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THERMAL REACTIVITIES OF POLYNUCLEAR AROMATIC HYDROCARBONS AND ALKYL DERIVATIVES

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Abstract—The HMO free valence, the PMO Dewar reactivity number, and the structure count ratio are correlated with thermal reactivities of polynuclear aromatic hydrocarbons and derivatives. The compounds are classified as thermally reactive if carbonaceous residues are observed upon heating to 750° (Experimental, Ref. 13). Radical intermediates are assumed to mediate the pyrolytic reactivities. The structure count ratio which is the ratio SC (radical intermediate) ÷ SC (reactant) is recommended as a simple working method for correlating and predicting thermal reactivity.

An understanding of the thermal reactions of polycyclic aromatic hydrocarbons and their derivatives has practical pertinence to coal chemistry and to chemical carcinogenesis. Yokono *et al.* have recently suggested[2] that the thermal reactivity of the polynuclear aromatic hydrocarbons can be understood in terms of the maximum value of the free valence as calculated by the Hückel molecular orbital (HMO) method.[3,4] This suggestion is based on a presumed correlation between free radical reactivities and free valence values. It is therefore of interest to critically examine free valence and other types of reactivity indices in this regard. In general, the free valence has not proved to be the most successful quantitative measure of reactivities in past structure-reactivity studies.[4]

The simplest HMO reactivity index is the Dewar number, calculated by perturbational MO theory.[5] Dewar numbers can be defined for deletion or addition of an orbital from or to a reactant π system, and the calculated indices correspond to the π-energy change for each reaction. In contrast to the free valence and other calculated HMO quantities ($\pi\Delta E$, bond orders, charge densities, etc), Dewar numbers are obtainable by simple hand calculation. Even so, PMO calculations have recently been shown to reproduce SCF and observed heats of formation of π radicals.[6] Any utility for correlating the thermal reactivity of π hydrocarbons would of course be related to the fact that the PMO method gives accurate π resonance energy differences between reactant and derived π radicals.

Resonance energy differences for formation of π hydrocarbon radicals can also be calculated using the empirical parameterized valence bond method termed structure-resonance theory.[1b,7-9] These calculations are likewise carried out by hand, and the results are in good quantitative agreement with SCF calculations[7] and with kinetic data[8-12] which experimentally model the differences in resonance energies between reactants and radical intermediates. The free valence index gave a relatively poor correlation with the same kinetic data,[8,10,11] sô one may infer that structure-resonance calculations would also be in better qualitative correspondence to thermal stabilities.

An appropriate qualitative resonance theory reactivity index is the structure count (SC) ratio, i.e. SC (radical intermediate) ÷ SC (reactant), and it is a particularly easy quantity to calculate. A comparison of thermal stabilities of aromatic hydrocarbons and derivatives[13] with SC ratios, Dewar numbers, and free valencies will therefore be given below in order to allow a judgement of relative usefulness. This comparison will be preceded by a brief listing of the results of some previous experimental and theoretical studies of π-hydrocarbon radical reactivities, including a short summary and a criticism of the work of Yokono *et al.*[2] A graph-theoretical structure count algorithm will be illustrated in an appendix.

π-Hydrocarbon radical reactivities and reactivity indices

Lewis and Edstrom[13] have provided qualitative thermal reactivity data of the type to be discussed in this paper. They classified polynuclear aromatic hydrocarbons as thermally reactive based on whether or not carbonaceous residues were observed after heating to 750°. Eighty-four polycyclic benzenoid hydrocarbons, polyphenyls, vinyl and alkyl derivatives, and nonalternant systems were tested, and 25 were found to be reactive. It was postulated that the pyrolyses of the active compounds involved free radical intermediates obtained by bond cleavages, condensations, hydrogan transfers, or thermal rearrangements.

Yokono *et al.*[2] proposed that the free valence at the most reactive position of a polynuclear aromatic hydrocarbon could account for the free radical activity. They examined a subset of 28 benzenoid compounds studied by Lewis and Edstrom, and they stated that a free valance value of 0.530 correctly delineated reactivity in 25 cases. As will be seen later, some of the other benzenoid and nonalternant compounds not included in their study also provide exceptions to their empirical choice of a critical free valence value. In addition, three of the 28 compounds which they list as having been investigated by Lewis and Edstrom[12] are not actually contained in the original experimental study. For these reasons, it is felt that the Yokono *et al.* results did not constitute a decisive reactivity index test.

