Effect of Overcrowding on Mass Spectra of Aromatic Hydrocarbons

Toyotoshi Ueda,* Reiko Yano, Mitsuru Ohno, and Satoshi Iwashima
Department of Chemistry, Meisei University, Hodokubo, Hinoshi, Tokyo 191, Japan
Minoru Takekawa and Junji Aoki
Department of Chemistry, Toho University, Funabashi-shi, Chiba 274, Japan
Teruo Kan
Tokyo Metropolitan Research Laboratory of Public Health, Shinjuku-ku, Tokyo 160, Japan

Mass spectra of condensed polycyclic aromatic hydrocarbons with or without overcrowding, which have three, four, five, and nine fused aromatic rings, were examined. Their patterns reflect the type of overcrowding and the number of overcrowded hydrogen atoms in the molecule. These facts were supported by the ionization efficiency curves and especially the lowering of appearance energies of the $[M-2]^{\cdot+}$ ions of benzo[*c*]phenanthrene and dibenzo[*c,g*]phenanthrene or the $[M-4]^{\cdot+}$ ions of tetrabenzo[*a,cd,j,lm*]perylene.

Previously we have reported the effects of overcrowding in the mass spectra of nanocyclic aromatic compounds.[1,2] The strongest peak in the molecular-family ions of highest valency for an overcrowded polycyclic aromatic hydrocarbon corresponds to the fragment ion which resulted from detaching all overcrowded hydrogen atoms from the parent molecular ion. The molecular ion gives the strongest peak for an uncrowded hydrocarbon.

In order to verify the validity of this rule, we studied a further series of aromatic hydrocarbons with or without overcrowding, which have three, four, five, and nine condensed rings, and also examined the dependence of relative intensities of fragment ions on the impact electric current, and on the impact electric voltage.

Experimental

Mass spectra were measured with a Shimadzu LKB 9000 gas-chromatograph mass spectrometer using a direct inlet (DI). About 0.2 mg of each sample was dissolved in 0.3 ml of the highest grade benzene (Wako Chem. Co.) and a few µl of the solution was inserted into the vacuum chamber of the ionization source. Normal measurement conditions were as follows: temperature in ionization chamber, 290 °C; DI temperature, varied from room temperature to 220 °C; ionization voltage, 70 V; emission current, 60 µA. Excess of benzene solution was used to keep the sample pressure almost constant during the measurement of voltage or current dependence. Variations in the sensitivity were corrected with a nitrogen peak before and after the measurement. The trap current was changed from 0 to 100 µA for every 1 or 0.5 V below 40 V and every 5 V above it.

Highly purified samples of anthracene (**1**),[3] phenanthrene (**2**),[4] chrysene (**3**),[5] benzo[*c*]phenanthrene (**4**),[6] anthra[9,1,2-*cde*]benzo[*rst*]pentaphene (violanthrene A) (**7**),[7] and tetrabenzo[*a,cd,j,lm*]perylene (**8**)[8] were prepared by the methods described in refs. 3—8, respectively. Dibenzo[*a,h*]anthracene (**5**) was purchased from Aldrich Chem. Co. and used without further purification. The synthesis of dibenzo[*c,g*]phenanthrene (**6**) was performed starting from α-tetralone according to the method described in ref. 9.*

