\mathrm{Bu})| < 0.02$ mT.

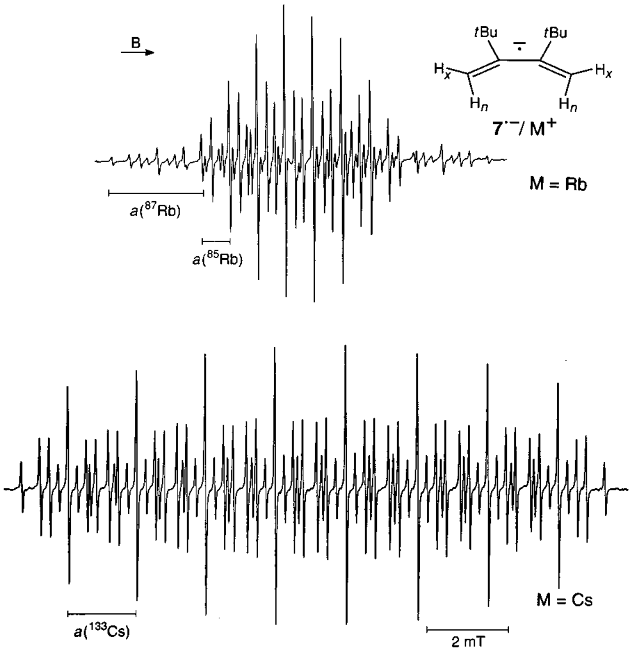

Figure 4. ESR spectra of **7**$^{\bullet-}$/Rb$^+$ (top) and **7**$^{\bullet-}$/Cs$^+$ (bottom). Solvent DME (top) and THF (bottom), temperature 220 (top) and 210 (bottom) K. For the structural formula, see the Discussion.

With the use of a rubidium mirror for the reduction of **7**, the radical anion could also be generated only in DME, while both DME and THF were appropriate solvents for the reaction of **7** with a cesium mirror. A rather persistent ion pair **7**$^{\bullet-}$/Cs$^+$ was produced by this reaction in THF, and its ESR spectra were studied up to high temperatures. With either rubidium (170−260 K) or cesium (150−320 K), loose ion pairs were no longer observed, even at the lowest temperatures, so that all ESR spectra had to be exclusively attributed to tight ion pairs **7**$^{\bullet-}$/Rb$^+$ and **7**$^{\bullet-}$/Cs$^+$. Examples of these spectra are shown in Figure 4, while Figure 5 reproduces the corresponding ENDOR signals from the α-protons and the alkali-metal nuclei. In addition, Figure 5 presents the ENDOR signals from the α-protons in the tight ion pair **7**$^{\bullet-}$/K$^+$; those from the ^{39}K nuclei could not be unequivocally spotted in this case. The small coupling constant $a(\mathrm{H}\text{-}t\mathrm{Bu})$ also escaped detection in the ESR spectra of **7**$^{\bullet-}$/Rb$^+$ and **7**$^{\bullet-}$/Cs$^+$, and the ENDOR signals from the pertinent γ-protons were not apparent for any of the ion pairs. A mixture of the two isotopic species was again observed for **7**$^{\bullet-}$/Rb$^+$ with the expected relative concentrations and the due ratio $|a(^{85}\mathrm{Rb})|:|a(^{87}\mathrm{Rb})|$. The hyperfine splittings from the ^{85}Rb, ^{87}Rb, and ^{133}Cs nuclei were considerably larger for **7**$^{\bullet-}$/Rb$^+$ and **7**$^{\bullet-}$/Cs$^+$ than for **6**$^{\bullet-}$/Rb$^+$ and **6**$^{\bullet-}$/Cs$^+$ under the same conditions. Consequently, these splittings dominated the ESR spectra of the former ion pairs (Figure 4) even more than those of the latter (Figure 2). Due to the extremely large coupling constant $a(^{133}\mathrm{Cs})$, the ESR spectrum of **7**$^{\bullet-}$/Cs$^+$ in THF at 320

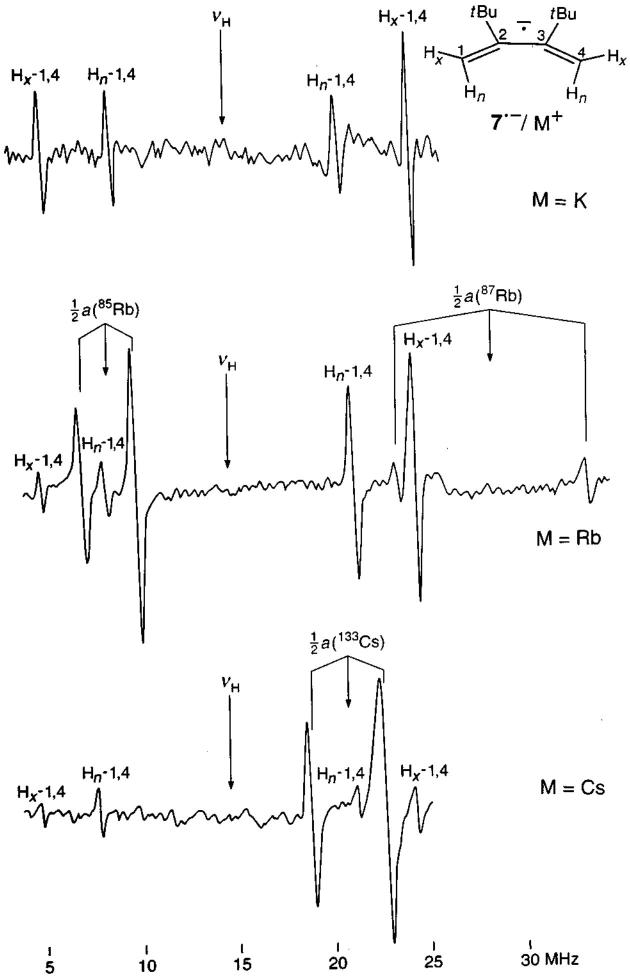

Figure 5. ^{1}H-(top), ^{1}H/^{85,87}Rb-(center), and ^{1}H/^{133}Cs-(bottom) ENDOR spectra of **7**$^{\bullet-}$/K$^+$, **7**$^{\bullet-}$/Rb$^+$, and **7**$^{\bullet-}$/Cs$^+$, respectively. Solvent DME, temperature 220 (top) and 200 (center and bottom) K. For the structural formula, see the Discussion.

