# The Additivity of NMR Carbon–Carbon Spin–Spin Coupling Constants

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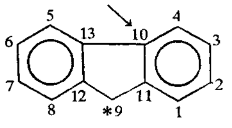
**Fluorene-9-$^{13}$C, fluorenone-9-$^{13}$C, acenaphthenone-11-$^{13}$C, acenaphthenone-12-$^{13}$C, 1-methylcyclopentanol-1-$^{13}$C and 1-methylcyclopentene-1-$^{13}$C were synthesized to obtain $J$(CC) values between the natural carbons and the labeled carbons. Each of these compounds possessed at least one asymmetric dual-path coupling, i.e., coupling between the labeled carbon and another carbon via simultaneous two- and three-bonded coupling paths. Model $^{13}$C-labeled compounds were synthesized where necessary to give expected values of the constituent mono-path couplings. Values of these dual-path couplings $^{(2+3)}J$ suggested that the observed value is the (at least approximate) algebraic sum of the two constituent $J$ values.**

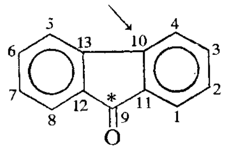
The additivity of NMR spin–spin coupling constants over more than one path has been implied in the literature,[1–7] and several examples exist of two simultaneous coupling pathways that do appear to be anomalously large.[3,5,6,8] However, other examples exist where a dual-path coupling appears reasonably low in value.[9–11] Because of the possibility of symmetry complications (all these dual-path couplings had two *identical* pathways) and because of the paucity of model compounds needed to determine the 'mono'-path $J$ value (e.g., what should the mono-path $^3J$(CC) value in benzene be?), it seemed desirable to explore systems with nonequivalent coupling paths. Carbon, with more than one bond, would lend itself to a greater variety of systems where different multiple pathways existed than would a proton, with only one bond. Hence, a study was initiated where carbon–carbon coupling constants could be determined in compounds involving two different coupling pathways. It was realized that the added complication of carbon–carbon coupling constant *sign* should be taken into consideration; fortunately, signs of $J$ values including virtually all types of *C—C—C—*C or *C—C—*C linkages involving sp$^3$, sp$^2$, or sp carbons are known.[12,13] An additional question potentially answerable in this study would be whether coupling constants were *algebraically* additive. Such a possibility could be explored if a system could be devised simultaneously possessing positive coupling and negative coupling pathways. The kind of systems chosen in this study involved simultaneous two- and three-bonded couplings and embraced compounds **1–6**.

## RESULTS

The method of obtaining carbon–carbon coupling constants was the same as before, i.e., by labeling a specific position in a molecule with >90% $^{13}$C and by subsequently observing the splitting in the natural abundance carbon signals.[16] Compounds synthesized and studied were fluorene-9-$^{13}$C (**1**), fluorenone-9-$^{13}$C (**2**), acenaphthenone-11-$^{13}$C (**3**), acenaphthenone-12-$^{13}$C (**4**), 1-methylcyclopentanol-1-$^{13}$C (**5**) and 1-methylcyclopentene-1-$^{13}$C (**6**). Chemical shifts and carbon–carbon coupling constants for **1–6** are given in Table 1.



**1**



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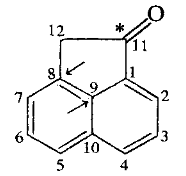

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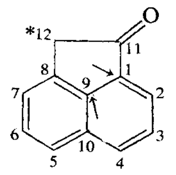

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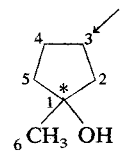

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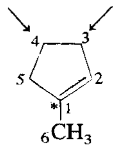

**6**

Although chemical shift assignments for **3–6** were straightforward, those for **1–2** were ambiguous. (Since this work was completed a study was reported[17] which included the chemical shifts of **1** and **2** and whose assignments agree with those of the present study.) Thus, specifically labeled deuterated compounds **1a,b** and **2a,b** were synthesized and analyzed by $^{13}$C NMR spectroscopy, and all chemical shift assignments for **1–6** are therefore certain. The chemical shift assignments for fluorene (**1**) suggest that literature assignments for indene[18] are incorrect: the $\delta$ values of C-1

