bromide falls on the Hammett plot with other meta- and para-substituted compounds studied by Yano et al.[18] using a σ^- value of 1.24 for the ortho nitro group that is based on the ionization of ortho-substituted phenols[17] (Figure 1).

This inversion in the trend of β values means that Hammett plots for these reactions, catalyzed by weaker base catalysts than the hydroxide ion, will show positive deviations for 2-(2,4-dinitrophenyl)ethyl bromide. This is because with weaker base catalysts, the decrease in rate constant will be greater for the *p*-nitro compound, which has the largest β value (0.61), than for *both* the less activated and the dinitro bromides which have smaller β values.

Positive deviations from Hammett plots, which characterized a change in mechanism, have been previously observed in the reactions of (2-arylethyl)quinuclidinium ions.[3] The results reported here suggest that positive deviations from Hammett plots are also expected in elimination reactions that do not reflect a change in mechanism, but rather a large change in the orientation of the reaction coordinate, and structure of the E2 transition state that occurs near the E1cB borderline.

Registry No. 2,4-$(NO_2)_2C_6H_3CH_2CH_2F$, 87902-03-2; 2,4-$(NO_2)_2C_6H_3CH_2CH_2Cl$, 63070-32-6; 2,4-$(NO_2)_2C_6H_3CH_2CH_2Br$, 60680-77-5; 2,4-$(NO_2)_2C_6H_3CH_2CH_2I$, 87902-04-3; 4-$NO_2C_6H_4CH_2CH_2Br$, 5339-26-4; 4-$NO_2C_6H_4CH_2CH_2F$, 56153-06-1; 4-$NO_2C_6H_4CH_2CH_2Cl$, 20264-95-3; 2,4-$(NO_2)_2C_6H_3CH{=}CH_2$, 2287-45-8; HO^-, 14280-30-9; $CF_3CH_2O^-$, 24265-37-0; $(CF_3)_2CHO^-$, 44870-01-1; $CH_3CH_2O^-$, 16331-64-9; 2-phenylethyl alcohol, 60-12-8; 2-phenylethyl chloride, 622-24-2.

Relative Rate Constants of Hydrogen Transfer to Benzyl Radical

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Contribution from the U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania 15236. *Received April 18, 1983*

Abstract: A method has been developed for measuring relative rate constants for hydrogen transfer from reactive donor compounds to the benzyl radical generated by thermolysis of dibenzylmercury. Relative rate constants were measured against the rate constant for a reference donor, triphenylsilane-*d*, for 23 hydrogen donor compounds at 170 °C. The values range from 0.12 for mesitylene to 37 for 9,10-dihydroanthracene. A correlation was found between the logarithm of the relative rates of hydrogen transfer from arylmethyl donors and estimates of the resonance stabilization energies of the arylmethyl radicals thus formed. The influence of stereoelectronic factors, steric inhibition to resonance, and angle strain on the relative rates is also discussed.

Investigations of the mechanism of direct coal liquefaction have often used benzyl radical as a model of reactive species generated under pyrolytic conditions. The quenching of such radicals by hydrogen transfer from so-called donor solvents is an important step in much of this chemistry.[1] Although some work has been reported concerning rates of hydrogen transfer to resonance-stabilized radicals,[2-7] information regarding patterns of selectivity of benzyl radical, especially toward hydroaromatic donors, is lacking. The present work employs a method based on competitive kinetics to obtain relative rate constants for hydrogen transfer transfer to benzyl radical from 23 compounds all measured against a common reference compound, the deuterium donor triphenylsilane-*d*.

Experimental Section

Materials. (Reference to a brand or company name is made to facilitate understanding and does not imply endorsement by the U.S. Department of Energy.) All hydrogen donors were determined to be greater than 98.5% pure by capillary gas chromatographic analysis unless otherwise noted. Dibenzylmercury (Alfa) was recrystallized three times from ethanol, mp 110.5-111.5 °C (lit. 111 °C). Dihydropyrene was a mixture of 53% dihydropyrene and 47% pyrene, prepared in our laboratory by the reduction of pyrene.[8] The 4,5,6,7-tetrahydrobenzothiophene, 99.5% by capillary gas chromatography, was kindly donated by R. Winans. Triphenylsilane-*Si-d* was synthesized after the method of Gilman and Dunn[9] by lithium aluminum deuteride (Aldrich, 98 atom % D) reduction of triphenylsilyl chloride or triphenylsilyl bromide in refluxing ether. Triphenylsilane-*d*, recrystallized from hexanes (mp 40.0-41.5 °C, uncorrected), was determined to be 98.5% deuterated by proton NMR spectroscopy employing standard addition techniques. Toluene-α-*d* was synthesized via the Grignard reaction with benzyl chloride and magnesium followed by quenching with deuterium oxide. Toluene-α-*d* prepared in this manner had a deuterium content of 96.5% as determined by the method of standard additions using proton NMR spectroscopy.