Dickerman *et al.* have obtained precise relative rate data for homolytic substitution of phenyl radicals in polycyclic aromatic hydrocarbons.[11] Unruh

$$C_6H_5\cdot + ArH \rightarrow [C_6H_5ArH\cdot] \rightarrow C_6H_5Ar \qquad (1)$$

and Gleicher determined relative rates for trichloromethyl radical abstraction from arylmethanes.[10] These data can be used to test the free valence and other

$$CCl_3\cdot + ArCH_3 \rightarrow [ArCH_2\cdot + HCCl_3] \rightarrow \text{Products} \quad (2)$$

calculated radical reactivity indices for quantitative correspondence of theory and experiment. Older homolytic substitution and abstraction data[14] are not as useful because product mixtures were not analyzed, and it has been established that several isomeric products are usually obtained in reactions of these types.

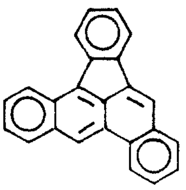
Correlation coefficients of theoretical calculations with ln (relative rate) values are given in Table 1.[8,10,11] The structure-resonance theory calculations assume that the resonance energy of a π-radical or of a neutral benzenoid hydrocarbon can be obtained by use of the algorithm $\beta \ln(SC)$ (β = constant). The justifications for this assumption have been discussed in detail previously,[8,15] and utility in correlating SCF π resonance energies[10] with the enthalpies of formation of highly stabilized arylmethyl π radicals has been demonstrated.[7,9] One concludes that a resonance theory approach or the Dewar number is reliable for the free radical reactivity data referred to in Table 1, and the free valence is found to be not as dependable.

Thermal reactivities of π-hydrocarbons

Polynuclear aromatic compounds. Structures for the fully aromatic compounds pyrolyzed by Lewis and Edstrom[13] are given in Fig. 1. Nonplanar polyphenyl-type compounds and molecules with essential double bonds are excluded and will be discussed separately. The Fig. 1 compounds are also listed in Table 2 in order of increasing SC ratio for the single position in each compound that would give rise to the most highly resonance stabilized radical. Homolytic radical addition and substitution is therefore implicitly assumed to be responsible for thermal reactivity. The SC which is used in this table is the corrected SC,[16] which in the case of the nonalternant radicals is actually less than the number of possible resonance structure drawings. The corrected SC does correspond to the number of canonical Kekule structures as explained by Pauling and Wheland,[17] and a graph-theoretical algorithm for determining the number of canonical Kekule structures is given in the appendix. It should be noted that Stein and Golden[7] have suggested that the Kekule SC for nonalternant radicals be halved to give a corrected SC value that corresponds to experimental values of π resonance stabilization energies. However, the use of corrected SC = canonical Kekule SC is consonant with the valence bond interpretation of resonance energies,[1b,8] and in any case gives values close to those assumed by Stein and Golden.

The critical values to predict thermal reactivity are SC ratio $\geqq 4.889$, Dewar number $\leqq 0.626$, and free valence > 0.520. These chosen values given the minimum number of incorrect prediction (3, 4 and 7, respectively) for each theoretical approach. However, two of the misclassified cases should not be considered as incorrect. The first, benzcoronene, actually has a minimum reaction temperature of 637° which is over 50° higher than that for any other active compound,[13] and which far exceeds the b.p. of any nonactive compound. Considering these facts, the thermal properties of benzocoronene are therefore consistent with its low SC ratio and high Dewar number.

