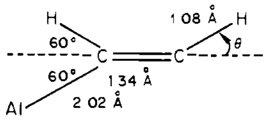
2 the essentially isotropic interaction with Al is the result of direct overlap possible between its 3s orbital and the semifilled orbital of the α carbon. The sign of the Al coupling elements given in eq 4 must therefore be positive. The z axis along which the smallest Al coupling constant is measured must then be perpendicular to the molecular plane. The smallest α-proton coupling constant was also observed along the z axis. It follows that the α-proton coupling constant of the Al-acetylene adduct is positive and its $C{=}C_\alpha{-}H_\alpha$ section is also bent.

As stated earlier the photoinduced spectral change observed with the $Al/C_2H_2/Ar$ system can be best understood in terms of the cis-trans isomerization of the vinyl form. We therefore examined the radical **2** by the EHT (extended Huckel type) molecular orbital theory. In particular, based on the structural parameters depicted below, the total energy of the radical and the isotropic Al coupling constant were examined as a function of θ, the angle of bend of the $C{=}C_\alpha{-}H_\alpha$ section. The results are shown in Figure 13. The EHT-MO theory thus states that the trans configuration at $\theta \simeq -40°$ is more stable than the linear structure ($\theta = 0°$) by $\sim$4 kcal. The energy vs. θ curve does not show a minimum in the $\theta > 0$ region; its shape, however, strongly suggests the possibility of a meta-stable cis configuration at $\theta \simeq 40°$. It thus appears that the addition reaction of Al to acetylene is symmetry restricted to yield only the cis form, and a barrier exists to prevent the conversion to the more stable trans isomer. The barrier need not be much higher than kT of the colliding atom/molecular beams since the conversion would be a unimolecular process at extremely low pressure ($\leq 10^{-5}$ torr), and the adduct remains at ambient temperature for only $\sim 10^{-5}$ s. Most interestingly, the EHT calculation (Figure 13) also showed that the cis-to-trans conversion should lead to a decrease of $\sim$20 G in the isotropic Al coupling constant as observed experimentally.



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Registry No. Al, 7429-90-5; C_2H_4, 74-85-1; C_2D_4, 683-73-8; C_2H_2, 74-86-2; C_2D_2, 1070-74-2.

Deuterium Nuclear Quadrupole Resonance Spectra of Nonlinear Hydrogen Bonds

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Abstract: The ^2H NQR spectra of several compounds having nonlinear hydrogen bonds ($O{-}H\cdots O$ angle of less than 150°) have been obtained at 77 K by a field-cycling double-resonance method: 1,3-diphenyl-1,3-propanedione, salicylamide, 1,4-dihydroxyanthraquinone, tropolone, salicyclic acid, 2-nitrophenol, 1-hydroxy-9-fluorenone, 3-hydroxy-2-naphthoic acid, and 1-hydroxy-2-naphthoic acid. The values obtained for the quadrupole coupling constants are higher than those found in a linear hydrogen bond of the same $O\cdots O$ distance. A single-crystal NMR study of 1,3-diphenyl-1,3-propanedione has been carried out at room temperature by a rotating-frame double-resonance experiment. The results show that the principal (z) axis of the deuterium electric field gradient tensor lies nearly along the O-H bond direction. Additional ^2H NQR spectra for several linear hydrogen-bonded systems in the crystalline benzoic acid, 4-chlorobenzoic acid, 2-bromobenzoic acid, 3-hydroxybenzoic acid, potassium acid phthalate, salicylamide, 3-hydroxy-2-naphthoic acid, and 1-hydroxy-2-naphthoic acid, have also been obtained. In addition, an X-ray structural study of 1-hydroxy-9-fluorenone has provided structural data to test for enhancement of the ^2H quadrupole coupling constant for the case of a relatively long nonlinear hydrogen bond.

Hydrogen bonding is widely recognized to be a fundamental feature of chemical and biological systems.[1-3] Numerous experimental techniques, including X-ray and neutron diffraction, infrared spectroscopy, and nuclear magnetic resonance spectroscopy, have been applied to the study of hydrogen bonding in solids. To a limited extent, deuterium nuclear quadrupole resonance (NQR) has also been employed. The results obtained thus far have demonstrated that the deuterium quadrupole constant (DQCC) is very dependent upon the hydrogen bond geometry,[4-10] and motional effects.[4,11-13] However, little work has been done on very short ($O\cdots O$ distance less than 2.55 Å) or highly nonlinear hydrogen bonds ($O{-}H\cdots O$ bond angle less than 150°). Neither have there been any reports of the use of nuclear quadrupole double resonance by level crossing (ADLF)[14,15] to study motional effects in the solid state.

We report the ^2H NQR data for a variety of hydrogen-bonded systems in the solid state as determined by the ADLF technique and the X-ray structure of 1-hydroxy-9-fluorenone, one of the substances studied by this method. The ^2H NQR data are interpreted in terms of the hydrogen bond geometry. In addition, we have completely determined the orientation of the electric field

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(1) Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman and Co.: San Francisco, 1960.

