

the anion stability as in dimerone by constraining the π system to a planar geometry which allows maximum charge delocalization.

References and Notes

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- (27) NOTE ADDED IN PROOF. Measurements just completed by M. French in our laboratory show that the measurement of the equilibrium $\text{CH}_3\text{COCH}_3 + \text{CNCH}_2^- = \text{CH}_3\text{COCH}_2^- + \text{CH}_3\text{CN}$ leads to $\Delta G^\circ = -2.6$ and not +2.5 kcal/mol as shown in Figure 1. This leaves $D - \text{EA}$ for acetone unchanged but gives for acetonitrile 52.7 kcal/mol (see Figure 1). This value leads to 29.6 kcal/mol for the EA of CH_2CN (see Table VI).

Long-Range Carbon-Carbon Spin-Spin Coupling Constants in Carboxyl Labeled Aromatic Carboxylic Acids and Dihydro Aromatic Carboxylic Acids

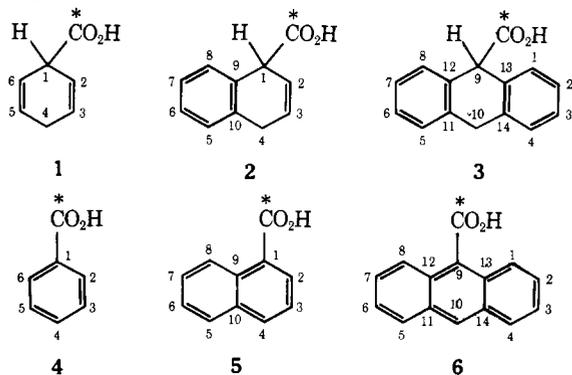
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Abstract: The following compounds, both natural and labeled in the carboxyl position with >90% ^{13}C , were synthesized and studied by carbon NMR to obtain carbon chemical shifts and all carbon-carbon coupling constants involving the labeled carboxyl carbon: 1,4-dihydrobenzoic acid (**1**), 1,4-dihydro-1-naphthoic acid (**2**), 9,10-dihydro-9-anthroic acid (**3**), benzoic acid (**4**), 1-naphthoic acid (**5**), and 9-anthroic acid (**6**). Chemical shift assignments for **1-6** were aided by the chemical shifts for the parent hydrocarbons **7-9**, generated in this study. A breakdown of the expected dihedral angular dependence of the three-bonded carbon-carbon coupling constants is experienced in the series **1-3**, and for a conformational analysis of this series, an analysis of longer-range couplings is necessary. These longer-range couplings appear to arise from an additional π contribution as the $\text{C}-\text{CO}_2\text{H}$ carbon-carbon bond becomes more nearly parallel to the aromatic p orbitals of **2** and **3**. Such longer-range couplings are not observed for the fully aromatic compounds **4-6**, even though a completely conjugated coupling route is available. This conformational analysis of the series **1-3** indicates that the degree of puckering in **2** is intermediate between that in **1** and that in **3**.

In this paper experimental and theoretical studies of $^{13}\text{C}-^{13}\text{C}$ coupling are extended to two classes of compounds: 1,4-dihydro aromatic carboxylic acids (**1-3**) and aromatic carboxylic acids (**4-6**). This has been accomplished by the



synthesis and carbon NMR spectroscopic studies of carboxyl labeled **1-6**. It is shown that the data generated thereby overcome certain inadequacies which were previously encountered in the use of proton-proton coupling constants in the conformational analysis of **1-3**.² Further, some rather interesting trends in the coupling constants of **4-6**, the synthetic precursors to **1-3**, are noted.

The vicinal $^{13}\text{C}-^{13}\text{C}$ coupling constants in aliphatic and alicyclic organic compounds have been shown to be related to dihedral angle,³ and it was anticipated that a similar relationship would be followed in the series of compounds studied here. For example, **1** is known to be flat⁴ and **3** is known to be puckered,⁵ so that the experimental values of $^3J_{\text{CC}}$ of **2** would be indicative of the extent of puckering of the dihydro ring.