The second case is the compound identified in the Lewis–Edstrom work[13] as dibenz[a,l]pyrene, **29** in Table 2. The compound formerly known as dibenz[a,l]pyrene was shown[18] to be dibenz[a,e]fluoranthene, **39**, subsequent to the Lewis–Edstrom publication. However, the recorded m.p.[19] of **39** is 6° higher than the compound



39

SC = 14
radical SC = 72
SC ratio = 5,143
m. pt. = 232°C

Table 1. Correlation coefficients, radical reactivities and reactivity indices

Type of Reaction	Type of Correlation with ln(relative rate)	Corr. coeff.
ArH + $C_6H_5\cdot$ (Meerwein arylation, 13 sites of reaction in 6 compounds)[a]	HMO Localization Energy	0.960[b]
	PMO Dewar Numbers	0.964[b]
	Free Valence	0.876[b]
	Structure-Resonance Theory	0.976[c]
Arylmethanes + CCl_3 (13 compounds)[d]	HMO $\Delta E(\pi$ Energy)	0.855[d]
	PMO Dewar Numbers	0.926[b]
	SCF $\Delta E(\pi$ Energy)	0.977[d]
	Free valence	0.828[e]
	Structure-resonance theory	0.951[c]

[a] Ref. 11. [b] This work. [c] Ref. 8. [d] Ref. 10. [e] Defined for the position adjacent to the methyl group. G. J. Gleicher, personal communication.