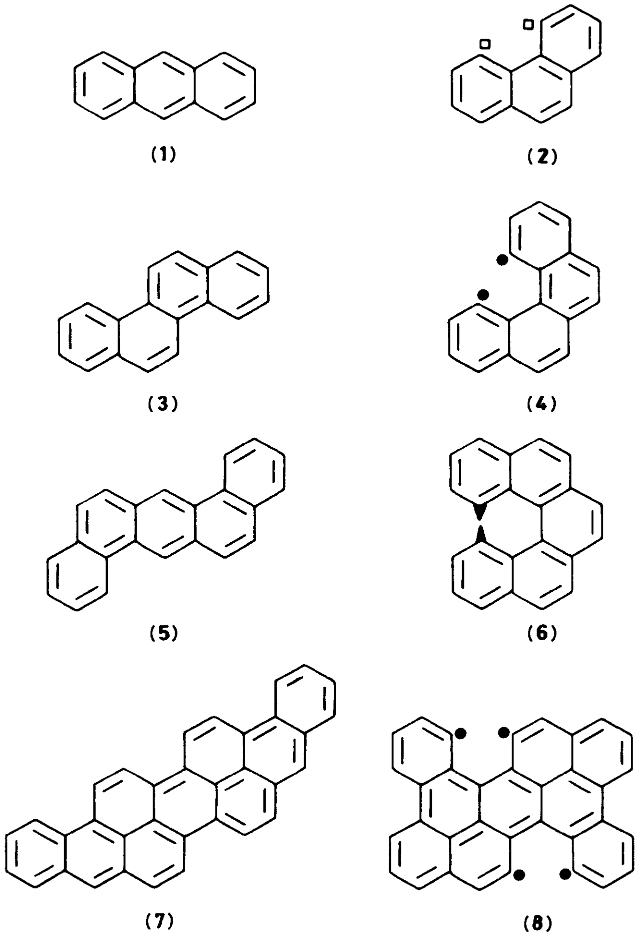
(**1**) (**2**) (**3**) (**4**) (**5**) (**6**) (**7**) (**8**)

Figure 1. Typical examples of overcrowded and uncrowded structures for tri-, tetra-, penta-, and nona-cyclic condensed hydrocarbons (**1**)—(**8**). Fjord-like overcrowding (**4**), (**8**) and crab-like overcrowding (**6**) are shown as ●● and ▲▲, respectively. An example of bay-like overcrowding is shown as □□ for (**2**)

Results

Comparison of Mass Spectra for Overcrowded Aromatic Hydrocarbons with Those of Uncrowded Ones.—We observed several kinds of overcrowding in polycyclic aromatic compounds, *e.g.* bay-like overcrowding (□□) in phenanthrene (**2**), fjord-like overcrowding (●●) in benzo[*c*]phenanthrene (**4**), and crab-like overcrowding (▲▲) in dibenzo[*c,g*]phenanthrene (**6**) as shown in Figure 1. Overcrowding refers to steric

---

* The method of ref. 9 should be modified to improve the yield. The details will be reported in a separate paper.

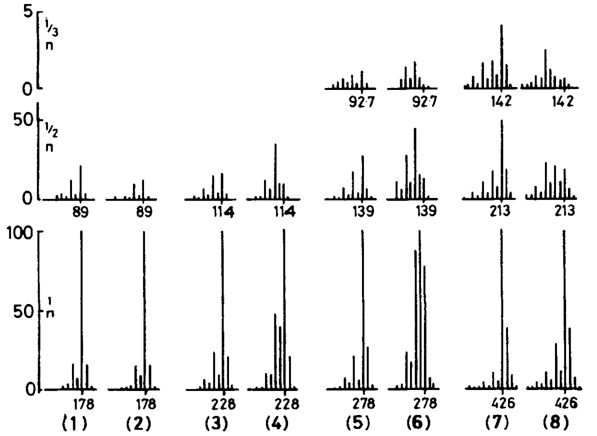

Figure 2. Mass spectrum patterns of singly, doubly, and triply charged ions of molecular families for (**1**)—(**8**). Ions with the same mass but different charge are arranged vertically for each isomer, and the intensity scale of triply charged ions is expanded ten times

