

Reduced HOMO–LUMO Gap as an Index of Kinetic Stability for Polycyclic Aromatic Hydrocarbons

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A reduced HOMO–LUMO gap, which is defined as the HOMO–LUMO energy separation of a molecule divided by that of the hypothetical polyene reference, can be used as an index of kinetic stability for a variety of polycyclic aromatic hydrocarbons (PAHs). The reduced HOMO–LUMO gap < 1.00 indicates that the HOMO contributes to the decrease in the topological resonance energy. In general, PAHs with reduced HOMO–LUMO gaps < 1.30 are chemically very reactive. Fully benzenoid hydrocarbons are kinetically very stable with very large reduced HOMO–LUMO gaps. Many of the PAH molecules with large reduced HOMO–LUMO gaps are closed-shell substructures of nonmetallic one-dimensional benzenoid polymers.

The kinetic stability of a molecule has a crucial influence on its synthetic accessibility and isolability. By kinetic stability we mean stability with respect to the activated complex of any further chemical reaction.¹ In order for a molecule to be isolable, it must be not only thermodynamically but also kinetically stable. Thermodynamic stability can easily be estimated experimentally and/or computationally. However, it is very difficult to estimate the degree of kinetic stability because it is related to innumerable chemical reactions.

The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy separation has been used as a simple indicator of kinetic stability.^{1–11} A large HOMO–LUMO gap implies high kinetic stability and low chemical reactivity, because it is energetically unfavorable to add electrons to a high-lying LUMO, to extract electrons from a low-lying HOMO, and so to form the activated complex of any potential reaction.¹ Pearson pointed out that the HOMO–LUMO gap represents the chemical hardness of a molecule.^{3,6,7,10} Zhou and Parr discussed the chemical reactivity of cyclic conjugated systems using the HOMO–LUMO gaps of the reactant and the transition state.⁸

Clar noted that the more highly colored a polycyclic aromatic or benzenoid hydrocarbon (PAH), the less stable it generally is in a kinetic sense.^{12,13} Thus, he ascribed kinetic instability to a small HOMO–LUMO gap. For benzenoid and nonbenzenoid hydrocarbons, the HOMO–LUMO energy separation is highly correlative with the Hess–Schaad resonance energy per π electron, a measure of thermodynamic stability due to cyclic conjugation.^{2,6,7} This correlation indicates that thermodynamically stable hydrocarbons are kinetically stable in general.

The kinetic stability of fullerenes has also been discussed in terms of the HOMO–LUMO energy gap.^{1,5,9,11} Fullerene isomers with very small HOMO–LUMO gaps indeed have not been isolated.^{9,14} In this context, Fowler pointed out that a HOMO–LUMO energy gap is not always suited for predicting the kinetic stability of fullerenes.¹⁵ As the cage size increases, the ratio of hexagonal to pentagonal rings increases, but the HOMO–LUMO gap must decrease. Highly aromatic graphite has no band gap.¹⁶ It follows that the HOMO–LUMO gap cannot be used as an index of kinetic stability for very large π -electronic systems.

We previously found that the HOMO–LUMO energy gap can be scaled to remove the effect of the size of the π -electronic system.^{17–19} A new index we proposed was a T value, defined as a HOMO–LUMO gap multiplied by the number of conjugated atoms. The definition of the T value was applied successfully to fullerenes with up to 100 carbon atoms. However, we noticed that the T value of a PAH molecule reflects not only kinetic stability but also some structural characteristics. In this paper, we propose another scaled HOMO–LUMO gap as a better index of kinetic stability for a variety of PAHs. It is defined as the HOMO–LUMO energy separation of a molecule, divided by that of the hypothetical polyene reference. Hückel molecular orbital (HMO) theory is used throughout this paper.

Definition of the Reduced HOMO–LUMO Gap

The physical meaning of the HOMO–LUMO energy gap multiplied by the number of conjugated atom or the T value has previously described.^{17,18} In brief, this index is supposed to represent the degree of kinetic stability corrected for the size of a molecule. The unweighted HOMO–LUMO energy gap does not permit comparison between different molecules, but the T value does. Thus, the difficulty with the use of the unweighted HOMO–LUMO energy separation apparently disappeared.

We now want to see if the concept of the T value is applicable to planar PAH molecules. We first examined the T values calculated for linear and angulated or zigzag polyacenes in Figures 1 and 2, respectively. Calculated T values are listed in Tables 1 and 2. Those of linear polyacenes **1–11** are rather acceptable, in that higher members have smaller values in accord with their chemistry. Note that higher members of linear polyacene are extremely reactive.^{12,13} In contrast, the T value of zigzag polyacene increases monotonically as the number of benzene rings increases. As a result, higher members of zigzag polyacene have unusually large T values.

The occurrence of large T values for large zigzag polyacene molecules is closely associated with the fact that infinitely long zigzag polyacene (**P5** in Figure 3) has a band gap of $0.764|\beta|$.^{20–22} Zigzag polyacenes **12–20** are closed-shell substructures of this polymer. Therefore, the T value for a sufficiently large zigzag polyacene molecule approaches $0.764N_C$, where N_C is the