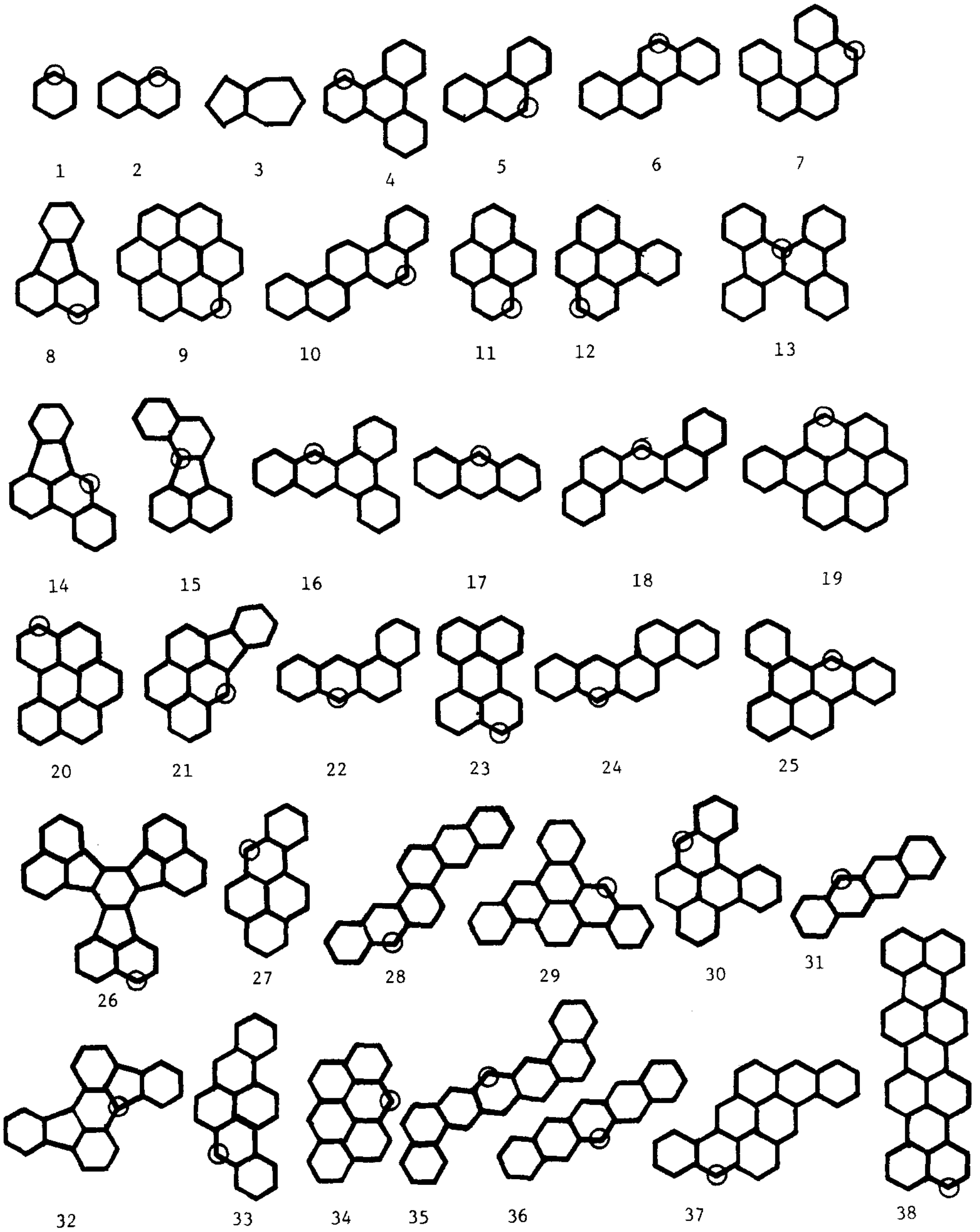


Fig. 1. Structures for compounds in Table 2. The calculated most reactive position is circled. Unsaturation is not depicted.

investigated by Lewis and Edstrom, so the true identity of **29** in the pyrolysis study must be considered to be in doubt. Using the SC method, the borderline compound benz[a]pyrene, **29**, SC ratio = 5.000, remains as the only real exception in classifying the thermally reactive compounds in Table 2. Three values of the free valence are not available in the current literature, but the inclusion of these values could not alter the conclusion that the SC ratio is the more dependable quantity for classifying thermal reactivity in this group of compounds.

Dewar numbers cannot be calculated for the nonalternant radical species in Table 2 because they do not possess a nonbonding MO.[20] In the alternant system cases, the Dewar number does seem to provide an excellent correlation of the experimental data, but the exclusion of nonalternant compounds is a definite liability. The Dewar numbers and the SC ratio values closely parallel one another, in agreement with the results summarized in Table 1, where both methods are in better agreement with the free radical kinetic data than is the free valence.

Alkyl derivatives. Aromatic compounds with attached saturated moieties are depicted in Fig. 2 and listed in Table 3. For this group of compounds, homolytic fission of a benzyl-type C–H bond or abstraction of a benzyl-type hydrogen atome is assumed to mediate the pyrolytic reactivity. In the case of 9,9′-bifluorenyl, **66**, CC bond fission is assumed. Using the same critical value of the SC ratio as determined for the compounds in Table 2, the only misclassified compound is 9-methylanthracene with a borderline structure count ratio of 5.000. The Dewar number also gives a reasonable correlation of the experimental data, if a new critical value of 0.54 is defined. Again, the Dewar number correlation is limited to the alternant systems.

The advantages of a structure-resonance theory approach are pointedly illustrated by the results for the compounds in Table 3. It is possible, of course, to calculate the free valence of the π-radical at the position of abstraction or bond fission. However, this calculated quantity has no theoretical relationship to the kinetic stability of the parent alkyl-substituted aromatic hydrocarbon. Therefore the thermal reactivity of these hydrocarbons cannot be rationalized using the free valence.

Failures. Structure-resonance theory assumes that a π molecular species can be described as a resonance hybrid of principal resonance structures, and effective resonance interactions require an essentially planar π system. Also, in the present applications to thermal reactivities, the primary reactions have been assumed to

Table 2. Structure count ratios, Dewar numbers, and free valancies for the most reactive position in polynuclear aromatic hydrocarbons[a]

