

A Study of the Electronic Spectrum of 3,4-Benzphenanthrene Cation Radical

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The electronic spectrum of 3,4-benzphenanthrene cation radical is studied for the first time experimentally as well as theoretically. The cation radicals have been produced in boric acid glass by photooxidation and the absorption spectrum is measured in the region 200–1400 nm. An interpretation of the spectrum is given on the basis of Pariser-Parr (PP) and Free Electron (FE) molecular orbital calculations using limited configuration interaction. It is found that the results based on the PP method are in better agreement with experiment as compared to the FE method. Furthermore, the spectral shifts and other variations observed between the spectra of the cation and anion radicals are attributed to the characteristics of these species.

A number of workers has studied the carcinogenic activity of polycyclic aromatic hydrocarbons^{1–3}, but so far the reason for their special biological activity has not been found. We feel that spectroscopy may, perhaps, provide a tool in such investigations, and a systematic study of such hydrocarbons should, therefore, be carried out.

We report here the electronic spectrum of the 3,4-benzphenanthrene cation radical which belongs to the mentioned class of carcinogens. The cation radicals have been produced in boric acid glass by the photo-oxidation technique^{4,5} and the absorption spectrum has been measured in the region 200 to 1400 nm (7–50 kK). An interpretation of the observed spectrum is given on the basis of the Pariser-Parr (PP) and Free Electron (FE) molecular orbital methods using limited configuration interaction.

Experimental

3,4-Benzphenanthrene of K & K (U.S.A.) was obtained from Professor C. P. Poole, Jr., and the boric acid was of 'AR' grade (Pfizer, Bombay). The details of the ultraviolet source of irradiation, the method for the preparation of boric acid films, and the apparatus used for recording the spectrum are described elsewhere⁴.

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Calculations

In the Pariser-Parr method^{6,7} the following parameters were used: $\beta_{cc} = -2.318$ eV, $\gamma_{cc} = 10.53$ eV, and the two-centre Coulomb repulsion integrals were evaluated according to the Mataga-Nishimoto approximation⁸. In the Free Electron calculations we used the same parameters as given by Ham and Ruedenberg⁹. Throughout the calculations a constant value of 1.395 Å was used for all the C–C bondlengths.

For the configuration interaction (CI) calculations a standard procedure was adopted where we used in addition to the ground state configuration, all the configurations arising from the one-electron excitations between the four highest doubly-occupied orbitals, the singly-occupied orbital, and the four lowest vacant orbitals. The CI matrix elements were calculated according to the formulas given by Wasilewski¹⁰.

The calculations were made on an IBM 1130 computer at the Computer Centre, Aligarh Muslim University.

Results and Discussion

The absorption spectrum of 3,4-benzphenanthrene cation in boric acid and the predicted electronic transitions are shown in Figure 1. A close look at the

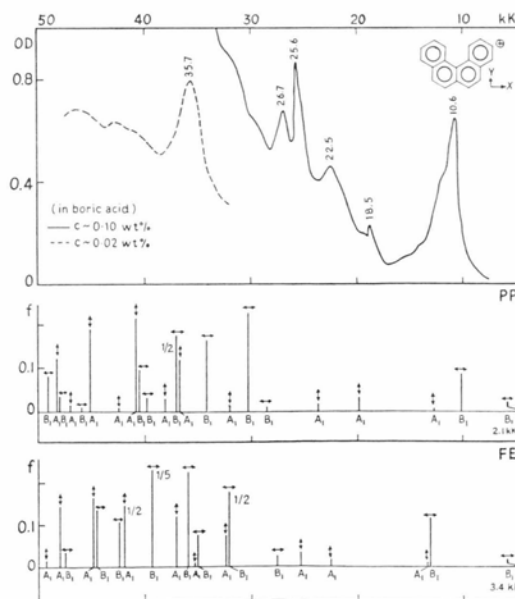


Fig. 1. Comparison of the observed and calculated electronic spectra of the 3,4-benzphenanthrene cation radical. The results for both the Pariser-Parr (PP) and Free Electron (FE) calculations are presented. The horizontal and vertical arrows correspond to the *x*- and *y*-axes of the molecule. The transitions are designated by the letters A_1 and B_1 .

Classification	Polarization ^b	Cation			Anion
		Present work (Boric acid)	Shida ¹² (sec-BuCl)	Shida ¹² (Freon mixture)	Shida ¹² (MTHF)
B ₁	<i>x</i>	10.6	10.6	10.6	9.3
A ₁	<i>y</i>	11.8	11.9	12.0	10.6
A ₁	<i>y</i>	18.5	18.0	18.2	16.9
		19.6	19.4	19.6	18.2
					20.5
					21.4
A ₁	<i>y</i>	22.5	22.7	22.7	21.8
			23.8	23.8	23.3
					25.0
B ₁	<i>x</i>	25.6	25.3	25.2	26.7
B ₁	<i>x</i>	26.7			
		29.4			
B ₁	<i>x</i>	35.7			

Table 1. Assignment of the observed electronic transitions of the 3,4-benzphenanthrene cation in boric acid glass and their comparison with other available data for the cation and anion^a.

^a Transition energies are in kilokaysers (kK).

^b The letters *x* and *y* correspond to the molecular axes shown in Figure 1.

figure shows that the results based on the Pariser-Parr method are in excellent agreement with the experiment. The Free Electron results also show a good correspondence with the observed spectrum except that the electronic transitions are blue-shifted in this method. The same trend is found in the calculations for other ion radicals also¹¹. Both calculations suggest that the lowest transition in the cation should be located in the spectral region 2–3 kK. This, however, could not be measured due to our experimental limitations.

An assignment of the observed electronic transitions of the 3,4-benzphenanthrene cation on the basis of the above calculations is given in Table 1 where the present results are compared with other available data for the cation and anion radicals¹². It is noticed that with regard to the positions of the electronic bands and their general appearance, there is a close resemblance in the spectra of the cation

radicals produced in different matrices, but a marked difference is noticed between the spectra of the cation and anion radicals. Similar results are found with other hydrocarbon ion radicals^{11,13}. This suggests that the variation is due to the characteristic spectra of the cation and anion radicals.

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