

## Photochemical Stability of Polycyclic Aromatic Hydrocarbons in the Interstellar Medium

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The astronomical IR spectra of molecular origin have been attributed to compact polycyclic aromatic hydrocarbons. This interpretation can be rationalized in terms of the percent resonance energies of the excited-state species. In general, large compact polycyclic aromatic hydrocarbons are not only thermodynamically stable but also photochemically stable. These hydrocarbons have large percent resonance energies in the excited state, and are expected to survive the rough conditions in space. In contrast, relatively small aromatic hydrocarbons are greatly destabilized when they are excited electronically or deprived of two  $\pi$  electrons.

The infrared astronomical satellite (IRAS) launched in 1983 initiated a new era of interstellar chemistry.<sup>1)</sup> Surprisingly, the IRAS satellite found that a series of discrete infrared (IR) bands are emitted from the interstellar medium (ISM). The emission maxima are located at 3.3, 6.2, 7.7, 8.6, and 11.3  $\mu\text{m}$ , all of which are always observed as a set.<sup>1)</sup> They are observed in a wide variety of astronomical objects: reflection nebulae, bipolar nebulae, planetary nebulae, and the whole regions of active galaxies.<sup>1)</sup> The five IR bands are obviously of molecular origin. Fundamental molecular vibrations must be responsible for these bands.

It was in 1984 that Léger and Puget reported that a similar set of bands appears in the IR absorption spectrum of coronene (**8**).<sup>2,3)</sup> They proposed that a mixture of various polycyclic aromatic hydrocarbons (PAHs) is responsible for the astronomical IR spectra. Allamandola et al. supported this view by showing the good agreement between the wavelengths of the astronomical IR bands and the Raman spectrum of automobile soot (a mixture of PAHs and small carbon particles).<sup>4–6)</sup>

The five discrete IR bands can really be assigned to fundamental vibrations of PAHs.<sup>1–8)</sup> The 3.3  $\mu\text{m}$  band is assignable to an aromatic C–H stretch. The 6.2  $\mu\text{m}$  band is assignable to a C=C stretch in an aromatic ring. The 7.7  $\mu\text{m}$  band is not found in benzene (**1**) and naphthalene (**3**), and may be specific to large PAHs such as coronene.<sup>3,8)</sup> The 8.6  $\mu\text{m}$  band is assignable to an in-plane aromatic C–H bend. Finally, the 11.3  $\mu\text{m}$  band is assignable to an out-of-plane aromatic C–H bend.

The wavelength position of the out-of-plane C–H bending mode is very sensitive to the number of adjacent hydrogen atoms on a ring.<sup>3,5,6)</sup> The more hydrogens which are adjacent on the same ring, the longer the wavelength of this bending mode becomes. The predominance of the 11.3  $\mu\text{m}$  emission in the 11–13  $\mu\text{m}$  region implies that most interstellar PAHs have many solo hydrogens (see Fig. 1).<sup>3)</sup> The emission observed in the 11.5–13  $\mu\text{m}$  region might indicate the presence of PAHs with duo and trio hydrogens (see Fig. 1).

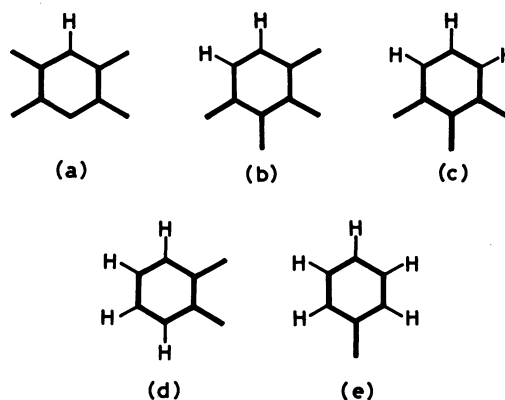


Fig. 1. Classification of hydrogens in PAHs: (a) solo hydrogen, (b) duo hydrogens, (c) trio hydrogens, (d) quartet hydrogens, and (e) quintet hydrogens.

These observations imply that rather compact PAHs with many solo hydrogens dominate the interstellar PAH mixture.<sup>1–6)</sup> Typical compact PAHs have only solo and duo hydrogens. Léger and d'Hendecourt then found that the astronomical IR spectra resemble the IR spectra of compact PAHs very closely.<sup>3)</sup> The fit with the IR spectra of non-compact PAHs is very poor. PAHs with quartet or quintet hydrogens (see Fig. 1) can be excluded because the emission bands concerned are very weak in the astronomical IR spectra.

