Theoretical Evidence for the Presence of Linear Polyacenes in the Interstellar Medium

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Duley and Jones recently proposed that small linear polyacenes (e.g., anthracene) were responsible for the IR emission observed in localized regions of some UV-excited nebulae. Linear polyacenes are relatively stable in the first excited state although they are not very stable in the ground state. This probably is the primary reason why this type of benzenoid hydrocarbons are observed in the interstellar medium.

The presence of polycyclic aromatic hydrocarbons (PAHs) in many celestrial objects such as planetary nebulae, reflection nebulae, and active galaxies is now generally accepted.[1-3] Evidence for the occurrence of PAHs derives primarily from the analysis of IR emission spectra. Major features occurring in the IR region were attributed reasonably to vibrational modes in large compact PAHs containing 20—50 carbon atoms per molecule. Many carbon atoms seemed to be required to stabilize the PAH molecule against destruction by the interstellar radiation field under diffuse cloud conditions.

Such an image of interstellar PAHs has changed a little during the past few years.[4-7] Geballe et al. noticed that the smallest PAHs in such objects as the Orion Bar (a ridge of emission in the Orion Nebula) and the Red Rectangle (a symmetric biconical nebula surrounding the star HD 44179) appeared to contain only 15—20 carbon atoms.[4] Woodward et al. in a study of the planetary nebula NGC 7027 concluded that the PAHs contained 13—27 carbon atoms and that small PAHs with about 10 carbon atoms per molecule might account for some of the IR emission features.[5] Thus, for the first time there appears to be clear observational evidence for the presence of small PAHs in UV-excited nebulae.

Quite recently Duley and Jones proposed that small linear polyacenes (**1**—**3**, **5**, and **10**) were responsible for the IR emission in the above nebulae and that these PAHs have only a transient existence in localized regions of the interstellar medium.[7] Small linear polyacenes were found to provide a close spectroscopic match to the major observed IR emission bands. Specifically, the spectrum of anthracene (**3**) gave an almost perfect representation of the observed emission spectra with lines at 3048, 1621, 1450, 1317, 1147, and 884 cm^{-1}. Duley and Jones also noted that the 2940 and 2850 cm^{-1} emission features were consistent with the anharmonicity of the CH stretching vibration in some small linear polyacenes. They suggested that two- to five-ring linear polyacenes could be important constituents in such objects as the Orion Bar.[7]

Of particular interest is the fact that there is no indication of nonlinear or angular polyacenes in objects where linear polyacenes are observable. Here, angular polyacenes refer to all possible benzenoid isomers of linear polyacenes (**4**, **6**—**9**, **11**—**21**). Duley and Jones analyzed the detailed spectrum of the Orion Bar reported by Roche et al.,[6] and interpreted the features in the 860—940 cm^{-1} region as arising from the superposition of emission from CH bending modes in naphthalene (**2**), anthracene (**3**), and naphthacene (tetracene, **5**), the three simpler linear polyacene molecules.[7] However, the CH bending modes in angular polyacenes such as phenanthrene (**4**) and chrysene (**7**) were not detectable in interstellar IR spectra.

Laboratory work so far done confirmed firmly that linear polyacenes were thermodynamically much less stable than the angular isomers.[8] Both linear and angular polyacenes occur in carbonaceous meteorites, but the abundances of linear polyacenes are much smaller than those of the angular analogues.[9-12] Therefore, it is a very queer thing that linear polyacenes, rather than angular ones, are present in some nebulae. It is the purpose of this paper to rationalize the predominance of small linear polyacenes in interstellar space in terms of photochemical stability.

Theory

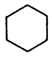
The topological resonance energies (TREs) of the ground- and excited-state species were calculated as previously described.[13,14] The percent resonance energy (%RE) is defined as 100 times the TRE, divided by the total π-electron energy of the graph-theoretically defined polyene reference.[15] The %RE is known to be an excellent measure of stability of a cyclic conjugated system in the electronic state concerned. The simple Hückel molecular orbital model was used.

