

Why are some polycyclic aromatic hydrocarbons extremely reactive?

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Higher members of the polyacene series are extremely reactive although they are aromatic in nature. This aspect of aromatic chemistry can be explained using conventional indices of kinetic stability, such as a localization energy and a HOMO–LUMO energy separation. Large polyacene molecules have smaller localization energies and smaller HOMO–LUMO energy separations than their respective polyene references defined using matching polynomials. These molecules are presumed to be thermodynamically more stable but kinetically less stable than non-aromatic polyolefins. The same situation is sometimes observed in other groups of polycyclic aromatic hydrocarbons (PAHs). Such highly reactive PAH molecules were found to be substructures of metallic one-dimensional benzenoid polymers.

Linear polyacene molecules are all aromatic in the sense that they have positive Dewar and topological resonance energies.^{1–4} However, it is true that higher members of the polyacene group are extremely reactive.^{5,6} Clar pointed out that the benzenoid character of a larger polyacene molecule will be gradually lost since one aromatic sextet is shared among all constituent rings.⁶ This reasoning is fully consistent with the reactivity of polyacene molecules, which increases rapidly as the number of benzene rings increases. Structural formulae of 22 polycyclic aromatic hydrocarbons (PAHs), including ten polyacene molecules, are presented in Fig. 1.

As is known very well, naphthalene (**2**) is more reactive than benzene (**1**) and is sulfonated by concentrated sulfuric acid at room temperature. Anthracene (**3**) is more reactive and is easily oxidized in the middle ring to anthraquinone. Tetracene or naphthacene (**4**) is readily oxidized in air and light in the middle ring. As pentacene (**5**) and hexacene (**6**) are very susceptible to photo-oxidation, they must be prepared and handled under nitrogen.⁶ Heptacene (**7**) is kinetically so unstable that it has never been obtained in a pure state.⁶

For many chemists, PAHs are still representatives of not only thermodynamically but also kinetically stable unsaturated molecules. This point of view ignores the existence of highly reactive polycyclic benzenoid hydrocarbons. The aims of this paper are to find the reason why large polyacene molecules and some other PAHs are highly reactive and then to identify structural features that these molecules have in common. Kinetic stability of PAH molecules is analyzed using some conventional indices defined by Hückel molecular orbital (HMO) theory.

Localization energies

One of the straightforward indices of chemical reactivity is a localization energy (LE),^{7–9} which is defined as the π -binding energy required to attach a proton or a hydride ion to a given π -electronic system. In the case of alternant hydrocarbons, such as PAHs, the LE values are the same for these two types of reactions.⁸ LE can be calculated in the same manner for a polyene reference defined using a matching polynomial.⁹ This reference structure by definition is a hypothetical non-aromatic one with the same geometry as a given molecule.^{2–4}

The LEs for all sites in three groups of PAH molecules and their polyene references are presented in Fig. 1. Smaller LE

values indicate higher reactivity toward electrophiles and nucleophiles. In general, the chemical reactivity and then the kinetic stability of a molecule is determined by the reactivity at the most reactive site in the molecule.^{10,11} Minimum LE (min LE) represents the smallest LE in the molecule, *i.e.*, the LE at the most reactive site.¹⁰ Benzene (**1**) is the least reactive species with the smallest min LE of $2.536 |\beta|$; here, β is the resonance integral defined in HMO theory. Min LEs occur at solo carbon atoms, if any, which are located between two carbon atoms at ring junctions.

Group A molecules are benzene (**1**) and linear polyacene molecules (**2–11**). It is obvious that the most reactive sites in these molecules are innermost solo carbon atoms. The min LE of a relatively small polyacene molecule is larger than that of the polyene reference, indicating that the entire molecule is kinetically stabilized by cyclic conjugation. For heptacene (**7**) and higher polyacene members (**8–11**), however, this is not true. The min LEs of such large polyacene molecules are smaller than those of their respective polyene references, implying that the entire molecule is kinetically less stable than the polyene reference. Carbon atoms at which the LEs are smaller than those at the corresponding sites in the polyene reference are denoted by asterisks. They are all solo carbon atoms.

