Table I. Parameters Used in the Extended Hückel Calculations

orbital	H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Cr 3d	−11.22	4.95	1.60	0.4876	0.7205
4s	−8.66	1.70			
4p	−5.24	1.70			
Mn 3d	−11.59	5.15	1.90	0.5320	0.6490
4s	−8.63	1.80			
4p	−5.06	1.80			
Fe 3d	−12.70	5.35	1.80	0.5366	0.6678
4s	−9.17	1.90			
4p	−5.37	1.90			
Co 3d	−12.28	5.55	2.10	0.5680	0.6060
4s	−9.51	2.00			
4p	−4.78	2.00			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
H 1s	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

any length here. The idea in **66** is that the "extra" double bond will stabilize the η^3 intermediate and, therefore, the haptotropic rearrangement will require less energy than in naphthalene–Cr$(CO)_3$. In fact, calculations predict that the η^5 structure where the $Cr(CO)_3$ group is coordinated to the five-membered ring will be 6 kcal/mol more stable than the normal η^6 isomer. Experimentally this is not true as evidenced by the room temperature ^{13}C NMR spectrum.[52] NMR experiments have been initiated to measure the activation energies for intramolecular exchange in **66** and other derivatives of naphthalene–$Cr(CO)_3$.[52] Efforts are also underway to prepare d^6 complexes of **67**.[53] There are some basic differences between the π topology of acepentalene and phenalenium. The bonding interaction analogous to **63** is not present in the acepentalene system. Accordingly, an η^4 structure is strongly avoided. There are also differences in the reaction path and associated activation energies depending upon whether the metal is d^6 or d^8. The complex behaves somewhat like pentalene–FeCp$^+$ (Figure 5) and the d^8 compound is analogous to pentalene–FeCp$^-$ (Figure 6). A full discussion of the stability, reactivity, and potential energy surfaces will be presented elsewhere.[54]

Acknowledgment. We are grateful to P. Stauffert for running the acepentalene–MCp calculations. We thank the Scientific Affairs Division of NATO (T.A.A. and P.H.), the Robert A. Welch Foundation (T.A.A.), Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie (P.H.), and the National Science Foundation (R.H.) for support of this work.

Appendix

The extended Hückel calculations[16] utilized a modified version of the Wolfsberg-Helmholz formula.[55] The parameters listed in Table I were taken from previous work.[17b] Idealized geometries for the polyenes were used with C–C = 1.41 Å and C–H = 1.09 Å. The M–Cp midpoint distance was fixed at 1.687 Å. For the $M(CO)_3$ groups the distances utilized were: Cr–C = 1.84 Å, Mn–C = 1.76 Å, Fe–C = 1.78 Å. All M–C–O and C–M–C angles were fixed at 180 and 90°, respectively. The C–O distance used was 1.14 Å.

Registry No. Naphthalene–$Cr(CO_3)_3$, 12110-37-1; indenyl–FeCp, 54845-16-8; pentalene–FeCp cation, 85304-57-0; pentalene–FeCp anion, 85304-58-1; bicycloheptatrienyl–CoCp cation, 85304-59-2; bicycloheptatrienyl–CoCp anion, 85304-60-5; phenalenium–$Cr(CO)_3$ cation, 85318-19-0; fluorenyl–FeCp, 61642-91-9.

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Nuclear Spin–Spin Coupling via Nonbonded Interactions. 5. The Orientational Dependence of α-Substituent Effects on Vicinal ^{13}C–^{13}C Coupling Constants

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Abstract: To investigate the role of nonbonded interactions on vicinal ^{13}C–^{13}C coupling constants, a series of 2,2-dimethylcyclopropanes with ^{13}C labeled substituents in the C1 position were synthesized and their NMR parameters were accurately measured. The vicinal ^{13}C–^{13}C coupling constants in the cis arrangement (ϕ = 0°) were found to be quite sensitive to substituent orientation. For example, the largest (3.40 Hz) and smallest (1.04 Hz) values of $^3J_{CC'}$ (0°) were found for the primary and tertiary alcohols, respectively. the ^1H chemical shifts and vicinal coupling constants were used to determine the conformations of the hydroxy group of the primary, secondary, and tertiary alcohols. The calculated INDO-FPT molecular orbital results for the Fermi contact contributions to the vicinal ^{13}C–^{13}C coupling constants are in good agreement with the experimental data. By means of a modified molecular orbital technique, it is demonstrated that the most important contributions to $^3J_{CC'}$ (0°) arise from the nonbonded interactions associated with the proximity and orientation of the hydrogens which are directly bonded to the coupled carbon atoms (C4 and C5). As a consequence, the larger value of $^3J_{CC'}$ (0°) occurs for the primary alcohol with two hydrogens on C4. The smaller values for the secondary alcohols depend on the H–C4 orientation. The smallest value of the cis coupling constants occurs for the tertiary alcohol which does not have any directly bonded hydrogens.

The conformational and substituent dependencies of vicinal ^{13}C–^{13}C coupling constants have been the subject of a number of studies from these and other laboratories.[2] Recent studies have emphasized the exceedingly important role of nonbonded inter-

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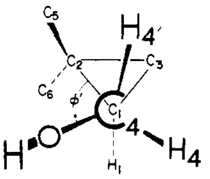


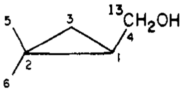
Figure 1. Specification of the dihedral angle ϕ' in the 2,2-dimethylcyclopropane derivatives. The dihedral angle is measured counterclockwise from the C2–C1 bond to the C4–O bond on looking along the C4–C1 bond.

Table I. Experimental Values of Cis ($\phi = 0°$) and Trans ($\phi = 145°$) Vicinal ^{13}C–^{13}C Coupling Constants in a Series of 1-Substituted 2,2-Dimethylcyclopropanes

	R	^3J(C4,C5), Hz	^3J(C4,C6), Hz
1	$^{13}CH_2OH$	3.40	0.46
2	$^{13}CH(CH_3)OH$ (*R*,*S*)	3.23	0.37
3	$^{13}CH(OH)CH_3$ (*R*,*R*)	2.72	0.73
4	^{13}CN	2.68	0.99
5	^{13}CHO	2.65	0.74
6	$^{13}CO_2H$	1.57	1.22
7	$^{13}C(NH_2)O$	1.5	1.0
8	$^{13}C(CH_3)O$	1.42	0.98
9	$^{13}C(CH_3)_2OH$	1.04	0.98

actions,[3] including γ-substituent effects,[4] and bridgehead interactions in multicyclic compounds.[5]

It has been proposed[6] that α-substituent effects would be dependent on the orientation of the α or C1 substituent, i.e., on the dihedral angle ϕ', which is depicted for substituted cyclopropanes in Figure 1. On the basis of a series of molecular orbital calculations for substituted butanes, it was suggested[6] that the most important effects would occur in those cases in which the substituents at C1 were in a anti ($\phi' = 180°$) arrangement with the coupled carbon atoms C4 and C5 in a cis ($\phi = 0°$) orientation. In this study a series of ^{13}C-enriched 1-substituted 2,2-dimethycyclopropanes **1–9** were synthesized, the experimental NMR parameters measured, and the proposed orientational dependence of the cis vicinal ^{13}C–^{13}C coupling constants is confirmed. Molecular orbital studies demonstrate that the dominant mechanisms for the α-substituent dependence of $^3J_{CC'}$ are the nonbonded interactions associated with the hydrogen atoms bonded to the coupled carbon atoms C4 and C5. To maintain conformity in the discussions, a consistent numbering scheme for compounds **1** and **9** was used throughout.