Results and Discussion

We previously presented theoretical evidence for the presence of large compact PAHs in many celestrial objects.[16-18] We examined the TREs of a wide variety of PAHs in detail, and found that the PAHs observed in the interstellar radiation field had to be photochemically stable with a sufficiently large %RE in the first electronic excited state. PAHs which

Table 1. Percent Resonance Enegies (%RE) of Linear Polyacenes and Related PAHs

Species		Ground state	Excited state
C_6H_6	**1**	3.528	−10.342
$C_{10}H_8$	**2**	2.924	−1.113
$C_{14}H_{10}$	**3**	2.519	0.947
	4	2.888	−0.453
$C_{18}H_{12}$	**5**	2.269	1.573
	6	2.630	0.904
	7	2.809	0.599
	8	2.802	0.205
	9	3.012	−0.453
$C_{22}H_{14}$	**10**	2.105	1.780
	11	2.416	1.574
	12	2.599	1.332
	13	2.593	1.238
	14	2.808	1.008
	15	2.682	1.000
	16	2.484	0.992
	17	2.773	0.929
	18	2.884	0.865
	19	2.765	0.699
	20	2.768	0.607
	21	2.598	0.244
$C_{16}H_{10}$	**22**	2.729	0.930
	23	2.636	0.323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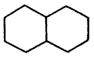
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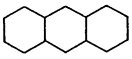
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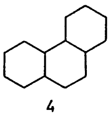
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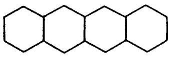
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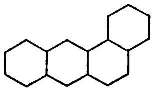
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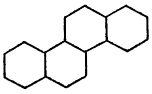
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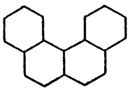
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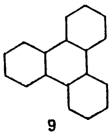
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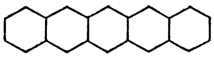
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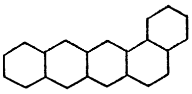
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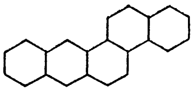
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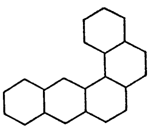
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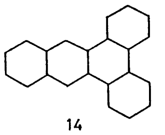
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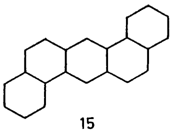
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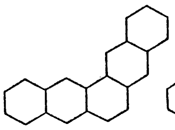
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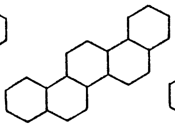
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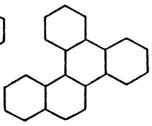
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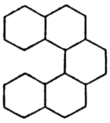
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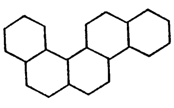
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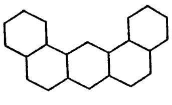
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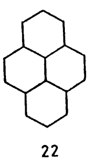
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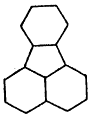
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satisfy this condition were restricted mostly to large compact ones.[16] Since the present study is concerned with small polyacenes, we examine relative stabilities of small linear and angular polyacenes (**1**—**23**). The %REs calculated for these PAHs both in the ground and in the first excited state are listed in Table 1.

In general, linear polyacenes show decreasing stability as the number of rings is increased.[8,19] Naphthalene (**2**) is a stable molecule, whereas pentacene (**10**) is very reactive. On the other hand, angular polyacenes are much more stable than their linear analogues. For example, picene (**18**) is considerably less reactive than pentacene.[8,19] The %REs of the ground-state species are in good agreement with their chemical behaviors. The %RE of the linear polyacenes decreases sharply, whereas the %RE of the angular ones decreases to a much lesser extent with increase in the number of rings.[16,18,20] Thus, linear polyacenes larger than naphthalene are never very stable in the ground state. It is obvious that the stability of a molecule in the ground state cannot rationalize its occurrence in the interstellar medium.

As suggested in previous papers,[16–18] the stability of the excited-state species is expected to give an important clue to the present problem since the interstellar polyacenes are exposed to intense UV light. Inspection of Table 1 shows that in marked contrast to the ground-state species, linear polyacenes in the first excited state have a larger %RE than the isomeric angular polyacenes in the same excited state. This implies that when light is absorbed, linear polyacenes become more stable than their angular isomers. This must be the primary reason why anthracene and other small linear polyacenes are observed in localized regions of some UV-excited nebulae. Such a way of reasoning is identical with that adopted previously to rationalize the occurrence of large compact PAHs in many objects.[16–18]

Clar has noted that the more highly colored a benzenoid hydrocarbon, the less stable it generally is.[14,19,20] He ascribed this relationship to a bathochromic shift of the p band as the stability decreases. The p band is due to an allowed electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).[19] We reported that for PAHs the HOMO-LUMO energy separation was highly correlative with the %RE.[14,20] It then follows that relatively unstable PAHs with a small HOMO-LUMO gap are destabilized to a lesser extent by light absorption and that the resulting excited-state species are fairly stable.

According to Duley and Jones,[7] anthracene (**3**) appears to be most abundant in interstellar space, followed by naphthalene (**2**) and then by naphthacene (**5**) and perhaps pentacene (**10**). They made no decision as to whether this represents a decomposition sequence with naphthalene derived from anthracene via photodissociation, or whether the observed relative abundances represent the initial abundance in the dust. We will show below that such a pattern of the PAH distribution can in principle be interpreted in terms of thermodynamic and photochemical stabilities of the individual PAHs.

