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ENDOR STUDIES OF [6]HELICENE ANION RADICAL

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Abstract—ESR, ENDOR and TRIPLE (electron-nuclear-nuclear triple) measurements on the reduction products of [6]helicene have been performed. From the ENDOR spectrum of the [6]helicene monoanion eight sets of equivalent protons could be deduced, being in agreement with the molecular structure. No ion-pairing was observed for the anion under the experimental conditions.

The chemical and physical properties of the helicene system such as synthesis, resolution, racemization and absolute configuration have been the subject of increasing attention[1] in recent years. The optical and magnetic properties of the reduction products of the best-known helicene, [6]helicene, were studied by Weissman and Chang.[2] Unfortunately, the resolution of the ESR spectra of the paramagnetic ions was rather poor and the hyperfine coupling constants (HFSC's) could not be determined. In such cases of very complex ESR spectra the ENDOR technique proved to be the method of choice. Actually Allendoerfer and Chang[3] performed an ENDOR study of the monoanion of [6]helicene and ten HFSC's were extracted from the ENDOR spectrum.

In this paper we report ENDOR and TRIPLE resonance experiments of the [6]helicene monoanion. As a result, the interpretation of the ENDOR spectrum of the monoanion as reported has been revised.

EXPERIMENTAL

[6]Helicene was synthesized as described.[4] The paramagnetic derivative was prepared on a high vacuum line by standard techniques[5] of [6]helicene with alkali metal in dimethoxyethane (DME) or in 2-methyl tetrahydrofuran (MTHF).

Instrumentation. The ENDOR spectrometer consists basically of a commercial AEG 20X ESR spectrometer with some modifications in the modulation/psd-section allowing the choice of three audio modulation frequencies (0.27, 1 and 10 kHz). The broadband ENDOR accessory was built in our laboratory by Dr. R. Biehl and is similar to one previously described.[6] Figure 1 shows the block diagram of the apparatus used in our experiments: The TM_{110} cavity contains a silver solenoid of 20 turns (30 mm length, 10 mm o.d., 1 mm diameter) directly mounted on the Dewar line. A 675A hp oscillator generates the rf which passes through an ENI A300 or L350 power amplifier, the solenoid, and a Bird 4230-058 power meter. Finally, the rf power is dissipated in a 50 Ω water-cooled resistor (Bird 871011). A linear ramp simultaneously sweeps the audio modulated frequency of the oscillator and drives the x-axis of the recorder hp 7004B. The phase sensitive detected (psd) changes of the absorbed microwave power generate the signal voltages driving the y-axis of the recorder. For the general TRIPLE experiments the output voltage of a second oscillator (hp 8601A) was added to that of the hp 675A via an ENI PM 12-2 power combiner before amplification by the ENI A300.

RESULTS AND DISCUSSION

From symmetry considerations one expects eight sets of HFSC's and $3^8 = 6561$ ESR lines for the paramagnetic monoanion of [6]helicene. Thus, only poorly resolved ESR spectra can be expected (Fig. 2, top). The simplifications obtained by performing the ENDOR technique are clearly demonstrated by comparison of the respective ESR and ENDOR spectra. Figures 3 and 4 (top) show ENDOR spectra of the monoanion and of the product from its further reduction, in solution.

ENDOR of [6]*helicene anion.* According to the ENDOR resonance condition $\nu_{ENDOR} = |\nu_H \pm a/2|$ each set of equivalent protons yields one pair of lines equidistant from the free proton frequency ν_H. From the ENDOR spectrum (Fig. 3, top), in agreement with the predictions from molecular symmetry, eight HFSC's can be deduced, in contrast to ten different HFSC's derived from a previous ENDOR study on this radical.[3] The alleged decrease in symmetry was accounted for by assuming ion-pairing with the potassium counter ion. However, it is possible, that the additional ENDOR lines were simply due to a paramagnetic by-product or decomposition product. Thus, the ENDOR line pattern and HFSC's remain nearly unaffected when Li, Na or K were used for generating the radical ions, even when the reaction was repeated in MTHF (Table 1). In addition, the reproduction of the experimental ESR spectrum by a computer simulation based on the ten couplings was ambiguous since the ESR spectrum can be simulated as well when only the eight HFSC's extracted from our ENDOR experiments were used (Fig. 2, bottom). Obviously the ESR spectrum[3] was too badly resolved for an accurate assurance of assignments and multiplicities. The additional very weak ENDOR lines (indicated in Fig. 3, top) have to be attributed to a paramagnetic by-product. The relative ENDOR line intensities were strongly dependent on the ESR field setting, which clearly indicates two different paramagnetic species in the sample.

