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An EPR study of the radicals produced by γ-irradiation of Acenaphthene single crystals

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Chimica. — *An* EPR *study of the radicals produced by γ-irradiation of Acenaphthene single crystals.* Nota di GABRIELLA POGGI e GIAN CARLO MARCONI, presentata (*) dal Socio G. SEMERANO.

RIASSUNTO. — Monocristalli Acenaftene di sono stati irradiati con raggi γ a temperatura ambiente, e si sono registrati gli spettri EPR delle speci prodotte variando l'orientazione del campo magnetico entro i tre piani cristallografici della sostanza. La risoluzione degli spettri è scarsa a causa della presenza di quattro molecole nella cella unitaria e di più di una specie paramagnetica. Tuttavia, entro due dei piani cristallografici esplorati è possibile selezionare una particolare orientazione in cui si possono distinguere due speci. Si sono effettuati calcoli teorici di densità di spin su sei speci paramagnetiche e sulla base dei risultati è possibile proporre una attribuzione per entrambi.

INTRODUCTION

γ-Irradiation of single crystals of aromatic hydrocarbons can lead essentially to the following kinds of radicals: charged hydrocarbon species, H abstraction radicals and H addition radicals. Acenaphthene, due to the presence of one aromatic and one aliphatic moiety, could possibly give rise to all three types of species. In order to investigate these radiation effects we have carried out an EPR study of room temperature γ-irradiated single crystals of Acenaphthene.

EXPERIMENTAL

Single crystals of Acenaphthene were grown both from solutions and from the melt in a Bridgman oven. As solvents, a mixture of ethyl acetate-carbon tetrachloride 1 : 1, as prescribed by Ehrlich [1], and acetone, were used. The starting material was reagent grade Acenaphthene by J. T. Baker Chemicals. Prior to application of the Bridgman procedure this was repeatedly crystallized from ethyl alcohol and zone-refined. Well characterized crystal planes were identified by means of a Leitz Ortholux polarizing microscope.

Irradiation was carried out in a ^{60}Co Gammacell source, with doses of circa 50 Mrad. For EPR measurements, a Varian 4500 Spectrometer with 100 KHz modulation and operating at 9.2 GHz was used. The effect of annealing at 70^0 was also investigated but no appreciable change in the EPR spectra was observed.

(*) Nella seduta del 13 novembre 1976.

RESULTS AND DISCUSSION

The spectra of γ-irradiated single crystals of Acenaphthene show an appreciable orientation dependence in all three planes explored, *ab*, *bc*, and *ac*, where the notation is as in Ref. [1]. The number of lines observed varies between five and eleven. Within the planes *ab* and *ac* it is possible to identify the components of a quintuplet, and to follow the associated splitting which varies smoothly through the planes, displaying the characteristic pattern due to site splitting.

Besides the quintuplet pattern, other lines are present, apparently due to a different species, for which a multiplet structure is not easily recognizable. Only in a very narrow range of orientations does the complex pattern give rise to a well characterized quadruplet structure.

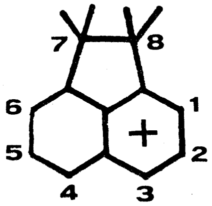
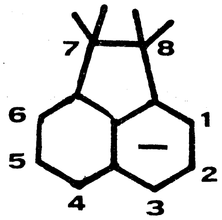
We will henceforth refer to the species characterized by a quintuplet structure within the *ab* and *ac* planes as R_1, and to the species characterized by a quadruplet structure over a very limited range in the same planes as R_2.

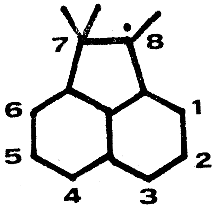
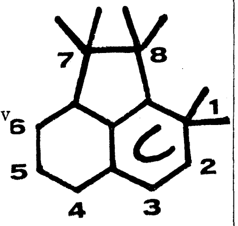
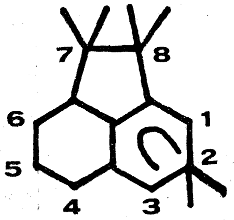
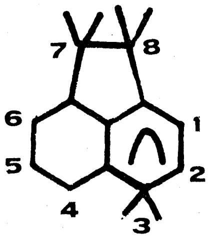
An identification of the above specified radicals has been attempted on the basis of theoretical spin density calculations performed on six radical species, i.e. Acenaphthene radical cation and anion (R_I , R_{II}), Acenaphthyl radical produced by H abstraction from the methylenic group (R_{III}) and Hydroacenaphthyl radicals produced by H addition to the aromati moiety (R_{IV} , R_V, R_{VI}). The last four species seem to be the most plausible candidates in view of previous results on similar systems [2, 3, 4]. However, one cannot exclude that charged species, although only stable at lower temperatures in other systems [2], might in the present case be present at room temperature. For R_I and R_{II}, spin density calculations are already available in the literature [5], along with the experimental values of the hyperfine splitting constants of R_{II}. However, we considered it worthwhile to reevaluate them with the same procedure applied to the other species, i.e. the INDO method.

