

Radical Anions of Sterically Protected Polyenes: An ESR and ENDOR Study

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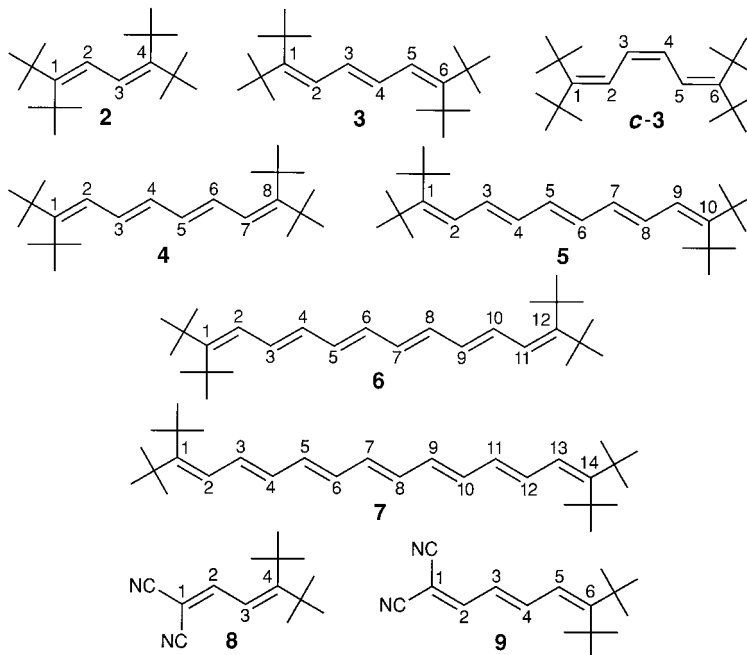
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Dedicated to Professor *Armin de Meijere* on the occasion of his 60th birthday

Owing to the steric protection by four bulky substituents in the terminal positions 1 and n , several conjugated polyenes could be reduced with K or Cs metal in 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) to fairly persistent radical anions. These compounds, denoted here as **2**, **3**, ... **7** (which corresponds to the number, $\frac{1}{2}n = 2, 3, \dots, 7$, of their formal double bonds) are 1,1, n , n -tetra(*tert*-butyl) derivatives of buta-1,3-diene, hexa-1,3,5-triene, octa-1,3,5,7-tetraene, deca-1,3,5,7,9-pentaene, dodeca-1,3,5,7,9,11-hexaene, and tetradeca-1,3,5,7,9,11,13-heptaene. In addition to the six polyenes **2–7** with all-*trans*-configuration, the studies comprised an isomer of **3**, the *trans,cis,trans*-triene, **c-3**. The radical anions **2^{•-}–7^{•-}** and **c-3^{•-}** were characterized by their hyperfine data acquired with ESR, ENDOR, and TRIPLE-resonance spectroscopy. The ¹H-coupling constants comply with the spin distribution predicted for the radical anions of such 'linear' π -systems by simple MO models. Ion pairs formed with K⁺ in DME were loose but became tighter with Cs⁺ in THF. Propensity to ion pairing decreased with the lengthening of the π -system on going from **2^{•-}** to **3^{•-}–7^{•-}**. Hyperfine data are likewise reported for the radical anions of all-*trans*-polyenes **8** and **9**, in which two *tert*-butyl substituents in one terminal position of **2** and **3**, respectively, were replaced by CN groups.