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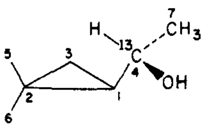

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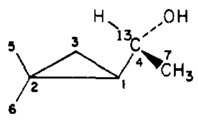

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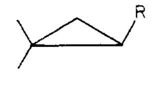
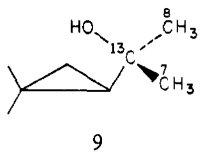


4, R = ^{13}CN
5, R = ^{13}CHO
6, R = $^{13}CO_2H$
7, R = $^{13}C(NH_2)O$
8, R = $^{13}C(CH_3)O$



9

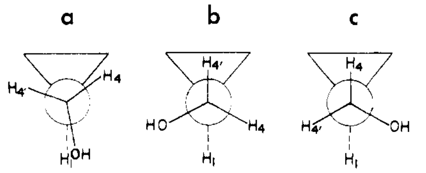


Figure 2. Three possible conformations a, b, and c of 2,2-dimethylcyclopropanemethanol.

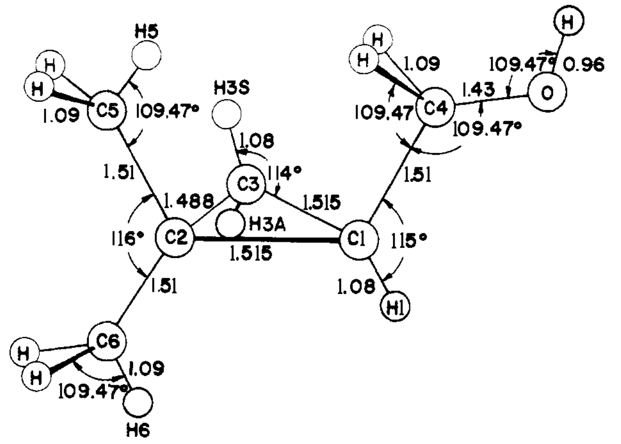


Figure 3. The geometry used for the MO calculations of the 1-substituted 2,2-dimethylcyclopropanes. It was assumed that the cyclopropane ring bisects the angles made by H3S–C3–H3A, C5–C2–C6, and H1–C1–C4. The dihedral angles H5–C5–C2–C6 and H6–C6–C2–C5 were set equal to 180°. The standard geometrical model[18] was used for the substituents.

α-Substituent Effects on Vicinal ^{13}C–^{13}C Coupling Constants. The experimental values of the cis and trans coupling constants ^3J(C4,C5) and ^3J(C4,C6) for the ^{13}C-labeled C1-substituted 2,2-dimethylcyclopropanes **1–9** are entered in Table I (these values are taken from Table II of the Experimental Section). From Table I it can be seen that the cis ($\phi = 0°$) coupling constants ^3J(C4,C5) between the ^{13}C labeled substituent and the C5 methyl carbon range from 1.05 to 3.40 Hz depending on the nature of substituents at C4. The trans coupling constants ($\phi = 145°$) between C4 and C6 exhibit a smaller range of values (1.22–0.37 Hz) but do not parallel the behavior of the cis coupling. The influence of α substitution on vicinal ^{13}C–^{13}C coupling constants has been mentioned in a number of studies of the conformational dependence of $^3J_{CC'}$.[2,6-11]

The vicinal ^{13}C–^{13}C coupling constants in Table I show no obvious correlation with the hybridization of the C4 carbon atom. In fact, the maximum and minimum values of ^3J(C4,C5) occur for the primary **1** and tertiary **9** alcohols, respectively, i.e., in cases in which C4 is sp^3 hybridized. As a consequence, the cis values of the vicinal ^{13}C–^{13}C coupling constants must be exceedingly sensitive to the orientations of the hydroxyl group in the various alcohols. An understanding of the electronic factors, which lead to the substituent orientational dependence, is to be found in the conformational differences for the four alcohols.

The orientations of the hydroxyl groups of the four alcohols **1–3** and **9** in solution are based on the ^1H chemical shifts and

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Table II. Carbon-13 Chemical Shifts and ^{13}C–^{13}C Coupling Constants (to C4) for Compounds 1–9[a]

compd		C1	C2	C3	C4	C5	C6	C7	C8
1[b]	δ	27.22 (3)	16.03 (3)	18.31 (3)	63.07 (3)	19.84 (3)	26.60 (3)		
	J	48.40 (4)	1.19 (4)	0.61 (4)		3.40 (4)	0.46 (4)		
2	δ	32.97 (1)	16.25 (1)	18.30 (1)	70.13 (1)	20.05 (1)	27.35 (1)	23.25 (1)	
	J	48.71 (7)	1.69 (7)	<0.2		3.23 (5)	0.37 (5)	39.17 (7)	
3	δ	32.86 (1)	16.15 (1)	18.35 (1)	69.78 (1)	20.29 (1)	27.47 (1)	23.89 (1)	
	J	47.69 (18)	<0.4	1.83 (7)		2.72 (7)	0.73 (5)	38.88 (7)	
4	δ	10.24 (3)	20.58 (3)	22.10 (3)	120.93 (9)	21.91 (3)	24.79 (3)		
	J	78.58 (12)	1.95 (12)	2.35 (12)		2.68 (12)	0.99 (12)		
5	δ	35.49 (6)	25.07 (6)	22.30 (6)	200.3 (1)	18.85 (6)	25.90 (6)		
	J	53.70 (7)	1.27 (7)	1.32 (7)		2.65 (7)	0.74 (7)		
6[b]	δ	26.96 (6)	23.80 (3)	22.63 (3)	177.82 (3)	18.85 (3)	26.96 (6)		
	J	73.71	1.52	1.48		1.57	1.22		
7[c]	δ	28.92 (6)	22.52 (6)	20.54 (6)	178.2 (1)	19.04 (6)	27.07 (6)		
	J	63.4 (8)	1.5 (2)	1.4 (1)		1.5 (1)	1.0 (2)		
8	δ	35.52 (1)	26.22 (1)	23.00 (1)	205.52 (1)	18.07 (1)	27.25 (1)	32.02 (1)	
	J	52.54 (4)	1.66 (2)	1.89 (6)		1.42 (3)	0.98 (3)	41.55 (4)	
9	δ	35.56 (1)	16.35 (1)	15.35 (1)	70.15 (1)	19.66 (1)	29.00 (1)	29.54 (1)	32.22 (1)
	J	47.82 (6)	1.44 (6)	1.71 (8)		1.04 (6)	0.98 (6)	39.83 (6)	39.22 (6)