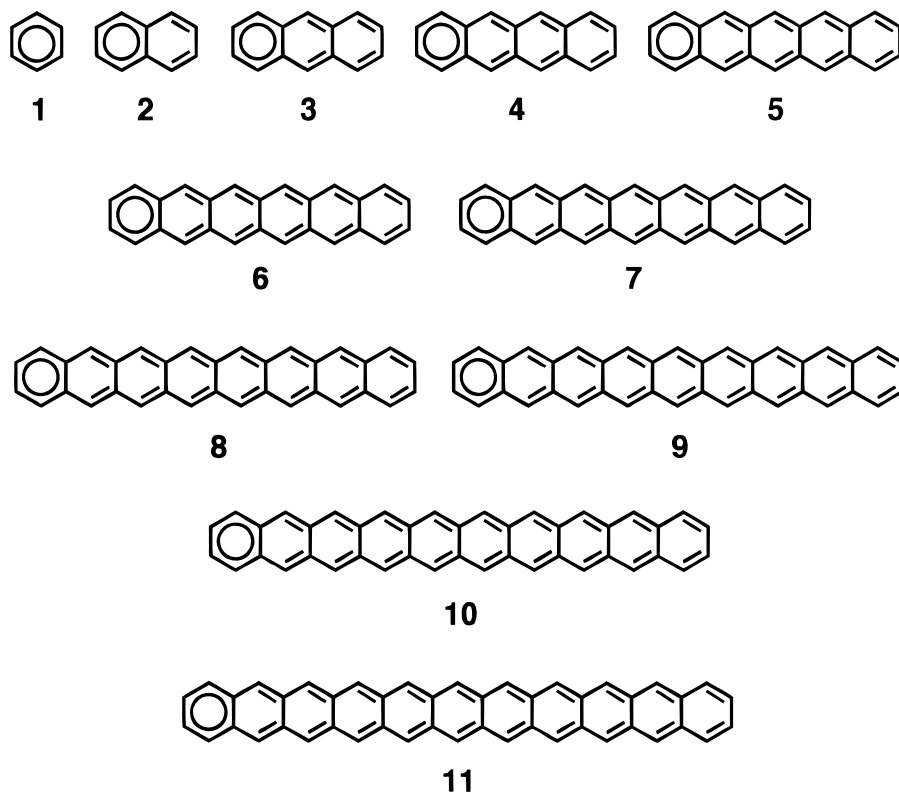


Figure 1. Clar structures of the linear polyacenes.

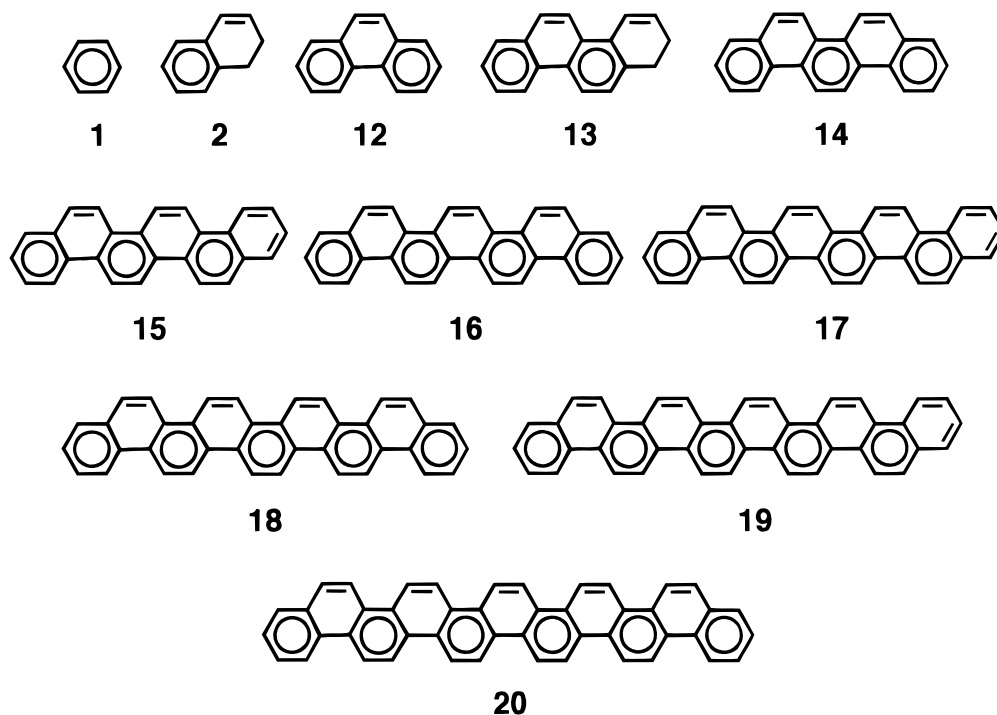


Figure 2. Clar structures of the zigzag polyacenes.

number of constituent carbon atoms. Infinitely large linear polyacene (**P1** in Figure 3) does not have a band gap.^{20–22} The T value for a sufficiently large linear polyacene molecule, which is a closed-shell substructure of this polymer, is close to zero. As shown in Figure 3 and Table 4, there are many benzenoid polymers with nonzero band gaps.^{20–22} In general, the T value is large for large closed-shell substructures of such polymers.

The chemical reactivity of a molecule might be determined primarily by the reactivity at the most reactive site in the molecule.^{11,23} Localization energy (LE) is a simple but realistic

measure of chemical reactivity.²⁴ Minimum LE (min LE) represents the LE at the site with the smallest LE in the molecule. As shown in Table 3, the min LE of linear polyacene monotonically decreases on going to higher members, whereas the min LE of zigzag polyacene is kept almost unchanged among fulminene (**15**) and higher members. Thus, very large T values of large zigzag polyacene molecules never imply very high kinetic stability.

