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Abstract

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INFRARED SPECTRA OF RADICAL ANIONS OF AROMATIC HYDROCARBONS

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The vibrational spectra of polyatomic radicals have been studied very little (1). In the present work, the IR spectra of the radical anions of naphthalene, anthracene, tetracene, and pentacene were investigated. The radical anions of naphthalene and anthracene are convenient objects for the study of IR spectra, since the vibrational spectra of naphthalene (2) and anthracene (3) are well known. Upon radicalization of the molecule, its configuration and symmetry do not change. The electronic state of radical anions and the distribution of electron density in them have repeatedly been obtained on the basis of ESR spectra and calculations by the Hückel MO method (4). Thus it is possible to trace the influence of the unpaired electron on various vibrations in the molecule. For a more reliable assignment of the bands of the radical anions, the IR spectra of the radical anions of fully deuterated naphthalene and anthracene were studied.

The radical anions of aromatic hydrocarbons were obtained by the known reaction of the hydrocarbon (5,6) on a mirror of metallic potassium in a solution of tetrahydrofuran (THF) under a vacuum of not less than $1 \cdot 10^{-5}$ mm Hg:

$$\text{hydrocarbon} + \text{K} \rightarrow (\text{hydrocarbon})^{-} + \text{K}^{+}.$$

The resulting intensely colored solution was transferred into an IR vacuum cell (windows of NaCl or KBr), 0.10-0.15 mm thick. We studied solutions in which naphthalene (or anthracene) had been converted into the radical by 80-90%. IR spectra were recorded on a UR-10 double-beam spectrometer in the region 400-3200 cm^{-1}. The spectral slit width was 5.5 cm^{-1} in the region 400-600 cm^{-1}; 3.5 cm^{-1} in the region 700-1000 cm^{-1}; 7.5 cm^{-1} at 1500 cm^{-1}, and 1.9 cm^{-1} at 2100 cm^{-1}.

The most intense absorption bands of THF are: 2800-3000, 850-960, 1030-1120, 1190-1250, 1450-1500, 650-670 cm^{-1}. Because of the lower solubility in THF of the deuterated products, tetracene, and pentacene, their solutions had to be recorded in cells of greater thickness (0.3-0.4 mm). Therefore the absorption of the solvent increased, and it was not possible to detect the absorption bands of the hydrocarbons in the region 1200-1600 cm^{-1}.

In the solutions obtained by us, molecules of the hydrocarbon and of its radical anion are present (Fig. 1). The absorption bands of the radical anion are most intense at the initial moment of formation of the radical and gradually disappear when air is admitted, in parallel with the decolorization of the solution.

In the spectrum of the naphthalene radical anion, a lowering of frequencies is observed in comparison with naphthalene (Table 1). In identifying the radical bands, we assumed that radicalization should cause identical shifts in both the deuterated and undeuterated hydrocarbon, since their electronic structure is the same. In fact, the frequency shifts naphthalene → radical proved to be approximately equal to the shifts naphthalene-d_8 → radical-d_8 for each absorption band (the latter are somewhat smaller, Table 1). In the region 1300-1600 cm^{-1}, the reliability of the assignment of the radical bands is complicated by the fact that in naphthalene-d_8 it was not poss—

was possible to observe bands of such intensity as in the d_8 radical.

In the spectrum of the anthracene anion and anthracene-d_{10}, intense absorption bands are also found, which can be associated with certain vibrations (Table 2). Our assignment of the bands of anthracene-d_{10} agrees with that proposed by Califano ([3]).

In the spectra of the hydrocarbons and anions of tetracene and pentacene, few bands were detected. In tetracene the frequency 750 cm^{-1}, and in pentacene 742 cm^{-1}, corresponds to out-of-plane C—H vibrations (B_{1u}); in the anions they are represented by frequencies of 728 and 723 cm^{-1}, respectively.

The general tendency toward a decrease in frequencies and intensities can be explained by the lower stability of the radical-anion molecule, since the unpaired electron is located in an antibonding orbital of the hydrocarbon molecule. This leads to weakening of all bonds in the molecule, to a decrease in the force constants of the corresponding bonds, and to an increase in bond lengths. The latter agrees with the results of calculations of bond orders obtained by Hoytink and co-workers ([7]) for alternant hydrocarbons and their anions.