There are also highly reactive carbon atoms in other groups of PAH molecules. Group B molecules comprise pyrene (**12**), anthanthrene or dibenzo[def,mno]chrysene (**13**), and higher homologues. As shown in Fig. 2, **15**, **16**, and **17** have smaller min LEs than their respective polyene references. Peripheral carbon atoms at the central rings are reaction centers in these molecules. Biphenyl (**18**), perylene (**19**), bisanthene or phenanthro[1,10,9,8-opqra]perylene (**20**), and higher homologues (**21**, **22**) constitute group C molecules. It is likely that **21** and **22** are very reactive since they have carbon atoms with asterisks. Thus, it has been confirmed that some PAHs are reactive or extremely reactive although they are polycyclic benzenoid systems.^{1–4}

It may be interesting to note that, for each group of PAH molecules in Fig. 1, the polyene references of higher members are predicted to be more reactive with smaller min LEs. This aspect of polyene references is essentially the same as that found in actual PAH molecules although the variation of the min LE is smaller. Among the molecules studied, **22** has the most reactive polyene reference with the smallest min LE ($1.669 |\beta|$).

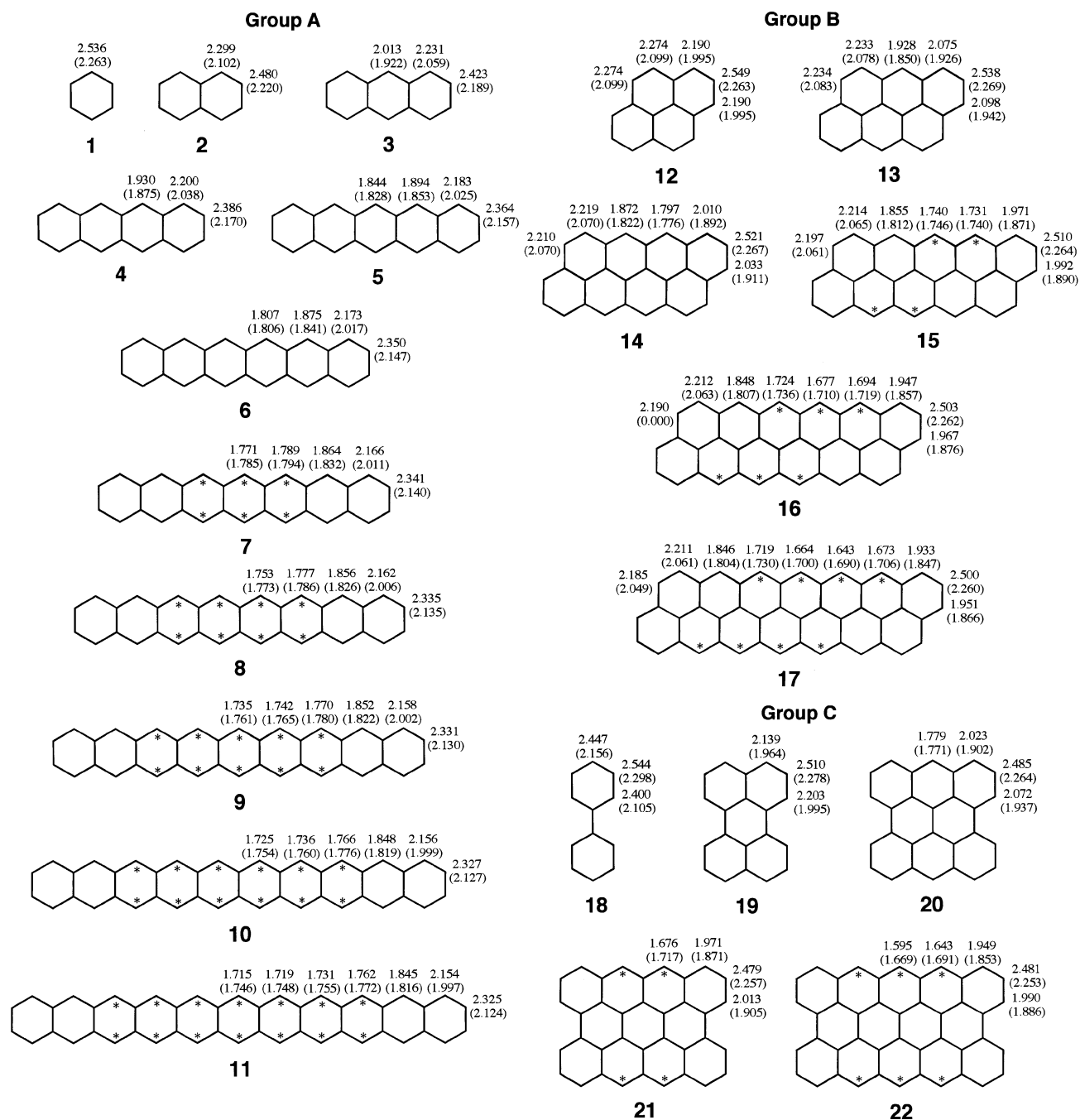


Fig. 1 Localization energies (LEs) in units of $|\beta|$ for all sites in 22 PAH molecules. Values in parentheses are those for the polyene references.

Topological resonance energies

