CONJUGATED RADICALS. XVII.*

ELECTRONIC SPECTRA OF RADICAL IONS DERIVED FROM PENTALENO[6,6a,1,2-def]HEPTALENE AND 2-PHENYLCYCLOPENT[cd]AZULENE AND SEMIEMPIRICAL OPEN SHELL PPP-LIKE CALCULATIONS

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Radical anions of the title compounds were prepared by alkali metal reduction in 1,2-dimethoxyethane and the corresponding radical cations electrochemically in dichloromethane. The recorded electronic spectra have been compared with the results of semiempirical open shell PPP-like calculations.

This paper, which represents a continuation of our earlier studies[1,2] on nonalternant radical ions, concerns two nonalternant systems, pentaleno[6,6a,1,2-def]heptalene and 2-phenylcyclopent[cd]azulene. We report here on the generation of the respective mononegative and monopositive ions and the interpretation of their electronic spectra by semiempirical calculations.

EXPERIMENTAL AND CALCULATIONS

Substances and solvents. The investigated systems were alkyl derivatives of the title compounds, *viz.* 4-methylpentaleno[6,6a,1,2-def]heptalene[3] (*Ia*) and 2-phenyl-3,5,7-trimethylcyclopent[cd]azulene[4] (*II*). Since in electrochemical oxidation of *Ia* filming on the electrode occurred, we were forced to use 4,7,9-trimethylpentaleno[6,6a,1,2-def]heptalene[5] (*Ib*). With this derivative filming was observed, too, but in this case it did not prevent radical generation because the film formed was soluble. Purification of the solvents was described previously[1,2].

Procedure. Monopositive ions were generated electrochemically in a 0·1M tetrabutylammonium tetrafluoroborate–dichloromethane system and mononegative ions were prepared by alkali metal reduction in 1,2-dimethoxyethane. The two experimental techniques are described in detail elsewhere[1,6].

Ia   *Ib*   *II*
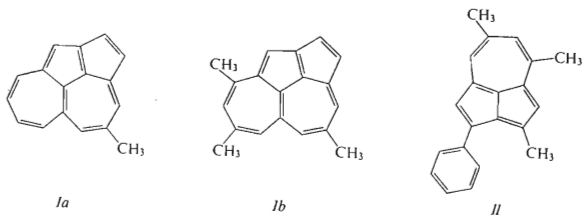
Calculations. These were of the PPP type, making use of the open shell SCF procedure of Longuet-Higgins and Pople and the variable β approximation (for detail see refs[1,7]). Methyl groups in *I* and *II* were disregarded in the calculations. As the phenyl group in the radical cation of *II* might be twisted out of the coplanarity, we also performed the calculation with a decreased
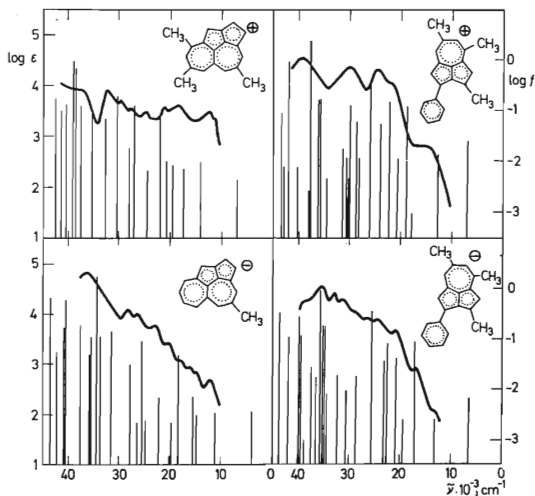

FIG. 1

Electronic Spectra of Monopositive and Mononegative Ions Derived from *I* and *II*

The results of semiempirical calculations are represented by vertical lines. The left-hand scale concerns experimental intensities, the right-hand scale the calculated ones (f theoretical oscillator strength).

value of the resonance integral for the critical CC bond. Using the formula $\beta'_{CC} = \beta_{CC} \cos \alpha$ and assuming the twist angle (α) of 60°, that integral was half the standard value. Even for this high α, the effect on the calculated spectral data was found unimportant.

RESULTS AND DISCUSSION

The observed electronic spectra and results of semiempirical calculations are presented in Fig. 1. It can be seen that the electronic spectra are very complex, in agreement with a great number of electronic transitions predicted by the theory. This complexity makes any assignment very difficult. One can only conclude that the theory correctly predicts the strong absorption of the studied radical ions over the entire spectral region from the near infrared to the ultraviolet. A striking feature of the calculations is a predicted transition below $10\,000 \text{ cm}^{-1}$. At present it is difficult to decide whether this is a failure of the theory, or whether these low energy transitions in radical ions *I* and *II* really take place: they could not be experimentally observed as the solvents used in these experiments exhibit strong absorption just over the spectral region in question.

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