***cis-exo*-2,3-Dideuteriobicyclo[2.1.0]pentane (7).** About 400 mL of an approximately 1% solution of bicyclo[2.1.0]pent-2-ene[16] in tetrahydrofuran was added to 20.0 g (0.118 mol) of potassium azodicarboxylate[19] in an ice bath cooled 1000-mL flask under nitrogen. The mixture was stirred and treated with 14 mL of CH_3COOD added dropwise over a 30-min period at 0 °C. The stirred reaction mixture was maintained at 0 °C another 2.5 h and then allowed to warm to room temperature. Two hours later, GLC analysis on a 3 mm × 5 m $\beta\beta\beta$ TCEP column at 25 °C showed that no bicyclopentene remained. The mixture was filtered and concentrated by distillation, first using a 50-cm Vigreux column and then a 60-cm Teflon spinning-band column; the labeled bicyclopentane **6** (768 mg) was obtained in pure form by preparative GLC on a 6 mm × 5 m $\beta\beta\beta$ TCEP column at 25 °C.

***cis-exo*-2,3-Dideuterio-1-methylbicyclo[2.1.0]pentane (10).** About 200 mL of an approximately 1% solution of methylbicyclo[2.1.0]pentenes[17] in tetrahydrofuran was combined with 5 g (0.03 mol) of potassium azodicarboxylate and then treated with 3.5 mL of CH_3COOD in a procedure analogous to that detailed above. When GLC analysis indicated that reduction by dideuteriodiimide was complete, the reaction mixture was filtered through coarse sintered glass at an aspirator; the filtrate was diluted with ice–water and extracted with pentane; the hydrocarbon phase was washed with 15 20-mL portions of water, and the labeled 1-methylbicyclo[2.1.0]pentane was obtained in pure form by preparative GLC on a 6 mm × 5 m $\beta\beta\beta$ TCEP column, first at 50 °C and for the second and final chromatography at 25 °C.

Two preparations on this scale gave 322 mg of the deuterated product **10**.

***exo*- and *endo*-5-Methylbicyclo[2.1.0]pentane (14 and 15).** 5-Methylcyclopentadiene was prepared by the method of McLean and Haynes.[21] To about 1000 mL of diglyme which had been freshly distilled from sodium was added 82.5 g (1.25 mol) of cyclopentadiene, followed by 28.75 g (1.25 mol) of sodium. The mixture was heated to reflux for 18 h. The resulting purple solution was cooled and added dropwise to 255 g (2.0 mol) of dimethyl sulfate cooled to −10 °C in a 2-L flask equipped with a mechanical stirrer. The reaction mixture was stirred and kept below −10 °C throughout the addition, stirred at −10 °C for another hour after addition was complete, and then stored for 2 h at −20 °C. Distillation from the flask at −10 °C (0.8 mm) gave 8.5 mL of product, which was placed in a 50-mL two-necked round-bottom flask cooled in an ice–salt bath and fitted with an addition funnel containing 15.7 g (0.091 mol) of diethyl azodicarboxylate in 15 mL of ether.[22] The addition was done over a 5-h period with magnetic stirring in a −20 °C cold room. The reaction mixture was placed in a +4 °C cold room overnight and then allowed to warm to room temperature. Solvent was removed at aspirator pressure to leave 21.1 g of a yellow oil. The NMR spectrum of this material (e.g., methyl doublet at δ 0.08, $J = 6$ Hz) was consistent with anticipations for diethyl 2,3-diaza-7-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**12**).

The Diels–Alder adduct was dissolved in 25 mL of absolute ethanol and hydrogenated over 100 mg of 5% palladium-on-carbon in a Parr bottle. The customary workup led to 20.7 g of yellow oil, shown by NMR to be completely reduced.

Dry nitrogen was bubbled for 20 min through 120 mL of mildly warmed ethylene glycol in a 250-mL three-necked flask fitted with magnetic stirrer, condenser, and thermometer. Potassium hydroxide pellets (27.5 g, 0.042 mol) were added in two portions, and the solution was heated to 125 °C. The diazabicycloheptane derivatives **13** (20.7 g, 0.081 mol) were added quickly; the reaction mixture was stirred for 1 h at 125 °C, allowed to cool, and poured slowly into a mechanically stirred mixture of 100 g each of ice and water and 45 mL of concentrated hydrochloric acid. This hydrolysis mixture was warmed to 40 °C and neutralized with 5 N ammonium hydroxide. Six 6-mL portions of 2 N cupric chloride solution were added with stirring. After each of the six additions, enough 5 N ammonium hydroxide was added to bring the pH to 5–6. The brick-red precipitate was collected by filtration; the filtrate was treated again with cupric chloride and ammonium hydroxide solutions, and a second crop of product was thus obtained. The combined precipitate was washed with 100 mL of 20% aqueous ammonium chloride, 200 mL of 95% ethanol, and 200 mL of water. It was sucked as dry as possible on the funnel, then slurried with 40 mL of water, and treated with a slowly added solution prepared from 6 g of sodium hydroxide and 10 mL of water. The resulting orange-yellow suspension was continuously extracted with pentane for 48 h. The hydrocarbon solution was dried over potassium carbonate; filtration and concentration gave 3.45 g of a brown oil. Another 48-h extraction led to another 40 mg of material. The NMR of the 3.49 g of intermediate was consistent with the 2,3-diaza-7-methylbicyclo[2.2.1]hept-2-ene structure **13** expected (yield 50.5% from reduced Diels–Alder adduct).