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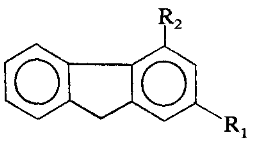
**Table 1. Chemical shifts and carbon–carbon coupling constants to labeled carbon in compounds 1–6[a]. $J$(CC), Hz ($\delta_C$, ppm)**

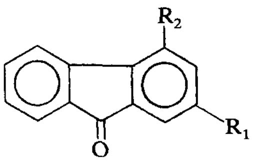
| | | | | | | | Carbon no.[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| **1** | 3.12 | 3.75 | 0.50 | 2.50 | 2.50 | 0.50 | 3.75 | 3.12 | L[d] | 4.50 | 42.25 | 42.25 | 4.50 |
| | (125.8) | (127.5) | (127.5) | (120.6) | (120.6) | (127.5) | (127.5) | (125.8) | (37.3) | (145.1) | (144.0) | (144.0) | (145.1) |
| **2** | 2.62 | 3.75 | 0.88 | 3.75 | 3.75 | 0.88 | 3.75 | 2.62 | L | 7.88 | [c] | [c] | 7.88 |
| | (124.4) | (129.8) | (135.4) | (121.4) | (121.4) | (135.4) | (129.8) | (124.4) | (205.7) | (145.1) | (133.0) | (133.0) | (145.1) |
| **3** | 54.81 | 1.83 | 4.03 | 0.98 | 0[e] | 0 | 4.15 | 3.66 | 9.80 | <2.0[f] | L | 42.72 | |
| | (134.9) | (120.8) | (127.4) | (130.9) | (123.4) | (127.8) | (120.5) | (133.9) | (142.2) | (130.3) | (190.4) | (42.0) | |
| **4** | 17.58 | 0 | 0 | 0 | 0 | 3.52 | 0 | 45.12 | 1.56 | 1.17 | | L | |
| **5** | L | 37.1 | 1.22 | 1.22 | 37.1 | 39.8 | | | | | | | |
| | (79.7) | (41.2) | (24.2) | (24.2) | (41.2) | (28.2) | | | | | | | |
| **6** | L | 72.0 | 4.88 | 1.71 | 38.1 | 44.7 | | | | | | | |
| | (139.6) | (123.9) | (32.6) | (23.9) | (36.8) | (16.4) | | | | | | | |

[a] Coupling constants appear first for each entry, chemical shifts are in parentheses. Chemical shifts referenced downfield to tetramethylsilane and are accurate to 0.1 ppm. $J$ values accurate and reproducible to 0.1 Hz.
[b] For numbering, see structures.
[c] Splitting obscured by other signals and not measured.
[d] L denotes labeled carbon.
[e] A value of 0 indicated no splitting and the $J$ value is considered to be less than 0.5 Hz.
[f] Obscured by other signals.

and C-4 in **1** (125.8 and 120.6, respectively) suggest the published values of C-1 and C-4 in indene[18] (120.8 and 123.5, respectively) should be reversed.



**1a:** $R_1 = D, R_2 = H$
**1b:** $R_1 = H, R_2 = D$



**2a:** $R_1 = D, R_2 = H$
**2b:** $R_1 = H, R_2 = D$

All compounds **1–6** possess simultaneous two- and three-bonded couplings. Since $^2J$(CC) and $^3J$(CC) values are generally substantial and measureable, a true test of additivity should be possible. Compounds **1** and **2** each possess one two- and one three-bonded coupling path to position 10 (or 13) from the labeled 9-position. Compounds **3** and **4** each have two possibilities for simultaneous two- and three-bonded pathways: to positions 8 and 9 from labeled position 11 in **3**, and to positions 1 and 9 from labeled position 12 in **4**. In **5** one such dual pathway exists, to position 3 (or 4) from position 1; in **6** two dual pathways exist, to positions 3 and 4 from the labeled 1-position. All of these positions of interest to which dual paths exist are marked by arrows in the drawn structures for **1–6**.