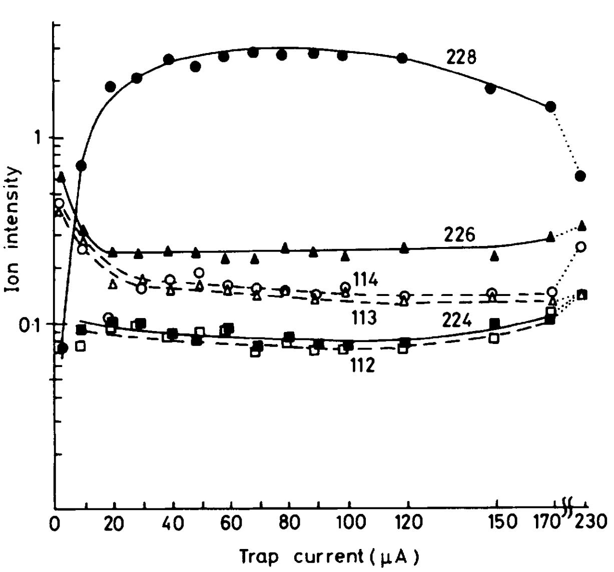

Figure 3. Dependence of ion intensities on trap current. Relative intensities of main fragment ions of chrysene are compared with a parent ion $[228]^{+\cdot}$. The curve for $[228]^{+\cdot}$ represents numerical figures of the ion current on an arbitrary scale under almost constant sample pressure. The current below 10 μA cannot be controlled and it was estimated by a scale of filament current

Table. Mass spectrum of dibenzo[*c,g*]phenanthrene*

$m/1$	Int.	$[m/2]$	Int.	$m/3$	Int.
280	3.6				
279	7.3	139.5	2.3		
278	77.7	139	12.9	92.7	0.3
277	100	138.5	15.4	92.3	0.6
276	87.3	138	44.3	92	1.6
275	17.5	137.5	11.0	91.7	0.6
274	23.1	137	27.1	91.3	1.3
273	3.6	136.5	6.3	91	0.6
272	2.4	136	10.6		
		132	2.2		
263	4.9	131.5	4.7		
		125	9.9		
		124.5	3.3		
248	3.7	124	9.6		
		123	6.7		
237	1.6	118.5	1.3		
		113	5.4		
224	1.1	112	5.9		

* Small peaks due to impurities such as $C_{22}H_{16}$ and $C_{22}H_{18}$ were eliminated by the simultaneous equations of three spectra with different compositions.

crowding caused by repulsive interactions between the neighbouring hydrogen atoms attached to the condensed aromatic rings, and it brings considerable strain into the ring system which should be intrinsically planar. However, we call 'overcrowded' a molecule which contains at least one sample of fjord-like or crab-like overcrowding, and 'uncrowded' a molecule which has no overcrowding or only bay-like overcrowding; the two hydrogens and two carbons in bay-like overcrowding are rather distant from each other so that its ring system can be almost planar. This definition may need to be rationalized since the mass spectra for phenanthrene show the same features as those for anthracene as seen in Figure 2, which shows the mass spectra of molecular ion families for these polycyclic hydrocarbons. In Figure 2, the molecular ions and their mass intervals are arranged at the same position and on the same scale for each charge group. Higher multi-charged ions appear as the number of condensed rings and the stability of a molecule become larger. Triply charged ions for molecules with more than four benzene rings are observed clearly. The largest peak in divalent ions of the overcrowded molecules (**4**), (**6**), and (**8**) corresponds to a fragment ion in which all overcrowded hydrogens have been detached, *i.e.* $[M - 2]^{2+}$ for benzo[*c*]phenanthrene and dibenzo[*c,g*]phenanthrene, and $[M - 4]^{2+}$ for tetrabenzoperylene. On the other hand, that of the uncrowded molecules (**1**)—(**3**), (**5**), and (**7**) corresponds to a molecular ion. These features are more prominent in trivalent ions. A singly charged ion $[M - 2]^{+\cdot}$ is in most cases the first fragment ion born of the precursor molecular ion $[M]^{+\cdot}$ with one pair of hydrogens lost. Thus, its relative intensity represents the instability of a parent ion. The overcrowded molecule always has a higher abundance of the $[M - 2]^{+\cdot}$ peak than the uncrowded one for the same number of rings. In dibenzo[*c,g*]phenanthrene (**6**) the highest peak is the $[M - 1]^{+}$ peak and the next highest is $[M - 2]^{+\cdot}$. Both of these are stronger than the molecular ion peak, which may be understood as follows. The crab-like overcrowding is so strong that the molecular plane is twisted completely and the two overcrowded carbons come nearer to each other and they are bridged even by the detachment of only one hydrogen. The enhancement of the $[M - 1]^{+}$ peak supports our previous determination of 5,14-diazatetrabenzo[*a,cd,lm,o*]perylene having crab-like overcrowding.[2] The highest peaks in multi-charged ions of (**6**) are again $[M - 2]^{2+}$ and $[M - 2]^{3+\cdot}$ ions mainly due to the cyclization at the position of overcrowded carbon atoms. The mass spectrum of dibenzo[*c,g*]phenanthrene is an original one and listed in the Table.

