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^{13}C-^{13}C COUPLING IN [1.1.1]PROPELLANE

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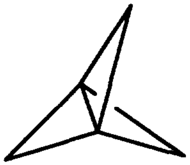
Abstract: The C1-C2 coupling constant in [1.1.1]propellane is measured to be 9.9 ± .1 Hz. The CH bond is $sp^{2.1}$ and the C-CH_2 bond is estimated to be $sp^{8.6}$-$sp^{4.8}$. The remaining orbital at each bridgehead carbon is $sp^{0.5}$.

Small ring propellanes[1,2] are an interesting class of hydrocarbons and [1.1.1]propellane (1, also known as tricyclo[1.1.1.$0^{1,3}$]pentane) is perhaps the most intriguing compound of the series. The nature of bonding within the molecule continues to receive much attention[3-7]. Theoretical treatments have been employed to calculate various features, such as orbital hybridization[8,9]. Since its initial synthesis[10] in 1982, 1 has been analyzed with various spectroscopic methods[11-13] and studied through chemical experimentation[14-16] as well. We now report the measurement of the C1-C2 coupling constant and estimation of orbital hybridization throughout 1.



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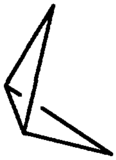

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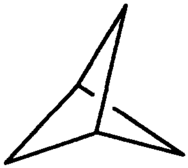

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Recent improvements[17] in the synthetic route have simplified generation of 1 in gram quantities. The two step procedure starts with a conventional dibromocarbene addition to 2-chloromethyl-3-chloro-1-propene (commercially available). The resulting tetrahalide is purified by sublimation and reacted with methyllithium to form 1. Purification (separation from methyl bromide and diethyl ether) is achieved by preparative gas chromatography (10% OV-101 column at 30 °C).

We have prepared samples of sufficient concentration to record the only measurable ^{13}C-^{13}C coupling constant in unenriched 1, using the INADEQUATE NMR experiment. Spectra were recorded and analyzed with Bruker AC-200 and AC-300 NMR spectrometers. Optimum parameters include a relaxation delay (D1) of 20 seconds, an evolution - refocus period (D2) of 0.075 seconds and a total of 3968 scans, as used in conjunction with the INADEQ2 pulse program (Ernst-type double quantum phase cycling).

The value for the ^{13}C-^{13}C coupling constant (Table 1) in **1** (like the value for J_{CH}) is comparable to that found for cyclopropane[18] but this value is less than half of that found for bicyclobutane[19,20] (2), which also has fused cyclopropane rings, and less than half of that estimated for [1.1.1]bicyclopentane (3), which also has three methylene units bound to two common carbons. The methine C-H coupling in **2** is 23% higher than that of **3** (and of course absent in **1**). The methylene C-H coupling in **1** is 14% higher than that of **3** and is only 2% greater than that of the average value found in **2**. Thus the methylene group in **1** appears to be more similar to that of **2** than of **3**.

Table 1. J (Hz) and Orbital Hybridization (%s)

	1		**2**		**3**	
C1-C2	9.9[a]	(10-17)	21.0	(22-18)	26[b]	(22-21)
C1/C3		(69)		(17)		
C-H	163.7	(33)	202[c]	(40)	164[c]	(33)
			170[d]	(34)	144[e]	(29)
			152[f]	(30)		

[a] ± 0.1 Hz, average taken from both carbon signals (acetone-d_6, -50 °C)
[b] using eq 2
[c] methine protons
[d] exo protons
[e] methylene protons
[f] endo protons

The measured values for J_{CC} and J_{CH} were used with empirical equations (assuming validity for **1**)[21] as a nonrigorous means to estimate orbital hybridization throughout **1** (Table 1). While many factors may affect the magnitude of observed spin-spin coupling constants, Fermi contact is the major contributor in C-H coupling; a correlation[22] has been demonstrated between orbital hybridization and J_{CH} (eq 1).

$$\%s = 0.2J_{CH} \qquad (1)$$

This correlation was used to determine the %s character in the equivalent C-H bonds of **1**. The %s character from C2 in each of the remaining CH_2-C bonds was determined by assuming 100%s about C2 and an equivalence between bridgehead carbons.

The magnitude of the one-bond C-C coupling constant has been shown to increase with increasing %s character and a rough correlation[22] between $^1J_{CC}$ and orbital hybridization has been demonstrated (eq 2).

$$\%s_{C1} = 18J_{C1\text{-}C2}/\%s_{C2} \qquad (2)$$

Although here other electronic factors appear to be important[23] and the correlation is not as strong or reliable as that found for C-H, this simple correlation has proven useful in the hybridization study of other small fused rings[24]. Similarily, the %s character from C1 in the CH_2-C bond of **1** was estimated from J_{CC} (eq 2). The remaining %s character about C1 (available for bridgehead-bridgehead bonding) was estimated assuming 100%s. This scheme for estimation of orbital hybridization was also applied to **2** and **3**, using additional literature values[25] for J_{CH} (Table 1).