Topological resonance energy (TRE) represents the extra stabilization energy due to cyclic conjugation.^{2–4} All molecules in Fig. 1 are aromatic with positive TREs. The percentage TRE (%TRE) is defined as 100 times the TRE, divided by the total π -binding energy of the polyene reference.¹⁰ This index is useful when one wants to compare the degrees of aromaticity in different molecules. Table 1 contains the TREs and the %TREs for 22 PAHs. For each group of PAH molecules, the %TRE decreases slowly on going to higher members. However, this does not support the presumption that some PAH molecules are chemically more reactive than their respective polyene references. All PAH molecules studied have %TREs > 1.7 , indicating that they are far from being anti-aromatic.

Fig. 2 shows how the TRE increases on protonation at each site of the PAH molecules. Here, hyperconjugation through a methylene group is disregarded for simplicity. Positive or

negative values indicate that the protonated species concerned is more or less aromatic than the parent molecule, respectively. For smaller PAH molecules, the TRE decreases on protonation. However, protonation at carbon atoms with asterisks in large PAH molecules increases the TRE. Thus, the increase in the TRE on protonation is closely related to the decrease in the LE at the same site. This can be considered as the primary reason why some large PAH molecules are very reactive. Note that the whole TRE is lost when a monocyclic aromatic molecule is protonated.

Clar structures

A Clar structure for a closed-shell PAH molecule is depicted as a combination of the maximum number of isolated aromatic sextets imaginable and localized double bonds.^{5,6} Clar accumulated a large amount of experimental stability data on PAHs, and found that the Clar structure represents the chemical reactivity of the PAH molecule very well.^{5,6} In general, the