(2) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

(3) Schuster, P., Zundel, G., Sandorfy, C., Eds. "The Hydrogen Bond"; North-Holland Publishing Co.: Amsterdam, 1976; Vols. I, II, and III.

(4) Chiba, T. *J. Chem. Phys.* **1963**, *39*, 947.

(5) Soda, G.; Chiba, T. *J. Phys. Soc. Jpn.* **1969**, *26*, 249.

(6) Soda, G.; Chiba, T. *J. Chem. Phys.* **1969**, *50*, 439.

(7) Hunt, M. J.; Mackay, A. L. *J. Magn. Reson.* **1974**, *15*, 402.

(8) Berglund, B.; Vaughan, R. W. *J. Chem. Phys.* **1980**, *75*, 2037.

(9) Berglund, B.; Lindgren, J. *J. Mol. Stuct.* **1978**, *179*, 43.

(10) Butler, L. G.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6541.

(11) Blinc, R., ref 3, Chapter 18.

(12) Looyestijn, W. J.; Klaassen, T. O.; Poulis, N. J. *Physica B + C (Amsterdam)* **1979**, *96B + C*, 303.

(13) Berglund, B.; Eriksson, A.; Lindgren, J.; Tegenfeldt, J. *J. Mol. Struct.* **1979**, *52*, 113.

(14) Edmonds, D. T. *Phys. Rep.* **1977**, *29C*, 233.

(15) Rubenacker, G. V.; Brown, T. L. *Inorg. Chem.* **1980**, *19*, 392.

0002-7863/82/1504-1172$01.25/0

gradient (EFG) tensor of the deuterium site in 1,3-diphenyl-1,3-propanedione. Since a conventional single-crystal NMR study employing direct detection of the ^{2}H transitions would be difficult in a proton-rich organic compound such as 1,3-diphenyl-1,3-propanedione, we have employed a double-resonance technique involving adiabatic demagnetization in the rotating frame (ADRF) for the observation of the ^{2}H transitions in high magnetic field.

In a recent high-resolution ^{13}C NMR study of naphthazarin a rapid proton motion in the solid state was deduced.[16] In the present work, the presence of proton motion in the hydrogen bond has been deduced from the behavior of the ^{2}H T_{1d} as a function of temperature.

Theory

In zero magnetic field, NQR transitions are observed between nuclear energy levels determined by the quadrupole Hamiltonian, $\mathcal{H}_Q$:

$$\mathcal{H}_Q = \frac{e^2Qq_{zz}}{4S(2S-1)}\left[3\mathbf{S}_z^2 - \mathbf{S}^2 + \frac{\eta}{2}(\mathbf{S}_+^2 + \mathbf{S}_-^2)\right] \qquad (1)$$

The quantity, e^2Qq_{zz}/h, is termed the quadrupole coupling constant, S is the nuclear spin, and η is the asymmetry parameter. The nuclear quadrupole moment, Q, for deuterium is 2.860×10^{-28} cm^2.[17] The electric field gradient (EFG), q, is a traceless second-order tensor. In the principal axis system, the EFG is diagonal; by convention the axis system is defined so that $|q_{zz}| \geq |q_{yy}| \geq q_{xx}|$. The asymmetry parameter, defined as $\eta = (q_{xx} - q_{yy})/q_{zz}$, has values between 0 and 1. The asymmetry parameter and quadrupole coupling constant completely describe the EFG tensor in the principal axis system.

The elements of the EFG tensor are the sum of electronic and nuclear contributions. For deuterium, the latter contributions are dominant.[18,19]

Three transitions labeled ν_+, ν_-, and ν_0 are expected for the $S = 1$ case. While the ν_0 transition is not observed for ^{2}H, the observation of ν_+ and ν_- serves to uniquely determine the DQCC and the asymmetry parameter.

In high magnetic field, the total Hamiltonian is given by a combination of quadrupolar and Zeeman interactions:

$$\mathcal{H}_{\text{total}} = -\gamma\hbar S'_z H_0 + \mathcal{H}_Q(S)$$

Note that S' is the spin operator in the laboratory frame while S is the spin operator in the principal axis system. For each crystallographically distinct $S = 1$ spin site in a single crystal, two transitions are expected, centered about the Larmor frequency ($\omega_0 = \gamma H_0$) assuming $\gamma H_0 >> e^2Qq_{zz}/h$. The splitting of the two transitions as a function of the crystal orientation in the magnetic field H_0 allows one to determine the principal axis system of the EFG tensor.[20]

One disadvantage of ADRF for the detection of ^{2}H transitions in the presence of a large static magnetic field is the high rf magnetic field that must be applied to satisfy the Hartmann–Hahn condition.[21] ADRF at a field of 1.4 T requires an rf magnetic field of about 10^{-3} T, whereas in ADLF, rf magnetic fields on the order of only 10^{-6} T may be employed.

