Quadrupole Coupling Parameters of Olefinic Deuterons: ^{2}H MAS NMR Spectroscopy of Photochromic Spiropyran and Merocyanines

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Three molecules with olefinic deuterons were obtained through H−D exchange of the C3 proton on the central bridging double bond of spiropyran photomerocyanines with deuterium oxide solution. Quadrupole coupling parameters were determined by simulation of the spinning sideband manifolds in spectra obtained using solid-state deuterium MAS NMR spectroscopy. The C3-deuterated forms of the closed-ring spiropyran 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2-indoline] (3D-6-nitro-BIPS) and the open-ring merocyanines 1′,3′,3′-trimethyl-6,8-dinitrospiro[2*H*-1-benzopyran-2,2-indoline] (3D-6,8-dinitro-BIPS) and 1′,3′,3′-trimethyl-6-nitro-8-bromospiro[2*H*-1-benzopyran-2,2-indoline] (3D-6-nitro-8-bromo-BIPS) had the same quadrupole coupling constants (QCCs) of 176 ± 4 kHz. This value, the second reported for an olefinic deuteron, is slightly less than the QCCs known for rigid aromatic deuterons (180−185 kHz). The asymmetry parameters (η) for the latter two molecules (open rings) were 0.10 ± 0.03, slightly larger than that observed for the closed-ring 3D-6-nitro-BIPS (0.00 ± 0.03). This slight asymmetry of the electric field gradient around deuterium in the merocyanines is attributed to a small deviation of the C−D bond from perfect axial symmetry, probably resulting from a through-space interaction between C3−D and C9−O.

1. Introduction

^{2}H NMR spectra of solids provide detailed information on the local (electronic) environment of the deuteron. The orientation-dependent line shape has been widely used to determine quadrupole coupling parameters and reveal molecular structure and dynamics in many types of solids and liquid crystals. Typical quadrupole coupling parameters for deuterons bonded to carbon have been reported for methyl, methylene, and aromatic functional groups.[1−4] However, olefinic deuteron studies are practically nonexistent. This is attributed to the very long longitudinal relaxation times (T_1) associated with these deuterons and to the difficulty of synthesizing molecules selectively deuterated in olefinic positions.

Recent studies of photochromic spiropyrans and merocyanines[5−8] have provided evidence of a surprisingly facile H−D exchange reaction for one of the bridging methine protons in solution. This reaction presents the exceptional opportunity of obtaining organic molecules, solid at room temperature, with olefinic deuterons. Thus, the principal aim of this work was to prepare these selectively deuterated molecules and perform ^{2}H NMR studies to obtain quadrupole coupling parameters for olefinic deuterons in a solid. A secondary objective was to investigate the local electronic environment of these labile hydrogen sites.

1.1. Quadrupole Coupling Parameters and ^{2}H MAS NMR Spectroscopy. Deuterium, being a quadrupolar nucleus (I = 1), has a nonspherically symmetric charge distribution in the nucleus, giving rise to a nuclear electric quadrupole moment (Q). "Coupling" of Q to the electric field gradient (eq) surrounding the nucleus gives rise to the quadrupolar interaction, which is mathematically described by a tensor. The directional dependence of this interaction (tensor) causes it to be highly sensitive to the electronic structure immediately around the nucleus. Valence electrons of the neighboring nuclei highly shield the nuclear part of this interaction (Q). The overlap charge density of the X−D bond determines the value of eq at the deuteron.[4]

Orientationally dependent NMR line shapes of quadrupolar nuclei in solids are used to quantify the quadrupolar interaction. Because the trace of the electric field gradient tensor in its principal axis system (x, y, z) is zero, only two parameters are required to describe it. By convention, the z axis has the largest principal component of the electric field gradient (q_{zz}) and lies parallel to the X−D bond. Spectral line shapes depend on the orientation of the principal axis system with respect to the laboratory fixed axes. The size, or strength, of the quadrupolar interaction is given by the quadrupole coupling constant (QCC)

$$\mathrm{QCC} = e^{2}q_{zz}Q/h \qquad (1)$$

Its magnitude depends on the amount of charge (electronic *and* nuclear) that lies along the z axis.[2] The shape of the interaction (electric field gradient tensor) is described by the asymmetry parameter (η), which ranges from 0 to 1

$$\eta = (q_{xx} - q_{yy})/q_{zz} \qquad (2)$$

Trends in QCC and η can be rationalized in terms of nuclear charge, bond distance (X−D), and local symmetry.[1] In general, a shorter bond gives a larger QCC because the nuclear

