

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.

Acknowledgements

We are highly grateful to Professor C. P. Poole, Jr., for his gift of the chemical 3,4-benzphenanthrene and to Dr. T. Shida for recording the spectra of its cation and anion radicals. Thanks are also due to Dr. J. Wasilewski for sending a corrected version of his paper¹⁰ and for his useful suggestions. One of us (Z. H. K.) gratefully acknowledges the Council of Scientific and Industrial Research, India for the financial support and to the University Grants Commission, New Delhi for a research grant.

¹ O. Chalvet, P. Daudel, R. Daudel, C. Moser, and G. Prodi, *Wave Mechanics and Molecular Biology* (Ed. Louis de Broglie), Addison-Wesely Publishing Company, Inc., Reading, Massachusetts, U.S.A., 1966, p. 101.

² A. Pullman and B. Pullman, *Adv. Cancer Res.* **3**, 129 [1971].

³ W. C. Herndon, *Trans. New York Acad. Sci.* **36**, 200 [1974].

⁴ Z. H. Khan and B. N. Khanna, *J. Chem. Phys.* **59**, 3015 [1973].

⁵ Z. H. Khan and B. N. Khanna, *Canad. J. Chem.* **52**, 827 [1974].

⁶ R. Pariser and R. G. Parr, *J. Chem. Phys.* **21**, 466, 767 [1953].

⁷ R. Pariser, *J. Chem. Phys.* **24**, 250 [1956].

⁸ N. Mataga and K. Nishimoto, *Z. Phys. Chem. Frankfurt (Main)* **13**, 140 [1957].

⁹ N. S. Ham and K. Ruedenberg, *J. Chem. Phys.* **25**, 1 [1956].

¹⁰ J. Wasilewski, *Acta Phys. Polon. A* **38**, 349 [1970].

¹¹ Z. H. Khan, Ph. D. Thesis, Aligarh Muslim University, Aligarh 1975.

¹² T. Shida, Private Communication.

¹³ T. Shida and S. Iwata, *J. Amer. Chem. Soc.* **95**, 3473 [1973].