Aromaticity under star dust conditions

Roberto Salcedo · Lioudmila Fomina

Abstract Astronomical observations have revealed diffuse interstellar bands ranging from blue in the visible spectrum to the near IR. It has been suggested that these bands exist, owing to the presence of polyaromatic hydrocarbons or fullerene in the vicinity of certain stars, and constitute residual material from stellar explosions. The intention here is to study the relative stability of these species, when exposed to extreme conditions. The aromaticity of polycarbon molecules is an important aspect of this explanation.

Keywords Star dust · Aromaticity · High temperature

Introduction

Certain interesting astronomical features exist which have been the subject of various research projects and written reports. The DIBs (diffuse interstellar bands) are absorption features in the near UV down to the visible, and also there are UIRs (unidentified IR emissions), both phenomena are subject of various research projects. In 1985, reports claimed [1, 2] that these emissions are produced by polycyclic aromatic hydrocarbons and not by graphite or chains of carbon. The spectroscopic features [3] are the infrared emission bands (UIRs) between 3 and 15 μm, the diffuse interstellar absorption bands (DIBs) observed in the optical range between 400 and 1000 nm and a strong absorption feature at 220 nm. The sharp UIRs have been correctly attributed to gaseous polycyclic aromatic

hydrocarbons [4–6] (PAHs), but the more than 300 DIBs may also be attributable to fullerene type molecules. Very recently, fullerene molecules were reported to be clearly detectable (C_{60} and C_{70}) in a planetary Nebula [7], and in this work, certain DIBs were totally assigned to these molecules without envisaging any contribution from PAHs. Therefore, both PAHs and fullerene can be found in the interstellar medium; however, the abundance of these molecules may vary by as much as one or two orders of magnitude, with fullerene being the predominant component. Indeed, it has been suggested that C_{60} and its ions may be the most abundant form of carbon in interstellar space [8].

The feature described above seems to contradict natural evidence, because the burning of several materials containing carbon forms graphite as its main product (although it is important to take into account that the two dimensional graphite, also known as graphene is a very elusive material [9–11]), whereas fullerenes are normally produced by the vaporization of this same graphite by arc discharge under low pressure in an inert gaseous atmosphere [12, 13]. This would indicate that a more sophisticated procedure may occur in the proximity of certain stars, where there are interstellar emission bands which indicate high temperatures. However, certain doubts exist concerning the predominance of this species, in comparison to the PAHs which have been regarded as molecularly defined models of graphite [14–18], so that coronene and ovalene as well as other large molecules of this kind provide apt models for the present comparison. Intrinsic aromaticity is an important aspect to be considered in this comparison, as it is thought to represent a stabilizing factor.

Thus the aim of the present study is to analyse the stability of these molecules in the environment of outer space and attempt to determine whether fullerenes are likely to

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constitute the dominant species. The study also seeks to define the best way of evaluating the aromaticity of these molecules. It is important to note that this aspect has been analyzed for many substances, substituting a temperature of 1000 K which is near the values quoted by a number of authors who have investigated the topic of aromatic molecules at high temperature, in both theoretical and experimental studies [19–21]. However, in this study, we propose a new method for evaluating the Aromatic Stabilization Energy (ASE) in fullerene, besides adapting alternative ones for PAHs, where homodesmotic reactions are employed.
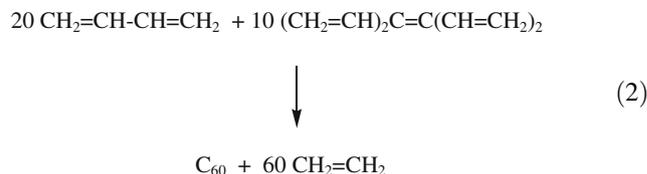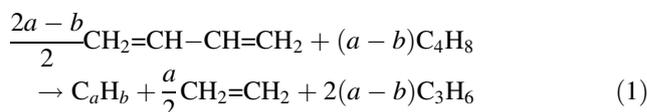
Computational methods

All structures, the neutral species as well as the corresponding cations, were optimized in the gas phase, employing the Jaguar 4.0 package [22]. A pure DFT method, comprising Becke's gradient corrections for exchange [23] and Perdew–Wang's for correlation [24], was used to carry out energy evaluations, and all calculations were performed using the 6-31G** basis set. Frequency calculations were carried out at the same level of theory, in order to confirm that optimized structures were at the minima of the potential surfaces. These frequencies were then used to evaluate the zero-point vibrational energy, the thermal vibrational corrections to enthalpy and total enthalpy values.

