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SIMPLE LINEAR POLYCYCLIC AROMATIC HYDROCARBON MOLECULES AND THE INFRARED EMISSION FEATURES: MOTHBALLS IN THE ORION RIDGE?

W. W. DULEY AND A. P. JONES
Department of Physics, York University
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ABSTRACT

We show that the IR emission spectrum in objects such as the Orion ridge is compatible with the presence of two- to five-ring linear PAH species in amorphous carbons; specifically the derivatives of naphthalene, anthracene, tetracene, and perhaps pentacene. An origin for these molecules in carbon dust is indicated and is consistent with the structure of laboratory hydrogenated amorphous carbons (a-C:H). Benzene and the simplest aromatic ring molecule, cyclopropenylidene, may be observable in sources which show the UIR emission features.

Subject headings: infrared: general — interstellar: grains — interstellar: molecules — line identifications — nebulae: general

I. INTRODUCTION

The presence of polynuclear aromatic molecular species in the interstellar medium is now generally accepted. Evidence for the occurrence of such species derives primarily from the analysis of infrared emission spectra first recorded by Gillett, Forrest, and Merrill (1973). Prominent features occur at or near 3040(3.29), 1615(6.2), 1310(7.6), 1150(8.7), and 885(11.3) $\mathrm{cm}^{-1}(\mu\mathrm{m})$ and can be associated, in principle, with vibrational modes in aromatic species (Duley and Williams 1981; Léger and Puget 1984; Allamandola, Tielens, and Barker 1985) although the exact class of molecule has not been identified. Localization of these features to regions adjacent to energetic sources (e.g., the Orion ridge) suggests that the species responsible may have a transient existence and, in fact, could be the products of the dissociation or sputtering of carbon grains (Duley and Williams 1986; Duley 1988).

Excitation and emission of radiation by interstellar PAHs has been discussed by Allamandola, Barker, and Tielens (1987) and Barker, Allamandola, and Tielens (1987). They conclude that spectral factors such as the shape, width, and relative intensities of the emission features are a strong function of the ambient interstellar radiation field. The predictions are in general agreement with the observations of spatial variations in emission within individual objects (Tokunaga *et al.* 1988; Geballe *et al.* 1989; Roche, Aitken, and Smith 1989), although there is still considerable uncertainty concerning the detailed behavior of several of the weaker features [e.g., 2940(3.40), 2890(3.46), 2850(3.51), and 2800(3.57) $\mathrm{cm}^{-1}(\mu\mathrm{m})$].

Attempts at a chemical identification of the IR emitters have focused on compact fused aromatic ring molecules such as pyrene $C_{16}H_{10}$, coronene $C_{24}H_{12}$, and ovalene $C_{32}H_{14}$ for which there are laboratory spectra (Allamandola, Tielens, and Barker 1985; Léger and Puget 1984). Such molecules have close to the 20–50 carbon atoms that seem to be required to stabilize the PAH against destruction by the interstellar radiation field for extended periods ($\sim 10^7$–10^8 yr) under diffuse cloud conditions.

Geballe *et al.* (1989) find that in the Orion bar and the Red Rectangle the smallest hydrogenated PAHs would appear to contain only 15–20 carbon atoms, and Woodward *et al.* (1989) conclude that in NGC 7027, the PAHs contain 13–27 carbon atoms. It is worth emphasizing that the stable PAHs within these size ranges are catacondensed and not compact structures. In this context, we note that a lower limit (Geballe *et al.* 1989), or an upper limit (Woodward *et al.* 1989), on the size of the hydrogenated PAHs severely constrains the range of molecules that can be present. Indeed, for the smaller stable PAHs the number of carbon atoms per PAH must be even. For a generic PAH C_nH_m, if $n = 14$ (three rings), only two structures are possible, for $n = 16$ (four rings) only one structure exists, and for $n = 18$ (four rings) five structures are possible. PAHs with $n \geq 20$ have many tens of isomers.

