The 6-X-Benzonorbornyl System: A New Motional Dynamics Probe

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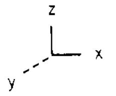
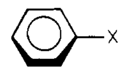
Abstract: ^{13}C NMR spin-lattice relaxation data have been used to probe solution molecular dynamics for a series of 6-X-benzonorbornene derivatives (X = NH_2, CH_3, NH_3^+). The benzonorbornyl system was chosen specifically because it possesses structural features that make it a powerful probe molecule: rigidity, many nonequivalent C–H vectors, and overall low symmetry, but high local "phenyl" symmetry at the X group. Preliminary data obtained by using this probe are given, showing its application to the analysis of solvent-restricted rotation of NH_3^+ in several solvent/anion systems. Overall molecular motion was also studied. The NMR relaxation data were analyzed by using a SIMPLEX optimizing interactive computer program based on the Woessner model for anisotropic motional diffusion. For the methyl and amine derivatives two factors were found to be important in determining overall motional anisotropy: (a) the inertial properties of the molecule and (b) the relative disturbance of neighboring solvent molecules arising from molecular rotation. Protonation of the amine resulted in decreased motion of the probe molecule as a whole as well as a considerable increase in the rate of internal spinning of the NH_3^+ group compared with NH_2 rotation/inversion, as determined from ^{15}N T_1^{DD} measurements.

^{13}C spin-lattice relaxation times have been extensively used to study molecular motion.[2-9] A number of the studies to date have been concerned with motion in substituted benzenes (**1**),[2,3,5] where





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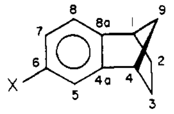
it has been shown that the preferred in-plane rotation occurs about the molecular axis coincident with the phenyl ring–substituent bond. This effect was found to be magnified when the substituent was increased in size or when it was associated.[3]

The usual approach applied in these studies was to determine the ratio of the T_1 value of either the ortho or meta carbons to that of the para carbon. A ratio of $T_{1(o,m)}/T_{1(p)}$ significantly greater than unity was assumed to indicate preferred motion about the in-plane C_2 axis (x). Subsequently, Bauer et al.[10] and Vold[11] showed that this simple approach was only valid when the substituent was large; otherwise, preferred rotation around the (z) axis perpendicular to the plane of the ring could lead to incorrect conclusions.

The major difficulty associated with motional studies in substituted benzenes is that all of the ring C–H vectors are coplanar and thus ^{13}C spin-lattice relaxation data can differentiate only two of the three rotational diffusion coefficients. In spite of this, these systems do have a number of important features (such as symmetry, rigidity, essentially equal C–H bond lengths, and off-axis C–H vectors which are close to the magic angle of 54.7°) which combine to make substituted benzenes a very useful motional probe. However, a much superior system would be one which possessed the above features but did not have the disadvantages of planar systems. In this preliminary paper we propose the 6-X-benzonorbornyl system (**2**) as a new molecular probe for motional dynamic studies.



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This system combines the advantages of the phenyl ring system with the rigid three-dimensionality of the norbornyl system: the overall symmetry of the molecule is low, giving 11 nonequivalent one bond C–H vectors. However, there is high local ("phenyl") symmetry at the X group which permits the investigation of changes in internal motional dynamics of this group. The effects of overall anisotropic tumbling of the molecule as a function of solvent (and counterion for charged substituents) can also be studied. The system is also ideally sized, i.e. not too large, so that it is possible to induce anisotropic motion when X is a group affected by intermolecular interactions or electrostatic effects.

All of the above features are critical for the evaluation of anisotropic molecular reorientation and the use of this phenomenon to probe solution effects such as ion pairing and hydrogen bonding. In this paper, as well as presenting the 6-X-benzonorbornyl system as a motional dynamics probe, we also show a first application to the study of CH_3 and NH_3^+ group rotation. First, however, a brief description of some relevant theoretical background is given below.

