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THE ELECTRONIC STRUCTURE AND REACTIVITY OF SMALL RING COMPOUNDS—VII

THE CMR SPECTRA OF 1-CYANOBICYCLO[1.1.0]BUTANE[1]

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Abstract—The 25·2 MHz CMR (FFT) spectra of 1-cyanobicyclo[1.1.0]butane are reported both with and without hydrogen decoupling. Chemical shifts are discussed in terms of dipolar resonance contributions to the ground state and the unsaturated nature of the bicyclobutane ring. The C-H coupling constants, including directly bonded and long range interactions, are reported. It is suggested that the large long range $H_{x'}$–C_2 coupling constant is a result of a favorable interaction between the $H_{x'}$–C_4 bond and C_2 and that the H_3-cyano carbon coupling constant results from a 0° dihedral angle and to a small extent, if at all, from a favorable geometry. The C_1–C_2 (22 Hz) and C_1–C_3 (16 Hz) ^{13}C–^{13}C coupling constants are presented, compared with the calculated values, and discussed in terms of hybridization. The possibility of a negative value for the C_1–C_3 coupling constant is also considered. It is pointed out that using coupling constant-hybridization relationships and extrapolating from several known to an unknown hybridization around a carbon atom can, in many cases, lead to a sizeable error in calculated hybridization.

INTRODUCTION

The chemical and physical properties of highly strained microcyclic compounds have been of considerable interest over the past several years. The large amount of strain in bicyclobutane[4] and derivatives[5] (64–68 kcal/mole) gives rise to rather interesting properties, both chemical and physical.[6] In addition, there is much current interest in long range ^{13}C–H spin-spin coupling constants,[7] which are now available from hydrogen coupled CMR spectra using Fourier techniques. These coupling constants are being studied as a diagnostic probe for structural assignments.

In this paper we present an analysis of the 25·2 MHz CMR spectra of 1-cyanobicyclo[1.1.0]butane which provides the chemical shifts from proton decoupled spectra and ^{13}C–H coupling constants, including long range interactions, from direct, coupled, spectra. In addition, ^{13}C–^{13}C coupling constants between directly bonded C atoms were obtained.[1]

EXPERIMENTAL

The sample of 1-cyanobicyclobutane was generously provided by Dr. S. C. Cherkofsky of E. I. DuPont de Nemours. For the 60 MHz ^1H spectra the sample was used as obtained, as a soln in CCl_4 containing TMS. For the 25·2 MHz ^{13}C spectra the sample and acetonitrile-d_3 (*ca* a 30:70 mixture of acetonitrile-d_3 and the cyanobicyclobutane respectively) were codistilled (bulb to bulb) at 10^{-5} Torr into a 12-mm tube, subjected to several freeze-thaw degassing cycles and sealed. The sample thus prepared was stored at −80°C (Dry Ice) or 77°K (liquid N_2). The PMR spectrum was recorded on a Varian A-60A spectrometer at ambient temperature. The CMR FFT spectra were recorded on a Varian XL-100 spectrometer at −30° using a pulse width of 75 μsec and a delay time of 15 sec. The ^{13}C–^{13}C coupling constants were obtained from a spectrum using 2613 transients.

RESULTS AND DISCUSSION

The PMR spectrum of 1-cyanobicyclo[1.1.0]butane was essentially the same as reported.[8] The chemical shift (δ, ppm) for the exo hydrogens H_X and $H_{X'}$ was found to be 1·20, for the endo hydrogens H_N and $H_{N'}$, 2·19 and for H_3, 2·49 (Fig. 1). Hall *et al.*[8] reported δ = 1·23, 2·22 and 2·52 ppm respectively.

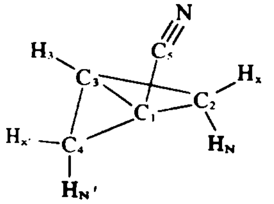


Fig 1.

The ^{13}C NMR spectrum was obtained using acetonitrile-d_3 both as deuterium lock and as the internal standard. If the nitrile carbon is taken as having a chemical shift of 75·6 ppm relative to CS_2[9a] or 117·2 ppm relative to TMS[9b] then the chemical shifts shown in Table 1 are obtained assuming no isotope effect on the chemical shift of the

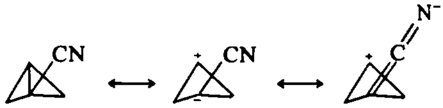
Table 1. ^{13}C chemical shifts of 1-cyanobicyclobutane (ppm relative to TMS)