As this study developed, it became apparent that the $^3J_{\text{CC}}$ couplings in **1-3** do not obey the expected dependence on dihedral angle. However, long-range couplings were observed in **2** and **3** which were absent in the fully aromatic compounds

Table I. Carbon-13 Chemical Shifts for 1-9

Compd	Chemical shift ^a of carbon atoms													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 ^b	42.2	122.2	126.2	26.4	126.2	122.2								
2	47.2	124.2	128.0	30.3	128.9	127.6	126.7	129.2	132.9	134.9				
3	129.1	127.0	128.0	128.7	128.7	128.0	127.0	129.1	53.5	36.2	137.7	135.5	135.5	137.7
4 ^b	131.0	130.2	128.5	134.4	128.5	130.2								
5	127.9	131.3	125.4	134.2	129.4	126.9	128.4	126.7	132.3	134.9				
6	126.0	127.7	126.4	129.5	129.5	126.4	127.7	126.0	127.1	129.7	132.0	128.8	128.8	132.0
7 ^c	25.7	124.1	124.1	25.7	124.1	124.1								
8	29.9	125.1	125.1	29.9	128.7	126.2	126.2	128.7	134.3	134.3				
9	127.8	126.6	126.6	127.8	127.8	126.6	126.6	127.8	36.4	36.4	137.4	137.4	137.4	137.4

^aIn ppm relative to internal standard tetramethylsilane, measured in acetone-*d*₆, except where noted otherwise. ^bMeasured neat, using benzene internal standard, converted relative to TMS using δ (benzene) = 128.6 [G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 90]. ^cTaken from H. Günther and G. Jikeli, *Chem. Ber.*, **106**, 1863 (1973); measured in 3:1 CCl₄:CDCl₃ with TMS internal standard. For easy comparison of 1 and 7, the numbering of the carbons in 7 starts at the methylene position.

Table II. Carbon-Carbon Coupling Constants Involving the Carboxyl Carbon of 1-6

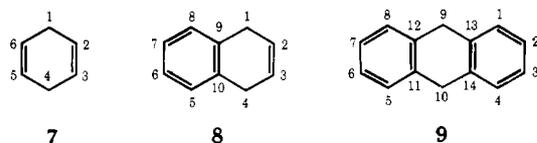
Compd	Coupling constant ^a of C*O ₂ H with carbon atom													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	55.5	2.8	3.2	0 ^b	3.2	2.8								
2	54.7	3.8	3.3	0.8	0 ^b	0.5	0 ^b	1.2	2.5	1.9				
3	1.3	0.8	1.0	0.8	0.8	1.0	0.8	1.3	54.8	0.8	1.5	2.9	2.9	1.5
4	71.9	2.5	4.5	0.9	4.5	2.5								
5	71.7	1.9	4.8	1.0	0 ^b	0 ^b	0 ^b	0.5	3.6	4.3				
6	2.4	0 ^b	2.4	^c	1.3	4.3	4.1	4.1	4.3					

^aIn Hz; considered to be accurate to 0.1 Hz. ^bSplitting not discerned; considered to be <0.5 Hz. ^cNot observed; obscured by other signals.

5 and 6, and these long-range couplings indicated a trend in the conformations of 1-3.

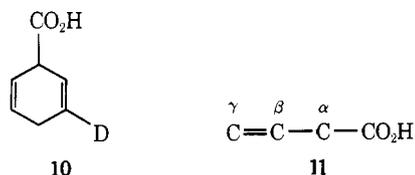
Chemical Shift Assignments

To help in the carbon chemical shift assignments for 1-3, the chemical shifts of the model hydrocarbon compounds 7-9



were used. The literature had previously suggested⁶ identical chemical shifts for the α carbon (C-1) and the β carbon (C-2) of 9; we investigated 9 and found the literature incorrect. Table I lists our assignments for 1-9.

Assignments for compounds 7-9, and for the methylene and methine carbons of 1-3, were straightforward. For the remaining assignments, the major uncertainty resided in correctly distinguishing the β and γ carbons of 1-6. Data from aliphatic systems suggest the β -carbon signal should be downfield to the γ -carbon signal,⁷ but *J* values obtained from such assignments did not appear to be self-consistent.⁸ To remove this uncertainty, 3-deuterio-1,4-dihydrobenzoic acid (10) was synthesized, whose carbon NMR spectrum established C-3 was indeed the downfield signal. Thus, for the moiety 11



the carboxyl group shields the β carbon and deshields the γ carbon (both by about 2 ppm).⁹ Arguments for the remaining chemical shift assignments appear in the Experimental Section.