[a] Chemical shifts δ are measured in part per million downfield from internal Me_4Si; ^{13}C–^{13}C coupling constants J are in hertz; the solvent is chloroform-d unless noted otherwise. [b] Acetone-d_6 solvent. [c] The solvent is a mixture of methanol and D_2O.

interproton coupling constants (see Experimental Section). Because of the importance of intermolecular hydrogen bonding in these systems, the molecular orbital results for the energies of the isolated molecules **1**–**3** were not considered to be reliable.

One criterion for the preferred orientation of the hydroxyl groups is the chemical shift of the H3S proton, which is dependent on the orientation of the hydroxyl group. The designations of the various hydrogen atoms are given in Figures 2 and 3. The H3S proton will be shielded or deshielded if the hydroxyl group is directed away from or toward the C3–H3S bond, respectively.[12] The ^1H chemical shift of cyclopropane is 0.20 ppm, which increased slightly to 0.22 ppm in 1,1-dimethylcyclopropane.[13] In contrast, the chemical shifts for the H3S proton of the four alcohols **1**–**3** and **9** are either greater or smaller than these values. In **9** the two bulky methyl groups force the hydroxyl group to be over the cyclopropane ring and close to the H3S proton, which is shifted downfield to 0.39 ppm. In compounds **1** and **2**, however, the hydroxyl groups are directed away from H3S and the shifts are only 0.07 and 0.03 ppm, respectively. The chemical shifts of the C5 methyl protons are also consistent with this interpretation, but the changes are somewhat smaller in magnitude.

2,2-Dimethylcyclopropanemethanol (1). The chemical shift of the H3S proton (0.07 ppm) and the C5 methyl protons in this alcohol indicate that the hydroxyl group is directed away from the cyclopropane ring. Also, steric interactions between the hydroxyl group and H1 make it unlikely that the lowest energy conformation is depicted in Figure 2a. It seems more likely that the minimum energy conformations are **b** and **c** in Figure 2 because the vicinal proton coupling constants between H4 and H4′ are 6.30 and 8.57 Hz, respectively, in good conformity with the molecular orbital results for an average of the conformations in which ϕ' is either 130° or 250°.

Calculated Fermi contact contributions to the various nuclear spin coupling constants were based on the finite perturbation (FPT) formulation for spin–spin coupling in the self-consistent field (SCF) molecular orbital (MO) approximation of intermediate neglect of differential overlap (INDO).[14] All calculations were performed on a Control Data Corp. CYBER 175 digital computer.

The geometry, which was adopted for 2,2-dimethylcyclopropanemethanol (**1**), is depicted in Figure 3. This is a composite of X-ray diffraction data,[15] microwave data,[16] ab initio MO calculations for similar compounds,[17] and a standard geometrical model.[18] The geometry of the substituents at C4 were based on the latter. In all of the MO calculations to be described herein, the methyl groups at the C2 carbon were held fixed as the substituent at C1 was rotated by 360°.

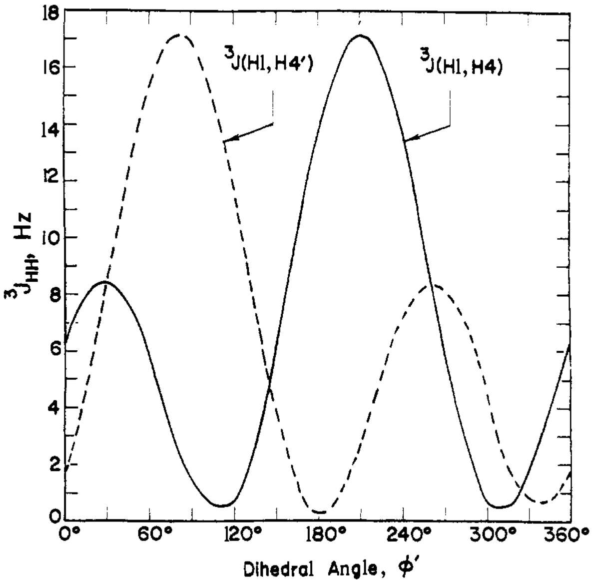

Figure 4. Calculated INDO FPT MO results for the vicinal ^1H–^1H coupling constants ^3J(H1,H4) and ^3J(H1,H4′) in 2,2-dimethylcyclopropanemethanol (**1**) plotted as a function of the dihedral angle ϕ'. Coupling constants to H4 and H4′ are given by the solid and the dashed curves, respectively.

Calculated INDO FPT MO results for the vicinal ^1H–^1H coupling constants ^3J(H1,H4) and ^3J(H1,H4′) are plotted in Figure 4 as a function of the dihedral angle ϕ'.[19] The dihedral angle is measured in a counterclockwise sense from the C2–C1 bond as one looks along the bond from C4 to C1 as depicted in Figure 1. Vicinal coupling from H1 to H4 and H4′ are given by the solid and dashed curves, respectively, in Figure 4. Note that these plots are shifted by 25° and 265°, respectively, from the usual "Karplus-type" plots in which the dihedral angle is measured from the cis arrangement of the protons. Assuming equal pop-

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[19] The calculated INDO FPT MO results for coupling constants and INDO energies are given at 30° intervals of the dihedral angle in the supplementary material.

