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# Polarizability-based computational astrochemistry of polycyclic aromatic hydrocarbons

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Polarizability of carbon-rich molecules is deeply studied. It is usually related to the molecule's behavior under external electric fields. However, we have shown that it is also applicable to assessing reactivity of the molecules [1, 2]. First of all, the correlations between the polarizabilities and the yields of compounds are typical for the molecules enriched with the  $sp^2$ -C atoms. The latter means that the molecule contains facily polarizable  $\pi$ -electrons such as fullerenes and polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons (PAHs) are assumedly widespread in space. Their stability and polarizability depend on their chemical structure. We report on the correlations between structures, energies, polarizabilities and abundances of PAHs. We choose polarizability as a key parameter as it relates to molecule's behavior under various irradiations [2]. All computations in this work were performed with relevant DFT methods. The hypotheses of this work: (a) planar PAH isomers have low energy whereas their nonplanar counterparts have low polarizability; (b) lower molecular polarizability relates to higher survivability of the molecules.

## (1) Linear vs kinked planar PAHs

In general, PAHs with the linearly condensed benzene rings (oligoacenes) are thermodynamically least favorable than their "kinked" isomers (phenacenes). Mean polarizability of these PAHs differently increases with molecular size: it increases linearly with the number of benzene rings in the case of phenacene series and the dependence is quadratic in the case of the oligoacene [3]. The mean polarizability of phenacene is lower in a 'phenacene-oligoacene' pair, and the gap between the polarizabilities of the isomers

becomes greater with increasing molecular size. Thus, minimum-energy and minimum-polarizability estimates within these regular series are consistent. Both quantities indicate that the growth of large PAH molecules is more preferable if it results in a kinked pattern, and vice versa: large linear interstellar PAHs are not favorable. Most recent experimental studies confirm this hypothesis [4].

## (2) Planar vs nonplanar PAHs

In wider sets of isomeric PAHs, the energy and polarizability trends do not coincide. Nonplanar helicoids have minimal (or very close to minimal) mean polarizabilities, i.e. these compounds are favored in terms of minimum polarizability principle. We noticed [5] that helicenes have never been in a focus of astrochemical research but the computed polarizabilities indicate their weak response to external fields/irradiations and, possibly, enhanced survivability under interstellar conditions. Our hypothesis was confirmed with the syntheses of PAHs in laboratory experiments simulating the conditions of circumstellar envelopes of carbon-rich stars [6]. The main products of these experiments were [4]- and higher helicenes. A very recent computational study [7] proposes the relevance of diffuse interstellar band 4502 Å to the high-molecular helicenes.

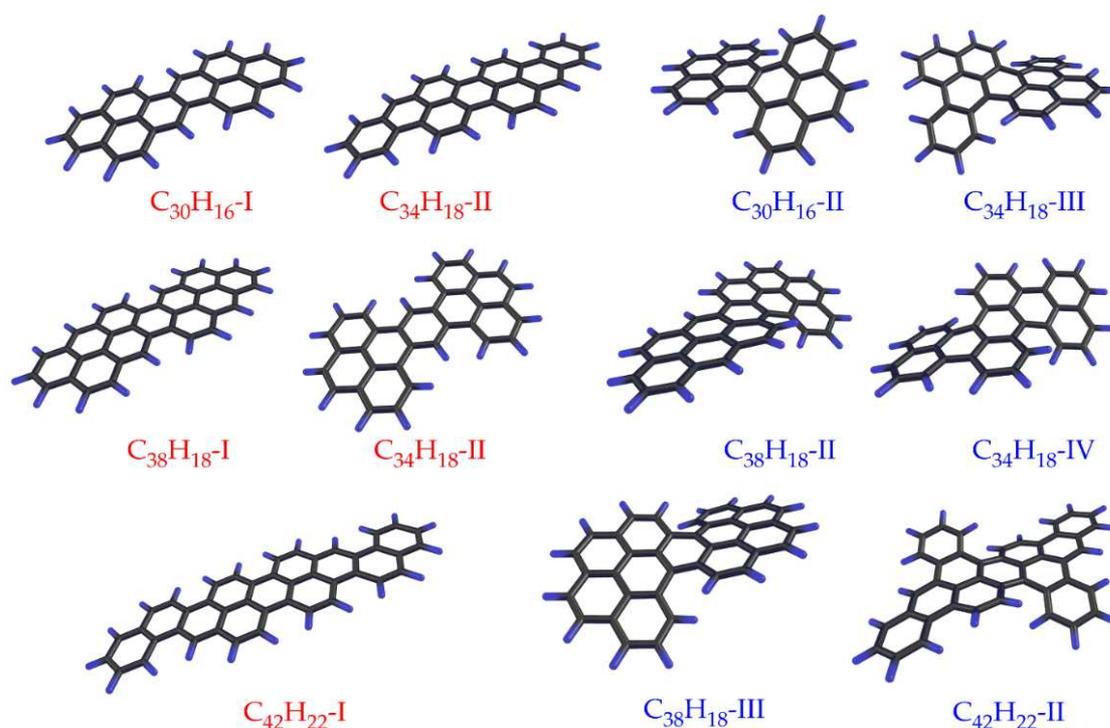


Fig. 1. The studied isomeric sets 'planar–nonplanar PAHs'. The color of designations correspond to planar, most stable (red) and nonplanar least polarizable (blue) structures.