Introduction. – The radical anions of buta-1,3-diene (**1**) and several of its Me-substituted derivatives have been produced electrolytically in liquid ammonia [1] or tetrahydrofuran (THF) [2]. In general, reaction of these compounds with an alkali metal in an ethereal solvent fails to yield a persistent radical anion, because of rapid polymerization to rubber-like products (see, *e.g.*, [3]). However, as has recently been shown [4], this process can be hindered by bulky substituents. Introduction of two *tert*-Bu groups into each of the terminal positions of **1** should endow its radical anion with an even greater persistence, and an analogous statement may also hold for longer conjugated polyenes. Recently, such 1,1, n , n -tetrasubstituted derivatives, **2–7** (with $\frac{1}{2}n = 2–7$ formal double bonds), have become synthetically available [5]. These compounds are 1,1,4,4-tetra(*tert*-butyl)buta-1,3-diene (**2**), 1,1,6,6-tetra(*tert*-butyl)hexa-1,3,5-triene (**3**), 1,1,8,8-tetra(*tert*-butyl)octa-1,3,5,7-tetraene (**4**), 1,1,10,10-tetra(*tert*-butyl)deca-1,3,5,7,9-pentaene (**5**), 1,1,12,12-tetra(*tert*-butyl)dodeca-1,3,5,7,9,11-hexaene (**6**), and 1,1,14,14-tetra(*tert*-butyl)tetradeca-1,3,5,7,9,11,13-heptaene (**7**). In the present paper, we report the ESR and ENDOR studies on the radical anions of **2–7** with all-*trans*-configuration, which is, however, not specifically expressed in this notation. In the case of the triene, the radical anion of the *trans,cis,trans*-isomer [6a] was also investigated and the notation **c-3** serves to distinguish it from its all-*trans*-

counterpart **3**. To our knowledge, radical anions of polyenes longer than **1** or those of their alkyl derivatives have not yet been studied by ESR spectroscopy. Merely, the ESR and ENDOR spectra of radical anions of 1,6-diphenylhexa-1,3,5-triene and 1,8-diphenylocta-1,3,5,7-tetraene were described in [7]. However, in terms of π -electron structure, these very persistent radical anions can hardly be considered as those of polyenes, because a substantial part of their spin population resides in the terminal Ph groups.



Apart from the spin distribution in the radical anions of **2–7** and **c-3**, the interest is focused on whether these species form unusually tight ion pairs with their alkali-metal counterions in an ethereal solvent, as do the radical anions of 1,4- and 2,3-di(*tert*-butyl)buta-1,3-dienes [4]. The occurrence of such ion pairs in DME and THF was strikingly demonstrated by the extremely large coupling constants of ^{39}K and ^{133}Cs nuclei in the associated cations K^+ and Cs^+ , $a_{\text{K}} + 0.12$ to $+0.16$ and $a_{\text{Cs}} + 0.7$ to $+2.6$ mT [4]. These values exceed by an order of magnitude those generally found for ion pairs of hydrocarbon π -radical anions in DME and THF, $|a_{\text{K}}| \approx 0.01$ and $|a_{\text{Cs}}| \approx 0.1$ mT [8a] [9].

The radical anions were also generated from 4,4-di(*tert*-butyl)buta-1,3-diene-1,1-dicarbonitrile (**8**) and 6,6-di(*tert*-butyl)hexa-1,3,5-triene-1,1-dicarbonitrile (**9**) [5] [6b] (see *Appendix*).

Results and Discussion. – *Source of Compounds.* The synthesis of the polyenes **2–7** will be described in a coming paper [5]. Formation of the most stable all-*trans*-isomers was ensured by photoequilibration of the raw-product mixtures. The isomeric trienes **3** and **c-3**, prepared by the *McMurry* coupling of 3-(*tert*-butyl)-4,4-dimethylpent-3-enal

(3,3-di(*tert*-butyl)acrolein), were separated by column chromatography and high-vacuum sublimation [5]. The dicyanonitriles **8** and **9** are readily available from the corresponding aldehydes by condensation with malonitrile [5][6b].

