Electron Spin Resonance Studies of Aromatic Hydrocarbon Radical Ions. Part IV.[1] t-Butylacenaphthene Anions

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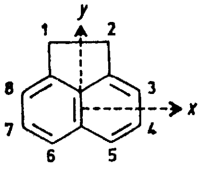
The radical anions of 3-, 4-, and 5-t-butylacenaphthene and 3, 8-di-t-butylacenaphthene have been prepared by reduction with alkali metals in ether solvents. Analysis of their e.s.r. spectra indicates the hyperfine coupling from the t-butyl groups is not resolved and hence leads to simplification of the spectra. The observed coupling constants are in agreement with those predicted by a Hückel inductive MO model for these compounds. Ion pairing effects are observed with different solvents and counterions and are related to a McClelland electrostatic ion pair model. Some paramagnetic decomposition products are observed and their possible structures are determined from their e.s.r. spectra.

It is well known that alkyl substitution leads to a marked perturbation of the distribution of electron density in aromatic hydrocarbons. The technique of e.s.r. provides an excellent method for the observation of such an effect by indicating changes in spin density at various atoms in the radical ions of these hydrocarbons upon substitution.[2]

In this paper, the results of e.s.r. studies of the effects of t-butyl substitution in acenaphthene are presented. In particular, the radical anions of the symmetrically substituted 3,8-di-t-butyl acenaphthene (3,8-DTACN) and the three asymmetrical 3-, 4-, and 5-t-butyl acenaphthenes (3-, 4-, 5-TACN) are considered in comparison with unsubstituted acenaphthene (ACN). The e.s.r. spectra of these species were analysed in terms of the effects of changes in (a) position of t-butyl substitution, (b) solvent, (c) alkali metal counterion and its consequent ion pairing effects.



ACN

Only one previous study [3] has been reported on t-butylacenaphthenes and this concerned the electrolytic generation, observation, and analysis of the e.s.r. spectra of the 4,7- and 3,8-di-t-butylacenaphthene radical anions.

The radical ions of very few asymmetrically alkyl substituted polycyclic hydrocarbons have been examined by e.s.r. because of the complex hyperfine structure arising from odd numbers of protons. We have found that t-butyl groups are particularly useful in alleviating this problem because the hyperfine coupling arising from the nine t-butyl protons is very small and hence only causes line broadening rather than resolvable hyperfine splitting. Thus the only hyperfine structure observed is that arising from the aromatic protons, and the methylene protons in the present case of acenaphthene derivatives. Similar simplification of the hyperfine structure has been observed in the e.s.r. spectra of asymmetrically substituted t-butyl naphthalene radical anions.[4]

EXPERIMENTAL

The t-butylacenaphthenes were synthesised using standard literature methods.

The radical anions were prepared by alkali metal reduction using normal high vacuum procedures.[5] 1,2-Dimethoxyethane (DME) (Aldrich), tetrahydrofuran (THF) (Eastman), and diethyl ether (DEE) (May and Baker) were stored in the presence of the anthracene radical anion. For lithium reduction, a small piece of lithium was placed in ethanol (or methanol) and allowed to react until a bright surface appeared on the metal. It was then transferred to the sample tube and the latter evacuated. The part of the tube in the immediate vicinity of the lithium was gently heated until the oxide coating peeled off leaving a ball of metal with a bright silver surface which could then be readily used for reduction.

All monosubstituted radical anions were olive green characteristic of naphthalene-type hydrocarbon radical anions. All Na–DME systems and 5-TACN–K–DME were stable at room temperature (r.t.) (*ca.* 18°) for indefinite periods of time. The 3- and 4-TACN–K, Li–DME systems were stable at −100° but decomposed at r.t. DTACN also formed olive green solutions upon reduction with Na and K while it formed brown solutions with Li in DME and THF after standing for 1—2 h at r.t.

The e.s.r. spectra were recorded with a Varian E-4 spectrometer and were simulated on a Burroughs B614 with an E.A.I. plotter using a program which calculates first- and second-order isotropic e.s.r. spectra.[6] Molecular orbital and ion pair calculations were calculated using a program MOCALC written by one of us (B.M.P.) Field linearity was checked with Fremey's salt and the estimated accuracy of hyperfine coupling constants is ±0.02 G.