The similar average methylene C-H coupling constants of about 160 Hz in **1** and **2**, suggest that these C-H bonds are approximately $sp^{2.1}$ ($sp^{2.5}$ for **3**). This means that the methylene carbons contribute a hybridized orbital of about $sp^{4.7}$ to the C-CH_2 bond in **1** and **2** ($sp^{3.7}$ in **3**). Thus the hybridization about the secondary carbons in **1** and **2** is essentially the same (less so for **1** and **3**). The difference in J_{CC} for **1** and **2** therefore reflects a difference in hybridization of the orbital about the bridgehead carbons, involved in the C-CH_2 bond: $sp^{8.6}$ for **1** and $sp^{3.7}$ for **2** ($sp^{3.5}$ for **3**). The methine C-H bond in **2** is $sp^{1.5}$ ($sp^{2.0}$ for **3** and of course absent in **1**). The remaining hybridized orbitals available for bonding about the bridgehead carbons is $sp^{5.0}$ for **2** and $sp^{0.5}$ for **1**. The estimated orbital hybridization, based on experimentally determined bonded nuclear couplings in **1**, is more consistent with the theoretical treatments[8] which suggest significant %s character for orbitals between bridgehead carbons.

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References

(1) Wiberg, K.B. *J. Amer. Chem. Soc.* **1983**, *105*, 1227-1233.

(2) Stohrer, W.D.; Hoffmann, R. *J. Amer. Chem. Soc.* **1972**, *94*, 779-786.

(3) Wiberg, K.B.; Bader, R.F.W.; Lau, C.D.H. *J. Amer. Chem. Soc.* **1987**, *109*, 985-1001.

(4) Feller, D.; Davidson, E.R. *J. Amer. Chem. Soc.* **1987**, *109*, 4133-4139.

(5) Messmer, R.P.; Schultz, P.A. *J. Amer. Chem. Soc.* **1986**, *108*, 7407-7408.

(6) Lee, I.; Yang, K.; Kim, H.S. *Tetrahedron* **1985**, *41*, 5007-5010.

(7) Jackson, J.E.; Allen, L.C. *J. Amer. Chem. Soc.* **1984**, *106*, 591-599.

(8) Newton, M.D.; Schulman, J.M. *J. Amer. Chem. Soc.* **1972**, 94, 773-778.

(9) Herr, M.L. *Tetrahedron* **1977**, *33*, 1897-1903.

(10) Wiberg, K.B.; Walker, F.H. *J. Amer. Chem. Soc.* **1982**, *104*, 5239-5240.

(11) Wiberg, K.B.; Dailey, W.P.; Walker, F.H.; Waddell, S.T.; Crocker, L.S.; Newton, M. *J. Amer. Chem. Soc.* **1985**, *107*, 7247-7257.

(12) Honegger, E.; Hanspeter, H.; Heilbronner, E.; Dailey, W.P.; Wiberg, K.B. *J. Amer. Chem. Soc.* **1985**, *107*, 7172-7174.

(13) Orendt, A.M.; Facelli, J.C.; Grant, D.M.; Michl, J.; Walker, F.H.; Dailey, W.P.; Waddell, S.T. *Theor. Chim. Acta.* **1985**, 68, 421-430.

(14) Wiberg, K.B.; Waddell, S.T. *Tetrahedron Lett.* **1988**, *29*, 289-282.

(15) Wiberg, K.B.; Waddell, S.T. *Tetrahedron Lett.* **1987**, *28*, 151-154.

(16) Wiberg, K.B.; Waddell, S.T.; Laidig, K.E. *Tetrahedron Lett.* **1986**, *27*, 1553-1556.

(17) Semmler, K.; Szeimies, G.; Belzner, J. *J. Amer. Chem. Soc.* **1985**, *107*, 6410-6411.

(18) Weigert, F.J.; Roberts, J.D. *J. Amer. Chem. Soc.* **1967**, *89*, 5962-5963.

(19) Schulman, J.M.; Newton, M.D. *J. Amer. Chem. Soc.* **1974**, *96*, 6295-6297.

(20) Newton, M.D.; Schulman, J.M.; Manus, M.M. *J. Amer. Chem. Soc.* **1974**, *96*, 17-23.

(21) Della, E.W.; Pigou, P.E. *J. Amer. Chem. Soc.* **1984**, *106*, 1085-1092.

(22) Frei, K.; Bernstein, H.J. *J. Chem. Phys.* **1963**, *38*, 1216-1226.

(23) Maciel, G.E; McIver, Jr., J.W.; Ostlund, N.S.; Pople, J.A. *J. Amer. Chem. Soc.* **1970**, *92*, 1-11.

(24) Bertrand, R.D.; Grant, D.M.; Allred, E.L.; Hinshaw, J.C.; Strong, A.B. *J. Amer. Chem. Soc.* **1972**, *94*, 997-999.

(25) Wiberg, K.B.; Lampman, G.M.; Ciula, R.P; Connor, D.S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749-2769.

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