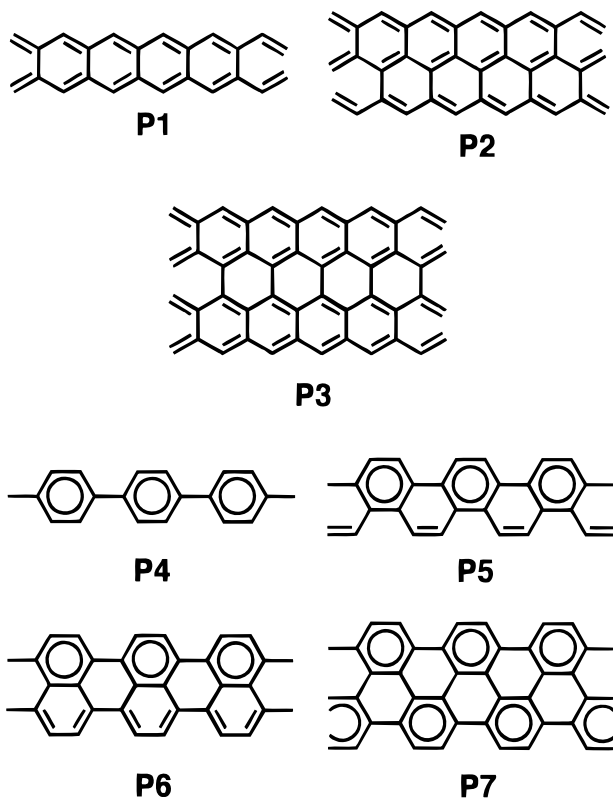
In this connection, we noticed that if a given molecule has a very large T value, its polyene reference also has a relatively

TABLE 1: Reduced HOMO–LUMO Gaps and Related Quantities for Linear Polyacenes

species	N_C	T value		reduced HOMO–LUMO gap	D_{as}
		polyene reference	real molecule		
benzene (1)	6	6.21	12.00	1.932	1.00
naphthalene (2)	10	7.07	12.36	1.748	0.60
anthracene (3)	14	7.38	11.60	1.571	0.43
naphthacene (4)	18	7.45	10.62	1.426	0.33
pentacene (5)	22	7.39	9.67	1.307	0.27
hexacene (6)	26	7.29	8.81	1.209	0.23
7	30	7.15	8.05	1.126	0.20
8	34	7.00	7.40	1.056	0.18
9	38	6.85	6.83	0.996	0.16
10	42	6.71	6.33	0.944	0.14
11	46	6.56	5.89	0.898	0.13
P1	∞		0		0

TABLE 2: Reduced HOMO–LUMO Gaps and Related Quantities for Zigzag Polyacenes

species	N_C	T value		reduced HOMO–LUMO gap	D_{as}
		polyene reference	real molecule		
benzene (1)	6	6.21	12.00	1.932	1.00
naphthalene (2)	10	7.07	12.36	1.748	0.60
phenanthrene (12)	14	8.14	16.95	2.082	0.86
chrysene (13)	18	8.92	18.73	2.099	0.67
picene (14)	22	9.78	22.08	2.258	0.82
fulminene (15)	26	10.59	24.51	2.316	0.69
16	30	11.41	27.49	2.409	0.80
17	34	12.23	30.18	2.467	0.71
18	38	13.07	33.07	2.531	0.79
19	42	13.90	35.87	2.580	0.71
20	46	14.75	38.76	2.628	0.78
P5	∞		∞		0.75

**Figure 3.** Typical benzenoid polymers.

large T value. Here, a polyene reference is a hypothetical nonaromatic structure with the same molecular geometry as a given molecule, which is defined using a reference or matching

TABLE 3: Minimum Localization Energies for Polyacenes

A. linear polyacenes		B. zigzag polyacenes	
species	min LE/ $ \beta $	species	min LE/ $ \beta $
1	2.536	1	2.536
2	2.299	2	2.299
3	2.013	12	2.298
4	1.930	13	2.254
5	1.844	14	2.254
6	1.807	15	2.250
7	1.771	16	2.250
8	1.753	17	2.250
9	1.735	18	2.250
10	1.725	19	2.250
11	1.715	20	2.250

TABLE 4: Band Gaps of Typical Benzenoid Polymers

species	band gap/ $ \beta $	D_{as}	species	band gap/ $ \beta $	D_{as}
P1	0.000	0.00	P5	0.764	0.75
P2	0.000	0.00	P6	0.000	0.60
P3	0.000	0.00	P7	0.494	1.00
P4	0.828	1.00			

polynomial.^{25,26} In general, if a molecule has a T value >20.0 , its polyene reference has a T value >9.0 . Typical such examples are higher members of zigzag polyacene. If a PAH molecule has a relatively small T value, its polyene references will also have a small T value. Such an in-phase variation of the T value is characteristic of PAH molecules. The T values for the polyene references of fullerenes with 20–100 carbon atoms lie in the very narrow range 5.78–7.60.^{17–19}

One should remember that higher members of zigzag polyacenes are presumably similar in chemical reactivity. Likewise, it can be assumed that polyene references of all PAH molecules are similar in chemical reactivity, even if they have varied T values. All polyene references are polyolefins by definition.^{25,26} With this assumption in mind, we propose a new scaled index of kinetic stability, which is defined as the T value of a molecule divided by that of the polyene reference. This index will be referred to as a reduced HOMO–LUMO gap because it is identical with the HOMO–LUMO energy separation of a molecule divided by that of the polyene reference.