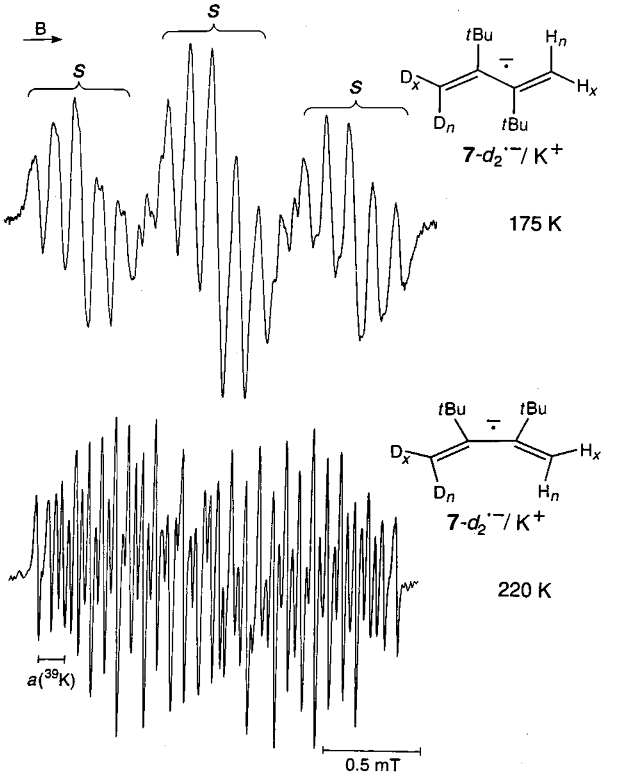

Figure 6. ESR spectra of **7**-$d_2^{\bullet-}$/K$^+$. Solvent DME, temperature as indicated. The lines due to the loose or solvent-separated ion pair are marked by ***s***. For the structural formulae, see the Discussion.

K extended over 20 mT, an unusually large width for an organic radical anion. The ^{1}H-hyperfine patterns of **7**$^{\bullet-}$/Rb$^+$ and **7**$^{\bullet-}$/Cs$^+$ resembled that of the tight ion pair **7**$^{\bullet-}$/K$^+$, with $|a(H_n\text{-}1,4)|$ being considerably smaller than $|a(H_x\text{-}1,4)|$.

On passing from **7**$^{\bullet-}$ to **7**-$d_2^{\bullet-}$, dideuterated in the 1-position, coupling constants of two α-protons were replaced by those of deuterons as was to be expected. For the loose ion pair, also present with K$^+$ in DME below 200 K, the five lines ***s*** from four quasi-equivalent α-protons with $|a(H_x\text{-}1,4)| \approx |a(H_n\text{-}1,4)| = 0.71$ mT were substituted in the ESR spectrum **7**-$d_2^{\bullet-}$/K$^+$ by three lines due to the same coupling constant $|a(H_x\text{-}4)| \approx |a(H_n\text{-}4)|$, now arising from two α-protons only; each of these lines was split into five by two α-deuterons with $|a(D_x\text{-}1)| \approx |a(D_n\text{-}1)| = 0.11$ mT. For the tight ion pairs **7**-$d_2^{\bullet-}$/K$^+$ and **7**-$d_2^{\bullet-}$/Rb$^+$ in DME, as well as for **7**-$d_2^{\bullet-}$/Cs$^+$ in DME and THF, the hyperfine pattern from the two sets of two α-protons with the strongly differing coupling constants changed into that stemming from two single α-protons and two single α-deuterons. With the larger absolute values assigned to the *exo*- and the smaller to the *endo*-positions (see the Discussion), the coupling constants $|a(H_x\text{-}1,4)| \approx 0.7$ and $|a(H_n\text{-}1,4)| \approx 0.4$ mT were thus replaced by $|a(H_x\text{-}4)| \approx 0.7$, $|a(H_n\text{-}4)| \approx 0.4$, $|a(D_x\text{-}1)| \approx 0.11$, and $|a(D_n\text{-}1)| \approx 0.06$ mT. Figure 6 presents ESR spectra of the loose (top) and tight ion pairs **7**-$d_2^{\bullet-}$/K$^+$ (bottom). Those of **7**-$d_2^{\bullet-}$/Rb$^+$ and **7**-$d_2^{\bullet-}$/Cs$^+$ are not shown here; they correspond exactly to the spectra of their undeuterated counterparts in Figure 4, when consideration is given to the above replacements.