Prolonged reduction of the monoanion resulted in changes of colour, complete loss of any paramagnetism and successive generation of a new paramagnetic species with significantly changed ESR and ENDOR spectra, (Fig. 4, top). This product has been assigned a [6]helicene trianion structure,[2] but we feel that all the hitherto existing arguments give no unequivocal identification of the trianion, and the formation of a paramagnetic decomposition product cannot be excluded. Since, to our knowledge, no stable paramagnetic hydrocarbon trianion with symmetry lower than threefold was ever clearly

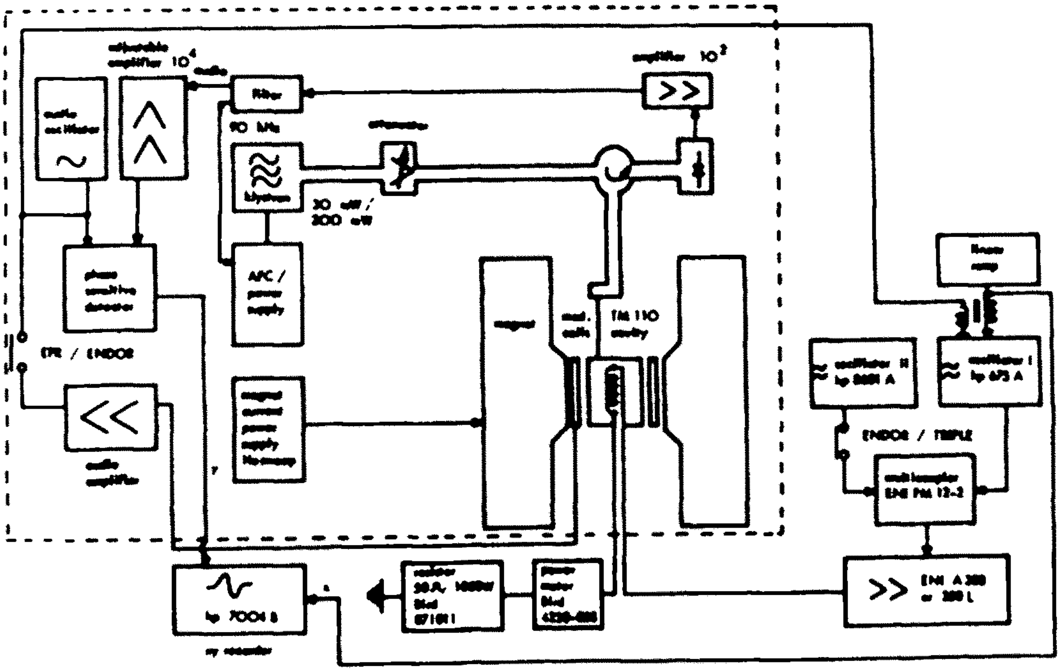

Fig. 1. Block diagram of the ENDOR/TRIPLE spectrometer. The part enclosed by the broken line represents the commercial AEG 20X ESR spectrometer.

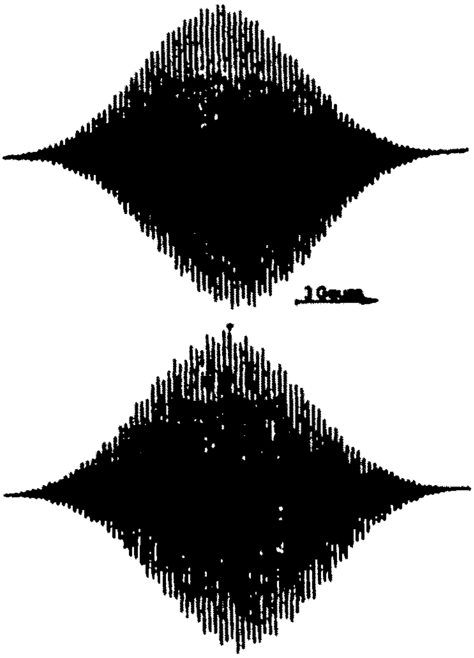

Fig. 2. Experimental (top) and computer simulated ESR spectra of the [6]helicene monoanion; solvent DME, temperature 190 K.