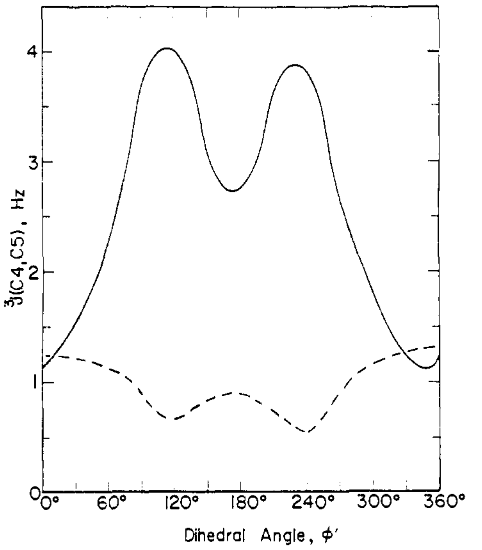

Figure 5. Calculated INDO FPT MO results for the vicinal $^{13}C-^{13}C$ coupling constant ^3J(C4,C5) (solid line) in 2,2-dimethylcyclopropanemethanol (**1**) plotted as a function of the dihedral angle ϕ'. Also plotted in the figure are the calculated results (dashed curve) for ^3J(C4,C5) in **1**, which were obtained on eliminating the interactions between the protons bonded to C4 and the protons of the C5 methyl group.

ulations of two rotamers, the averaged vicinal H-H coupling constants are given by the expressions

$$\langle {}^3J_{\mathrm{H1,H4}} \rangle = [{}^3J_{\mathrm{H1,H4}}(\phi') + {}^3J_{\mathrm{H1,H4}}(\phi' + 120°)]/2$$

$$\langle {}^3J_{\mathrm{H1,H4'}} \rangle = [{}^3J_{\mathrm{H1,H4'}}(\phi') + {}^3J_{\mathrm{H1,H4'}}(\phi' + 120°)]/2$$

Experimental values of $^3J_{\mathrm{H1,H4}}$ and $^3J_{\mathrm{H1,H4'}}$ are 6.30 and 8.57 Hz to be compared with the calculated values of 6.40 and 8.50 Hz, respectively, corresponding to dihedral angles of 40° (and 160°) or 130° (and 250°). Since the chemical shifts for the H3S proton and the C5 methyl protons indicate that the hydroxyl group is directed away from the ring, it seems likely that the conformers with the larger dihedral angles (130° and 250° corresponding to parts b and c, respectively, of Figure 2) will be substantially more populated. With these assumptions it is possible to compare the experimental data for **1** with the MO results.

The calculated INDO FPT MO results for vicinal $^{13}C-^{13}C$ coupling constants[19] between the C4 and C5 carbon atoms of 2,2-dimethylcyclopropanemethanol (**1**) are plotted (solid curve) in Figure 5 at 30° intervals of the dihedral angle ϕ'. The two maxima in the curve occur for dihedral angles near 120° and 240°, i.e., in situations in which the hydrogens H4' and H4, respectively, are in closest proximity to the C5 methyl group. A relative minimum occurs near the arrangement ($\phi' = 180°$) in which the hydroxyl is directed away from the C5 methyl, and the minimum occurs in the situation in which the hydroxyl is pointed in the direction of the C5 methyl. If it is again assumed that the rotamers **1b** and **1c** in Figure 2 are equally populated and have dihedral angles of 130° and 250°, then the average $^{13}C-^{13}C$ coupling constant ^3J(C4,C5) from Figure 5 is 3.6 Hz. This is in reasonably good agreement with the experimental value of 3.4 Hz in Table I and provides further confidence in the assignments, conformations, and populations deduced from the ^1H NMR data.

In order to investigate the importance of the nonbonded interactions associated with the interactions between the hydrogens of the hydroxymethyl group and those of the C5 methyl group on vicinal $^{13}C-^{13}C$ coupling constants, a procedure used in the previous papers[3-5] in this series was also adopted here. Elements of the Fock matrices associated with the hydrogen atoms on the C4 carbon atoms and the hydrogen atoms on the C5 carbon atoms were set equal to zero in each cycle of the SCF procedure. The coupling constants were recalculated as a function of the dihedral angle ϕ',[19] and the results are plotted (dashed line) in Figure 6. The maxima in the calculated results for $^3J_{\mathrm{CC'}}$ are decreased by 2.5–3 Hz. This shows clearly that the nonbonded interactions between hydrogens on the coupled carbon atoms are the dominant factor controlling vicinal $^{13}C-^{13}C$ coupling in the cis arrangement. It should be remembered, however, that many other nonbonded interactions are not negligible[6] and that this is something of an oversimplification of the physical situation.

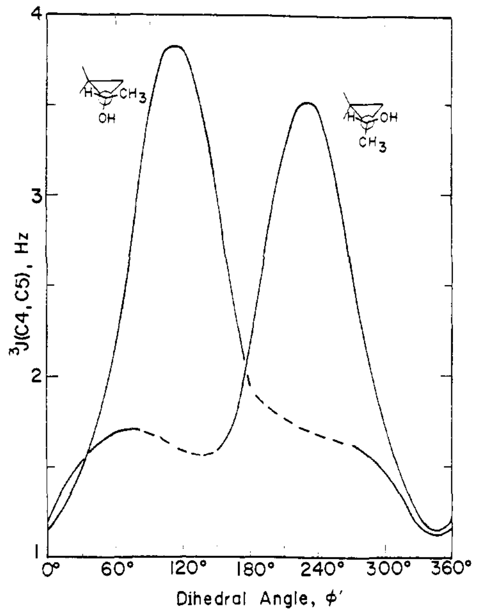

Figure 6. Calculated INDO FPT MO results for ^3J(C4,C5) in the (*R*,*S*) and (*R*,*R*) diastereomers of α,2,2-trimethylcyclopropanemethanol **2** and **3**, respectively, plotted as a function of the dihedral angle ϕ'. The (*R*,*S*) and (*R*,*R*) diastereomers have maxima near 120° and 240°, respectively. The dashed parts of the curves correspond to regions in which the hydrogens of the C7 methyl and the C4 methyl are so close. (<1 Å) that the calculated results are not reliable.

(*R*,*S*)- and (*R*,*R*)-α,2,2-Trimethylcyclopropanemethanol (2 and 3). The chemical shifts of the H3S proton of **2** and **3** are 0.03 and 0.24 ppm, respectively, i.e., values substantially smaller, and slightly greater than the value in cyclopropane. It seems likely, therefore, that the hydroxyl group in **2** is directed away from the cyclopropane ring, whereas for **3** it is pointing toward the ring. The near equality of the vicinal $^1H-^1H$ coupling constants ^3J(H1,H4') = 9.60 Hz in **2** and 9.48 Hz in **3** suggests that the H–C–C–H dihedral angles are about the same. From the $^{13}C-^{13}C$ coupling constant data it appears that the protons on C1 and C4 are near trans arrangements in both **2** and **3**. In the trans arrangements the INDO-FPT MO method substantially overestimates vicinal $^1H-^1H$ coupling constants.[14,20] Moreover, the assumption of rotational averaging between two conformers does not appear to be consistent with the coupling constant data described herein.