In general, when molecular motion is not isotropic or is outside the range of extreme narrowing or when the decay of the autocorrelation function is nonexponential, the equations relating spin-lattice relaxation times and terms related to molecular motion are complex.[12-14] For simple anisotropic or internal motional

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dynamics the Woessner[15] formulation has found much application. For the case of a *rigid* molecule tumbling anisotropically in solution, the T_1 value for a given carbon can be expressed as a function of three diffusion constants and three direction cosines (eq 1).

$$1/T_1^{DD} = f(R_1, R_2, R_3, l, m, n) \qquad (1)$$

Here R_1, R_2, and R_3 are the diffusion constants describing rotational motion about three mutually perpendicular axes. As an initial approximation it is normally assumed that the diffusion axis system is coincident with the inertial axis system (i.e., the axis system in which the inertial tensor is diagonalized).[6,9] The direction cosines l, m, and n represent the angles subtended by each C–H vector with respect to the three principal axes. These terms impart a geometrical dependence to the T_1 values. Further details relating to the exact functional form of eq 1 are given in the Appendix.

Recently it has been pointed out that this type of analysis must be carried out with a careful regard for the appropriate limitations of the method.[16] If this is done, then it is possible to semiquantitatively determine motional anisotropy and to interpret this motion in terms of the inertial or interacting properties of the system under investigation. In this type of study it is particularly important that T_1 values are measured carefully and are determined to the highest possible accuracy. It is also imperative that the iteration procedure used is suited to the determination of an optimum point in a relatively shallow response surface. We have found our SIMPLEX approach most applicable in this regard.

It should also be noted that the application of the Woessner equation presumes the presence of only isolated ^{13}C–H dipolar autocorrelation terms. It is possible that cross-correlation effects may make some contribution to the relaxation of the three methylene groups in **2**. However, for the proton-decoupled ^{13}C data discussed here such effects are of second order and are expected to contribute errors of less than 5%. Several groups[11,17] have examined in detail the use of multiple relaxation interactions for the determination of diffusion tensors.

Experimental Section

The 6-X-benzonorbornene derivatives, with X = CH_3 and NH_2 (or NH_3^+) were synthesized by using adapted procedures from the literature.[18-23] For the methyl derivative, 0.1 mol (15.1 g) of 2-amino-5-methylbenzoic acid in 80 mL of THF was added dropwise over 5 h to a refluxing solution of 0.2 mol (13.2 g) of cyclopentadiene and 0.12 mol (12.3 g) of isoamyl nitrite in 300 mL of dichloromethane. The mixture was refluxed overnight, the solvent evaporated, and the residue extracted with 400 mL of heptane, passed through a short column of alumina, concentrated, and distilled. A 7.2-g sample of 6-methylbenzonorbornadiene (114 °C, 25mmHg) was obtained. 6-Methylbenzonorbornene was obtained quantitatively by hydrogenation in ethyl acetate with 10% Pd/C. For an increase in the sensitivity of the ^{15}N NMR experiment, the amine and its salts were isotopically enriched in ^{15}N as follows: Benzonorbornadiene was reduced with H_2/Pd–C in ethyl acetate at 2–3 atmospheric pressure.[19] The resultant benzonorbornene was nitrated with a $HNO_3/H_2SO_4/H_2O$ mixture (containing 15% ^{15}N-labeled HNO_3) in nitromethane at 0 °C.[20] The product was essentially the 6-NO_2 isomer containing few percent of the 5-NO_2 isomer. Separation was achieved by silica gel liquid chromatography. The 6-NO_2-benzonorbornene was reduced to the amine by using Zn dust in ethanol and $CaCl_2$.[21]

Table I. Chemical Shifts of Benzonorbornene and Some 6-Substituted Derivatives[a]

X	1	2	3	4	4a	5
H	43.8	27.1			148.1	120.4
NO_2	43.8	26.4	26.4	43.8	149.6	115.9
NH_2	43.0	27.8	27.3	44.0	149.7	108.8
NH_3[b]	43.4	26.4	26.4	43.8	151.0[c]	115.0
CH_3	43.9	27.5[c]	27.4[c]	43.5	148.5	121.6

