

CONJUGATED RADICALS. XIV.*

ELECTRONIC SPECTRA AND SEMIEMPIRICAL CALCULATIONS
ON RADICAL ANIONS OF ACENAPHTHYLENE, FLUORANTHENE
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Acenaphthylene, fluoranthene and 2,4-dimethylaceheptylene radical anions have been prepared in dimethoxyethane by alkali metal reduction and in acetonitrile by electrochemical generation. Electronic spectra measured in these media correspond well to one another and are in agreement with semiempirical open shell PPP-like calculations.

This series is concerned with the semiempirical PPP-like treatments of radicals, with the object of calculating ground-state properties and transition energies. It was found possible to interpret satisfactorily the electronic spectra of alternant hydrocarbon radicals and radical ions of various types¹⁻⁴. With respect to an important role of non-alternant systems in theoretical chemistry we decided to devote the present paper to the study of acenaphthylene, fluoranthene and aceheptylene anion radicals (Fig. 1). These radicals have been already studied both experimentally⁵⁻⁹ and theoretically¹⁰, but with emphasis only on the electron spin resonance. The electronic spectra have not been studied, to our knowledge the only attempt reported so far is that of Pointeau and Favade¹¹, who recorded the absorption of the fluoranthene anion radical in the region of 400–700 m μ . In order to judge the results of the calculations against the reliable data, we prepared the radicals in two independent ways: by electrolysis and by alkali metal reduction. The latter method enabled us also to prepare the solutions of the corresponding dianions.

EXPERIMENTAL

Substances and solvents. Acenaphthylene and fluoranthene were obtained commercially and purified by vacuum sublimation. The synthesis of 2,4-dimethylaceheptylene was reported previously¹². Tetrabutylammonium perchlorate was prepared by mixing a hot aqueous solution of

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tetrabutylammonium bromide and perchloric acid; the precipitate was repeatedly recrystallized from ethyl acetate and vacuum-dried. Acetonitrile was purified by refluxing with calcium hydride, followed by fractional distillation from calcium hydride¹³. Dimethoxyethane was refluxed with an Na-K alloy and distilled under purified nitrogen, repeating this procedure several times.

Electrochemical generation of radicals. Controlled potential electrolysis and polarographic measurements were carried out in acetonitrile with the use of 0.1M tetrabutylammonium perchlorate as a supporting electrolyte. A description of the electrochemical cell and the procedure was given previously¹⁴. Measurements of half-wave potentials were performed in a three-electrode arrangement using an OH-102 polarograph (Radelkis, Budapest) with a built-in electronic potential drop compensator. An aqueous saturated calomel electrode with an asbestos fibre was used as a reference electrode. The half-wave potentials were determined against a recommended standard bis-diphenylchromium (I) iodide¹⁵ ($E_{1/2} = -0.640$ V vs S.C.E.) and are believed to be precise to within 10 mV. The electrochemical cell was placed directly in a cell compartment of an Optica Milano CF-4 spectrophotometer. Concentration of a radical formed in electrolysis was estimated polarographically from the magnitude of the anodic current.

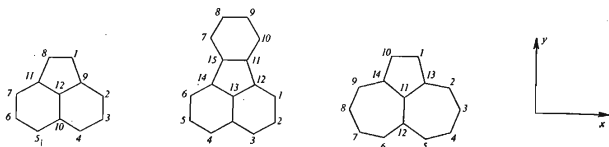
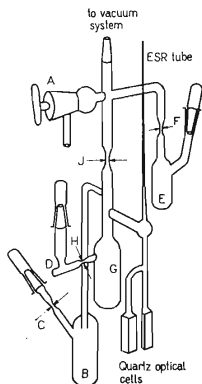


FIG. 1

Skeletons of the Systems Studied

Experimental results for acceptylene concern the 2,4-dimethyl derivative, in the theoretical approach the methyl groups were ignored.



Alkali metal reduction. Although this method is very popular and widely used, we think it is worthy of being described here, as our attempts to employ the apparatus according to the designs reported in literature¹⁶⁻¹⁸ were met with some difficulties, which led us to modifications in the reaction vessel. Our apparatus is shown in Fig. 2. The solutions of mono-negative and dinegative ions were prepared by the following procedure. On connecting the entire vessel to the vacuum system, traces of water and oxygen on the wall were removed by heating and discharging with a Tesla coil. Then the apparatus was filled with purified nitrogen through A, the weighed sample of the hydrocarbon was put into B through C, a piece of sodium was put into D, and dimethoxyethane was distilled into E, where a small amount of an Na-K alloy was added.

