An Electron Spin Resonance Study of the Radical Anions of 5*H*-Dibenzo[*a*,*d*]cycloheptene and Related Compounds

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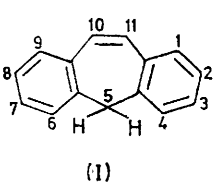
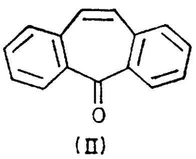
The e.s.r. spectra of the radical anions of 5*H*-dibenzo[*a*,*d*]cycloheptene (I) and two related ketones 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (II) and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (III) have been obtained and interpreted. Coupling constants have been assigned to sets of equivalent protons for the radical anions of (II) and (III) with the aid of simple Hückel MO and McLachlan SCF calculations. In the latter radical anion the four β protons exist as two equivalent pairs at the temperature of the measurements. The e.s.r. spectrum of the radical anion of (I) varies markedly with temperature and counterion. At −70 °C the radical anion exists as a single conformer with quite different coupling constants for the two β protons. As the temperature is raised an e.s.r. spectrum is obtained (with Li^+ as the counterion; at +48 °C) which can be satisfactorily interpreted in terms of two equivalent β protons. However the e.s.r. spectrum of this radical anion is much more complex at +45 °C when Na^+ is the counterion.

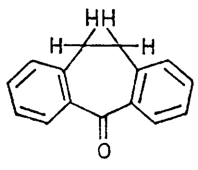
RADICAL anions of many aromatic hydrocarbons have been prepared for e.s.r. studies. For some time we have been particularly interested in the radical anions of hydrocarbons containing a methylene bridge (*e.g.* the fluorene radical anion).[1,2] Our interest in such radical anions led us to consider a group of similar compounds, based on 5*H*-dibenzo[*a*,*d*]cycloheptene (I). The compounds 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (II) and 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (III) completed the series of three interesting and related compounds. Reports of the e.s.r. spectra of the triplet state of dibenzo[*a*,*d*]cycloheptenylidene,[3] the dianion radical obtained from (I),[4] and the radical anion of tropone [5] have appeared in the literature, but there has been no systematic study of the radical anions of (I)—(III).



(I)



(II)



(III)

RESULTS AND DISCUSSION

5H-*Dibenzo*[a,d]*cyclohepten-5-one* (II).—When a dimethylformamide solution of (II) was reduced electrolytically at room temperature a blue colour quickly developed at the cathode. The e.s.r. spectrum associated with this blue solution at −50 °C is shown in Figure 1*a* and may be satisfactorily interpreted in terms of three 1 : 2 : 1 triplet splittings (of 0·350, 0·304, and 0·081 mT) and a 1 : 4 : 6 : 4 : 1 quintet (of 0·034 mT). This interpretation of the spectrum was confirmed by computer reconstruction (Figure 1*b*), and is consistent with the formation of the radical anion of (II).

A sample of (II) was also reduced in tetrahydrofuran solution using lithium, sodium, potassium, and caesium metals. Again the characteristic blue colour quickly developed but the e.s.r. spectra obtained were complicated by the presence of additional splitting from the alkali metal counterion. When either lithium or sodium was the counterion the most satisfactory interpretation of the spectra gave values for the coupling constants very similar to those obtained in the electrolytic reduction. However, in the spectrum obtained when potassium was the counterion the computer reconstruction was improved by replacement of the 0·034 mT quintet by two triplets with coupling constants 0·045 and 0·030 mT.

The assignment of the coupling constants to particular positions in the molecule was made by a comparison of the experimental coupling constants with the unpaired spin densities calculated from simple Hückel MO theory. A further calculation was also performed using McLachlan's SCF method ($\lambda = 1·2$).[6] The values

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[1] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1969, 887.

[2] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1970, 1560.

[3] I. Moritani, S.-I. Murahashi, M. Nishino, Y. Yamamota. K. Itoh, and N. Mataga, *J. Amer. Chem. Soc.*, 1967, **89**, 1259.

[4] N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, 1967, **89**, 5417.

[5] Y. Ikegami and S. Seto, *Bull. Chem. Soc. Japan*, 1968, **41**, 2225.

[6] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

of the experimental and calculated coupling constants are summarised in Table 1.