Dependence of Trap Current.—We examined the dependence of relative ion intensities on the trap current and the impact voltage of colliding electrons, in order to understand the overcrowding effects on mass patterns. The current dependence may tell us whether our ionization process is due to the impact of one or more electrons. If a fragment ion, especially a doubly or triply charged ion, is produced by a multi-ionization process, *i.e.* the impact of *n* electrons, then its ion intensity should increase with the *n*th power of impact current. As seen in Figure 3 for chrysene, the relative intensities of fragment ions were almost constant in the range 20—120 μA. Those of multi-

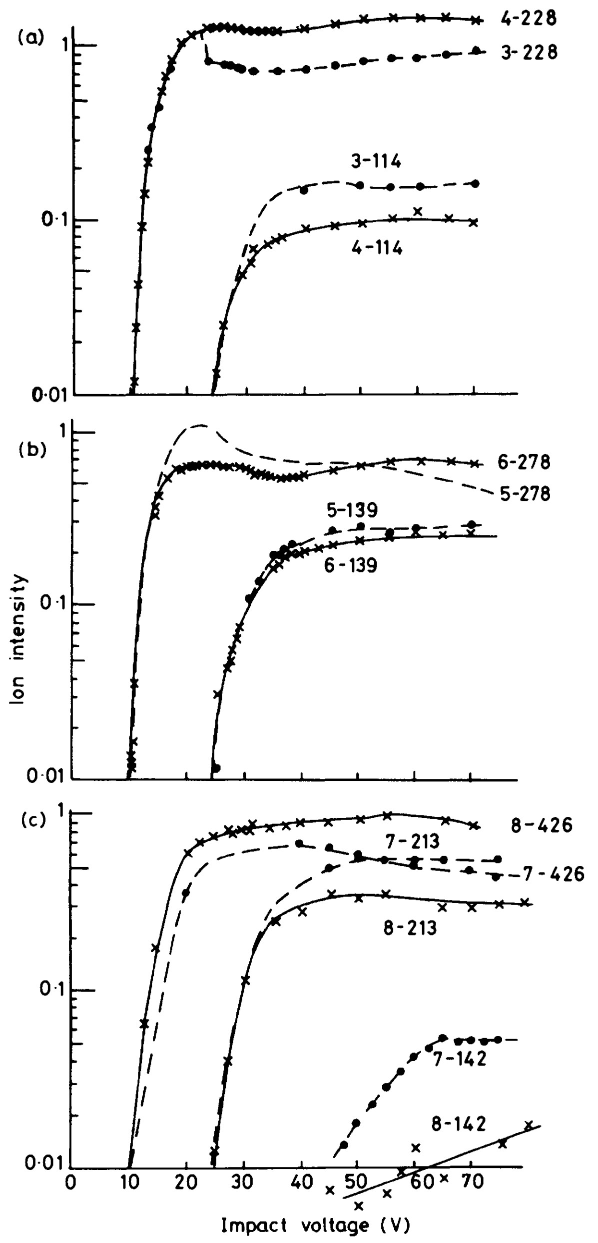

Figure 4. Ionization efficiency curves of molecular ions $[M]^{i+\cdot}$ (i = 1—3). The ratio of the intensity of ions to that of a parent ion $[M]^{+\cdot}$ is plotted *versus* the impact voltage. The curve for $[M]^{+\cdot}$ represents numerical figures of the ion current in an arbitrary scale under almost constant pressure of samples. The number before the value of *m/z*, *e.g.* 4—114, means structure (4). a, Tetra-, b, penta-, and c, nona-cyclic hydrocarbons, respectively. Solid lines correspond to overcrowded molecules, while broken lines to uncrowded ones