FIG. 2

Apparatus for the Preparation of Negative Ions

After new pumping to vacuum the solvent was distilled from E into B, the bulb E was sealed off at F, and the sodium was sublimed to form a mirror on the wall of the bulb G. On sealing off the capillaries C and H, the apparatus was pumped to high vacuum for one hour and then sealed off at J. The solution of the hydrocarbon was poured from B into G. After a time varying from several minutes to several hours, a colour was observed, and the sample was ready for optical and ESR measurements. Extinction molar coefficients were estimated from the titrimetrically determined concentration of the sodium hydroxide formed in the hydrolyzed sample.

Course of the electrolysis. The electrolytic reduction of acenaphthylene, fluoranthene and 2,4-dimethylaceheptylene was carried out at a potential of 0.3 V more negative with respect to the half-wave potential of the first wave (Table I). Under these conditions the radical anions formed should be free of the corresponding dinegative ions, as a rather large gap between the first and second wave indicates a high value of the semiquinone formation constant with all three hydrocarbons studied (Table I). Disproportionation of the mononegative ions therefore appears to be improbable. The highest concentration of the radicals was reached in about 20 minutes after the beginning of the electrolysis. All these radicals were sensitive to oxidation. Although being under purified nitrogen, they were converted reversibly into the parent hydrocarbons within one minute after interrupting the electrolysis. This was proved both polarographically and spectrophotometrically.

Course of the alkali-metal reduction. With all three hydrocarbons studied the reduction proceeded with an appearance and increase of a brown colour and ESR signal in intensity. At this stage after a transfer from the bulb containing sodium (from G to B, Fig. 2), solutions of radicals were stable for several days. Their recorded ESR spectra were in agreement with those reported in the literature^{6,19}. On prolonged reduction, the ESR signal decreased and deep emerald-green acenaphthylene and 2,4-dimethylaceheptylene dianions and reddish-brown fluoranthene dianion were formed. After about 30 hours the reduction was completed, exhibiting no ESR signal. In some runs only one half of the hydrocarbon solution was allowed to stay in contact with sodium, while the other one was kept in the bulb B. After proving by ESR measurements that the reduction was completed and no radical was present any longer, the solutions were mixed in the bulb B. Colour change and appearance of a strong ESR signal indicated the comproportionation reaction $R^{2-} + R \rightarrow 2R^-$ proceeded. Both optical and ESR spectra of radicals prepared in this way were identical with those recorded after a one-electron reduction. This treatment afforded also strong evidence for the presence of dinegative ions in the oxidation-reduction system.

TABLE I
Half-Wave Potentials and Estimated Semiquinone Formation Constant^a (*K*) for Radical Anions

Compound	$E_{1/2}^b$		log <i>K</i> ^c
	first wave	second wave	
Acenaphthylene	1.60	2.30	11.7
Fluoranthene	1.70	2.27	9.5
2,4-Dimethylaceheptylene	1.28	2.16	14.7

^a Concerning the $R + R^{2-} \rightleftharpoons 2R^-$ equilibrium; ^b In volts vs s.c.e.; ^c $\Delta E_{1/2}$ (V) = 0.06 log *K*; $\Delta E_{1/2}$ (V) is the half-wave potential difference of the first and the second polarographic wave²⁴.

On further staying on sodium for several days, no changes in the electronic spectra of dinegative ions (these will be discussed in a later paper) were observed. After complete one-electron or two-electron reduction the samples were exposed to air, and the measured electronic spectra were compared with those of the parent hydrocarbons to confirm the measured absorption for the mononegative and dinegative ions, respectively.

CALCULATIONS

The calculations undertaken on the radical anions were of the PPP-type combining the open shell SCF procedure of Longuet-Higgins and Pople²⁰ with the configuration interaction. For