## DISCUSSION

The most difficult problem in assessing possible additivity of couplings in **1–6** would be obtaining the correct values for the constituent mono-path couplings. Hence, model compounds were synthesized where necessary to complement previous literature data. Unfortunately, *exact* models for mono-path couplings were virtually impossible, owing to electronic and steric differences. Nevertheless, the model compounds used appeared sufficiently close to ideality to

**Table 2. Chemical shifts and carbon–carbon coupling constants to the labeled carbon for model compounds[a]. $J$(CC), Hz ($\delta_C$, ppm)**

| | | | | | | | Carbon no.[b] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| **7** | 1.37 | 2.56 | 0[c] | 0 | 0 | 0 | 0 | 0 | 3.17 | 0.77 | 57.04 | L[d] | |
| | (129.4) | (127.8) | (125.1) | (127.9) | (128.4) | (125.5, | 126.2) | (123.3) | (131.7) | (133.5) | (39.2) | (177.9) | |
| **8** | 45.1 | 2.83 | 4.30 | 0 | 0 | 0 | 0 | 2.93 | 2.15 | 2.54 | L | 54.93 | |
| **9** | 13.7 | 8.4 | 0 | 0 | 0 | 8.4 | 42.7 | L | | | | | |
| | (135.8) | (128.5) | (128.5) | (131.1) | (128.5) | (128.5) | (188.1) | (20.2) | | | | | |
| **10** | 2.68 | [e] | 1.70 | 4.70 | 1.0 | 2.68 | 1.10 | 0 | 0 | 0 | 0 | 0 | L |
| | (142.7) | | (130.0) | (128.7) | (131.6) | (130.5) | (140.3) | (127.4) | (127.8) | (126.5) | (127.8) | (127.4) | |
| **11** | 47.36 | 2.93 | 3.42 | 0 | 0 | 0 | 0 | 1.34 | 2.69 | 2.69 | L | | |
| | (135.7) | (124.7) | (123.0) | (127.9) | (127.7) | (125.1, | 125.6) | (124.5) | (130.5) | (133.1) | (62.8) | | |

[a] Coupling constants appear first for each entry, chemical shifts are in parentheses. Chemical shifts referenced downfield to tetramethylsilane and are accurate to 0.1 ppm. $J$ values accurate and reproducible to 0.1 Hz.
[b] For numbering, see structures.
[c] A value of 0 indicates no splitting and the $J$ value is considered to be less than 0.5 Hz.
[d] L denotes labeled carbon.
[e] Not observed.

allow meaningful comparisons. Carbon–carbon coupling constants taken from the model compounds synthesized in this study appear in Table 2.

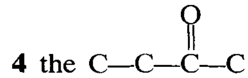
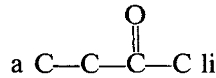
For **1** and **2**, the dual-path *J* values are larger than one would have anticipated considering only one coupling pathway, and thus it appears that the two pathways (both of which should be positive in sign[12,13]) are at least roughly additive. For **1**, the anticipated $^2J$ contribution (from toluene,[19] benzyl alcohol,[10] *o*-methylbenzyl alcohol,[20] *o*-methylbenzyl chloride[20]) should be *c.* 3 Hz, and the $^3J$ contribution from a number of *o*-disubstituted benzene compounds[20] should be *c.* 2–3 Hz. The observed dual *J* value in **1** is 4.5 Hz, less than the sum of the $^2J$ and $^3J$ model values, but larger than either the $^2J$ or $^3J$ value alone.

For **2**, the anticipated $^2J$ contribution can vary from 2–6 Hz for various aromatic carbonyl compounds; the value is typically 2–3 Hz in toluic derivatives[20] but increases to 5.8 Hz for the $^2J$(CO,C-2) value in 1-naphthaldehyde.[21] A conformational dependence of *J*(CC) on the orientation of the carbonyl group exists. This $^2J$ value for aromatic carbonyl compounds appears to be potentially quite large when the carbonyl group is ideally planar with the aromatic ring,[21] as is the case with **2** where the carbonyl group is locked rigidly into planarity with the aromatic ring. The anticipated $^3J$ contribution (as from toluic derivatives[20]) should be 2–3 Hz. The observed dual *J* value in **2** is actually 7.9 Hz. Thus, for the fluorene compounds **1** and **2** a rough additivity of the constituent $^2J$ and $^3J$ contributions appears to be taking place.