We utilize kinetic aspects of a Clar structure^{12,13} to test the reasonableness of the reduced HOMO–LUMO gap. A Clar structure for a PAH molecule is depicted as a combination of the maximum number of isolated aromatic sextets imaginable for the molecule and localized double bonds.^{12,13} Clar accumulated a large amount of experimental stability data on PAHs and noted that the Clar structure represents the chemical reactivity of the PAH molecule. Hosoya et al. showed that the Clar structure represents bonding character of some high-lying occupied MOs, which are responsible for chemical reactions.^{27,28}

In general, a PAH molecule with a given number of aromatic sextets is kinetically more stable than its isomers with less aromatic sextets. To visualize such a situation, the density of aromatic sextets in a Clar structure is defined as 6 times the number of aromatic sextets, divided by the number of carbon atoms. This quantity will be denoted by D_{as} , which lies in the range 0.0–1.0. The D_{as} value for linear polyacene approaches zero on going to higher members, whereas that for zigzag polyacene approaches 0.75. Thus, if the reduced HOMO–LUMO gap is a meaningful index of kinetic stability, it must be more or less correlative with D_{as} .

Numerical Values and Discussion

Reduced HOMO–LUMO gaps for many PAHs and their polyene references are listed and compared with the D_{as} values

in Table 5. Their Clar structures are shown in Figure 4. These PAHs were classified into 10 groups according to their molecular structures. Some PAH molecules belong to more than one group. Polyphenyls are included as group J molecules, although they are not so-called PAHs. Many of the PAH molecules are kinetically stable. For each group of molecules, the T value has a tendency to diverge to infinity or to converge to zero on going to higher members.

Group A molecules consist of pyrene (**21**), anthanthrene (**22**), and higher homologues (**23–26**), all of which are closed-shell substructures of benzenoid polymer **P2** with no band gap. As each member is a composite of two linear polyacene molecules with several bonds in common, there always are only two aromatic sextets in the Clar structure. The two aromatic sextets are diluted in higher members. Therefore, higher members must be chemically reactive with smaller D_{as} values. The reduced HOMO–LUMO gap of **26** is less than unity, suggesting that it might be more reactive than cyclic polyolefins.

Group B molecules (**21, 27–29**) are closed-shell substructures of benzenoid polymer **P6**. This polymer has no band gap, although its D_{as} value is as large as 0.60.^{20–22} All group B molecules are predicted to be kinetically stable with moderately large reduced HOMO–LUMO gaps. Group C molecules (**2, 30–32**) likewise are substructures of **P6** with their edge structures being different from those of group B molecules. They have moderately large reduced HOMO–LUMO gaps, indicating that all members are kinetically as stable as naphthalene (**2**).

Group D molecules (**1, 33–39**) are all fully benzenoid hydrocarbons or total resonant sextet benzenoids in Dias's terminology.²⁹ All carbon atoms belong to any of the sextets. There are no localized double bonds in the Clar structures. These molecules are substructures of fully benzenoid polymer **P7**. This polymer has a band gap of $0.494|\beta|$.²² All members have very large reduced HOMO–LUMO gaps and are kinetically very stable with a D_{as} value of 1.00.^{12,13} Group E molecules (**2, 21, 40–44**) are also closed-shell substructures of **P7**. The D_{as} value approaches rapidly to 1.00 on going to higher members. Like fully benzenoid hydrocarbons, large group E molecules have very large reduced HOMO–LUMO gaps, so must be kinetically very stable.

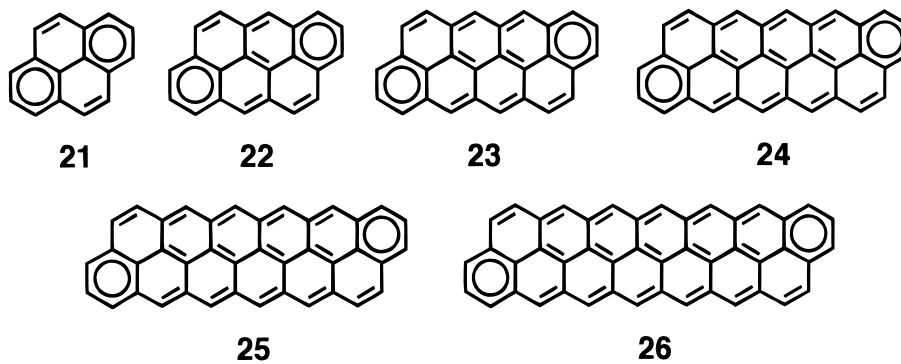
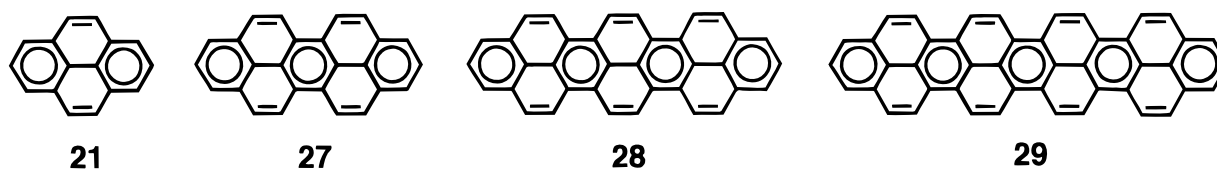
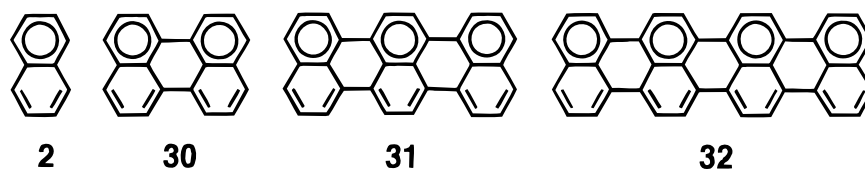
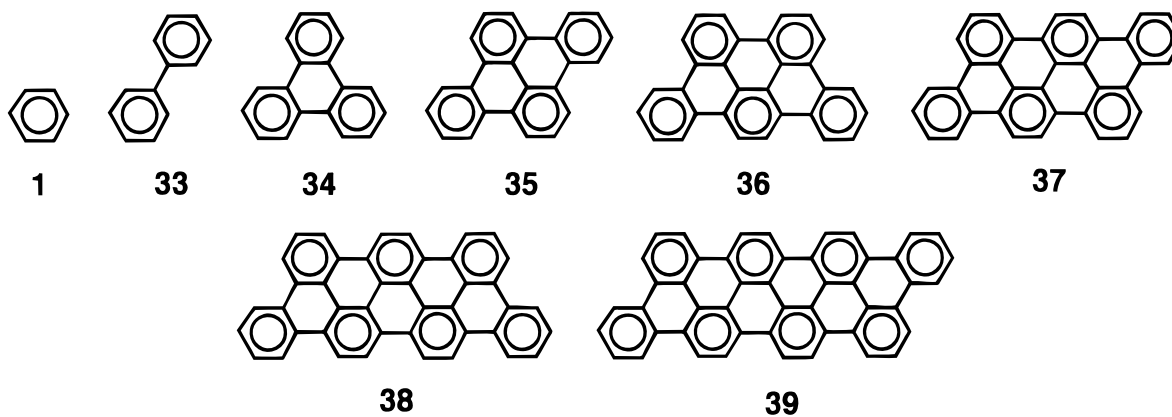
Group F molecules are substructures of benzenoid polymer **P3** with no band gap.^{20–22} Pyrene (**21**) and coronene (**45**) have two and three aromatic sextets, respectively. Since higher members (**46–48**) have four aromatic sextets in the Clar structure, aromatic sextets are gradually diluted. The reduced HOMO–LUMO gap decreases on going to higher members, reflecting the magnitude of the D_{as} value. It is noteworthy that the reduced HOMO–LUMO gap of **45** is exceptionally very large. Clar noted that this molecule is kinetically as stable as fully benzenoid hydrocarbons.^{12,13}