Assignment	Chemical shift
C_1	−8·9[a]
C_2, C_4	36·5
C_3	12·4
C_5	120·4

[a] Upfield from TMS.

acetonitrile-d_3 cyano carbon. The relative chemical shifts are considered accurate to better than 0·1 ppm. These compare favorably with other nitrile carbon chemical shifts[9a] and with the C_1 and C_2 resonances in bicyclobutane itself, $\delta_{TMS} = -4$ and 32 ppm respectively.[10*]

The observation that in cycanobicyclobutane C_1 is more shielded and C_3 is more deshielded than the corresponding C atoms in bicyclobutane is readily explained on the basis of the dipolar resonance forms pictured. The positive charge at C_3 and the negative charge at C_1 would tend to shield and deshield these respective carbon atoms. The same phenomenon[11a] is observed in acrylonitrile where



C_α is shielded by about 16 ppm and C_β is deshielded by 15 ppm relative to the carbons of ethylene. In addition, the contribution to the resonance hybrid of polar canonical forms is also shown in ethyl vinyl ether where C_α (vinyl) is now deshielded by 30 ppm and C_β is shielded by 38 ppm relative to ethylene.[11a]

$$CH_2{=}CH{-}CN \leftrightarrow \overset{+}{C}H_2{-}\overset{-}{C}H{-}C{\equiv}N \leftrightarrow \overset{+}{C}H_2{-}CH{=}C{=}\overset{-}{N}$$

$$CH_2{=}CH{-}O{-}C_2H_5 \leftrightarrow \overset{-}{C}H_2{-}\overset{+}{C}{-}O{-}C_2H_5$$

$$\leftrightarrow \overset{-}{C}H_2{-}CH{=}\overset{+}{O}{-}C_2H_5.$$

It should be pointed out that the methylene groups in cyanobicyclobutane are also deshielded relative to bicyclobutane by 4·5 ppm which indicates some contribution to the resonance hybrid of cyclopropylcarbinyl cation type forms. These observations of deshielded carbons β to the cyano group and shielded carbons α to the cyano group, once again, point up the unsaturated nature of the bicyclobutane ring system and the high degree of p-character in the C-C bonds, particularly in the 1-3 bond.[6a,12-15]

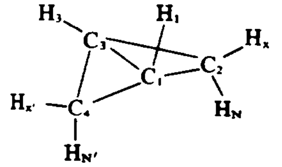
The differences in chemical shift of the α and β carbons of a series of nitriles are as follows: propionitrile, 3 ppm;[11b] cyclopropanecarbonitrile, 10 ppm;[11c] bicyclobutane-1-carbonitrile, 21 ppm, and acrylonitrile, 31 ppm.[11a] This is exactly the order which would be expected based on the extent of the contribution of dipolar canonical forms to the resonance hybrid.

By examining the ^{13}C spectrum directly without noise decoupling each of the carbon resonances split into first order multiplets from which the coupling constants shown in Table 2 were obtained. Also in this table for comparison are the corresponding coupling constants in bicyclobutane. The values obtained in this work are accurate to ±0·5 Hz while those from ref.[10] are as indicated.

It is obvious from Table 2 that the agreement between the two bicyclobutanes is quite good. Thus, using the Muller-Pritchard relationship,[16] one can calculate that the carbon orbital bonding to the bridgehead hydrogen is hybridized $sp^{1\cdot40}$ (41·6% s-character). In addition, the orbital bonding the exo hydrogen is $sp^{2\cdot15}$ (31·6% s-character) and that bonding the endo hydrogen is $sp^{1\cdot87}$ (34·8% s-character). These values agree fairly well with hybridization obtained from *ab-initio*,[12] INDO,[12] maximum overlap,[13] CNDO,[14] extended Hückel[15] as well as very simple zeroth order Hückel[6a] calculations on bicyclobutane itself.

Table 2. ^{13}C–H coupling constants (Hz)

1-Cyanobicyclobutane		Bicyclobutane[10](Fig. 2)	
Assignment	$\lvert J\rvert(\pm 0\cdot5\ Hz)$	Assignment	J(Hz)
$J_{C_3-H_3}$	207·8	$J_{C_1-H_1}$	205 ± 2
$J_{C_2-H_N}$	174·0	$J_{C_2-H_N}$	169 ± 1
$J_{C_2-H_X}$	158·3	$J_{C_2-H_X}$	153 ± 1
$J_{C_1-H_3}$	2·1	$J_{C_1-H_3}$	3·3 ± 0·2
$\left.\begin{matrix}J_{C_1-H_X}\\J_{C_1-H_N}\end{matrix}\right\}$	4·3 and 0	$\left.\begin{matrix}J_{C_1-H_X}\\J_{C_1-H_N}\end{matrix}\right\}$	3·3 or 0 ± 0·2
$\left.\begin{matrix}J_{C_3-H_X}\\J_{C_3-H_N}\end{matrix}\right\}$	3·8 and 0		
$J_{C_2-H_3} = J_{C_2-H_{N'}}$	4·7	$J_{C_2-H_1} = J_{C_2-H_{N'}}$	5·3 ± 0·2
$J_{C_2-H_{X'}}$	14·1	$J_{C_2-H_{X'}}$	16·0 ± 0·5
$J_{C_3-H_3}$	8·4		