TABLE II

Results of the Semiempirical Calculations on Anion Radicals

Transition energy ^a	f^b	$\log f$	Polarization ^c	Main contributions ^d
Acenaphthylene anion radical				
14-34	0-000	-3-413	x	B (7 → 8) 67-7; A (6 → 7) 24-0
17-78	0-032	-1-500	x	A (6 → 7) 62-7; B (7 → 8) 26-0
19-28	0-002	-2-598	y	A (5 → 7) 47-4; B (7 → 9) 45-6
23-13	0-024	-1-615	x	B (7 → 10) 78-7; A (4 → 7) 7-6
25-35	0-213	-0-671	y	A (5 → 7) 40-4; B (7 → 9) 40-3
30-94	0-059	-1-232	x	A (4 → 7) 76-0; C _α (5 → 8) 11-2
33-36	0-020	-1-702	y	B (7 → 11) 71-0; C _β (4 → 8) 9-6
35-58	0-004	-2-354	x	A (3 → 7) 40-3; C _β (6 → 9) 17-9
37-22	0-001	-3-151	y	C _β (6 → 8) 64-8; C _β (4 → 8) 24-1
38-57	0-020	-1-689	y	C ₂ (6 → 8) 83-2; B (7 → 11) 5-4
40-36	0-502	-0-299	x	C _β (5 → 8) 41-1; C _α (5 → 8) 35-8
Fluoranthene anion radical				
13-47	0-020	-1-701	x	B (9 → 10) 88-4; C _β (8 → 10) 5-1
14-50	0-001	-3-099	x	B (9 → 11) 95-0; A (7 → 9) 1-3
18-87	0-031	-1-513	y	B (9 → 12) 63-8; A (8 → 9) 32-1
22-64	0-000	-3-642	x	A (7 → 9) 43-8; B (9 → 13) 37-3
23-87	0-384	-0-416	y	A (8 → 9) 56-6; B (9 → 12) 28-7
25-46	0-037	-1-428	x	B (9 → 13) 44-8; A (7 → 9) 42-4
31-39	0-036	-1-443	x	A (6 → 9) 71-3; C _α (8 → 11) 17-6
34-67	0-001	-2-971	y	C _β (7 → 10) 43-4; A (5 → 9) 36-3
34-68	0-036	-1-447	x	C _β (5 → 10) 33-1; C _β (8 → 10) 28-2
35-89	0-093	-1-030	y	C _α (7 → 10) 33-3; C _β (7 → 10) 25-8
37-87	0-278	-0-555	x	C _β (8 → 11) 28-6; C _α (8 → 11) 27-8
39-38	0-193	-0-715	y	C _β (6 → 11) 32-8; C _α (7 → 10) 21-1
39-78	0-082	-1-084	x	C _α (8 → 10) 65-2; C _β (5 → 10) 9-2
40-14	0-406	-0-391	y	C _α (7 → 10) 27-0; C _β (6 → 11) 22-1

TABLE II
(Continued)

Transition energy ^a	f^b	$\log f$	Polarization ^c	Main contributions ^d
Aceheptylene anion radical				
9.55	0.025	-1.606	<i>x</i>	B (8 → 9) 83.9; A (7 → 8) 6.7
11.40	0.000	-3.724	<i>y</i>	B (8 → 10) 94.6; A (4 → 8) 1.4
15.10	0.008	-2.125	<i>x</i>	A (7 → 8) 89.3; B (8 → 9) 5.5
21.31	0.056	-1.250	<i>y</i>	$C_\beta(7 \rightarrow 9)$ 59.9; $C_\alpha(7 \rightarrow 9)$ 26.9
21.66	0.016	-1.809	<i>x</i>	$C_\beta(7 \rightarrow 10)$ 84.7; B (8 → 11) 8.5
23.50	0.000	-6.372	<i>y</i>	A (6 → 8) 68.5; $C_\beta(7 \rightarrow 9)$ 12.8
27.89	0.015	-1.816	<i>x</i>	B (8 → 11) 58.1; A (5 → 8) 11.5
28.01	0.115	-0.937	<i>y</i>	$C_\alpha(7 \rightarrow 9)$ 40.5; A (6 → 8) 17.2
29.32	0.149	-0.825	<i>x</i>	$C_\alpha(7 \rightarrow 10)$ 62.6; A (5 → 8) 23.3
33.45	0.060	-1.222	<i>x</i>	$C_\alpha(6 \rightarrow 9)$ 39.7; B (8 → 11) 16.7
35.24	0.008	-2.112	<i>y</i>	B (8 → 12) 36.1; $C_\beta(6 \rightarrow 10)$ 25.2
37.02	0.009	-2.041	<i>y</i>	A (4 → 8) 42.2; $C_\beta(7 \rightarrow 11)$ 27.1
37.54	0.518	-0.285	<i>x</i>	$C_\beta(6 \rightarrow 9)$ 39.6; $C_\alpha(6 \rightarrow 9)$ 27.0
39.13	0.384	-0.416	<i>y</i>	$C_\beta(6 \rightarrow 10)$ 44.5; B (8 → 12) 26.4