RESULTS

3-, 4-, *and* 5-*TACN–DME*.—Typical spectra for 3-TACN reduced with K, and 4-TACN reduced with Li (at −100°) are shown in Figures 1 (a) and (b) respectively. Reduction of both 3- and 4-TACN with Na gave identical spectra. These observed spectra together with that for 5-TACN$^-$

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[1] (*a*) Part I, R. F. C. Claridge, D. R. A. Leonard, and B. M. Peake, *Mol. Phys.*, 1971, **19**, 737; (*b*) Part II, R. F. C. Claridge and B. M. Peake, *Austral. J. Chem.*, 1972, **25**, 2353; (*c*) Part III, F. Gerson, B. M. Peake, and G. M. Whitesides, *Org. Magnetic Resonance*, 1972, **4**, 361.

[2] *E.g.* R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, 1969, **51**, 1765 and references therein.

[3] S. F. Nelsen, *J. Amer. Chem. Soc.*, 1967, **89**, 5925.

[4] I. Goldberg, R. Franck, and B. M. Peake, unpublished results.

[5] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, 1964, **40**, 3307.

[6] Details of this program and associated e.s.r. spectral data processing programs, B. M. Peake and K. J. Walker, unpublished results.

produced by K or Na reduction could be simulated using the coupling constants given in Table 1.

The 4-TACN–K–DME system was found to be unstable even at low temperatures giving the spectrum shown in Figure 1 (c). Similarly reduction of 4-TACN with Li at low temperatures gave a stable paramagnetic species [Figure 1 (b)] which on raising the temperature formed another paramagnetic species whose spectrum at −100° is shown in Figure 1 (d). This latter spectrum was also observed for the 4-TACN–K–DME system after a time (*ca.* 0.5 h).

TABLE 1

Observed and calculated proton hyperfine coupling constants for the asymmetric t-butylacenaphthene radical anions

Hyperfine coupling constants (G)

Species	a_1 †*	a_2 *	a_2		a_4		a_5		a_6		a_7		a_8	
	Obs. ‡	Obs.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
3-TACN$^{\cdot-}$	7.31	7.17			2.56	2.16	4.33	4.12	4.40	4.26	1.32	1.23	2.00	1,86
4-TACN$^{\cdot-}$	7.62	7.48	2.67	2.22			4.00	3.39	4.15	3.90	1.30	1.26	0.89	1.30
5-TACN$^{\cdot-}$	7.80	6.89	2.10	1.71	0.85	0.89			4.27	4.67	1.25	1.41	2.64	1.89

* Cannot be unambiguously assigned. † Subscript refers to numbering of acenaphthene. ‡ All observed values obtained by simulation of spectra observed at −100°.

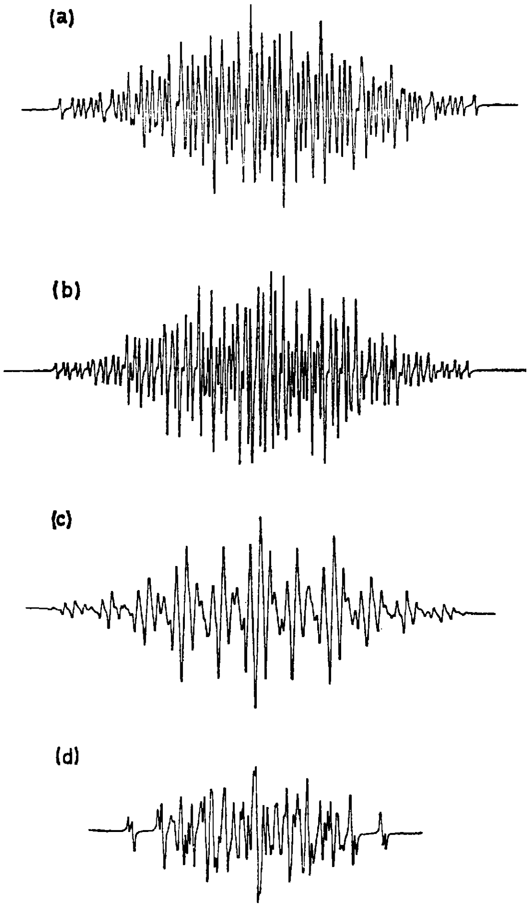

FIGURE 1 Observed spectra for 3-TACN$^{\cdot-}$ and 4-TACN$^{\cdot-}$ at −100°: (a) 3-TACN–K–DME; (b) 4-TACN–Li–DME; (c) 4-TACN–K–DME; (d) 4-TACN–Li–DME after raising the sample temperature and 4-TACN–K–DME after 0.5 h