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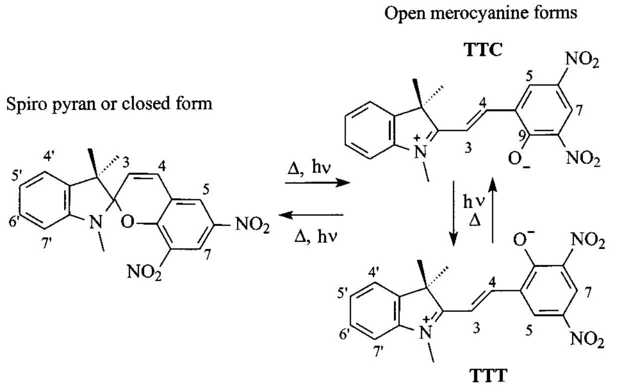
SCHEME 1: Photochemical and Thermal Isomerization Pathways for Exchange between the SP and MC Forms of 6,8-Dinitro-BIPS



contribution is larger. η is zero if the symmetry of the electric field gradient at the deuteron is C_3 or higher.

Typical experimental values reported[2-4] for ^{2}H QCCs in *rigid* C−D bonds show a dependence on the bond hybridization of the carbon nucleus: for sp^3 sites, QCC = 170−175 kHz; for sp^2 sites, 180−185 kHz; and for sp sites, >200 kHz. Molecular motion, or more precisely movement of the C−D bond with respect to the external magnetic field, will cause a reduction in these values. The inevitably fast rotation of methyl groups (around the pseudo-3-fold spinning axis) in organic solids at room temperature, gives QCCs in the 45−55-kHz range (with $\eta = 0$).[1]

Application of the magic angle spinning (MAS) technique to solid-state ^{2}H NMR studies, first demonstrated in 1979 by Ackerman et al.,[9] offers considerable advantages over static measurements.[10-12] MAS causes line narrowing because it removes first-order quadrupolar broadening from the spectra. It provides greater sensitivity and finer resolution of chemical types. MAS can also decrease the lengthy longitudinal relaxation times (T_1) often encountered in solids by enhancing spectral spin diffusion. Under MAS, the ^{2}H spectrum is broken up into spinning sidebands, because the quadrupolar interaction is refocused by rotation. The manifold of these spinning sidebands can be simulated with high precision to yield accurate quadrupole parameters[10,12] and the isotropic shift. MAS was employed here because the deuteron line shapes are expected to be very broad (low S/N) and the recycle time for signal accumulation is expected to be long (large T_1).

1.2. Spiropyrans and Merocyanines. Spiropyrans (SPs) are interesting molecules because they undergo light-activated photoisomerization reactions that can be applied to photoswitching processes. The finer points of the SP reaction mechanism have remained elusive for a long time. Recently, the thermal and photochemical isomerization pathways (Scheme 1) for 6,8-dinitro-BIPS (1′,3′,3′-trimethyl-6,8-dinitrospiro[2*H*-1-benzopyran-2,2-indoline]) and its merocyanine (MC) forms were established.[5] A similar reaction scheme was proposed for 6-nitro-8-bromo-BIPS (1′,3′,3′-trimethyl-6-nitro-8-bromospiro[2*H*-1-benzopyran-2,2-indoline]).[7] The MC forms of these two SPs exist predominantly as the TTC (trans−trans−cis) isomer in all of the solutions investigated.[5-8]