Steric perturbation of the carboxyl group on C-1 (C-8) in 3 and C-8 in 2, a potentially shielding phenomenon,^{3a} is ap-

parently playing an insignificant role. That this perturbation is minor is consistent with previous conclusions that the carboxylate group in 2² and 3⁵ is axial and away from C-8.

Discussion

Table II lists the carbon-carbon coupling constants involving the carboxylate group of compounds 1-6.

General Trends. The geminal ¹³C-¹³C coupling constants (²*J*_{CC}) in 1-3 are the largest yet observed in aliphatic systems (2.5-3.8 Hz), but appear to be consistent with previous observations that ²*J*_{CC} couplings involving the CO₂H group,⁸ or involving aliphatic coupling to an sp²-hybridized carbon,¹⁰ are large. Apparently both factors are operating in 1-3 to produce an even larger ²*J*_{CC} value.

The three-bonded ¹³C-¹³C coupling constants (³*J*_{CC}) in 1-3 are consistently larger when involving the olefinic carbons (*J*_{C-C₃} = 3.2 in 1, 3.3 in 2) than when involving the aromatic carbons (*J*_{C-C₁₀} = 1.9 in 2; *J*_{C-C₁₁} = 1.5 in 3). Apparently the lower π -bond order along the aromatic route is reducing the aromatic couplings. Taking into consideration this difference between olefinic and aromatic couplings, there emerges a trend wherein ³*J*_{CC} remains rather constant throughout the series 1-3.

A further remarkable observation is that longer-range couplings (i.e., more than three bonds) become quite noticeable in the dihydro aromatic series. In 2 one longer-range coupling can be observed (*J*_{C-C₆} = 0.5 Hz) and *all* longer-range aromatic couplings in 3 are significant (*J*_{C-C₂}, *J*_{C-C₃}, *J*_{C-C₄} are 0.8-1.0 Hz). These longer-range couplings are *not* observed in the fully aromatic compounds 4-6 (even though a completely conjugated coupling route is available), except when this coupling route remains within one ring (i.e., the *cis* ⁴*J*_{CC} couplings to the para carbon in 4-6).

The *cis* ³*J*_{C-C₈} in 5 is rather small for a three-bonded coupling (0.5 Hz). This small coupling is in contrast to the larger ³*J*_{C-C₁} in 6 (2.4 Hz), but parallels the small ³*J*_{cis} in 1-pyrene-carboxylate (12)¹¹ (1.0 Hz). Perhaps the peri interaction in

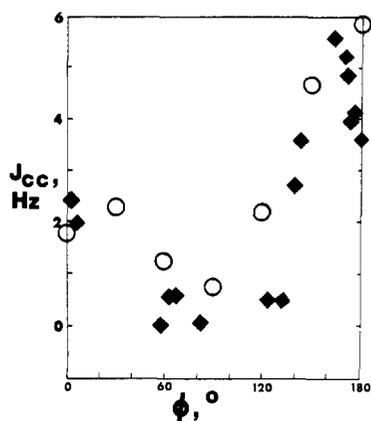
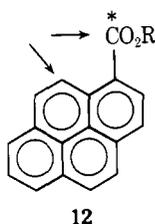


Figure 1. Experimental ${}^3J_{CC}$ values (\blacklozenge) for aliphatic and alicyclic carboxylic acids compared with theoretical ${}^3J_{CC}$ values (\circ) for butanoic acid, plotted vs. the dihedral angle ϕ .

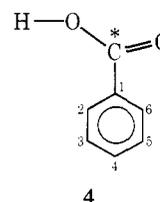


5 and 12 moves the carboxylate group laterally, thereby reducing the coupling. It is to be noted that in **6** peri interactions flank both sides of the carboxylate group. Another possible explanation is different rotational orientations of the carboxylate group, possibly giving rise to negative coupling contributions.^{3c}

Finally, the "allylic" longer-range coupling over four bonds (${}^4J_{C-C_4}$ in **1**, ${}^4J_{C-C_4}$ in **2**, and ${}^4J_{C-C_{10}}$ in **3**) is measurable in **2** and **3** but is small in **1**.