Experimental Section

The zero field ^{2}H NQR transitions that we report for polycrystalline samples were determined with one of two ADLF spectrometers. Spectra at 77 K were obtained by using a spectrometer which has been described elsewhere.[22,23] In addition, a new ADLF spectrometer of similar design was constructed. This new instrument is capable of variable temperature operation in the range 20–300 K. Spectra can be obtained on 200 mg of sample. If necessary, computer-controlled signal averaging of repeated scans can be performed. A description of the computer-controlled S channel tuning system is presented elsewhere.[24]

Table I. Positional Parameters in the Crystal Structure of 1-Hydroxy-9-fluorenone

atom	x/a	y/b	z/c
O1	0.2145 (1)	0.3494 (1)	−0.0058 (4)
O2	0.1792 (1)	0.4894 (1)	0.3969 (3)
C1	0.1228 (2)	0.3170 (1)	0.1212 (5)
C1A	0.0718 (2)	0.3576 (1)	0.3291 (5)
C2	0.0767 (2)	0.2380 (2)	0.0382 (5)
C3	−0.0184 (2)	0.2032 (1)	0.1578 (6)
C4	−0.0719 (2)	0.2448 (1)	0.3642 (5)
C4A	−0.0264 (2)	0.3221 (1)	0.4477 (4)
C5	−0.1536 (2)	0.3779 (2)	0.8223 (5)
C5A	−0.0632 (2)	0.3826 (1)	0.6522 (5)
C6	−0.1688 (2)	0.4452 (2)	0.9965 (5)
C7	−0.0944 (2)	0.5150 (2)	1.0025 (5)
C8	−0.0023 (2)	0.5202 (1)	0.8334 (5)
C8A	0.0115 (2)	0.4542 (1)	0.6580 (4)
C9	0.0997 (2)	0.4411 (1)	0.4532 (4)
HO1	0.230 (3)	0.406 (2)	0.037 (7)
H2	0.112 (2)	0.207 (2)	−0.107 (6)
H3	−0.050 (2)	0.147 (2)	0.074 (6)
H4	−0.144 (2)	0.223 (2)	0.440 (6)
H5	−0.205 (2)	0.327 (2)	0.822 (5)
H6	−0.231 (2)	0.445 (2)	1.117 (6)
H7	−0.102 (2)	0.558 (2)	1.133 (6)
H8	0.055 (2)	0.571 (2)	0.839 (6)

The single-crystal NMR study was performed at room temperature by using an ADRF spectrometer which has been described previously.[25] The Larmor frequencies for ^{1}H and ^{2}H are 60.1 (0.002) and 9.2267 (0.001) MHz, respectively. For a DQCC of 200 kHz, ^{2}H transitions are expected in the range of 9080–9380 kHz.

Most samples were deuterated either by refluxing in D_2O or D_2O/alcohol. 2-Bromobenzoic acid and 4-chlorobenzoic acid were deuterated by acidification of an aqueous solution of the sodium salt with DCl. Although different crystallographic modifications of 1,4-dihydroxyanthraquinone have been reported,[26] samples recrystallized from benzene, diethyl ether, and glacial acetic acid showed no significant differences in X-ray powder diffraction pattern; this was taken as evidence that the NQR sample contained a single polymorph.

Single crystals of 1,3-diphenyl-1,3-propanedione were grown by slow evaporation of a cyclohexane solution. Single crystals used in the ADRF experiment were on the order of 300–500 mg. Crystal orientations were determined by measurement of the interfacial angles and with reference to the ^{2}H NMR of the C–^{2}H site which also becomes deuterated by refluxing in D_2O. The orientation of the z axis of the efg at the carbon-bound deuterium should lie along the C^{2}H bond direction.[27] As the space group for 1,3-diphenyl-1,3-propanedione is $Pbca$,[28,29] four signals (two pair) are expected at certain rotation angles for both the C–^{2}H and the O–^{2}H sites.

X-ray Experiments. Golden yellow needles of 1-hydroxy-9-fluorenone, $C_{13}H_8O_2$, were grown from ethyl acetate solution. Crystal data: orthorhombic, $P2_12_12_1$, $a = 11.672$ (4) Å, $b = 15.409$ (3) Å, $c = 5.203$ (2) Å, $V = 935.9$ (6) Å^3, $F(000) = 408.0$, $Z = 4$, $\rho_{\text{calcd}} = 1.39$ g/mL, μ(Cu Kα) = 6.71 cm^{-1}. Cell data were obtained by a least-squares fit to the settings for 15 reflections ($37° < 2\theta < 45°$) on a Syntex P2$_1$ diffractometer equipped with a graphite monochromator. Using a variable scan rate of 2–29°/min, the $+h,+k,+l$ octant of data up to a maximum of 135° in 2θ(Cu Kα) was collected. The data were scaled according to the behavior of the intensities of the standard reflections, but there was no fluctuation greater than 5% of the original intensity. Of the 1009 unique reflections collected 865 had intensity greater than $3\sigma(I)$ and these were used in the subsequent structural analysis. No correction for absorption was warranted, but the excellent crystal quality necessitated an isotropic correction for secondary extinction,[30] the final value for the coefficient being 4.7×10^{-6}.

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(16) Shiau, W.; Duesler, E. N.; Paul, I. C.; Curtain, D. Y.; Blann, W. G.; Fyfe, C. A. *J. Am. Chem. Soc.* **1980**, *102*, 4546.

(17) Reid, R. V., Jr.; Vaida, M. L. *Phys. Rev. Lett.* **1975**, *34*, 1064.