3,8-*DTACN–DME*.—The spectrum for 3,8-DTACN reduced with K at −100° could be readily simulated using the coupling constants given in Table 2. Spectra for the Na and Li reduced species were of the same basic hyperfine pattern but in order to simulate these spectra, it was found necessary to use slightly different values for the proton coupling constants (Table 2).

3,8-*DTACN–THF*.—The spectrum obtained at −100° for Li reduction in this solvent was identical to that of Li–DME. However, a comparison of spectrum obtained at −100° by K reduction in THF compared with that in DME indicates some marked changes.

TABLE 2

Observed and calculated proton hyperfine coupling constants for the 3,8-di-t-butylacenapthene radical anion

Counter ion	$a_{1,2}$ * Obs.	$a_{4,7}$ Obs.	$a_{4,7}$ Calc.	$a_{5,8}$ Obs.	$a_{5,8}$ Calc.
Li$^+$	7.13	2.14	1.90	4.39	4.47
Na$^+$	7.02	2.10	1.90	4.42	4.47
K$^+$	7.01	2.10	1.90	4.37	4.47

* Subscript refers to numbering of acenaphthene.

TABLE 3

Observed proton hyperfine coupling constants for 3,8-DTACN–Na–THF

T/°C	No. of protons	Coupling constant (G)
−100	4	7.15
	2	4.37
	2	2.12
−40	4	7.25
	2	4.30
	2	2.26
	1	2.70
	1	1.36

Spectra were observed for the Na reduced species at various temperatures and those at −100 and −40° were simulated using the hyperfine coupling constants given in Table 3.

3,8-*DTACN–DEE*.—The spectrum observed at −100° for K reduction in this solvent did not change over the temperature range −100 to −40°. Above −40° the paramagnetic signal disappeared.

DISCUSSION

The observed line width of at least 0.20 G of all anion species compared with that of 0.090 G which was measured from the spectrum of ACN$^{\cdot-}$ prepared by reduction with K–DME indicated that the t-butyl protons may well have a hyperfine coupling constant which was too small to be resolved but large enough to contribute to the linewidth. Confirmation of this effect was obtained by the successful simulation of spectra using coupling constants given in Tables 1 and 2 for protons at only the aromatic and methylene bridge positions.

The number of sets of equivalent protons obtained from the successful simulations at −100° correlates well with the number expected for either mono- or di-substitution in the aromatic ring system. In order to assign the coupling constants to specific proton positions, simple Hückel molecular orbital (SHMO) calculations were performed using the following model: the t-butyl group was regarded as having only an inductive effect such that the Coulomb integral for the ring C atom at the position of substitution was given by $\alpha_{\mathrm{Ar}} = \alpha_0 + h_{\mathrm{Ar}}\beta_0$ where h_{Ar} was varied from −0.10 to −0.60 at 0.025 intervals. The other parameters were given the same values as those used in an earlier SHMO study [7] of ACN$^{\overline{\cdot}}$.