X	6	7	8	8a	9	CH_3
H	125.5				49.4	
NO_2	146.6	120.8	122.0	155.9	49.4	
NH_2	144.3	111.7	120.9	138.7	49.1	
NH_3[b]	126.1	119.7	121.7	150.2[c]	49.4	
CH_3	134.9	126.0	120.3	145.3	49.5	21.64

[a] In parts per million from Me_4Si, 0.1 M solutions in $C_2D_2Cl_4$. [b] Trifluoroacetate salt. [c] Assignment may be reversed.

^{13}C and ^{15}N spectra were obtained on two superconducting solenoid-based spectrometers, at 37.7 and 27.4 MHz, respectively. The ^{13}C resonances of the benzonorbornene derivatives were assigned by using ^{13}C additivity rules and comparisons with related compounds, shift reagents, paramagnetic relaxation (PAR) reagents, and decoupling techniques. ^{13}C and ^{15}N T_1 values were determined by using the FIRFT[24] technique with delay times of 3–5 s between the —(180–τ–90)—sequences. A total of 10–15 τ values ranging from ~0.01 s to 5T_1 s were used to obtain a given T_1 data set. The T_1 values given in Table II were obtained by using a three parameter exponential fit[24] and are estimated to be accurate to ±5%. Careful NOE measurements (using the gated decoupling technique with a delay of ~10T_1 between pulses) showed full enhancements for the protonated ring and methylene carbons, confirming the dominance of dipolar relaxation at these sites. A full NOE was not obtained for the methyl group in 6-methylbenzonorbornene, presumably because of a contribution from the spin–rotation relaxation mechanism. Within experimental error the maximum expected ^{15}N NOE of –4.93 was obtained for the amine; however, smaller enhancements were noted in the protonated derivatives. Again, this most likely reflects spin–rotation contributions, as the NH_3 group undergoes faster internal motion than does NH_2.

The calculations of the diffusion constants was carried out by using a FORTRAN 5 (Data General) program developed in our laboratories for an Eclipse S/130 minicomputer. For input, the program requires molecular coordinates in an arbitrary reference frame, the experimentally determined dipole–dipole T_1 values (T_1^{DD}) for three or more carbon atoms in the molecule, and initial guesses for the diffusion constants. The heavy-atom coordinates were obtained from a rudimentary molecular mechanics calculation. The hydrogen atom positions were calculated by assuming standard values for the carbon–hydrogen bond lengths[25] (1.09 Å for the aliphatic protons and 1.08 Å for the aromatic protons). Small deviations from these values are not expected to change the calculated diffusion constants, within the error limits specified in Table III. ^{15}N–^{1}H bond lengths were set at 1.01 Å.[25] The program iteratively determines a set of diffusion constants which minimizes the sum of the squares of the deviations of the calculated and observed T_1 values. Both nonlinear least squares and SIMPLEX techniques were used for iteration, with the latter method being found more satisfactory.

Results and Discussion

^{13}C chemical shift data for some of the substituted derivatives of (**2**) are given in Table I. ^{13}C and ^{15}N T_1^{DD} data are given in Table II. It is apparent from the ^{13}C dipolar T_1 data for the methyl derivative that some degree of anisotropy is present in the motion. This can be seen, for example, in the nonequivalence of the T_1 values for the ring carbon positions 5, 7, and 8; the T_1 of carbon 7 is significantly shorter than those for carbons 5 and 8.