Results and discussion

The molecules being studied are presented in Fig. 1. Coronene (**2**) and ovalene (**3**) are both molecules which should be considered in this analysis, because several reports indicate that both act as carriers of DIBs [4–6]. Likewise, the other two PAHs presented in this figure, hexa-peri-hexabenzocoronene (**4**) and graphite disk (**5**) that also belong to the family of the graphenes [25], were also taken into consideration as representing large models of aromatic molecules, in order to make comparisons between them as possible larger carriers of DIBs.

The calculation and comparison of aromaticity in fullerenes and PAHs is not a straightforward task. Indeed, in the case of PAHs, aromaticity is only considered in the rings, whereas no spherical aromaticity is presented by the fullerene molecule [26, 27], although the importance of analysing this feature is recognised. Not only does aromaticity vary in the different rings, but so do the PAHs molecules, as revealed in Clar's theorem [28–31]. Thus, in the present study, we take these factors into consideration.

Only one previous report has combined the approximation of experimental with theoretical data for both kinds of molecules, also taking into account heat formation [32]. Cyranski [33] has also proposed a value for the process of closing an open topological precursor, in order to yield C_{60}. All these studies assume that the molecules involved are being assessed under standard conditions; however, we have devised a study which includes both the standard and the extreme. In this work, we propose a method for making this estimation using relative results, i.e. proposing a set of relative, thermodynamic values which are applicable for comparing both families of hydrocarbons. However, there are two aspects which must be considered; firstly, there are strong differences between the structure of PAHs and fullerenes, in the first case quaternary sp^2 carbons appear and in the second the carbon atoms present a certain degree of pyramidalization; factors which should account for different results in terms of energy yields (and stability). Secondly, the intrinsic aromaticity of the sphere in fullerene should also be considered; thus the next step consists in evaluating the aromatic stabilization energy (ASE) for each kind of species, i.e. the George's homodesmotic one for PAHs, as opposed to the homodesmotic one for fullerene, with the general application of the homodesmotic reactions (Eqs. 1 and 2).

$$\frac{2a-b}{2}CH_2=CH-CH=CH_2 + (a-b)C_4H_8$$
$$\rightarrow C_aH_b + \frac{a}{2}CH_2=CH_2 + 2(a-b)C_3H_6 \qquad (1)$$

$$20\ CH_2=CH-CH=CH_2\ +\ 10\ (CH_2=CH)_2C=C(CH=CH_2)_2$$

$$\downarrow \qquad\qquad (2)$$

$$C_{60}\ +\ 60\ CH_2=CH_2$$

It is very important to consider the spherical aromaticity in fullerene, as this feature also provides this molecule with additional stability [34]. This characteristic has been evaluated by means of magnetic [27, 33, 35, 36], reactivity [27, 37] and in terms of energetic criteria [33, 38–40]. The Fowler et al. [38] reference is particularly relevant for the present case, as these authors used the recourse of an isodesmic reaction. Our study makes an indirect estimation of the spherical aromaticity of fullerene, in terms of energetic criteria, i.e. assessing a set of values relating to relative enthalpy, using the homodesmotic reaction shown as Eq. 2, as reported previously [40]. On the other hand, other homodesmotic reactions are used in the case of the PAHs for comparison purposes; the corresponding homodesmotic reaction for estimating the ASE of PAHs is shown as Eq. 1

Fig. 1 Molecules in the study
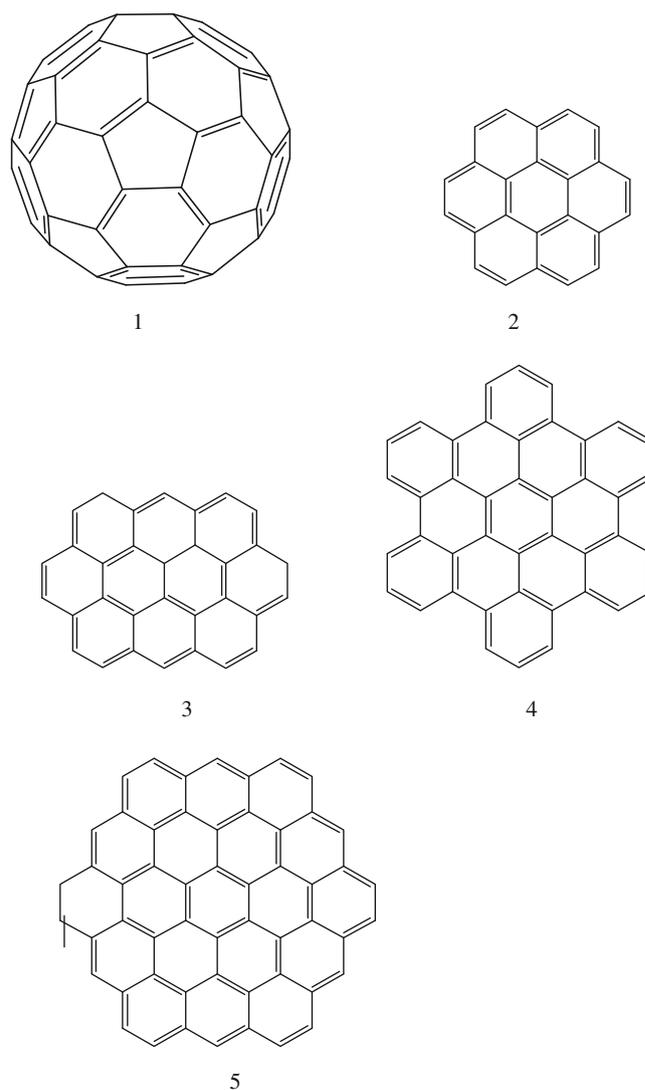
and is the same as that suggested by George and his co-workers [41, 42], this reaction involves quaternary sp² carbon atoms that also are found in the PAHs under study. Both equations yield results that are shown below, however, it is important to note that we are going to compare the enthalpy values obtained by two different models as a general situation as it has been made by other authors [43], because there is not a general homodesmotic equation for both PAHs and fullerenes, however, the results seems to be appropriated and interesting.