Calculated values of the cis ^3J(C4,C5) in the secondary alcohols **2** and **3** are plotted as a function of the dihedral angle ϕ' in Figure 6.[19] These plots again show the importance of the proximity of the hydrogens to the methyls; the coupling constant drops off rapidly as the protons are moved in either direction away from the C5 methyl group. Furthermore, the replacement of a proton by a methyl group greatly attenuates the nonbonded coupling mechanism. Note that the assumptions of fixed methyl groups for compounds **2** and **3** leads to conformations in which the protons are very close; the energies become sufficiently large that the molecules would distort. These conformations are indicated by the dashed lines in Figure 6. The relaxation of the various angles would remove this problem, but it would not change the conclusions of this study.

The MO results for ^3J(C4,C5), which are plotted as a function of ϕ' in Figure 6, suggest that the experimental result of 3.2 Hz in **2** should have ϕ' equal to ~30 or ~145°. In either case, as noted from the proton chemical shift data, the hydroxyl group

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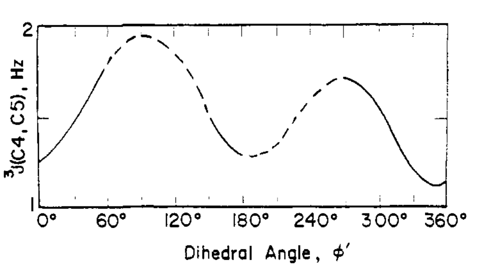

Figure 7. Calculated INDO FPT MO results for ^3J(C4,C5) in the tertiary alcohol **9** plotted as a function of the dihedral angle ϕ'.

is directed away from the ring. The vicinal ^{13}C–^{13}C coupling constants ^3J(C2,C7) and ^3J(C3,C7) from the dilabeled compound **2b** (from Table III, these are 3.45 and 0.34 Hz, respectively) are only consistent with $\phi' = 80°$. From the INDO FPT MO results for $^3J_{CC'}$ in 2-butanol,[8] $\phi' = 80°$ gives ^3J(C2,C7) = 3.6 Hz and ^3J(C3,C7) = 0.5 Hz, in good conformity with the experimental results. In contrast, the respective values for $\phi' = 145°$ are 0.5 and 4.0 Hz, which are at variance with the experimental data.

From Figure 6 it can also be inferred that the experimental coupling constant of 2.7 Hz between C4 and C5 in **3** would be consistent with $\phi' = \sim 195°$ or $\sim 265°$. In the dilabeled compound **3b** ^3J(C2,C7) was not observed and ^3J(C3,C7) = 3.23 Hz. From the calculated results for 2-butanol[8] the smaller value of the dihedral angle leads to ^3J(C2,C7) = 0.9 Hz, ^3J(C3,C7) = 3.4 Hz, whereas $\phi' = 265°$ gives 2.5 and 2.6 Hz, respectively. Thus, it appears that the preferred conformation is that for which ϕ' is $\sim 195°$.

Additional confirmation of these conformations of **2** and **3** is to be found in the agreement between the experimental geminal ^{13}C–^{13}C coupling constant data in Table II and results based on a recently developed[21] semiempirical expression for the angular dependence of $^2J_{CC'}$. A value of $\phi' = \sim 80°$ for **2** gives calculated values of −2.3 and 0.04 Hz in comparison with the experimental values of ±1.69 and <0.2 Hz, respectively. Similarly, $\phi' = 195°$ in **3** leads to calculated values ^2J(C2,C4) = 0.5 and ^2J(C3,C4) = −2.0 Hz in comparison with the experimental values of <0.4 and ±1.83 Hz, respectively.

***α,α,*2,2-Tetramethylcyclopropanemethanol (9).** The larger size of the methyl groups will tend to put the hydroxyl group toward the cyclopropane ring in conformity with the expectation from the relatively large (0.39 ppm) shift of the H3S proton of **9**. In this case, the results are consistent with the minimum energy conformations near 30 and 300° in the INDO MO calculations for this molecule.[19] Calculated INDO FPT MO results for vicinal ^{13}C–^{13}C coupling constants between the C4 and C5 carbon atoms of **9** are plotted as a function of the dihedral angle ϕ' in Figure 7. Again, the dashed part of the curve corresponds to calculated values which are not physically meaningful because the energies are too large. Because there are no protons on the C4 carbon, the very important nonbonded coupling mechanism does not occur in this molecule, and the ^{13}C–^{13}C coupling constants in Figure 7 are less than 2 Hz. Furthermore, the calculated values in the minimum energy conformations are about 1.5 Hz, which is significantly smaller than any of the other values which were calculated for the series of alcohols. This may be compared with the experimental value of 1.0 Hz in Table I. It is now clear why this is the smallest value found in the series of dimethylcyclopropanes.

Trans (ϕ = *145°*) Coupling in the Series of Compounds 1–3 and 9. Calculated results for the "trans" ^{13}C–^{13}C coupling constants between the C4 and C6 carbons of the various 2,2-dimethylcyclopropanes were also obtained in this study for the series of molecules **1**–**3** and **9**.[19] The calculated values range from 1.0 to 1.7 Hz with no correlations with substituents or orientation of the hydrogens on the C4 carbon. The calculated values for each of the four compounds follow a consistent pattern in which there is a relatively steep maximum for a dihedral angle ϕ' of about 340°, i.e., a conformation in which the hydroxyl group lies over the cyclopropane ring.

Conclusions

Vicinal ^{13}C–^{13}C coupling in the cis arrangement is very sensitive to the nature and orientation of the α substituents. The α-substituent effects are shown to be dominated by nonbonded interactions involving the hydrogen atoms which are directly attached to the coupled carbon atoms. The presence of a hydrogen atom on the C_α carbon and directed toward a C_δ methyl group produces large values of cis ^{13}C–^{13}C coupling constants. Replacement of this hydrogen by other groups such as hydroxyl or methyl groups greatly attenuates the coupling constants. As a consequence, the maximum value of the experimentally determined ^{13}C–^{13}C coupling constants occurs for the 2,2-dimethylcyclopropane **1** with the hydroxymethyl group having the hydroxyl group directed away from the C5 methyl, and the minimum value occurs for the tertiary alcohol **9**, which does not have any hydrogens on the C4 carbon atom. The intermediate values for the carboxylic acid derivative and the other compounds **4**–**7** in Table I are also attributable to the number and orientation of hydrogen atoms on the substituent.

Experimental Section

Syntheses. Carbon-13 labeled carbon dioxde (>90% isotopically enriched) was purchased from Prochem Chemical Co., B.O.C., Ltd., Deer Park Road, London SW19 3UF U.K. Isobutylene was purchased from Matheson Co., East Rutherford, NJ. Methyl iodide was obtained from Aldrich Chemical Co., Milwaukee, WI. Proton NMR spectra were recorded on a Perkin-Elmer R-24B NMR spectrometer.