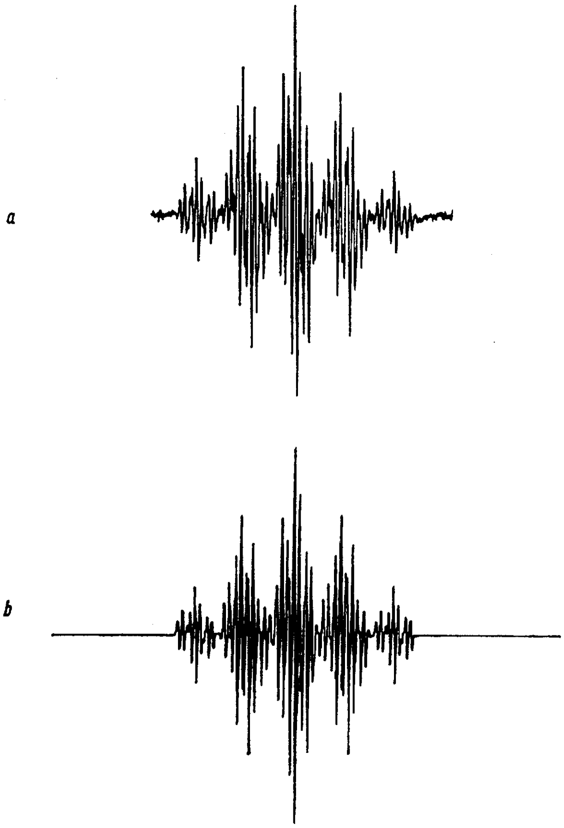


FIGURE 1 *a*, The e.s.r. spectrum, recorded at -50 °C, obtained by the electrolytic reduction of (II) in dimethylformamide; *b*, a computer reconstruction based on the coupling constants given in Table 1

*10,11-Dihydro-*5H*-dibenzo*[a,d]*cyclohepten-5-one* (III).—Following the successful reduction of (II) to form the corresponding radical anion it was anticipated that (III) could also be reduced to form a radical anion. As with (II), when a dimethylformamide solution of (III) was electrolytically reduced, a blue colour quickly appeared at the cathode. The e.s.r. spectrum associated with this blue solution at 0 °C is shown in Figure 2*a* and can be satisfactorily interpreted in terms of four 1 : 2 : 1 triplets (of 0·358, 0·088, 0·060, and 0·028 mT) and a 1 : 4 : 6 : 4 : 1 quintet (of 0·296 mT). This interpretation was confirmed by a computer reconstruction (Figure 2*b*) and is again consistent with the formation of the corresponding radical anion.

TABLE 1

A comparison of experimental and calculated coupling constants (mT) for the radical anion of (II)

	Position					
	1	2	3	4	11	Counterion
Experimental [a]	0·034	0·304	0·081	0·350	0·034	
Experimental [b]	0·030	0·300	0·075	0·345	0·045	0·015
Hückel ($Q = \|3{\cdot}5\|$) [c]	0·087	0·308	0·007	0·340	0·098	
McLachlan ($Q = \|2{\cdot}5\|$) [c]	$-0{\cdot}009$	0·322	$-0{\cdot}102$	0·354	0·047	

[a] In dimethylformamide, electrolytic reduction recorded at -50 °C. [b] In tetrahydrofuran, potassium as the counterion, recorded at -70 °C. [c] $\alpha_o = \alpha_c + 1{\cdot}0\beta_{co}$, $\beta_{co} = \beta_{co}$.

Unfortunately the assignment of the coupling constants to particular positions in the radical anion is not straight forward. Possibly the 0·296 mT quintet is associated with the four methylene protons at positions 10 and 11 which must therefore be equivalent. However, it might also be expected that the coupling constants associated with the ring protons would not be too dissimilar to those found for the benzophenone radical anion. In this latter radical anion two large triplet coupling constants are found to be associated with the ring protons. Hence in the radical anion of (III) a large a(2H) value may be assigned to positions 2 and 8 and a second slightly smaller a(2H) value would be expected for positions 4 and 6. However some redistribution of spin density is probable in the radical anion of (III) compared to the radical anion of benzophenone for two reasons. First, (III) is not planar and secondly the effect of the ethylene carbon bridge has to be considered. A series of simple Hückel MO calculations were therefore made allowing for these two considerations in the usual way, *i.e.* $\beta_{5,13} = \beta_{5,15} = \beta_{cc}\cos\theta$ and $\alpha_{12} = \alpha_{14} = \alpha_c + h\beta_{cc}$. The results of these calculations (summarised in Table 2) confirm that the theoretical spin distribution in the radical anion of