Hyperfine splitting constants for the six species are reported in Table I, along with the values taken from Ref. [5]. As a first result of the comparison between theoretical estimates and experiment one can exclude the presence of H addition radicals, since the overall spread of the spectra observed is circa 70 Gauss, while even the lowest spectral width from one of the three species would turn out to be more than twice this quantity. Second, it seems quite reasonable to attribute the R_I structure to R_1, since the major quintuplet splitting associated with the latter varies from 14.5 G to 18.0 G, the average 16.5 G being very close to the theoretical expectation 15.52 obtained in the present work, and also to the value calculated in Ref. [5]. As far as the aromatic splittings are concerned, our results show for all positions a value lower than the ones of Colpa and De Boer [5]. In particular, the highest aromatic splitting decreases from 5.42 to 3.98 G, and under the prevailing resolution conditions, dominated by hyperfine splitting anisotropy plus site splitting, one would not expect such coupling to be detectable.

TABLE I

Hyperfine splitting constants for R_{I} , R_{II} R_{III} , R_{IV} , R_{V} , R_{VI}

Species	Position	$(a_H)_{INDO}$	$(a_H)_{th.}$ Ref. [5]	$(a_H)_{exptl.}$ Ref. [5]
R_{I} 	1,6	2.34	2.70	
	2,5	0.14	1.41	
	3,4	3.98	5.42	
	7,8	15.52	18.34	
R_{II} 	1,6	1,05	2.01	1.04
	2,5	0.75	1.89	2.42
	3,4	3.54	4.77	4.17
	7,8	7.40	8.29	7.53

Species	Position	$(a_H)_{INDO}$	Species	Position	$(a_H)_{INDO}$
R_{III} 	1	4.22	R_{IV} 	1	76.92
	2	1.85		2	4.97
	3	2.66		3	2.52
	4	1.00		4	2.57
	5	1.03		5	4.14
	6	1.14		6	2.77
	7	27.80		7	4.58
	8	16.03		8	18.77
R_{V} 	1	5.23	R_{VI} 	1	4.52
	2	107.09		2	12.01
	3	10.41		3	80.63
	4	3.25		4	12.86
	5	2.76		5	1.60
	6	3.92		6	2.60
	7	3.91		7	1.78
	8	4.67		8	2.82

The attribution of a given structure to R_2 poses a much more difficult interpretation problem in that, as explained, a simple multiplet structure for it is only observable through a range of about 20°, and consequently one cannot extract from it the isotropic component to be compared with the calculated value. However, one can single out the two major calculated splittings, which would separately give rise to a triplet of doublets. It is conceivable that their anisotropies might act so as to produce a near degeneracy of the two, not unlike the situation observed in the radical produced by H abstraction from succinic acid [6], with the consequent appearance of an overall quadruplet patterns. In the present case, due to the presence of other unresolved splittings and of site splittings, this could be indistinguishable from a real quadruplet.