The azo compound (1.41 g) was placed in a 5-mL flask which was fitted with a 20-cm unpacked column connecting directly to a receiver cooled in a dry ice–acetone bath. The flask was kept at 200–220 °C by an oil bath for 9 h, giving 485 mg of colorless liquid in the receiver. Analytical GLC on a 3 mm × 2.4 m $\beta\beta$ ODPN column at 25 °C showed traces (<2%) of 1-methylbicyclopentane and bicyclopentane and two major products. These were collected by preparative GLC on a 6 mm × 5 m $\beta\beta\beta$ TCEP column at 35 °C and identified through proton and carbon NMR spectra as *exo*-(shorter retention time) and *endo*-5-methylbicyclo[2.1.0]pentane in a 3.5:1 ratio.[23]

Kinetics of the gas-phase isomerizations were determined by using a well-seasoned 300-mL round-bottomed glass vessel with a length of 9-mm glass tubing connected through a "greaseless" Teflon stopcock to a vacuum line. The bath design and temperature control system have been described elsewhere.[25] After each run, hydrocarbons were condensed back in the vacuum line and analyzed either by NMR spectroscopy or GLC. The results are summarized in Table I.

Acknowledgment. Partial support of this work by the National Science Foundation and Hoffmann-LaRoche, Inc., is gratefully acknowledged.

Registry No. 6, 5164-35-2; **7**, 51794-28-6; **8**, 60426-74-6; **9**, 36112-14-8; **10**, 76847-16-0; **11**, 76898-64-1; **12**, 76847-17-1; **13**, 76847-18-2; **14**, 76898-65-2; **15**, 50338-79-9; 5-methylcyclopentadiene, 96-38-8; diethyl azodicarboxylate, 1972-28-7.

Resonance Energies of π Hydrocarbon Radicals. Radical Reactivities of Polycyclic Aromatic Hydrocarbons[1]

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Resonance energies for π hydrocarbon radicals can be calculated by using the empirical, parameterized, valence-bond method called structure-resonance theory. The calculations are in good agreement with kinetic data which experimentally model the difference in resonance energies between reactants and radical intermediates.

Quantitative aspects of aromatic hydrocarbon reactivities are well-described by structure-resonance theory calculations.[2] A recent example[3] involved kinetic studies of the Diels–Alder reactions of 46 polycyclic benzenoid hydrocarbons with second-order rate constants spanning a range of seven powers of ten. The calculations require counting Kekule structures for reactants and products, and the logarithm of the ratio of structure count (SC), e.g., ln ($SC_{product}/SC_{reactant}$), serves as a precise (correlation coefficient 0.99) reactivity index. This index correlates the rate data to a significantly higher degree than do Hückel MO para-localization energies, free valencies, or Dewar reactivity numbers. Since previous work[4] has shown that ln SC is an accurate algorithm for resonance energy, the obtained correlation strongly suggests that the change in π resonance energy is the main variable factor affecting the activation energies of these cycloaddition reactions.

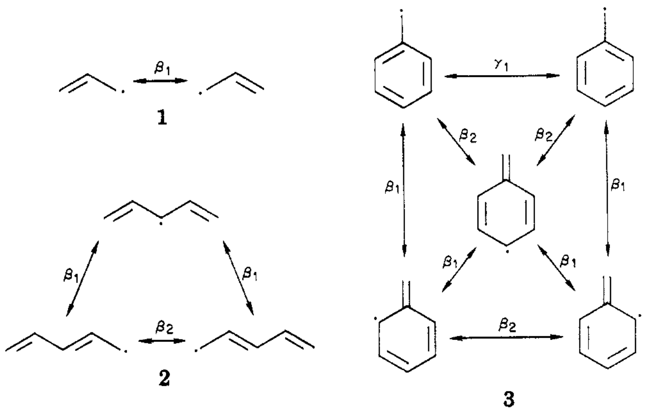
In earlier work,[2] electrophilic and nucleophilic substitution rates, hydrocarbon acidities, and solvolytic reactivities[5] were successfully correlated with calculations involving the counting of principal resonance structures for presumed cationic or anionic intermediates. In these cases, the reaction index used was ln ($SC_{intermediate}/SC_{reactant}$). The index was also compared with resonance energy differences between reactant and intermediate obtained by using LCAO-MO-SCF techniques,[5] and correlation coefficients were always 0.98 or higher. Again, one concludes that differences in π-resonance energies control differences in reactivities. One notes that the extremely simple structure-resonance theory calculations seem to provide a description of π-resonance energies tantamount to that obtained by using SCF-MO procedures.

In this paper, the structure-resonance theory calculations of π-resonance energies will be extended to π hydrocarbon radicals. A partial justification of the empirical structure-resonance theory procedures will be established by comparing the results with resonance energies calculated by the valence-bond method.[6] It has already been demonstrated[7] that relative values of resonance energies for benzyl-type polycyclic aromatic radicals as calculated by SCF-MO methods[8] closely correspond to resonance energies calculated by the resonance theory approach. However, the comparisons with relevant experimental data are lacking and will therefore be given here. In addition, other types of radicals derived from aromatic hydrocarbons will be examined so that other types of radical reactions may be treated. Finally, some comparative remarks will be made regarding recently suggested methods for calculating π-resonance energies which are based on Hess-Schaad-type Hückel MO calculations[9] and graph theory.[10]

Theoretical Procedures

Valence-Bond Theory. The results of the valence bond calculations to be used in this paper were first obtained by Pauling and Wheland.[6a] The calculations were repeated here because of reported[6b] numerical errors in the initial work. Among many assumptions, the calculations are restricted to the π-system structures, and all exchange integrals are neglected except single-exchange integrals involving orbitals topologically adjacent in the molecular graph. Resonance energies will be given in terms of this exchange integral, J.[11] A complete and lucid exposition of the calculation procedures has been given by Sandorfy.[12]