Kinetic Measurements. Kinetic experiments were performed in microautoclaves made from $^1/_2$ in. by 2 in. stainless steel threaded unions fitted with Swagelok caps. In all cases, both hydrogen and deuterium donors were added to the microautoclave in 10-fold excess (or more) over the yield of toluene, thus assuring that pseudo-first-order kinetics was maintained with regard to both the hydrogen donor and triphenylsilane-*d*. The Swagelok cap was tightened and the contents mixed. The reactors were placed in an air convection oven at 170 ± 2 °C for 18 h. After reaction, the solutions were transferred to Teflon-capped vials and stored at -10 °C until analysis, usually within 1 week. Reaction products were analyzed for the ratio of toluene to toluene-α-*d* by using either GC/MS or high-resolution mass spectrometry (KRATOS MS-50). In the latter case, toluene was separated and collected on a gas chromatograph prior to analysis. The entire collected sample was introduced into the mass spectrometer and analyzed at an ionizing voltage of 70 eV with resolution never less than 1:50 000.

In a typical experiment, tetralin, triphenylsilane-*d*, dibenzylmercury, and *tert*-butylbenzene were weighed into five microreactors. The weight of triphenylsilane-*d* was kept constant (0.520 g, 2.00 mmol) while that of tetralin was increased from reactor to reactor, providing mole ratios of tetralin to triphenylsilane-*d* of 0.252, 0.504, 1.00, 1.54, and 2.01. The total volume was kept to approximately 2.0 mL by reducing the weight

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of solvent (*tert*-butylbenzene) to compensate for the increasing tetralin concentration. Dibenzylmercury was also kept constant (38 mg, 0.100 mmol). After completion of the reaction, total yields of toluene ranged from 2 to 5 mg.

Product Analysis. Method A: Combined GC/MS. A sample of the entire reaction product was injected into a Hewlett-Packard 5985 GC/MS. By use of a 0.29 mm × 15 m SE-52 WCOT glass column, toluene was cleanly separated from all other chromatographic peaks. The ionizing voltage of the mass spectrometer was 70 eV. Mass numbers 91, 92, 93, and 94 were monitored for the toluene peak of each injection. Peak heights were corrected for the natural abundance of ^{13}C, yielding a set of corrected heights for masses 91, 92, and 93. These peaks are due to the parent ions from toluene (92) and deuterated toluene (93), tropylium ion resulting from loss of hydrogen or deuterium by the parent ions (91), and deuterated tropylium ion (92). The decay of the parent ion to tropylium ion has been studied in detail,[10] and its implications were fully taken into account in the reduction of the GC/MS data.

Method B: Preparative GC followed by High-Resolution Mass Spectrometry. Toluene samples were collected from a Varian 2700 gas chromatograph with dual SP2100 packed columns ($^1/_4$ in. × 10 ft) operating isothermally at 115 °C at a flow rate of 40 mL/min during collection. Samples were collected in a glass wool packed U-tube immersed in a dry ice/acetone bath, then sealed with Teflon tape and quickly frozen in liquid nitrogen. The toluene to toluene-α-*d* radio was determined by measuring the relative intensities at masses 92.0626 and 93.0689. Since the spectrometer resolves the parent ions from all other ions at nominal masses 92 or 93, the analysis is made without interference caused by the formation of tropylium ion. The method was shown to be precise and accurate by using authentic samples of toluene-α-*d* of known deuterium content.

Results and Discussion

The selectivity of benzyl radical in hydrogen atom abstraction reactions was determined by establishing a competition between individual donors and a reference donor. Triphenylsilane-*d* was chosen as the reference donor because of its thermal stability, high reactivity, and ease of preparation. Thermal decomposition of dibenzylmercury has been used by others as a convenient source of free benzyl radicals in solution.[11] Values for the rate constant, activation energy, and preexponential factor for the dissociation of dibenzylmercury in toluene have been published.[12] From these data, the half-life of dibenzylmercury at the nominal reaction temperature of 170 °C was calculated to be approximately 18 min.