No.	Compound	SC(R•)/SC(RH)	SC ratio	Dewar No.	Free Valence
1	Benzene	5/2	1.500	1.155	0.399
2	Naphthalene	7/3	2.333	0.905	0.453
3	Azulene	5/2	2.500		0.482
4	Triphenylene	23/9	2.556	1.000	0.439
5	Phenanthrene	13/5	2.600	0.891	0.451
6	Chrysene	26/8	3.250	0.834	0.457
7	Dibenz[c,g]phenanthrene	43/13	3.307	0.870	0.453
8	Fluoranthene	20/6	3.333		0.469
9	Coronene	68/20	3.400	0.898	0.449
10	Picene	45/13	3.462	0.834	0.457
11	Pyrene	21/6	3.500	0.756	0.468
12	Benz[e]pyrene	40/11	3.636	0.815	0.463
13	Tetrabenznaphthalene	88/24	3.667	0.885	
14	Benz[b]fluoranthene	38/10	3.800		0.507
15	Benz[j]fluoranthene	35/9	3.889		0.473
16	Dibenz[a,c]anthracene	51/13	3.923	0.752	0.499
17	Anthracene	16/4	4.000	0.632	0.520
18	Dibenz[a,h]anthracene	48/12	4.000	0.756	0.498
19	Benzcoronene	136/34	4.000*	0.838*	
20	Benz[g,h,i]perylene	56/14	4.000	0.773	0.456
21	1,10-*o*-Phenylenepyrene	49/12	4.083		
22	Benz[a]anthracene	29/7	4.143	0.711	0.515
23	Perylene	40/9	4.444	0.667	0.473
24	Dibenz[a,h]phenanthrene	49/11	4.455	0.645	0.517
25	Dibenz[a,e]pyrene	83/17	4.882	0.681	0.512
26	Decacyclene	264/54	4.889		0.472*
27	Benz[a]pyrene	45/9	5.000*	0.577*	0.530*
28	Dibenz[b,k]chrysene	75/15	5.000	0.626	0.517*
29	Tribenz[a,e,i]pyrene	145/27	5.370	0.650*	0.513*
30	Dibenz[a,l]pyrene[b]	86/16	5.375*,[b]	0.608*,[b]	0.526*,[b]
31	Tetracene	27/5	5.400	0.513	0.529
32	Rubicene	88/16	5.500		0.468*
33	Dibenz[a,i]pyrene	80/14	5.714	0.557	0.531
34	Anthanthrene	58/10	5.800	0.513	0.531
35	Dibenz[a,i]pentacene	140/20	7.000	0.478	0.536
36	Pentacene	45/6	7.500	0.400	0.540
37	Pyranthene	195/25	7.800	0.457	0.539
38	Quaterrylene	688/81	8.494	0.485	0.476*

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[a] Thermally reactive compounds (ref. 13) are underlined. Incorrectly classified compounds are starred. [b] Misidentified compound. See text.

be radical reactions. Figure 3 gives the structures, and Table 4 summarizes reactivity indices for compounds in which one or both of these restrictions may be violated. A compound is calculated to be reactive using the same index as used for the compounds in Table 2.

Misclassified compounds **71**, **73** and **77** contain CC double bonds conjugated with aromatic moieties. Pryor and Lasswell have shown that these types of compounds can undergo spontaneous polymerization via Diels–Alder-type condensation reactions,[21] and this kind of reaction could then account for the anomalous predicted non-reactivity. Even though the reactivity of **76**, 9-benzylidenefluorene is hard to explain on this basis, it is felt that thermal reactions of this type will be generally observed for vinyl-substituted aromatic compounds.

The remaining misclassified compounds, **79**, **81**, **82** and **83** all contain phenyl group substituents and are expected to be substantially nonplanar. If radicals derived by homolytic addition are also nonplanar, the calculated reactivities would be greater than what is experimentally observed. Whatever the correct explanation, the fact remains that the SC ratio is not successful in correlating the pyrolysis of this group of compounds.

CONCLUSION

The least satisfactory aspect of this work is the non-quantitative nature of the experimental data. Acknowledging this limitation, the SC ratio provides a simple working method to correlate and predict the qualitative aspects of the thermal behavior of π polynuclear hydrocarbons. There are some exceptions but the anomalous cases can be easily understood on the basis of structural or mechanistic considerations.

Several examples of congruities between the quantitative aspects of structure-resonance theory and SCF or HMO calculations have been recently demonstrated.[1b] One can conclude that all three methods give reasonable results, although the structure-resonance method involves less computational effort. Considering this ease of application, and the good correspondence of calculations with experimental properties, the structure resonance method seems to provide a useful alternative to MO calculations for correlating structure-reactivity data.