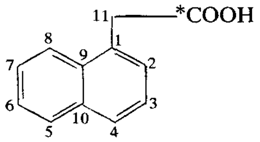
Compounds **3** and **4** each have two dual path ($^2J+{}^3J$) possibilities. First, **3** has an observed $^{(2+3)}J$ of 3.7 Hz to C-8. The model $^2J$ value could be derived from 1-naphthylacetic acid (**7**, see Table 2), viz., 1.4 Hz. The model $^3J$ value could be obtained from toluic derivatives[20] and should be 2–3 Hz. Thus, it appears that the observed $^{(2+3)}J$ value is additive (both $^2J$ and $^3J$ contributions should be positive in sign.[12,13]

Compound **3** also has an observed dual *J* of 9.8 Hz to C-9. The model $^2J$ value is the same as for **2** and can range from 2 to 6 Hz. The model $^3J$ should be *c.* 3 Hz from 1-naphthylacetic acid, albeit a severe conformational difference exists between the involved C—C—C—C linkages in **3** and **7**. Thus, as for **2**, it appears that a rough additivity is taking place, and that a large (*c.* 8–10 Hz) $^{(2+3)}J$ results when a $^2J$ aromatic contribution is included which involves a O═C—C(sp$^2$)—C(sp$^2$) linkage. That the observed $^{(2+3)}J$ in **3** is 2 Hz larger than in **2** may merely reflect the fact that the $^3J$ contribution is partially *aliphatic* in **3** and should be larger than the purely aromatic $^3J$ contribution in **2**.[20] The signs of $^2J$ and $^3J$ should both be positive.[13,14]

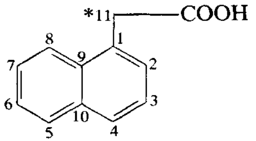
In **4**, an observed $^{(2+3)}J$ value of 17.6 Hz to C-1 is observed. The model $^2J$ of 13.7 Hz is taken from acetophenone (**9**) and the model $^3J$ of 2.9 Hz is taken from **8** (both *J* values should be positive[12,13]). For these two model values no conformational complications are anticipated (i.e., no conformational differences exist between **4** and **8** and between **4** and **9** which would lead to anticipated differences between the model *J* value and the expected *J* contribution in **4**), and in fact the sum of the model values 13.7 + 2.9 = 16.6 Hz is close to the observed value of 17.6 Hz.

The other dual *J* value in **4** is 1.6 Hz to C-9. A model $^2J$ value of 2.2 Hz is taken from compound **8**. For the $^3J$ model value, a satisfactory model compound is difficult to find. Acetophenone (**9**) suggests a value of 8.4 Hz, although in **4** the  $\mathrm{C{-}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C}$ linkage is frozen *cis*. Little is known of the dependence of $^3J$ on the conformation of a  $\mathrm{C{-}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C}$ linkage. However, values of $^3J$(HH) from conformationally frozen (low temperature) formamide are much lower for *cis* (2.1 Hz) than for *trans* (12.9 Hz[22]). Thus, a true model $^3J$ value for **4** to position C-9 may be substantially less than the observed value of 8.4 Hz in **9**. Nonetheless, it is clear that the observed dual *J* value of 1.6 Hz to position C-9 in **4** does not agree at all with the sum of anticipated model $^2J$ and $^3J$ values. Hence, in this instance either (1) additivity is shown not to operate or (2) one of the signs of the model *J* values is negative and the model *J* values are *algebraically* additive. In fact, it has been observed that in some cases $^2J$(CC) values in sp$^3$–sp$^2$–sp$^2$ (aromatic) systems can be negative.[23]

In view of the unresolved questions remaining after a study of the systems **1**–**4**, it was concluded that it would be desirable to explore a system that (1) had no conformational ambiguities of the kind discussed above, (2) had good model systems whose $^2J$ and $^3J$ values could be determined, and (3) would have $^2J$ and $^3J$ contributions of *opposite* sign to ascertain if *J* values were algebraically additive. The systems chosen to meet all of these criteria were **5** and **6**.