Scheme I

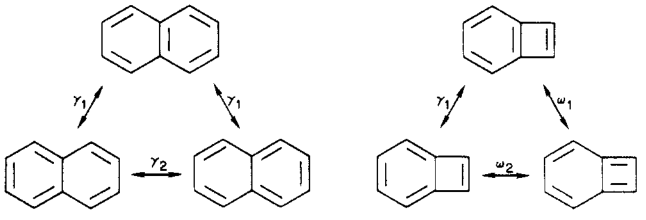


1

2

3

Scheme II



γ_1 = 19.39 kcal
γ_2 = 7.76 kcal

ω_1 = −14.99 kcal
ω_2 = −6.00 kcal

4

Structure-Resonance Theory. This approach uses the formulism of valence-bond theory.[13] The isoenergetic basis functions are taken to be represented by the principal resonance structure as shown in **1**–**3** (Scheme I) for allyl, pentadienyl, and benzyl radicals. The interactions "between" the structures are the Hamiltonian matrix elements that give rise to the resonance energy. The resonance energy is the difference between the ground-state radical π energy and the energy of a basis structure. A significant simplification is provided if one assumes that the ground state is an equally weighted hybrid of the structures. The ground-state wave function is then given by eq 1, and the ground-state resonance energy is given by eq 2.

$$\Psi = (1/SC^{1/2})(\Psi_1 + \Psi_2 + \ldots \Psi_i) \qquad (1)$$

$$RE = (2/SC)(\sum H_{ij}) \qquad (2)$$

Examination of the resonance structures **1**–**3** shows that the H_{ij} correspond to resonance integrals that result from permutations of electron pairs. As discussed previously,[13] the H_{ij} can be evaluated theoretically or empirically from experimental data. After comparison with a large number

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(1) (a) This work was presented in part at the Symposium on Polynuclear Aromatics, The 2nd Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980. (b) Applications of Structure-Resonance Theory. 17. For the previous paper see Herndon, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 1538–41. For a review see: Herndon, W. C. *Isr. J. Chem.* **1980**, *20*, 270–5.

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(10) Ilić, P.; Trinajstić, N. *J. Org. Chem.* **1980**, *45*, 1738–48.

(11) The exchange integral J varies somewhat with bond length as discussed by: Coulson, C. A.; Dixon, W. T. *Tetrahedron* **1962**, *17*, 215–28. All J values are assumed to be equal in the present cases.

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of aromatic hydrocarbon resonance energies calculated by an LCAO-MO-SCF method,[14,15] the best correlative value of γ_1 is 19.39 kcal (0.841 eV), and the values of the other established resonance integrals are defined and listed in structures 4 (Scheme II). Although conjugated circuits[16] larger than those containing ten carbon atoms (characterized by γ_2) could conceivably contribute to resonance energies, the energy contributions of the larger circuits decrease rapidly with increasing circuit size. Their effects are presumably incorporated in the empirically obtained parameters determined by the regression analysis of the SCF resonance energies.

The values of the integrals β_1 and β_2 can be obtained empirically as follows. From structure-resonance theory, the resonance energies of allyl, pentadienyl, and benzyl are as shown in eq 3–5. The numerical values of resonance

$$\mathrm{RE(allyl)} = {}^2\!/_2(\beta_1) = 11.4 \text{ kcal} \tag{3}$$

$$\mathrm{RE(pentadienyl)} = {}^2\!/_3(2\beta_1 + \beta_2) = 18.5 \text{ kcal} \tag{4}$$

$$\mathrm{RE(benzyl)} = {}^2\!/_5(\gamma_1 + 4\beta_1 + 3\beta_2) = 30.1 \text{ kcal} \tag{5}$$

energies in eq 3–5 are deduced from recent kinetic and thermodynamic data.[17-20] Using γ_1 = 19.39 kcal and rearranging to linear form, one obtains eq 3a–5a. This yields

$$11.4 = 0.0\beta_2 + \beta_1 \tag{3a}$$

$$13.875 = 0.5\beta_2 + \beta_1 \tag{4a}$$

$$13.965 = 0.75\beta_2 + \beta_1 \tag{5a}$$

(regression analysis) β_1 = 11.56 kcal and β_2 = 3.64 kcal. Along with the other parameters given in Scheme II, these values will be used in the calculations to be reported in the next section.

It is not necessary to draw all resonance structures of a particular radical species in order to obtain the resonance energy (eq 2). The radical molecular graph is composed of subgraphs represented by allyl, pentadienyl, and four-, six-, eight-, and ten-member rings, each of which makes a contribution to resonance energy. One can count the H_{ij} that arise from each resonance interaction by summing the SC values of the fragment graphs that remain after deletion of the corresponding resonance subgraph from the original molecular graph in all possible ways. For example, deletion of the allyl subgraph can be made from the benzyl radical graph in four different ways. The remaining fragment subgraphs each have SC = 1 (butadiene π system). Therefore four β_1 resonance interactions contribute to the resonance energy.

This process is conveniently carried out on a single molecular graph of the radical system. Details are given in the appendix, where the calculations are shown to be further simplified by the use of procedures involving the coefficients of nonbonding molecular orbitals.