(18) Kern, C. W.; Karplus, M. *J. Chem. Phys.* **1965**, *42*, 1062.

(19) Snyder, L. C. *J. Chem. Phys.* **1978**, *68*, 291.

(20) Cohen, M. H.; Reif, F. In "Solid State Physics"; Seitz, F., Turnbull, D., Eds.; Academic Press: New York, 1957; Vol. V.

(21) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.

(22) Hsieh, Y.; Ireland, P. S.; Brown, T. L. *J. Magn. Reson.* **1976**, *21*, 445.

(23) Hsieh, Y.; Rubenacker, G. V.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1384.

(24) Butler, L. G.; Reiner, C.; Brown, T. L., submitted for publication.

(25) Hiyama, Y.; Brown, T. L. *J. Chem. Phys.* **1981**, *75*, 114.

(26) Borgen, O. *Acta Chem. Scand.* **1966**, *20*, 2885.

(27) Ragle, J. L.; Minott, III, G. L. *Adv. Nucl. Quad. Reson.* **1978**, 3, 205.

(28) Williams, E. E. *Acta Crystallogr.* **1966**, *21*, 340.

(29) Jones, R. D. G. *Acta Crystallogr. Sect. B* **1976**, *B32*, 1807.

(30) W. H. Zachariasen, *Acta Crystallogr.* **1963**, *16*, 1139; *Acta Crystallogr., Sect. A* **1968**, *A24*, 212.

Table II. Intramolecular Distances (Å) and Angles (Deg)

Distances

O1	C1	1.353 (3)	C4A	C5A	1.479 (3)
O1	HO1	0.93 (3)	C5	C5A	1.380 (3)
O2	C9	1.226 (2)	C5	C6	1.388 (4)
C1	C1A	1.384 (3)	C5	H5	0.98 (2)
C1	C2	1.401 (3)	C5A	C8A	1.406 (3)
C1A	C4A	1.412 (3)	C6	C7	1.383 (4)
C1A	C9	1.475 (3)	C6	H6	0.96 (3)
C2	C3	1.381 (3)	C7	C9	1.392 (3)
C2	H2	0.98 (3)	C7	H7	0.95 (3)
C3	C4	1.398 (4)	C8	C8A	1.376 (3)
C3	H3	1.04 (3)	C9	H8	1.03 (2)
C4	C4A	1.374 (3)	C8A	C9	1.495 (3)
C4	H4	0.99 (3)			

Angles

C1	O1	HO1	113 (2)	C5A	C5	H5	120 (1)
O1	C1	C1O	123.8 (2)	C6	C5	H5	121 (1)
O1	C1	C2	118.3 (2)	C4A	C5A	C5	130.6 (2)
C1A	C1	C2	118.0 (2)	C4A	C5A	C8A	109.2 (2)
C1	C1A	C4A	121.0 (2)	C5	C5A	C8A	120.1 (2)
C1	C1A	C9	129.8 (2)	C5	C6	C7	121.0 (2)
C4A	C1A	C9	109.0 (2)	C5	C6	H6	121 (2)
C1	C2	C3	120.5 (2)	C7	C6	H6	118 (2)
C1	C2	H2	120 (2)	C6	C7	C8	121.0 (2)
C3	C2	H2	120 (2)	C6	C7	H7	120 (2)
C2	C3	C4	121.8 (2)	C8	C7	H7	119 (2)
C2	C3	H3	115 (1)	C7	C8	C8A	117.8 (2)
C4	C3	H3	123 (1)	C7	C8	H8	122 (1)
C3	C4	C4A	117.9 (2)	C8A	C8	H8	121 (1)
C3	C4	H4	122 (2)	C5A	C8A	C8	121.4 (2)
C4A	C4	H4	120 (2)	C5A	C8A	C9	107.8 (2)
C1A	C4A	C4	120.8 (2)	C8	C8A	C9	130.7 (2)
C1A	C4A	C5A	107.8 (2)	O2	C9	C1A	126.3 (2)
C4	C4A	C5A	131.4 (2)	O2	C9	C8A	127.6 (2)
C5A	C5	C6	118.5 (2)	O1A	C9	C8A	106.1 (2)

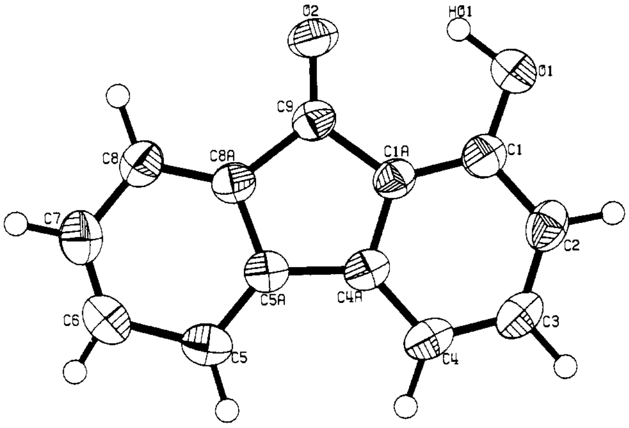

Figure 1. ORTEP view of the 1-hydroxy-9-fluorenone molecule. Only the intramolecular hydrogen bond is shown here.

