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Possible Fluorescence from the Polycyclic Aromatic Hydrocarbons in the Interstellar Medium

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Large compact polycyclic aromatic hydrocarbons (PAHs) are photochemically very stable. These PAHs have been considered as excellent candidates for explaining the interstellar infrared emission lines. Since the large compact PAHs exhibit the first electronic absorption band in a rather low-energy region, it is possible and very probable that fluorescence from such PAHs are responsible for the red emission humps of several nebulae such as the Red Rectangle, a nebula surrounding the binary star HD 44179.

The Red Rectangle is a symmetric biconical nebula centered at the bright binary star HD 44179.[1] Since its discovery in 1975, it has been a target of various spectroscopic observations.[1-4] The visible emission spectrum of the Red Rectangle consists of two major components.[2] They are: (1) The scattered stellar light, which is fairly uniform in intensity over the visible region, and (2) a broad emission hump, which spreads in the wavenumber range 13000—18600 cm^{-1} with a maximum around 15700 cm^{-1}. The latter component gives the red color to the nebula. The rough contour of this red emission hump is reproduced in Fig. 1. Recently several other nebulae were found to exhibit extended red emission similar to that from the Red Rectangle.[5,6]

Duley proposed that the red emission hump of the Red Rectangle could be due to fluorescence from small particles of hydrogenated amorphous carbon (HAC).[7,8] An argument for this hypothesis is the similarity to the observed fluorescence from the HAC particles.[9] Wdowiak attributed the red emission hump to the PAHs clumped together on the surfaces or interiors of grain mantles.[10] He inferred that excimers are formed on the surfaces of grains, and that excimer fluorescence might be responsible for the hump. These explanations require that the molecules responsible for the emission hump must be aggregated on grains.

Discrete infrared lines are emitted coincidentally from the Red Rectange and the like nebulae.[1,5] Léger and Puget and Allamandola et al. ascribed these infrared lines to polycyclic aromatic hydrocarbons (PAHs) in the gas phase, but not in the condensed phase.[11-14] If infrared and red emissions arise from the same source, it must be these PAHs in the gaseous state. In 1986 d'Hendecourt et al. stressed that isolated PAHs can provide broad emission spectra.[15] They suggested that phosphorescence, rather than fluorescence, might be responsible for the red emission hump of the Red Rectangle. Chlewicki and Laureijs also proposed that the most likely source of the red emission hump is phosphorescence from aromatic molecules.[16]

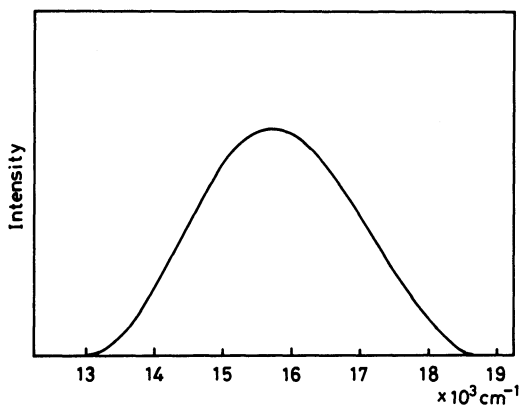


Fig. 1. Rough contour of the red emission hump of the Red Rectangle.

Since the light-emitting interstellar PAHs, if any, are placed in the intense radiation field, they must be fairly resistant to the field. Therefore, photochemically stable PAHs are qualified for explaining the interstellar infrared spectra. In a previous paper,[17] we showed that it is very probable that many of large compact PAHs are stable in the radiation field. They have large percent resonance energies (%REs)[18-20] in the excited state. In this paper, the peculiar red emission hump is interpreted with this characteristic of large compact PAHs in mind. The Hückel molecular orbital model is used throughout this paper.