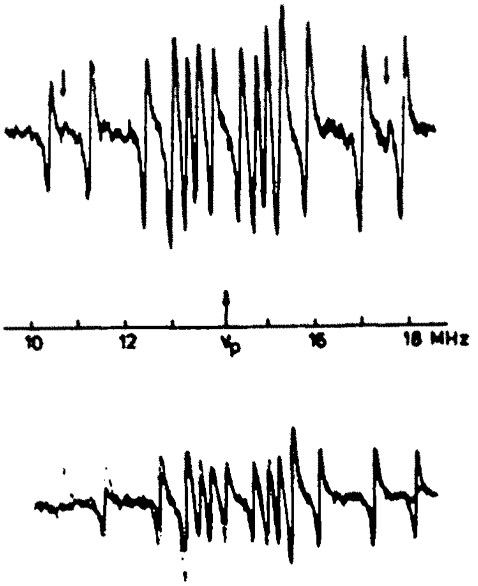

Fig. 3. ENDOR (top) and TRIPLE spectra of the [6]helicene monoanion, DME/K, 190 K. Two slightly different HFSC's contribute to the most intense and broader line pair at 13.01 and 15.23 MHz, as could be shown by higher resolution.

established, we intend to perform some careful experiments on this subject, e.g. cyclic polarography, quantitative symproportionation reactions.

General TRIPLE experiments. The recently described[7] electron-nuclear-nuclear TRIPLE resonance technique has proved to be of significant value because the relative signs of the HFSC's become accessible. Figures 3 and 4 (bottom) depict the TRIPLE spectra of both paramagnetic species derived from [6]helicene. From the spectra it is obvious that in both anions all HFSC's have the same (negative) sign except one (positive). This is in agreement with a HMO-McLachlan calculation on the [6]helicene monoanion[3] yielding a positive sign of only one HFSC (Table 1). However, the combination of relative signs of HFSC's with the quantummechanical approach still yields no unambiguous assignments of the experimental couplings to molecular positions (Table 1).

Table 1. Proton HFSC's of the [6]helicene monoanion a/MHz ±0.01

Li/DME 190 K	Na/DME 190 K	Na/MTHF 150 K	K/DME 190 K	K/DME[a]	calculated[b]
- 7,42	- 7.40	- 7.41	- 7.40	7.46	- 7.84
				6,86	
- 5,67	- 5,68	- 5,68	- 5,69	5,70	- 6,46
				5,90	
- 3,35	- 3,35	- 3,38	- 3,36	3,35	- 5,41
				2,85	
- 2,28					- 4,10
	- 2,23[c]	- 2,25[c]	- 2,23[c]	2,30	
- 2,17					- 3,05
- 1,66	- 1,67	- 1,62	- 1,66	1,60	- 0,86
- 0,59	- 0,58	- 0,59	- 0,58	0,55	- 0,08
+ 1,22	+ 1,20	+ 1,20	+ 1,22	1,21	+ 1,10

[a] Values from ref 3. Seven HFSC's are nearly identical with our values, while three additional ones are reported in ref 3 (see ordering of rows).

[b] Calculated values given in ref 3 (McLachlan).

[c] Average value of two HFSC's, see caption of Fig. 3.

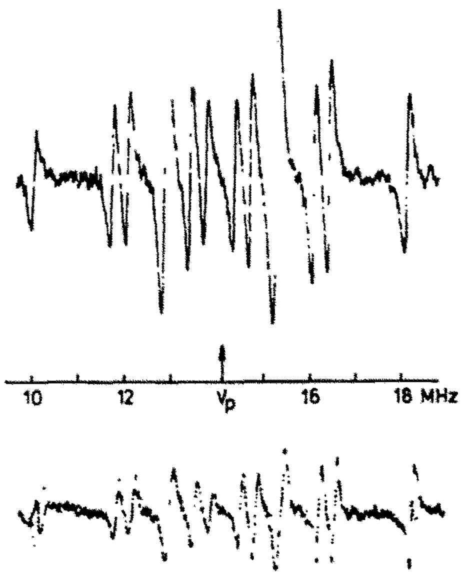

Fig. 4. ENDOR (top) and TRIPLE spectra of the radical obtained by progressive reduction of the [6]helicene monoanion, DME/K, 190 K. As in the monoanion two slightly different couplings—here with opposite sign (bottom)—contribute to the larger lines at 12.93 MHz and 15.31 MHz. The proton HFSC's (MHz) are measured to be $a_1 = -7.99$, $a_2 = -4.65$, $a_3 = -3.97$, $a_4 = -2.47$, $a_5 = -1.30$, $a_6 = -0.66$, $a_7 = +2.31$.

CONCLUSION

ENDOR and TRIPLE experiments can successfully be performed on the alkali metal reduction products generated from [6]helicene. In the monoanion significant ion-pairing could be excluded, in contrast with previous ENDOR studies,[3] and therefore no asymmetric spin density distribution has to be taken into account. However, an unambiguous assignment of all the HFSC's calls for more detailed investigations, e.g. selective deuteration. Further work on paramagnetic helicene systems is in progress including more sophisticated quantum-mechanical approaches, e.g. all valence electron calculations (INDO, MINDO/3).

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