Structure-Count Algorithms. Reference has already been made to work showing that ln SC is an accurate algorithm for SCF resonance energies of benzenoid hydrocarbons[4] and arylmethyl π radicals.[7] In many cases, the ratio SC(intermediate)/SC(reactant) be used as a quantitative index of reactivity, although one generally expects that the proportionality constant between ln SC and resonance energy will be different for ground-state aromatic molecules and various types of reactive intermediates. An equation of the type shown in eq 6 is

$$\ln k = A_0 + A_1 \ln \mathrm{SC(intermediate)} + A_2 \ln \mathrm{SC(reactant)} \tag{6}$$

therefore expected to correlate rate data in radical reactions. The constants could be determined by a regression analysis, and sensible results require that A_1 and A_2 should have positive and negative values, respectively. This type of equation has been found to be useful in the correlation of ionization potentials[21] and in examining rate data for reactions that involve carbocation intermediates.[22]

The counting of structures for radicals is also carried out by using the coefficients of nonbinding molecular orbitals. As shown in the appendix, the coefficients define a corrected structure count (CSC[23,24]) for the radical species. In the previous empirical correlations of ln SC with resonance energy,[4,7] the CSC was found to be a more accurate representation of relative stabilities than the SC. The present results are consistent with this observation, so the CSC will be used in the present work where appropriate.

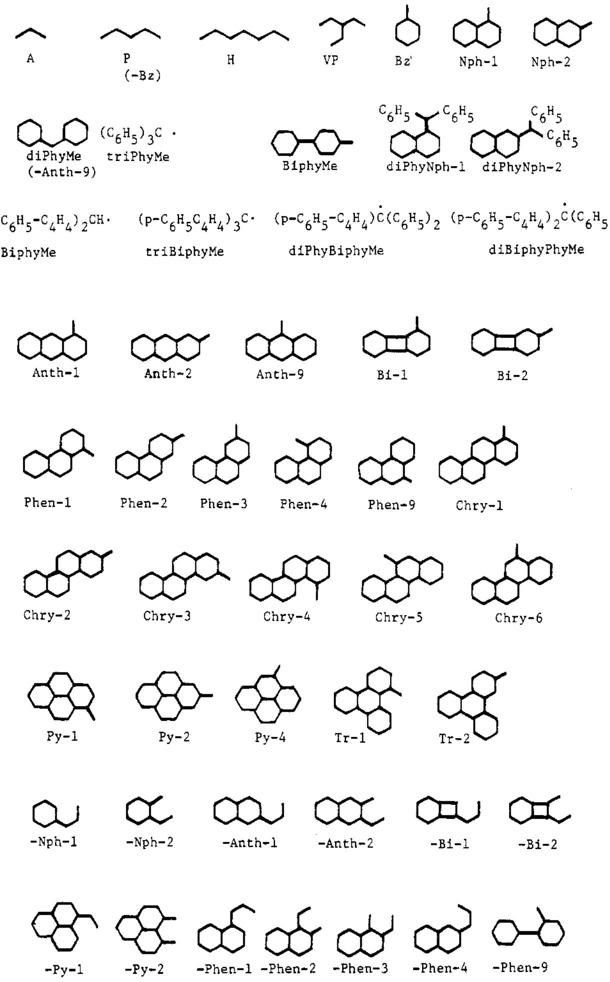

Figure 1. Molecular graphs and abbreviations for π radicals.

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Table I. Resonance Energies (Valence-Bond and Structure-Resonance Theory)[d]

radical (Figure 1)	SC	RE(VB)[a]	RE(SRT)[b]
A	2	0.50[c]	11.6
P	3	0.82[c]	17.8
H	4	1.05[c]	21.0
VP	4	1.08[c]	22.8
Bz	5	1.41	30.6
Nph-2	9	2.00	41.7
Nph-1	10	2.12	44.4
BiphyMe	13	2.36	49.5
diPhyMe	16	2.64	54.6
triPhyMe	44	3.81	77.5
diPhyNph-2	72	4.34	88.1
diPhyNph-1	76	4.40	89.2
diBiphyMe	88	4.51[c]	91.6
diPhyBiphyMe	100	4.73	95.6
diBiphyPhyMe	224	5.65	114.0
TriBiphyMe	496	6.58	133.1

[a] Units of VB exchange integral.[6] [b] In kilocalories. [c] This work. [d] Correlation coefficients: RE(VB):RE(SRT), 0.99995; ln SC:RE(SRT), 0.99960.

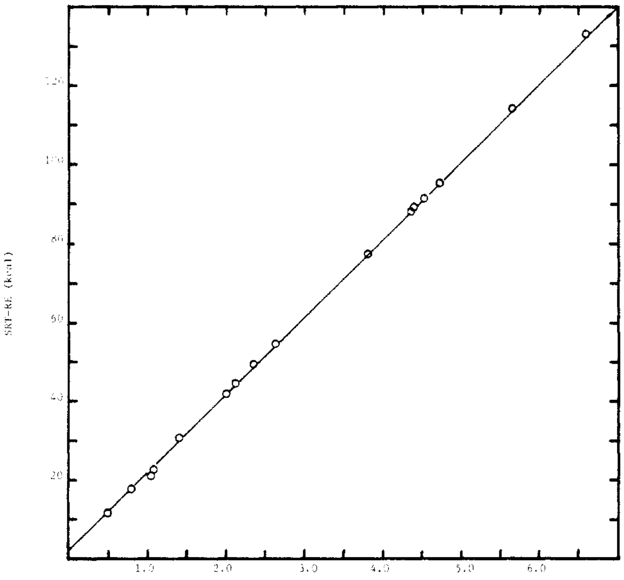


Figure 2. Valence bond resonance energies from Table I are plotted vs. structure-resonance theory resonance energies.

Results

Resonance energies for the π radicals depicted in Figure 1 were calculated by structure-resonance theory using the parameters given in the preceeding section. Valence-bond resonance energies are available for the first 16 of these radicals.[6] The valence bond calculations for the open-chain radicals and for dibiphenylmethyl (diBiphyMe) radical are new, and the remaining values were checked for errors. The two sets of theoretical results and the algorithm ln SC are compared in Table I.