charged ions showed the same tendency as singly charged ions. The independence of relative ion intensities from the increase in trap current may suggest that most of our vaporized molecules pass through an ion source chamber under the impact of one electron. Let us check our experimental conditions. The flow of sample molecules I_s is estimated to be 1×10^{13} s^{-1}, since 3 μg of sample with molecular weight 150—450 sublime and disappear in 10 min. The flow of electrons I_e is calculated to be 4×10^{14} s^{-1} from the current value of 60 μA. If we take an average cross-section of a molecule as 10 Å^2 and cross-section area of an ion-source chamber $A_i \doteqdot 1$ cm^2, then the ratio of collision cross-section for an electron is $r_s = A_sI_s/A_i$. Therefore, the ratio of the molecules impacted by an electron is $r_sI_e/I_s = A_sI_e/A_i \doteqdot 0.4$. The ion intensity of $[M]^{+\cdot}$ is shown to increase approximately with the first power of I_e below 70 μA from its log–log plot. We may conclude that the ionization process of a molecule is mainly due to one-electron impact, and that multi-charged ions are produced by the intramolecular multi-scattering of one electron. Thus, our mass spectrum can reflect the intrinsic property of a molecule.

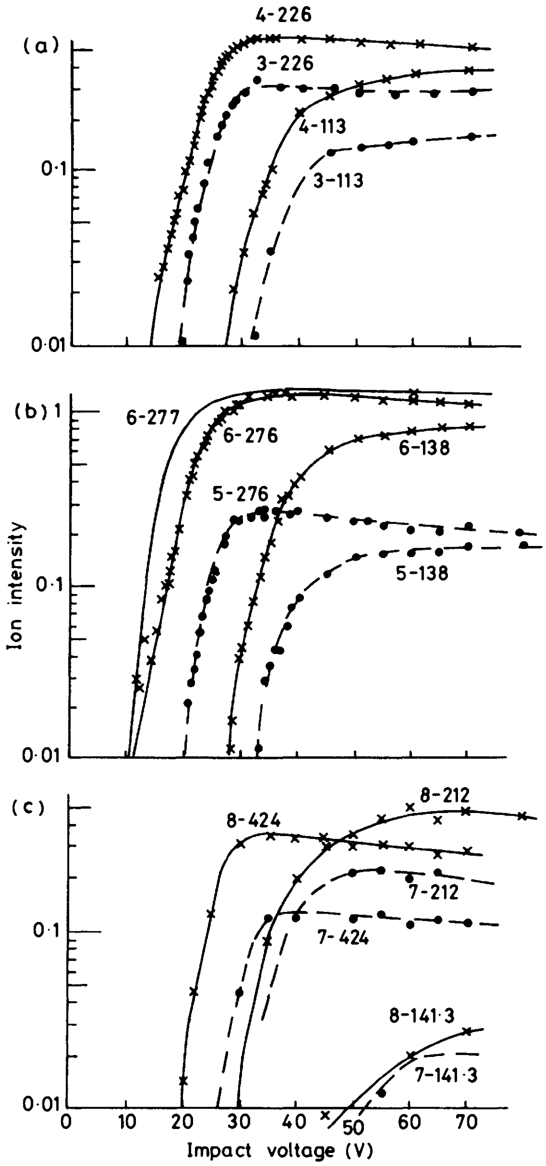

Figure 5. Ionization efficiency curves for $[M - 2]^{i+}$ ions. We also plotted that of $[M - 1]^{+}$ for dibenzo[*c,g*]phenanthrene (6-277 in b). See Figure 4