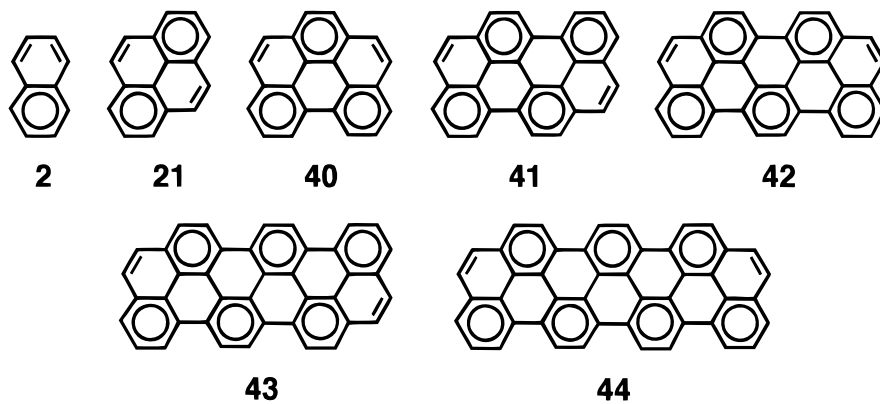
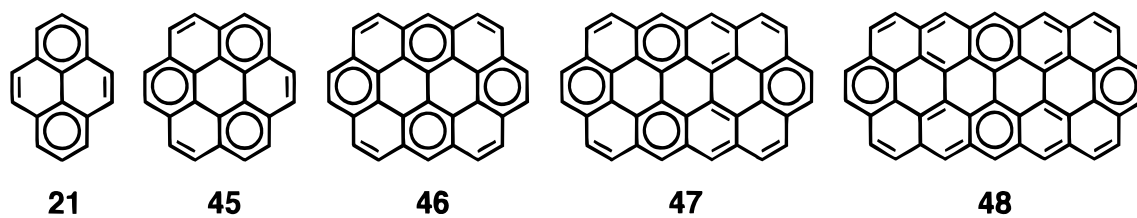
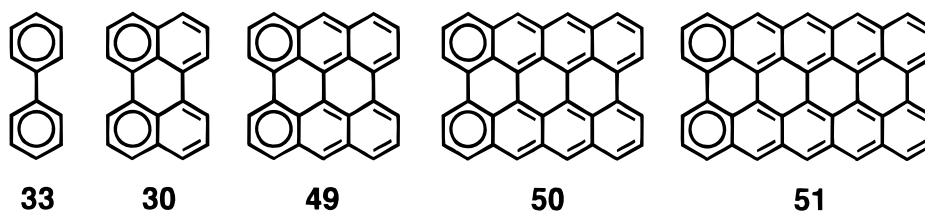
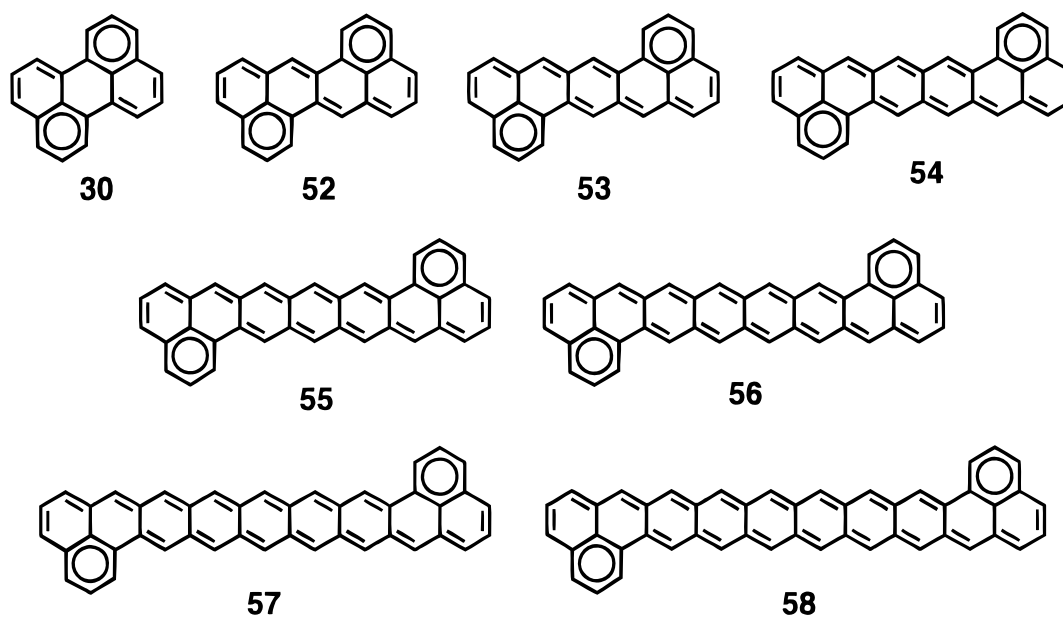
Group G molecules (**33, 30, 49–51**) are also closed-shell substructures of **P3** with no band gap.^{20,22} As there always are only two aromatic sextets in the Clar structure, higher members must be kinetically very unstable with much smaller D_{as} values. The reduced HOMO–LUMO gap of **51** is less than unity, so it must be extremely reactive.