^a In $\text{cm}^{-1} \cdot 10^{-3}$; ^b oscillator strength; ^c for definition of *x* and *y* axis see Fig. 1; ^d weights of singly excited configurations of the A, B, C_α , and C_β types in %.

parameters and computational details see¹. In the present open shell calculations we employed a variable β approximation²¹

$$\beta_{\mu\nu} = \beta_{\mu\nu}^0 \exp(-1.862r_{\mu\nu} + 2.597),$$

$$r_{\mu\nu} = 1.517 - 0.18p_{\mu\nu},$$

where for β^0 we use the value -2.318 eV, and $p_{\mu\nu}$ and $r_{\mu\nu}$ stand for bond orders and interatomic distances.

RESULTS AND DISCUSSION

Electronic spectra of the radical anions under study are seen in Fig. 3 to be rather complex. Absorption curves obtained by two experimental techniques are in a good correspondence, particularly the wavelengths of absorption maxima are in good agreement. Observed differences in spectral intensities are believed to be more likely due to uncertainties in the determination of radical concentration than to a solvent effect. The only qualitative disagreement in the spectra was found for the fluoranthene radical anion in the ultraviolet region, where even in the range of about 25000 to

29000 cm^{-1} we were not able to estimate the absorption of the radical anion owing to a strong absorption of both the parent hydrocarbon and its dinegative ion in that

TABLE III
ESR Coupling Constants

Position ^a	Calculated ^b	Observed ^c	Position ^a	Calculated ^b	Observed ^c
Acenaphthylene ⁻			Fluorathene ⁻		
1	2.565	3.09	3	5.427	5.20
2	4.158	4.63	7	0.027	(0)
3	-0.405	0.55 ^d	8	0.891	1.30
4	6.426	5.71			
Fluoranthene ⁻			Aceheptylene ⁻		
1	3.807	3.90	1	0.513	0.32 ^{d,e}
2	0.189	(0)	3	-0.918	1.28 ^{d,e}
			6	-1.053	0.99 ^{d,e}

^a For numbering see Fig. 1; ^b McConnell relation $a_{\mu}^H = 27\varrho_{\mu}$ was employed, ϱ_{μ} stands for the calculated spin densities; ^c Refs^{6,9,19}; ^d The sign of the spin density was not determined experimentally; ^e Coupling constants were measured for the 2,4,7,9-tetramethyl derivative.

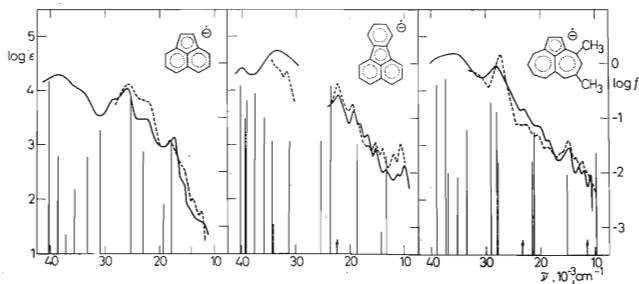


FIG. 3

Electronic Spectra of Acenaphthylene, Fluoranthene and 2,4-Dimethylaceheptylene Anion Radicals and Results of the Semiempirical Calculations

Anion radicals were prepared by alkali metal reduction — solid curves, electrochemically — dashed curves. Vertical lines — the results of the semiempirical calculations; full lines — allowed transitions, wavy lines with arrows — forbidden transitions. The left side scale concerns experimental intensities, the right side scale the calculated ones, (f theoretical oscillator strengths).

region. Results of semiempirical calculations, summarized in Table II, afford a reasonable interpretation of the complex nature of the spectra. As seen in Fig. 3, the theory predicts a great number of allowed electronic transitions within the whole spectral range studied. Generally speaking, the shapes of the absorption curves correspond to the theoretical predictions, although *e.g.* the first absorption bands are not estimated as accurately as those of alternant hydrocarbon radical anions^{2,4}. For the 2,4-dimethylaceptylene radical anion we tried to estimate the effect of methyl groups on the location of the first absorption maximum by means of the first-order perturbation treatment²², however, this effect was found to be negligible.

Finally, it is worth mentioning that our calculations also provide a reasonable interpretation of ESR spectra (Table III). It should be pointed out that the spin densities were calculated without any change in the SCF-CI computational scheme²³ and without any change in the semiempirical parameters adopted.

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