Ionization Efficiency Curves and Lowering of Appearance Potential.—The dependence of fragment ions on the impact voltage gives us a hint of its fragmentation mechanism. In Figures 4—6 are shown the voltage dependences of ion intensities for $[M]^{i+}$, $[M - 2]^{i+}$, and $[M - 4]^{i+}$ (i = 1—3), respectively. In each Figure we illustrated the different behaviour of the overcrowded molecules (4), (6), and (8) from that of uncrowded ones (3), (5), and (7) for tetra-, penta-, and

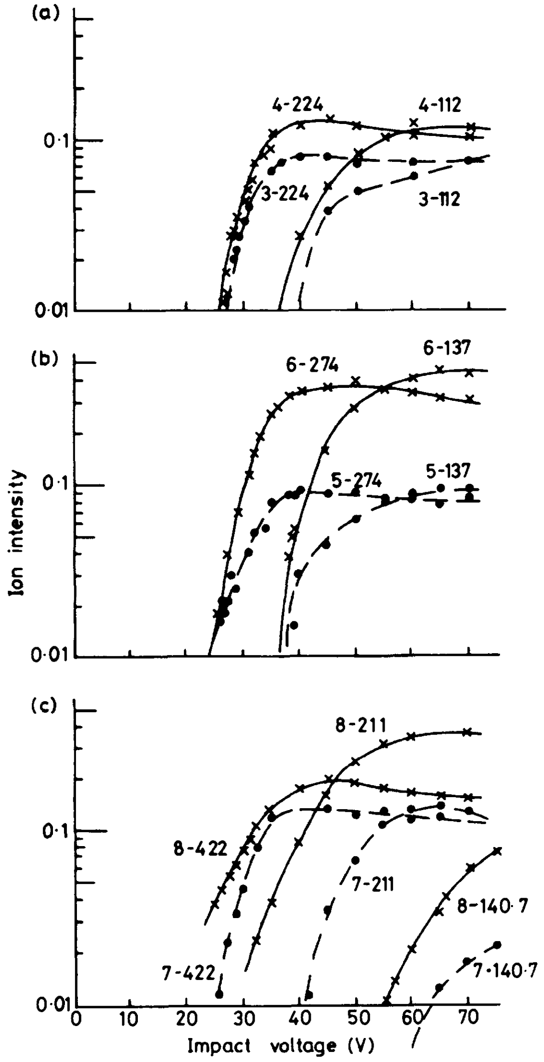

Figure 6. Ionization efficiency curves for $[M - 4]^{i+}$ ions. See Figure 4

nona-cyclic aromatic compounds. Unfortunately, the detector of our mass spectrometer is not so sensitive and the electron energy is non-homogeneous, and thus the appearance energy should be considered as an apparent appearance energy and the upper limit of its value. As seen from Figure 4, the appearance energy of molecular ions is not so sensitive to the overcrowding phenomenon. That of $[M]^{+\cdot}$ is < 10 V, and that of $[M]^{2+}$ is *ca.* 24 V for all molecules investigated. The formation of molecular ions is a simple ionization process involving no fragmentation and is not affected much by molecular strain. The higher abundance of multi-charged molecular ions for uncrowded molecules suggests their higher stability in the region of excess energy.