The structure was solved by direct phasing methods by using the SHELX 76 program.[31] All nonhydrogen atoms were located from an E map and after least-squares refinement of their positional and anisotropic thermal parameters, all hydrogen atoms were located from a difference Fourier map. Full-matrix least-squares refinement of positional parameters for all atoms, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms led to final agreement values of $R = 0.030$ and $R_w = 0.0391$,[32] where $w = 1.306/[\sigma(F_o)^2 + 0.0003(F_o)^2]$; the final observation to variable ratio was 5.1:1.[33]

Table III. Hydrogen Bonding Distances

	O2···HO1–O1 angle, deg	O2···HO1, Å	HO1–O1, Å	O2···O1, Å
intramolecular[a]	131 (3)	2.35 (4)	0.93 (3)	3.036 (2)
intermolecular[b]	140 (3)	2.05 (3)	0.93 (3)	2.822 (2)

[a] With O2 at (x, y, z). [b] With O2 at ($^1/_2 - y, 1 - y, {}^1/_2 + z$).

Scattering curves were taken from the analytical expressions in ref 34. The final atomic coordinates are listed in Table I; thermal parameters and structure factors are included as supplementary material.

A labeled single molecule of 1-hydroxy-9-fluorenone is shown in Figure 1; intramolecular distances and angles are given in Table II. The carbon–carbon distances are within the range of those expected for aromatic systems of this type, with the formally single C9–C1A and C9–C8A bond lengths being diminished slightly from 1.54 Å due to resonance stabilization. The C9–O2 length of 1.226 (2) Å and the C1–O1 length of 1.353 (3) Å are those expected for aliphatic ketones and aromatic alcohols, respectively. That is, there is no evidence that the two C–O bonds are equivalent due to dynamic disorder of HO1 between O1 and O2, as was the case for naphthazarin B where the analogous C–O bond lengths were 1.290 (3) and 1.299 (3) Å, respectively.[16] The C1–HO1 bond length, without correction for bond shortening, of 0.93 (3) Å and reasonable thermal parameter for HO1 also evidence the absence of hydrogen exchange.

The carbon framework of the molecule is essentially planar with no carbon atom lying farther than 0.025 Å out of the plane; O2 also lies in this plane, but O1 and HO1 are 0.071 and 0.247 Å out of the plane. HO1 participates in an intramolecular hydrogen bond with O2 of the reference molecule and a *stronger* intermolecular hydrogen bond with O2 of the molecule at $^1/_2 - x$, $1 - y$, $^1/_2 + z$. The dimensions of these interactions are summarized in Table III. The intramolecular O2–HO1 hydrogen bond completes an essentially planar six-membered ring containing HO1, O1, C1, C1A, C9, and O2, with HO1 0.18 (3) Å out of the plane.

The arrangement of molecules in the unit cell is depicted in Figure 2. Hydrogen bonding dominates the packing features in this crystal. There is no ring stacking except for the 5.2 Å repeat along the crystallographic c axis. The molecules are linked together into spiral chains by the intermolecular hydrogen bond noted above; these chains are roughly parallel to the crystallographic c axis. The HO1, O1, C1, C1A, C9, O2 "hydrogen-bond plane" of one molecule makes an angle of 103° with the analogous plane in an adjacent molecule of the spiral; the O1–HO1···O2···HO1 network is clearly not coplanar. It is probably this intermolecular interaction which pulls HO1 out of the plane of the molecule and out of the intramolecular "hydrogen bonding plane".

Results

The ^{2}H NQR data for nonlinear hydrogen bonds are listed in Table IV. For compounds having one ^{2}H site in the molecule, assignment of the spectrum is straighforward. In the case of 1,3-diphenyl-1,3-propanedione, which is found in the enol tautomer in the solid state,[29] the transitions due to the C–^{2}H site were identified based on the similarity of the EFG parameters to those reported for other sp^2 C–^{2}H sites.[27] Assignment of the ^{2}H spectrum of salicylamide was aided by the observation of ^{2}H satellites about the ^{14}N ν_+ transition due to directly bound ^{2}H.[7,35] Also, the ^{2}H ν_+ and ν_- transitions are distinguishable by a characteristic perturbation of the transition line shapes caused by application of a small static magnetic field (ca. 10^{-4} T).[14] Deuterium transitions resulting from sites involved in linear hydrogen bonds were assigned on the basis of the well-characterized relationship between the DQCC and the O···O bond distance for linear hydrogen bonds.[4-10] It has been reported that dipolar coupling between neighboring deuterium nuclei can lead to an increase in the observed line width.[36] Thus, one would expect the deuterium resonances of carboxylic acid dimers to have a larger line width that those found for single hydrogen-bonded systems; this behavior was observed. The ^{2}H NQR data found for linear hydrogen bonded systems are given in Table V. Miscellaneous

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(31) G. M. Sheldrick, SHELX 76, a program for crystal structure determination, University of Cambridge, England, 1976.