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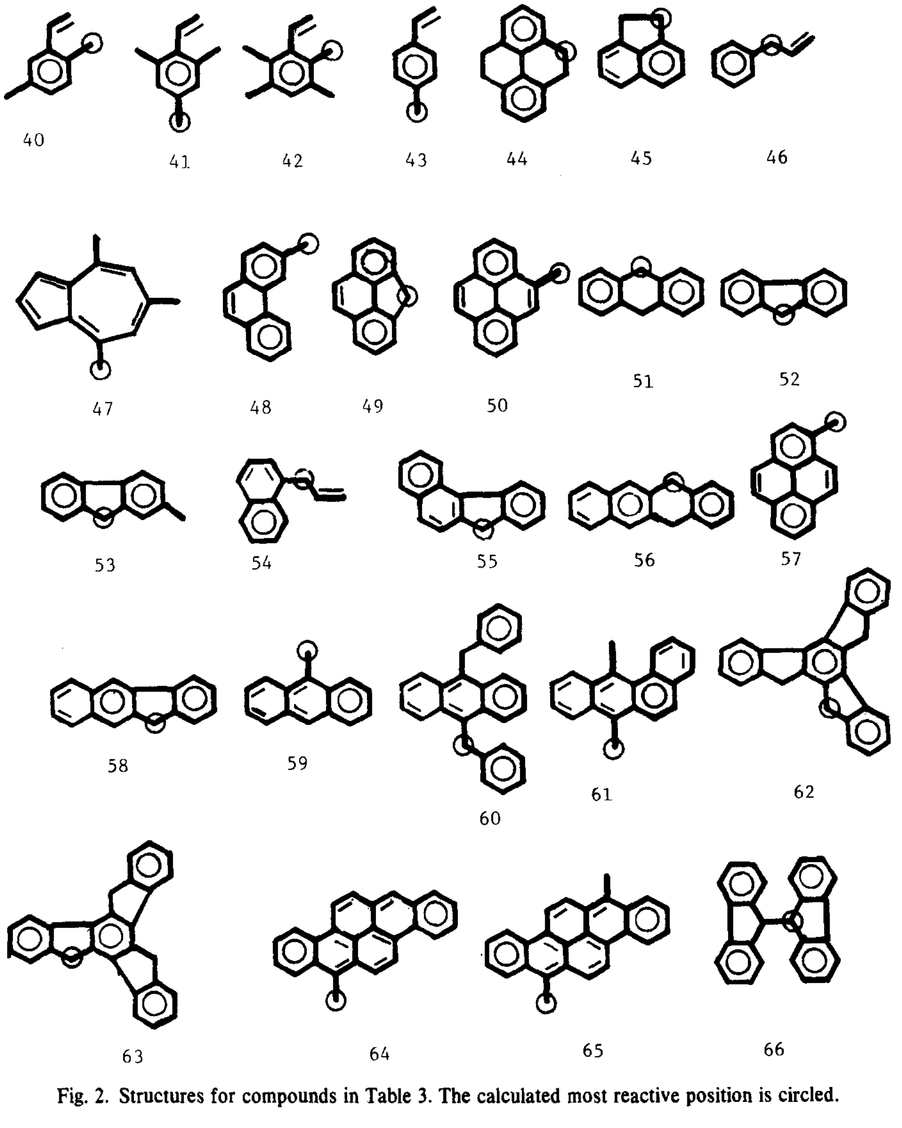

Fig. 2. Structures for compounds in Table 3. The calculated most reactive position is circled.

Table 3. Structure count ratios and Dewar numbers for the most reactive position in alkyl derivatives of aromatic hydrocarbons[a]