The major reaction steps of the competition experiment are given in eq 1–6. In the absence of hydrogen donors[7,11] or other free-radical traps,[13] reaction 4 dominates and bibenzyl is formed as the stable product. In the presence of hydrogen donors, significant quantities of toluene are also produced.[7,13] The competition between reactions 2 and 3 is of chief interest here. It may be shown that under pseudo-first-order conditions

$$\mathrm{PhCH_2{-}Hg{-}CH_2Ph \rightarrow 2PhCH_2\cdot + Hg} \tag{1}$$

$$\mathrm{PhCH_2\cdot + RH \rightarrow PhCH_3 + R\cdot} \tag{2}$$

$$\mathrm{PhCH_2\cdot + Ph_3SiD \rightarrow PhCH_2D + Ph_3Si\cdot} \tag{3}$$

$$\mathrm{2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph} \tag{4}$$

$$\mathrm{PhCH_2\cdot + R'H \rightarrow PhCH_3 + R'\cdot} \tag{5}$$

$$\mathrm{PhCH_2\cdot + R\cdot \rightarrow PhCH_2R} \tag{6}$$

$$\frac{[\mathrm{PhCH_3}]}{[\mathrm{PhCH_2D}]} = \frac{k_2[\mathrm{RH}]}{k_3[\mathrm{Ph_3SiD}]} + \frac{k_5[\mathrm{R'H}]}{k_3[\mathrm{Ph_3SiD}]} \tag{7}$$

Thus, a plot of the ratio of toluene to deuteriotoluene vs. the ratio of a donor compound to the reference donor should yield the ratio of rate constants, k_2/k_3, as the slope. The value of the intercept would be governed by donation from all other possible sources of hydrogen in the system, including any nondeuterated triphenylsilane, that is always present in small amounts as an unavoidable impurity.

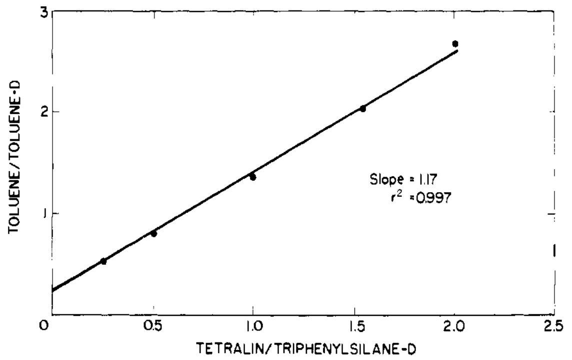

Figure 1. Determination of the ratio of rate constants for abstraction of hydrogen from tetralin and deuterium from triphenylsilane by benzyl radical in *tert*-butylbenzene solvent at 170 °C. Deuterium content of toluene determined by high resolution mass spectrometry.

In order to test the validity of the proposed kinetic analysis, dibenzylmercury was decomposed in the presence of hydrogen donor compounds and triphenylsilane-*d*, and the deuterium content of the toluene so produced was determined as described in the Experimental Section. In all cases, *tert*-butylbenzene was used as solvent. This relatively high boiling solvent has the virtues of being a very poor hydrogen donor toward benzyl radical under these conditions[4,7] and a very good solvent for most of the donor compounds used here. Figure 1 contains data from an experiment using tetralin as a hydrogen donor. As may be seen, a linear relationship between toluene/toluene-*d* and tetralin/triphenylsilane-*d* was found, as expected on the basis of eq 7. The slope of the line is taken to be the ratio of rate constants, k_2/k_3, for tetralin.

As described in the Experimental Section, two methods of analysis for deuterium content in toluene were developed. The relative rate factors obtained by using the two methods are in excellent agreement. The relative rate constant for tetralin was found to be 1.13 ± 0.05 for three separate determinations like the determination shown in Figure 1 using the high-resolution mass spectrometry method. An average value of 1.04 ± 0.15 was found by using the GC/MS method for three separate determinations. The majority of the data reported were obtained by the high-resolution mass spectrometry method, which provided the more precise data.