(32) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

(33) Since 1-hydroxy-9-fluorenone crystallizes in a noncentrosymmetric space group, an attempt was made to determine absolute configuration by refining the "enantiomeric" positions for the atoms. The final residuals for this model were not significantly different from those above, and it was concluded that absolute configuration of this compound could not be determined in this simple manner.

(34) Ibers, J. A., Hamilton, W. C., Eds. "International Tables for X-ray Crystallography"; Kynock Press: Birmingham, England, 1974; pp 99–102.

(35) D'Avignon, D. A.; Brown, T. L. *J. Phys. Chem.*, in press.

(36) Edmonds, D. T.; White, A. A. L. *J. Magn. Reson.* **1978**, *31*, 149.

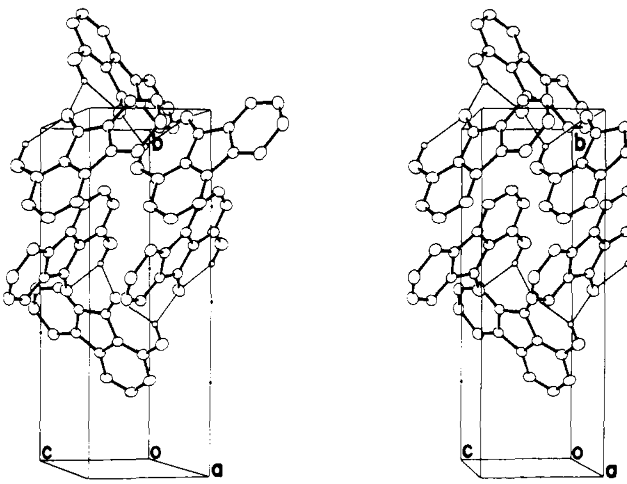


Figure 2. Stereoview of unit cell, showing both intra and intermolecular hydrogen bonding. The reference molecule is the one closest to the origin.

Table IV. Deuterium Quadrupole Resonance Spectra in Nonlinear Hydrogen-Bonded Systems

compd	temp, K	$\nu_+{}^a$	$\nu_-{}^a$	e^2Qq_{zz}/h^a	η	O···O, Å	O^2HO, deg	$O\cdots{}^2H$, Å	$O-{}^2H$, Å
1 1,3-diphenyl-1,3-propanedione	77	100.4 (1)	80.7 (1)	120.7 (1)	0.326 (4)	2.459[b]	155	1.36	1.16
	198	94.5 (1)	not observed						
	300	94 (1)	79 (1)	115.3 (13)	0.26 (4)				
2 salicylamide	77	133.0 (2)	116.8 (2)	166.5 (2)	0.195 (5)	2.49[c]	164	1.68	0.87
3 1,4-dihydroxyanthraquinone	77	153.0 (1)	140.0 (1)	195.0 (2)	0.133 (4)	2.576[d]	145		0.90, 0.91
4 tropolone	77	163.0 (2)	154.4 (2)	211.6 (3)	0.081 (5)	2.553[e]	118	1.98	0.94
	200, 300	not observed							
5 salicylic acid	77	170.0 (2)	155.0 (2)	216.7 (2)	0.138 (4)	2.606[f]	145	1.766	0.957
6 *o*-nitrophenol	77	172.6 (2)	159.2 (2)	221.1 (2)	0.121 (4)	2.587[g]	140	1.84	0.88
7 1-hydroxy-9-fluorenone	77	176.5 (1)	165.5 (1)	228.0 (1)	0.096 (2)	2.822[h]	140	2.05	0.93
	198	175.7 (3)	164.2 (3)	226.6 (4)	0.102 (5)				
	300	174.0 (5)	164.0 (5)	225.3 (7)	0.089 (9)				
8 3-hydroxy-2-naphthoic acid	77	173.0 (1)	156.0 (1)	219.3 (1)	0.155 (2)	2.66[i]	165		
9 1-hydroxy-2-naphthoic acid	77	164.3 (1)	149.0 (1)	208.9 (1)	0.147 (2)	2.58[j]	130		

[a] in kHz. [b] Reference 29. [c] Sasada, Y; Takano, T; Kakudo, M. *Bull. Chem. Soc. Jpn.* 1964, *37*, 940. Hsu, I.-N.; Craven, B. M. *Acta Crystallogr., Sect. B* 1974, *B30*, 843. [d] Nigam, G. D.; Deppish, B. *Z. Kristallogr.* 1980, *151*, 185. [e] Reference 37. [f] Bacon, G. E.; Jude, R. J. *Z. Kristallogr.* 1973, *138*, 19. [g] Assumed to be the same as that for 2-nitro-4-chlorophenol: Kawai, R.; Kashino, S.; Haisa, M. *Acta Crystallogr. Sect. B* 1976, *B32*, 1972. [h] This work. [i] Gupta, M. P.; Dutta, B. P. *Cryst. Struct. Commun.* 1975, *4*, 37. [j] Gupta, M. P.; Mahata, A. P. *Cryst. Struct. Commun.* 1976, *5*, 553. OHO angle is estimated; uncertainty about ±5°.