A qualitative examination of the dipolar T_1 data for the amine and derivatives reveals a large decrease in overall motion upon protonation with trifluorosulfonic or trifluoroacetic acid. This is indicative of strong solvation or ion pairing. Interestingly, the data also indicate that protonation by acetic acid does not restrict the overall motion nearly as much. In a recent ^{15}N and ^{13}C relaxation study[5] of aniline and aminobenzoic acid anions, neutral

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Table II. 37.71-MHz ^{13}C T_1^{DD} Data for 0.5 M Derivatives and Salts[a] of the 6-X-Benzonorbornyl System in $CDCl_2CDCl_2$ at 21 °C

X	counterion	C-1	C-2	C-3	C-4	C-5	C-7	C-8	C-9	CH_3	$NH_{2,3}$[b]
NH_2		1.41	0.57	0.59	1.55	1.71	1.35	1.58	0.58		6.3 (−4.82)[c]
NH_3^+	CH_3COO^-	1.15	0.48	0.46	1.24	1.42	1.16	1.25	0.48		4.3 (−4.54)
NH_3^+	CF_3COO^-	0.40	0.13	0.13	0.35	0.43	0.37	0.37	0.13		1.1 (−3.88)
NH_3^+	$CF_3SO_3^-$	0.40	0.16	0.16	0.35	0.44	0.37	0.38	0.15		2.3 (−3.31)
CH_3		2.10	0.87	0.87	2.23	2.42	1.89	2.22	0.80	8.0 (1, 19)[c]	

[a] The salts were prepared by adding a 10% excess of the appropriate acid to the amine. [b] ^{15}N $T_1{}^{DD}{}_s$ and NOEFs at 27.36 MHz. [c] NOEF values are given in parentheses for CH_3, NH_2 and NH_3^+. The theoretical maximum NOEF values were observed for all other protonated carbons.

species, and cations, the activation energy for overall molecular reorientation and for the composite internal overall motion of the $-NH_2$ and $-NH_3^+$ groups was estimated.[5] It was found that although the $-NH_3^+$ groups spins faster than $-NH_2$, its rotation was quite restricted compared to $-CH_3$ rotation in analogous systems. However, diprotonation of *m*-aminobenzoic acid with the nonnucleophilic superacid CF_3SO_6H gave T_1 data indicative of extremely rapid $-NH_3^+$ group internal rotation relative to overall reorientation.

It is apparent from the current study that the NH_3^+ group of **2** undergoes rapid spinning in the presence of the $CF_3SO_3^-$ counterion. This can be seen, for example, by noting that the carbon T_1 data sets for the trifluoroacetate and trifluorosulfonate salts are very similar, but the nitrogen dipolar T_1 values are more than a factor of 2 different. The larger T_1^{DD} value for the NH_3^+ group in the trifluorosulfonate salt indicates faster NH_3^+ rotational motion.

The ^{15}N NOE values in Table II confirm these general conclusions. The full enhancement (theoretical −4.93, observed −4.8) noted for the amine NH_2 group decreases upon protonation in the order $CH_3COO^- > CF_3COO^- > CF_3SO_3^-$. The smallest NOE (−3.31) for the trifluoroacetate salt indicate a reduced contribution from the dipolar relaxation mechanism at the nitrogen site, presumably reflecting a larger spin–rotation contribution due to increased NH_3^+ spinning.

Quantitative Assessments

Diffusion constants for these systems were determined by using our anisotropic rotor computer program. Good fits of the calculated to the observed T_1 values were obtained. (For calculations involving the simultaneous fitting of eight T_1 values, the maximum variation between calculated and observed values was less than 10%.) For example, the calculated and observed dipolar T_1 values (in s) for the 6-methyl derivative were as follows: C1 (2.06, 2.22), C2 (0.87, 0.85), C3 (0.87, 0.86), C4 (2.23, 2.18), C5 (2.42, 2.28), C7 (1.88, 1.90), C8 (2.22, 2.25), C9 (0.80, 0.80).

An analysis of the calculated diffusion constants in Table III reveals several important features not discernible from the qualitative analysis given above. It is convenient to begin the discussion with the data for the 6-methyl derivative, as in this case the assumption of coincident inertial and diffusion frames is most likely to be valid. (This compound contains neither any polar or polarizable groups nor any disproportionately heavy atoms.) The approximate orientation of the principal inertial axis system is shown in Table III.