No.	Compound	SC(R·)/SC(RH)	SC ratio	Dewar Number
40	Vinylxylene	6/2	3.000	0.707
41	Vinylmesitylene	6/2	3.000	0.707
42	Vinyldurene	6/2	3.000	0.707
43	Vinyltoluene	6/2	3.000	0.707
44	Tetrahydropyrene	13/4	3.250	0.718
45	Acenaphthene	10/3	3.333	0.671
46	3-Phenylpropene	7/2	3.500	0.603
47	4,6,8-Trimethylazulene	7/2	3.500	
48	3-Methylphenanthrene	19/5	3.800	0.714
49	4,5-Methylenephenanthrene	19/5	3.800	
50	4-Methylpyrene	23/6	3.833	0.643
51	9,10-Dihydroanthracene	16/4	4.000	0.632
52	Fluorene	16/4	4.000	
53	2-Methylfluorene	16/4	4.000	
54	1-Allylnaphthalene	13/3	4.333	0.557
55	Benz[a]fluorene	26/6	4.333	
56	5,12-Dihydronaphthacene	27/6	4.500	0.616
57	1-Methylpyrene	27/6	4.500	0.603
58	Benz[b]fluorene	27/6	4.500	
59	9-Methylanthracene	20/4	5.000*	0.534
60	9,10-Dibenzylanthracene	40/8	5.000	0.485
61	7,12-Dimethylbenz[a]anthracene	36/7	5.143	0.560*
62	10,15-Dihydro-5H-diendeno[1,2-a:1′,2′-c]fluorene	88/16	5.500	
63	10,15-Dihydro-5H-diendeno[2,1-a:1′,2′-c]fluorene	88/16	5.500	
64	1-Methyldibenz[b,i]pyrene	96/13	7.385	0.452
65	1,6-Dimethydibenz[b,i]pyrene	96/13	7.385	0.452
66	9,9′-Bifluorenyl	256/16	16.000[b]	

[a] Thermally reactive compounds (ref. 13) are underlined. Incorrectly classified comcompounds are starred. [b] CC bond cleavage to give fluorenyl radicals is assumed.

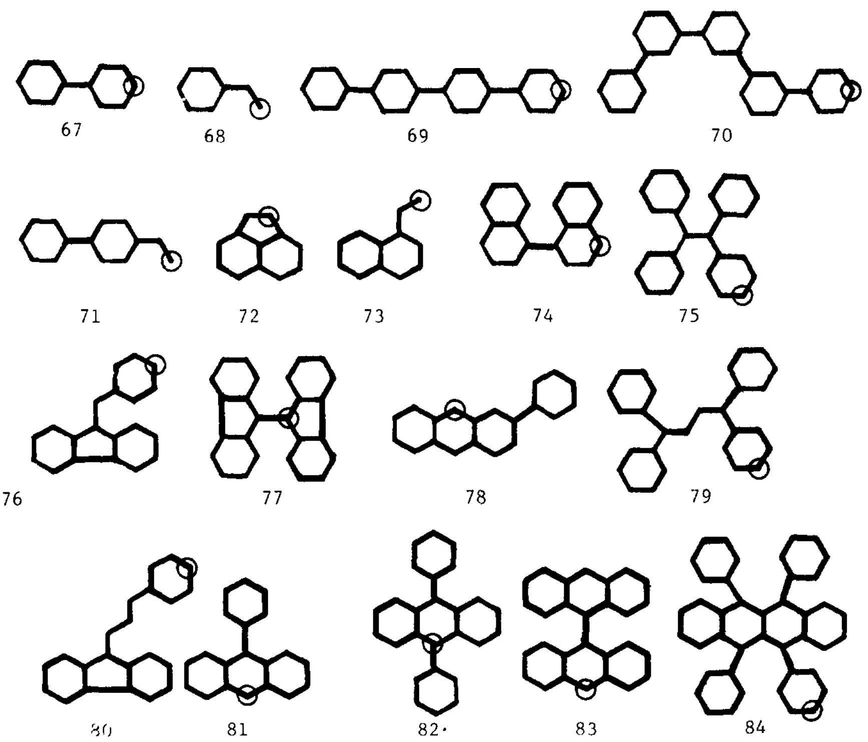

Fig. 3. Structures for compounds in Table 4. The calculated most reactive position is circled. Unsaturation is not depicted.

