for valuable comments concerning the interpretation of these results.

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Nuclear Magnetic Resonance Spectroscopy. Long-Range Spin–Spin Couplings Involving Carbon-13[1]

Sir:

Relatively few studies have been reported of spin–spin couplings involving carbon and atoms more than one bond removed. Such couplings can often be seen as ^{13}C satellites in spectra of the other nuclei, but unless the spectra are simple, and even if the "inner" satellites can be detected, specific coupling assignments may not be possible. In such circumstances, specific isotopic enrichment can be of great value.[2] Carbon–fluorine[3] and carbon–phosphorus couplings[4] have been directly observed in the natural-abundance ^{13}C satellites. Internuclear double-resonance experiments utilizing observations of proton spectra have been used to study couplings between carbon and nondirectly bonded phosphorus[5] and nitrogen[6] where the proton spectra are relatively simple. We report here some nonbonded couplings between carbon and other nuclei measured directly from ^{13}C spectra in which the protons are decoupled.

Some couplings involving aromatic carbons are given in Table I. With complete proton decoupling, the ^{13}C spectrum of fluorobenzene consists of four doublets. The signs were determined by partial decoupling techniques and analysis of the second-order proton-decoupled ^{13}C spectra of the difluorobenzenes. The proton-decoupled ^{13}C spectrum of 1-fluoronaphthalene consists of ten doublets arising from carbon–fluorine couplings ranging from 0.8 to 250 Hz, while the ^{13}C spectrum of 2-fluoronaphthalene consists of six doublets and four singlets. Substituent effects on carbon–fluorine coupling in fluorobenzenes have been measured for some 30 compounds and will be discussed in detail elsewhere.

Two-bond, carbon–carbon coupling constants have been observed in molecules in which these couplings would be expected to be large on the basis of carbon–proton couplings in similar bonding situations. The C-1,C-3 coupling in 2-butanone is 15.1 Hz and the C-1,C-3 coupling in propyne is 11.8 Hz.[7] A large, three-bond carbon–carbon coupling of 13.95 Hz in pyridine has no analogy in carbon–proton coupling. The signs of the carbon–carbon coupling constants are unknown.

Table I. Coupling of Carbon to Other Elements in $(C_6H_5)_nX^a$

X	n	$J_{CX}{}^b$	$J_{CCX}{}^b$	$J_{CCCX}{}^b$	$J_{CCCCX}{}^b$
F	1	−245.3	+21.0	+7.7	+3.3
P	3	12.4	19.55	*c*	0
P^+	4^d	88.4	10.9	12.8	2.9
Hg	2	1186	88	101.6	17.8
B^-	4	49.5^e		2.6^e	
H^f	1	157.5	+1.0	+7.4	−1.1

[a] Signs refer to reduced coupling constants. [b] In hertz. [c] Three lines with spacings of 6.7, 5.1, and 1.6 Hz are seen for the *meta* and *para* carbons. That 6.7 Hz is correct for this splitting has been kindly verified at 25 MHz in unpublished work by Dr. G. S. Reddy of the Central Research Department, Du Pont. [d] Triphenylmethylphosphonium bromide. [e] Boron-11. [f] F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 2967 (1967).

Two-bond, carbon–metal couplings in organometallic compounds may be correlated by the relationships derived by Karabatsos[2] to correlate carbon–proton couplings with proton–proton couplings.[8,9] Three-bond couplings involving carbon in aliphatic compounds (see Table II) have nearly the same magnitudes as three-bond couplings involving protons,[10] although according to the Karabatsos relations one would expect $J_{CX} = 0.3J_{HX}$. On the other hand, couplings involving carbon in aromatic derivatives correlate rather well with $J_{CX} = 0.4J_{HX}$ for the analogous couplings involving protons in vinyl derivatives, although not quite as quantitatively as the corresponding couplings involving benzene and ethylene derivatives[11] (see Table I).

Table II. Coupling of Carbon to Other Elements in $(C_nH_{2n-1})_mX^a$

X	m	n	$J_{CX}{}^b$	$J_{CCX}{}^b$	$J_{CCCX}{}^b$
F	1	6	−166.6	+19.9	5.25
P	3	4	−10.9	+11.7	12.5
P^+	4	4	+47.6	−4.3	15.4
Hg	2	4	+656	−26.3	100
Sn	4	2	+307.4 321.5	−23.5	
H^c	1	2	+125	−4.5	

[a] Signs refer to reduced coupling constants. [b] In hertz. [c] See Lynden-Bell and Sheppard.[7]

Differences in the signs of the one-bond, carbon–phosphorus coupling in phosphines and phosphonium ions have been noted previously,[5b,12] but not explained.