Proton NMR spectra of the substituted 2,2-dimethylcyclopropane alcohols were recorded at 250.13 MHz on a Bruker Instruments WM-250 FT NMR spectrometer. Spectral analyses were performed via iterative techniques using Bruker Instruments' PANIC.80 spectral simulation program[22] on the Aspect 2000A computer. Chemical shifts and coupling constants are included in this section; in all cases the root-mean-square errors were less than 0.13 Hz. Melting points were determined by using a Thomas-Hoover apparatus. Infrared spectra were recorded on a Beckman IR-33 infrared spectrophotometer. Mass spectra were recorded by using a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer.

1,1-Dibromo-2,2-dimethylcyclopropane.[23] A mixture of potassium *tert*-butoxide in *tert*-butyl alcohol/pentane was produced by adding potassium (58.5 g) to 946 mL of *tert*-butyl alcohol in a 3-L three-neck flask under argon and then adding 946 mL of pentane. To this stirring mixture, cooled in a salt-ice bath, was injected liquid isobutylene (250 mL), and then 87 mL of bromoform was injected in 10-mL portions. The stirring mixture was held at 0 °C for 14 h, warmed, washed with 12 500-mL portions of water, dried (anhydrous magnesium sulfate), and concentrated in vacuo to give 213 g (93% based on bromoform) of a pale yellow liquid: IR (neat, cm^{-1}) 3000, 2970, 2940, 2890, 1465, 1455, 1445, 1390, 1270, 1130, 1110, 1055, 1010, 975, 850, 700; ^{1}H NMR (CDCl$_3$) δ 1.65 (s, 2 H), 1.60 (s, 6 H); mass spectrum, *m/e* 226, 228, 230 (ratio 1:3:1), B 147, 149 (ratio 1:1).

1-Bromo-2,2-dimethylcyclopropane.[24] To rapidly stirring 1,1-dibromo-2,2-dimethylcyclopropane (103.2 g) under argon in a 250-mL flask was added dropwise, 131.5 g of tri-*n*-butyl hydride (synthesized by the usual procedure[25]), while the reaction contents were kept below 15 °C by means of an ice bath. Then the mixture was distilled to give a pale yellow liquid, 65.2 g (96% based on the dibromide). Redistillation gave a clear liquid: bp 107–108 °C (lit.[24] bp 107–108 °C); IR (neat, cm^{-1}) 3180, 2940, 2920, 2870, 2750, 1470, 1450, 1290, 1215, 1130, 1095, 1080, 1035, 970, 925, 835; ^{1}H NMR (CDCl$_3$) δ 2.64 (d of d, 1 H), 1.24 (s, 3 H), 1.12 (s, 3 H), 0.93 (d of d, 1 H), 0.6 (d of d, 1 H); mass spectrum, *m/e* 148, 150, B 41.

2,2-Dimethylcyclopropanecarboxylic-*carboxyl*-^{13}*C* Acid (6).[26–29] To a stirring mixture of 1.32 g of lithium sand (prepared by shaking a hot

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flask of molten lithium in mineral oil and hexane under argon, cooling, and washing with ether) in 250 mL of anhydrous ether under argon in a 500-mL flask cooled by means of an ice bath was added 13.0 g of 1-bromo-2,2-dimethylcyclopropane over a period of 2 h. After an additional hour of stirring, the ethereal layer was decanted into a round-bottom flask and carbonated[7,29] and worked up in the usual manner[7] to give 6.7 g of crude product (68% based on the bromide). Distillation gave a clear liquid: bp 85 °C (5 torr) (lit.[27] bp 198–201 ° (1 atm)); IR (neat, cm^{-1}) 3500–2400, 1650 (^{13}C-labeled) or 1700 (unlabeled), 1460, 1440, 1400, 1325, 1290, 1230, 1140, 1120, 1065, 985, 865; ^{1}H NMR[13] (CDCl$_3$) δ 11.5 (s, 1 H), 1.40 (d of d, 1 H), 1.21 (s, 3 H), 1.11 (s, 3 H), 0.99 (d of d, 1 H), 0.79 (d of d, 1 H); ^{13}C NMR, see Table II; mass spectrum, *m/e* 114 (115 for ^{13}C labeled), B 69.

2,2-Dimethylcyclopropanemethanol-*carbinol*-^{13}*C* (1). Lithium aluminum hydride reduction of the carboxylic acid **6** in the usual manner[9] gave 85% of the alcohol **1**: IR (neat, cm^{-1}) 3500–3100, 3050, 3000, 2950, 2875, 2750, 1460, 1425, 1390, 1315, 1280, 1240, 1170, 1140, 1120, 1040, 965, 875, 815; ^{1}H NMR (CDCl$_3$) δ 3.39 (complex, 2 H, system additionally split, J = 138 Hz), 0.95 (s, 3 H), 0.91 (s, 3 H), 0.95 to −0.10 (complex, 3 H); ^{13}C NMR see Table II; mass spectrum *m/e* 83 (labeled) or 82 (unlabeled), B 41. A detailed ^{1}H NMR analysis using PANIC.80[22] gave the following ^{1}H NMR parameters: δ 0.85 (H1), 0.40 (H3A), 0.07 (H3S), 3.41, 3.63 (H4, H4′), 1.10 (H5), 1.05 (H6), 4.41 (OH); J = 8.59 (1,3A), 5.27 (1,3S), 8.57 (1,4), 6.30 (1,4′), −4.27 (3S,3A), −11.25 Hz (4,4′).

2,2-Dimethylcyclopropanecarboxaldehyde-*carbonyl*-^{13}*C* (5).[27] Oxidation of the alcohol **1** (2.79 g) using 8.95 g of pyridinium chlorochromate[30] in 100 mL of dichloromethane gave 2.0 g (72%) of a pale yellow liquid: ^{1}H NMR (CDCl$_3$) δ 9.05 (d, 1 H, J = 6 Hz; system additionally split, J = 167 Hz), 1.19 (s, 3 H), 1.09 (s, 3 H), 0.5–1.5 (3 H, complex); ^{13}C NMR, see Table II. This material was extremely sensitive to air (oxidized rapidly to the carboxylic acid) and was immediately carried on in the synthetic sequence.