Comparisons with Theoretical Results. Molecular orbital (MO) calculations of ${}^{13}C$ - ${}^{13}C$ coupling constants were based on the finite perturbation theory (FPT) formulation^{12,13} in the INDO (intermediate neglect of differential overlap) approximation of self-consistent-field (SCF) molecular orbital theory. For comparison with the vicinal ${}^{13}C$ - ${}^{13}C$ coupling constants in compounds **1-6**, calculated values of ${}^3J_{C_1-C_4}$ in butanoic acid^{3c} are plotted in Figure 1 as a function of the dihedral angle ϕ . This dihedral angle is measured about the C_2-C_3 bond of butanoic acid. The experimental data^{3a} for the series of aliphatic and alicyclic carboxylic acids are also included in Figure 1. The agreement between the INDO-FPT results and the experimental data is not unreasonable.¹⁴ The major disparity is the appearance of the maximum in the experimental data at a somewhat smaller dihedral angle than 180° , which is probably due to the neglect of conformation changes in the carboxyl group as the dihedral angle was varied and/or the inadequacy of the use of *butanoic acid* as a model system for the actual alicyclic compounds from which the coupling constant data were extracted.^{3a,14} Except for the much smaller cis/trans ratio in Figure 1, the form of the angular dependence follows a form similar to that noted for the vicinal H-C-C-H group¹⁵ and other types of vicinal coupling.^{3a} Therefore, it appears that the dominant mechanism for vicinal ${}^{13}C$ - ${}^{13}C$ coupling in *aliphatic* systems in conformations with dihedral angles greater than about 60° is the direct^{14,16} (electron mediated) one associated with the interactions between the two vicinal C-C bonds. A similar mechanism is expected in the series of carboxylic acids **1-6**, but additional π -electron coupling paths are expected to modify the form of angular dependence of the ${}^3J_{CC}$ values. Furthermore, in the cases of

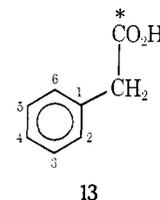
Table III. Calculated Carbon-Carbon Coupling Constants of Benzoic Acid (**4**)



Calculated J_{C-CO_2H} for carbon atom ^a					
2	3	4	5	6	
-8.55	7.46	-3.26	7.86	-6.95	

^a J values in Hz.

Table IV. Calculated Carbon-Carbon Coupling Constants of Phenylacetic Acid (**13**) with Different Orientations of the C-CO₂H Bond with Respect to the Plane of the Phenyl Ring



ϕ , ^a deg	Calculated J_{C-CO_2H} for carbon atom ^b					
	1	2	3	4	5	6
90	-6.99	3.50	-2.34	2.67	-2.34	3.52
60	-6.72	4.45	-1.66	2.08	-1.91	3.20
30	-6.19	6.12	-0.46	0.91	-0.99	2.73
0	-5.98	8.72	0.01	0.53	-0.84	1.97

^a Defined as the dihedral angle between the C-CO₂H carbon-carbon bond and the plane of the phenyl ring, as depicted in Figure 2. ^b J values in Hz.

${}^{13}C$ - ${}^{13}C$ coupling constants over more than three bonds, these π -electron mechanisms are dominant in analogy with long-range H-H coupling constants¹⁷ and because of the generally smaller magnitudes of ${}^{13}C$ - ${}^{13}C$ coupling constants.

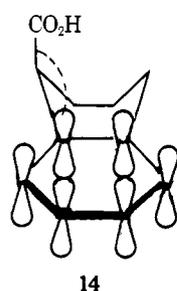
Calculated INDO-FPT results for ${}^{13}C$ - ${}^{13}C$ coupling constants associated with the carboxyl carbons were performed for the model compounds benzoic acid (**4**) (see Table III) and phenylacetic acid (**13**) (see Table IV). Structural data for use in the calculations were based on those for analogous molecules in the compilation of Sutton.¹⁸ The calculated results for phenylacetic acid (**13**) were obtained at 30° intervals of the dihedral angle ϕ , which is measured from the plane of the aromatic ring as depicted in Figure 2.