The quality of the congruity between the valence-bond and the resonance theory calculations can be judged from the regression analysis, illustrated by Figure 2, which gives a correlation coefficient of essentially unity for eq 7. The

$$\mathrm{RE(SRT)} = 19.86\mathrm{RE(VB)} + 2.01 \qquad (7)$$

linear correlation of calculated resonance energies with the algorithm ln SC is also excellent as exemplified in Figure 3, which also includes data points for the other radicals to be discussed. Therefore, any of the three procedures give linearly related results, and either procedure gives an equally valid estimate of resonance energies. The most important conclusion is that the simplified parameterized resonance theory approach or the quantity ln SC can be assumed in further applications to give resonance energies that will be equivalent to those obtained by a more sophisticated valence-bond calculation.

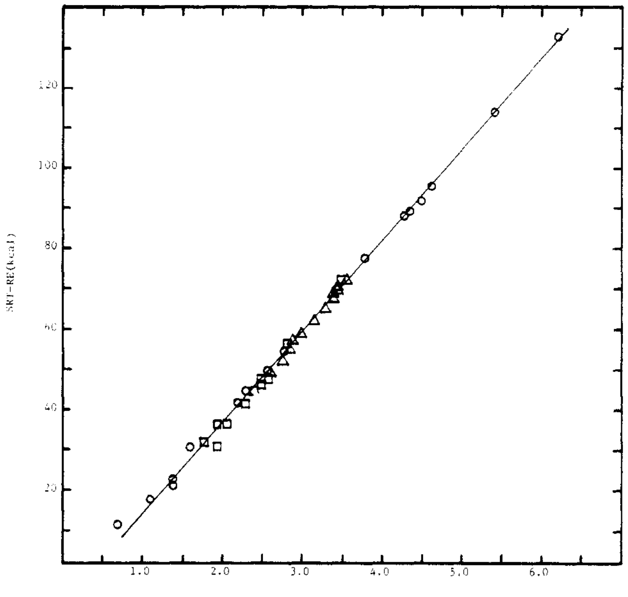


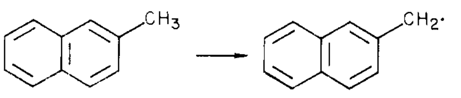
Figure 3. Natural logrithms of structure-count are plotted vs. structure-resonance theory resonance energies: ○, Table I; ▲, Table II, □, Table III. A few points have been omitted for clarity of presentation.

Table II. Resonance Energies (Arylmethyl Radicals)[e]

radical (Figure 1)	SC	RE-(SRT)[a]	ln (rel rate)[b]	ΔRE[a]	SC ratio
Bz	5	30.6	−1.760	10.1[c]	2.500
Nph-2	9	41.7	−0.383	10.7	3.000
Nph-1	10	44.4	0.000	13.4	3.333
BiphyMe	13	49.5			3.250
Anth-2	14	49.2	1.773	12.4	3.500
Anth-1	16	52.2	2.573	15.4	4.000
Phen-2	16	54.1			3.200
Phen-3	17	54.6	−0.603	9.6	3.400
Phen-4	17	55.5			3.400
Phen-1	18	56.7	−0.564	11.7	3.600
Phen-9	18	57.1	−0.168	12.1	3.600
Py-2	19	57.3			3.800
Anth-9	20	58.6	4.718	21.8	5.000
Py-4	23	62.1			3.833
Chry-2	27	65.2			3.375
Py-1	29 (27)[d]	65.5	2.929	16.4	4.500
Chry-3	29	67.2			3.625
Chry-5	29	67.8			3.625
Chry-4	29	68.1			3.625
Chry-1	31	69.3			3.875
Tr-2	31	70.3	−0.929	9.1	3.444
Tr-1	32	70.8	−1.016	9.6	3.556
Chry-6	34	72.2	0.784	14.0	4.250

[a] In kilocalories. [b] Reaction with CCl_3 (70 °C).[8] [c] Experimental value.[20] [d] Corrected structure count, CSC. See text. [e] Correlation coefficients: ln (rel rate):ΔRE, 0.933, 0.838 (β-methylnaphthyl-type compounds), 0.964 (α-methylnaphthyl-type compounds; ln (rel rate):ln (SC ratio), 0.829; eq 8, 0.951.

Radical Astraction Reactions. Resonance energies for the arylmethyl radicals (Figure 1) are listed in Table II. Also listed are relative rate data for trichloromethyl radical abstraction of hydrogen from the corresponding arylmethanes, along with resonance energy differences[25] and SC's pertinent to a radical abstraction reaction of this type, e.g.



RE = 31.0 kcal SC = 3 — RE = 41.7 kcal SC = 9

ΔRE = 41.7 − 31.0 = 11.7; SC ratio = 9/3

SCF calculations of resonance energies[8] and comparisons with SC ratios have already been extensively discussed,[7] so this point will not be reviewed further here.

