

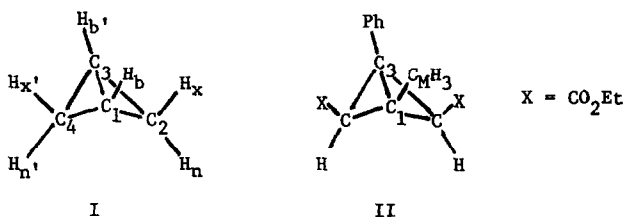
NUCLEAR SPIN-SPIN COUPLING CONSTANTS OF BICYCLOBUTANES

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Recently, it has been predicted^{1,2} that the sign of the nmr spin-spin coupling constant for directly-bonded bridgehead carbons, $^1J_{C_1C_3}$, of bicyclo[1.1.0]butane(I) and its derivatives would be negative, in contrast to the signs of all known $^1J_{CC}$ values. The particular values calculated for bicyclobutane were -5.6 ± 3.4 Hz and -8.4 ± 2.4 Hz based, respectively, on semiempirical coupled Hartree-Fock perturbation theory¹ and an independent argument using INDO localized-orbital hybridizations². An experiment which appears to confirm this prediction has recently been performed. Pomerantz, *et al.*³ have measured the bridgehead coupling constant of the methyl, phenyl bicyclobutane *di-exo* ester(II), triply labeled at C_1, C_3 , and C_M and obtained $^1J_{C_1C_3} = -5.4 \pm 0.5$ Hz. The effects of methyl and phenyl substitution at the bridgehead and carboxyethyl substitution further removed should be quite small. For example, our calculations on 1-methylbicyclobutane indicate the effect of methyl substitution to be +0.8 Hz while phenyl substitution in alkanes and alkenes tends to alter one-bond coupling constants by ca. 5% -- here, 0.3 Hz. Thus, the experimental value for I, itself, should be quite close to both the perturbation-theoretic and hybridization predictions.



The importance of this result lies in its confirmation (by inference) of the unusual hybridization, sp^{18} (INDO) and sp^{24} (ab-initio), in the bicyclobutane central bond. This bond then differs from what one might expect from the high bridgehead proton acidity, the large $^1J_{CH}$ bridgehead coupling constant of 205 Hz⁴ or consideration of Walsh symmetry orbitals unmixed in a variational calculation, all of which would lead to an ethylenic or acetylenic central bond with hybridization intermediate to sp^1 and sp^2 ⁵. Moreover, merely counting ligands gives the "nominal" hybridization, sp^3 . In point of fact, the bicyclobutane bond is an example of a rather unusual (nearly) pure p-p single bond which is also bent with respect to its interatomic vector⁶. The experiment has also demonstrated a predictive role for hybridization which is most often relegated to the less consequential realm of interpretation. Finally, since the dominant negative contribution in the coupled Hartree-Fock calculation arises from the orbital and spin-dipolar terms it seems likely that this experiment furnishes the first unambiguous detection of these coupling mechanisms in carbon-carbon coupling.

It is perhaps useful to examine the results of the coupled Hartree-Fock method for the remaining 18 coupling constants of bicyclobutane most of which are known only in magnitude. Moreover, the experiment of Pomerantz, et al. provides six signed coupling constants for the bridgehead carbons and methyl nuclei of (II) which can be used for comparison with the calculated results on 1-methylbicyclobutane.

Since there has been some discussion of uncertainty in the geometry of bicyclobutane^{7,8}, particularly in the location of the protons, calculations were performed at both the experimental microwave⁹ and the ab initio STO-3G optimized geometries¹⁰, the results of which are given in Table I. The five one-bond constants are in good agreement with experiment; indeed, one bond constants represent the best application of this method of calculation. Quite similar results are obtained from the INDO localized hybrids, and the observed exo-endo separation can be obtained by "rocking" the methylene group exo as discussed by Newton⁸. For the long range coupling constants hybridization arguments no longer apply and we must rely on the results of the coupled Hartree-Fock method. There is found qualitative agreement for the three and four bond coupling constants; however for two bond couplings,

particularly the methylene geminal constant the results are poor. Calculation at the STO-3G geometry gives an improvement in the coupling constants ($^1J_{C_2X}$ excepted) particularly for coupling constants involving the endo protons, although the geminal coupling constant is not much improved. (A problem also occurs with cyclopropane for which $J_{gem} = +0.7$, is computed at the experimental geometry whereas -4.3 is observed¹¹. On the other hand, in unstrained systems the agreement for geminal coupling constants is much better¹²).