General Procedure. The tetra(*tert*-butyl)-substituted polyenes **2–7** and **c-3** were reduced to their radical anions with a K or a Cs mirror in DME or THF. Li and Na were not employed to this aim, because they proved to have insufficient reducing power for alkyl-substituted buta-1,3-dienes [4]. Although the ease of formation (thermodynamic stability) of the radical anions gradually increased on going from **2**^{•−} to its longer counterparts, their persistence (kinetic stability) decreased in the same order. Thus, reduction of the pentaene **5** with Cs in THF led to a relatively weak ESR spectrum of its radical anion, while the hexaene **6** and the heptaene **7** did not yield sufficiently long-lived radical anions under these conditions. ESR and ENDOR studies of **6**^{•−} and **7**^{•−} were, therefore, restricted to radical anions generated with K in DME. Evidently, with the lengthening of the polyene, the *t*-Bu groups in the terminal positions can less efficiently protect the central part of the molecule. ESR Spectra of **2**^{•−}–**7**^{•−}, and **c-3**^{•−} (*Varian-E9* instrument) were recorded at 200 K and followed up to 270 K. The hyperfine data refer to 200 K, the temperature at which the corresponding ENDOR and general-TRIPLE-resonance spectra [10] (*Bruker-ESP-300* system) were observed. Assignment of the coupling constants, a_{H} , to pairs of α -protons¹⁾ is based on the *Hückel-McLachlan* procedure [11] which proved adequate for planar π radicals [8b]. The signs allotted to the a_{H} values are those required by theory, and they comply with the general-TRIPLE-resonance spectra which provided the relative signs. The *g* factor of all radical anions, **2**^{•−} to **7**^{•−}, and **c-3**^{•−}, generated with K in DME, was 2.0027 within the limits of experimental error (± 0.0001); those of **2**^{•−}, **3**^{•−}, **c-3**^{•−}, **4**^{•−}, and **5**^{•−}, produced with Cs in THF, were 2.0039, 2.0036, 2.0036, 2.0034, and 2.0032, respectively.

1,1,4,4-Tetra(tert-butyl)buta-1,3-diene (2). The radical anion **2**^{•−}, formed by contact of **2** with a K mirror in DME, gave rise to a single unresolved ESR signal of 0.18 mT width (peak-to-peak distance). The corresponding ENDOR spectrum (*Fig. 1*, top) revealed three coupling constants $|a_{\text{H}}|$ 0.059, 0.027, and 0.010 mT (exper. error ± 0.001 mT). Using these hyperfine data, computer simulation reproduced the ESR signal when the largest $|a_{\text{H}}|$ value was assigned to the two α -protons at C(2) and C(3), leaving the two smaller ones for the sets of 18 γ -protons¹⁾ in the *t*-Bu substituents. An observable splitting (> 0.005 mT) from the ³⁹K nucleus of the counterion was not needed for a correct simulation. TRIPLE-Resonance experiments indicated that the sign of 0.059 mT, which should be negative according to theory, is the same as that of 0.010 mT and opposite to that of 0.027 mT. The spectra did not markedly change upon raising the temperature. They are attributed to a loose or solvent-separated ion pair **2**^{•−}/K⁺.

When Cs replaced K as the reducing metal in DME, the ESR signal of **2**^{•−}, due to a loose ion pair, was flanked by hyperfine components arising from the ¹³³Cs nucleus ($I = 7/2$) of the counterion and spaced by the coupling constant $|a_{\text{Cs}}|$ 0.315 ± 0.005 mT

¹⁾ In ESR spectroscopy, protons separated from a π -center by 0, 1, 2 ... sp³-hybridized C-atoms are denoted α , β , γ , Thus, α specifies protons directly attached to the π -centers of the polyenes, while γ refers to those in the *t*-Bu substituents.

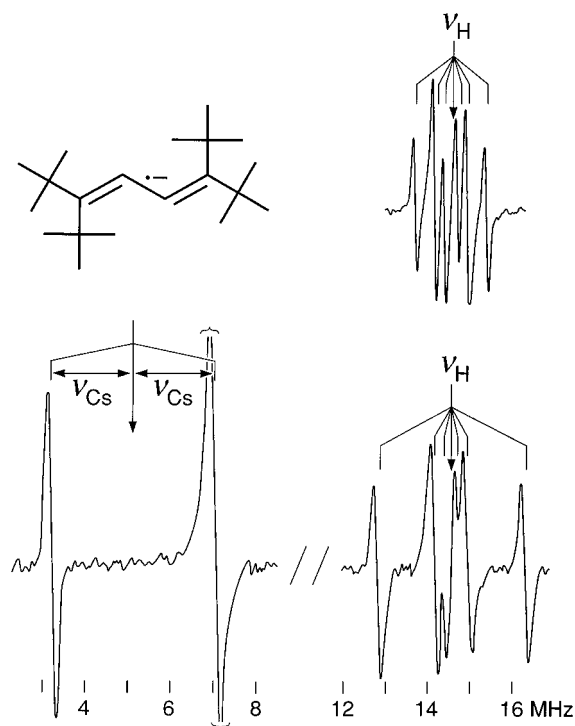


Fig. 1. ^1H - and ^{133}Cs -ENDOR Spectra of the radical anion $2^{\bullet-}$ at 200 K. Top: Solvent DME, counterion K^+ . Bottom: Solvent THF, counterion Cs^+ .