As noted by Duley and Williams (1981) the absorption spectra of compact molecules such as coronene provide a close, but not exact, spectroscopic match to the major interstellar IR emission features. In particular, a poor correlation exists between laboratory and astronomical data in the region near 885 cm^{-1}; the relatively sharp nature of the interstellar 885 cm^{-1} feature would seem to imply a limited range of emitters. The recent detection of additional sharp emission features at 905 cm^{-1} (11.05 μm) and 787 cm^{-1} (12.70 μm) led Roche, Aitken, and Smith (1989) to note that "we are seeing emission from a single species of molecule or a relatively small number of dominant species."

II. LINEAR POLYCYCLIC AROMATIC HYDROCARBON SPECIES AND THE INFRARED EMISSION

In this *Letter* we propose that small linear, fused ring molecules are responsible for the IR emission and that these molecules have only a transient existence in localized regions of the interstellar medium. The absorption spectrum of these molecules is characterized by a close match to all the major observed IR emission bands (Table 1). Specifically, the spectrum of the simple three-ring linear PAH, anthracene $C_{14}H_{10}$, gives (on its own) an almost perfect representation of the observed emission spectrum with lines at 3048, 1621, 1450, 1317, 1147, and 884 cm^{-1}. Agreement between the energy of the CH bending vibration (884 cm^{-1}) and the observed energy of the interstellar peak (885 cm^{-1}) is particularly significant in view of the sensitivity of the CH bend energy to environment (Bellamy 1964). The feature at 1905 cm^{-1} (5.25 μm) (Allamandola 1989) is also observed in the spectrum of anthracene. We also note that the 2940 cm^{-1} and 2850 cm^{-1} features are consistent with the anharmonicity of the C–H stretching

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TABLE 1

ABSORPTION BANDS AND INTERSTELLAR EMISSION FEATURES[a]

Species	Absorption and Emission Features (cm^{-1})																
Interstellar	3040	1905	1754	1615	...	1460	1315–1250	...	1150	...	...	905	885	787	...
Naphthalene	3048	...	...	1593	1504	...	1271	...	1123	...	959	...	...	782	...
Anthracene	3048	1910	1775	1621	1530	1450	1317	1270	1162/1147	1000	954	...	884	...	727
Tetracene	3043	...	...	...	1538	...	1297	...	1122	996	958	904	...	...	741
Pentacene	3043	...	...	...	...	...	1296	...	...	990	958	908	836	...	732

[a] Comparison of energies of major absorption bands in simple polyacenes with interstellar spectra. Laboratory spectra are from Nujol solutions.

vibration (2–1 and 3–2 transitions) in benzene, naphthalene, and anthracene (Geballe *et al.* 1989).

The spectrum reported by Roche, Aitken, and Smith (1989) between 860 and 940 cm^{-1} can now be understood as arising from the superposition of emission from CH bending modes in naphthalene (782 cm^{-1}), anthracene (884 cm^{-1}), and tetracene (904 cm^{-1}), the three simplest linear polyacene molecules. Emission from pentacene at 908 cm^{-1} could also contribute to the 905 cm^{-1} interstellar feature; however, anthracene also absorbs at this energy (Fig. 1). We note that emission by two-, three-, and to some extent four-ring molecules will be intrinsically narrow because of the limited range of molecular conformations available in such simple molecules.

Woodward *et al.* (1989) in a study of NGC 7027 conclude that small PAHs with about 10 carbon atoms per molecule (i.e., naphthalene) may account for some of the observed UIR emission, especially in the neutral region. Thus, for the first time there appears to be clear observational evidence for small PAHs in a planetary nebula.

The existence of relatively small PAH molecules is compatible with the model for the structure of hydrogenated amorphous carbon (HAC) recently proposed by Duley (1987). In this model, which is based on the analysis of laboratory data by Robertson and O'Reilly (1987) and Smith (1984), HAC consists of a collection of PAH clusters loosely bonded by polymeric material. Erosion of these clusters is expected under the energetic conditions that exist in objects such as the Orion ridge where clusters with fewer than five rings are the most highly excited and the first to be removed due to their low thermal heat capacity (Duley 1988). Observation of emission from the two- to five-ring linear polyacenes is therefore consistent with the dissolution of HAC dust. It is uncertain, however, whether IR emission occurs before or after ejection of these fragments from dust (Duley 1988; Allamandola 1989). The good agreement between the spectrum of condensed anthracene (Fig. 1) and the UIR spectrum suggests that the molecules may be emitting before leaving the HAC surface.