2,2-Dimethylcyclopropyl Methyl Ketone-*carbonyl*-^{13}C (1-Acetyl-2,2-dimethylcyclopropane-*carbonyl*-^{13}C) (8).[27,31] To a 250-mL flask charged with 0.33 g of lithium hydride and 50 mL of anhydrous ether under argon was added 4.26 g of the carboxylic acid (**6**) in 15 mL of anhydrous ether over a 10-min period. The stirring white suspension was heated under reflux for 2.5 h and cooled to produce a lithium carboxylate suspension. (Methyl-^{13}C)lithium was prepared by adding lithium sand (6 g, vide supra under **6**), washed with 100 mL of anhydrous ether, into a 100-mL flask and by then adding 10.5 g of methyl-^{13}C iodide in 25 mL of anhydrous ether, followed by 1 h of reflux. The methyllithium solution was added to the lithium carboxylate suspension (cooled in an ice bath) with stirring over a 30-min period. The resulting mixture was allowed to warm to room temperature and to stir overnight. A solution of 10 g of sodium thiosulfate pentahydrate in 400 mL of water was added to the rapidly stirring organic solution. The resulting solution was extracted with three 100-mL portions of ether. The combined ethereal extracts were dried (anhydrous sodium sulfate) and concentrated in vacuo to give 2.07 g (48%) of a pale yellow liquid: ^{1}H NMR (CDCl$_3$) δ 2.1 (s, 3 H, d for labeled compound with J = 6 Hz), 1.71 (d of d, ^{1}H, complex for labeled compound), 1.15 (s, 3 H), 1.05 (s, 3 H), 0.75 (d of d, 2 H, complex for labeled compound); ^{13}C NMR, see Table II; mass spectrum, *m/e* 112 (113 for labeled compound) B 41. This material was extremely sensitive to acidic conditions during workup and decomposed readily.

(*R*,*S*)- and (*R*,*R*)-α,2,2-Trimethylcyclopropanemethanol-*carbinol*-^{13}*C* (2a and 3a) and (*R*,*S*)- and (*R*,*R*)-α,2,2-Trimethylcyclopropanemethanol-α-^{13}*C*,*carbinol*-^{13}*C* (2b and 3b).[27] Lithium aluminum hydide reduction of the ketone **8** in the usual manner[9] gave a 86:14 mixture of the RS and RR diastereomers,[32] respectively, in an 85% yield: ^{1}H NMR (CDCl$_3$) for unlabeled compound, δ 3.2 (1 H, multiplet), 1.15 (d, 3 H), 1.05 (s, 3 H), 0.95 (s, 3 H), methylene and methine signals obscured by the methyl signals; ^{1}H NMR (CDCl$_3$) for 1,2-^{13}C dilabeled compound showed additional J = 138 Hz at δ 3.2 and J = 126 Hz at δ 1.15; ^{13}C NMR, see Table II: mass spectrum, *m/e* 96 (for unlabeled), 98 (for dilabeled), B 59. Methyl Grignard addition to the aldehyde **5** gave a respective ratio of 53:47 of *RS*:*RR*. A detailed ^{1}H NMR analysis using PANIC.80[22] gave the following ^{1}H NMR parameters: δ (for *RS*) 0.70 (H1), 0.46 (H3A), 0.03 (H3S), 3.38 (H4), 1.18 (H5), 1.06 (H6), 1.29 (H7); J (for *RS*) = 8.71 (1,3A), 5.30 (1,3S), 9.60 (1,4), −4.38 (3A,3S), 6.18 Hz (4,7); δ (for *RR*) 0.66 (H1), 0.49 (H3A), 0.24 (H3S), 3.34 (H4), 1.07 (H5), 1.04 (H6), 1.28 (H7); J (for *RR*) = 8.18 (1,3A), 5.42 (1,3S), 9.48 (1,4), −4.30 (3A,3S), 6.18 Hz (4,7). This PANIC.80 analysis for the ^{13}C-labeled compound gave the following carbon-proton couplings: J (for *RS*) = 1.42 (C4,H1), 4.21 (C4,H3A), 141.17 (C4,H4), 4.40 Hz (C4,H7); J (for *RS*) = 1.42 (C4,H1), 4.21 (C4,3A), 141.17 (C4,H4), 4.40 Hz (C4,H7); J (for *RR*) = 1.53 (C4,H1), 2.10 (C4,H3A), 5.40 (C4,H3S), 141.7 (C4,H4), 4.40 Hz (C4,H7).

Table III. Carbon–Carbon Coupling Constants in the Dilabeled Compounds **2b**, **3b**, and **9b**

carbon X	**2b** $J(X,\mathrm{C7})$, Hz	**3b** $J(X,\mathrm{C7})$, Hz	**9b** $J(X,\mathrm{C8})$, Hz
1	1.10 (7)	*a*	3.11 (9)
2	3.45 (7)	*a*	2.62 (5)
3	0.34 (7)	3.23 (7)	1.03 (9)
4	39.17 (7)	38.88 (7)	39.2 (2)
5	<0.2	<0.2	<0.2
6	<0.1	<0.1	<0.6
7			*a*

[a] No splitting was observed.

α,α,2,2-Tetramethylcyclopropanemethanol-*carbinol*-^{13}C (9).[27,33] The ketone **8** was reacted with (methyl-^{13}*C*)lithium (vide supra under **8**) and worked up in the same manner to give 0.2 g (20%) of the tertiary alcohol **9**: ^{1}H NMR (CDCl$_3$) δ 1.15 (s, 6 H), 1.10 (s, 3 H), 0.91 (s, 3 H), 0.51–0.21 (3 H, m); ^{13}C NMR, see Table II; mass spectrum, *m/e* 128, B 59. A detailed ^{1}H NMR analysis using PANIC.80[22] gave the following ^{1}H NMR parameters: δ 0.64 (H1), 0.35 (H3A), 0.39 (H3S), 1.25 (H5), 1.04 (H6), 1.30 (H7), 1.31 (H8); J = 9.12 (H1,H3A), 6.22 (H1,H3S), 0.10 (H1,H7), 0.18 (H1,H8), −4.26 (H3S,H3A), 0.43 Hz (H7,H8). This PANIC.80 analysis for the ^{13}C-labeled compound gave the following carbon–proton couplings: J = 2.15 (C4,H1), 1.95 (C4,H3A), 4.51 (C4,H3S), 4.14 (C4,H7), 4.14 Hz (C4,H8). This alcohol was extremely sensitive to atmospheric conditions and rapidly decomposed.

2,2-Dimethylcyclopropanecarboxamide-*carbonyl*-^{13}*C* (7).[34,35] The carboxylic acid (6, 5.62 g) was reacted with 6.4 g of thionyl chloride, heated to remove excess thionyl chloride, reacted with 150 mL of concentrated ammonium hydroxide, and concentrated by heating. The residue was extracted with hot ethyl acetate. Cooling of the ethyl acetate gave 2.0 g of the amide (35%): mp 174.5–176.5 °C (lit.[35] mp 177–177.5 °C); IR (KBr, cm^{-1}) 3380, 3220, 3000, 2980, 2900, 1685, 1645, 1400, 1355, 1320, 1270, 1160, 1140, 1115, 985, 870; ^{1}H NMR (CDCl$_3$) δ 1.5–1.2 (1 H, m), 1.05 (s, 3 H), 1.0 (s, 3 H), 0.9–0.5 (2 H, m); ^{13}C NMR, see Table II; mass spectrum, *m/e* B 113 (114 for labeled compound).

