LITERATURVERZEICHNIS

[1] 30. Mitteilung: *M. Viscontini & H. Leidner*, Helv. *53*, 789 (1970)
[2] Dissertation *G. Mattern*, Naturw. Fakultät, Universität Zürich 1969.
[3] *M. Viscontini & G. Mattern*, Helv. *50*, 1664 (1967).
[4] *M. Viscontini & G. Mattern*, Helv. *53*, 372, 377 (1970).
[5] *C. Nofre, J. P. Charrier & A. Cier*, Bull. Soc. Chim. biol. *45*, 913 (1963).

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96. ESR. Spectra of the Radical Ions of Indeno[1,2,3-*cd*]fluoranthene

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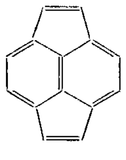
(2. IV. 70)

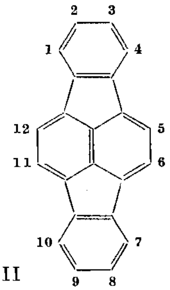
Summary. The ESR. spectra of the radical anion and the radical cation of indeno[1,2,3-*cd*]-fluoranthene have been recorded. Their hyperfine structures are consistent with those expected on the basis of simple MO models.

In the last few years, there has been a great deal of interest in the radical ions of nonalternant hydrocarbons [1] [2] [3]. The ESR. spectra of such ions were successfully used as an experimental test for the MO prediction that the radical anion and the radical cation of the same nonalternant compound should in general have different spin populations.

This short communication presents the ESR. results for indeno[1,2,3-*cd*]fluoranthene (II), first synthesized by *Stubbs & Tucker* [4]. The compound II is a dibenzo derivative of a nonalternant hydrocarbon, pyracylene (I), which has not yet been prepared [5].



I



II

The radical anion $II^{\ominus}$ can be readily produced by conventional methods such as reaction with an alkali metal in 1,2-dimethoxyethane or electrolytic reduction in N,N-dimethylformamide with tetraalkylammonium perchlorate as supporting salt. Attempts to generate the radical cation $II^{\oplus}$ by dissolving the neutral hydrocarbon II in conc. sulfuric acid failed, since no ESR. signal could be detected. Use of unpurified antimony trichloride as a solvent at +80°C (with the pentachloride impurity as a presumable oxidizing agent) [6] resulted in a broad absorption which did not show any indication of hyperfine structure. A similar unresolved signal, but only of 3 gauss width, was observed on the oxidation of II by $SbCl_5$ in methylene chloride at −70°C [2]. This signal arises from a paramagnetic material which is insoluble at low temperature. On warming the solution, the unresolved signal was gradually replaced by a multiline spectrum; however, at the same time, the overall intensity decreased, owing to radical decay (half life 10 min. at room temperature).

An optimal spectrum of sufficient intensity and resolution was obtained at +10°C. This spectrum, which can safely be ascribed to the radical cation $\mathrm{II}^{\oplus}$, is reproduced in Figure 1, below the spectrum of the corresponding radical anion $\mathrm{II}^{\ominus}$.