Léger et al. further noticed that the extinction coefficient per solo hydrogen is much larger than that per duo hydrogen in the two measured PAHs ovalene (**28**) and dicoronene,<sup>9)</sup> which have both solo and duo hydrogens.<sup>3)</sup> The large extinction coefficient of a solo hydrogen is commonly found in many smaller PAHs.<sup>8)</sup> Therefore, it is reasonable to assume that PAHs in the ISM can have some duo or trio hydrogens in addition to not a few solo hydrogens. This feature is consistent with the molecular structure of large compact PAHs, in which there must be some duo and/or trio hydrogens.

It is now fairly clear that interstellar PAHs, if any, must be limited to a large compact type. If so, we must seek for the reason why such PAHs are dominant

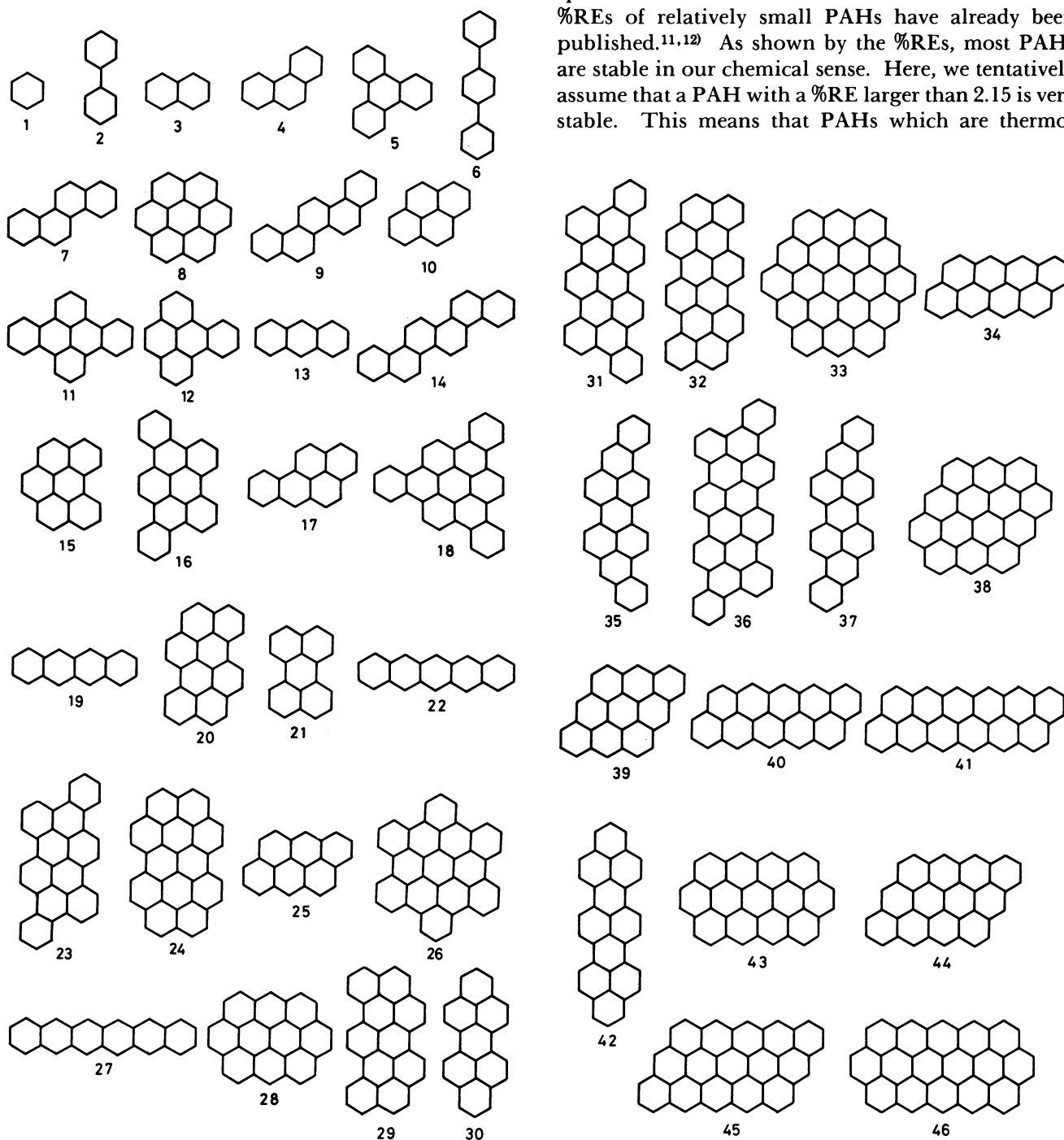
in space. Are these PAHs really stable enough to survive the rough conditions in the ISM? In order to find a clue to this problem, our graph theory of aromaticity<sup>10-13)</sup> was applied to a variety of PAHs including those which have so far been the candidates for explaining astronomical IR data.