The calculated geminal coupling constants in Tables III and IV are substantially larger in magnitude than the experimental ones in Table II. The inadequacy of the INDO-FPT method for describing geminal coupling constants is general and was noted in the previous study of aliphatic compounds.^{3c}

It is disappointing to note that the calculated results for vicinal ${}^{13}C$ - ${}^{13}C$ coupling constants in Tables III and IV are significantly larger in magnitude than the experimental values for ${}^3J_{CC}$ in Table II. These calculated vicinal couplings are also larger than the ones calculated and observed for butanoic acid (Figure 1). In the latter case these differences must largely reflect contributions from mechanisms involving π -electron paths. For example, in benzoic acid (**4**) the σ bonds at the carboxyl carbon can interact with the $2p_z$ atomic orbitals via the σ - π exchange interaction, followed by delocalization in the carboxyl aromatic π -electron system, and finally σ - π exchange to the three σ bonds at each of the carbon atoms of the ring. A comparison of the experimental results in Table II with those

in Table III indicates that these types of π -electron mechanisms are overestimated by the INDO-FPT method. This is true for the longer-range ^{13}C - ^{13}C coupling constants as well as the vicinal ones. Inadequacies of the INDO-FPT scheme for describing coupling in aromatic systems have also been noted and discussed¹⁹ in a recent study of ^{13}C - ^{19}F coupling constants in a series of fluorinated and trifluoromethylated aromatic compounds. The results presented here would seem to substantiate the suggestion¹⁹ that the major source of difficulty may be related to the failure of the INDO scheme to describe coupling in aromatic systems rather than the neglect of orbital and dipolar terms in the Hamiltonian operator.

In the compounds 1-3, for which phenylacetic acid (13) provides the model compound, another type of π -electron mechanism is expected to contribute to the various ^{13}C - ^{13}C coupling constants to the carboxyl carbon. As the carboxyl group in Figure 2 is twisted out of the plane of the aromatic ring, the hyperconjugative interaction between the C-CO₂H bond and the $2p_z$ atomic orbital of the C-1 ring carbon will assume its maximum value for $\phi = 90^\circ$. Structure 14 illustrates



this maximum interaction for compound 3. In the case of vicinal ^{13}C - ^{13}C coupling, the resulting π mechanism will be superimposed on the σ -electron contributions, which should have an angular dependence roughly of the form of that shown in Figure 1. In Table IV the calculated values for $\phi = 90^\circ$ are 3.5 Hz in phenylacetic acid. This amount should be almost entirely due to the π -electron mechanism.

As noted above (under "general trends"), the three-bonded carbon-carbon coupling constants in 1-3 are rather constant, after the difference between olefinic and aromatic couplings is taken into consideration. To be noted are the olefinic couplings ($J_{\text{C}-\text{C}_3} = 3.2$ in 1 and $J_{\text{C}-\text{C}_3} = 3.3$ in 2), the trans aromatic couplings ($J_{\text{C}-\text{C}_{10}} = 1.9$ in 2 and $J_{\text{C}-\text{C}_{11}} = 1.5$ in 3), and the cis aromatic couplings ($J_{\text{C}-\text{C}_8} = 1.2$ in 2 and $J_{\text{C}-\text{C}_1} = 1.3$ in 3). This constancy in $^3J_{\text{CC}}$ prevails even when 1 is flat and 3 is puckered with an axial substituent. Thus, three-bonded carbon-carbon coupling constants are of no help in the conformational analysis of the series 1-3. Reasons for this constancy in $^3J_{\text{C}-\text{C}}$ are afforded by the π mechanism discussed above when one realizes the σ contribution (maximum when $\phi = 0^\circ$) and the π contribution (maximum when $\phi = 90^\circ$) may fortuitously balance one another such that the net observed $^3J_{\text{C}-\text{C}}$ does not vary much over the expected range of ϕ through the series 1-3 (perhaps $90^\circ > \phi > 55^\circ$). Supporting this view, the calculated results of Table IV suggest $J_{\text{C}-\text{C}}$ over this range of ϕ should be 1 Hz or less.