Table 2 lists the hyperfine data for the α-protons and alkali-metal nuclei in **7**$^{\bullet-}$/K$^+$ and **7**$^{\bullet-}$/Rb$^+$ in DME and **7**$^{\bullet-}$/Cs$^+$ in DME and THF at several temperatures. Allotment of a negative sign to $a(H_x\text{-}1,4)$ and $a(H_n\text{-}1,4)$ and a positive one to $a(^{39}K)$, $a(^{85}Rb)$, $a(^{87}Rb)$, and $a(^{133}Cs)$ is justified by the same arguments as those presented above for the corresponding coupling constants in the ion pairs of **6**$^{\bullet-}$. Whereas the decrease in $|a(H_x\text{-}1,4)|$ for **7**$^{\bullet-}$/M$^+$ (M = K, Rb, Cs) on raising the temperature was comparable to that in $|a(H_n\text{-}1,4)|$ for **6**$^{\bullet-}$/M$^+$, the concomitant fall of $|a(H_n\text{-}1,4)|$ for **7**$^{\bullet-}$/M$^+$ was much steeper, as was the increase in the coupling constants of the alkali-metal nuclei. Thus, for **7**$^{\bullet-}$/Cs$^+$ in THF, $a(H_n\text{-}1,4)$ and $a(^{133}Cs)$ changed from -0.51 and $+1.15$ mT at 150 K to -0.39 and $+2.57$ mT, respectively, at 320 K. As in the case of **6**$^{\bullet-}$/M$^+$, the *g* factor of **7**$^{\bullet-}$/M$^+$ depended more distinctly on the counterion M$^+$ than on the solvent and temperature. Such a dependence was, however, less pronounced for **7**$^{\bullet-}$/M$^+$ than for **6**$^{\bullet-}$/M$^+$, and in contrast to **6**$^{\bullet-}$/M$^+$, the *g* factor of **7**$^{\bullet-}$/M$^+$ decreased with the growing size of the alkali-metal counterion. The difference in *g* factor of the loose and tight ion pairs **7**$^{\bullet-}$/K$^+$ was smaller than the experimental error of ±0.0001. Actually, as is evident from the spectrum taken at 195 K with both pairs coexisting (Figure 2, center), the *g* factor of the loose ion pair was larger by 0.000 03 than that of the tight one.

1,1,4,4-Tetramethylbuta-1,3-diene (4). Upon reaction of **4** with a potassium mirror in DME, a low-intensity ESR spectrum of **4**$^{\bullet-}$ appeared ($g = 2.0027 \pm 0.0001$) showing two coupling constants, $|a(H_x\text{-Me})| = 0.95$ and $|a(H_n\text{-Me})| = 0.86$ mT, each for the six methyl *β*-protons in the *exo*- or *endo*-positions of the 1,4-substituents, and $|a(H\text{-}2,3)| = 0.13$ mT for the two α-protons[25] (experimental error ±0.01 mT). A hyperfine splitting from the ^{39}K nucleus of the counterion was not

Table 2. Coupling Constants of Protons and Alkali-Metal Nuclei (mT) and g Factors for Ion Pairs of the 2,3-Di-*tert*-butylbuta-1,3-diene Radical Anion ($\mathbf{7}^{\bullet -}$) with K$^+$, Rb$^+$, and Cs$^+$

counterion	solvent	temp (K)	a(H$_x$-1,4)	a(H$_n$-1,4)			g^a
					$a(^{39}\mathrm{K})$		2.0027
K$^{+\,b}$	DME	175	*−0.71*	*−0.71*	<0.02		
K$^{+\,c}$	DME	195	−0.695	−0.445	+0.119		
		220	−0.686	−0.428	+0.134		
		240	−0.678	−0.414	+0.144		
		260	−0.672	−0.398	+0.155		
					$a(^{85}\mathrm{Rb})$	$a(^{87}\mathrm{Rb})$	2.0024
Rb$^{+\,c}$	DME	170	−0.709	−0.472	+0.483	+1.64	
		200	−0.697	−0.456	+0.597	+2.01	
		220	−0.689	−0.441	+0.683	+2.32	
		240	−0.680	−0.423	+0.767	+2.59	
		260	−0.677	−0.411	+0.840	+2.84	
					$a(^{133}\mathrm{Cs})$		2.0017
Cs$^{+\,d}$	DME	200	−0.70	−0.48	+1.46		
		220	−0.69	−0.46	+1.59		
		240	−0.68	−0.45	+1.65		
	THF	150	−0.72	−0.51	+1.15		
		180	−0.70	−0.49	+1.40		
		210	−0.69	−0.47	+1.68		
		240	−0.69	−0.44	+1.92		
		270	−0.67	−0.42	+2.19		
		300	−0.65	−0.39	+2.47		
		320	−0.65	−0.39	+2.57		

[a] Experimental error ±0.0001. [b] The a(H) values (italic) in this line refer to a loose ion pair; experimental error ±0.01 mT. [c] Experimental error ±0.004 mT in a(H) and $a(^{85}\mathrm{Rb})$, ±0.002 mT in $a(^{39}\mathrm{K})$, and ±0.01 mT in $a(^{87}\mathrm{Rb})$. [d] Experimental error ±0.01 mT in a(H) and $a(^{133}\mathrm{Cs})$.

observed (<0.02 mT). Use of rubidium and cesium as the reducing agents failed to yield an ESR spectrum of $\mathbf{4}^{\bullet -}$, presumably because of polymerization.