Polycyclic aromatic hydrocarbons may have irregular structure combining linear and zigzag, flat and nonplanar moieties. In general, we can talk about the correlation: *planar PAH isomers have low energy whereas their nonplanar counterparts have low polarizability*. We exemplify this statement with the PBE/3 $\zeta$  calculations of the selected isomeric sets taken from [8] (Figure 1). Of course, the energy and polarizability values of the hydrocarbons result from the balance between the structural features, so the correlation has some exceptions. Anyway, both most stable and least polarizable PAHs must be considered as possible participants of interstellar and circumstellar chemistry.

### (3) Monitoring polarizability in the stepward graphitization of hexaphenylbenzene (Scholl reaction)

The increase in polarizability is also observed for related (non-isomeric) PAHs. We demonstrated the correlation between planarity and polarizability on the example of stepward conversion of hexaphenylbenzene  $C_{42}H_{30}$  to hexabenzocoronene  $C_{42}H_{18}$ , a completely planar molecule (Figure 2). Here, both planarity and polarizability increase with the condensation (number of benzene rings in the molecule) [9, 10].

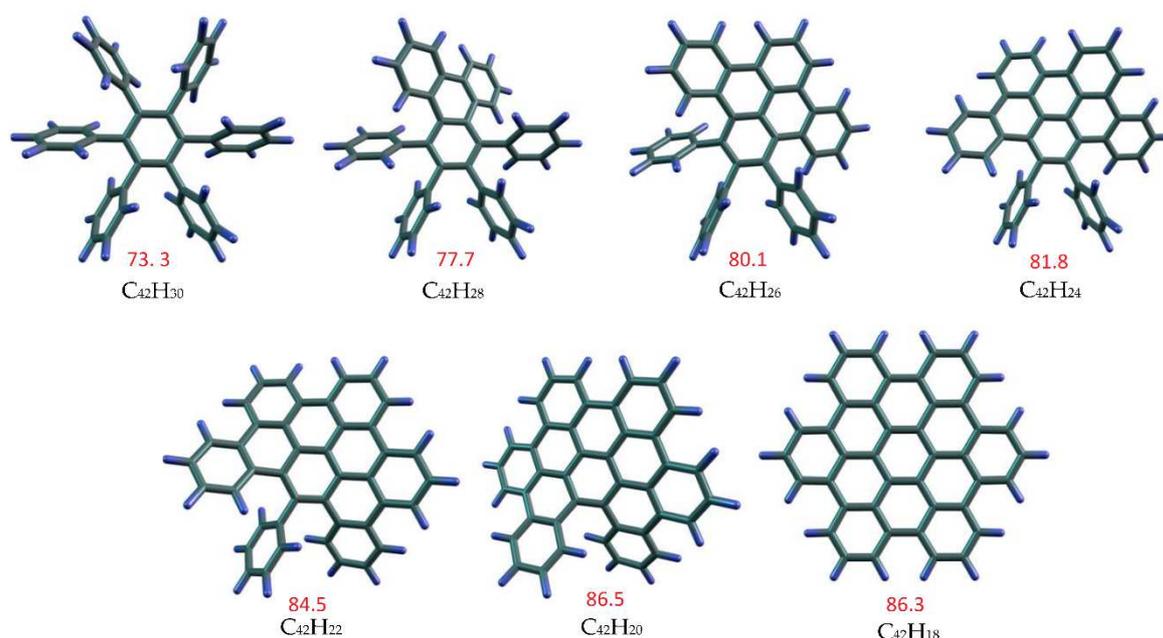


Fig. 2. Planarity and polarizability increases with the number of benzene rings in PAHs, which are initial, intermediate and final states of the Scholl reaction starting from hexaphenylbenzene  $C_{42}H_{30}$ . The PBE/3 $\zeta$ -computed mean polarizabilities are shown in  $\text{\AA}^3$  (red numbers).

## Conclusion

We computationally demonstrated the correlation between planarity, polarizability and energy of PAHs. Experiments reveal that low-polarizability molecules are more survivable under laboratory experiments simulating interstellar media. Helicenes and other nonplanar PAHs have low polarizability as compared with their planar isomers / analogs. Hence, we hypothesize that they may be most abundant among other PAHs. In continuation of these studies, we plan to invoke structural descriptors such as Wiener-based topological indices. The first steps in this direction have been taken [11].

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