### Results and Discussion

We have developed the graph theory of aromaticity since 1975.<sup>10-13)</sup> We defined a new type of resonance energy in graph-theoretical terms. The percent res-

onance energy (%RE) of a given molecule is then defined as 100 times the resonance energy, divided by the total  $\pi$ -electron energy of its olefinic reference structure.<sup>11,12)</sup> The %RE has been recognized as an excellent index for determining the degree of thermodynamic stability of a cyclic conjugated molecule. The %RE is approximately proportional to the resonance energy per  $\pi$  electron.<sup>14,15)</sup> A PAH with a large %RE is considered to be thermodynamically stable and typically aromatic in nature.<sup>11,12)</sup>

We calculated the %REs of a variety of PAHs (1-46) to test the above interpretation of the astronomical IR spectra. The obtained %REs are listed in Table 1. The %REs of relatively small PAHs have already been published.<sup>11,12)</sup> As shown by the %REs, most PAHs are stable in our chemical sense. Here, we tentatively assume that a PAH with a %RE larger than 2.15 is very stable. This means that PAHs which are thermo-



dynamically more stable than pentacene (**22**) must be very stable.

First of all, there are a group of very stable PAHs called fully benzenoid hydrocarbons (or fully benzenoid PAHs).<sup>16-18</sup> They are PAHs whose Clar structures consist of aromatic sextets alone.<sup>16</sup> PAHs **1**,

**5**, **11**, **16**, **18**, **23**, **26**, **31**, and **36** are such PAHs. Since double bond character is scarcely localized anywhere in each of these PAHs, they provide the ultimate in stability which synthetic chemistry can offer.<sup>15</sup> The energy of the highest occupied molecular orbital (HOMO) in these PAHs is very low in energy, indicating that the HOMO contributes much to the thermodynamic stability of the entire molecule.<sup>11,15</sup> The %REs are all larger than 2.80.

Accordingly, it is quite natural that Schmidt et al. regarded such fully benzenoid PAHs as attractive candidates to account for the astrophysical IR data.<sup>16,17</sup> The PAHs chosen by them are highly symmetric hexa-*peri*-benzocoronene (**26**) and tribenzocoronene (**18**). However, there is one serious difficulty with these PAHs. They have no solo hydrogens. Compact fully benzenoid PAHs have only duo and quartet hydrogens, and exhibit no 11.3  $\mu\text{m}$  emission line. Therefore, they are not a major molecular component of the ISM although they are thermodynamically very stable. Benzene (**1**) is the most stable PAH with the largest %RE conceivable. However, there is no evidence for the existence of this molecule in the ISM. These facts strongly suggest that the ground-state stability is not a sufficient condition of the interstellar PAHs.

In this context, it may be worth noting that all IR-emitting PAHs must be placed in the strong radiation field since they must first be excited electronically to emit IR lines.<sup>1-6</sup> In other words, we can observe only PAHs in the emission zone. If a given PAH is fragile in the excited state, it cannot survive the severe radiation field in the ISM. Therefore, the stability of the excited-state species or the photochemical stability must be the most important factor in the present interstellar chemistry. In order to see the photochemical stability, we then calculated the %REs of all PAHs in the first excited state.<sup>19</sup> They are listed in Table 1.

Furthermore, it is very probable that the radiation field in the emission zone is intense enough to ionize many of the PAHs.<sup>3,5,21</sup> The PAHs were estimated to exist in cationic forms to more than 50% in extent.<sup>4,20</sup> The importance of double ionization was stressed by Leach.<sup>22</sup> d'Hendecourt pointed out in Ref. 23 that the radiation field in reflection nebulae is so high that most of the PAHs are probably ionized. From this point of view, the stability of the dications, as well as that of the excited-state species, must be taken into account when the type of interstellar PAHs is sought.