On ejection from the grain surface it is likely that small linear PAH species with fewer than 20 carbon atoms will rapidly be destroyed by stellar photons of energy greater than ~5 eV (Leach 1989). This rapid destruction should yield $C_2H_2^+$ and $C_3H_3^+$ products which are likely to be the precursors of the abundant cyclopropenylidene molecule, C_3H_2 (Leach 1989).

Substitution of sidegroups of naphthalene, anthracene, and tetracene has little effect on the 884 cm^{-1} or 1620 cm^{-1} absorption bands (Table 2). However, substituents yield a range of absorption features that could contribute to the continuum between the 787 and 885 cm^{-1} emission peaks or to the "plateau" emission (de Muizon *et al.* 1986) on the low-energy side of the 885 cm^{-1} feature. The CH bending modes in the nonlinear PAHs phenanthrene (three rings), $C_{14}H_{10}$, and chrysene (four rings), $C_{18}H_{12}$, lie at 873 cm^{-1} and 864 cm^{-1}. Neither features are present in the interstellar spectra; however, a low concentration of these PAH molecules could contribute to the 800–900 cm^{-1} continuum.

It is significant that spectra of anthracene and tetracene show absorption features near 727 cm^{-1} corresponding to the excitation of four adjacent CH oscillators (Bellamy 1964). Detection of an emission band at such an energy would be an important confirmation of the presence of small hydrogenated polyacene molecules. However, substitution has the effect of weakening this band while leaving most other features unchanged. Table 2 shows that substitution also has the effect of slightly increasing the energy of the 884 cm^{-1} feature. A shift of the 884 cm^{-1} feature to 891 cm^{-1} as seen, for example, by Witteborn *et al.* (1989) could be due to the presence of anthra-

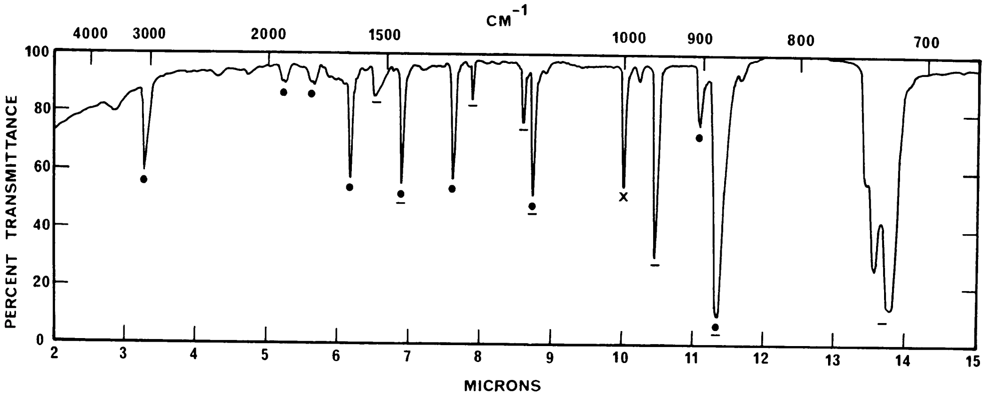

FIG. 1.—Infrared absorption spectrum of anthracene in KBr. Filled circles denote the observed UIR features; a cross (minus sign) denote spectral lines that disappear (weaken) on substitution or dehydrogenation.

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TABLE 2

Effect of Substitution on Absorption Spectra

Molecule	Substituent	Observed Energy (cm^{-1})				
Naphthalene	...	1593	...	...	782	...
	1-methyl	1599	...	...	770–790	...
	2-methyl	1601	885	848	811	740
Anthracene	...	1621	884	...	...	725
	2-methyl	1635	892	...	803	737
	9-methyl	1622	887	...	778	723
	2-ethyl	1626	893	...	810	740
	9,10-dimethyl	1619	...	...	815	744
	9-vinyl	1621	881	842	790	734
	9-acetyl	1620	892	...	789	732
	9-carbonitrile	1620	899	847	781	...

cene derivatives. Substitution with CH_3 groups would also produce a feature in the 2940 cm^{-1} (3.4 μm) region.