A good correlation of the rate data with ΔRE for all of the reactants considered as a single group was not expected. Unruh and Gleicher[8] found that Hückel MO calculations of ΔRE were more congruous with the rate data if the α-methylnaphthalene-like compounds were considered separately from the β-methylnaphthalene analogues. However, this is certainly not true with the present calculations as is apparent from the correlation coefficients given in Table II. ΔRE gives a reasonable correlation of all of the data and is not improved significantly as a reactivity index if this dissection is made. It should be noted that a dual correlation of data is not required if SCF methods are used to calculate the ΔRE.[8]

In this case the SC ratio only provides a qualitative measure of relative reactivities since the correlation coefficient is less than 0.9. The best resonance theory results are obtained if the rate data are correlated with the ln SC algorithm for resonance energy according to eq 8. The improvement over the use of the SC ratio alone or HMO-calculated ΔRE's (correlation coefficient 0.855)[8] is considerable.

$$\ln (\text{rel rate}) = -10.94 + 11.68 \ln \text{SC}(\text{ArCH}_2\cdot) - 13.93 \ln \text{CSC}(\text{ArCH}_3) \quad (8)$$

Homolytic Aromatic Substitution. Partial rate factors for phenylation at 15 sites in six different aromatic hydrocarbons have been measured by Dickerman et al.[26] The remaining radicals in Figure 1 are the presumed radical intermediates in reactions of this type. Although other homolytic reaction rate studies are available,[26,27] only the Meerwein arylation reaction data[26] will be analyzed in this work. Resonance energies and the relative rates are summarized in Table III.

The correlations of calculated resonance theory reactivity indices with the reactivity data are good. The results are not significantly better than those obtained by using HMO localization energies[26] (correlation coefficient 0.961). Again, the best correlation of the data is obtained from an equation involving separate terms for the CSC of reactants and intermediates (eq 9). SCF calculations of the radicals involved in these reactions have not been carried out.

$$\ln (\text{rel rate}) = -2.45 + 7.07 \ln \text{SC(int)} - 8.01 \ln \text{SC(reactant)} \quad (9)$$

Discussion and Conclusions

The calculations and rate data summarized in Tables I–III lead one to conclude that structure-resonance theory can be used to quantitatively correlate and predict rates of π-radical reactions as well as do MO calculations. The use of the algorithm ln SC for resonance energy with eq 6 has the advantages of being extremely easy and highly correlative of experimental data. The agreement between ln SC and structure-resonance theory resonance energies is illustrated in Figure 3 for all of the species in the tables.

Table III. Resonance Energies (Homolytic Substitution Radical Intermediates)[e]

radical (Figure 1)	SC	RE-(SRT)[a]	ln (rel rate)[b]	ΔRE[a]	SC ratio
-Bz (pentadienyl)	3	17.8	0.000	−1.5	1.500
-Nph-2	6	31.8	1.327	0.7	2.000
-Bi-1	11 (7)[c]	30.6	1.914	0.6[d]	2.333
-Nph-1	7	36.1	3.006	5.0	2.333
-Bi-2	10 (8)[c]	36.3	3.144	6.3[d]	2.667
-Anth-2	10	41.3	2.681	4.4	2.500
-Phen-2	11	44.5	1.797	−0.5	2.200
-Phen-3	12	45.9	1.899	0.9	2.400
-Phen-4	12	47.2	2.442	2.2	2.400
-Anth-1	12	47.2	3.839	10.3	3.000
-Py-2	13	47.1		−2.0	2.167
-Phen-1	13	48.4	2.580	3.4	2.600
-Phen-9	13	49.5	2.821	4.5	2.600
-Anth-9	16	54.6	6.503	17.7	4.000
-Py-4	17	55.9	3.600	6.8	2.833
-Py-1	23 (21)[c]	62.0	4.449	12.9	3.500

[a] In kilocalories. [b] Reaction with phenyl radicals at room temperature. [c] Corrected structure count, CSC. See text. [d] Biphenylene calculated resonance energy = 30.0 kcal.[4] SCF value is 31.1 kcal.[14] [e] Correlation coefficients: ln (rel rate):ΔRE, 0.961; ln (rel rate):ln (SC ratio), 0.963; eq 9, 0.977.

The general equivalence of the various theoretical techniques in correlating actual rate data should not be taken to imply that no significant differences in predicted reactivity exist. An examination of Hückel MO localization energies[28] and ΔRE's in Tables II and III shows that several large discrepancies in calculated localization energies do exist. Perhaps the most easily discernible difference is that structure-resonance theory predicts that nearly all radicals produced by homolytic addition to aromatic hydrocarbons (Table III) are more resonance stabilized than the precursor hydrocarbons, while HMO theory gives the opposite result. As expected, relative energy differences agree better than do the actual signed numerical values but still do not account for the largely comparable rate-data correlations. The equivalence is probably due to the character of the difficult to obtain data itself.[8,26] Especially in the case of CCl_3 hydrogen abstractions,[8] the relative rates are calculated only after assumptions regarding relative rates of abstraction and addition reactions, and the products were not analyzed. Perhaps more experimental studies might allow a choice of correlative theories.

One must also realize that the generally good agreement of theory and experiment cannot be considered as sufficient to validate the theoretical procedures. The valence-bond calculations given in Table I are a good example of this fallacy. They were once used in semiquantitative discussions[6] of radical stabilities based on equilibria data for the association of triarylmethyl radicals to give hexa-

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(25) The resonance energy of the arylmethane is taken to be the resonance energy of the corresponding benzenoid hydrocarbon. See ref 13 for a list of resonance energies.

(26) Dickerman, S. C.; Feigenbaum, W. M.; Fryd, M.; Milstein, N.; Vermont, G. B.; Zimmerman, I.; McOmie, J. F. W. *J. Am. Chem. Soc.* **1973**, *95*, 4624–31.

(27) See ref 26 for literature citations.

(28) Streitwieser, A., Jr.; Brauman, J. I.; Coulson, C. A. "Supplemental Tables of Molecular Orbital Calculations with a Dictionary of π-Electron Calculations"; Pergamon Press: New York, 1965.