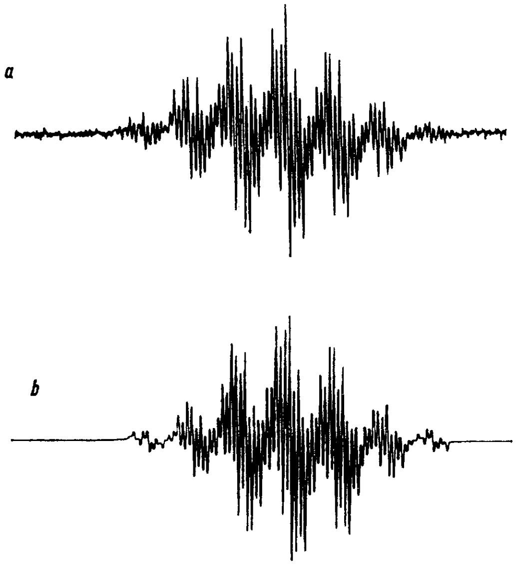


FIGURE 2 *a*, The e.s.r. spectrum, recorded at -40 °C, obtained by the electrolytic reduction of (III) in dimethylformamide; *b*, a computer reconstruction based on the coupling constants given in Table 2

(III) is indeed similar to that observed for the radical anion of benzophenone.

In view of the results of these calculations it seems unreasonable to associate a(4H) = 0·296 mT with the four β protons at positions 10 and 11. Indeed one would only expect all the protons at these positions to be equivalent if there is rapid interconversion between the possible radical anion conformers at the temperature of the measurements. It appears therefore that the quintet could well result from the accidental equivalence of two sets of protons with the radical anion existing as a single conformer (as far as e.s.r. measurements are concerned) at the temperature of the measurements. The results of McLachlan SCF calculations (with λ = 1·2) are also summarised in Table 2. It is interesting to note that these latter calculations predict near equivalence for positions 2, 4, 6, and 8 when θ lies between 20 and 30°. In view of this result it is tempting, and probably quite reasonable to assign a(4H) = 0·296 mT to those positions. The values of a(2H) = 0·358 and 0·031 mT are then assigned to the β protons.

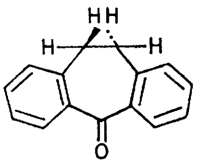
Table 2

A comparison of experimental and calculated coupling constants (mT) for the radical anion of (III)

	Position					
	1	2	3	4	β_{ax}	β_{eq}
Experimental	0·060	0·296	0·088	0·296	0·358	0·028
McLachlan [a] θ = 20°	−0·069	0·299	−0·102	0·297	0·345—0·377 [b]	
McLachlan [a] θ = 30°	−0·062	0·280	−0·092	0·275	0·315—0·345 [b]	

[a] $Q = |2{\cdot}5|$, $\lambda = 1{\cdot}2$, $\alpha_o = \alpha_c + 1{\cdot}0\beta_{cc}$, $\beta_{co} = \beta_{cc}$. [b] Values for ψ over the range 25—30° [from equation (1)].

With a single conformer, corresponding to the most planar π arrangement for the radical anion, two 'axial' and two 'equatorial' protons result (IIIa). In this arrangement the value of a(2H) = 0·358 mT would be associated with the β_{ax} protons with a much smaller value [presumably a(2H) = 0·028 mT] assigned to the β_{eq} protons. This assignments receives further support from a consideration of the values of β_{ax} predicted from the relationship[7] (1) (see Table 2) which lie encouragingly close to the experimental value of 0·358 mT.



(IIIa)

$$\alpha_\beta = \rho^\pi(B_0 + B\cos^2\psi) \qquad (1)$$

5H-*Dibenzo*[a,d]*cycloheptene* (I).—When a tetrahydrofuran solution of (I) was brought into contact with lithium, sodium, or potassium at room temperature an orange-yellow solution with an associated e.s.r. spectrum immediately developed. Unlike the spectra obtained for the radical anions of (II) and (III) the spectra obtained for the radical anion of (I) varied markedly with temperature and counterion. (The linewidth of the spectra also varied over the range of temperatures studied.) The radical anion was quite stable over the range +60 to −105 °C and the changes in the spectrum were reversible. Indeed measurements made on the sample tube over a period of two years gave identical spectra at each temperature.