Table I. Coupling constants of bicyclobutane(Hz)

coupling constant	calculated (experimental geom.)	calculated (STO-3G geom.)	calculated (hybridization) ^a	expt
carbon-carbon ^b				
$^1J_{C_1C_3}$	-5.6	-5.4	-8.4	-5.4 ^c
$^1J_{C_1C_2}$	21.4	19.9	23.2	21.0 ^d
$^1J_{C_2C_4}$	-6.1	-5.8 ^e		
carbon-proton ^f				
$^1J_{1b}$	190 ^g	203	202	205 ^h
$^1J_{2x}$	148 ^g	139	157	153
$^1J_{2n}$	165 ^g	168	158	169
$^2J_{1b'}$	-0.1	-0.3		3.3
$^2J_{1x}$	-5.3	-4.2		3.3 ⁱ
$^2J_{1n}$	4.6	1.4		0.0 ⁱ
$^2J_{2b}$	-0.3	-0.4		5.3
$^3J_{2x'}$	11.3	11.8		16.0
$^3J_{2n'}$	2.8	4.0		5.3
proton-proton ^f				
$^2J_{nx}$	10.6	10.3		0.4, 0.6
$^3J_{bb'}$	5.6	4.2		10.4
$^3J_{bx}$	1.5	1.1		2.9
$^3J_{bn}$	2.1	0.5		1.2
$^4J_{xx'}$	5.2	5.8		5.9
$^4J_{xn'}$	-0.5	-0.6		0.4, 0.6
$^4J_{nn'}$	2.5	2.2		1.1

a) Based on eqs. (1) and (2) of ref. 2. b) The calculated values are based on $S_C^2(0) = 3.54, \langle r^{-3} \rangle_C = 2.50$ in a_0^{-3} . c) The only coupling constant whose sign is known; the result for II. d) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, J. Amer. Chem. Soc. **94**, 997 (1972). e) The orbital and spin dipolar contributions were negligible. f) The calculated values are based on $S_C^2(0) = 4.0318, S_H^2(0) = 0.3724$ of J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, J. Chem. Phys. **49**, 2965 (1968). g) Reported previously by Newton and Schulman, ref. 6 and P. D. Ellis and G. Maciel, J. Amer. Chem. Soc. **92**, 5829 (1970).

h) All CC and CH proton coupling constants are those of Ref.4. 1) The ambiguity between $^2J_{1x}$ and $^2J_{1n}$ reported in ref.4 can be removed through results on exo-substituted bicyclobutanes, M.Pomerantz(private communication). The correct assignment is given here.

Quite good results are obtained by the method for methylbicyclobutane, where only one of the coupled nuclei is in the strained framework, as shown in Table II for six of the coupling constants. In each case, including two bond couplings, the correct signs are obtained and the magnitudes are in reasonable agreement with the experimental values.

Table II. Coupling Constants of 1-methylbicyclo[1.1.0]butane(Hz)

coupling constant	calculated value ^a	experimental for II ^b
$^1J_{C_1C_3}$	-4.8	-5.4
$^1J_{C_1C_M}$	47.5	53.2
$^2J_{C_3C_M}$	-0.6	-2.4
$^1J_{C_MH_M}$	121	129
$^2J_{C_1H_M}$	-6.3	-7.3
$^3J_{C_3H_M}$	1.3	2.7

a) The geometry used was that of bicyclobutane with one bridgehead proton replaced by a tetrahedral methyl group. The C_1H_M and C_1C_M bond lengths were 1.09A and 1.50A, respectively and one C_1H_M bond had a dihedral angle of 0° with C_1C_3 . The coupling constants involving H_M were computed as the statistical average of the three methyl protons.

b) Ref. 3.

References

1. J.M.Schulman and M.D.Newton, J.Amer.Chem.Soc. 96,6295(1974).
2. M.D.Newton,J.M.Schulman and M.M.Manus, J.Amer.Chem.Soc. 96,17(1974).
3. M.Pomerantz,R.Fink and G.A.Gray, J.Amer.Chem.Soc. 98,291 (1976).
4. K.Wuthrich,S.Meiboom,L.C.Snyder, J.Chem.Phys. 52,230(1970).
5. M.Pomerantz and E.W.Abrahamson, J.Amer.Chem.Soc. 88,3970(1966).
6. The calculated angle is 31° , see M.D.Newton and J.M.Schulman, J.Amer.Chem.Soc. 94 767(1972). Examples of unbent essentially p-p bonding may be anticipated in the early members of the propellane series, e.g. (2.2.2) propellane has $sp^{1.0}$ hybridization (see ref.1).
7. S.Meiboom and L.C.Snyder,Accounts of Chemical Research,4,81(1971).
8. M.D.Newton, "Modern Theoretical Chemistry, Vol.II", H.F.Schaefer,III,ed.,(Plenum Press, New York,1976).
9. K.W.Cox,M.D.Harmony,G.Nelson and K.B.Wiberg,J.Chem.Phys. 50,1976(1969).
10. W.J.Hehre and J.A.Pople, J.Amer.Chem.Soc. 97,6941(1975).
11. V.S.Watts and J.H.Goldstein, J.Chem.Phys. 46, 4165 (1967).
12. G.E.Maciel,J.W.McIver,Jr.,N.S.Ostlund and J.A. Pople, J.Chem.Phys. 92, 4151(1970).