2,3-Diisopropylbuta-1,3-diene (5) and 1,3-Di-*tert*-butylbuta-1,3-diene (9). Reaction of **5** and **9** with an alkali-metal mirror caused polymerization, but ESR spectra of $\mathbf{5}^{\bullet -}$ and $\mathbf{9}^{\bullet -}$ were observed upon electrolytic reduction in THF. For $\mathbf{5}^{\bullet -}$ (g = 2.0027 ± 0.0001), the hyperfine pattern was due to $|a(\mathrm{H}_x\text{-1,4})| \approx |a(\mathrm{H}_n\text{-1,4})| = 0.71$ mT for the four α-protons and $|a(\mathrm{H}\text{-}i\mathrm{Pr})| = 0.14$ mT for the two methine β-protons in the 2,3-isopropyl substituents (experimental error ±0.01 mT). The ESR spectrum of $\mathbf{9}^{\bullet -}$ (g = 2.0025 ± 0.0001) exhibited coupling constants of the four α-protons with two of them having indistinguishable values. Assignments are made in terms of $|a(\mathrm{H}_x\text{-4})| = 0.83$, $|a(\mathrm{H}_n\text{-1})| \approx |a(\mathrm{H}_n\text{-4})| = 0.61$ and $|a(\mathrm{H}\text{-2})| = 0.19$ mT (experimental error ±0.02 mT). Hyperfine splittings from the γ-protons in the 2,3-isopropyl and the 1,4-*tert*-butyl substituents of $\mathbf{5}^{\bullet -}$ (<0.02 mT) and $\mathbf{9}^{\bullet -}$ (<0.03 mT), respectively, were unresolved.

1,2-Di-*tert*-butylbuta-1,3-diene (8). The radical anion $\mathbf{8}^{\bullet -}$ was generated from **8** by reaction with a potassium, rubidium, or cesium mirror in DME. As in the case of $\mathbf{9}^{\bullet -}$, the ESR spectrum of $\mathbf{8}^{\bullet -}$ (g = 2.0026 ± 0.0001) showed the coupling constants of the four α-protons, one value of which was the same for two protons within the spectral resolution (experimental error ±0.02 mT). Tentative assignments are $|a(\mathrm{H}_x\text{-1})| = 0.89$, $|a(\mathrm{H}_x\text{-4})| \approx |a(\mathrm{H}_n\text{-4})| = 0.69$ and $|a(\mathrm{H}\text{-3})| = 0.31$ mT. γ-Protons in the 1,2-*tert*-butyl substituents and the ^{39}K nucleus of the counterion did not give rise to resolvable hyperfine splittings (<0.03 mT). On the other hand, the two Rb isotopes and the ^{133}Cs nucleus had observable coupling constants $|a(^{85}\mathrm{Rb})| = 0.11$, $|a(^{87}\mathrm{Rb})| = 0.37$, and $|a(^{133}\mathrm{Cs})| = 0.36$ mT.

1,4-Di-*tert*-butylcyclohexa-1,3-diene (11). Reaction of **11** with a potassium or rubidium mirror in DME led to an ESR spectrum of $\mathbf{11}^{\bullet -}$ (g = 2.0028 ± 0.001) with two coupling constants, $|a(\mathrm{H}_{ax}\text{-5,6})| = 1.23$ and $|a(\mathrm{H}_{eq}\text{-5,6})| = 0.95$ mT, each for the two methylene β-protons in their quasi-axial and quasi-equatorial positions, and $|a(\mathrm{H}\text{-2,3})| = 0.20$ mT for the two α-protons (experimental error ±0.02 mT). The values 1.23 and 0.95 mT tended to an average $|a(\mathrm{H}\text{-5,6})| = 1.08$ mT upon raising the temperature from 195 to 240 K. Hyperfine splittings from the γ-protons of the 1,4-*tert*-butyl substituents and from the ^{39}K nucleus of the counterion were not perceivable (<0.03 mT), but the two Rb isotopes gave rise to detectable coupling constants, $|a(^{85}\mathrm{Rb})| = 0.040$ and $|a(^{87}\mathrm{Rb})| = 0.136$ mT. With cesium as the reducing agent, the ESR spectrum of the radical anion of 1,4-di-*tert*-butylbenzene was observed,[27] due to the "aromatization" of the six-membered ring.

1,2-Dimethylenecyclohexane (12). Both reaction with a potassium mirror in DME and electrolytic reduction in THF failed to yield the radical anion $\mathbf{12}^{\bullet -}$.

Discussion

Table 3 summarizes the hyperfine data for the hitherto studied radical anions of buta-1,3-diene (**1**) and its alkyl derivatives **2**−**9**, including those of structurally related cyclohexa-1,3-diene (**10**) and its 1,4-di-*tert*-butyl derivative (**11**). All data refer to α- and β-protons, while the small coupling constants of the γ-protons (which were determined only for $\mathbf{6}^{\bullet -}$) are omitted.[25] Use is made of low-temperature values (175−220 K) and, for the radical anions generated with alkali metals, only of one solvent (DME) and one counterion (K$^+$). The signs of the coupling constants are those required by theory.[3b]

With one notable exception discussed below (−0.43 mT for $\mathbf{7}^{\bullet -}$ at 220 K), the coupling constants of the α-protons, H$_x$ and H$_n$, in the 1,4-*exo*- and -*endo*-positions lie between −0.61 and −0.89 mT, while those of the β-protons in the alkyl groups attached to these positions range between +0.86 and +1.23 mT. The α-protons in the 2,3-positions have values of −0.12 to −0.31 mT, while the β-protons in the 2,3-substituents give rise to coupling constants of +0.12 to +0.34 mT. Apart from $\mathbf{6}^{\bullet -}$ and $\mathbf{7}^{\bullet -}$, extremely large hyperfine splittings from the alkali-metal nuclei of the counterions were in no case observed. This statement holds, in particular for $\mathbf{8}^{\bullet -}$ and $\mathbf{11}^{\bullet -}$ which have likewise two *tert*-butyl substituents and could also be generated

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[27] Gerson, F.; Heckendorn, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 556−557.