Group H molecules are **30**, zethrene (**52**), and related PAHs with fixed double bonds (**53–58**). They are formally substructures of **P1**, although there is one additional benzene ring at each edge. There are two aromatic sextets localized on the four edge rings. Since there are many polyene-like fixed double bonds in other rings, these molecules must be very reactive with very small D_{as} values. In line with this prediction, they have very small reduced HOMO–LUMO gaps. Heptazethrene (**53**)

TABLE 5: Reduced HOMO–LUMO Gaps and Related Quantities for Typical PAHs and Poly(*p*-phenyl)s

species	N_C	T value		reduced HOMO–LUMO gap	D_{as}
		polyene reference	real molecule		
Group A					
pyrene (21)	16	7.86	14.24	1.811	0.75
anthanthrene (22)	22	8.00	12.80	1.599	0.55
23	28	7.85	10.87	1.385	0.43
24	34	7.56	9.08	1.201	0.35
25	40	7.23	7.57	1.048	0.30
26	46	6.88	6.35	0.923	0.26
Group B					
pyrene (21)	16	7.86	14.24	1.811	0.75
peropyrene (27)	26	8.41	14.80	1.761	0.69
28	36	8.70	15.05	1.731	0.67
29	46	8.88	15.19	1.712	0.65
Group C					
naphthalene (2)	10	7.07	12.36	1.748	0.60
perylene (30)	20	8.50	13.89	1.634	0.60
terrylene (31)	30	8.96	14.46	1.615	0.60
quaterylene (32)	40	9.16	14.76	1.611	0.60
Group D					
benzene (1)	6	6.21	12.00	1.932	1.00
biphenyl (33)	12	8.75	16.91	1.932	1.00
triphenylene (34)	18	9.36	24.63	2.630	1.00
35	24	10.36	26.64	2.571	1.00
36	30	11.03	30.18	2.736	1.00
37	36	11.77	32.54	2.763	1.00
38	40	12.42	35.13	2.829	1.00
39	46	13.07	37.58	2.874	1.00
Group E					
naphthalene (2)	10	7.07	12.36	1.748	0.60
pyrene (21)	16	7.86	14.24	1.811	0.75
40	22	8.92	19.33	2.166	0.82
41	28	9.74	21.97	2.256	0.86
42	34	10.53	25.64	2.436	0.88
43	40	11.28	28.55	2.531	0.90
44	46	11.99	31.66	2.641	0.91
Group F					
pyrene (21)	16	7.86	14.24	1.811	0.75
coronene (45)	24	8.96	25.88	2.888	0.75
ovalene (46)	32	9.26	21.50	2.321	0.75
circumanthracene (47)	40	9.08	17.05	1.877	0.60
48	48	8.66	13.22	1.526	0.50
Group G					
biphenyl (33)	12	8.75	16.91	1.932	1.00
perylene (30)	20	8.50	13.89	1.634	0.60
bisanthene (49)	28	7.61	9.94	1.306	0.43
50	36	6.68	6.82	1.022	0.33
51	44	5.84	4.69	0.803	0.27
Group H					
perylene (30)	20	8.50	13.89	1.634	0.60
zethrene (52)	24	7.52	9.54	1.268	0.50
heptazethrene (53)	28	6.85	7.17	1.047	0.43
54	32	6.36	5.72	0.901	0.38
55	36	5.98	4.76	0.797	0.33
56	40	5.67	4.07	0.718	0.30
57	44	5.42	3.56	0.656	0.27
58	48	5.21	3.16	0.607	0.25
Group I					
biphenyl (33)	12	8.75	16.91	1.932	1.00
triphenylene (34)	18	9.36	24.63	2.630	1.00
35	24	10.36	26.64	2.571	1.00
36	30	11.03	30.18	2.736	1.00
59	36	11.68	36.51	3.126	1.00
60	42	11.56	39.04	3.376	1.00
Group J					
benzene (1)	6	6.21	12.00	1.932	1.00
biphenyl (33)	12	8.75	16.91	1.932	1.00
61	18	10.54	21.34	2.024	1.00
62	24	12.14	25.73	2.120	1.00
63	30	13.68	30.19	2.207	1.00
64	36	15.20	34.71	2.283	1.00
65	42	16.73	39.28	2.348	1.00
66	48	18.27	43.91	2.403	1.00