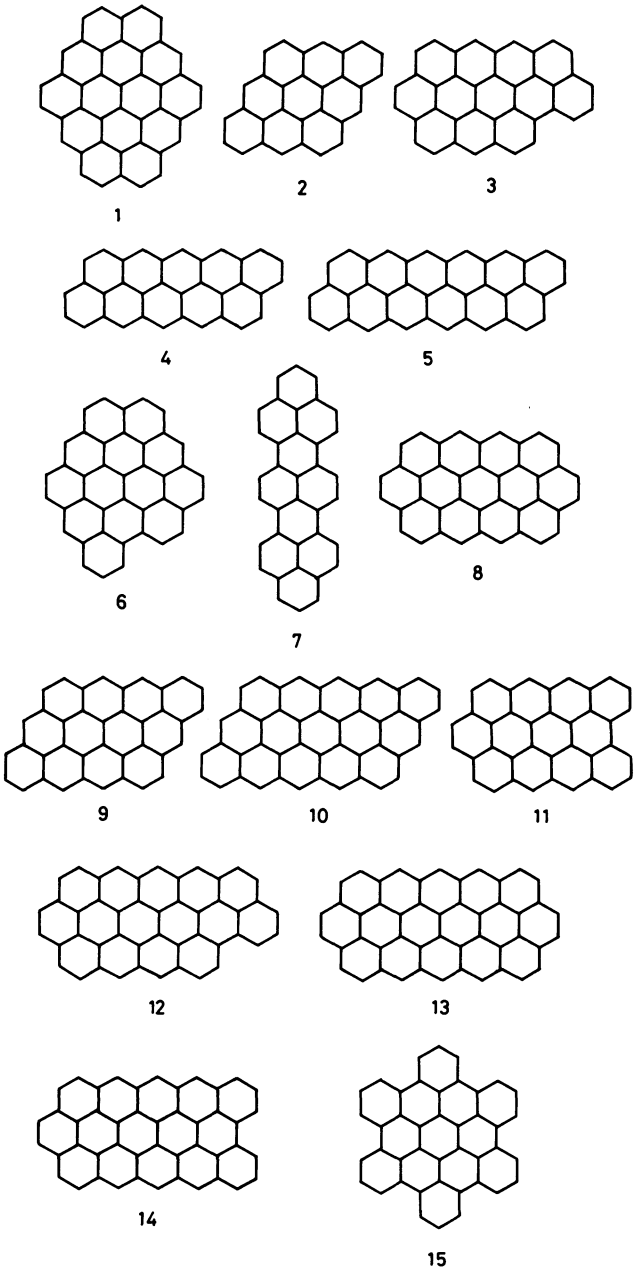
Results and Discussion

We have developed the graph theory of aromaticity.[18-23] The %RE of a molecule is given as 100 times the graph-theoretically defined resonance energy, divided by the π-electron energy of the olefinic reference structure.[18-20] The %RE can be defined for any conjugated system in any electronic state. It has been established that most of the conjugated molecules with large %REs are stable or fairly unreactive. In the case of polyacenes, naphthalene, anthracene, and naphthacene are relatively stable, but pentacene and higher members are not stable. In general, PAHs with %RE$>$2.15 are stable in our chemical sense.[17]

We previously calculated %REs of a variety of PAHs both in the ground and excited states.[17] As shown in Table 1, **1—14** have the %REs larger than 2.15 both in the ground and excited states. Many large compact

Table 1. The HOMO Energies of the PAHs Having Large %REs in the Excited State

PAH	%RE		m_{HOMO}	$\nu_p/10^3\,cm^{-1}$
	Ground state	Excited state		
1	2.668	2.156	0.271	20.8
2	2.414	2.172	0.186	17.6
3	2.637	2.173	0.251	20.1
4	2.278	2.194	0.134	15.6
5	2.217	2.209	0.095	14.1
6	2.665	2.218	0.249	20.0
7	2.564	2.225	0.209	18.5
8	2.593	2.252	0.213	18.6
9	2.348	2.287	0.118	15.0
10	2.309	2.316	0.076	13.4
11	2.500	2.349	0.150	16.2
12	2.547	2.358	0.162	16.7
13	2.515	2.383	0.138	15.8
14	2.436	2.410	0.091	14.0
15	2.917	1.828	0.465	28.2



PAHs have large %REs both in the ground and excited states.[17] This implies that these PAHs are possibly stable not only at high temperature but also in the strong radiation field in the interstellar medium. As pointed out by Léger and Puget and Allamandola et al.,[11-14] the PAHs having not a few solo hydrogens are consistent with the infrared emission spectra of the interstellar medium. Therefore, large compact PAHs are the best candidates conceivable for explaining the infrared emission from the interstellar medium.

Fully benzenoid hydrocarbons are the PAHs whose Clar structures consist of aromatic sextets only.[24] There are no formal double bonds in them. This type of PAHs are indeed extremely stable. d'Hendecourt et al. found that the phosphorescence spectrum of hexabenzocoronene (**15**), a typical fully benzenoid hydrocarbon, resembles the red emission hump of the Red Rectangle.[15] However, we previously pointed out that fully benzenoid hydrocarbons are greatly destabilized in the excited state.[17] At present, there is no spectroscopic evidence for the presence of this type of PAHs in the interstellar medium. Compact fully benzenoid hydrocarbons do not have solo hydrogens.[17]

For PAHs having very large %REs or very large resonance energies per π electron in the ground state, the highest occupied molecular orbital (HOMO) is very low in energy,[21,25] and the lowest unoccupied molecular orbital (LUMO) is necessarily very high in energy. This implies that, in general, the energy of the first electronic transition of a fully benzenoid hydrocarbon is too large to exhibit red fluorescence. In other words, fluorescence from such PAHs as **15** cannot reproduce the red emission hump. A situation is essentially the same for relatively small PAHs. It is probably for this reason that Wdowiak and d'Hendecourt et al. were forced to fit excimer fluorescence or phosphorescence to the red emission hump.[10,15] Both excimer fluorescence and phosphorescence are much lower in energy than the fluorescence band of an isolated molecule.