(Fig. 2, top). On raising the temperature, these components, which represent a tight ion pair $2^{\bullet-}/\text{Cs}^+$, were enhanced at the expense of the central signal (Fig. 2, bottom). Association with the counterion was still more strongly favored with THF as solvent, and the ESR spectrum of a tight ion pair $2^{\bullet-}/\text{Cs}^+$ was the only one observed. The corresponding ENDOR spectrum (Fig. 1, bottom) exhibited the expected ^1H and ^{133}Cs signals [10]. The negative coupling constant of the two α -protons was increased in absolute value from $|a_{\text{H}}| 0.059 \pm 0.001$ for $2^{\bullet-}/\text{K}^+$ in DME to 0.123 ± 0.001 mT for $2^{\bullet-}/\text{Cs}^+$ in THF. The ^{133}Cs -coupling constant was $|a_{\text{Cs}}| 0.370 \pm 0.005$ mT; its sign is opposite to that of 0.123 mT and should, therefore, be positive.

1,1,6,6-Tetra(tert-butyl)hexa-1,3,5-trienes (3 and c-3). Reduction of both all-*trans*-(**3**) and *trans,cis,trans*-isomers (*c-3*) by K in DME led to ESR spectra showing a two-proton triplet split by another one. The coupling constants $|a_{\text{H}}|$, determined from the ENDOR spectra, were slightly different for $3^{\bullet-}$ and *c-3* $^{\bullet-}$. In the case of $3^{\bullet-}$, these were 0.453 ± 0.002 and 0.090 ± 0.001 mT, each for two α -protons, and to 0.019 ± 0.001 mT for 18 γ -protons in two 1,6-*t*-Bu substituents. The corresponding $|a_{\text{H}}|$ values for *c-3* $^{\bullet-}$ were 0.465 ± 0.002 , 0.108 ± 0.001 , and 0.019 ± 0.001 mT. Evidently, the coupling constant of the 18 γ -protons in two remaining 1,6-*t*-Bu substituents of $3^{\bullet-}$ and *c-3* $^{\bullet-}$ was too small to be observed (< 0.005 mT). An analogous statement holds for the hyperfine splitting from the ^{39}K nucleus of the counterion which was not required for the computer simulation of the ESR spectra. This finding points to formation of loose ion pairs $3^{\bullet-}/\text{K}^+$

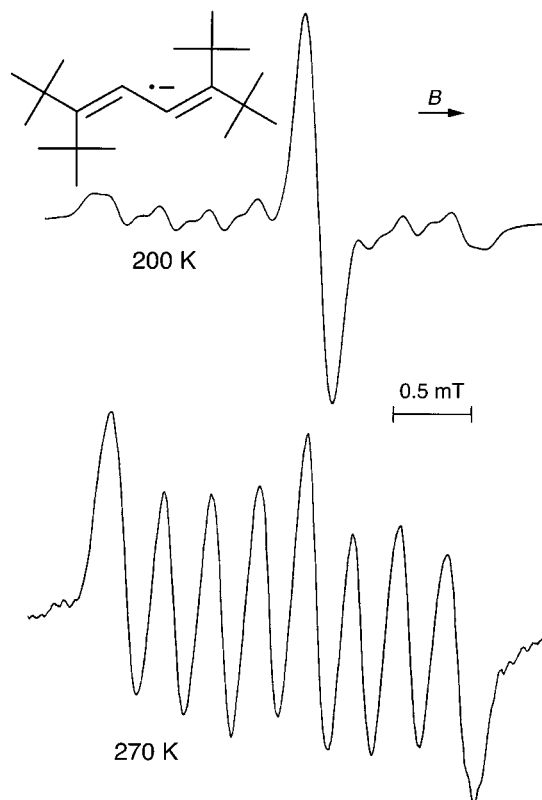


Fig. 2. ESR Spectra of the radical anion $2^{\bullet-}$. Solvent DME, counterion Cs^+ , temperature as indicated.

and $c\text{-}3^{\bullet-}/\text{K}^+$ in DME. The largest $|a_{\text{H}}|$ value was assigned, with a negative sign, to the α -protons at C(3) and at C(4), leaving the smaller one, with a positive sign, for those at C(2) and C(5). The observed coupling constant of the *t*-Bu γ -protons should be positive.