Group A**Group B****Group C****Group D**

Group E**Group F****Group G****Group H**

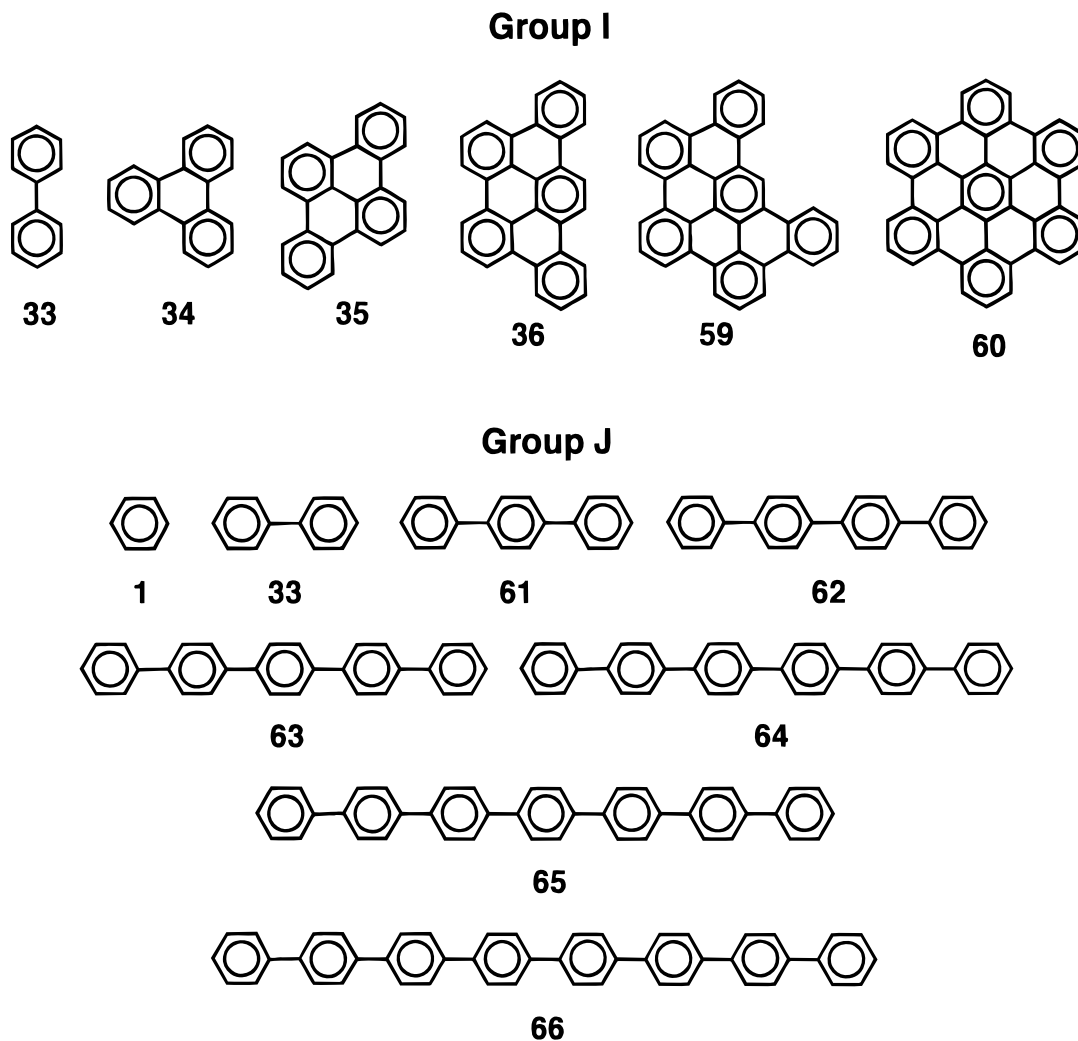


Figure 4. Clar structures of typical PAHs.

is highly reactive.^{12,13} Higher members have reduced HOMO–LUMO gaps < 1.00 .

Group I molecules consist of hexabenzo[*bc,ef,hi,kl,no,qr*]-coronene (**60**) and its fully benzenoid substructures (**33–36**, **59**). Like group D molecules, these fully benzenoid species are kinetically very stable, with D_{as} values of 1.00. They have very large reduced HOMO–LUMO gaps, in line with their chemistry. Indeed, **60** is one of the kinetically most stable PAH molecules ever prepared.^{12,13} It has the largest reduced HOMO–LUMO gap among the molecules listed in Table 5.

As already mentioned, group J molecules are polyphenyls (**1**, **33**, **61–66**). Infinitely large polyphenyl (**P3**) has a large band gap of $0.828|\beta|$.²² Therefore, higher members of polyphenyl have larger reduced HOMO–LUMO gaps. The high kinetic stability of benzene is preserved in the benzene rings of biphenyl (**33**) and higher members of polyphenyl. The D_{as} values for all members are equal to unity, indicating that they are a kind of fully benzenoid hydrocarbons.