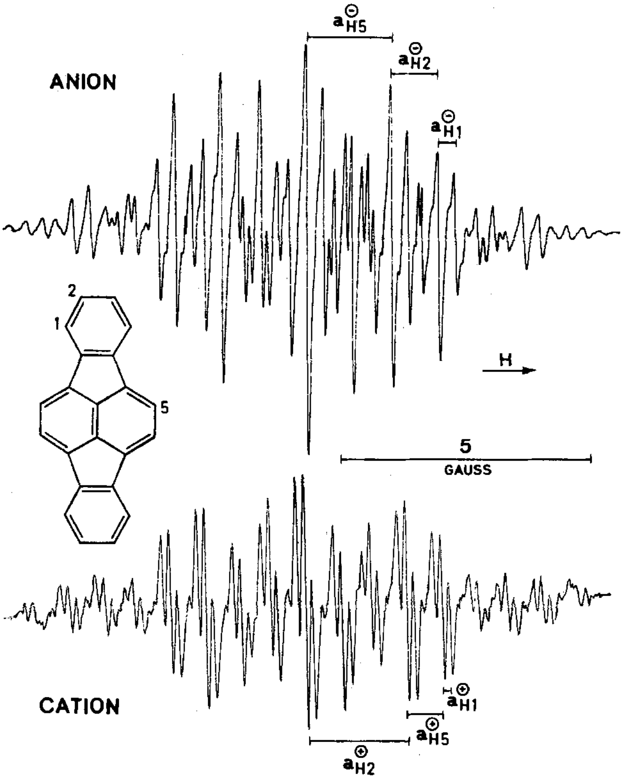


Figure 1. *ESR. Spectra of indeno[1,2,3-*cd*]fluoranthene radical ions*
Top: anion; solvent: N,N-dimethylformamide; gegenion: $(C_2H_5)_4N^{\oplus}$; room temperature
Bottom: cation; solvent: methylene chloride; gegenion: $Cl^{\ominus}$; temperature: +10°C

The coupling constants $a^{\ominus}_{\mathrm{H}\mu}$ and $a^{\oplus}_{\mathrm{H}\mu}$ of the ring protons at the centers μ of $\mathrm{II}^{\ominus}$ and $\mathrm{II}^{\oplus}$ are listed in Table 1. The experimental data compare favorably with the squares of the HMO coefficients $c_{a\mu}$ ($\mathrm{II}^{\ominus}$) and $c_{b\mu}$ ($\mathrm{II}^{\oplus}$), where the subscripts a and b stand for the lowest antibonding (ψ_a) and the highest bonding (ψ_b) orbitals of the indeno[1,2,3-*cd*]fluoranthene system. The HMO values $c^2_{a\mu}$ and $c^2_{b\mu}$ are also given in Table 1, along with the spin populations $\varrho^{\ominus}_{\mu}$ and $\varrho^{\oplus}_{\mu}$ computed from them by the procedure of *McLachlan* [7] (parameter $\lambda = 1.2$). The assignment of $a^{\ominus}_{\mathrm{H}\mu}$ and $a^{\oplus}_{\mathrm{H}\mu}$ to sets of four equivalent ring protons at centers μ is based on comparison with the calculated values.

The relevant orbitals ψ_a and ψ_b are schematically depicted in Figure 2. Together with the calculated values of Table 1, the two schemes give evidence that in both radical ions the spin population is greatest at the «blind» centers which are void of protons. The summed squares of the HMO coefficients $c_{a\mu}$ and $c_{b\mu}$ at the proton-carrying centers μ amount to 0.46 and 0.36, respectively. The corresponding values obtained by the procedure of *McLachlan* are 0.44 for the sum of $|\varrho_\mu^{\ominus}|$ and 0.36 for that of $|\varrho_\mu^{\oplus}|$ (cf. Table 1). In accord with these numbers, the ESR. spectra extend over ranges of only 11.7 ($II^{\ominus}$) and 11.4 ($II^{\oplus}$) gauss. The resulting proportionality factor Q_{CH} of the *McConnell* relation has thus the following absolute values: 11.7/0.46 (or 11.7/0.44) $\approx$ 26 gauss for the radical anion and 11.4/0.36 $\approx$ 31 gauss for the radical cation.

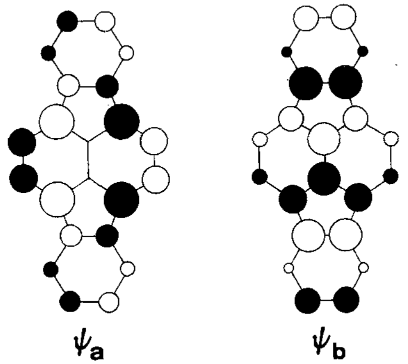


Figure 2. *Lowest antibonding* (ψ_a) *and highest bonding* (ψ_b) *HMO's of indeno[1,2,3-*cd*]fluoranthene* The radii of the circles are proportional to $|c_{a\mu}|$ or $|c_{b\mu}|$. Blank and filled surfaces refer to different signs of $c_{a\mu}$ or $c_{b\mu}$.