**7**



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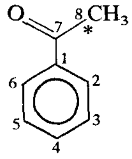

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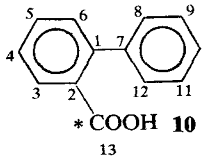

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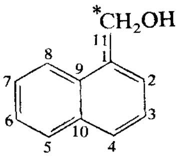

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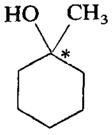
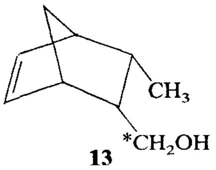


**12**



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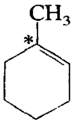
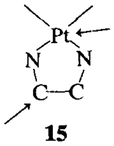
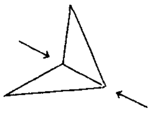


**14**



**15**



**16**

In **5** the observed $^{(2+3)}J$ value (to C-3) was 1.22 Hz. The model $^2J$ value (expected to be negative[12b]) was taken from 1-methylcyclohexanol-1-$^{13}$C (**12**)[16] and was (−)1.7 Hz. The model $^3J$ value of 4.6 Hz was taken from *endo,endo*-5-methylol-6-methylnorbornene-8-$^{13}$C (**13**),[24] whose analogous C—C—C—C*—OH linkage had the same *cis* geometry (differences of the relative orientation of the hydroxyl group in **5** and **13** should be small, but in any case this should be a minor consideration[24]). Therefore, there does indeed appear to be a dramatic decrease in the observed $^{(2+3)}J$ value, which strikes one as curiously small for a coupling involving carbons so closely situated until it is realized that algebraic addition of coupling contributions must be taking place.

In **6** two dual path $^{(2+3)}J$ values exist. For the coupling to C-3 (4.9 Hz) the constituent couplings would be $^2J \simeq 0$[25] and $^3J = 4$–$5$ Hz. [For $^3J$(CC) the olefin functionality has little effect, whether it is internal (C═C—C—C), external (C═C—C—C—C), or absent (Ref. 25). For a cisoid butane linkage, $^3J$(CC) should be 4–5 Hz (Ref. 24).] Thus, the observed value of 4.9 Hz in **6** merely reflects that the $^2J$ contribution is negligible.

The other dual path coupling in **6** was to C-4 and was observed to be 1.7 Hz. The model $^2J$ value, expected to be negative,[12b] was taken from 1-methylcyclohexene-1-$^{13}$C (**14**)[25] and was (−)2.0 Hz The model $^3J$ value was again 4–5 Hz.[24] Thus, again there was attenuation of the $^{(2+3)}J$ value, explicable if there was algebraic addition of constituent coupling constants.

## CONCLUSIONS

For dual-path carbon–carbon couplings involving a $^2J$ and a $^3J$ contribution, the observed $J$ value appears to be at least roughly equal to the sum of the constituent $J$ contributions. It is unclear whether this phenomenon of additivity is only approximate because exact model compounds (with equivalent electronic and steric environments) are impossible to obtain or whether coupling constant contributions are not strictly additive.[4] Nevertheless, where contributing couplings are opposite in sign, an attenuation of the observed dual-path coupling is observed, and therefore the sum of the constituent $J$ contributions appears to be algebraic.

A previous example exists in the literature where it appears that dual-path spin–spin coupling constants are algebraically additive.[26] In certain bipyridyl diaminoethane platinum complexes, the $^{195}$Pt–$^{13}$C coupling constant is significantly attenuated when a $^{2+3}J$ situation occurs (see **15**). It is argued[26] that the $^2J$ contribution should be negative in sign and that the $^3J$ contribution should be positive in sign, and that the observed $^{2+3}J$ is consequently quite small.

That coupling contributions appear to be algebraically additive may have significance upon previous conclusions that the directly-bonded [$^1J$(CC)] coupling constant in bicyclobutane (**16**) is negative (−5.4 Hz).[15] In this example, $^2J$ contributions were ignored. In bicyclobutane the geminal [$^2J$(CC)] couplings should be much less (algebraically) than in unstrained aliphatic systems,[7] and there are two such negative coupling contributions. It is quite possible, therefore, that geminal contributions to $J$(CC) in bicyclobutane could surpass the observed value of −5.4 Hz, and that the actual $^1J$(CC) value [minus the $^2J$(CC) contributions] in bicyclobutane is positive.

## EXPERIMENTAL

$^{13}$C-Carbon dioxide (90% isotopic purity) was purchased from the Monsanto Research Corporation, Mound Laboratory, Miamisburg, Ohio. The labeled carbon dioxide was introduced into the samples by the technique previously described.[16]

The $^{13}$C NMR spectra were recorded in chloroform-*d* as a solvent and internal lock, with tetramethylsilane as internal standard, on a Bruker WH-90 NMR spectrometer operating at 22.63 MHz (the fluorene samples) and on a JEOL PFT-100 NMR spectrometer, operating at 25.16 MHz (all other samples). Chemical shifts were determined by using natural compounds (i.e., not $^{13}$C-labeled). The $J$(CC) values, obtained by measuring the splitting in the natural carbon signals and by using 8K data points over a 500 or 600 Hz spectral width, were reproducible to 0.1 Hz and are considered to be accurate to 0.1 Hz.