Carbonaceous chondrites contain various extraterrestrial organic molecules.[21)] PAHs extracted from the chondrites are naphthalene (**2**), acenaphthene, phenanthrene (**4**), fluoranthene (**23**), and pyrene (**22**), which are arranged in order of decreasing abundance.[9,10)] It is worth noting that anthracene is not abundant in meteorites. In the antarctic meteorite Yamato-791198, phenanthrene is about 13 times more abundant than anthracene.[10)] A similar PAH distribution was observed in the Murchison chondrite.[9)] A polymeric organic material in carbonaceous chondrites also contain much more phenathrene nuclei than anthracene nuclei.[12)] The predominance of phenanthrene over anthracene can be attributed primarily to the fact that phenanthrene is thermodynamically more stable than anthracene. The heat of atomization of phenanthrene is 6.2 kcal mol^{-1} larger than that of anthracene.[8)] Thus, phenanthrene is more easily formed in nature than anthracene. The relative abundances of these two PAHs in meteorites[9,10)] are consistent with their relative %RE values in the ground state.

Duley and Jones thought of hydrogenated amorphous carbon (HAC) as a source of interstellar polyacenes.[7,22)] HAC consists of randomly oriented PAH molecules bound to each other by aliphatic hydrocarbon bridges. If they are correct, HAC dust is expected to erode under the energetic conditions that exist in objects such as the Orion Bar, where small PAHs are the most highly excited and the first to be removed due to their low heat capacity.[7,23)] However, it seems very likely that linear polyacenes are minor components in HAC dust as in the case of carbonaceous chondrites. In particular, naphthacene (**5**) and pentacene (**10**) are thermodynamically much less stable than their angular analogues.[8)] Blumer pointed out that these linear polyacenes did not survive in nature on the Earth.[24)]

Relative abundances of polyacenes observed in the interstellar medium must then be a function of the initial abundance and the photochemical stability. Angular polyacenes must decompose rapidly before or after ejection from HAC dust since they have a much smaller %RE in the excited state than the isomeric linear polyacenes. Smaller linear polyacenes are possibly present much more abundantly in HAC dust than larger linear polyacenes, but larger linear polyacenes are expected to be more stable in the radiation field. These conflicting tendencies of polyacenes can in principle account for the relative abundance of anthracene maximized in some localized regions of UV-exclted nebulae. Note that anthracene in the excited state is aromatic with a positive %RE, whereas phenanthrene in the excited state is antiaromatic with a negative %RE.

Duley and Jones examined the spatial distribution of anthracene and naphthalene in some nebulae, and suggested that the destruction rate for naphthalene was larger than that for anthracene.[7)] This presumably is due to the antiaromaticity of naphthalene in the excited state. Therefore, whether or not this molecule is really observable in the interstellar medium depends on its initial abundance, i.e, the amount of naphthalene which is continuously liberated from the HAC dust there. HAC dust then must be very rich in this PAH. Since small PAHs are not so stable in the excited state as large compact ones,[16,18)] they must anyway be very transient species under harsh conditions.

Duley and Jones suggest that the possible presence of a PAH molecule as small as naphthalene might be an indication of the presence of benzene in some objects.[7)] However, organic photochemstry tells us that benzene is highly reactive in the excited state.[25)] In fact, benzene has a large negative %RE in the excited state. Therefore, there must be little possibility of detecting benzene in the intense radiation field. Pyrene (**22**) and fluoranthene (**23**) are found abundantly in carbonaceous meteorites.[9–11)] Pyrene is fairly aromatic in the excited state. This PAH is likely to be present in nebulae where linear polyacenes are detectable.

Concluding Remarks

In the interstellar medium PAH molecules susceptible to photodecomposition processes will be weeded out, leaving a mixture dominated by the photochemically stable structures. The %REs of the excited-state species provide theoretical support to the presence of small linear polyacenes in some UV-exclted nebulae. The present way of reasoning is consistent with that devised previously to rationalize the presence of large compact PAHs in many celestial objects.[16–18)] In both cases high photochemical stability seems to be essential to the survival in the strong radiation field. The rate of photodecomposition, rather than the initial abundance, determines the relative abundances of PAHs in the radiation field.

For alternant hydrocarbons such as PAHs, the %RE of the excited-state species is equal to that of the dication.[16)] Therefore, PAHs with a large %RE in the excited state must be resistant to photodecomposition even if they are deprived of one or two π electrons in the intense radiation field. Fluoranthene (**23**) alone is not an alternant hydrocarbon. Its dication is antiaromatic with a %RE of -0.830, which is not favorable to the survival in the radiation field.

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