Several physical−chemical observations have provided evidence that the open merocyanine forms are zwitterions with peculiar properties: (a) the C3−H bond is labile,[5] (b) C3−H is magnetically deshielded (^{1}H shift = 8.8 ppm) compared to a typical olefinic proton,[5] (c) ^{13}C shifts reveal a polarized C3−C4 double bond with C3 δ^- and C4 δ^+ charged,[6] (d) H−D exchange of the C3−H causes a large ^{13}C deuterium isotope shift at C9,[6] and (e) the ^{13}C shift of C9 (182 ppm) is 25 ppm upfield from a typical carbonyl carbon and 25 ppm downfield from a typical alcohol carbon.[6] These findings indicate some type of interaction between C3−H and C9−O. In this work, an alternative method for characterizing these peculiar MCs was made through determination of quadrupole coupling parameters for the C3−D forms.

2. Experimental Section

2.1. Sample Preparation. 6-Nitro-BIPS was purchased from Aldrich. 6,8-Dinitro-BIPS and 6-nitro-8-bromo-BIPS were prepared by standard synthetic routes.[13] The preparation of the C3-deuterated forms was described previously.[5-7] It involves exchange from deuterium oxide layered over the MC forms dissolved in chloroform or evaporation of the solvent from a CH_3OD solution. $NaDCO_3$ was prepared by saturating a solution of $NaHCO_3$ in hot D_2O and then precipitating the powdered product by cooling.

Isotopic purities were established using solution-state ^{1}H NMR spectroscopy. 6,8-Dinitro-BIPS was 100% deuterated, whereas 6-nitro-8-bromo-BIPS and 6-nitro-BIPS were ca. 80% deuterated.

2.2. ^{2}H MAS NMR Spectroscopy. Spectra were obtained at 46.072 MHz on a Bruker ASX-300 spectrometer using powdered samples (ca. 200 mg) contained in 7-mm zirconia rotors spinning at 5 kHz. Spectra, consisting of 200−2000 scans, were collected at room temperature using the following parameters: an effective 90° rf pulse for ^{2}H of 2.9 μs [equal to $(I + {}^1/_2)^{-1}$ or $^2/_3$ the value for liquid D_2O], a 200-μs preacquisition delay (one rotor revolution), a 400-kHz spectral window, 24K time domain points, a 29-ms acquisition time, and a long recycle delay (90 s for $NaDCO_3$, 240 s otherwise). Longitudinal relaxation times for the molecules studied here are expected to be greater than 1 min. Chemical shifts were referenced to heavy water (D_2O) at 4.8 ppm. A Lorentzian line broadening of 20 Hz was applied before Fourier transformation.

The magic angle was finely adjusted by maximizing the FID length of $NaDCO_3$ in GS mode. This procedure gave a more accurate setting than can be obtained with KBr and ^{79}Br NMR spectroscopy. The symmetry of the receiver phase glitch (impedance match between probe and transmitter) was carefully set to give minimum asymmetry (<5%) in the height of the spectral “horns” (Pake doublet envelope) of $NaDCO_3$ by moving the probe tuning slightly (ca. 50 kHz to lower frequency) away from its optimum value.

Spectra were simulated with the Q-1 MAS All routine of WINFIT 96 (Bruker, version 960624). This simulates the MAS sideband pattern for the first-order quadrupolar interaction of all transitions. Peaks with 40% Gaussian character having line widths of 60 and 140 Hz were used to simulate the $NaDCO_3$ and chromophore spectra, respectively.