*Diphenyl-2-carboxylic acid-carboxyl-*$^{13}$*C* (**10**). To a solution of diphenyl-2-magnesium bromide, prepared by the reaction of 0.6 g of magnesium turnings and 5.18 g of 2-bromobiphenyl in 60 ml of anhydrous diethyl ether, was added 1.0 g of $^{13}$C-carbon dioxide. The usual workup[16] yielded 2.9 g (66%) of **10**, mp 111–112 °C (lit.[27] mp 113–114 °C).

*Fluorenone-9-*$^{13}$*C* (**2**). A mixture of 0.8 g of **10** and 10 ml of 80% aqueous sulfuric acid was heated at 85 °C for ½ h, poured over ice water, and filtered to give 0.71 g (98%) of **2**, mp 78–79 °C (lit.[27] mp 79–80 °C).

*Fluorene-9-*$^{13}$*C* (**1**). A solution of 0.5 g of **2**, 1.6 ml of hydrazine hydrate, and 16 ml of ethylene glycol was stirred and heated under reflux for 5 h, cooled, mixed with 100 ml of 5% aqueous hydrochloric acid, and extracted with diethyl ether. The ethereal extract was dried (anhydrous magnesium sulfate) and concentrated under reduced pressure to yield 0.4 g of **1** (89%), mp 113–114 °C (lit.[28] mp 112–114 °C).

*2-Deuteriofluorene* (**1a**). 2-Bromofluorene (0.50 g) (Aldrich Chemical Company, Milwaukee, Wisconsin) was reduced with sodium borodeuteride (0.84 g) with palladium chloride catalyst (0.72 g) and methanol-O-*d* solvent (14.0 ml), using the procedure of Bosin[29], to give 0.31 g (91%) of **1a**, whose carbon NMR signal at 127.5 ppm was reduced in intensity.

*2-Deuteriofluorenone* (**2a**) was prepared by the air oxidation of **1a** (0.25 g), using 200 mg of 18-crown-6 (Aldrich Chemical Company), 0.125 g of potassium hydroxide, and 2 ml of benzene and vigorously stirring for 1 h. The benzene solution was washed with 5 ml of 6N hydrochloric acid, 2 × 5 ml of brine solution, dried (anhydrous magnesium sulfate), and concentrated under reduced pressure to give 0.26 g (100%) of **2a**. A recrystallized sample of **2a** (mp 78–80 °C) displayed a carbon NMR spectrum whose signal at 129.8 ppm was reduced in intensity.

4-*Bromofluorenone* was prepared by the diazotization of 4-aminofluorenone (2.0 g) by adding 40 ml of glacial acetic acid and 10 ml of 48% aqueous hydrobromic acid, by cooling in an ice/salt bath, and by then adding a solution of 0.45 g of sodium nitrite in 5 ml of water below the surface of the stirring mixture over a period of 10 min. After 8 min more of stirring, 0.1 g of urea was added for a further 8 min of stirring. The reaction mixture was poured into a boiling solution of 1.95 g of cuprous bromide in 20 ml of 6n hydrochloric acid. After 5 min of further heating, the reaction mixture was allowed to cool and stand overnight. The product was collected by filtration, washed with 80 ml of water, and recrystallized from 95% ethyl alcohol to give 2.0 g of 4-bromofluorenone (75%), mp 123–124 °C (lit.[30] mp 125–126 °C).

4-*Bromofluorene* was prepared by the Wolff-Kishner reaction for 4-bromofluorene as for **1** above, to give 0.62 g (97%), mp 57–59 °C (lit.[30] mp 61 °C).

4-*Deuteriofluorene* (**1b**) was synthesized from 4-bromofluorene using the same procedure as above for **1a** to give 0.28 g (96%), whose carbon NMR signal at 120.6 ppm was reduced in intensity.

4-*Deuteriofluorenone* (**2b**) was prepared from **1b** as described above to give 0.04 g (80%), whose carbon NMR signal at 121.4 ppm was reduced in intensity.