The HMO energies of ψ_a and ψ_b, $E_a = \alpha - 0.186\beta$ and $E_b = \alpha + 0.580\beta$, point to a high electron affinity and to a relatively high ionisation potential of compound II, as confirmed by its ease of reduction and reluctance to oxidation. It is noteworthy that the next lower bonding orbital lies rather close to ψ_b. However, an occupancy of this orbital by the unpaired electron in $II^{\oplus}$ would lead to $|Q_{CH}| \approx 18$ gauss, a quite unrealistic value for a radical cation.

Table 1. *Proton coupling constants* (in gauss) *and spin populations of indeno[1,2,3-*cd*]fluoranthene radical ions*

μ	Radical anion			Radical cation		
	$a_{H\mu}^{\ominus}$ 1)	$c_{a\mu}^2$	$\varrho_\mu^{\ominus}$	$a_{H\mu}^{\oplus}$ 1)	$c_{b\mu}^2$	$\varrho_\mu^{\oplus}$
1,4,7,10	0.33	0.020	0.012	0.15 2)	0.009	–0.012
2,3,8,9	0.92	0.030	0.030	1.99	0.053	0.059
5,6,11,12	1.68	0.066	0.068	0.70 2)	0.019	0.009

1) Experimental error 0.01 to 0.02 gauss.
2) Assignment uncertain.

We thank Dr. *K. D. Warren*, University College of South Wales and Monmouthshire, Cardiff, for a generous gift of a sample of indeno[1,2,3-*cd*]fluoranthene.

This work was supported by the *Swiss National Foundation* (Project 4651). One of us (*Ch. E.*) is obliged to the *Volkswagen Foundation* for a research fellowship.

LITERATURE

[1] *F. Gerson & J. Heinzer*, Chem. Commun. *1965*, 488; Helv. *49*, 7 (1966).
[2] *I. C. Lewis & L. S. Singer*, J. chem. Phys. *43*, 2712 (1965); *44*, 2082 (1966).
[3] *M. D. Sevilla, S. H. Flaiser, G. Vincow, & H. J. Dauben, Jr.*, J. Amer. chem. Soc. *91*, 4139 (1969).
[4] *H. W. D. Stubbs & S. H. Tucker*, J. chem. Soc. *1951*, 2936.
[5] *A. G. Anderson, Jr. & R. G. Anderson*, J. org. Chemistry *23*, 517 (1958); *B. M. Trost*, J. Amer. chem. Soc. *88*, 853 (1966).
[6] *E. C. Baughan, T. P. Jones, & L. G. Stoodley*, Proc. Chem. Soc. (London) *1963*, 274; *F. Gerson & J. Heinzer*, Helv. *50*, 1852 (1967).
[7] *A. D. McLachlan*, Mol. Physics *3*, 233 (1960).

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97. Zur Stereochemie des (+)-Davanons

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(30. IV. 70)

Zusammenfassung. Durch stereospezifische Synthese wird die Konstitution des natürlichen (+)-Davanons bestätigt und seine Konfiguration mit der des (–)-Nerolidols verknüpft.

Seit einiger Zeit [1] an 1,4-Epoxy-Derivaten des Nerolidols interessiert, erregte das Epoxyketon (+)-Davanon [2] aus dem ätherischen Öl von *Artemisia pallens Wall.* unsere Aufmerksamkeit. Während seine Struktur von *Sipma & van der Wal* [2] aus spektroskopischen Daten und Abbauversuchen abgeleitet werden konnte, wurden die 4 Racemate dieses Sesquiterpens von *Naegeli & Weber* [3] hergestellt. Letztere Arbeit jedoch veranlasste uns, über eigene Untersuchungen im Zusammenhang mit der Struktur und absoluten Stereochemie des natürlichen Davanons in vorläufiger Form zu berichten, da es uns durch eine stereospezifische Synthese gelungen ist, die beiden am