3. Results and Discussion

The ^{2}H MAS NMR spectrum of $NaDCO_3$ is shown at the bottom of Figure 1. This is an ideal molecule for setting the spectrometer acquisition conditions to observe a deuterium site with a large QCC. The spinning sideband manifold covers a large frequency range (ca. 240 kHz). The simulated spectrum (Figure 1, top) provides a good fit of the experimental data, with the largest deviation being noted at the extremes. The lower intensity of the outermost spinning sidebands in the experimental spectrum compared to the simulated one is attributed to the reduced efficiency of the excitation profile at frequencies distant

TABLE 1: Isotropic ^{2}H NMR Chemical Shifts (δ_{iso}) and Quadrupole Coupling Parameters (QCC, η) Determined Experimentally for Selected Molecules

sample	δ_{iso}[a] (ppm)	QCC[a] (kHz)	η[a]	method[b]	reference
$NaDCO_3$	12 (5)	149 (10)	0.182 (5)	MAS	14
$NaDCO_3$	13.5 (5)	149 (2)	0.20 (3)	MAS	this work
3D-6-nitro-BIPS	4.7 (4)	174 (2)	0.00 (3)	MAS	this work
3D-6,8-dinitro-BIPS	6.9 (5)	178 (2)	0.10 (3)	MAS	this work
3D-6-nitro-8-bromo-BIPS	7.5 (5)	177 (2)	0.10 (3)	MAS	this work
2D-1,3-diphenyl-1-hydroxypropene-3-one	nd[c]	188.5 (1)	0.118 (2)	ADLF	15
benzene-D_6 (at 87 K)	nd[c]	183 (1)	0.040 (5)	QE	16
1,4-dibromobenzene-D_4	nd[c]	176 (5)	0.09 (2)	MAS	12
$HDC{=}O$	nd[c]	170 (2)	<0.15	μwave	3
α-$(COOH)_2 \cdot 2D_2O$ (at 203 K)	8.2	230 (2), 219 (2)	0.062 (6), 0.16 (3)	QE	16

[a] Error margin (±) of last decimal given in parentheses. [b] MAS = ^{2}H MAS NMR spectroscopy at 298 K, ADLF = nuclear quadrupole resonance by level crossing (at 77 K), QE = quadrupole echo ^{2}H (static) NMR spectroscopy at low temperature of the solid state, μwave = microwave spectroscopy of the gaseous state. [c] nd = not determined.

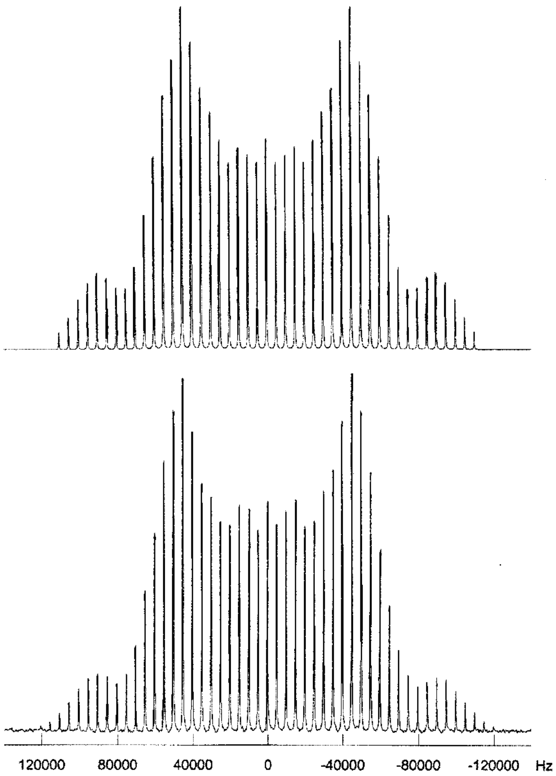


Figure 1. ^{2}H MAS NMR spectra of $NaDCO_3$: experimental spectrum (bottom), simulated spectrum with QCC = 149 kHz and η = 0.20 (top).