The ASE value for fullerene is 560.68 kcal/mol, calculated using our homodesmotic reaction [40]. This value is similar to the theoretical value which Fowler calculated, applying the equation for an isodesmic reaction (536.57 kcal/mol) designed by this researcher and his group. In Table 1, the ASE values for all the molecules are presented, and clearly the fullerene molecule has the most aromatic character. The ASE per π electron (ASE/π electron) [43] is also shown in the same table. The ASE/π electron values are very important; the highest value for the PAHs is that of graphite disk, but the corresponding value for fullerene is more than twice this, therefore the 'extra' stability derived from this aromaticity could be almost 2.5 times greater than that coming from any planar molecule. Fullerene thus makes two contributions to aromaticity; firstly that coming from the surface and secondly that generated by the sphere. Together, these yield a very high value, when compared to values relating to PAHs.

However, in the interstellar environment, we should also consider the high temperature factor. It has been demonstrated that the aromaticity of PAHs [20, 44, 45] and of fullerenes [19] can prevail at high temperatures, but a change in the enthalpy value is expected as a result of the temperature. This change can be quantified by applying Eq. 3.

Table 1 Obtained values for ASE

Compound	1	2	3	4	5
ASE (kcal/mol) (Cv cal/mol °K)	−560.68 (119.85)	−94.75 (66.70)	−126.38 (85.24)	−165.85 (110.10)	−222.70 (140.58)
ASE$_{1000 \text{ K}}$ (kcal/mol)	−475.161	−47.930	−66.543	−88.560	−128.38
ASE/π (kcal/mol)	−9.341	−3.902	−3.951	−4.138	−4.638
ASE/$\pi_{1000 \text{ K}}$ (kcal/mol)	−7.919	−1.997	−2.082	−2.216	−2.675

Assuming a temperature of 1000 K in the interstellar dust medium [4–6, 19–21], the ASE values will change to become less negative in all cases, but as is evident in Table 1 for PAHs, the effect is so strong that two cases exist which manifest a decrement of more than half the room temperature value. On the other hand, fullerene appears to vary from the original only by about 15%. It has been suggested that this phenomenon is a consequence of the spherical shape of this compound [46, 47], as the spherical molecules of fullerene are able to rotate as the temperature increases so that no strong interactions occur between them. Indeed, it has been suggested that in terms of properties which depend on this interaction, fullerenes can be treated as large, rare, spherical gas atoms [47].

$$\Delta HT = \Delta H_{\text{To}} + \int_{\text{To}}^{T} Cp\,dT. \tag{3}$$

Besides this, the ASE/π at 1000 K indicates the same behaviour, where the highest value for the PAHs is that referring to the grapheme disk, but again the value obtained for fullerene is almost 4 times greater than the corresponding value of circulene; thus, the situation under star dust conditions once again suggests that fullerenes must be the predominant species. These results are an example of LeChatelier's principle, but the consequence is that fullerene is able to be the predominant molecule because its combustion heat is better able to support the temperature changes, due to its intrinsic extra aromaticity, i.e. its spherical aromaticity. Fullerene is thus predicted to be the predominant allotropic form of carbon in star dust and likewise it was possible to predict that the extreme conditions of the interstellar environment will result in the natural formation of fullerene and other stable nanostructures.