Table IV. Resonance Energies (Three Different Methods)[e]

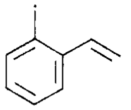
radical (Figure 1)	RE(SRT)[a]	H/S[b]	GT[c]
A (allyl)	11.5	0.165	0.0
P (pentadienyl)	17.8	0.265	0.0
H (heptatrienyl)	21.0	0.320	0.0
-Bi-1	30.6	0.294[d]	-0.156[d]
Bz (benzyl)	30.6	0.509[d]	0.155
-Nph-2	31.8	0.523[d]	0.129[d]
-Nph-1	36.1	0.535[d]	0.192[d]
-Bi-2	36.3	0.421[d]	-0.009[d]
Nph-2	41.7	0.704[d]	0.266
Nph-1	44.4	0.734[d]	0.287
diPhyMe	54.6	0.929[d]	0.383
triPhyMe	77.5	1.322[d]	0.627

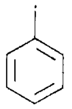
[a] In kilocalories. [b] Hess-Schaad;[9] units of β. [c] Graph theory;[10] units of β. [d] This work. [e] Correlation coefficients: RE(SRT):H/S, 0.967 (9 compounds); RE(SRT): GT, 0.882 (9 compounds).

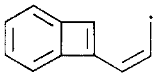
arylethanes. Agreement was remarkably good and was in part taken to support the theoretical approach. However, the later elucidation of correct quinoid structures of triarymethyl radical dimers counteracted the argument.[29] Presumably the reactants and intermediates are correctly identified in the present cases, and the theory–experiment agreement is valid.

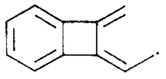
The structure-resonance theory calculations are essentially empirical and properly evaluated by comparison with experimental data. However, two other procedures have recently been suggested for calculating the resonance energies of π radicals that are advocated as simple working methods.[9,10] Both methods are based on Hückel MO theory. The first uses the familiar Hess–Schaad approach[30] of defining a reference π energy with additive bond energy terms, and the resonance energy is taken as the difference between the reference structure energy and the usual Hückel MO π energy. The second method uses a graph–theoretical definition[31,32] of the reference structure which eliminates the contributions of cyclic components to the π energy. A comparison of obtained resonance energies is given in Table IV.

The relatively better agreement of the resonance theory resonance energies with the Hess–Schaad results was expected. It is well understood that the graph theory approach only gives resonance energies attributable to cyclic conjugation, and as a consequence, graph theory resonance energies are zero for the open-chain radicals. In addition the 2-vinylbenzyl radical (–Nph-2) is calculated to have less resonance energy than benzyl radical, and the radicals obtained by excision of an orbital from the biphenylene system, –Bi-1 and –Bi-2, are found to be antiaromatic rather than resonance stabilized. The graph theory calculation evidently overestimates the destabilizing influence of the cyclobutadienoid ring. These results are emphasized because Ilič and Trinajstič have claimed[10] that the graph theory method "is generally applicable to any conjugated ion, radical, or radical-ion" whether the species be "neutral closed shell, neutral open shell, or charged, both closed and open shell". One must conclude that these statements are incorrect and that further modifications are necessary before the concept of graph–theoretical resonance energy can be applied to ionic and radical π systems.


2-vinylbenzyl(-Nph-2)


benzyl


-Bi-1

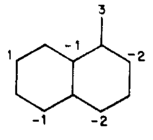

-Bi-2

On consideration of the ease of application and the congruities of resonance theory results with those from Hückel MO and SCF calculations, the structure-resonance method does seem to provide a viable alternative to MO calculations for quantitative π-radical structure-reactivity problems. At present, Hückel MO, SCF–MO, and structure-resonance theory all must be judged as reasonable procedures in this regard. For qualitative predictions, the SC ratio (intermediate/reactant) can be obtained by pencil and paper procedures with little effort and can therefore be recommended for quick predictions and pedagogical purposes.

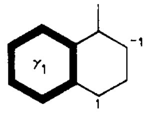
Acknowledgment. Financial support of the Robert A. Welch Foundation of Houston, TX, is gratefully acknowledged.

Appendix

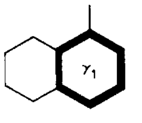
Calculation of Resonance Energies. The resonance-energy calculation is illustrated below for the α-methylnaphthyl radical. The SC is the sum of the absolute values of the unnormalized coefficients of a nonbonding molecular orbital. The coefficients follow the zero-sum rule and can be written by inspection. The resonance energy is given by eq 2, where the H_{ij} are the resonance integrals. The number of each H_{ij} is determined by deletion of the structural fragment corresponding to the resonance interaction. For example, the γ_1 resonance integral refers to resonance of the type found in the benzene π system, i.e., permutation of three pairs of electrons in a six-membered ring. A six-membered ring can be deleted from the α-methylnaphthyl graph in two different ways as given by the heavy lines in the graphs shown below.



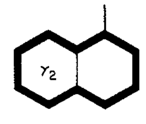
SC(Nph-1) = 10



residual SC = 3



residual SC = 1



residual SC = 1

The residual graphs have SC's of 3 and 1, respectively. Therefore, four γ_1 resonance terms contribute to the resonance energy expression. In a similar way, one enumerates a single γ_2 term (naphthalene 10-membered-ring resonance).

The allyl resonance defines the β_1 resonance integral. Deletion of the allyl fragment from the α-naphthylmethyl

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[29] For a historical account, see: McBride, J. M. *Tetrahedron* **1974**, *30*, 2009–22.

[30] Schaad, L. J.; Hess, B. A., Jr. *J. Chem. Educ.* **1974**, *51*, 640–3.

[31] Aihara, J.-I. *J. Am. Chem. Soc.* **1976**, *98*, 2750–8, 6840–44; *J. Org. Chem.* **1976**, *41*, 2488–90.

[32] Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692–704.

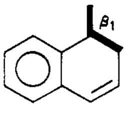
[33] Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1947**, *192*, 16–32. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265–74.

