Triply-charged Ions in the Mass Spectrum of Triptycene

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MULTIPLY-CHARGED IONS are commonly found in the mass spectra of compounds containing heteroatoms, on which some of the positive charge may be localized. Thus, the mass spectra of alkylindoles[1] show doubly-charged parent ions of greater than 10% relative intensity; octamethyltrisiloxane shows triply-charged parent and $(P - CH_3)$ ions.[2]

I now report the observation of triply-charged ions produced by electron impact from a hydrocarbon. The mass spectrum† of triptycene (9,10-dihydro-9,10-*o*-benzenoanthracene) shows a parent ion at m/e 254, accompanied by ions produced by loss of hydrogen at lower m/e values, and by ^{13}C-substituted ions at higher m/e values. Between m/e 123 and 128, spaced at half-mass units, is a group of doubly charged ions, and between m/e 82 and 85 a group of peaks separated by one-third units are assigned to triply-charged parent and associated ions. These assignments have been confirmed by accurate mass measurements, and the relevant values, together with the relative intensities of the various peaks, are listed in the Table. The high relative abundances of the doubly-charged (up to 12%) and triply-charged (up to 0·51%) ions are noteworthy.

Of interest are the variations in relative intensities within the groups. In the singly-charged group, P^+ and $(P - H)^+$ are most intense, and are also the strongest peaks in the spectrum. The ions $(P - H)^{2+}$ and $(P - 2H)^{2+}$ are the most abundant in the doubly-charged group, although the relative intensity of the latter ion also necessarily includes any contribution from the ion $C_{10}H_6^+$. In the triply-charged group, $(P - 2H)^{3+}$ and $(P - 4H)^{3+}$ are the strongest ions; the mass matching determinations showed that the triply-charged ions were the only ones present, *i.e.*, no other ion of m/e 83 or 84 contributed to these peaks. No evidence was found for any ions bearing a higher charge.

Consideration of possible structures for these ions provides an explanation for these relative intensities. Triptycene can lose a hydrogen from one of its bridgehead carbons in a similar manner to triphenylmethane, forming a cation (I) which may be stabilized in a similar manner to trityl cation. Thus it may be expected that the ion (I)

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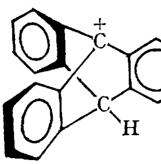
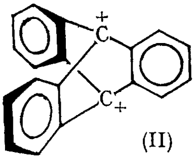
† Obtained with an AEI MS9 mass spectrometer operating at 70 ev ionising energy.

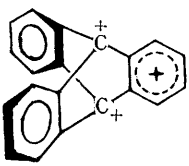
TABLE

Some ions in the mass spectrum of triptycene ($C_{20}H_{14}$)

Ion	Relative intensity (%)	Mass (a.m.u.)	
		Found	Calculated
(a) Singly-charged Ions			
$C_{17}{}^{13}C_3H_{14}^{+}$	0·24	257	—
$C_{18}{}^{13}C_2H_{14}^{+}$	3·1	256·1170	256·1161
$C_{19}{}^{13}CH_{14}^{+}$	22	255·1134	255·1128
$C_{20}H_{14}^{+}$	100	254·1089	254·1095
$C_{20}H_{13}^{+}$	100	253·1016	253·1017
$C_{20}H_{12}^{+}$	51·5	252·0943	252·0939
$C_{20}H_{11}^{+}$	7·5	251·0836	251·0861
$C_{20}H_{10}^{+}$	15·5	250·0787	250·0782
$C_{20}H_{9}^{+}$	2·8	249·0705	249·0704
$C_{20}H_{8}^{+}$	3·2	248·0625	248·0626
$C_{20}H_{7}^{+}$	0·4	247	—
$C_{20}H_{6}^{+}$	0·15	246	—
(b) Doubly-charged Ions			
$C_{18}{}^{13}C_2H_{14}^{2+}$	0·72 ($+C_9{}^{13}CH_7^{+}$)	128	—
$C_{19}{}^{13}CH_{14}^{2+}$	2·0	127·5567	127·5564
$C_{20}H_{14}^{2+}$	8·0 ($+C_{10}H_7^{+}$)	127·0545	127·0548
$C_{20}H_{13}^{2+}$	12	126·5498	126·5509
$C_{20}H_{12}^{2+}$	26 ($+C_{10}H_6^{+}$)	126·0464	126·0470
$C_{20}H_{11}^{2+}$	5·4	125·5414	125·5431
$C_{20}H_{10}^{2+}$	11 ($+C_{10}H_5^{+}$)	125·0413	125·0391
$C_{20}H_{9}^{2+}$	2·0	124·5362	124·5352
$C_{20}H_{8}^{2+}$	2·8 ($+C_{10}H_4^{+}$)	124·0317	124·0313
$C_{20}H_{7}^{2+}$	0·35	123·5	—
$C_{20}H_{6}^{2+}$	0·36 ($+C_{10}H_3^{+}$)	123	—
(c) Triply-charged Ions			
$C_{19}{}^{13}CH_{14}^{3+}$	0·1	85	—
$C_{20}H_{14}^{3+}$	0·08	84·67	—
$C_{20}H_{13}^{3+}$	0·17	84·3653	84·3672
$C_{20}H_{12}^{3+}$	0·51	84·0313	84·0313
$C_{20}H_{11}^{3+}$	0·23	83·6948	83·6954
$C_{20}H_{10}^{3+}$	0·47	83·3599	83·3594
$C_{20}H_{9}^{3+}$	0·21	83	—
$C_{20}H_{8}^{3+}$	0·04	82·67	—
$C_{20}H_{7}^{3+}$	0·05	82·33	—
$C_{20}H_{6}^{3+}$	0·06	82	—


(I)


(II)


(III)

would have a high relative abundance in the mass spectrum. Similar loss of hydrogen from the second bridgehead carbon gives the dipositive ion (II). Further loss of an electron from these ions might lead to an ion of the type (III), but the heavy accumulation of charge makes unlikely the formation of higher-charged species. Since the third electron is presumably lost from an aromatic ring, the relatively high abundance of the triply-charged ions may be explained by considering the statistical effect of there being three rings equally able to lose the electron.

As with alkylindoles, loss of hydrogen occurs easily from the multiply-charged ions, and indeed triply-charged ions up to at least $(P - 7\text{H})^{3+}$ and perhaps $(P - 8\text{H})^{3+}$ are found, albeit in low abundance. However, the intensities of ions with less hydrogen than $(P - 6\text{H})^{+}$, $(P - 6\text{H})^{2+}$, or $(P - 4\text{H})^{3+}$ were too low to allow accurate mass measurement.

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[1] J. H. Beynon and A. E. Williams, *Appl. Spectroscopy*, 1959, **13**, 101; 1960, **14**, 27.

[2] V. H. Dibeler, F. L. Mohler, and R. M. Reese, *J. Chem. Phys.*, 1953, **21**, 180.