Table 3. Coupling Constants of α- and β-Protons and ^{39}K Nuclei, *a*(H) and *a*(^{39}K) (mT) for the Radical Anions of Buta-1,3-diene (**1**), Its Alkyl Derivatives **2**−**9**, Cyclohexa-1,3-diene (**10**), and Its 1,4-Di-*tert*-butyl Derivative (**11**)

	solvent	counterion	temp (K)	*a*(H_x-1)	*a*(H_n-1)	*a*(H-2)	*a*(H-3)	*a*(H_x-4)	*a*(H_n-4)	*a*(^{39}K)	ref
$\mathbf{1}^{\bullet-}$	NH_3	Me_4N^+	195	−0.76	−0.76	−0.28	−0.28	−0.76	−0.76		15
	THF	Bu_4N^+	197	−0.77	−0.77	−0.27	−0.27	−0.77	−0.77		17
$\mathbf{2}^{\bullet-}$	NH_3	Me_4N^+	195	−0.79	−0.65[a]	+0.34[b]	−0.31	−0.79[a]	−0.65		16
$\mathbf{3}^{\bullet-}$	NH_3	Me_4N^+	195	−0.72	−0.70	+0.12[b]	+0.12[b]	−0.72	−0.70		16
$\mathbf{4}^{\bullet-}$	THF	Bu_4N^+	197	+0.99[b]	+0.88[b]	−0.12	−0.12	+0.99[b]	+0.88[b]		17
	DME	K^+	195	+0.95[b]	+0.86[b]	−0.13	−0.13	+0.95[b]	+0.86[b]	<0.02	this work
$\mathbf{5}^{\bullet-}$	THF	Bu_4N^+	200	−0.71	−0.71	+0.14[c]	+0.14[c]	−0.71	−0.71		this work
$\mathbf{6}^{\bullet-}$	DME	K^+	200	*d*	−0.73	−0.24	−0.24	*d*	−0.73	+0.13	this work
$\mathbf{7}^{\bullet-}$	DME	K^+	175	−0.71	−0.71	*d*	*d*	−0.71	−0.71	<0.02	this work
	DME	K^+	220	−0.69	−0.43	*d*	*d*	−0.69	−0.43	+0.13	this work
$\mathbf{8}^{\bullet-}$	DME	K^+	200	−0.89[e]	*d*	*d*	−0.31	−0.69[e]	−0.69	<0.03	this work
$\mathbf{9}^{\bullet-}$	THF	Bu_4N^+	210	*d*	−0.61	−0.19	*d*	−0.83	−0.61		this work
$\mathbf{10}^{\bullet-}$	NH_3	Me_4N^+	195	−0.82	+1.11[f]	−0.20	−0.20	−0.82	+1.11[f]		16
$\mathbf{11}^{\bullet-}$	DME	K^+	200	*d*	+1.23[g] +0.95[g]	−0.20	−0.20	*d*	+1.23[g] +0.95[g]	<0.03	this work

[a] Assignment different from that in ref 16. [b] Methyl protons. [c] Isopropyl CH-protons. [d] Substituted by *tert*-butyl groups. [e] Tentative assignment. [f] Four 5,6-CH_2-protons. [g] Two 5,6-CH_2-protons.

with an alkali-metal mirror. Although the ion pairs formed by **8**$^{\bullet-}$ with Rb^+ and Cs^+ and by **11**$^{\bullet-}$ with Rb^+ exhibited hyperfine splittings from alkali-metal nuclei, the pertinent coupling constants were considerably smaller than those observed for the corresponding ion pairs of **6**$^{\bullet-}$ and **7**$^{\bullet-}$. One is, therefore, confronted with the question of which structural features predestinate **6**$^{\bullet-}$ and **7**$^{\bullet-}$ for the formation of such ion pairs with the unusually large hyperfine splittings from the alkali-metal nuclei of the counterions. These features should also make the two radical anions markedly more persistent than those of buta-1,3-diene and its other alkyl derivatives. Taking into account the variety of steric and electronic interactions between the radical anions substituted by the bulky *tert*-butyl groups, the cations of heavy alkali metals, and the molecules of the ethereal solvent, the answer to the above question on the structure of the tight ion pairs of **6**$^{\bullet-}$ and **7**$^{\bullet-}$ is, by no means, a trivial task, even with the use of a sophisticated MO theory. In such circumstances, the following sections represent an attempt to describe this structure with some aid of semiempirical calculations. As the interest is largely focused on the preferred conformations of the radical anions, their absolute energies are less relevant. Thus, the AM1 method[28] was used, because it has proved to be reliable for predicting the geometry of radical ions,[29] although it may be less appropriate for reproducing exactly the absolute energies.[30]

Prior to considering the conformations of **6**$^{\bullet-}$ and **7**$^{\bullet-}$, one has to recall that, in any case, the LUMO of buta-1,3-diene is bonding between C(2) and C(3), so that this bond should be considerably strengthened on passing from the neutral molecule to its radical anion. With the counterion situated in the antinode between the π-centers 2 and 3 (see below), a direct transfer of the spin population from the singly occupied MO of the radical anions of buta-1,3-diene and its alkyl derivatives into the alkali-metal *n*s-AO ($n = 3$, 4, and 5 for K, Rb, and Cs, respectively) is allowed by symmetry; such a delocalization of the spin population complies with the positive sign allotted to the coupling constants *a*(^{39}K), *a*(^{85}Rb), *a*(^{87}Rb), and *a*(^{133}Cs). The amount of population transferred to the counterion is comparable for all threee cations K^+, Rb^+, and Cs^+, as the pertinent coupling constants are roughly proportional to the atomic parameters for a unit spin in the *n*s-AOs of K, Rb, and Cs.[31] Therefore, the structure of the ion pairs of **6**$^{\bullet-}$ and **7**$^{\bullet-}$ should not essentially alter on passing from one counterion to another.

