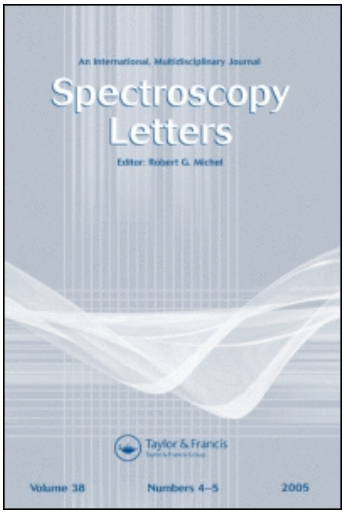

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ALTERNATE π-BOND ROUTES FOR CARBON-13-CARBON-13 SPIN-SPIN COUPLING -- HYPERCONJUGATIVE σ-π VS NON-CLASSICAL p-p INTERACTIONS

Key words: Acetyl[2.2]paracyclophane, Phenylacetic acid, Carbon-13-labeled compounds, Carbon-13 nuclear magnetic resonance

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In a previous report[1] longer-range carbon-13-carbon-13 spin-spin coupling up to five bonds was noted in ^{13}C-carboxyl-9,10-dihydro-9-anthroic acid. Although many types of longer-range proton-proton couplings in various π-systems are known[2] (e.g., cumulenes) which may portend analogous π-systems in carbon-carbon couplings, this type of carbon-carbon coupling observed in 9,10-dihydro-9-anthroic acid has no analogy in proton-proton coupling, since proton cannot be incorporated within a ring.

In the present study two new systems were explored which potentially were capable of carbon-carbon coupling via π-interactions and which had no proton-proton analogy. Accordingly, ^{13}C-carboxyl-labeled 1 and 2 were synthesized. In 1 (^{13}C-carboxyl-phenylacetic acid) a σ-π "hyperconjugative" route is present (see 3), and in 2 (^{13}C-carboxyl-2-acetyl[2.2]paracyclophane) a π-π "non-classical"[3] coupling is potentially available (see 4).

Compound 1 was synthesized by reacting benzyl Grignard reagent with >90%-^{13}C-carbon dioxide utilizing the technique previously described,[4] and compound 2 was synthesized with >90%-^{13}C incorporation by reacting ^{13}C-carboxyl-acetyl chloride[5] with [2.2]paracyclophane.[6] The carbon-carbon couplings involving the labeled carboxyl carbon were then determined in 1 and 2 by directly measuring the splitting in each of the natural carbon signals. Table 1 gives the chemical shifts and coupling constants derived in this study for 1 and 2.

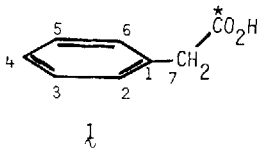
TABLE 1

Carbon-13 Chemical Shifts, and Carbon-Carbon Coupling Constants Involving the Labeled Carbon, for Compounds 1 and 2

Carbon No.	Chemical Shifts, δ[a] (Coupling Constants, J[b]) for Compound:	
	1[c]	2[c]
1	135.0 (2.0)	140.8 (1.7)
2	129.9 (1.9)	137.3 (53.7)
3	128.9 (0.5)	135.6 (3.9[e])[f]
4	127.3 (0.7)	139.1 (4.4)
5	128.9 (0.5)	135.7 (<1.0[e])
6	129.9 (1.9)	133.6 (3.9)
1'		138.5 (0.[g])
2'		130.6 (0.[g])[h]
3'		131.5 (0.[g])
4'		139.6 (0.[g])
5',6'[d]		132.3 (0.[g])
		132.5 (0.[g])
7,8,9,10[d]	41.1 (55.9)	34.9-35.8[i]
CH_3		28.4 (41.8)[j]

[a] In ppm, referenced to internal standard TMS; considered to be accurate within 0.1 ppm. Carbon-13 spectra recorded on a JEOL PS-100 nmr spectrometer with resolution better than 0.1 Hz. [b] In Hz, accurate to 0.1 Hz, except where noted. [c] Chemical shift assignments for 1 were trivial, and for 2 were done on the basis of additivity parameters, coupling patterns, and steric perturbation effects. [d] Assignments not differentiated. [e] Interference of these two signals rendered the accuracy of the Js to 0.5 Hz. [f] Proton nmr spectrum gave $^3J(C^*\text{-}H_3) = 4.8$ Hz. [g] Less than 0.5 Hz. [h] No evidence of coupling from the labeled carbon to the H(2') proton was seen in the proton nmr spectrum. [i] Overlapping signals. [j] Proton nmr spectrum gave $^2J(C^*\text{-}H) = 5.8$ Hz.

The data of Table 1 show that longer-range coupling (i.e., longer than three bonds) is significant in 1 and that σ-π interactions are indeed apparently operating here. These couplings are akin to the "allylic" type



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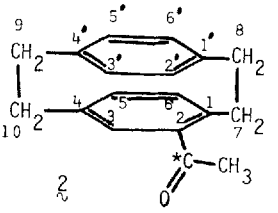

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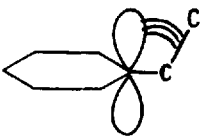

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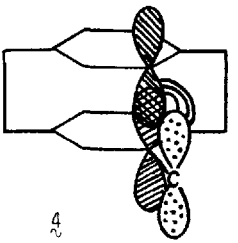

4

σ-π interactions in proton-proton couplings[7] but operate at longer range. The existence of these couplings in 1 is in agreement with such a "hyperconjugative" effect suggested by theoretical calculations (SCF-INDO-FPT) conducted for compound 1 itself.[1]

Regarding compound 2, the extensive electronic interactions between the two decks of [2.2]paracyclophane have been thoroughly documented (ultraviolet spectra,[8] orientation effects in electrophilic substitution[9] and in Birch reductions[10]), and one might have expected rather efficient transmittal of the spin information from one deck to the other in spin-spin coupling. That in fact no coupling is observed between the two decks indicates that either (1) the excited state phenomena in [2.2]paracyclophane do not carry over to the ground-state phenomenon of spin-spin coupling; and/or (2) in planar π-systems the carbon-carbon coupling is transmitted predominately through the σ-electrons. If this latter explanation is correct, then the observation that three-bonded couplings in aromatic compounds depend upon the π-bond order of the coupling path[11] may merely reflect the shorter bonds associated with higher π-bond order.

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