The e.s.r. spectra of the coloured solutions depended on the counterion to a lesser extent than on the temperature. In order to investigate if the changes in the spectra with temperature were related to the alkali metal counterion, a sample of (I) was electrolytically reduced in dimethylformamide. The characteristic orange-yellow colour developed at the cathode. Unfortunately it was only possible to record the e.s.r. spectrum of the electrolytically reduced species over a relatively small temperature range (−30 to −70 °C). However the spectra of the electrolytically reduced species were very similar to those obtained when potassium was the counterion and also to those obtained at −90 °C when either lithium or sodium was the counterion, except for small differences in the magnitude of the coupling constants (see Table 3).

When either Li$^+$ or Na$^+$ was the counterion, a narrow line spectrum was obtained at −70 °C (see Figure 3*a*). This was readily interpreted in terms of an a(4H) quintet (0·414 mT), three a(2H) triplets (0·225, 0·101, and 0·050 mT) and one a(1H) doublet (0·110 mT). A computer reconstruction based on these coupling constants confirms this interpretation (see Figure 3*b*). Again as with the radical anion of (III) the quintet may arise by accidental equivalence. A preliminary assignment of coupling constants may be made by comparison with the stilbene radical anion.[8] Hence the quintet can be assigned to positions 3, 7, 10, and 11, the 0·225 mT triplet to positions 1 and 9, the 0·101 mT triplet to positions 2 and 8, and the 0·050 mT triplet to positions 4 and 6. The single proton coupling constant (0·110 mT) must be associated with position 5, the remaining 5-H proton having a coupling constant close to zero. At this temperature, therefore, the rate of interconversion beteeen the two possible conformers for the radical anion of (I) must be slow leading to different environments for the two β protons. An examination of a molecular model of (I) indicates that one of the β protons lies very close to 90 °C to the

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[7] C. Heller and H. M. McConnell, *J. Chem. Phys.*, 1960, **32**, 1535.

[8] N. M. Atherton, F. Gerson, and J. N. Ockwell, *J. Chem. Soc.* (*A*), 1966, 109.

p orbitals of the π system and this would therefore account for the lack of a splitting constant associated with this proton.

As the temperature was raised the spectrum changed until, at −20 °C, the spectrum shown in Figure 3*c* was obtained. Above this temperature, the spectrum changed only slightly when Li^+ was the counterion, but continued to change quite markedly when Na^+ was the counterion. At high temperatures where interconversion between conformers is rapid a 1 : 2 : 1 triplet with coupling constant $a_{\beta_{av}} = \frac{1}{2}(a_{\beta_1} + a_{\beta_2})$ (*i.e.* 0·055 mT) would be expected. When the rate of interconversion is comparable to the frequency difference between the two coupling constants, linewidth alternation would be expected leading to broadening of the central line of the triplet and resulting in a 1 : 1 doublet with coupling constant $\bar{a}_\beta = (a_{\beta_2} + a_{\beta_1})$ (*i.e.* 0·110 mT). Certainly the spectrum at +48 °C with Li^+ as the counterion responds well to the interpretation based on rapid interconversion (see Table 3). The interpretation of the spectrum at −20 °C with Li^+ as the counterion is perhaps a little less certain. An interpretation based on the anticipated situation for an intermediate rate of interconversion is acceptably close to the experimental spectrum. Unfortunately, however, as both the spectra at −20 and at +48 °C have more or less the same linewidth it is not possible to make the distinction between the two as clearly as we would have wished. However, the interpretation of the spectrum is consistent with the anticipated temperature dependence.

TABLE 3

A summary of the experimental coupling constants (mT) for the radical anion of (I) over a range of different temperatures and/or different counterions

		Coupling constant								
Counterion	t (°C)	a_1	a_2	a_3	a_4	a_{10}	a_{β_1}	a_{β_2}	$a_{\beta_{av}}$	$\bar{a}_\beta$
Li^+	−70	0·225	0·101	0·414	0·050	0·414	0·110	0·000		
	+48	0·220	0·110	0·420	0·055	0·420			0·055	
Na^+	−70	0·225	0·101	0·414	0·050	0·414	0·110	0·000		
	+45 [a]	0·205	0·090	0·405	0·045	0·405			0·045	
	+45 [b]	0·205	0·090	0·405	0·045	0·405				0·090
K^+	−80	0·230	0·103	0·419	0·051	0·419	0·103	0·000		
Electrolytic	−70	0·230	0·103	0·419	0·051	0·419	0·103	0·000		

[a] Assigned to the solvent separated ion pair. [b] Assigned to the contact ion pair.