The absence of a 727 cm^{-1} emission feature may provide an important indication of the source of the PAH molecules responsible for the UIR features. The accepted model for the structure of HAC (Smith 1984) involves aromatic and diamond-like molecular groups bonded through a polymeric structure. Such structures, e.g., pendant benzene in a-C:H, have been confirmed by laboratory experiments (Tamor *et al.* 1989). Liberation of PAH molecules from this material will involve the breaking of single C—C bonds (Fig. 2). The resulting naphthalene or anthracene molecule would either retain a CH_n group, or be dehydrogenated, at these sites. Any PAH–matrix bond is statistically more likely to be on one of the terminating rings in linear PAHs. Thus, dissociation events would yield molecules in which the proportion of four adjacent CH oscillators is reduced and the corresponding 727 cm^{-1} emission feature suppressed. Indeed, it would be absent if bonds were broken at both ends of the molecule (Fig. 2). The nonobservation of a 727 cm^{-1} emission band may then provide clear evidence that the PAH UIR emitters derive from the dissolution of HAC. If IR emission by these species occurs before the molecules leave the surface, then the 727 cm^{-1} feature would of course also not be observed because of bonding at these terminal sites (Fig. 2).

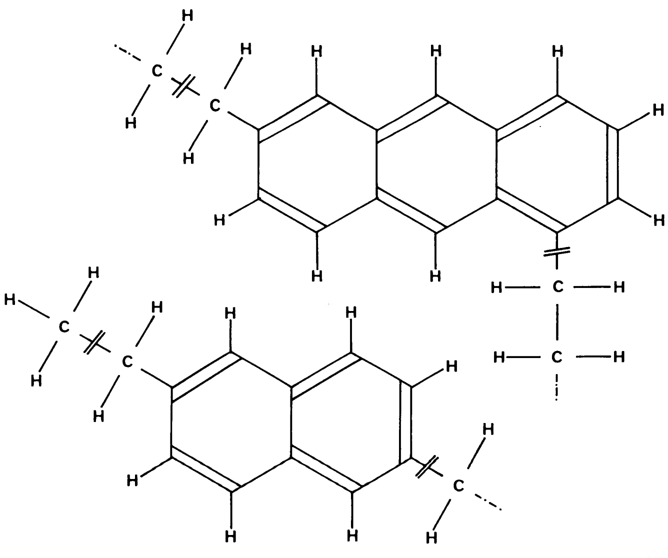

Fig. 2.—Schematic representation of naphthalene and anthracene bonding to polymer (alkane) in HAC. Liberation of anthracene would likely involve bond breaking as shown forming a gas phase molecule with only one, two, or three adjacent C—H oscillators and no 727 cm^{-1} emission band.

Figure 1 shows several lines in the spectrum of anthracene that have not yet been observed in interstellar spectra. The strongest of these lines (in absorption) occur at 1530(6.5), 1270(7.9), 1162(8.6), 1000(10.0), 954(10.5), and 727(13.8) cm^{-1}(μm). Some of these features could be present in the spectrum of NGC 7027 (Russell, Soifer, and Willner 1977) and in HD 44179 (Witteborn *et al.* 1989). Others such as the 954 cm^{-1} line may be confused with ionic lines. For example, Aitken and Roche (1982) have reported a feature at ~10.5 μm in the spectra of several nebulae which has been attributed to S iv. An explanation for the lack or weakness of these features is compatible with the structure of HAC (Fig. 2), namely, that end ring substitutions in linear PAHs lead to a weakening or disappearance of these bands. For example, 2-methyl-, 2-ethyl-, and 2-(*tert*-butyl)- anthracenes show no 1000 cm^{-1} feature and a considerably weakened 954 cm^{-1} feature. Di-substituted naphthalenes (2,5-dimethyl, 1,6-dimethyl-, and 2,6-dimethyl-) with one substituent on each ring show the same behavior and also the presence of solo, duo, and trio CH bending modes. Substitution on small linear PAH species (naphthalene and anthracene) leads to the loss or weakening of the 1162, 1000, and 954 cm^{-1} features, a weakening of the 727 cm^{-1} feature and corresponding appearance of the 787 cm^{-1} band, and the presence of a ~885 cm^{-1} (solo H) band in substituted naphthalenes where no such band is present in naphthalene. We also note that a weakening of the 1450, 1147 and 884 cm^{-1} features in mono-substituted anthracenes is compatible with the observed UIR emission features in NGC 7027 and HD 44179. The absence of 1000 cm^{-1} and 727 cm^{-1} emission lines in interstellar spectra suggests that the emitters either contain CH_n substituents or are dehydrogenated at terminal bonding sites.