Reduced HOMO–LUMO gaps for some other PAHs are listed in Table 6. Their Clar structures are presented in Figure 5. Pyranthrene (**67**), violanthrene (**68**), and isoviolanthrene (**69**) are kinetically stable with moderately large reduced HOMO–LUMO gaps. Circobiphenyl (**70**) has very large reduced HOMO–LUMO gap. Clar noted that this molecule is kinetically as stable as fully benzenoid hydrocarbons.^{12,13} Kekulene (**71**) is also kinetically very stable.³⁰ Its Clar structure resembles those of the zigzag polyacenes, in that aromatic sextets are placed

TABLE 6: Reduced HOMO–LUMO Gaps and Related Quantities for Some Other PAHs

species	N_C	T value		reduced HOMO–LUMO gap	D_{as}
		polyene reference	real molecule		
pyranthrene (67)	30	8.96	15.48	1.727	0.60
violanthrene (68)	34	9.12	16.00	1.754	0.71
isoviolanthrene (69)	34	8.97	15.40	1.716	0.53
circobiphenyl (70)	38	10.30	31.18	3.027	0.79
kekulene (71)	48	12.74	41.97	3.294	0.75
72	26	10.73	26.60	2.479	0.92
vinylcoronene (73)	26	9.28	24.21	2.608	0.69

alternately with localized double bonds along the linear array of benzene rings. This may be the reason the reduced HOMO–LUMO gap of **71** is very large. Note that higher members of the zigzag polyacenes have very large reduced HOMO–LUMO gaps.

We have shown that the definition of the reduced HOMO–LUMO gap can be applied fairly reasonably to a variety of PAH molecules. However, there is no guarantee that it can be applied satisfactorily to all PAH molecules. In particular, the reduced HOMO–LUMO gap of a molecule with extremely reactive sites may fail to predict the kinetic instability of the molecule. As shown in Figure 5, **72** has as many as four aromatic sextets in its Clar structure. Therefore, the reduced HOMO–LUMO gap of this molecule is comparable to those of fully benzenoid hydrocarbons. However, the central double bond is very reactive

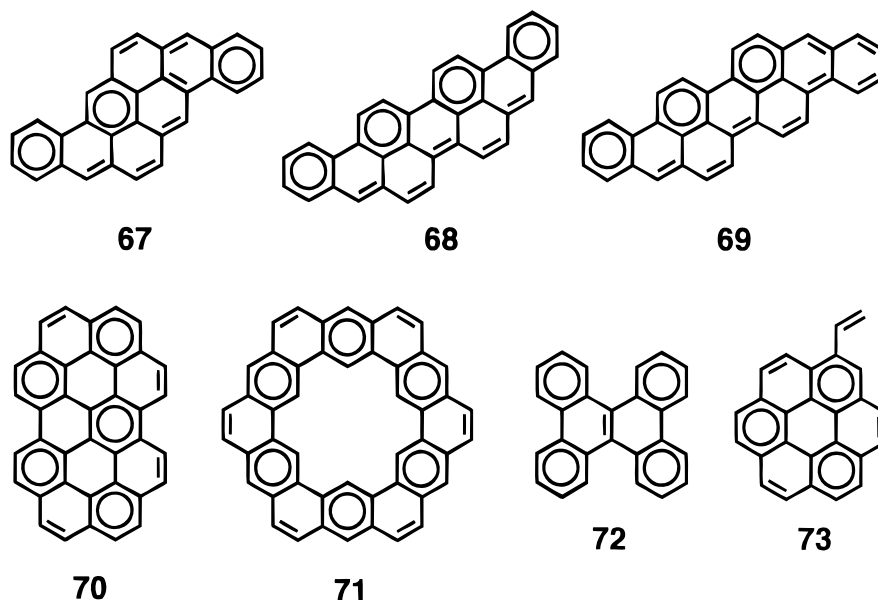


Figure 5. Clar structures of some other PAHs.

and is readily oxidized, with retention of four aromatic sextets.^{12,13} The reduced HOMO–LUMO gap of vinylcoronene (**73**) is comparable to that of coronene (**45**), although the former must be chemically reactive at the substituent.

Concluding Remarks

The very successful application of the T value to fullerenes may be partly due to the fact that they all are homologous, in the sense that all carbon atoms are connected to three other ones.^{17–19} As mentioned, the T values for the polyene references of fullerenes investigated are very close to each other. In marked contrast, the polyene references of PAH molecules have widely varied HOMO–LUMO gaps. As shown in Figure 4, many different homologous series are conceivable for PAH molecules. In this view, it seems that the reduced HOMO–LUMO gap is preferred as an index of kinetic stability to the T value.

It is noteworthy that PAHs with the reduced HOMO–LUMO gaps < 1.30 are chemically very reactive in general. Most of them have D_{as} values < 0.40 . Thus, aromatic benzenoid systems are not always kinetically stable. The reduced HOMO–LUMO gap < 1.00 indicates that the HOMO of the molecule contributes to the decrease in the topological resonance energy.^{25,26} Kinetically stable PAHs have larger reduced HOMO–LUMO gaps. However, we cannot differentiate, say, the kinetic stabilities of molecules with reduced HOMO–LUMO gaps > 2.00 . Many of the PAH molecules with large reduced HOMO–LUMO gaps are closed-shell substructures of nonmetallic one-dimensional benzenoid polymers.

In fact, it seems that the T value is still useful if only we assume that PAH molecules with large or very large T values are all kinetically stable. These molecules really have fairly or very large D_{as} values. We might say rather safely that PAH molecules with the T values < 10.0 are fairly or very reactive. In the case of isolated-pentagon fullerene isomers, those with the T values < 11.0 were presumed to be kinetically unstable under harsh experimental conditions.^{17,19} For reference, T values for linear polyenes lie in the range 4.00–6.28.

It is very true that the HOMO and the LUMO play a dominant role in many chemical reactions.³¹ However, when it comes to molecules formed by many atoms, many high-lying occupied

MOs and low-lying unoccupied MOs must in principle be taken into account to predict kinetic stability.³² Therefore, it is somewhat strange that a fairly acceptable prediction of kinetic stability can be made in terms of the reduced HOMO–LUMO energy separation. We cannot fully understand why this can be done. All we can say at present is that the reduced HOMO–LUMO gap by definition is closely related to aromaticity.

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