Because of the greater absorption of the solvent in the region 2800-3000 cm^{-1}, it was not possible to reliably detect the frequencies of the stretching vibrations of the radical C—H; however, in the naphthalene-d_8 anion the frequency of the C—D vibration is 31 cm^{-1} lower than the frequency of the corresponding vibration of naphthalene, and in the anthracene-d_{10} anion it is 18-22 cm^{-1} lower than in anthracene-d_{10}. The smaller shift for anthracene than for naphthalene is understandable, since in anthracene-d_{10} each C—D bond carries a smaller electron density.

Fig. 1. IR spectra of hydrocarbons and their radical-anions in THF. Band designations: P —radical-anion, H —naphthalene, A —anthracene, T —tetracene, —pentacene.

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Assignment of IR bands of the radical anions of naphthalene and naphthalene-d_8

Naphthalene, cm^{-1}	Radical anion	$\Delta\nu$	Deuteronaphthalene	Radical anion	$\Delta\nu$	Symmetry class	Form of vibrations
480	470	10	408	398	10	B_{1u}	Skeletal vibrations, non-planar
618	595	23	593	574	19	B_{3u}	Skeletal vibrations, planar
788	720	68	634	574	60	B_{1u}	C—H (D) out-of-plane vibrations
(960)	840		800	685	115	B_{1u}	C—H (D) out-of-plane vibrations

Naphthalene, cm^{-1}	Radical anion	$\Delta\nu$	Deuteronaphthalene	Radical anion	$\Delta\nu$	Symmetry class	Form of vibrations
1010	994	16	834	819	15	B_{3u}	C—H (D) in-plane vibrations
	1185						
	1360			1355			
	1487			1415			
3055			2278	2247	31		C—H (D) stretching vibrations

Clearer results were obtained by us in the analysis of the band of C—H out-of-plane vibrations (B_{1u}). This characteristic band, assigned to the out-of-plane vibrations of four adjacent hydrogens and located in the region 790-735 cm^{-1}, is the most intense in the spectra of hydrocarbons. The corresponding band in the radical anion is traced throughout the entire series of hydrocarbons investigated by us (Fig. 1). The difference in frequency between the hydrocarbon and the radical anion clearly decreases with increasing number of rings in the molecule. This is connected with the corresponding decrease in the electron density of the unpaired electron on the carbon atoms. It turned out that the shift of the C—H vibration frequency depends linearly on the total spin density falling on the α- and β-carbon atoms of the radical anions (Fig. 2).

Fig. 2. Dependence of the lowering of the band of out-of-plane C—H vibrations of hydrocarbon radical anions ($\Delta\nu$) on the spin density (ρ) on the carbons participating in this vibration ([4])

The decrease in the frequency of the stretching and deformation vibrations of C—H(D) in the anion is in general agreement with the results of Joesten and Jeba ([8]) and Bellamy ([8]), who studied the displacement of the frequencies of the stretching and deformation vibrations of C—H in various monosubstituted benzenes as a function of the electron-donor and electron-acceptor ability of the substituents. The frequencies decreased as the electron density on the carbons of the ring increased. The absence of such a clear linear dependence as in our case is explained by the fact that the substituents not only changed the electron density on the ring, but also made their own contribution to the vibrations of the molecules, since they had different configurations and masses.

The increased sensitivity of C—H out-of-plane vibrations to the π-electron density on carbon can be explained by the interaction of the sp^2 orbital participating in the C—H bond with the π-electron cloud during out-of-plane vibrations (^{9}). With increasing π-electron charge, the overlap increases, and the vibrations occur at a lower frequency.

In conclusion I express my gratitude to Academician of the Academy of Sciences of the Ukrainian SSR A. I. Brodsky for suggesting the topic of the work, to Academician of the Academy of Sciences of the USSR,

Table 2

Assignment of IR bands of the radical anions of anthracene and anthracene-d_{10}

Anthracene, cm^{-1}	Radical anion	$\Delta\nu$	Deuterated anthracene	Radical anion	$\Delta\nu$	Symmetry class	Form of vibrations
473	465	8	403	–		B_{1u}	Out-of-plane skeletal vibrations
603	–		583	–		B_{1u}	Out-of-plane skeletal vibrations
735	695	40	567	527	40	B_{1u}	C—H out-of-plane vibrations
(884)	777	107	728	630	98	B_{1u}	Same
(960)	803	157	790			B_{1u}	””
	1320						
	1380						
	1510						

Anthracene, cm^{-1}	Radical anion	$\Delta\nu$	Deuterated anthracene	Radical anion	$\Delta\nu$	Symmetry class	Form of vibrations
	1560		2273	2250–2255	18–23		C–D stretching vibrations

Note. The frequencies in parentheses were taken from the literature, since we did not observe them, and their assignment is tentative.

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