The calculated spin densities were fitted to the observed coupling constants using a least square procedure. Assuming the McConnell relationship of $a^{\mathrm{H}}_{\mathrm{CH}} = Q^{\mathrm{H}}_{\mathrm{CH}}\rho$ the inductive parameter, h_{Ar}, which gave best agreement as shown by the minimum variance of $Q^{\mathrm{H}}_{\mathrm{CH}}$ was found to be −0.30 corresponding to $Q^{\mathrm{H}}_{\mathrm{CH}} = 23.2 \pm 1.6$ G. This inductive parameter is comparable to that found to give best fit for a number of t-butyl-substituted naphthalene anions.[8] The variance is considerably larger than that observed for methyl substitution in naphthalene [2] and may indicate the occurence of steric effects due to the bulky t-butyl group and inherent strain in the acenaphthene bridge, since similar calculations [9] for unsubstituted ACN$^{\overline{\cdot}}$ are markedly different compared with the observed coupling constants for ACN$^{\overline{\cdot}}$. Use of the McLachlan procedure (λ 1.2) did not improve the fit. The hyperfine coupling constants calculated from the above $Q^{\mathrm{H}}_{\mathrm{CH}}$ value and the theoretical spin densities are given in Tables 1—3 and these were used to assign the aromatic protons coupling constants to specific proton positions. It should be noted that SHMO calculations did not enable the methylene proton coupling constants in the asymmetric anions to be unambiguously assigned to either the 1 or 2 positions.

The assignment of the two protons coupling constants for 3,8-DTACN$^{\overline{\cdot}}$ was confirmed by using an additivity model. This method has been used successfully to assign the aromatic proton coupling constants in methyl substituted naphthalene anions.[2] Using the observed values for the coupling constants for 3-TACN$^{\overline{\cdot}}$ compared with those for ACN$^{\overline{\cdot}}$, the predicted coupling constants for 3,8- and 4,7-DTACN$^{\overline{\cdot}}$ are given in Table 4. In comparison with the observed values, it can be seen that only reasonable agreement is obtained. This may be due to the fact that the additivity relationship is expected to hold only when the substituent effects are small and the groups do not interact.[2] In the case of 3,8- and 4,7-DTACN$^{\overline{\cdot}}$ no such direct interaction can occur because of the positions of substitution on separate rings. However the bulky nature of the t-butyl group may well lead to steric interaction with adjacent protons. This would be expected to be more marked for 4,7-DTACN$^{\overline{\cdot}}$ than 3,8-DTACN$^{\overline{\cdot}}$ and hence may well account for the differences between additivity and observed coupling constants for these species.

In view of the small number of lines and the symmetry in the spectrum of 3,8-DTACN–Na–DME it was considered that this anion species could well be prepared in other solvents and with different counterions in order to observe possible ion pairing effects.

TABLE 4

Comparison of experimental coupling constants with additivity model predictions

Species	Proton position	Coupling constant (G) Additivity	Experimental
3,8-DTACN$^{\overline{\cdot}}$	4,7	1.51	2.10
	5,6	4.59	4.42
4,7-DTACN$^{\overline{\cdot}}$	3,8	2.48	0.99 *
	5,6	3.95	3.79 *

* Ref. 3.

No alkali metal splitting was observed at any temperature for any system. This would be expected in view of the average linewidths of at least 0.20 G observed for all spectra. A comparison of these spectra in THF and DEE with that in DME indicates some marked changes in the proton coupling constants with changes in solvent polarity. Similar changes had previously been observed for ACN$^{\overline{\cdot}}$ with different counter ions [9] and had been ascribed to ion pair formation. We conclude that these spectral changes observed for 3,8-DTACN$^{\overline{\cdot}}$ are also due to the formation of K$^+$(3,8-DTACN$^{\overline{\cdot}}$) ion pairs.

A comparison of the spectrum of the 3,8-DTACN–K–THF system with that of 3,8-DTACN–K–DME indicates that the lines associated with $M_{\mathrm{CH_2}} = \pm 1$ (where $M_{\mathrm{CH_2}}$ is the total angular momentum number for the four methylene protons) are broader for the former system. This was confirmed by the observation of a discrepancy between the amplitudes of lines in these regions in the observed spectra compared with a simulated spectrum for 3,8-DTACN–K–THF which reproduced all other features of that spectrum. This linewidth alternation effect was observed over the temperature range −100 to 40°. Such an effect had also been observed for ACN$^{\overline{\cdot}}$[9] and for the 9,10-dihydroanthracene anion.[10]

No such linewidth alternation effects were observed for 3,8-DTACN–K–DEE but in this case there appears to be two different methylene protons coupling constants. The variation of this coupling constant with solvent and K$^+$ as counterion is given in Table 5. Again such an effect had been observed previously for the ACN–K–DEE system [9] and was ascribed to an ion pair.