There are several other observations concerned with the carbon-hydrogen couplings which should be discussed. Just as in bicyclobutane,[10] the bridgehead carbon atoms couple to either the exo or the endo hydrogens but not both. We cannot at this time speculate which of the two possibilities obtains.

Recently Wasylishen and Schaefer[17a] used the INDO method to calculate the dependence of vicinal ^{13}C–H coupling constants, $^3J_{HCCC}$, in propane on dihedral angle and obtained a result similar to the Karplus relationship for H-H coupling constant and vicinal dihedral angle. A study of several systems[17b,c] seems to substantiate the calculations and that at a dihedral angle of about 90° the coupling constant is a minimum. The dihedral angle between C_2–C_1–C_4–$H_{N'}$ in cyanobicyclobutane is 59°[18] and, using the propane model,[17a] the coupling constant should be about 2 Hz as compared with the observed value of 4·7 Hz. The dihedral angle C_2–C_1–C_4–$H_{X'}$ is 155°[18] which, using the propane calculation, indicates a coupling constant of 7·5 Hz. Comparison of this to the observed value of 14·1 Hz and 16·0 Hz for cyanobicyclobutane and bicyclobutane respectively suggests that perhaps the rear lobe of the C_4–$H_{X'}$ bond is interacting with C_2 so as to enhance the coupling. This type of interaction is

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[*] The chemical shifts reported[10] are $\delta_{C_1} = 197 \pm 2$ and $\delta_{C_2} = 161 \pm 2$ ppm relative to CS_2. Using $\delta_{TMS} = 193 - \delta_{CS_2}$ the chemical shifts relative to TMS are obtained.

suggested to explain the large long range H-H couplings in various small ring compounds.[19]

The observation that the cyano carbon resonance is a doublet ($J = 8{\cdot}5 \pm 0{\cdot}5$ Hz) implies that this carbon is coupled to H_3 and not (or very minimally) to H_x or H_N. Comparison of this coupling constant to those in other nitriles [i.e. $^3J_{HCCC(N)}$] indicates that this one is considerably larger. In propionitrile $^3J_{HCCC(N)}$ is 4·28 Hz,[9a] in α-methylpropionitrile it is 4·2 Hz,[9a] and in α,α-dimethylpropionitrile it is 4·08[9a] or 5·4 Hz.[20] It is interesting that the average coupling constant calculated[17a] for a freely rotating group, where the dihedral angles are averaged between two 60° and one 180° angles, is 4·26 Hz. Thus the acyclic systems appear to be rotating freely and conversely the observation of a coupling constant of about 4·2 Hz supports the calculations. For a 0° dihedral angle, as H_3–C_3–C_1–C(N) in cyanobicyclobutane, the calculated coupling constant[17a] is 6·8 Hz. The slightly larger value observed, if significant, may be due to a more favorable interaction between the H_3–C_3 bond and C_1–C(N) bond through the rear lobes which would be absent in an unstrained system.[19]

The ^{13}C–^{13}C coupling constants were obtained from both of the satellite bands around the carbon resonance of each of the carbons involved. Thus the peaks corresponding to carbons 2 and 4 showed a single coupling constant to carbons 1 and 3 of $22 \pm 0{\cdot}5$ Hz. This is in excellent agreement with the value of 21 Hz reported recently by Grant and Allred and co-workers for bicyclobutane itself.[21] These authors were unable, because of the symmetry of the system, to obtain a value for the C_1–C_3 coupling constant. In the present case the value for the C_1–C_3 coupling constant, obtained from the side bands of both the C_1 and C_3 resonances, was $16 \pm 0{\cdot}5$ Hz. In addition C_1 and C_3 were coupled by 22 Hz to C_2 and C_4.