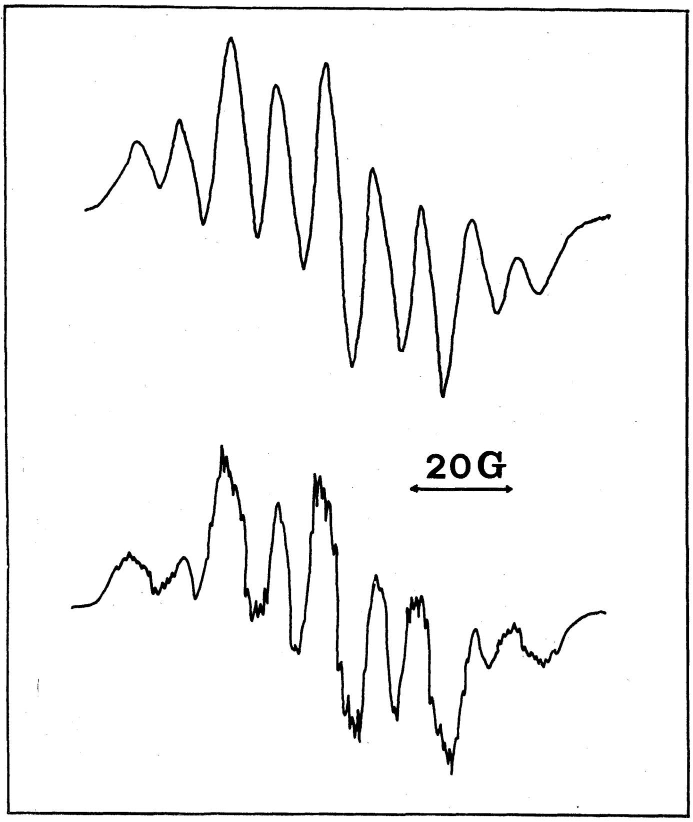


Fig. 1. – Experimental (top trace) and simulated (lower trace) spectrum. Plane *ab*, 40° fron the *b* axis. See text for explanations.

In order to check this hypothesis one can envisage a situation in which the planar hydrogen splitting is maximum and the CH_2 splittings are close to the minimum value; in Ref. [6], for example, the planar splitting and one of the two different CH_2 splittings become degenerate at one particular orientation (120°). In our case, due to the constraints imposed by the ring structure, one would not expect them to be inequivalent with respect to the molecular plane. If one assumes anisotropies of the same order as the ones observed in Ref. [6], one can estimate a maximum value of circa 19 G for the planar coupling and a minimum value of circa 24 for the methylenic proton splitting. The average of the two is not far from the experimental value of 19 G. If one now takes into account the possible error of INDO hyperfine splitting constants [7], it appears that the difference between isotropic values might be overestimated by the present calculation and that the effect of anisotropy might be thus more instrumental in simulating degeneracy than estimated above. In this connection, we have also carried out a different calculation, utilizing the Pople Pariser Parr π-electron method, along with the McConnell formula for the planar hydrogens and the well tested relationship $a_H = B \rho \cos^2 \vartheta$ for the methylenic hydrogens [8]. Spin densities were treated with an approximate projection technique already applied by one of us to the study of a radical containing methylenic hydrogens [2]. The isotropic coupling constants obtained from ρ_{av} defined in Ref. [2] are as follows: $a_{CH_2} = 21 \cdot G$ and $a_{H8} = 13 \cdot G$, the separation between the two being significantly smaller than in the INDO results.

In conclusion, it is felt that the attribution of the R_{III} structure to species R_2 cannot be ruled out. In fig. 1, under the experimental spectrum, an " ad hoc " simulation is presented. This has been obtained with a set of coupling constants taken partly from calculation (all minor splittings) and partly from esperiment (18 G for the major splitting, as measured at this particular orientation). R_2 has likewise been characterized by a mixed set, i.e. by the minor splittings given in Table I for R_{III} and by a major splitting of 19 G.

It must be pointed out that, although the single crystal features of the spectra are in the present case considerably obscured by the existence of relevant site splitting, still the angular variation study has been exploited in that a position has been identified for which an interpretation of the spectrum can be proposed.

REFERENCES

[1] H. W. W. EHRLICH (1957) – « Acta Cryst. », *16*, 699.

[2] G. ORLANDI, G. POGGI, F. BARIGELLETTI and A. BRECCIA (1973) – « J. Phys. Chem. », *77*, 1102.

[3] F. BARIGELLETTI, G. ORLANDI, G. GIRO and G. POGGI (1975) – « J. Chem. Soc. Faraday Trans., II », *71*, 1436.

[4] N. ITOH and T. OKUBO (1972) – « Mol. Cryst. Liquid Cryst. », *17*, 303.

[5] J. P. COLPA and E. DE BOER (1963) – « Mol. Phys. », *7*, 333.

[6] C. HELLER and H. M. MCCONNELL (1960) – « J. Chem. Phys. », *32*, 535.

[7] J. A. POPLE, D. L. BEVERIDGE and P. A. DOBOSH (1968) – « J. Am. Chem. Soc. », *90*, 420.

[8] E. W. STONE and A. H. MAKI (1962) – « J. Chem. Phys. », *37*, 1327.