All PAHs are alternant hydrocarbons. Therefore, the energy of the lowest unoccupied molecular orbital (LUMO) is equal to the negative of the energy of the HOMO. Then, the %RE of the dianion of any PAH is equal to that of the dication. The %RE of a given PAH in the first excited state is also equal to that of the dication. Accordingly, we do not need to calculate

Table 1. Percent Resonance Energies of PAHs

Species	%RE	
	Ground state	Excited state
1	3.528	-10.342
2	3.159	-1.175
3	2.924	-1.113
4	2.888	-0.453
5	3.012	-0.453
6	3.022	0.541
7	2.809	0.599
8	2.817	0.729
9	2.773	0.929
10	2.729	0.930
11	2.963	0.931
12	2.872	0.946
13	2.519	0.947
14	2.743	1.257
15	2.792	1.261
16	2.933	1.420
17	2.635	1.468
18	2.922	1.510
19	2.269	1.573
20	2.791	1.693
21	2.689	1.735
22	2.105	1.780
23	2.914	1.783
24	2.816	1.808
25	2.512	1.818
26	2.917	1.828
27	1.992	1.842
28	2.703	1.870
29	2.798	1.882
30	2.607	1.944
31	2.818	1.957
32	2.801	2.048
33	2.696	2.070
34	2.369	2.108
35	2.543	2.128
36	2.889	2.145
37	2.534	2.147
38	2.668	2.156
39	2.414	2.172
40	2.278	2.194
41	2.217	2.209
42	2.564	2.225
43	2.593	2.252
44	2.348	2.287
45	2.309	2.316
46	2.515	2.383

the %REs of the dications. The %REs of the excited-state species in Table 1 automatically represent the %REs of the dications. The %RE of the monocation or the monanion can readily be obtained by averaging the %REs of the ground-state species and the dication.

As can be seen from Table 1, fully benzenoid hydrocarbons are unable to form stable dications. The %REs of tribenzocoronene (**18**) and hexa-*peri*-benzocoronene (**26**) decrease much when they are excited electronically or doubly ionized. The same is fairly true for other fully benzenoid hydrocarbons. This is possibly the primary reason why such fully benzenoid PAHs do not contribute appreciably to the astronomical IR spectra. Polyphenyls, such as biphenyl (**2**) and terphenyl (**6**), are a kind of fully benzenoid PAHs. They are also supposed to be photochemically unstable.

There are many solo hydrogens in large linear polyacenes. However, none of them are thermodynamically very stable in the ground state.<sup>11,15</sup> Pentacene (**22**) and hexacene (**27**) must be handled under nitrogen since they are very oxidizable.<sup>10</sup> Higher members of this series are not isolable. Angulated polyacenes, such as phenanthrene (**4**), chrysene (**7**), picene (**9**), and fulminene (**14**), are very stable in the ground state. However, both linear and angulated polyacenes are unstable in the excited state. Therefore, they are not qualified for the PAHs in the ISM. All polyacenes have quartet hydrogens, the presence of which are also inconsistent with the astronomical IR spectra. Angulated polyacene do not have solo hydrogens.

Léger and Puget<sup>20</sup> and Allamandola et al.<sup>50</sup> estimated the carbon content of the interstellar PAHs to lie in the range of 20–50 carbon atoms. PAHs having less than 20 carbons must be much less abundant in the ISM. As shown in Table 1, this suggestion corresponds to the fact that dications derived from relatively small PAHs are not stable. For small PAHs the contribution of the HOMO to the RE is very large. Therefore, they become fairly unstable by losing two  $\pi$  electrons in the HOMO. Among the PAHs in Table 1 those having 30 or less carbon atoms behave in this manner. Dications of PAHs **1**–**5** are antiaromatic with negative %REs. Many of small PAHs do not have solo hydrogens.

Finally, large compact PAHs with solo hydrogens constitute the group of PAHs which have large %REs both in the ground and excited states. They are best exemplified by circumnaphthacene (**46**), dibenzocircumanthracene (**45**), dibenzovalene (**44**), circumanthracene (**43**), and circumpylene (**38**). The %REs of these PAHs are all larger than 2.15 both in the ground state and in the excited or doubly ionized states. Accordingly, they must be fairly stable not only at high temperature but also in the strong radiation field. Since these PAHs have not a few solo hydrogens, they

presumably match the pattern of the astronomical IR spectra. The large compact PAHs can be considered as the best candidates for the interstellar PAHs. The abundance of large compact PAHs has thus been explained satisfactorily.

It should be noted that large compact PAHs are not always qualified for the interstellar PAHs. Only those having large %REs in the excited state are eligible for them. Many compact PAHs do not have solo hydrogens, and their dications have small %REs. PAHs **8**, **20**, **24**, and **28** are all large and compact in shape. However, they are greatly destabilized in the excited state. As stated above, all fully benzenoid PAHs are not stable in the excited or doubly ionized states. Although hexa-*peri*-benzocoronene (**26**) is a large compact PAH, it is not an exception. All fully benzenoid PAHs investigated have no solo hydrogens.