On passing from K in DME to Cs in THF, the loose ion pairs $3^{\bullet-}/\text{K}^+$ and $c\text{-}3^{\bullet-}/\text{K}^+$ turned into tight ones $3^{\bullet-}/\text{Cs}^+$ and $c\text{-}3^{\bullet-}/\text{Cs}^+$. The coupling constants derived from the ENDOR spectrum, were again slightly different for $3^{\bullet-}$ and $c\text{-}3^{\bullet-}$. The ion pair $3^{\bullet-}/\text{Cs}^+$ had $|a_{\text{H}}|$ values of 0.462 ± 0.002 and 0.113 ± 0.001 mT for the α -protons at C(3) and C(4), and C(2) and C(5), respectively, 0.021 ± 0.001 mT for 18 *t*-Bu γ -protons, and an $|a_{\text{Cs}}|$ value of 0.364 ± 0.002 mT for the ^{133}Cs nucleus of the counterion. In the case of $c\text{-}3^{\bullet-}/\text{Cs}^+$, the corresponding $|a_{\text{H}}|$ values were 0.476 ± 0.002 , 0.134 ± 0.001 , and 0.021 ± 0.001 mT, while $|a_{\text{Cs}}|$ was 0.394 ± 0.002 mT. The ^1H -coupling constants should have the same sign as their counterparts for the loose ion pairs, that of the ^{133}Cs nucleus again being positive.

1,1,8,8-Tetra(tert-butyl)octa-1,3,5,7-tetraene (4) and *1,1,10,10-Tetra(tert-butyl)deca-1,3,5,7,9-pentaene (5)*. The radical anions generated from **4** and **5** with K in DME were diagnostic of loose ion pairs $4^{\bullet-}/\text{K}^+$ and $5^{\bullet-}/\text{K}^+$. Replacement of K by Cs and of DME by THF led to complex ESR spectra which were due to mixtures of the respective loose

and tight ion pairs $4^{\cdot-}/\text{Cs}^+$ and $5^{\cdot-}/\text{Cs}^+$. The ^1H - and ^{133}Cs -hyperfine data for both radical anions and for either solvent and counterion are listed in *Table 1*, along with compiled values for $2^{\cdot-}$, $3^{\cdot-}$, and $c\text{-}3^{\cdot-}$. For a given radical anion, ^1H -coupling constants were quite similar, the main difference in the spectra of the loose and tight ion pairs being due to an additional splitting from the ^{133}Cs nucleus in the latter species. The $|a_{\text{Cs}}|$ values were 0.235 ± 0.002 mT for $4^{\cdot-}/\text{Cs}^+$ and 0.155 ± 0.005 mT for $5^{\cdot-}/\text{Cs}^+$ (sign positive).

1,1,12,12-Tetra(tert-butyl)dodeca-1,3,5,7,9,11-hexaene (6) and *1,1,14,14-Tetra(tert-butyl)tetradeca-1,3,5,7,9,11,13-heptaene (7)*. As stated above, the only radical anions of **6** and **7** studied by ESR and ENDOR spectroscopy were those produced with K in DME. They formed loose ion pairs $6^{\cdot-}/\text{K}^+$ and $7^{\cdot-}/\text{K}$; their ^1H -coupling constants are also given in *Table 1*.