2,2-Dimethylcyclopropanecarbonitrile-*carbonitrile*-^{13}*C* (4).[35,36] Reaction of the amide (**7**, 1.36 g) with 1.1 g of thionyl chloride at 75–80 °C for 4.5 h, followed by workup with cold aqueous 50% sodium hydroxide, extraction with 100 mL of benzene, washing with aqueous sodium bicarbonate and water, drying (anhydrous magnesium sulfate), concentration in vacuo, and trap-to-trap distillation, gave 0.350 g (30%) of a clear liquid: IR (neat, cm^{-1}) 2980, 2940, 2860, 2260, 1735, 1460, 1390, 1280, 1105, 1040, 815; ^{1}H NMR (CDCl$_3$) δ 1.17 (s, 3 H), 0.98 (s, 3 H), 0.78 (2 H, d of d, complex for labeled), methine obscured by methyl and methylene signals; ^{13}C NMR, see Table II; mass spectrum, *m/e* 95 (96 for labeled compound), B 68.

Carbon-13 NMR Spectra. Carbon-13 NMR spectra were recorded at 22.63 and 62.86 MHz on Bruker Instruments WH-90 FT NMR and WM-250 superconducting FT NMR spectrometers, respectively. Either chloroform-*d*, acetone-d_6, or a mixture of methanol and deuterium oxide were used as solvents and internal lock materials. All chemical shifts are referenced downfield from internal tetramethylsilane (Me$_4$Si). The digital resolution, as determined by spectral widths and memory blocks, was better than the estimated errors in parentheses.

The experimental ^{13}C NMR data for the 1-substituted 2,2-dimethyl cyclopropanes **1–9** are given in Table II. Chemical shift assignments were based on single frequency off-resonance decoupling; the C5 carbon is shifted upfield of C6 due to the steric shift of the cis substituent.[37]

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These were also identified by the relative sizes of the vicinal $^{13}C-^{13}C$ coupling constants. To confirm the structure of the diastereomers **2** and **3** the C7-position was ^{13}C enriched (**2b** and **3b**) to observe the vicinal coupling constants to C2 and C3; the results for the dilabeled compound **2b**, **3b**, and **9b** are given in Table III.

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Registry No. 1, 85370-53-2; **2**, 85370-54-3; **3**, 85370-55-4; **4**, 85370-56-5; **5**, 85370-57-6; **6**, 85389-80-6; **7**, 85370-58-7; **8**, 85370-59-8; **9**, 85370-60-1; 1,1-dibromo-2,2-dimethylcyclopropane, 32264-50-9; isobutylene, 115-11-7; bromoform, 75-25-2; 1-bromo-2,2-dimethylcyclopropane, 3815-09-6; 1-lithio-2,2-dimethylcyclopropane, 82684-51-3.

Supplementary Material Available: Tables of calculated INDO FPT MO results for vicinal $^{1}H-^{1}H$ and $^{13}C-^{13}C$ coupling constants in **1**, $^{13}C-^{13}C$ coupling constants in **2**, and $^{13}C-^{13}C$ coupling constants in **4** (4 pages). Ordering information is given on any current masthead page.

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Site of Protonation and Conformational Effects on Gas-Phase Basicity in β-Amino Alcohols. The Nature of Internal H Bonding in β-Hydroxy Ammonium Ions

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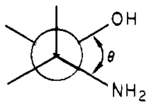
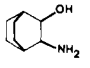
Abstract: The influence of interfunctional distance on the gas-phase basicity of β-amino alcohols is investigated by the method of equilibrium proton-transfer reactions in an ion cyclotron resonance (ICR) spectrometer. It is found that in the protonated species, interaction between the most basic center (amino group) with the hydroxy group results in stabilization of the system. The stabilization energy increases as the interfunctional distance decreases to reach a maximum value of about 7 kcal/mol for coplanar systems. Comparison with the values determined by ab initio calculations indicates that internal H bonding can be described in terms of the ion–dipole potential energy between the ammonium ion and the hydroxy group. External vs. internal ion solvation effects are also discussed.

The determination of basicity properties of isolated molecules is a rapidly expanding field of gas-phase chemistry. From the large number of data already accumulated on monofunctional compounds, a detailed picture of the effects of substituents has emerged (see ref 1 for a recent review). Useful comparisons can be made with the numerous solution results in order to evaluate the influence of solvation on molecular properties. Another challenge is provided by multifunctional systems in which one has to distinguish between different possible sites for protonation and thus different basicity values associated with each reaction site.[2]

The purpose of the present study is the determination of the gas-phase basicity (GB) of seven conformationnally stable β-amino alcohols, compounds **1–7**, in which the dihedral angle θ (CO–CN) ranges from 0° to 180°, according to



1, θ = 0°
2, θ = 30°
3, θ = 60°
4, θ = 90°
5, θ = 120°
6, θ = 150°
7, θ = 180°



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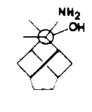

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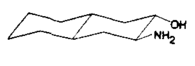

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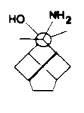

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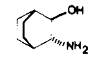

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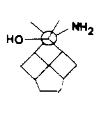

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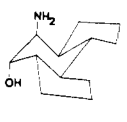

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In a previous investigation of the chemical ionization mass spectra of these compounds,[3] it has been shown that there is a relationship between the interfunctional distance and the loss of water from the protonated amino alcohol. It was then found that water loss becomes significant only when θ ≥ 120°, and these results suggested the possibility for internal proton transfer to form stable N-protonated species.

We want to establish quantitatively the gas-phase basicity of these compounds by the method of equilibrium proton transfer in an ion cyclotron resonance spectrometer (ICR)[4] in order to determine first the site of protonation in these amino alcohols. Another question is related to the possibility for interaction be-

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(1) D. H. Aue and M. T. Bowers, in "Gas Phase Ion Chemistry", M. T. Bowers, Ed., Academic Press, New York, 1979, Chapter 9.

(2) R. Houriet, H. Schwarz, W. Zummack, J. G. Andrade, and P. v. R. Schleyer, *Nouv. J. Chim.*, **5**, 505 (1981).

(3) P. Longevialle, J. P. Girard, J. C. Rossi, and M. Tichý. *Org. Mass Spectrom.*, **14**, 414 (1979).

(4) T. A. Lehmann and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley-Interscience, New York, 1976.

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