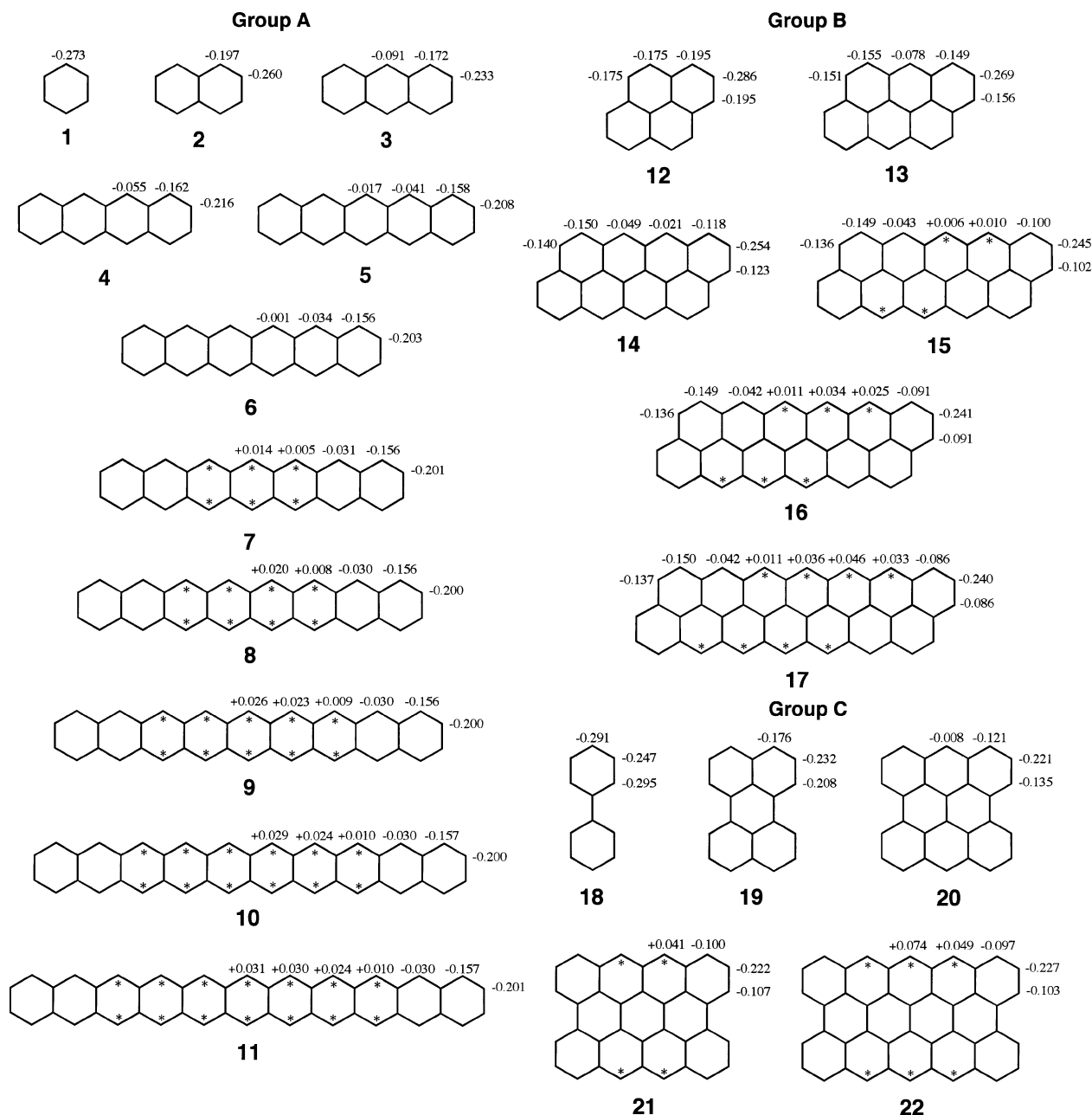


Fig. 2 Increase in the topological resonance energy (TRE) by protonation. Increments are given in units of $|\beta|$ with plus signs.

kinetic stability of the PAH isomers increases as the density of aromatic sextets in the Clar structure increases. Hosoya *et al.* showed that the Clar structure represents the bonding character of some high-lying occupied molecular orbitals, which are responsible for chemical reactions.^{11,12}

The increase in TRE on protonation can be qualitatively justified by comparing the Clar structure of a given molecule with that of the protonated species. As exemplified by **7a** in Fig. 3, only one aromatic sextet can be chosen from any polyacene molecule. In contrast, two aromatic sextets can be chosen from the protonated species (**7b**), in harmony with the increased TRE. For all polyacene molecules, the number of aromatic sextets increases on the protonation at inner rings. When a polyacene molecule is oxidized to the quinonoid species (**7c**), one more aromatic sextet is created.