Tielens et al. inferred that hexagonally symmetric PAHs, such as coronene (**8**) and circumcoronene (**33**), might dominate the interstellar PAH mixture.<sup>20</sup> This type of PAHs have doubly degenerate HOMOs. Benzene (**1**) also belongs to this type of PAHs. Dianions of such PAHs necessarily have much smaller %REs than those of other PAHs of similar size. Therefore, the compact PAHs responsible for the astronomical IR spectra must be less symmetric than coronene and circumcoronene. Coronene forms one of the most unstable dications among the PAHs investigated.

PAHs in Table 1 are numbered in such a manner that the excited-state species are arranged in order of increasing %RE. It is evident that rather large compact PAHs come later. Many PAHs with large %REs have not a few solo hydrogens. Circumnaphthacene (**46**) and circumanthracene (**43**) appear to be excellent candidates conceivable at present. These two PAHs are thermodynamically very stable as indicated by the large %REs of the ground-state species. They are also photochemically very stable as indicated by the large %REs of the dianions or the excited-state species.

As shown in Table 1, there are some non-compact PAHs which are photochemically as stable as large compact ones. PAHs **40**–**42** are examples of this kind. PAH **42** does not have solo hydrogens. If there are synthetic routes to these PAHs in the ISM, they must also contribute more or less to the interstellar IR emission.

### Concluding Remarks

In general, benzene and fully benzenoid hydrocarbons constitute the most stable group of PAHs. The absence of this group in the ISM suggests that there must be another criterion for determining the type of interstellar PAHs. Fully benzenoid hydrocarbons and most of relatively small PAHs were found to be photochemically unstable. Considering that the IR-emission zone are situated in the strong radiation

field, these photochemically unstable PAHs can be excluded. Then, large compact PAHs remained.

Fortunately, large compact PAHs have many solo hydrogens, and can be considered as excellent candidates for explaining the astronomical IR spectra taken by the IRAS satellite. Thus, it is photochemical stability that determines the type of PAHs in the ISM. The ground-state stability is of course important. However, almost all PAHs satisfy this condition. We believe that the existence of large compact PAHs in the interstellar IR-emission zone<sup>1)</sup> has thus been rationalized.

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#### References

- 1) "Polycyclic Aromatic Hydrocarbons and Astrophysics," ed by A. Léger, L. d'Hendecourt, and N. Boccara, D. Reidel, Dordrecht, The Netherlands (1987).
- 2) A. Léger and J. Puget, *Astron. Astrophys.*, **137**, L5 (1984).
- 3) A. Léger and L. d'Hendecourt in Ref. 1, pp. 223—254.
- 4) L. J. Allamandola, A. G. G. M. Tielens, and J. R. Barker, *Astrophys. J.*, **290**, L25 (1985).
- 5) L. J. Allamandola, A. G. G. M. Tielens, and J. R. Barker in Ref. 1, pp. 255—271.
- 6) A. G. G. M. Tielens, L. J. Allamandola, and J. R. Barker, and M. Cohen in Ref. 1, pp. 273—286.
- 7) L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," 2nd ed, Wiley, New York (1966).
- 8) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," 2nd ed, Aldrich Chemical, Milwaukee, Wisconsin (1975).
- 9) H. J. Lempka, S. Obenland, and W. Schmidt, *Chem. Phys.*, **96**, 349 (1985).
- 10) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976); *Netsu Sokutei*, **12**, 61 (1985).
- 11) J. Aihara, *J. Am. Chem. Soc.*, **99**, 2048 (1977).
- 12) J. Aihara, *Pure Appl. Chem.*, **54**, 1115 (1982).
- 13) I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977); N. Trinajstić, "Chemical Graph Theory," CRC Press, Boca Raton, Florida (1983), Vol. II, Chap. 1.
- 14) B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 305 (1971).
- 15) B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, **93**, 2413 (1971).
- 16) E. Clar, "The Aromatic Sextet," Wiley, London (1972).
- 17) W. Hendel, Z. H. Khan, and W. Schmidt, *Tetrahedron*, **42**, 1127 (1986).
- 18) S. Obenland and W. Schmidt in Ref. 1, pp. 165—172.
- 19) J. Aihara, *Bull. Chem. Soc. Jpn.*, **51**, 1788 (1978).
- 20) A. Léger and L. d'Hendecourt, *Astron. Astrophys.*, **146**, 81 (1985).
- 21) A. Omont, *Astron. Astrophys.*, **164**, 159 (1986).
- 22) S. Leach, *J. Electron Spectrosc. Relat. Phenom.*, **41**, 427 (1986); Ref. 1, pp. 99—127.
- 23) M. Jura in Ref. 1, pp. 367—370.
- 24) A. G. G. M. Tielens, L. J. Allamandola, J. R. Barker, and M. Cohen in Ref. 1, pp. 273—286.