Structure of the Ion Pairs of 6$^{\bullet-}$**.** According to calculations by molecular mechanics (MM3) and *ab initio* method (HF/3-21G) carried out in a previous work on the neutral 1,4-di-*tert*-butylbuta-1,3-diene (**6**),[32] the energy profile of **6** as a function of the dihedral angle C═C−C═C (φ) closely follows that of the parent buta-1,3-diene (**1**). The preferred conformation is clearly *trans* ($\varphi = 180°$) with the space demanding *tert*-butyl substituents in the sterically unhindered *exo*-positions. This geometry of **6** is confirmed by AM1 calculations performed in the present work, which also predict that it should be retained in the radical anion **6**$^{\bullet-}$ (Figure 7, top). Moreover, due to the strengthening of the C(2)−C(3) bond on passing from **6** to **6**$^{\bullet-}$, the barrier to rotation about this bond is drastically enhanced. Although the AM1 calculations hold for an “isolated” radical anion **6**$^{\bullet-}$, it is improbable that the tightly paired one, **6**$^{\bullet-}$/M^+ (M = K, Rb, Cs), would adopt a markedly different geometry. The alkali-metal counterion M^+ should be situated on the 2-fold symmetry axis above or below the molecular plane (Figure 7, bottom). Such a structure of C_2 symmetry is consistent with the hyperfine data for **6**$^{\bullet-}$/M^+.

Structure of the Ion Pairs of 7$^{\bullet-}$**.** MM3 and HF/3-21G calculations were also previously carried out on the neutral 2,3-di-*tert*-butylbuta-1,3-diene (**7**),[32,33] and the predicted geometry of **7** agreed with the results of an electron diffraction study.[33] Both theory and experiment point to an almost perpendicular orientation of the two $H_2C{=}CtBu$ moieties. This geometry is also obtained by AM1 calculations which yield substantial energy barriers separating the perpendicular conformation ($\varphi \approx 100°$ or 260°) from the planar *trans* ($\varphi = 180°$) and *cis* ($\varphi = 0°$ or 360°) ones (Figure 8, top). On passing from the neutral **7** to its radical anion **7**$^{\bullet-}$, the molecule should flatten, because of the strengthening of the C(2)−C(3) bond. Indeed, AM1 calculations on **7**$^{\bullet-}$ yield an energy profile which strongly differs from that of **7**. The perpendicular conformation is no longer the preferred one, as the two energy minima at $\varphi \approx 100°$ or 260° are replaced by those at $\varphi \approx 135°$ or 225° and at $\varphi \approx$

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(28) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

(29) See, e. g.: Gerson, F.; Schmidlin R.; de Meijere, A.; Späth, T. *J. Am. Chem. Soc.* **1995**, *117*, 8431−8434.

(30) It follows from the AM1 calculations on the preferred conformations of buta-1,3-dienes and their radical anions that the heats of formation, ΔH_f, for **1**$^{\bullet-}$ and **6**$^{\bullet-}$ are less positive than for **1** and **6** by 17 and 38 kJ mol^{-1}, respectively, while the corresponding value for **7**$^{\bullet-}$ is more positive than for **7** by 10 kJ mol^{-1}.

(31) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577−582.

(32) Trætteberg, M.; Bakken, P.; Hopf, H.; Hänel, R. *Chem. Ber.* **1994**, *127*, 1469−1478.

(33) Trætteberg, M.; Hopf, H.; Lipka, H.; Hänel, R. *Chem. Ber.* **1994**, *127*, 1459−1467.

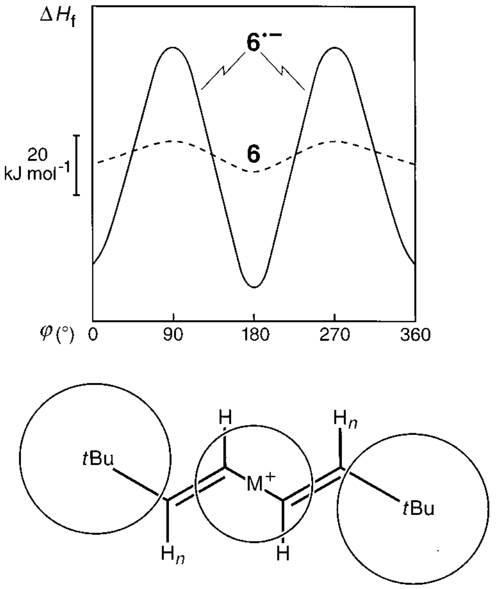

Figure 7. Top: Relative heats of formation, ΔH_f , vs the dihedral angle C═C—C═C, φ, calculated by the AM1 method for 1,4-di-*tert*-butylbuta-1,3-diene (**6**, dotted line) and its isolated radical anion ($\mathbf{6}^{\bullet-}$, full line). Bottom: Structural model of the tight or contact ion pair $\mathbf{6}^{\bullet-}$/M$^+$ (M = K, Rb, Cs).