Conclusions. – The spin distribution in $3^{\cdot-} - 7^{\cdot-}$ and $c\text{-}3^{\cdot-}$ agrees with that expected for the radical anions of the pertinent polyenes, as verified by calculations in the frame of simple MO methods. The tetra-(*tert*-butyl) substitutions at the terminal positions can thus be considered as a perturbation of the π -systems. A *cis,trans*-isomerization of $c\text{-}3^{\cdot-}$ to $3^{\cdot-}$ about their central $\text{C}=\text{C}$ double bond was not observed, and their structural difference has only a slight effect on the spin distribution. The propensity to form tight ion pairs with the alkali-metal counterions is in line with the findings for hydrocarbon π -radical anions. The factors that favor such a propensity are: *i*) decrease in the solvating power of the ether on going from DME to THF, and also on raising the temperature of the solution; *ii*) increase in the size of the alkali-metal cation on replacing K^+ by Cs^+ as the counterion; *iii*) smallness of the π -system which, in the

Table 1. ^1H - and ^{133}Cs -Coupling Constants, a_{H} and a_{Cs} in mT^{a} , for the Radical Anions $2^{\cdot-} - 7^{\cdot-}$, and $c\text{-}3^{\cdot-}$

| Radical anion | Solvent, counterion | Position ^{b)} | | | | | | | Cs^+ (1Cs) |
|-----------------------|---------------------|--|----------------------|-----------|----------------------|-----------|----------------------|-----------|------------------------|
| | | 1,n(4 <i>t</i> -Bu) | 2,n-1(2H) | 3,n-2(2H) | 4,n-3(2H) | 5,n-4(2H) | 6,n-5(2H) | 7,n-6(2H) | |
| $2^{\cdot-}$ | DME, K^+ | +0.027 ^{c)} -0.010 ^{c)} | -0.059 | | | | | | |
| | THF, Cs^+ | +0.028 ^{c)} -0.010 ^{c)} | -0.123 | | | | | | +0.370 |
| $3^{\cdot-}$ | DME, K^+ | +0.019 ^{d)} | +0.090 | -0.453 | | | | | |
| | THF, Cs^+ | +0.021 ^{d)} | +0.113 | -0.462 | | | | | +0.364 |
| $c\text{-}3^{\cdot-}$ | DME, K^+ | +0.019 ^{d)} | +0.108 | -0.465 | | | | | |
| | THF, Cs^+ | +0.021 ^{d)} | +0.134 | -0.476 | | | | | +0.394 |
| $4^{\cdot-}$ | DME, K^+ | +0.017 ^{d)} | +0.152 ^{e)} | -0.515 | -0.152 ^{e)} | | | | |
| | THF, Cs^+ | +0.018 ^{d)} | +0.153 ^{e)} | -0.521 | -0.153 ^{e)} | | | | +0.235 |
| $5^{\cdot-}$ | DME, K^+ | +0.014 ^{d)} | +0.155 | -0.519 | <0.005 ^{f)} | -0.280 | | | |
| | THF, Cs^+ | +0.014 ^{d)} | +0.160 | -0.524 | <0.005 ^{f)} | -0.286 | | | +0.155 |
| $6^{\cdot-}$ | DME, K^+ | +0.011 ^{d)} | +0.149 | -0.478 | +0.055 | -0.348 | -0.128 | | |
| $7^{\cdot-}$ | DME, K^+ | +0.009 ^{d)} | +0.138 | -0.436 | +0.091 | -0.371 | <0.005 ^{f)} | -0.213 | |

^{a)} Experimental error: for $|a_{\text{H}}|$ in $2^{\cdot-}$, $3^{\cdot-}$, and $c\text{-}3^{\cdot-}$, and for $|a_{\text{Cs}}|$, see text; for $|a_{\text{H}}|$ in $4^{\cdot-} - 7^{\cdot-}$, ± 0.001 mT in $|a_{\text{H}}| < 0.1$ mT and $\pm 1\%$ in larger $|a_{\text{H}}|$ values. ^{b)} $n = 4, 6, 8, 10, 12, 14$ for **2**, **3**, **4**, **5**, **6**, **7**. ^{c)} 18 *t*-Bu protons. ^{d)} 18 *t*-Bu protons; hyperfine splittings from the remaining 18 not observed. ^{e)} Accidental equality of the absolute values within the limits of spectral resolution. ^{f)} Not observed.