The same is essentially true for group B and C molecules. As exemplified by **15a** and **21a**, two aromatic sextets can be chosen from any group B or group C molecule. One or two more aromatic sextets are created in the protonated (*e.g.*, **15b** and **21b**) and quinonoid species (*e.g.*, **15c** and **21c**), indicating that the reaction products are much more aromatic than the

starting molecules.^{13–15} Therefore, there is no doubt that these PAH molecules have many reaction pathways to generate more aromatic products. As a general rule, a reaction route to a thermodynamically more stable product is accompanied by a smaller activation energy.¹⁶

HOMO–LUMO energy separations

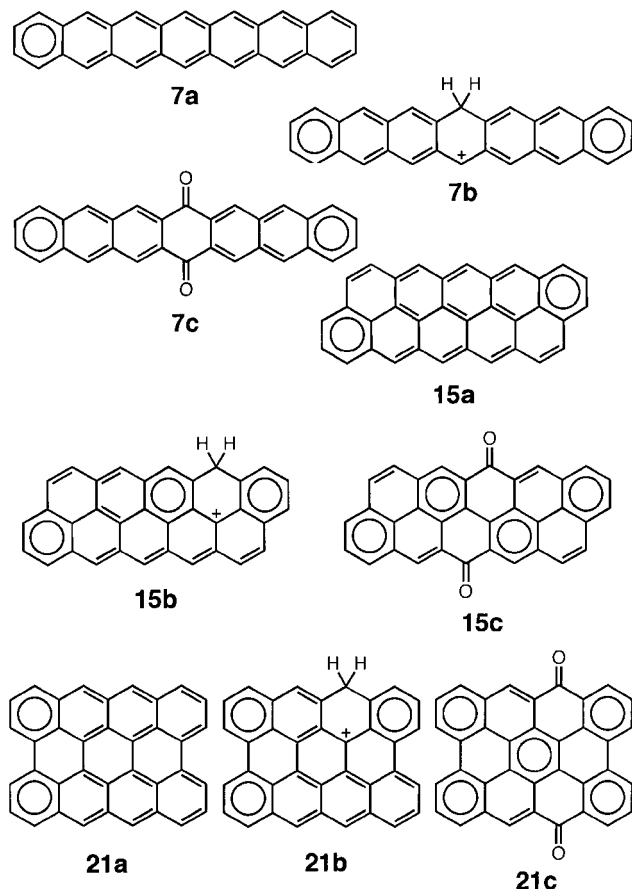
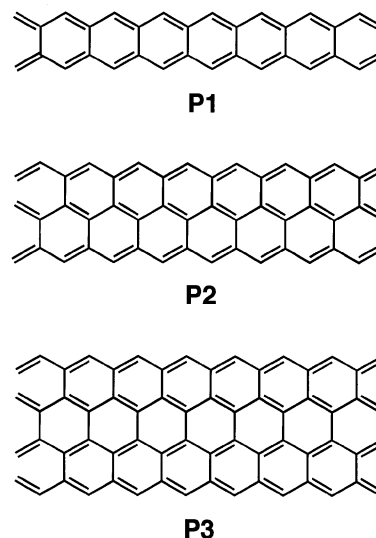
The HOMO–LUMO energy separation has been used as a simple but general measure of kinetic stability.^{17–21} Clar pointed out that the more highly colored a PAH molecule, the less stable it generally is in a kinetic sense.^{5,6} He tacitly ascribed kinetic instability to a small HOMO–LUMO energy gap. For PAH molecules, the HOMO–LUMO gap is highly correlated with the Hess–Schaad resonance energy per π electron, a measure of aromaticity somewhat similar to %TRE.¹⁷ This correlation indicates that thermodynamically stable benzenoid systems are kinetically stable.