By using the linear relationship between ^{13}C–^{13}C coupling constant and the s-characters of the carbon orbitals making up the bond:

$$J_{^{13}C-^{13}C} = 550(S_{1(2)})(S_{2(1)})$$

as suggested by Bernstein,[22a] Pople[22b] and Roberts[22c] and most recently, in a somewhat modified form, by Newton[22d] and assuming a symmetrical C_1–C_3 bond (i.e. the CN group exerts only a minimal perturbation) one obtains a hybridization of $sp^{4{\cdot}85}$–$sp^{4{\cdot}85}$ or 17·1% s-character in each orbital. The small effect of a neighboring CN group on a particular bond is shown by the fact that the C–C coupling constants change by about 5% in going from ethane ($J_{CC} = 34{\cdot}6$ Hz)[23] to propionitrile ($J_{CC} = 33$ Hz)[24] and from ethylene ($J_{CC} = 67{\cdot}6$ Hz) to acrylonitrile ($J_{CC} = 70{\cdot}6$ Hz). Similarly a comparison of J_{CC} for the C_1–C_2 bond in bicyclobutane and 1-cyanobicyclobutane shows a 5% difference, 21 Hz[21] vs 22 Hz.

By assuming the equivalence of the C_1–C_2 and C_2–C_3 bonds and using the carbon-hydrogen coupling constants given above along with the Muller-Pritchard relationship[16] the orbitals on C_2 bonding to C_1 and C_3 can be shown to contain 16·8% s-character each. From the observed coupling constant of 22 Hz and the equation given above relating J_{CC} to s-character it can be shown that the orbitals on carbon 3 (and 1) bonding to C_2 and C_4 contain 23·8% s-character.* This would indicate that the peripheral bonds are $sp^{3{\cdot}20}$-$sp^{4{\cdot}95}$ and C_2 and C_4 are cyclopropane-like. Now, since $J_{C_3\text{-}H} = 207{\cdot}8$ Hz and the total s-character around C_3 must be unity this would leave 10·8% s-character for the C_3 orbital bonding to C_1, or $sp^{8\ 26}$. Since the "direct" measurement gave 17·1% s-character or $sp^{4{\cdot}85}$ one is led to question the errors involved in summing the s-characters around a given carbon atom and also the validity of coupling constant-hybridization equations, particularly for small ring systems. An inspection of the literature shows that errors of the size obtained here are often observed when adding together the s-characters of each orbital around a carbon atom obtained from coupling constant-hybridization equations. For example† the terminal carbon of phenylacetylene shows a total s-character of 1·07, the methyl carbon of 1-phenyl-1-propyne shows 1·04 and the tertiary carbon of methylcyclopropane shows 0·93. Thus it is clear that estimates of the s-character of a particular orbital based on the s-character of the other orbitals around a carbon atom obtained from coupling constants must be done with due caution.[21]

There are a nymber of suggestions that the coupling-constant hybridization equations may break down for highly strained small ring systems. For most saturated systems the orbital and dipolar terms are small and for unstrained systems the contact term is large and positive and predominates.[25] However Schulman and Newton[22d,26] have recently refined their original INDO calculations[12] and have shown that for bicyclobutane, and benzvalene the 1,3-bond is abnormal in that the contact term is not large and positive but small and negative as are the dipolar and orbital terms. Thus the value calculated for the C_1–C_3 coupling constant is $-5{\cdot}6$ Hz for bicyclobutane and $-12{\cdot}2$ Hz for benzvalene. The calculated values for the C_1–C_2 bonds in these compounds are more normal and are $+21{\cdot}4$ Hz and $+23{\cdot}2$ Hz respectively. The negative value calculated for the C_1–C_3 coupling constant obviously cannot be accommodated by the simple equation[22c] which relates the coupling constant directly to the hybridization but the equation must include an additional, negative term as suggested by Newton and Schulman.[22d,26] Other calculations, however, predict a positive value for this coupling constant. The maximum overlap method[13,27] comes very close, in absolute magnitude, to the observed values for both $J_{C_1-C_3}$ and $J_{C_2-C_3}$. For bicyclobutane this method predicts 17·8 and 19·4 Hz respectively. The simplest calculations of hybridization,[6a] combined with the equation presented above relating J_{CC} to hybridization predicts a C_1–C_2 coupling constant of 20 and 15 Hz for the sp^2 and sp models respectively and a C_1–C_3 coupling constant of 27 and 15 Hz for these respective bicyclobutane models.

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*See Ref. 21 for a discussion of the C_1–C_2 bonds in bicyclobutane itself.

†See Ref. 1 footnote 23 for a discussion and additional references.

The foregoing discussion points up the necessity of determining the sign of the C_1–C_3 coupling constant. Work is now in progress toward this end.

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