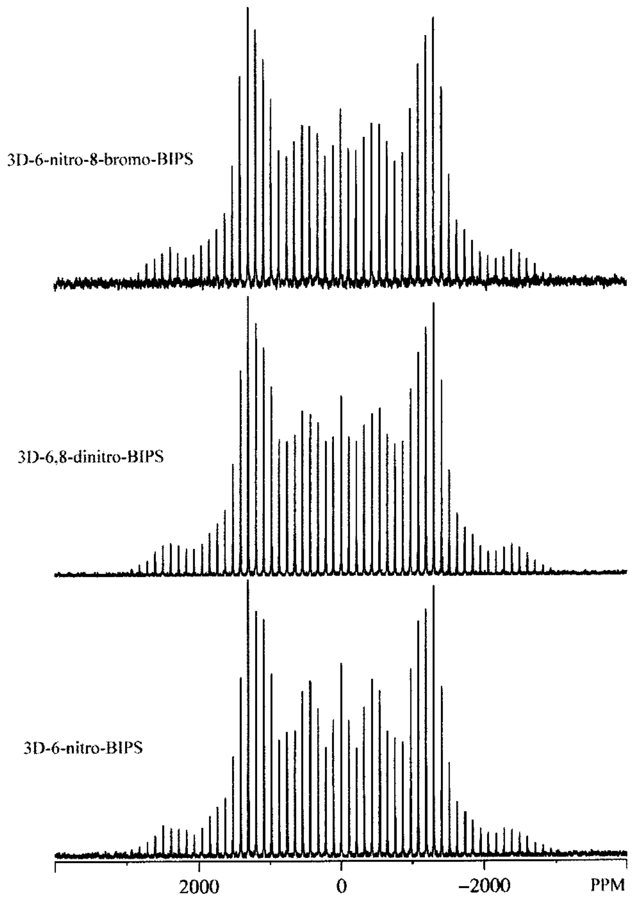


Figure 2. ^{2}H MAS NMR spectra of the deuterated chromophores: spiropyran (bottom) and two merocyanines.

from the carrier. Stated differently, the simulation program used here considers the rf excitation pulse to be ideal (infinitely short) when, in fact, it is not. The quadrupole coupling parameters obtained from the simulated spectrum (Figure 1) are given in Table 1. The agreement with values reported previously by Kim and Butler,[14] whose simulation program did account for the nonideality of the excitation pulse, assured us of our methods.

^{2}H MAS NMR spectra for the three deuterated chromophores are shown in Figure 2. Unlike the MC compounds, the methine deuteron in the closed-ring SP (3D-6-nitro-BIPS) has no zwitterionic character. Its isotropic chemical shift (Table 1) calculated by spectral simulation is that of a normal olefin (4.7 ± 0.4 ppm) in agreement with the 5.5-ppm shift observed by solution-state ^{1}H NMR spectroscopy.[5] The 174-kHz QCC found for 3D-6-nitro-BIPS is somewhat smaller than those known for deuterons bonded to sp^2-hybridized carbons. Literature data for two molecules containing such deuterons, benzene (183 kHz) and 1,3-diphenyl-1-hydroxypropene-3-one (188 kHz), are included in Table 1 for comparison. To our knowledge, the only quadrupole coupling parameters reported previously for an olefinic deuteron are those of 2D-1,3-diphenyl-1-hydroxypropene-3-one.[15]

The deuterium spectra in Figure 2 are not due to D_2O (crystalline water of hydration) introduced during deuteration. The deuterons of water molecules in solid hydrates have QCCs above 200 kHz. For example, the literature values for the water molecules in oxalic acid dihydrate are given in Table 1.

The two open-ring MC forms exhibit the same QCC values as found for the SP compound (Table 1). The spectral simulation for 3D-6,8-dinitro-BIPS is shown in Figure 3. It suggests that the predicted increase in the nuclear component of the quadrupolar interaction on passing from the SP to the MC compounds (on the basis of other experimental measurements) is not large enough to influence the QCC significantly. In other words, the