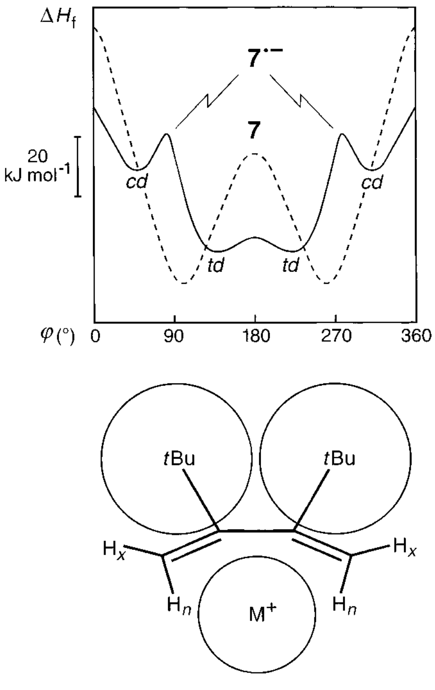

Figure 8. Top: Relative heats of formation, ΔH_f, vs the dihedral angle C═C—C═C, φ, calculated by the AM1 method for 2,3-di-*tert*-butylbuta-1,3-diene (**7**, dotted line) and its isolated radical anion ($\mathbf{7}^{\bullet-}$, full line); *td* = *transoid* and *cd* = *cisoid* conformation. Bottom: Structural model of the tight or contact ion pair $\mathbf{7}^{\bullet-}$/M$^+$ (M = K, Rb, Cs).

45° or 315°, denoted as *transoid* (*td*) and *cisoid* (*cd*) conformations, respectively (Figure 8, top). In both of them, the C_2 symmetry is consistent with the hyperfine data for $\mathbf{7}^{\bullet-}$/M$^+$; the counterion M$^+$ must again be situated on the 2-fold symmetry axis. For an "isolated" radical anion $\mathbf{7}^{\bullet-}$, considered in the AM1 calculations, the *transoid* conformation is energetically favored over the *cisoid* one (Figure 8, top). One is tempted to assume that this statement also holds for the radical anion in the loose or solvent-separated ion pair $\mathbf{7}^{\bullet-}$/K$^+$, the ESR spectrum of which predominates in DME at 175 K. On the other hand, the *cisoid* conformation should be favored for the radical anion in the tight or contact ion pairs of $\mathbf{7}^{\bullet-}$ which prevail above 210 K with K$^+$ and throughout the whole temperature range of investigation with Rb$^+$ and Cs$^+$ as the counterion. This is because the *cisoid* conformation places the two bulky *tert*-butyl substituents on "one side" of the molecule, so that the alkali-metal counterion can closely approach the radical anion from "the other side" (Figure 8, bottom). Moreover, in this conformation, the striking reduction in the absolute value of $a(\mathrm{H}_n\text{-}1,4)$ for the tight ion pairs is readily rationalized in terms of the two *endo*-protons being particularly prone to interact with the proximate counterion in such a structure. Finally, the finding that loose and tight ion pairs $\mathbf{7}^{\bullet-}$/K$^+$ coexist in DME at temperatures below 200 K without undergoing interconversion on the hyperfine time scale is in line with the distinctly different structures of these ion pairs separated by a substantial energy barrier.

The essential features of the energy profile, as indicated for $\mathbf{7}^{\bullet-}$ by the AM1 calculations, are also predicted by the UHF/3-21G* *ab initio* method.[34] This statement holds particularly for the energy minima representing the favored conformations. Merely, the flattening of the molecule on going from **7** to $\mathbf{7}^{\bullet-}$, as a consequence of the strengthening of the C(2)—C(3) bond, is more pronounced than with the AM1 calculations. Thus, both the energy difference between the (lower) *transoid* and the (higher) *cisoid* conformation and the barrier separating them are greatly enhanced. Furthermore, the *transoid* conformation is now shifted to $\varphi \approx 150°$ or 210°, while its *cisoid* counterpart appears at $\varphi \approx 35°$ to 325°.

Conclusions

Occurrence of tight ion pairs for the radical anions of 1,4- and 2,3-di-*tert*-butylbuta-1,3-diene ($\mathbf{6}^{\bullet-}$ and $\mathbf{7}^{\bullet-}$) associated with their alkali-metal counterions K$^+$, Rb$^+$, and Cs$^+$ can be traced back to the particular structures promoting a close contact between the oppositely charged particles (Figures 7 and 8, bottom). The cations are situated on a 2-fold axis in a half-cage flanked by the bulky *tert*-butyl groups which prevent their departure to positions where they would be solvent-separated from the radical anion. This structure of the tight ion pairs $\mathbf{6}^{\bullet-}$/M$^+$ and $\mathbf{7}^{\bullet-}$/M$^+$ (M = K, Rb, Cs) must also be responsible for their exceptional persistence which surpasses that of radical anions of other alkyl-substituted buta-1,3-dienes associated with alkali-metal counterions.

Experimental Section

1,1-Dideuterio-3-chloropropargyl Alcohol (14). To a solution of 12.7 g (0.17 mol) of propargyl chloride (**13**) in 90 mL of anhydrous diethyl ether was added a 1.6 M solution of *n*-butyllithium in *n*-hexane (97 mL, ca. 0.155 mol) under stirring at −70 to −90 °C. The reaction mixture was further stirred for 15 min, and 5 g (0.156 mol) of perdeuterioformaldehyde (Acros) was quickly added at −70 °C. The temperature was raised to −40 °C, and the mixture was again stirred for 2^1/$_2$ h at this temperature. After removal of the cooling bath, stirring was continued overnight at room temperature. During this process, the color changed from faintly yellow to brown-orange. Cooling to 0 °C in an ice bath and addition of 80 mL of ice water followed. The raw product mixture was filtered, and thoroughly extracted, first with dichloromethane and then with ether. The combined organic phases were dried (MgSO$_4$), and the solvent was removed by rotary evaporation. The remaining alcohol **14** (8.72 g, 53%) could be used in the next step without further purification. IR (film): $\tilde{\nu}$ 3357 (vs, br), 2997 (s), 2957 (s), 2935 (s), 2211 (s), 2167 (s), 2108 (m), 2077 (s), 1430

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[34] Spartan, Version 3.1.5. Wavefunction Inc., Irvine, CA, 1993. See also: Hehre, W. J.; Radom, L.; Schleyer, P.v.R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(m), 1264 (vs), 1178 (vs), 1079 (s), 1044 (s), 966 cm^{-1} (s). ^{1}H-NMR (400.1 MHz, $CDCl_3$): δ 4.16 (s, C*H*$_2$), 2.69 (s, br, O*H*). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 84.60 (s), 80.31 (s), 50.26 (m, *C*D$_2$), 30.35 (t, *C*H$_2$). MS (70 eV): *m*/*z* (%) 106 (8), 104 (10) [M$^+$], 71 (76) [M$^+$ − Cl], 43 (100).