A marked difference exists, however, between the longer-range aromatic couplings in 2 ($J_{\text{C}-\text{C}_5}, J_{\text{C}-\text{C}_7} = 0, J_{\text{C}-\text{C}_6} = 0.5$) and in 3 ($J_{\text{C}-\text{C}_5}, J_{\text{C}-\text{C}_7} = 0.8, J_{\text{C}-\text{C}_6} = 1.0$); the couplings in 3 are at least twice the corresponding values in 2. For these longer-range couplings the π mechanism appears to be primarily responsible; Table IV indicates the σ contributions to these couplings (when $\phi = 0^\circ$) are minimal. Furthermore, these longer-range couplings in the aromatic series 4-6 (where $\phi = 0^\circ$) are not observed. These longer-range couplings, therefore, afford a method for conformational analysis of 2 and 3. Table IV suggests these longer-range couplings should vary

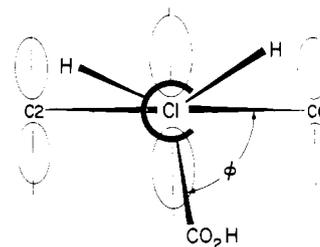


Figure 2. Schematic representation of the geometry of phenylacetic acid (13) used in the calculations given in Table IV.

by several tenths of a hertz as ϕ varies from 55° (for a flat 1) to 90° (for a highly puckered 3). Indeed, the longer-range couplings in 3 are at least 0.5 Hz larger than the corresponding values in 2. The longer-range couplings in 2 and 3, therefore, suggest 3 is definitely more highly puckered than 2. That 2 is somewhat flattened is consistent with the expected behavior of homoallylic proton-proton coupling constants^{2a} but is at variance with recent conclusions of Rabideau.^{2b}

In the cases of the "allylic" longer-range ^{13}C - ^{13}C coupling over four bonds ($^4J_{\text{CC}}$) in 1-3, there is a slight increase in the series ($^4J_{\text{C}-\text{C}_4} \leq 0.5$ Hz in 1 and $^4J_{\text{C}-\text{C}_4} = ^4J_{\text{C}-\text{C}_{10}} = 0.8$ Hz in 2 and 3, respectively). This is in accord with the expectation that this type of coupling would be greatest in 1 and smallest in 3 because of the decreased π -bond order in the latter. However, the increase in the coupling constants by as much as 0.8 to 0.3 Hz suggests (in conformity with the magnitudes of the changes in Table IV) that the increase in the dihedral angle in the series 1-3 could be as much as 30° .

Experimental Section

Labeled compounds 4-6 were synthesized by reacting carbon dioxide- ^{13}C (>90% isotopic purity; obtained from Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio) with the appropriate Grignard reagent utilizing the vacuum line technique previously described.^{3a}

Natural and labeled dihydro compounds 1-3 were synthesized according to the previously described Birch reduction procedure.^{2a,20}

Compound 7 was synthesized by the previously described procedure²⁰ used on 3-deuteriobenzoic acid.⁶

Carbon NMR spectra were recorded on a Bruker WH-90 Fourier transform NMR spectrometer operating at 22.63 MHz. Saturated solutions of the natural and labeled compounds were prepared in acetone- d_6 , which served as an internal ^2H lock. Chemical shifts of 1-9 were independently determined on natural samples using tetramethylsilane as an internal standard. The J_{CC} values of 1-6 were obtained using 8K data points over a 600 Hz spectral width. Splittings down to 0.5 Hz were reproducibly measured. These J_{CC} values were reproducible to 0.1 Hz and are considered to be accurate within 0.1 Hz. Couplings obtained on this instrument have been compared with those obtained on JEOL PS-100 and Varian CFT-20 NMR spectrometers and agree within 0.1 Hz.

Chemical Shift Assignments. In addition to the assignments discussed in the main text, the following methods were utilized.