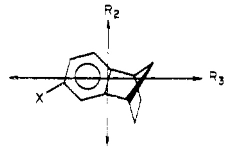
The rotational rates about the fastest (R_1) and slowest (R_2) axes are only a factor of 3 different. That the fastest rotation occurs about the axis perpendicular to the benzene ring serves to clearly illustrate the necessity of designing a motional probe having linearly independent C–H vectors in all three spatial dimensions.

The rotation rates about the R_1 and R_3 axes are similar. Relatively rapid rotation about the latter axis might be expected because of its associated lower moment of inertia. However, the rotational process in the solution phase involves not only the inertial properties of the molecule itself but also very importantly the "frictional" properties[26] of surrounding molecules and the solvent. The volume swept out by the R_1 rotation apparently reduces the disruption to the solvent compared with rotation about the other axes. Axelson and Holloway[8] have drawn similar conclusions for several planar or nearly planar systems.

Table III. Calculated Diffusion Constants[a,b] for 6-X-Benzonorbornenes

	CH_3	NH_3^+ $CH_3CO_2^-$	NH_3^+ $CF_3CO_2^-$	NH_3^+ $CF_3SO_3^-$	NH_2
R_1	10.9	8.0	3.1	4.7	8.4
R_2	3.3	1.8	0.4	0.3	2.1
R_3	7.0	3.1	0.8	0.6	4.4

[a] × 10^9 rad/s; estimated error ±20–30%. [b] The orientation of the principal axis system is shown below



R_1 is perpendicular to the plane of the benzene ring

^{13}C T_1 values were determined at five temperatures in the range 6–57 °C for the 6-methyl derivative. From the observed increase in T_1 values with temperature an activation energy for overall molecular reorientation of 3.0 kcal/mol was calculated. It is interesting to note that over the temperature range studied (~50 °C) no significant change in the motional anisotropy was detected. Although the calculated diffusion constants did increase as expected with temperature, the ratio R_1:R_2:R_3 remained approximately constant.

The barrier to methyl group rotation in toluenes is known to be extremely small. This is indeed confirmed from our data for the 6-methylbenzonorbornene derivative. On the basis of the diffusion constants in Table III, the T_1^{DD} value for a fixed (nonspinning) methyl group is predicted to be 0.6 s. The much longer observed value of 8 s shows that the methyl group is spinning very rapidly, compared with overall molecular reorientation. It is important to note here that the methyl carbon T_1 value of 0.6 s was derived by using the model of a *fixed* group attached to a framework undergoing *anisotropic* motion. We are currently developing the theory for the case of a *spinning* group attached to a framework undergoing *anisotropic* motion. This will allow us to calculate an accurate value for methyl group rotation using the observed dipolar T_1 value. Previous estimates of methyl group rotational rates have been based on models which assume overall isotropic motion or axially symmetric anisotropic motion.

Summary

This first study of system **2** demonstrates that the 6-X-benzonorbornyl molecular framework is an excellent probe for motional studies. Several features are currently being added to our computer program to allow more accurate results to be obtained. These features include the option of iteratively determining the diffusion axis (i.e., relaxing the assumption that it is coincident with the inertial axis) and the ability to calculate internal motional rates in the presence of overall anisotropic molecular motion.

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Appendix

Molecular tumbling in a magnetic field brings about a modulation of the $^{13}C–^1H$ dipole–dipole interaction, the frequency distribution of which is described by the spectral density function $J(\omega)$. The dipolar spin–lattice relaxation time (T_1^{DD}) for a single $^{13}C–^1H$ vector is linked to the spectral density function via eq A1.

$$\frac{1}{T_1^{DD}} = \left(\frac{1}{20}\right)\frac{\gamma_H^2\gamma_C^2\hbar^2}{r_{C-H}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (A1)$$

Here the γ terms are the magnetogyric ratios, $\hbar$ is Planck's constant divided by 2π, r_{C-H} is the carbon–hydrogen internuclear distance, and the ω terms are the appropriate Larmor frequencies (in rad/s).

