

ELECTRONIC SPECTRA OF AZULENE MONONEGATIVE AND MONOPOSITIVE IONS AND SEMIEMPIRICAL OPEN SHELL PPP-LIKE CALCULATIONS

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Azulene radical anion was generated by pulse radiolysis in aqueous isopropyl alcohol, electrochemically in hexamethylphosphoramide, and by γ -irradiation in 2-methyltetrahydrofuran glass. 1,3-Di-tert-butylazulene radical cation was generated electrochemically in dichloromethane. The electronic spectra of both radical ions are compared with the results of semiempirical PPP-like calculations based on the open shell SCF method of Longuet-Higgins and Pople.

Semiempirical MO calculations have proved useful for interpreting electronic spectra of conjugated radicals of various types¹. Among classes of radicals which have been little studied, the nonalternant systems represent one of the most interesting groups. In an earlier paper² we discussed the radical anions derived from three nonalternant hydrocarbons: acenaphthylene, fluoranthene, and 2,4-dimethylaceheptylene. The present paper extends this discussion to azulene radical ions. As the azulene mononegative ion is a highly reactive species, we produced it in three different ways in order to obtain reliable spectral data.

EXPERIMENTAL AND CALCULATIONS

Substances and solvents. Azulene was obtained commercially and 1,3-di-tert-butylazulene was kindly provided by Prof. K. Hafner (Technische Hochschule, Darmstadt, Germany). Hexamethylphosphoramide was dried with calcium hydride and distilled twice *in vacuo*³. Dichloromethane was dried with P₂O₅ and distilled. The purification of 2-methyltetrahydrofuran is described elsewhere^{4,5}. Tetrabutylammonium tetrafluoroborate was prepared from tetrabutylammonium hydroxide and tetrafluoroboric acid, the precipitate being thrice crystallized⁶ from aqueous methanol (1 : 1) and vacuum dried at 70°C.

Electrochemical generation. The equipment and procedure are described in detail elsewhere⁷. The azulene mononegative ion was generated in a 0.1M tetrabutylammonium tetrafluoroborate-hexamethylphosphoramide system, and the 1,3-di-tert-butylazulene monopositive ion in a 0.1M

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tetrabutylammonium tetrafluoroborate–dichloromethane system. Electrochemical oxidation of the unsubstituted azulene was unsuccessful owing to filming on the electrode. With the 1,3-di-*t*-butyl derivative, however, no filming was observed, presumably because the bulky alkyl groups prevent adsorption of the flat azulene system on the electrode surface. The concentration of the azulene anion was determined from the height of polarographic waves⁸ and the decrease of the absorption maximum of azulene at 580 nm. The somewhat higher stability of the cation radical permitted coulometric determination of the concentration.

Pulse radiolysis. As a pulse source we used a Van de Graaff generator^{9–11}. Azulene was dissolved in isopropyl alcohol and diluted by water so that the samples for irradiation were $8 \cdot 10^{-5} M$ in azulene and $0.1 M$ in isopropyl alcohol. Under these conditions the azulene molecules are attacked only by e_{aq}^- species provided the $\cdot C(CH_3)_2OH$ radical does not react with azulene. The $\cdot C(CH_3)_2OH$ radicals are known¹¹ to react with organic molecules not by substitution but by selective charge transfer. If such a charge transfer occurred here, the concentration of azulene anions would be about doubled, and the extinction coefficient about half the estimated value. This, however, seems improbable as the other two methods yield higher extinction coefficients. The estimation of radical concentration was based on the known yield¹² of radicals in water after the 100 eV energy absorption ($G_{e_{aq}^-} = 2.65$).

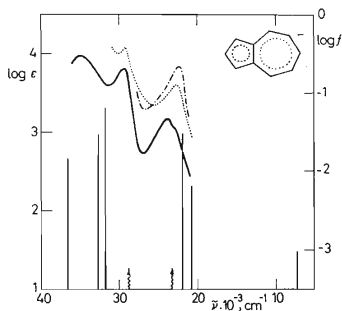


FIG. 1

Electronic Spectra and Results of Semiempirical Calculations for Azulene Radical Anion

Methods of radical generation: pulse radiolysis (—); electrolysis (·····); γ -irradiation (----). The calculated transition energies are represented by the vertical lines, the forbidden transitions by wavy lines with arrows. The right-hand scale concerns the calculated oscillator strengths.

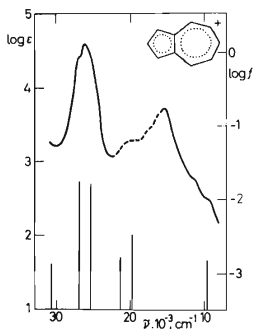


FIG. 2

Electronic Spectrum of the Electrogenerated 1,3-Di-*t*-butylazulene Radical Cation and Results of Semiempirical Calculations

High absorption of the 1,3-di-*t*-butylazulene prevents accurate determination of the molar extinction coefficient for the radical cation in the region $16\,100$ – $22\,200\text{ cm}^{-1}$ (dashed line). The calculated transitions are represented by vertical lines. The right-hand scale concerns the calculated oscillator strengths.

γ -Irradiation. Azulene ($3.4 \cdot 10^{-3} \text{M}$) in 2-methyltetrahydrofuran at 24°C was frozen at 77K . After γ -irradiation with the dose of $9.20 \cdot 10^{19} \text{eV/g}$ and photobleaching with light of $\lambda > 690 \text{nm}$ the absorption curve was recorded⁴. The extinction coefficient of the anion band at 440nm was determined from the decrease of the azulene band at 687nm .

Calculations. These were of the PPP type, combining the open shell SCF procedure of Longuet-Higgins and Pople¹³ with the configuration interaction treatment. We considered all singly excited states of the A, B, C_α , and C_β types (for definitions see¹), *i.e.* altogether 50 configurations (including the ground state configuration). An idealized geometry was used, with the value of 1.40\AA for all C—C bond distances. The parameter set and computational details are described in our earlier paper¹⁴.

RESULTS AND DISCUSSION

The observed electronic spectra and the results of semiempirical calculations are presented in Figs 1 and 2. The absorption curves of the azulene radical anion obtained by the three methods are consistent concerning the location of absorption maxima: the differences in estimated intensities are probably due to instability. The absorption band in the visible was also recorded by Sioda¹⁵ in dimethylformamide under electrolysis, his spectral data ($\lambda_{\text{max}} 445 \text{nm}$, $\epsilon \sim 3400$) being in agreement with ours. With the monopositive ion, the calculations refer to the unsubstituted system whereas the absorption curve was recorded for the 1,3-di-*tert*-butyl derivative. We think, however, that this alkyl substitution affects the nature of the absorption curve rather little. It is noteworthy that the first-order perturbation treatment¹⁶ predicts a negligible change in the first transition energy of the azulene radical cation upon alkyl substitution in 1 and 3 positions.

The overall agreement between calculated and observed spectra can be characterized as moderately successful. The shape of the first cation band (Fig. 2) strongly suggests that it is due to several electronic transitions. The theory predicts three transition in that region but overestimates the second and the third transition energy. A predicted band for the radical anion in the near infrared is difficult to confirm experimentally. First, its predicted intensity is very low which means that this reactive radical is likely to be observable only if generated in high concentrations and, second, the choice of solvents is very restricted owing to C—H valence bond absorption in that region.

Recently Roberts and Warren reported¹⁷ non-empirical π -electron calculations on azulene radical ions. Their results are very close to ours, however, with the azulene radical anion the spectrum is reproduced somewhat better by the non-empirical calculation.

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