For 2, the olefin signals were differentiated from the aromatic signals by selective proton-decoupling experiments. Of the aromatic signals of 2, C-5 through C-8 were distinguished from C-9 and C-10 by their much larger signals. The signal with the relatively large coupling ($J = 1.2$ Hz) was assigned as C-8 because of the three-bonded coupling available here. The remaining downfield signal was assigned as C-5, its being an α carbon.⁶ For the two β carbons (C-6 and C-7), additivity parameters were utilized.²¹ Signals C-9 and C-10 were assigned by allowing the β carbon to be upfield. Thus assigned, the chemical shifts for C-10 in 2 and in the model compound 8 are about the same. This parallels the observation that the meta quaternary carbon in substituted aromatics has a similar chemical shift to that in the unsubstituted analogue²² (cf. also 5 with naphthalene²³).

For **3**, the aromatic carbons of **3** were assigned in a manner identical with that for **2**. Thus assigned, it was observed that the same relative order of coupling constants occurred, viz., $J_{C-C_8} < J_{C-C_6} < J_{C-C_7} \sim J_{C-C_5}$ in both **2** and **3**. To verify that the α carbons in **3** (C-8 and C-5) were downfield from the β carbons (C-6 and C-7), a proton-coupled pattern²⁴ carbon NMR spectrum of **3** was recorded.

The analysis of **4** has been previously described.²⁵

For **5**, a proton-coupled pattern²⁴ spectrum differentiated the α and β carbons; furthermore, C-3, with no three-bonded carbon-proton coupling, appeared merely as a doublet. The three α carbons C-4, C-5, and C-8 were differentiated by: (1) the expectation that C-4 should be the furthest downfield;^{23,26} (2) steric perturbation of the carboxyl group on C-8 rendering its signal the furthest upfield.^{3a,26} The β carbons C-2, C-3, C-6, and C-7 were differentiated by: (1) the proton-coupled pattern of C-3 (vide supra); (2) the expectation that C-2 should be the furthest downfield;^{23,26} (3) the expectation that C-7 should be downfield from C-6.²³ The two γ carbons C-9 and C-10 were assigned by the expectation that $^3J_{CC} > ^2J_{CC}$. Thus assigned, the C-9 signal was upfield to the C-10 signal, consistent with previous reports of this "steric perturbation effect" on C-9 of 1-substituted naphthalenes.²³ These chemical shift assignments for **5** are consistent with the published chemical shifts of the structurally related 1-acetylnaphthalene.²⁷

For **6**, chemical shift assignments were done as previously reported for 9-anthracene derivatives.²² Chemical shifts for **6** thus parallel those for other 9-anthracene derivatives: (1) C-1 (C-8) and C-12 (C-13) are shielded relative to anthracene.²⁸ This imitates the "steric perturbation effect" observed in **5**. (2) The chemical shift of C-11 (C-14) is about the same as in anthracene²⁸ (compare 132.0 and 132.4 ppm).

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An Experimental Determination of the Free Energy of Hydrogen Bonding to an Anion Radical

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Abstract: The free energies for the hydrogen bond exchange reaction between the proton acceptors hexamethylphosphoramide (HMPA) and *p*-dinitrobenzene (PDNB) anion radical ($X\text{-PhC}\equiv\text{CH}\cdots\text{HMPA} + \text{PDNB}^{\cdot-} \rightleftharpoons X\text{-PhC}\equiv\text{CH}\cdots\text{PDNB}^{\cdot-} + \text{HMPA}$) were determined by the use of ESR. The free energies of hydrogen bond formation between the substituted phenylacetylenes and HMPA were determined separately from the NMR chemical shifts. These two free energies were then added in a thermochemical cycle to yield the free energies of hydrogen bonding to the anion radical, ΔG_a° . ΔG_a° was found to vary linearly with the σ^+ value for the para substituent on the donor. When this σ value is zero or greater, ΔG_a° is negative, indicating that the *p*-dinitrobenzene anion radical is a strong proton acceptor, whereas the neutral molecule is a very poor proton acceptor. This represents the first report of free energies of hydrogen bonding to an anion radical.

A wealth of information has been compiled on the thermodynamic parameters controlling the formation of hydrogen bonds between proton donors and neutral proton acceptors.¹ However, the literature is essentially devoid of reports of thermodynamic parameters for systems where anion radicals

serve as the hydrogen bond acceptor. This is true despite the fact that the extra negative charge should make these acceptors particularly viable proton acceptors and the fact that a number of reports dealing with equilibrium constants for systems with anion radicals as proton acceptors have appeared.²