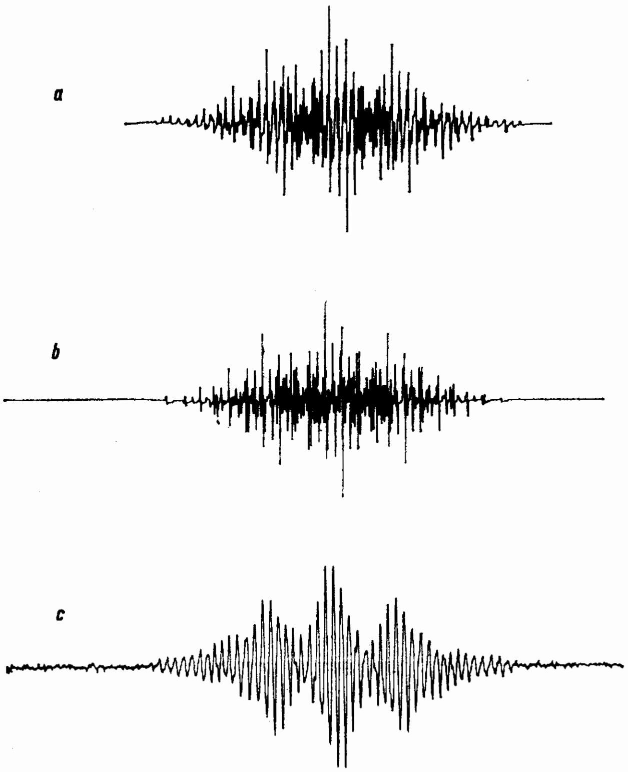

FIGURE 3 *a*, The e.s.r. spectrum, recorded at −60 °C, of the radical anion of (I) with Na^+ as the counterion in tetrahydrofuran; *b*, a computer reconstruction based on the coupling constants given in Table 3; *c*, the e.s.r. spectrum, recorded at −20 °C, of the radical anion of (I) with Li^+ as the counterion in tetrahydrofuran

The changes which occur in the spectrum when Na^+ is the counterion do not fit neatly into the above discussion. At these higher temperatures (*i.e.* > −20 °C) the spectra when Na^+ is the counterion are quite different to those when Li^+ is the counterion. In the former case the spectra become asymmetric at *ca.* +10 °C, although the asymmetry becomes less marked and the linewidth becomes much smaller than the corresponding spectra with Li^+ as the counterion as the temperature is raised further.

The asymmetric Na^+ spectrum at +48 °C can be interpreted in terms of the superimposition of two spectra (of approximately equal intensity) with centres removed by *ca.* 0·045 mT (see Figure 4*a*). The coupling constants of one of the two species are consistent with rapid interconversion between conformers, and of the other are consistent with an intermediate rate of interconversion (*cf.* Li^+ and Na^+ at −20 °C, see Table 3). Since the observed differences between the Na^+ and Li^+ systems result solely from a change in the counterion an explanation could lie in the ion-pairing properties of the radical anion of (I). If it is assumed that both contact and solvent separated ion pairs are present (Scheme) and that the rate of equilibration between them is slow compared with the e.s.r. time scale, then the two types of ion pair would contribute separately to the e.s.r. spectrum. If the rate of interconversion between conformers in the contact ion pair is much slower than in the solvent separated ion pair (a study of molecular models entirely supports this viewpoint) the solvent separated ion pairs could lead to the spectrum in Figure 4*b* and the contact ion pairs to the spectrum in Figure 4*c*. The *g* value of spectrum 4*c* is greater than that of spectrum 4*b* which adds further support to this suggestion.

$$\begin{tikzcd}
\text{Conformer 1, } (\mathrm{I})^{\overline{\cdot}}\ \mathrm{Na}^+ \arrow[d, shift left, "\text{slow}"] \arrow[r, shift left, "\text{slow}"] & \text{Conformer 1, } (\mathrm{I})^{\overline{\cdot}}\|\mathrm{Na}^+ \arrow[d, shift left, "\text{fast}"] \arrow[l, shift left] \\
\text{Conformer 2, } (\mathrm{I})^{\overline{\cdot}}\ \mathrm{Na}^+ \arrow[u, shift left] & \text{Conformer 2, } (\mathrm{I})^{\overline{\cdot}}\|\mathrm{Na}^+ \arrow[u, shift left]
\end{tikzcd}$$

Contact ion pairs Solvent separated ion pairs

SCHEME

EXPERIMENTAL

Materials.—Tetrahydrofuran, lithium, sodium, and potassium were purified as described.[9] Tetra-n-butylammonium iodide and dimethylformamide were obtained commercially and were used without further purification. 10,11-Dihydro-5*H*-dibenzo[*a,d*]cyclohepten-5-one (Aldrich) was used as supplied. 5*H*-Dibenzo[*a,d*]cyclohepten-5-one (Aldrich) was recrystallised twice from AnalaR benzene and dried *in vacuo* over P_2O_5 and silica gel.

