Stability of Large Polycyclic Aromatic Hydrocarbons in the Diffuse Interstellar Medium

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Synopsis. Fragmentation patterns of polycyclic aromatic hydrocarbons (PAHs) observed in mass spectra support the view that sufficiently large compact PAHs have a large possibility of surviving long in the diffuse interstellar medium. Multivalent molecular cations of these PAHs are moderately aromatic.

Unidentified IR features at 3.3, 6.2, 7.7, 8.6, and 11.2 μm dominate the emission from many UV-excited celestial objects, such as planetary nebulae, reflection nebulae, and HII regions.[1—4] Polycyclic aromatic hydrocarbons (PAHs) have been proposed to account for these emission features.[1—4] Considerable controversy has been evoked as to what types of PAHs are really present in space.[1—6] We previously presented theoretical evidence for the idea that the astronomical PAHs might be a mixture of large compact ones such as **1**—**3**.[7—9] Although these molecules have not been synthesized yet, they must be highly aromatic both in the ground state and in the first excited state.[7,8]

When PAH molecules are placed in the intense UV radiation field, they are not only excited electronically but also singly or multiply ionized.[5,6] PAHs are singly ionized with radiation of less than the ionization energy of a hydrogen atom (13.6 eV). An efficient way of forming PAH^{2+} in the interstellar medium is a sequential two-stage excitation process.[6] For larger members of the PAHs the ionization energy of PAH^{+} to PAH^{2+} is again less than 13.6 eV.[6] Therefore, the formation of PAH^{2+} is very possible even in HI regions of UV-excited nebulae.

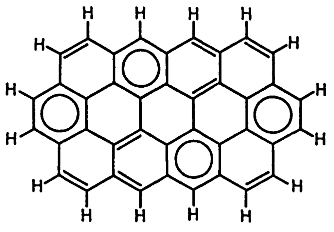
Mass spectrometry is useful for examining the stability of molecular ions. A beam of 70 eV electrons is usually employed to ionize molecules in a mass spectrometer. This energy is large enough to produce multivalent cations of PAHs. The direct formation of PAH^{2+} from PAH occurrs in the 20—40 eV range.[6] If an electron of 70 eV does not break a given PAH into fragments, it must be very stable even in space.

In this note we point out that an important clue to the nature of interstellar PAHs can be obtained from the mass spectra of PAHs. Hückel molecular orbital theory is used to calculate topological resonance energies (TREs) and percent resonance energies (%REs).

Results and Discussion

Hexabenzo[*bc,ef,hi,kl,no,qr*]coronene (**4**)[10,11] and kekulene (**5**)[12,13] are two of the largest PAHs available at present. The molecular structure of **4** does not conform to interstellar IR spectra since it does not have solo hydrogens. Here, solo hydrogens represent CH bonds with no adjacent CH bonds, such as those at 9- and 10-positions in anthracene. The presence of **5** in space cannot be conceived because of its peculiar molecular structure. Nevertheless, it is worthy of note that these PAHs contain as many atoms as the ones possibly present in typical reflection nebulae.[1—4] PAHs **4** and **5** would exhibit similar emission color temperatures if they were placed in such nebulae. Therefore, these large symmetric PAHs serve as a kind of model interstellar molecules.

The %RE represents the degree of aromaticity or the tendency of a cyclic conjugated system to preserve its own conjugated system.[7—9] This qunatity is given as 100 times the TRE, divided by the total π-electron energy of the graph-theoretically defined polyene reference. PAHs **4** and **5** have large %REs in the ground



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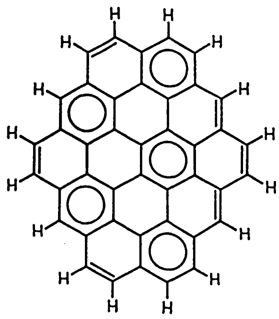

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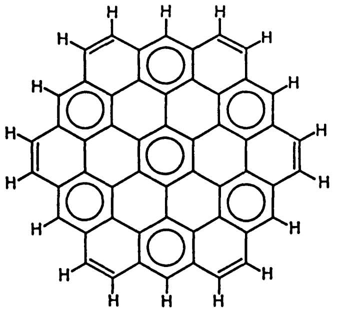

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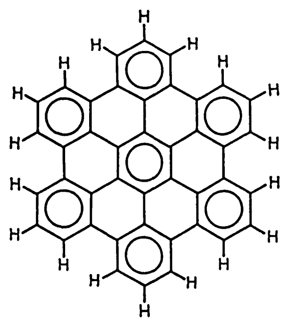

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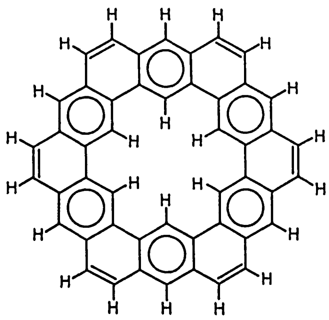

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state, being robust to high temperatures.10—12) In particular, **4** is a fully benzenoid hydrocarbon with a very large %RE.10) Although **4** and **5** have somewhat smaller %REs in the excited state than typical large compact PAHs **1**—**3**,7—9) they still are moderately aromatic in the excited state.

Mass spectra have been measured for **4** and **5**.10—13) In general, a mass spectrum of a PAH shows an intense signal of a molecular ion in contrast to saturated or heteroatom compounds. PAHs **4** and **5** are especially impressive in that their molecular cations are extremely resistant to decomposition. PAH **4** forms mono-, di-, and trivalent cations with some dehydrogenated ions.10,13) According to Diederich and Staab,11) the mass spectrum of **5** contains only the signals of mono-, di-, and trivalent molecular ions. Thus, the carbon skeletons of such large PAHs as **4** and **5** are preserved even if they are deprived of two or three π-electrons. This demonstrates the high stability of large PAH ions.