We note that both naphthalene and anthracene show an absorption feature at ~21 μm (483 and 47 cm^{-1}, respectively) and suggest that this feature may also be observable in emission.

III. FORMATION AND EXCITATION

The interpretation of the IR spectra given here suggests that two- to five-ring linear polyacenes could be important constituents in emission objects such as the Orion ridge. Anthracene (three rings) would appear to be most abundant, followed by naphthalene (two rings) and then by tetracene (four rings) and perhaps pentacene (five rings). It is unknown 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. If photodissociation is important, then the ratio $I(787)/I(885)$ which measures the relative concentration of two- and three-ring molecules will be sensitive to ambient conditions. The model for HAC proposed by Robertson and O'Reilly (1987) predicts that small ring clusters are more abundant than larger clusters. On the basis of this model, a reduction in $I(787)/I(885)$ would indicate an enhanced destruction rate for naphthalene relative to anthracene.

An analysis of the spatial dependence of the IR emission features across the Orion ridge using the data of Geballe *et al.* (1989) and Roche, Aitken, and Smith (1989) shows that the optical depth, τ_{UV}, for pumping of this emission increases more or less monotonically from position 4 to 20″ south of position

4. The value of τ_{UV} for both the 3040 and 884 cm^{-1} features is ~ 2 at 20″ south. Since the UV absorption cross sections for anthracene and naphthalene are known (Birks 1970), it is of interest to examine whether τ_{UV} could arise from self-shielding by these molecules. With the Orion ridge at a distance of 450 pc (Witt and Lillie 1978), the path length through from position 4 to 20″ south is 1.35×10^{17} cm. With σ(anthracene) $= 8.4 \times 10^{-16}$ cm^2, n(anthracene) $\sim 1.8 \times 10^{-2}$ cm^{-3} if self-shielding dominates. Expressed differently, one can conclude that the space density of PAH cannot be much larger than 1.8×10^{-2} cm^{-3} in this region or τ_{UV} would exceed the observed value.

Extinction by dust will also contribute to τ_{UV}. With $A_{UV} \sim 1.7 \times 10^{-21} n_H L$, the observed UV optical depth implies $n_H \sim 10^4$ cm^{-3}. Then n(anthracene)/$n_H \leq 1.8 \times 10^{-6}$ in this object. This corresponds to ≤ 0.07 of the available carbon abundance $n_C = 3.7 \times 10^{-4} n_H$.

The possible presence of a PAH molecule as small as naphthalene suggests that benzene, C_6H_6, may also be observable in objects with strong 787 cm^{-1} emission. Emission from benzene is expected at 675 cm^{-1} The contour of this emission band should be a clear indicator of the physical state of the emitter since gaseous molecules will show *P* and *R* branches in addition to *Q* branch–emission (Daunt and Shurvell 1976). Emission by cyclopropenylidene C_3H_2, the simplest aromatic ring molecule, may be a tracer of PAH decomposition (Leach 1989) and should be searched for in aromatic IR emission sources.

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W. W. DULEY and A. P. JONES: Department of Physics, York University, 4700 Keele Street, North York, Ontario, Canada, M3J 1P3