present work, is true for diene **2** but is gradually lost by its extension to the longer polyenes **3–7**. The finding that association of the radical anions with their alkali-metal counterions becomes weaker upon lengthening of the π -system is indicated by the occurrence of the loose ion pairs even with Cs^+ in THF, as well as by the lesser changes in the ^1H -coupling constants and in the g factor and by the decreasing $|a_{\text{Cs}}|$ value. Although the ^{133}Cs -coupling constants observed for $\mathbf{2}^{\cdot-}$ – $\mathbf{4}^{\cdot-}$ and $\mathbf{c}\text{-}\mathbf{3}^{\cdot-}$ are larger than those generally found for the ion pairs of hydrocarbon π -radical anions, they do not reach by far the $|a_{\text{Cs}}|$ values attained for the radical anions of 1,4- and 2,3-di(*tert*-butyl)buta-1,3-dienes [4]. Obviously, as stated in [4], the geometry of these two species represents an exceptionally favorable case for the formation of unusually tight ion pairs. Introduction of additional bulky *t*-Bu groups seems to prevent a closer approach of the alkali-metal cations to the radical anions, notably for that of the shortest polyene **2**.

Appendix. – 4,4-Di(*tert*-butyl)buta-1,3-diene-1,1-dicarbonitrile (**8**) and 6,6-Di(*tert*-butyl)hexa-1,3,5-triene-1,1-dicarbonitrile (**9**). Substitution by electron-attracting CN groups is expected to facilitate the reduction of the π -system and enhance the persistence of the radical anion thus formed, whereby a large part of the charge and spin population should be accommodated in these groups. However, such an expectation was not borne out by the present studies on the radical anions $\mathbf{8}^{\cdot-}$ and $\mathbf{9}^{\cdot-}$; these anions proved to be much less persistent than the corresponding tetra(*tert*-butyl)-substituted species $\mathbf{2}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$. Their generation was preferably carried out by electrolysis in THF with tetrabutylammonium fluoroborate as the supporting salt. A cylindrical cell with a helical cathode of amalgamated gold and a Pt-wire anode in the axis served for this purpose [12]. The ESR spectra ($g = 2.0026 \pm 0.0001$) were obtained at 200 K, with no multiresonance experiments being practicable during the electrolysis. Moreover, the hyperfine data (Table 2) revealed that the CN groups bear only a minor part of the spin population. The experimental findings are in accord with the spin distribution as calculated by the Hückel-McLachlan procedure [11] (heteroatom parameters $a_{\text{N}} = \alpha + \beta$, $\beta_{\text{CN}} = 2\beta$), which served for the assignment of the coupling constants and for the allotment of their signs.

Table 2. ^1H - and ^{14}N -Coupling Constants, a_{H} and a_{N} in mT^{a} , for the Radical Anions $\mathbf{8}^{\cdot-}$ and $\mathbf{9}^{\cdot-}$

| Radical anion | Solvent, counterion | Position | | | | | | | |
|-----------------------|------------------------------|----------------------|--------|------------------------|------------------------|--------|----------------------|------------------------|--|
| | | 1(1 N) | 2(1 H) | 3(1 H) | 4(2 <i>t</i> -Bu) | 4(1 H) | 5(1 H) | 6(2 <i>t</i> -Bu) | |
| $\mathbf{8}^{\cdot-}$ | THF, Bu_4N^+ | – 0.09 ^{b)} | – 1.02 | + 0.33 | + 0.025 ^{c)} | | | | |
| | | – 0.08 ^{b)} | | | < 0.02 ^{c,d)} | | | | |
| $\mathbf{9}^{\cdot-}$ | THF, Bu_4N^+ | – 0.07 ^{b)} | – 0.89 | < 0.02 ^{d,e)} | | – 1.00 | + 0.27 ^{e)} | < 0.02 ^{c,d)} | |
| | | – 0.06 ^{b)} | | | | | | < 0.02 ^{c,d)} | |

^{a)} Experimental error: ± 0.01 mT. ^{b)} ^{14}N Nucleus in one CN substituent. ^{c)} Nine *t*-Bu protons. ^{d)} Not resolved. ^{e)} Assignments of these values to the 3- and 5-positions may be reversed.

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