Table V. Deuterium Quadrupole Resonance Spectra in Linear Hydrogen-Bonded Systems

compd	temp, K	$\nu_+{}^a$	$\nu_-{}^a$	e^2Qq_{zz}/h^a	η	O···O, Å
potassium acid phthalate	77	95.4 (1)	88.6 (1)	122.7 (2)	0.111 (3)	2.546[b]
	234	97.5 (2)	91.0 (2)	125.7 (3)	0.103 (6)	
4-chlorobenzoic acid	77	not observed				
	200	128.0 (5)	114.5 (5)	161.7 (7)	0.167 (12)	2.615[c]
	300	129 (1)	116 (1)	163 (2)	0.16 (2)	
benzoic acid	77	not observed				
	300	131.5 (5)	119.5 (10)	167.3 (3)	0.14 (2)	2.633[d]
2-bromobenzoic acid	77	133.2 (2)	120.4 (2)	169.1 (3)	0.151 (5)	2.64[e]
	200, 300	not observed				
3-hydroxy-2-naphthoic acid	77	135.8 (4)	123.5 (4)	172.9 (8)	0.142 (8)	2.66[f]
salicylic acid	77	137.2 (2)	124.0 (2)	174.1 (4)	0.152 (4)	2.636[g]
1-hydroxy-2-naphthoic acid	77	135.5 (2)	123.2 (2)	172.5 (3)	0.143 (2)	2.67[h]

[a] In kHz. [b] Okaya, Y. *Acta Crstallogr.* 1965, *19*, 879. [c] Miller, R. S.; Paul, I. C.; Curtin; D. Y. *J. Am. Chem. Soc.* 1974, *96*, 6334. [d] Sim, G. A.; Robertson, J. M.; Goodwin, T. H. *Acta Crystallogr.* 1955, *8*, 157. Bruno, G.; Randaccio, L. *Acta Crystallogr., Sect. B* 1980, *B36*, 1711, 2857. [e] Ferguson, G.; Sim, G. A. *Acta Crystallogr.* 1962, *15*, 346. [f] Reference *i* in Table IV. [g] Reference *f* in Table IV. [h] Reference *j* in Table IV.

^2H and ^{14}N NQR data are listed in Table VI.

The spin-lattice relaxation time of the proton system in a deuterated 1,3-diphenyl-1,3-propanediol crystal, T_{1AD} (which is generally different than $T_{1\rho}$), is about 100 ms. This is long enough to perform the double resonance in the rotating-frame experiment for the ^1H–^2H system. Since the heat capacity of the deuterium spin system is much smaller than that of the proton system, the rf irradiation applied to the deuterium spin system was phase shifted every 500 μs to increase the sensitivity of detection of the ^2H transitions. The detection sensitivity of the ADRF technique is a strong function of the extent of dipolar coupling between the deuterium and proton spin systems.[21] For this reason, the transitions due to the C–^2H site are more intense than those due to the O–^2H site; the closest ^2H–^1H distances are 2.19 and 2.44 Å, respectively. Transitions due to the O–^2H site could be easily seen at most rotation angles, although computer-controlled signal averaging was required for rotation angles in the range of 40–140°. The rotation pattern about the crystallographic *c* axis is shown in Figure 3. At 0°, the crystallographic *a* axis is parallel to the applied magnetic field.

Table VI. Miscellaneous NQR data

compd	site	temp, K	$\nu_+{}^a$	$\nu_-{}^a$	$\nu_0{}^a$	e^2Qq_{zz}/h^a	η
1,3-diphenyl-1,3-propanedione[b]	${}^2H{-}C$	77	146.9 (1)	135.8 (1)		188.5 (1)	0.118 (2)
		198	145.0 (5)	133.5 (5)		185.7 (7)	0.124 (11)
		300	142.5 (5)	132.7 (5)		183.5 (7)	0.107 (11)
salicylamide[c]	$N{-}{}^2H\cdots O$ 2.94	77	153.0 (1)	135.5 (1)		192.3 (1)	0.182 (2)
	$N{-}{}^2H\cdots O$ 3.04	77	168.8 (1)	151.5 (1)		213.5 (1)	0.162 (2)
	${}^{14}NH_2$	77	2270 (1)	1740 (5)	530 (5)	2673 (10)	0.397 (10)
	${}^{14}N^2H_2$	77	2283 (1)	not tried			
3-hydroxybenzaldehyde[d]		77	161.1 (1)	144.9 (1)		204.0 (2)	0.159 (2)

[a] In kHz. [b] Reference b in Table IV. [c] Reference c in Table IV. [d] Assumed to be a linear hydrogen bond system (crystal structure unknown).