Conclusions

Interstellar dust is formed partly from carbon aggregates which consist predominantly of fullerene, as well as polyaromatic hydrocarbons (PAHs). The predominance of fullerene is due to its intrinsically high ASE, the limited change in ASE when the temperature increases, its high ionization potential and the concomitant stability of its ions

and also because it has a limited tendency to react and transform to become large molecules, when compared to other PAHs.

References

1. Puget JL, Léger A, Boulanger F (1985) A&A 142:L19
2. Léger A, d'Hendecourt L (1985) A&A 146:81
3. Ehrenfreund P, Sephton MA (2006) Faraday Discuss 133:277
4. Allamandola LJ, Hudgins DL, Sanford SA (1999) Astrophys J 511:115
5. Bréchignac Ph, Schmidt M, Masso A, Pno T, Parneix P, Bréichignac C (2005) A&A 42:239
6. Ruiterkamp R, Peeters Z, Moore M, Hudson R, Ehrenfreund P (2005) A&A 440:391
7. Cami J, Bernard-Salas J, Peeters E, Malek SE (2010) Science 329:1180
8. Ehrenfreund P, Foing BH (1995) Planet Space Sci 43:1183
9. Dinadayalene TC, Leszczynski J (2010) Struc Chem. doi: 10.1007/s11224-010-9670-2
10. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA (2004) Science 306:666
11. Allen MJ, Tung VC, Kaner RB (2010) Chem Rev 110:132
12. Kratschmer W, Lamb LD, Fostiropoulos K, Hoffman DR (1990) Nature 347:354
13. David T, Gimzewski JK, Durdie D, Rheil B, Schlitter RR (1994) Phys Rev B50:5810
14. Diederich F, Rubin Y (1992) Angew Chem Int Ed Engl 31:1101
15. Müller M, Kübel C, Müllen K (1998) Chem Eur J 4:2009
16. Dötz F, Brand JD, Ito S, Gherghel L, Müllen K (2000) J Am Chem Soc 122:7707
17. Gallegos EJ (1968) J Phys Chem 72:3452
18. Donaldson DM, Robertson JM (1953) Proc R Soc Lond Ser A 220:157
19. Cui Y-H, Chen D-L, Tian WQ, Feng J-K (2007) J Phys Chem A 111:7933
20. Rosgonyl T, Bártok-Partay A, Stirling A (2010) J Phys Chem A 114:1207
21. Cataldo F, Iglesias-Groth S, Manchado A (2010) Nanotub Carbon Nanostruct 18:224

22. Jaguar 4.0, Schrödinger, Inc., Portland, OR, 1991–2000
23. Becke AD (1988) Phys Rev A 38:3098
24. Perdew JP, Wang Y (1992) Phys Rev B 45:13244
25. Wu J, Pisula W, Mullen K (2007) Chem Rev 107:718
26. Bühl M (1998) Chem Eur J 4:734
27. Chen Z, King RB (2005) Chem Rev 105:3613
28. Clar E (1972) The aromatic sextet. Wiley, London
29. Clar E, Mullen A (1968) Tetrahedron 24:6719
30. Suresh C, Gadre SR (1999) J Org Chem 64:2505
31. Dias JR (1987) Handbook of polycyclic hydrocarbons: Part A. benzenoid hydrocarbons. Elsevier, Amsterdam
32. Yu J, Sumathi R, Green WH (2004) J Am Chem Soc 126:12685
33. Cyranski MK, Howard ST, Chodkiewicz ML (2004) Chem Commun 2458
34. Bühl M, Hirsch A (2001) Chem Rev 101:1153
35. Elser V, Haddon RC (1987) Nature 325:792
36. Rouff RS, Beach D, Cuomo J, McGuire T, Whetten RL, Diederich F (1991) J Phys Chem 95:3457
37. Zhang BI, Wang CZ, Ho KM (1992) Chem Phys Lett 193:225
38. Fowler PW, Collins DJ, Austin SJ (1993) J Chem Soc Perkin Trans 2:275
39. Matsuzawa N, Dixon DA, Fukunaga T (1992) J Phys Chem 96:7594
40. Salcedo R, Fomina L (2007) Tetrahedron Lett 48:3949
41. George P, Trachtman M, Bock CW, Brett AM (1976) J Chem Soc Perkin Trans 2:1222
42. George P, Trachtman M, Bock CW, Brett AM (1975) Theor Chim Acta 38:121
43. Slayden SW, Liebman JF (2001) Chem Rev 101:1541
44. Stein SE (1978) J Phys Chem 82:566
45. Weisman JL, Lee TJ, Salama F, Head-Gordon M (2003) Astrophys J 587:256
46. Mederos L, Navascués G (1994) Phys Rev 50:1301
47. Girifalco LA (1992) J Phys Chem 96:858