1,1-Dideuterio-1,4-dichlorobut-2-yne (15). To a mixture of 7.91 g (74.2 mmol) of **14** and 0.56 mL of pyridine was added 9.5 g (79.8 mmol) of freshly distilled thionyl chloride within 5 min at −40 °C. The solution was allowed to warm to 0 °C within 2 h, and the reaction was completed by stirring for 5 h at room temperature. Excess thionyl chloride was distilled off *in vacuo*, and the residue was carefully hydrolyzed and thoroughly extracted with ether. After drying ($MgSO_4$), the solvent was removed and **15** was obtained (8.43 g, 85%) as a brown oil which could be used directly in the next step. IR (film): $\tilde{\nu}$ 2994 (m), 2956 (m), 2871 (m), 2255 (s), 2179 (s), 2137 (s), 1429 (m), 1264 (vs), 1189 (vs), 1045 (m), 965 cm^{-1} (s). ^{1}H-NMR (400.1 MHz, $CDCl_3$): δ 4.14 (s, C*H*$_2$). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 81.04 (s), 80.96 (s), 23.2 (t, *C*H$_2$), 29.64 (m, *C*D$_2$).

1,1-Dideuterio-2,3-di-*tert*-butylbuta-1,3-diene (7-*d*$_2$). A solution of 7.83 g (62.4 mmol) of **15** in 40 mL of anhydrous tetrahydrofuran was placed in a flame-dried flask, and 300 mg (1.05 mmol) of cuprous bromide was added under dinitrogen. The suspension was cooled to −35 °C, and 100 mL of a 1.0 M solution (0.1 mol) of *tert*-butylmagnesium chloride in tetrahydrofuran was added under vigorous stirring within 30 min. After being stirred for additional 2^{3}/$_{4}$ h at 0 °C, the reaction mixture was poured into 300 mL of a saturated aqueous solution of ammonium chloride, which was then carefully extracted with ether. The combined organic phases were washed with brine, dilute hydrochloric acid, bicarbonate solution, and again with brine. Drying ($MgSO_4$) and removal of the solvent *in vacuo* provided 8.95 g of a brown oil which was subjected to further purification by chromatography on alumina with pentane and Kugelrohr distillation (70 °C, 11 Torr). A yield 5.30 g (60%) of **7**-*d*$_2$ as a colorless oil was obtained. The sample used for the ESR study was finally purified by preparative gas chromatography (3 m, Carbowax 90 °C). IR (film): $\tilde{\nu}$ 3088 (s), 2967 (vs), 2907 (s-m), 2870 (m), 1622 (s-m), 1566 (s-m), 1479 (m), 1463 (m), 1391 (m), 1362 (m), 1200 (m), 1069 (m), 902 cm^{-1} (m). ^{1}H-NMR (400.1 MHz, $CDCl_3$): δ 5.09 (d, *J* = 1.5 Hz, ═C*H*), 4.72 (d, *J* = 1.5 Hz, ═C*H*), 1.11 (s, 18 H, *t*Bu). ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 159.3 (s), 159.1 (s), 110.95 (t, ═*C*H$_2$), 110.38 (m, ═*C*D$_2$), 35.83 (s), 35.78 (s), 31.42 (s, *C*H$_3$). MS (70 eV): *m*/*z* (%) 168 (12) [M$^+$], 153 (16), 112 (50), 111 (35), 97 (48), 57 (100)

1,3-Di-*tert*-butylbuta-1,3-diene (9). A suspension of 0.85 g (2.37 mmol) of methyltriphenylphosphonium bromide in 8 mL of anhydrous tetrahydrofuran was cooled to 0 °C under stirring, and 0.26 g (2.27 mmol) of potassium *tert*-butylate was added. The color of the reaction mixture turned yellow and dark after a short time. Stirring at room temperature for 1^{3}/$_{4}$ h and addition of 0.26 g (1.53 mmol) of 1,3-di-*tert*-butyl-2-propenone (**16**)[23] in 3 mL of anhydrous tetrahydrofuran followed. The cooling bath was removed, and after further stirring for 3 h at room temperature, 1 mL of water and 15 mL of *n*-pentane were added. The solution was filtered over a short column filled with alumina, washed several times with *n*-pentane, and finally concentrated to about 10% of its volume. Preparative column chromatography (3 m, Carbowax, 90 °C) provided 0.21 g (83%) of analytically pure **9** identical in its spectroscopic properties with those of a sample prepared by photoisomerization of 2,3-di-*tert*-butylbuta-1,3-diene (**7**).[35]

Instrumental Details. The ESR and ENDOR spectra were taken on a Bruker-ESP-300 system, equipped with a variable temperature accessory. The *g* factors were measured by a Bruker-NMR-Gaussmeter ER035M and a Marconi-Instruments Microwave Counter 2440.

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(35) Hopf, H.; Lipka, H.; Trætteberg, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 204−205.