*Acenaphthenone*-11-$^{13}$*C* (**3**) and *acenaphthenone*-12-$^{13}$*C* (**4**) were synthesized by the same synthetic sequence, except for the step wherein the $^{13}$C-carbon dioxide was introduced. First, natural or $^{13}$C-carboxyl-1-napthoic acid[31] was reduced to give 1-naphthylmethanol, natural or $^{13}$C-labeled (**11**), 5.0 g (90%), mp 57–59 °C (lit.[32] mp 59.5–60.0 °C), which was converted with thionyl chloride to natural or labeled 1-naphthylmethyl chloride (5.0 g, 90%). This product without further purification was converted to the Grignard reagent[33] and carboxylated with either $^{13}$C or natural carbon dioxide to give 1-naphthylacetic acid-*carboxyl*-$^{13}$C (**7**), 1.4 g (30%), mp 131 °C (lit.[33] mp 133 °C) or 1-naphthylacetic acid-11-$^{13}$C (**8**), 1.6 g (30%), mp 132 °C. The specifically $^{13}$C-labeled **7** and **8** were then converted to the respective $^{13}$C-labeled acenaphthenone by the procedure of Snyder[34] (0.5 g of **7** or **8**, 10 ml of polyphosphoric acid heated at 100 °C for $\frac{1}{2}$ h) to give 0.14 g of **3** (30%), mp 116–119 °C (lit.[35] mp 119–120 °C) and 0.060 g of **4** (15%), mp 115–118 °C.

*Acetophenone*-8-$^{13}$*C* (**9**) was prepared in 95% yield (1.9 g) by the pyridinium chlorochromate[36] oxidation of 1-phenyl-1-ethanol-2-$^{13}$C, prepared in 78% yield (2.0 g) by the reaction of benzaldehyde (2.2 g) with $^{13}$C-methylmagnesium iodide[14] (3.0 g).

1-*Methylcyclopentanol*-1-$^{13}$*C* (**5**). To an initiated Grignard mixture of 0.1 g of 1-bromobutane, 5 g of magnesium turnings, and 50 ml of dry diethyl ether was added 10 g of 1,4-dibromobutane, (prepared by the reaction of 1,4-butanediol with phosphorous tribromide and subsequent distillation, 101 °C/10 mm, 70% yield) in 100 ml of dry diethyl ether over a period of 1 h. After 3 h of subsequent stirring, 3.5 ml of ethyl acetate-*carboxyl*-$^{13}$C[19] in 25 ml of dry diethyl ether was added, while the reaction mixture was cooled in an ice bath. After 24 h of subsequent stirring at room temperature, water (200 ml) was added and the organic phase was removed, and the aqueous phase was extracted (2 × 50 ml) with diethyl ether. The combined ethereal extracts were washed with saturated aqueous sodium bicarbonate solution, dried (anhydrous magnesium sulfate) and distilled to give 2.2 g (64%) of **5**, 40 °C/10 mm.

1-*Methylcyclopentene*-1-$^{13}$-*C* (**6**). A mixture of 2.2 g of **5** and 0.1 g of iodine was slowly heated[19] and distilled to produce a mixture of **6** and water. The product (1.2 g, 65%) was decanted and was proved by carbon NMR spectroscopy to be pure for clean analysis.

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## REFERENCES

1. (a) M. Barfield, R. J. Spear and S. Sternhell, *J. Am. Chem. Soc.* **93**, 5322 (1971); (b) M. Barfield, R. J. Spear and S. Sternhell, *J. Am. Chem. Soc.*, **97**, 5160 (1975); (c) M. Barfield and B. Chakrabarti; *J. Am. Chem. Soc.*, **91**, 4346 (1969).

2 H. Günther, *Tetrahedron Lett.* 2967 (1967).

3. F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.* **94**, 6021 (1972).
4. R. Lozac'h and B. Braillon, *J. Magn. Reson.* **12**, 244 (1973).

5 E. W. Garbisch Jr and M. G. Griffith, *J. Am. Chem. Soc.* **90**, 3590 (1968).

6 L. J. Durham, J. Studebaker and M. J. Perkins, *Chem. Commun.* 456 (1965).

7. J. N. Murrell, *The Theory of Nuclear Spin–Spin Coupling in High Resolution NMR Spectroscopy*, Ed. by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Vol. 6, p. 1. Pergamon Press, New York (1970).