However, as pointed out by Fowler,²² the HOMO–LUMO energy separation in general is smaller for a larger conjugated system, whether or not it is kinetically stable. We previously

Table 1 TREs and T values for selected PAHs and their polyene references

Species ^a	TRE/ $ \beta $	%TRE	<i>T</i> value	
			Polyene reference	Real molecule
Group A				
1	0.273	3.53	6.21	12.00
2	0.389	2.92	7.07	12.36
3	0.475	2.52	7.38	11.60
4	0.553	2.27	7.45	10.62
5	0.630	2.11	7.39	9.67
6	0.706	1.99	7.29	8.81
7	0.783	1.91	7.15	8.05
8	0.859	1.85	7.00	7.40
9*	0.936	1.80	6.85	6.83
10*	1.013	1.76	6.71	6.33
11*	1.090	1.73	6.56	5.89
Group B				
12	0.598	2.73	7.86	14.24
13	0.766	2.51	8.00	12.80
14	0.925	2.37	7.85	10.87
15	1.085	2.28	7.56	9.08
16	1.246	2.22	7.23	7.57
17*	1.408	2.17	6.88	6.35
Group C				
18	0.502	3.16	8.75	16.91
19	0.740	2.69	8.50	13.89
20	0.968	2.48	7.61	9.94
21	1.214	2.39	6.68	6.82
22*	1.469	2.36	5.84	4.69

^a Species with asterisks have smaller T values than their respective polyene references.

**Fig. 3** Clar structures of some polycyclic aromatic hydrocarbon (PAH) molecules and related species.**Fig. 4** Benzenoid polymers with zero band gaps.

showed that the HOMO–LUMO energy separation, multiplied by the number of conjugated atoms, is better as an index of kinetic stability than the HOMO–LUMO energy separation itself.^{23,24} This index has been referred to as the T value. Calculated T values are given in Table 1. For each group of PAH molecules, higher members have smaller T values in accord with their chemistry. They have smaller T values than their respective polyene references. This also reminds us that these PAH molecules are highly reactive.

Common structural features

Three one-dimensional benzenoid polymers are shown in Fig. 4. Many PAH molecules can be defined as partial structures of these polymers. Polyacene molecules represent closed-shell benzenoid substructures of benzenoid polymer **P1**. Likewise, group B and C molecules are closed-shell substructures of **P2** and **P3**, respectively. These benzenoid polymers, which are structurally related to PAHs in Fig. 1, have some common electronic properties. They are metallic with a vanishing band gap.^{25–28} Since no aromatic sextets can be chosen from these polymers, they must be olefinic in nature. Thus, the chemical formulae given in Fig. 4 are exactly the Clar structures.

It might then follow that, if a given large PAH molecule corresponds to a substructure of a one-dimensional benzenoid polymer with no band gap, it will be chemically reactive with a small HOMO–LUMO energy separation and even a very small T value. The chemical reactivity of PAH molecules in Fig. 1 can be predicted at least qualitatively on this basis. For highly reactive PAH molecules, the density of aromatic sextets in the Clar structure is necessarily small. One or two more aromatic sextets can be created in the protonated species.

Concluding remarks

Most PAH molecules are stable not only thermodynamically but also kinetically. This is in marked contrast to the chemistry of nonbenzenoid aromatic hydrocarbons.⁹ There are often very reactive sites in nonbenzenoid species even if they have sufficiently large %TREs. In this context, it is intriguing that, among a variety of PAH molecules, some are exceptionally reactive. In order to analyze the high chemical reactivity of these molecules, an approach based on LE and TRE proved to be most appropriate.

Some PAH molecules were found to be thermodynamically more but kinetically less stable than their respective polyene references. These molecules are presumably chemically very

reactive although they are moderately aromatic with positive %TREs. What is noteworthy in this context is that not only thermodynamic stabilization but also high chemical reactivity arise from the same cyclic conjugation. Such a situation cannot arise for monocyclic aromatic molecules. Extremely reactive benzenoid hydrocarbons are substructures of metallic one-dimensional benzenoid polymers.

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