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[1] Supported in part by the National Science Foundation and the Public Health Service, Research Grant GM-11072-07 from the Division of General Medical Sciences.

[2] G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **84**, 37 (1962).

[3] N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963); J. Reuben and A. Demiel, *J. Chem. Phys.*, **44**, 2216 (1966).

[4] E. A. Pier in "High Resolution Nuclear Magnetic Resonance Spectroscopy," J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1966, pp 1053–1054.

[5] (a) W. McFarlane, *J. Chem. Soc., A*, 1148 (1967); (b) *Proc. Roy. Soc.* (London), **A306**, 165 (1968).

[6] W. McFarlane, *Mol. Phys.*, **10**, 603 (1966).

[7] Analogies are $J_{CCH} = +26.6$ Hz for acetaldehyde (E. Sackmann and H. Dreeskamp, *Spectrochim. Acta.*, 21, 2005 (1965)) and $J_{CCH} = +49.4$ Hz in acetylene (R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A296**, 385 (1962)).

[8] G. W. Smith (*J. Chem. Phys.*, **39**, 2031 (1963)) has extended the correlation to two-bond, metal–proton coupling.

[9] F. J. Weigert, M. Winokur, and J. D. Roberts (*J. Am. Chem. Soc.*, **90**, 1566 (1968)) showed that the correlation could be extended to one-bond, metal–carbon coupling in organometallic compounds.

[10] Reference 4, pp 688–689.

[11] See Table I, footnote *f*.

[12] W. McFarlane, *Chem. Commun.*, **58** (1967).

The two-bond, carbon–phosphorus coupling in phosphines turns out to be positive, like the two-bond, carbon–fluorine coupling in *n*-hexyl fluoride. The two-bond, carbon–phosphorus coupling in phosphonium ions is negative, like the two-bond, carbon–proton coupling in ethane. The three-bond, carbon–phosphorus couplings are similar in magnitude and, as yet, of unknown sign. Phosphorus in phosphines, like fluorine, uses nearly pure p orbitals to form bonds to carbon.[13] In phosphonium ions it is reasonable to presume that hybrid orbitals are used. Negative one-bond couplings can occur when the energy difference between the valence s and p electrons becomes large, a situation implied by the formation of bonds involving unhybridized orbitals.[14]

Although the observed carbon–nitrogen couplings are internally consistent with the simplified formalism of the average-energy approximation,[15] a significant negative contribution to the couplings is apparent when these are compared with carbon–carbon couplings in similar situations.

More detailed discussion of these points along with comparisons of trends observed in nondirectly bonded and one-bond coupling constants will be presented later.

(13) From promotion energy arguments summarized by J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(14) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(15) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964).

(16) National Science Foundation Predoctoral Fellow, 1965–1968.

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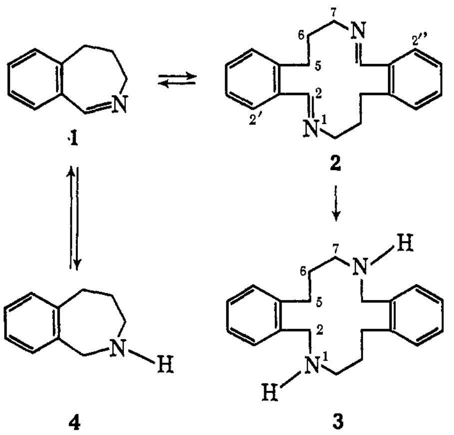
A Novel Schiff Base Dimerization Reaction. Interconversions Involving the 3,4-Dihydro-5H-2-benzazepine and 3,4,10,11-Dibenzo-1,8-diazacyclotetradeca-1,3,8,10-tetraene Ring Systems

Sir:

We have observed that the crude monomeric product **1**, obtained by Bischler–Napieralski cyclization of N-formyl-3-phenylpropylamine with polyphosphoric acid–phosphorus pentoxide at 160° for 16 hr, is transformed on standing for 16 hr to a crystalline dimer, 3,4,10,11-dibenzo-1,8-*trans,trans*-1,8-diazacyclotetradeca-1,3,8,10-tetraene (**2**): mp 172–173°; ir ($CHCl_3$) 6.11, 6.24, and 6.36 (w) μ; nmr ($CDCl_3$, TMS) δ 8.46 (2, broad s, $H_{2,9}$), 7.87 (2, m, $H_{2',2''}$), 7.28 (6, m), 3.37 (4, m, NCH_2), 2.93 (4, t, J = 6.5 Hz), and 2.18 ppm (4, m); mass spectrum, *m/e* 290 (m$^+$). Assignment of the *trans,trans*-di-Schiff base structure rests on (a) the azomethine proton absorption at 8.46 ppm, (b) the observed deshielding[1] ($\Delta = -0.59$ ppm) of $H_{2'}$ and $H_{2''}$, and (c) sodium borohydride reduction to the diamine **3**: mp 164–164.5°; nmr ($CDCl_3$, TMS) δ 7.18 (8, s), 3.70 (4, s, $H_{2,9}$), 2.90 (4, t, J = 7.5 Hz, $H_{5,12}$), 2.75 (4, m, $H_{7,14}$), 1.95 (4, m), and 2.07 ppm (2, broad s, NH); mass spectrum, *m/e* 294 (m$^+$).



Insight into the dimerization mechanism[2] was derived from the observation that the *reverse reaction*, conversion of dimer **2** to monomer **1**, occurred readily when ir and nmr samples of **2** were left standing in chloroform solution for several hours. In a controlled experiment dimer **2** was unchanged during 1 hr in solution in purified $CDCl_3$ (nmr); addition of 0.1 mole of trifluoroacetic acid led, in 70 min, to essentially complete conversion to **1**: nmr ($CDCl_3$, TMS) δ 8.49 (1, broad s), 7.27 (4, m), 3.62 (2, t, J = 6 Hz, NCH_2), 2.76 (2, *t*, J = 6.5 Hz), and 2.22 ppm (2, m); ir ($CDCl_3$) 6.10 (m), 6.17, 6.26 (vw), and 6.36 μ; mass spectrum, *m/e* 145 (m$^+$); picrate mp 159–160°. Evaporation of the $CDCl_3$ *in vacuo* afforded oil **1** which dimerized rapidly: within 1 min the oil became viscous; within 3 min dimer **2** began to crystallize out. Rapid treatment of the oil **1** with an excess of methanolic sodium borohydride afforded the amine **4**: mass spectrum, *m/e* 147 (m$^+$); hydrochloride mp 220–222° (lit.[3] mp 223–225°).

The instability of both dimer **2** in solution and monomer **1** neat, in the presence of acid, is in marked contrast to the behavior of **2** and **1** in the absence of acid. A pure sample of **1**, obtained by oxidation of **4** in refluxing benzene for 10 min with azeotropically activated manganese dioxide,[4] remained liquid for more than 1 hr. Upon standing overnight, however, about 50% conversion to dimer **2** resulted. Dimer **2** is thermally stable, small samples subliming at 145° (0.03 mm) or distilling at 185° (0.03 mm) without change.

It can be concluded on the basis of the present data that, while other pathways may be available, the facile interconversions involving **1** and **2** in this work are acid catalyzed. The observation of essentially complete monomerization of **2** in acidic chloroform solution, and dimerization of **1** neat, suggest comparable stabilities for monomer and dimer. Studies to determine the equilibrium constant for this reaction are in progress.

A simple stepwise scheme, involving a 1,3-diazetidine intermediate, can be envisioned for the acid-catalyzed interconversions of **1** and **2**. Schiff base dimerizations

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(1) *Cf.* lower field proton resonances for comparably disposed *ortho* protons in the *trans* rings for a variety of imines: D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Am. Chem. Soc.*, **88**, 2775 (1966).

(2) The dimerization could result from an uncatalyzed, acid-catalyzed, or water-catalyzed process. For example, the hydrolysis of **1** by a catalytic amount of water to an open-chain amino aldehyde followed by dehydrative dimerization could yield **2**. M. E. Derieg, R. M. Schweininger and R. I. Fryer, *J. Org. Chem.*, **34**, 179 (1969), have observed the formation of a 3,4,11,12-dibenzo-1,5,9,13-tetraazacyclohexadeca-1,3,9,-11-tetraene-6,14-dione from a 3,4-dihydro-1,5-benzodiazocine-2-one precursor.

(3) N. S. Hjelte and T. Agback, *Acta Chem. Scand.*, **18**, 191 (1964).

(4) I. M. Goldman, *J. Org. Chem.*, **34**, 1979 (1969).