Table 4. Reactivity indices for polyphenyl-type and compounds containing essential CC double bonds[a]

No.	Compound	SC(R•)/SC(RH)	SC ratio	Dewar No.	Free Valence
67	Biphenyl	9/4	2.250	1.033	0.399
68	Styrene	5/2	2.500	0.756	0.821*
69	p-Quarterphenyl	45/16	2.813	1.002	0.438
70	m-Quinquephenyl	96/32	3.000	0.943	
71	4-Vinylbiphenyl	13/4	3.250*	0.718*	0.825
72	Acenaphthylene	10/3	3.333		0.478
73	1-Vinylnaphthalene	10/3	3.333*	0.671*	0.833
74	1,1'-Binaphthyl	35/9	3.890	0.753	0.469
75	Tetraphenylethylene	64/16	4.000	0.632	0.447
76	9-Benzylidenefluorene	32/8	4.000		
77	9,9'-Bifluorenylidene	64/16	4.000*		0.447
78	2-Phenylanthracene	38/8	4.750	0.610*	
79	1,1,4,4-Tetraphenylbutadiene	80/16	5.000*	0.535*	
80	9-Cinnamylidenefluorene	40/8	5.000		
81	9-Phenylanthracene	44/8	5.500*	0.555*	
82	9,10-Diphenylanthracene	88/16	5.500*	0.555*	
83	9,9'-Bianthryl	128/16	8.000*	0.447*	
84	5,6,11,12-Tetraphenylnaphthacene	672/80	8.400	0.432	

[a] Thermally reactive compounds (ref. 13) are underlined. Incorrectly classified compounds are starred.

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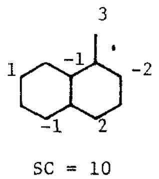
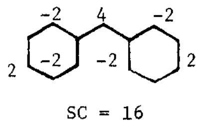
APPENDIX

Structure count. The number of principal[22] resonance structures is the sum of the absolute values of the unnormalized coefficients of a nonbonding molecular orbital. The coefficients follow the zero-sum rule and can be written by inspection. The procedure is illustrated below for α-methylnaphthyl and diphenylmethyl radicals. Each coefficient corresponds to the number of principal resonance structures that can be drawn with the odd electron localized at the site of the coefficient. For this reason, the smallest coefficient in the diphenylmethyl molecular graph is two rather than unity.



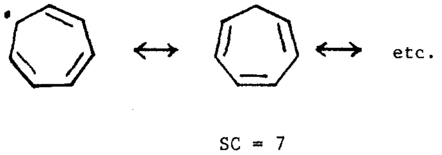
SC = 10



SC = 16

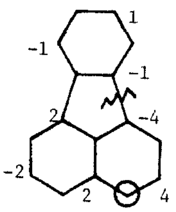
Canonical Kekule structure count. In alternant systems, the SC as obtained above corresponds to the number of canonical Kekule structures. The reader is referred to Pauling and Wheland[17] for the definition of a cononical structure. In general, nonalternant systems have fewer canonical Kekule structures than the total number of resonance structures. For example, cyclopentadienyl and cycloheptatrienyl radicals possess 3 and 4 canonical Kekule structures, respectively.

SC = 5
CSC = 3

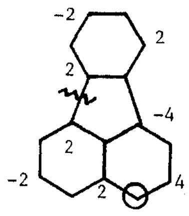


SC = 7
CSC = 4

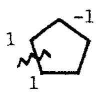
The canonical Kekule structure count is obtained by the following procedure, illustrated for 9-vinylfluorenyl. This is the radical one could obtain by homolytic substitution at the 3-position of fluoranthene or by abstraction of hydrogen from 9-ethylidenefluorene.



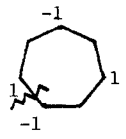
CSC = 15



CSC = 20



CSC = 3



CSC = 4

Odd-membered rings in the nonalternant molecular graph are severed in all possible ways so as to leave an alternant molecular graph. The zero-sum rule coefficients are obtained for each of the alternant systems, and the correct canonical Kekule SC is the largest so obtained, e.g. CSC = 20 for 9-vinylfluorenyl. In the same way, CSC = 3 for cyclopentadienyl and CSC = 4 for cycloheptatrienyl. It is possible to verify that this procedure works by making use of the Rumer-Pauling[24,25] diagramatic methods for drawing all canonical structures. The fact that some Kekule structures in nonalternant systems are noncanonical was first pointed out by Pauling and Wheland.[17]