A control experiment was performed to determine if the deuterium label on toluene might be lost to other radical species in solution during the course of the experiment. A typical experimental solution using dibenzylmercury, dihydrophenanthrene, and *tert*-butylbenzene was prepared. A small amount of toluene of known deuterium content (78.2% D) was added along with naphthalene to serve as an internal standard. After decomposition of the dibenzylmercury, the amount of additional toluene formed was determined by GC analysis. The deuterium content expected solely on the basis of dilution by the additional toluene formed was 61.9%. The deuterium content determined by GC/MS was 60.7%, which agrees with the expected value within the limits of experimental error. Thus, loss of deuterium label over the course of a typical experiment is negligible.

The intercept of the plot in Figure 1 is greater than zero, as was the case in nearly all of the other examples. Equation 7 indicates that the intercept should be proportional to the rate of donation from all other sources of hydrogen beside the added donor compound. This includes the nondeuterated triphenylsilane present in the reference donor as an impurity. Considering only this source of hydrogen, the measured relative rate factor of 3.9 for triphenylsilane, and its relative concentration (~1.5%), a value of 0.06 would be expected for the intercept. The difference between this value and the observed values must then be due to other sources of hydrogen, including the solvent, which is not completely inert.

The relative rate constants for a number of compounds all obtained from five-point plots similar to that shown inFigure 1 are gathered in Table I. The values span somewhat more than

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(11) Bass, K. C. *Organomet. Chem. Rev.* **1966**, *1*, 391–433.

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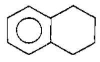
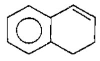
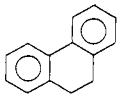
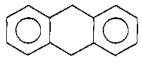
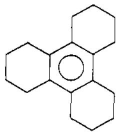
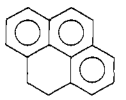
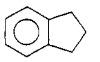
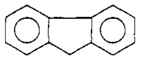
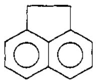
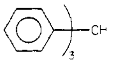
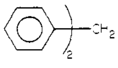
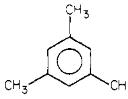
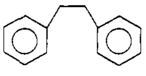
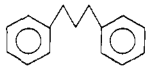
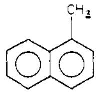
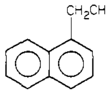
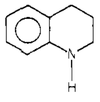
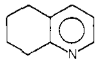
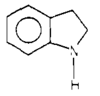
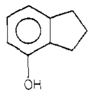
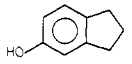
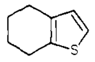
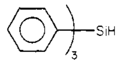
Table I. Rate Constants for Hydrogen Transfer to Benzyl Radical at 170 °C Relative to Triphenylsilane-*d*

compound	relative rate constant: per mol	relative rate constant: per active hydrogen	intercept	product analysis[a]
	1.1	0.28	0.26	A,B
	3.7	0.93	0.79	A[b]
	1.7	0.43	0.18	A
	37	9.3	0.17	B
	3.2	0.27	0.42	A
	4.1	1.0	0.29	A
	0.57	0.14	0.58	A
	4.4	2.2	0.95	B
	1.4	0.35	0.34	B
	1.2	1.2	0.54	B
	0.54	0.27	0.34	B
	0.12	0.013	0.24	B
	0.23	0.058	0.39	B
	0.33	0.083	0.32	A
	0.15	0.050	0.29	B
	0.25	0.13	0.22	B
	1.7		0.17	A
	1.5	0.38	0.63	A
	6.7		0.13	A
	2.7		-0.07	A
	3.5		-0.03	A
	1.2	0.30	0.25	B
	3.9	3.9	0.39	B

[a] See Experimental Section for details. [b] Analysis of the product by gas chromatography indicates dihydronaphthalene was not depleted by radical initiated polymerization.

2 orders of magnitude from the least reactive donor, mesitylene, to the most reactive, 9,10-dihydroanthracene. Several structural features seem to be important in determining the relative reactivity of the various donors.