The appearance potential of fragment ions for overcrowded molecules are, in general, lower than those for uncrowded ones (see Figures 5 and 6). This is probably because of the elimination of overcrowded hydrogen atoms followed by formation of a new ring. The molecular ion loses the overcrowded hydrogen atoms on contact, and the resultant unpaired electrons may form a new ring at that position. The leaving hydrogens may also make a bond under favourable conditions of close contact. The large decrease in free energy for this fragmentation process brings about a decrease in its appearance potential and the increase in its ion intensity.[10] In the case of crab-like overcrowding the molecule is twisted heavily and the overcrowded carbon atoms are kept in close contact. The elimination of one hydrogen is enough to make a new bridge between the adjacent carbons.

An $[M - 2]^{+\cdot}$ ion is usually a specific fragment ion which appears first as a result of the decomposition of an $[M]^{+\cdot}$ ion. In the case of uncrowded molecules, the potential value increases monotonically with the increase in the number of condensed rings, *i.e.* it increases by *ca.* 2 V per ring (see Figure 5). This is probably because the excess of energy can be distributed all over the rings. On the other hand, the appearance energy for overcrowded molecules is lower by 4 or 8 V than in the former case. The difference of appearance energy between these two cases can be understood as the extra energy released from overcrowding and ring formation.

As seen from Figure 6, the lowering of the appearance energy for $[M - 4]^{+\cdot}$ ion becomes small in the upper two cases, perhaps because normal unstrained hydrogens must be eliminated in addition to the pair of overcrowded hydrogens. In the case of tetrabenzo[*a,cd,j,lm*]perylene, it has two pairs of overcrowded hydrogens and the lowering of the appearance energy is still large.

The theoretical approach of mass spectra is very difficult. The fragmentation mechanism of a molecular ion has not been solved so far, because the excess of energy of tens of eV may produce many activated complexes and a number of reaction paths such as bond cleavage and ring rearrangement.[10] The result of our simple process of fragmentation with extremely strained molecules may suggest some important approximations had to be involved in the future development of its theoretical interpretation.

In conclusion, the high abundance of specific fragment ions at 70 V is correlated with the lowering of its appearance energy, *i.e.* a rough measure of the releasing energy of molecular strain and cyclization accompanied by the formation of the specific fragment ions.

Therefore, we consider the following rule has been established for aromatic polycyclic hydrocarbons: the mass difference between a molecular ion and the most intense fragment ion in the ion-family of highest valency corresponds to the number of overcrowded hydrogen atoms, and their mass patterns are different with the type of overcrowding, *i.e.* fjord-like or crab-like overcrowding.

References

1 T. Ueda, M. Ohno, H. Harada, S. Iwashima, J. Aoki, and T. Kan, *Org. Mass Spectrom.*, 1983, **18**, 105.
2 S. Iwashima, T. Ueda, H. Honda, T. Tsujioka, M. Ohno, J. Aoki, and T. Kan, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2177.
3 S. Iwashima, K. Ogino, and J. Aoki, *Nippon Kagaku Zasshi*, 1968, **89**, 338.
4 S. Iwashima, M. Kuramachi, T. Sawada, T. Kobayashi, M. Takekawa, S. Fujisawa, and J. Aoki, *Nippon Kagaku Kaishi*, 1974, 841.
5 S. Iwashima, T. Kobayashi, and J. Aoki, *Nippon Kagaku Kaishi*, 1972, 686.
6 J. Szmuszkovicz and E. J. Modest, *J. Am. Chem. Soc.*, 1948, **70**, 2542.
7 J. Aoki, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 1356.
8 S. Iwashima, H. Honda, J. Aoki, and M. Takekawa, *Nippon Kagaku Kaishi*, 1979, 443; S. Iwashima, H. Honda, J. Aoki, and H. Inokuchi, *Mol. Cryst. Liq. Cryst.*, 1980, **59**, 207.
9 Y. Altman and D. Ginsburg, *J. Chem. Soc.*, 1959, 466.
10 F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Am. Chem. Soc.*, 1970, **92**, 6867.

Received 4*th October* 1984; *Paper* 4/1719