In general, the first electronic absorption band of a PAH can be assigned to the transition from the HOMO to the LUMO. According to Streitwieser,[26] the energy of the first allowed transition (i.e, the p band in Clar's terminology[24]) is linearly related to the energy of the HOMO:

$$\nu_p/\mathrm{cm}^{-1} = 38040\, m_{\mathrm{HOMO}} + 10520 \quad (1)$$

where ν_p is the wavenumber of the p band, and m_{HOMO} is the energy coefficient of the HOMO or the energy of the HOMO given in units of β. This relationship holds for alternant hydrocarbons such as PAHs, for which m_{LUMO} is the negative of m_{HOMO}. It is useful for estimating the absorption edge of an unknown PAH. A p band is sometimes preceded by an α band assignable to a very weak electronic transition.[26] An α band sometimes shifts the absorption edge to a lower-energy side.

In a previous paper, a photochemically stable PAH was defined as the one whose %RE is greater than 2.15 in the excited states.[17] In this sense, **1**—**14** are thermodynamically and photochemically stable. The m_{HOMO} value is less than 0.28 for these PAHs. It follows that the HOMOs of these PAHs are relatively high in energy, as compared with those of fully benzenoid hydrocarbons. Then, photochemically stable PAHs must have the first absorption band in a relatively low-energy region. The m_{HOMO} values of **1**—**14** are listed in Table 1.

For example, m_{HOMO}=0.213 for circumanthracene (**8**).[27] This PAH has been regarded as one of the best candidates for the interstellar molecular species.[17] From Eq. 1 this PAH is predicted to have a p band around 18600 cm^{-1}. Clar et al. devised the relationship between the π-electron ionization potentials and the absorption maximum of the p band,[27] and predicted the location of this band at 2.24 eV or 18100 cm^{-1} in the gas phase. For **8** the p band is the lowest-energy band in the electronic absorption spectrum.[27] The red emission hump appears to give a mirror image of this absorption band. Therefore, it is highly probable that fluorescence from **8** constitutes a part of the red emission hump. Phosphorescence from this PAH is not responsible for it because it is too low in energy.

The wavenumbers of the p bands estimated using Eq. 1 are also presented in Table 1. Fluorescence from **1**—**3**, **6**—**8**, and **11**—**13** might appear in the energy region covered by the red emission hump, and can in principle reproduce the whole or a part of the red emission hump. Thus, there are many qualified large compact PAHs. It is noteworthy that **7** is an exceptionally non-compact PAH with no solo hydrogen. Since these photochemically stable PAHs are expected to exhibit fluorescence in a rather low-energy region, neither phosphorescence nor excimer fluorescence is necessary to explain the red emission hump of the Red Rectangle and other nebulae.

Other PAHs with somewhat larger m_{HOMO} values may also contribute to the red emission hump. If these PAHs coexist with those given in Table 1, the high-energy part of the fluorescence from the former PAHs are absorbed by the latter ones. On the other hand, the PAHs having very small m_{HOMO} values, such as **4**, **5**, **9**, **10**, and **14**, are not desirable as the candidates for explaining the red emission hump. Their fluorescence bands must be located in the infrared region. Among the PAHs in Table 1, these ones have relatively small %REs in the ground state. This might indicate that the ground-state stability is still very important in the interstellar medium.

Aromatic molecules typically have high fluorescence yields.[28] In general, PAHs are much more fluorescent than phosphorescent. Measurements of fluorescence from jet-cooled naphthalene, anthracene, and naphthacene have been made.[29–32] No one has reported the observation of phosphorescence from these PAHs in a supersonic jet. Phosphorescence must follow the intersystem crossing, which is formally a forbidden electronic process for most organic molecules.[28] Therefore, fluorescence is likely to be a much more natural electronic process than phosphorescence even in the interstellar medium. This may further support the assignment of the red emission hump to fluorescence from a group of PAHs.

Concluding Remarks

Large compact PAHs are rich in carbon atoms. If PAHs are formed in a carbon-rich environment, they must be large and compact in shape. Most of them happened to be photochemically very stable.[17] Interestingly, rather large compact PAHs are formed by combustion of light oil in a Diesel engine.[33] This fact might suggest possible formation mechanisms of PAHs in the interstellar medium. As has been seen above, if we accept the existence of abundant large compact PAHs in the interstellar medium, we can rationalize both discrete infrared and broad red emission bands of the Red Rectange and other nebulae in terms of fluorescence spectroscopy. It is very true that most PAHs are more fluorescent than phosphorescent, at least in solution.[28] PAHs emit exclusively from the first excited state.

Hexabenzocoronene (**15**) is a yellow fully benzenoid hydrocarbon of extreme stability.[34,35] Clar reported that this PAH shows an orange-red phosphorescence of very long life at low temperature.[24] If it is generally ture that a large compact PAH tends to undergo intersystem crossing from the singlet excited state to the lowest triplet state at high temperature, the contribution of phosphorescence to the red emission hump must be taken into consideration. At present, it is not at all clear whether there are large compact or fully benzenoid PAHs which are very phosphorescent at high temperature in the gaseous state. This question can only be answered by detailed laboratory measure-

ments of the appropriate materials and processes.

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