In the present case of 3,8-DTACN$^{\overline{\cdot}}$, the aromatic proton coupling constants remain the same as for the free ion and hence it may be deduced that a similar

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[7] J. P. Colpa and E. de Boer, *Mol. Phys.*, 1964, **7**, 333.

[8] B. Darragh, personal communication.

[9] M. Iwaizumi, M. Suzuki, T. Isobe, and H. Azumi, *Bull. Chem. Soc. Japan*, 1967, **40**, 2754.

[10] M. Iwaizumi and J. R. Bolton, *J. Magnetic Resonance*, 1970, **2**, 278.

effect is occurring for the 3,8-DTACN–K–DEE system with the cation situated somewhere along the *y* axis or in rapid exchange between two positions symmetrically spaced about the *y* axis. No linewidth alternation effects were observed for this system over the temperature range −100 to 40° and hence to account for two distinct methylene coupling constants one must postulate that the cation is either fixed or undergoing slow exchange between positions above and below the plane of the molecule thus giving two sets of nonequivalent methylene protons. Experimental verifications of this scheme could be obtained from the observation of the spectra from the 3,8-DTACN–K–DEE system where the two protons at one methylene carbon atom were replaced by deuterium, but this compound was not available for the present study.

TABLE 5

Variation of the methylene proton coupling constant with solvent for 3,8-DTACN–K

	Coupling constant (G)		
Solvent	a(4H)	a(2H)	a'(2H)
DME	7.01		
THF	7.25		
DEE		7.54	6.98

In an attempt to ascertain the cation position more precisely, ion pair calculations[11] were performed using the SHMO method for 3,8-DTACN$^{\cdot-}$. An inductive parameter of $h_{\mathrm{Ar}} = -0.30$ was used to allow for the effect of the t-butyl groups as outlined above. Bond lengths of 0.139 nm for the aromatic carbons and 0.154 nm for the methylene carbon–aromatic carbon distances were used. Plots of the cation–anion interaction energy (units of $\beta_0 = -2.5$ eV) along the x and y axes are shown in Figure 2. These indicate that for a cation at a distance of 0.3 nm above the aromatic plane, it is most likely to be undergoing fast exchange between two positions centred on either side of the y axis rather than moving along the x axis. Such a conclusion has also been reached for ACN$^{\cdot-}$[9] and the 9,10-dihydroanthracene anion.[10]

Marked changes in the spectra of some systems were observed over time or often by raising the sample temperature above −40°. For example, the spectra of 4-TACN–K–DME after 0.5 h [Figure 1 (c)] or 4-TACN–Li–DME above −40° [Figure 1 (d)] have a strong centre line and their hyperfine structure is quite different from that in the spectrum of 4-TACN–Li–DME at lower temperatures [Figure 1 (b)].

In view of the successful simulation of the latter spectrum in terms of hyperfine coupling constants (observed values in Table 1) which are in agreement with the structure of 4-TACN and MO calculations of spin densities for 4-TACN$^{\cdot-}$, it is considered that this spectrum [Figure 1 (b)] represents that of the free ion and the other spectra are those of either ion pair species or decomposition products. The spectrum for 4-TACN–K–DME at −100° [Figure 1 (c)] was successfully simulated in terms of two paramagnetic species [(1) and (2)] with the coupling constants given in Table 6 and in the ratio of 1.00 of species (1) to 0.10 of (2). There was no evidence of any 4-TACN$^{\cdot-}$ being present at all.