Resonance stabilization effects are made readily apparent by comparison of mesitylene, diphenylmethane, and triphenylmethane. If statistical corrections are made for the number of benzylic hydrogens on each donor, the relative reactivities are in the proportion of 1:21:91, respectively. This is in excellent agreement with the order of 1:28:84 reported for transfer of hydrogen from toluene, diphenylmethane, and triphenylmethane to polystyryl radical at 60 °C.[3]

A strong dependence of the reactivity of benzylic hydrogen on the degree of phenyl substitution is usually rationalized on the basis of differences in resonance stabilization energies generated during the formation of the transition state. Resonance stabilization energies of benzylic systems have been calculated by using a simple method based on counting the number of stable Kekulé isomers that may be drawn for the radical and its parent hydrocarbon.[14,15] The resonance stabilization energy was defined as the difference between the heat of dissociation for the reaction that forms the benzylic radical of interest and the heat of dissociation for the corresponding reaction that forms the alkyl radical from the totally saturated analogue. In Figure 2, the logarithm of the relative rate constants per hydrogen is plotted vs. the resonance stabilization energies calculated by using eq 5 of ref 15 for the four aromatic substituted methanes found in Table I.[16]

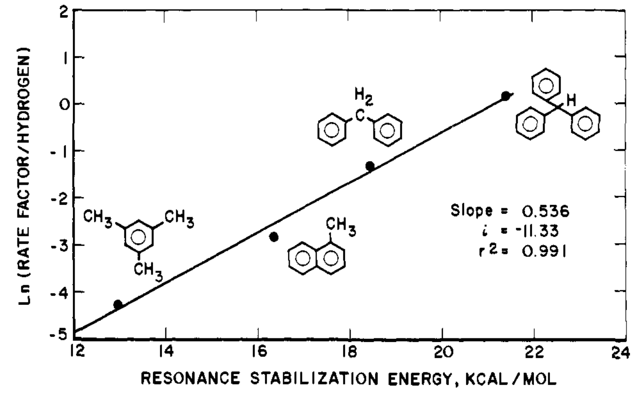


Figure 2. Logarithm of the relative rate factor per active hydrogen vs. the resonance stabilization energy calculated after Stein and Golden[15] for the radicals produced by abstraction of hydrogen from arylmethyl donors. The slope of the line is 0.54 with a correlation coefficient r^2 = 0.99.

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(14) Herndon, W. C. *J. Org. Chem.* **1981**, *46*, 2119–2125.
(15) Stein, S. E.; Golden, D. M. *J. Org. Chem.* **1977**, *42*, 839–841.

These limited data are fit well ($r^2 = 0.991$) by a straight line of slope 0.54. Other donors in Table I do not fall close to this line, indicating that other structural factors, as well as resonance stabilization energy, must also come into play. With the limited data available, it appears that hydroaromatic donors and donors with five-membered fused rings fall on separate parallel lines in resonance energy plots like the plot shown in Figure 2.

A significant increase in the reactivity of hydrogen donors occurs when a benzylic carbon is locked into a five- or six-membered ring in such a way that the resonance interaction between the developing p orbital and the aromatic ring(s) may occur without need of freezing out an internal rotation. This point is illustrated most clearly by comparisons of diphenylmethane with either fluorene or 9,10-dihydroanthracene. On a per hydrogen basis, the relative rate factors are 0.27, 2.2, and 9.3, respectively. In the latter two cases, resonance energy is available without need of freezing out the free rotation of the two phenyl rings. This argument is based strictly on entropy effects. Other examples of this effect are provided by comparison of mesitylene with tetralin or indan, and methylnaphthalene or ethylnaphthalene with acenaphthene. An additional factor that may contribute to the relatively high reactivity of acenaphthene is the relief of the steric interactions between the eclipsed benzylic hydrogens of the parent compound on formation of the radical.

In addition to entropy effects, another factor to be considered is steric inhibition to resonance. In neither di- nor triphenylmethane may the phenyl groups be brought to lie in the same plane simultaneously due to their steric interactions. On the other hand, the phenyl groups of the fused-ring compounds are already constrained to lie close to the nodal plane of the p orbital developing at the benzylic site during formation of the transition state. Thus, the reactivity of diphenylmethane may be depressed relative to the fused-ring analogues because only the former may experience steric inhibition to resonance. Both the entropy effect[19] and the steric inhibition to resonance[20] have been shown to play a role in the reactivity of similar benzylic hydrogen donors toward trichloromethyl radical.

The influence of angle strain is evident in comparing five- and six-membered ring systems, as in fluorene with 9,10-dihydroanthracene and indan with tetralin. The hydrogen of 9,10-dihydroanthracene is 4.1 times as reactive as that of fluorene, while the corresponding factor between tetralin and indan is 2.1. The differences in stereoelectronic and resonance energy factors between the members of these pairs are probably very small. Thus, the greater difficulty in bringing an additional sp^2 carbon into a five- rather than a six-membered ring probably accounts for the lower relative reactivity of both fluorene and indan. The more pronounced effect in the former case may be expected, since a fifth sp^2 carbon must be added to the five-membered ring of fluorene, while only the third must be added to that of indan.