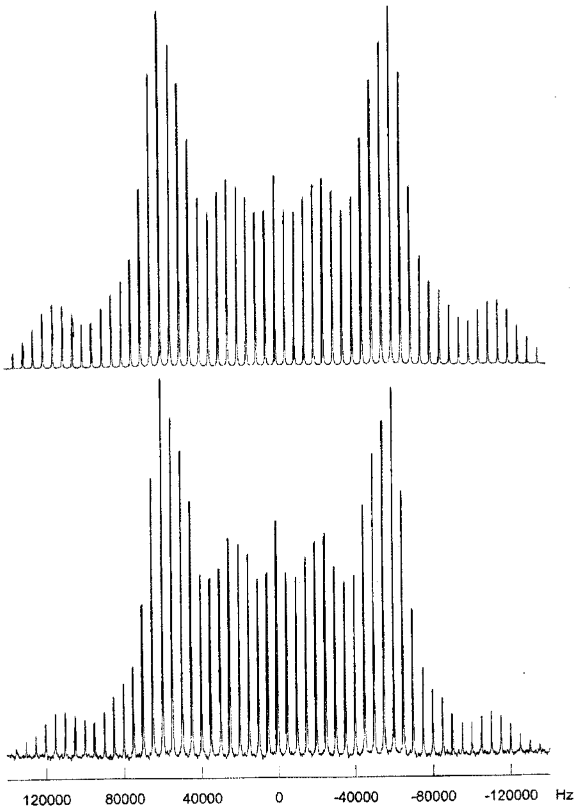


Figure 3. ^{2}H MAS NMR spectra of 3D-6,8-dinitro-BIPS: experimental spectrum (bottom), simulated spectrum with QCC = 178 kHz and η = 0.10 (top).

C3−H bond polarization in MC is too small to affect the QCC appreciably.

However, significant changes in other NMR parameters were observed on passing from SP to MC forms. High isotropic chemical shifts were calculated for C3−D on the MCs (ca. 7 ppm, Table 1). This finding is supported by solution-state ^{1}H NMR studies (8.82 ppm for 6,8-dinitro-BIPS in chloroform[5] and 8.88 ppm for 6-nitro-8-bromo-BIPS in methylene chloride[7]) and demonstrates the much longer-range sensitivity of chemical shifts compared to QCCs. The deuterium in MC experiences a more deshielded environment because of transmission, via the conjugated bond system, of electron withdrawal by distant electronegative substituents (Br, NO_2). Also, the indoline nitrogen−oxygen conjugation is important.

The electric field gradient asymmetry (η) indicates another distinction between the SP and MC forms. The small nonzero η value determined for the MCs reveals a less-symmetrical electric field gradient at the deuterium. Thus, the C−D bond in MC deviates slightly from perfect axial symmetry. The bulk MC solid phases prepared here were unsuitable for X-ray analysis. However, all of the available data from solution equilibria[5−8] and crystallographic studies[18−20] indicate that the most probable structure for the MCs in the bulk crystalline phases is the more thermodynamically stable TTC isomer, for which C3−D is in close proximity to C9−O. The nonzero values of η are consistent with the expected electric field asymmetry in this TTC isomeric form. A contracted internuclear distance between C9−O and C3−H was reported for this isomer,[18,20] in agreement with some type of through-space interaction (H-bonding or dipolar).

4. Conclusions

Solid-state ^{2}H-MAS NMR spectroscopy was used to probe the local electronic environment of rigid olefinic deuterons in a closed-ring SP (3D-6-nitro-BIPS) and two open-ring MCs (3D-6,8-dinitro-BIPS and 3D-6-nitro-8-bromo-BIPS). The QCCs determined for these chromophore molecules (174−178 kHz) are the same (within experimental error) and smaller than that of 2D-1,3-diphenyl-1-hydroxypropene-3-one (188 kHz), the only value reported previously for an olefinic deuteron. Thus, the expected longer and more-polar C3−D bond in the MCs compared to the SP (implied by chemical shifts and other studies) gave no appreciable change in the QCC. However, significant differences were found in the electric field asymmetries (η). The slightly larger η found for the MCs (compared to the SP) is attributed to a small deviation in the C3−D bond from axial symmetry, probably caused by proximity of the C9−oxygen bond. This proximity is consistent with the finding of a long-range D-isotope shift at C9 upon C3 deuteration, which was ascribed to a dipolar interaction. The nature of this through-space interaction (H-bonding or dipolar) will be the subject of future work.

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