5*H*-Dibenzo[*a,d*]cycloheptene was prepared from (II) as follows.[10] Compound (II) (2·02 g) and aluminium isopropoxide (8·05 g) were thoroughly mixed and heated between 240 and 260 °C. White, fluorescent plates of (I), isolated directly from the reaction mixture by sublimation, were recrystallised from AnalaR acetone. The purity of (I)—(III) was confirmed by m.p.s and by n.m.r. spectra.

Procedure.—Solutions of (I)—(III) in tetrahydrofuran were prepared as described using standard high vacuum techniques.[9] The concentrations of the resulting solutions were *ca.* 10^{-3}M. The solutions of the radical anions were prepared for e.s.r. study as described [1] by passing over a film of the alkali metal (except in the case of lithium when finely cut pieces of metal were used).

Dimethylformamide solutions for electrolytic reduction were in the range 0·5—2·0 × 10^{-3}M with 0·1M-tetra-n-butylammonium iodide as supporting electrolyte. A 4 mm sample tube with a mercury cathode and platinum anode was used and dry nitrogen was bubbled through the solutions for 10 min before reduction. The samples were reduced *in situ* by carefully raising the applied voltage until the radical anions were formed as indicated by the appearance of an e.s.r. spectrum.

Spectroscopic Measurements.—E.s.r. spectra were recorded on a Varian E3 spectrometer and temperature control of the samples by means of a Varian E 4557 variable temperature accessory. Computer simulation of spectra were on a Digico Micro 16 computer.

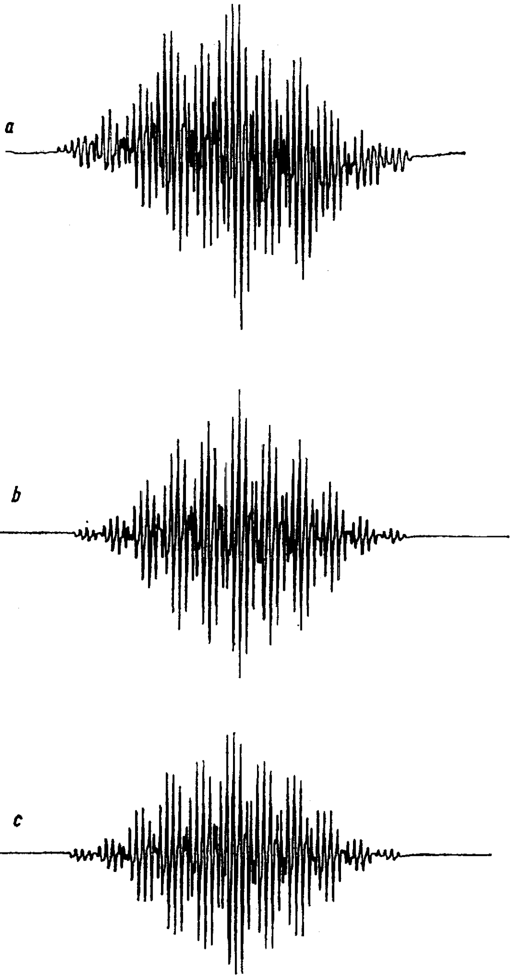

FIGURE 4 *a*, The e.s.r. spectrum, recorded at +45 °C, of the radical anion of (I) with Na^+ as the counterion in tetrahydrofuran; *b*, a computer reconstruction of one of the component spectra contributing to the e.s.r. spectrum of Figure 4*a*, possibly due to solvent separated ion pairs; *c*, a computer reconstruction of one of the component spectra contributing to the e.s.r. spectrum of Figure 4*a*, possibly due to contact ion pairs

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[9] D. Casson and B. J. Tabner, *J. Chem. Soc.* (*B*), 1971, 479.

[10] R. D. Hoffsommer, D. Taub, and N. L. Wendler, *Chem. and Ind.*, 1964, 482.