For cations of **4** and **5** the %RE decreases as the positive charge increases: $\mathrm{PAH}>\mathrm{PAH}^{+}>\mathrm{PAH}^{2+}>\mathrm{PAH}^{3+}$. As shown in Table 1, these PAHs are aromatic with large positive %REs even if they are multiply ionized. These PAH ions must be thermodynamlcally stable with a greatly diminished possibility of isomerization and fragmentation. Mass spectra of **4** and **5** are consistent with this way of reasoning based on the %REs. Large compact PAHs such as **1**—**3** are also aromatic in various electronic states. For cations of these PAHs the %RE likewise decreases as the positive charge increases. Even the trivalent cations have %REs larger than 1.6. For alternant hydrocarbons such as PAHs, the %RE of the molecule in the first excited state is equal to that of the divalent cation.

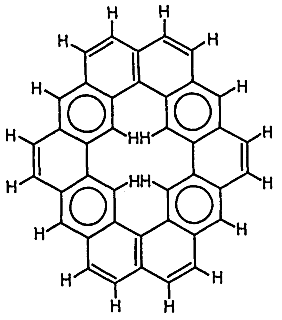
Mass spectra of smaller PAHs exhibit many ions formed by the fragmentation of carbon skeletons.14) For these PAHs the %RE often is negative in sign in the excited state and/or in ionized states.7,9) Many PAHs, including large ones such as **4**, have a tendency to lose two or four hydrogen atoms when they are excited by high-energy electrons.14) This phenomenon is not necessarily relevant to the instability of the π-electron system, indicating that part of the excitation energy is used to split weak σ bonds. Note that CH bonds are much weaker than conjugated C–C bonds. Dehydrogenation of PAHs has likewise been predicted to occur commonly in the interstellar radiation field.1—5)

Table 1. TREs of Large PAHs in Various Electronic States

PAH	Electronic state	TRE/$\lvert\beta\rvert$	%RE
1	0	1.476	2.59
	+1	1.376	2.42
	+2	1.276	2.25
	+3	0.959	1.70
2	0	1.600	2.67
	+1	1.444	2.41
	+2	1.288	2.16
	+3	1.006	1.69
3	0	2.096	2.70
	+1	1.851	2.38
	+2	1.606	2.07
	+3	1.480	1.91
4	0	1.739	2.92
	+1	1.412	2.37
	+2	1.085	1.83
	+3	0.912	1.54
5	0	1.569	2.34
	+1	1.264	1.89
	+2	0.960	1.44
	+3	0.753	1.13

As a molecule with N atoms has 3N-6 vibrational modes, **4** and **5** have 174 and 210 vibrational modes, respectively. Even if such large PAHs partition a considerable part of excitation energy among the vibrational modes, few C–C bonds can acquire the vibrational energy needed to dissociate themselves.1—4) Therefore, it seems very likely that large compact PAHs in space owe their long lifetime not only to high aromaticity in the neutral and ionized states but also to many vibrational modes. Multivalent cations can be kept out of Coulomb explosion if they are sufficiently large.6) The fact that electrons of several tens of eV are not energetic enough to fragment large PAHs suggests that such PAHs must be very stable in the UV-excited nebulae, where the light intensity is maximized somewhere in the 10—15 eV range.6) Poincaré fluorescence would further reduce the probability of photodissociation.15)

PAH **6** is as large a molecule as **1**. However, it loses four hydrogen atoms by electron-impact excitation.16) It is known that overcrowded hydrogen atoms tend to dissociate even if they reside in large PAHs.17,18) Overcrowded hydrogen atoms such as those in benzo[*c*]phenanthrene (**7**) readily dissociate when the molecule absorbs the energy of 70 eV.17,18) Hydrogen atoms ejected from **6** are presumably the inner overcrowded ones.16) If interstellar PAHs are actually large and compact in shape, they must be devoid of overcrowded hydrogen atoms.



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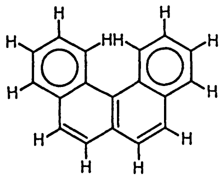

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Concluding Remarks

As has been seen above, mass spectra of **4** and **5** can be used as a strong argument in favor of the presence of large PAHs in UV-excited nebulae. Cations of **1**—**3** have numerous vibrational modes and slightly larger positive %REs than **4** and **5**. Therefore, such large compact PAHs must be highly radiation resistant to decomposition in the diffuse interstellar medium. Despite their high stability, **4** and **5** have not been considered as good candidates for interstellar PAHs. Interstellar or circumstellar chemical reactions must be unsuitable for the formation of these PAHs.

Kekulene (**5**) is interesting in two more respects. The outer periphery of **5** is identical with that of dodecabenzocoronene (**3**), one of the best candidates conceivable for interstellar PAHs.[1,5] It is highly probable that **3** is much more stable in space than **5** because multivalent cations of **5** has larger %REs and more vibrational modes. Balm and Kroto suggested that partly broken and partly hydrogenated fullerene-like carbon clusters might be responsible for the interstellar infrared bands.[19] These curved particles differ from normal PAHs in that the edges are internal rather like those in **5**. The inner solo hydrogens of **5** may give rise to bands which allow a satisfactory fit to the interstellar IR data.[19]

Addendum. After submission of this note, a paper describing the synthesis of circumanthracene (**1**) appeared (R. D. Broene and F. Diederich, *Tetrahedron Lett.*, **1991**, 5227). The electron-impact mass spectrum of **1** shows no fragment ions in the $m/z > 100$ range.

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