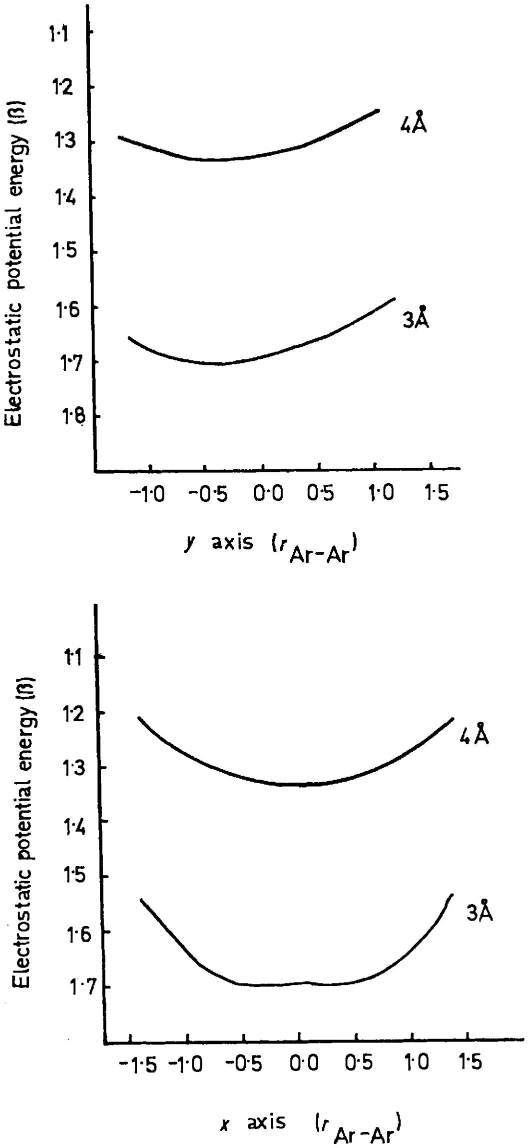

FIGURE 2 Cation–anion interaction energies for 3,8-DTACN$^{\cdot-}$ ion pairs

TABLE 6

Observed hyperfine coupling constants for 4-TACN–K–DME at −100°

	Coupling constant (G)	
No. of protons	Species (1)	Species (2)
4	7.70	7.53
2	1.05	1.09
2		2.39
2	3.90	4.14

A comparison of the values obtained for the successful simulation of the observed spectra at −100° for ACN–Na–DME which were within experimental error of those

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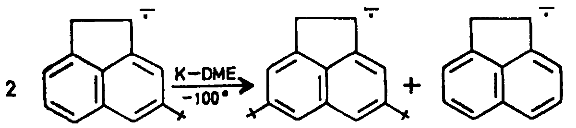
[11] B. J. McClelland, *Trans. Faraday Soc.*, 1961, **57**, 1458.

reported previously in the literature for ACN–K–DME,[7] with those of species (1), show that this latter species is most likely to be the unsubstituted acenaphthene anion. Similarly the values given for species (2) are in good agreement with those reported previously[3] for 4,7-DTACN$^{\overline{\cdot}}$ prepared by electrolysis. Hence we conclude that reaction (1) is taking place at −100° for 4-TACN$^{\overline{\cdot}}$ formed by K reduction in DME.



(1)

From this reaction one would predict an equal ratio of 4,7-DTACN$^{\overline{\cdot}}$ and ACN$^{\overline{\cdot}}$. That the observed ratio was 10 : 1 would suggest that some other diamagnetic decomposition products involving ACN$^{\overline{\cdot}}$ may be formed as well as the two paramagnetic species. Evidence for the absence of any 4,7-DTACN in the 4-TACN starting material comes from no apparent contribution from spectra of 4,7-DTACN$^{\overline{\cdot}}$ in other spectra of 4-TACN$^{\overline{\cdot}}$ [for example Figure 1 (b)] and the absence of 4,7-DTACN in a mass spectrometric analysis. The mechanism of this t-butyl group transfer under these experimental conditions is unknown.

Finally a comparison of the observed spectra of 3,8-DTACN–Na–THF at −40° with the spectra at −100° indicates substantial changes have occurred and this is reflected in the two quite different sets of coupling constants which were found to give good simulation of spectra at these two temperatures (Table **3**). All attempts to suggest a reasonable structure in terms of the magnitude and number of proton coupling constants for the paramagnetic species at −40° were unsuccessful.

To summarise, we conclude that the use of t-butyl groups as substituents in aromatic systems leads to considerable simplification of the e.s.r. spectra of the anions of these species. The results reported in this paper for some t-butyl-substituted acenaphthene anions are in substantial agreement with those reported previously for the anions of other alkyl-substituted aromatic compounds and for unsubstituted acenaphthene anion.

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