Woessner[15] originally derived expressions for the spectral density function in terms of both geometrical and motional parameters for a rigid molecule undergoing anisotropic motion. However, because of a singularity in the Woessner formalism for the case when motion is isotropic, we have used the transformed equations of Bleich et al.[6]

$$J(\omega_i) = \frac{12Rd(\omega_i^2 + 36L^2)}{(1/\tau_+^2 + \omega_i^2)(1/\tau_-^2 + \omega_i^2)} - \frac{12e(\omega_i^2 - 36L^2)}{(1/\tau_+^2 + \omega_i^2)(1/\tau_-^2 + \omega_i^2)} + \frac{C_1\tau_1}{(1 + \omega_i^2\tau_1^2)} + \frac{C_2\tau_2}{(1 + \omega_i^2\tau_2^2)} + \frac{C_3\tau_3}{(1 + \omega_i^2\tau_3^2)} \quad (A2)$$

where $R = {}^1/_3(R_1 + R_2 + R_3)$, $L^2 = {}^1/_3(R_1R_2 + R_1R_3 + R_2R_3)$, $1/\tau_+ = 6[R + (R^2 - L^2)^{1/2}]$, $1/\tau_- = 6[R - (R^2 - L^2)^{1/2}]$, $1/\tau_1 = 4R_1 + R_2 + R_3$, $1/\tau_2 = R_1 + 4R_2 + R_3$, $1/\tau_3 = R_1 + R_2 + 4R_3$, $d = {}^1/_2[3(l^4 + m^4 + n^4) - 1]$, $e = {}^1/_6\{\delta_1[(3l^4 + 6m^2n^2) - 1] + \delta_2[(3m^4 + 6l^2n^2) - 1] + \delta_3[(3n^4 + 6l^2m^2) - 1]\}$, $C_1 = 6m^2n^2$, $C_2 = 6l^2n^2$, $C_3 = 6l^2m^2$, $\delta_1 = R_1 - R$, $\delta_2 = R_2 - R$, and $\delta_3 = R_3 - R$.

In these equations *l*, *m*, and *n* are the direction cosines of the C–H vector with respect to the principal axes. R_1, R_2, and R_3 are the rotational diffusion coefficients about these axes.

In our program the calculated T_1^{DD} value was obtained by summing the contribution to eq A1 from every C–H interaction in the molecule.

Registry No. **2** (X = H), 4486-29-7; **2** ($X = NO_2$), 4228-30-2; **2** ($X = NH_2$), 35391-92-5; **2** ($X = NH_2$) trifluoroacetate salt, 79664-54-3; **2** ($X = CH_3$), 16499-70-0.

Propagation of a Redox Reaction through a Quinoid Polymer Film on an Electrode

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Abstract: Quinoid polymers were prepared by reacting acryloyl or methacryloyl chloride with dopamine. The polymers were coated onto glassy carbon electrodes. Using aqueous, pH 7 solutions and cyclic voltammetry, it is shown that for polymer layers with less than one equivalent monolayer of dopamine (<0.6 nmol cm^{-2}), most units are electroactive and can be converted to dopaquinone units. In thicker films only this inner monolayer is electroactive on the time scale of cyclic voltammetry. This behavior is compared with that for *N*-acetyldopamine as a soluble analogue. It is shown that the oxidation of the bulk polymer layer can be accelerated if compounds with reversible one-electron couples like bis(hydroxymethyl)ferrocene or *N,N,N′,N′*-tetramethylphenylenediamine are present at millimolar levels in the solution. It is suggested that these couples mediate the oxidation past the inner layer. Using mixed organic/aqueous solvents also serves to propagate the oxidation through the bulk layer. In this case, the mixed solvents swell the layer, making polymer chain motion more rapid so that the oxidation rate goes up.

There is currently considerable interest in the properties of electrodes which have molecular surfaces.[1] One attractive method for producing such electrodes is to coat the surface of a conductor with an ultrathin, 10–1000 Å, layer of polymer.[2-15] If the polymer contains electroactive groups or can sequester electroactive species from solution, the electrode acquires some very unusual properties.

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