[34] Herndon, W. C. *J. Chem. Educ.* **1974**, *51*, 10–5.

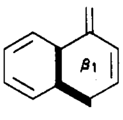
graph can be accomplished in seven different ways, two of which are exemplified below, giving nine β_1 contributions to the resonance energy. Analogously, one counts nine β_2 terms, corresponding to the pentadienyl resonance interaction. The resonance energy is then determined to be as shown in eq 10. These procedures can be verified by

$$RE = \tfrac{7}{10}(4\gamma_1 + \gamma_2 + 9\beta_1 + 9\beta_2) \qquad (10)$$

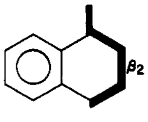
drawing all structures. For moderately sized systems, the resonance energy can be determined by utilizing a single graph of the π radical.



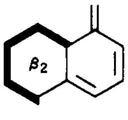
residual
SC = 2



residual
SC = 1

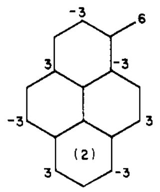


residual
SC = 2

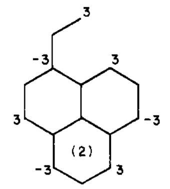


residual
SC = 1

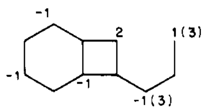
Corrected Structure Count (CSC). In isolated instances the sum of the absolute values of the coefficients of a nonbonding MO does not correspond to the actual number of valence bond structures (cf. entries for Py-1 in Table II and –Bi-1, –Bi-2, and –Py-1 in Table III). In agreement with earlier results,[13,24] the sum of the absolute values of the coefficients is defined as the CSC, and it is postulated that the CSC will be a more accurate predictor of stability than the SC for qualitative purposes. In the cases of systems incorporating cyclic 4*n* rings (cyclobutadiene, biphenylene, etc.), the background and theory supporting a calculated diminished resonance energy have been previously discussed in detail.[13]



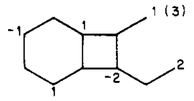
SC(Py-1) = 29
CSC = 27



SC(–Py-1) = 23
CSC = 21



SC(–Bi-1) = 11
CSC = 7



SC(–Bi-2) = 10
CSC = 8

Registry No. A, 1981-80-2; P, 3808-35-3; H, 15671-45-1; VP, 76613-39-3; Bz, 2154-56-5; Nph-2, 7419-61-6; Nph-1, 7419-60-5; BiphyMe, 4939-76-8; diPhyMe, 4471-17-4; triPhyMe, 2216-49-1; diPhyNph-2, 7094-19-1; diPhyNph-1, 7094-18-0; triBiphyMe, 76613-40-6; diPhyBiphyMe, 7261-23-6; diBiphyPhyMe, 20694-33-1; triBiphyMe, 6418-50-4; Anth-2, 19003-81-7; Anth-1, 19003-80-6; Phen-2, 19003-84-0; Phen-3, 19004-14-9; Phen-4, 19004-15-0; Phen-1, 19003-83-9; Phen-9, 19004-16-1; Py-2, 76613-41-7; Anth-9, 16407-06-0; Py-4, 76613-42-8; Chry-2, 76613-43-9; Py-1, 76613-44-0; Chry-3, 76613-45-1; Chry-5, 76613-46-2; Chry-4, 76613-47-3; Chry-1, 76613-48-4; Tr-2, 76613-49-5; Tr-1, 76613-50-8; Chry-6, 76613-51-9; -Nph-2, 55185-63-2; -Bi-1, 76613-52-0; -Nph-1, 20671-30-1; -Bi-2, 76613-53-1; -Anth-2, 76613-54-2; -Phen-2, 76613-55-3; -Phen-3, 76613-56-4; -Phen-4, 76613-57-5; -Anth-1, 76613-57-5; -Py-2, 76613-58-6; -Phen-1, 76613-59-7; -Phen-9, 20671-31-2; -Py-1, 76630-72-3.

Polymer-Supported Phase-Transfer Catalysts. Crown Ethers and Cryptands Bonded by a Long Alkyl Chain to a Polystyrene Matrix

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The synthesis of ω-aminononyl-substituted 18-crown-6 and [2.2.2]cryptand is described. These are easily bonded to chloromethylated polystyrene cross-linked with varying amounts of *p*-divinylbenzene. The polymer-bound polyethers can be successfully used as catalysts (0.01 molar equiv) in anion-promoted phase-transfer reactions. As is the case for the analogous soluble systems, the catalytic activity of the cryptands is higher than that of the crown ethers and quaternary onium salts. Due to their high chemical stability, polymer-bound polyethers are more advantageous than polymer-bound quaternary onium salts and can be recycled several times with no chemical degradation. However, loss of mechanical properties due to the grinding of the polymer matrix remains a problem. Methods allowing titration of polyether centers on the resin are also described.

Polymer-supported quaternary ammonium and phosphonium salts allow a radical simplification of the process of phase-transfer catalysis, provided that the reactivity of the immobilized catalyst is comparable with that of the analogous soluble catalysts.[1] When working under fluid-bed conditions, the polymer-bound catalyst can be filtered at the end of reaction and reused for another run. The product is directly isolated by separation from the immiscible aqueous phase and evaporation of the solvent.[1] This aspect becomes more important in the case of more sophisticated or more expensive catalysts, such as crown ethers or cryptands. Indeed the use of these systems is often discouraged by the difficulties of recovery at the end of reaction although, especially in the case of lipophilic cryptands, the much higher chemical stability and the

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[1] Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920.

0022-3263/81/1946-2125$01.25/0 © 1981 American Chemical Society