A small positive effect with increasing alkyl substitution is apparent by comparing the relative rate constants per hydrogen of methylnaphthalene (0.05) with ethylnaphthalene (0.13), or mesitylene (0.013) with bibenzyl (0.058) and 1,3-diphenylpropane (0.083). The latter two compounds have been widely used as model compounds under coal liquefaction conditions. Determination that they are modestly active hydrogen donors is important, especially in the case of 1,3-diphenylpropane, which may, following loss of a benzylic hydrogen, undergo a facile β-scission reaction at higher temperatures to form benzyl radical and styrene.[21-23]

Comparison of the hydroaromatic compounds allows the following order of reactivity to be set down on a per hydrogen basis: 9,10-dihydroanthracene (9.3) $\gg$ 4,5-dihydropyrene (1.0) $\sim$ 1,2-dihydronaphthalene (0.93) > 9,10-dihydrophenanthrene (0.43) > tetralin (0.28) $\sim$ dodecahydrotriphenylene (0.27). The similarity in reactivity of the latter two compounds provides some basis for assuming that the reactivity of other hydroaromatic compounds with structures closely related to those shown in Table I could be estimated by simple addition of the appropriate relative rate constants. For example, we expect the relative rate constant for 1,2,3,4,5,6,7,8-octahydrophenanthrene to be approximately twice that of tetralin, and tetrahydropyrene twice that of 9,10-dihydrophenanthrene.

The heteroatom-containing compounds also provide several interesting comparisons. The relative rate constants for tetralin and 1,2,3,4-tetrahydrobenzothiophene are essentially the same. Delocalization over the thiophene ring seems equivalent to delocalization over the phenyl ring. In the cases of nitrogen-containing compounds, 5,6,7,8-tetrahydroquinoline is more reactive than tetralin. Placement of nitrogen in the alicyclic ring, as in 1,2,3,4-tetrahydroquinoline, is activating to about the same degree as when the nitrogen is in the aromatic ring. The reactivity of indoline as opposed to indan is truly remarkable and awaits explanation. Both indanols exhibit high reactivity. We presume that the phenolic hydrogen is mostly responsible for this high reactivity. In support of this assumption, hydrogen transfer to the polystyryl radical at 60 °C is 336 times faster from the hydroxyl group on phenol as from the benzylic sites on toluene.[24] Since the C–H and O–H bond strengths in toluene and phenol are coincidentally the same, this rate difference is due to a much lower intrinsic activation energy for hydrogen removal from phenol.

The relative rate constant given in Table I for triphenylsilane is equivalent to the kinetic deuterium isotope effect for this reaction, $k_H/k_D = 3.9$. This is a large effect. The implications of the magnitude of this effect are under study.

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Registry No. $PhCH_2\cdot$, 2154-56-5; D, 7782-39-0; tetralin, 119-64-2; 1,2-dihydronaphthalene, 447-53-0; 9,10-dihydrophenanthrene, 776-35-2; 9,10-dihydroanthracene, 613-31-0; 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene, 1610-39-5; 4,5-dihydropyrene, 6628-98-4; indan, 496-11-7; fluorene, 86-73-7; acenaphthene, 83-32-9; triphenylmethane, 519-73-3; diphenylmethane, 101-81-5; mesitylene, 108-67-8; bibenzyl, 103-29-7; 1,3-diphenylpropane, 1081-75-0; 1-methylnaphthalene, 90-12-0; 1-ethylnaphthalene, 1127-76-0; 1,2,3,4-tetrahydroquinoline, 635-46-1; 5,6,7,8-tetrahydroquinoline, 10500-57-9; indoline, 496-15-1; 4-indanol, 1641-41-4; 5-indanol, 1470-94-6; 4,5,6,7-tetrahydrobenzo[*b*]thiophene, 13129-17-4; triphenylsilane, 789-25-3.

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(16) Resonance stabilization energies calculated with this equation are scaled to the value for benzyl radical $E_{RSE} = 13.0$ kcal/mol. If more recently reported values of 11 kcal/mol[17] or 10.1 kcal/mol[18] are used, all other calculated resonance stabilization energies are reduced in proportion. However, the slope and fit of the line in Figure 2 is virtually unchanged.

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