8 J. L. Marshall, L. G. Faehl, C. R. McDaniel Jr and N. D. Ledford, *J. Am. Chem. Soc.* **99**, 321 (1977).

9. J. L. Marshall, A. M. Ihrig and D. E. Miiler, *J. Magn. Reson.* **16**, 439 (1974).
10. A. M. Ihrig and J. L. Marshall, *J. Am. Chem. Soc.* **94**, 1756 (1972).
11. J. L. Marshall and A. M. Ihrig, *Org. Magn. Reson.* **5**, 235 (1973).
12. (a) P. E. Hansen and A. Berg, *Org. Magn. Reson.* **8**, 591 (1976); (b) P. E. Hansen, O. K. Poulsen and A. Berg, *Org. Magn. Reson.* **8**, 632 (1976); (c) P. E. Hansen, O. K. Poulsen and A. Berg, *Org. Magn. Reson.* **7**, 405 (1975).
13. (a) S. A. Linde and H. J. Jakobsen, *J. Am. Chem. Soc.* **98**, 1041 (1976); (b) S. Sorensen, R. S. Hansen and H. J. Jakobsen, *J. Am. Chem. Soc.* **95**, 5080 (1973); (c) S. Sorensen, R. S. Hansen and H. J. Jakobsen, *J. Magn. Reson.* **14**, 243 (1974); (d) H. J. Jakobsen, T. Bundgaard and R. S. Hansen, *Mol. Phys.* **23**, 197 (1972).
14. J. L. Marshall, D. E. Miiller, H. C. Dorn and G. E. Maciel, *J. Am. Chem. Soc.* **97**, 460 (1975).
15. M. Pomerantz, R. Fink and G. A. Gray, *J. Am. Chem. Soc.* **98**, 291 (1976).
16. J. L. Marshall and D. E. Miiller, *J. Am. Chem. Soc.* **95**, 8305 (1973).
17. J. B. Stothers, C. T. Tan, and N. K. Wilson, *Org. Magn. Reson.* **9**, 408 (1977).

18. N. Platzer, J. J. Basselier and P. Demereman, *Bull. Soc. Chim. Fr.* **5, 6,** 905 (1974).
19. J. L. Marshall, A. M. Ihrig and D. E. Miiller, *J. Mol. Spectrosc.* **43,** 323 (1972).
20. J. L. Marshall, L. G. Faehl and R. Kattner, *Org. Magn. Reson.* **12,** 169 (1979).
21. P. E. Hansen, O. K. Poulsen and A. Berg, *Org. Magn. Reson.* **9,** 650 (1977).
22. B. Sunners, L. H. Piette and W. G. Schneider, *Can. J. Chem.* **38,** 681 (1960).
23. P. E. Hansen, private communication.
24. J. L. Marshall, S. A. Conn and M. Barfield, *Org. Magn. Reson.* **9,** 404 (1977).
25. J. L. Marshall and D. E. Miiller, *Org. Magn. Reson.* **6,** 395 (1974).
26. L. E. Erickson, J. E. Sarneski and C. N. Reilley, *Inorg. Chem.* **14,** 3007 (1975).
27. C. H. Heidelberger and H. S. Ricke, *Cancer Res.* **11,** 640 (1951).
28. A. S. Harris, E. N. White and D. McNeil, *J. Chem. Soc.* 4216 (1955).
29. T. B. Basin, *Tetrahedron Lett.* 4699 (1973).
30. K. Suzuki, S. Kajigaeshi and S. Katio, *Yûki Gôsei Dagaku Kyôkai Shi*, **16,** 304 (1978).
31. J. L. Marshall, L. G. Faehl, A. M. Ihrig and M. Barfield, *J. Am. Chem. Soc.* **98,** 3406 (1976).
32. K. Ziegler, *Ber.* **54,** 737 (1921).
33. H. Gilman and J. E. Kirby, *J. Am. Chem. Soc.* **51,** 3475 (1929).
34. H. R. Snyder and F. X. Werber, *J. Am. Chem. Soc.* **72,** 2965 (1950).
35. A. L. Green and D. H. Hey, *J. Chem. Soc.* 4306 (1954).
36. E. J. Corey and J. W. Suggs, *Tetrahedron Lett.* 2647 (1975).

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