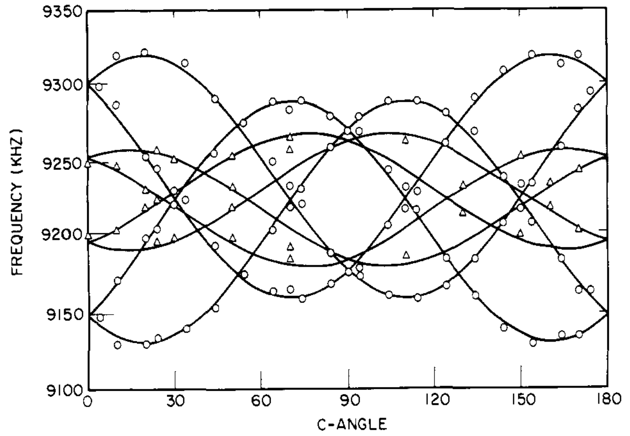


Figure 3. The splitting of the resonance lines due to the ${}^2H$ nucleus in the OHO bond (△) and that in the C–H bond (○) of single crystal 1,3-diphenyl-1,3-propanedione, at high magnetic field, as a function of rotation about the c axis. The a axis is parallel to the magnetic field at 0°.

In general, one must obtain rotation patterns about three orthogonal axes to completely determine the elements of the EFG tensor. However, when the DQCC and asymmetry parameter have been independently determined by the ADLF technique, the orientation of the EFG tensor can be uniquely determined from only two orientations of the crystal with respect to the applied magnetic field.

Discussion

DQCC of Nonlinear Hydrogen Bonds. Several detailed analyses of ${}^2H$ EFG parameters as a function of the hydrogen bond length have been presented.[4,7,10] All of these analyses have dealt with linear and nearly linear hydrogen bonds (O–H···O bond angle greater than 150°). The results have shown that the EFG at deuterium is mainly due to the directly bound oxygen and that the quadrupole coupling constant decreases with increasing O–H distance. In a recent study a large body of ${}^2H$ NQR data relating to the dependence of the DQCC upon O···O distance was fit to a third-order polynomial.[10] The relationship is depicted by the line in Figure 4. Also shown in the figure are the DQCC determined for the nonlinear hydrogen bonds of Table IV. As can readily be seen, the DQCC in the nonlinear hydrogen bonds are substantially larger than the values predicted for linear hydrogen bonds with the same O···O distances. Note also that when the O···O distance is short, even a relatively small departure from linearity (e.g., salicylamide) gives rise to enhanced DQCC values.

There are three possible origins for the observed discrepancy of DQCC between linear and nonlinear hydrogen bonds: (a) a change in orientation of the principal axis system, which renders comparison of the ${}^2H$ NQR data between linear and nonlinear hydrogen bonds meaningless, (b) a large dependence of the EFG upon the hydrogen bond angle in a manner which should be reflected in theoretical calculations of the DQCC, and (c) a dependence of the $O{-}{}^2H$ bond distance upon the hydrogen bond angle which is in turn reflected in the value of the DQCC.

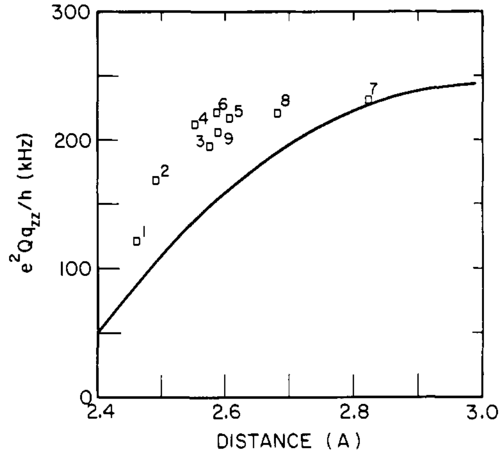
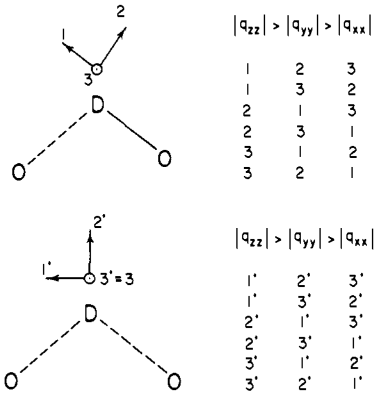


Figure 4. Quadrupole coupling constants for deuterium in nonlinear hydrogen bonds (□) as compared with the empirically established relationship between DQCC and O···O distance for linear hydrogen bond systems (solid line).[10]



$\lvert q_{zz}\rvert$ >	$\lvert q_{yy}\rvert$ >	$\lvert q_{xx}\rvert$
1	2	3
1	3	2
2	1	3
2	3	1
3	1	2
3	2	1

$\lvert q_{zz}\rvert$ >	$\lvert q_{yy}\rvert$ >	$\lvert q_{xx}\rvert$
1'	2'	3'
1'	3'	2'
2'	1'	3'
2'	3'	1'
3'	1'	2'
3'	2'	1'

Figure 5. Alternative assignments for the relative magnitudes of the EFG components of deuterium in hydrogen bonds, for assumed nonsymmetric (C_s) and symmetric (C_{2v}) hydrogen bond geometries. Vectors 3,3′ are normal to the page.

A theoretical analysis of the enol tautomer of malondialdehyde, which is structurally similar to 1,3-diphenyl-1,3-propanedione, indicates that for a *symmetric hydrogen bond*, the z axis of the efg would be normal to the molecular plane[37,38] rather than aligned with the $O{-}{}^2H$ bond direction. Since a neutron diffraction study of 1,3-diphenyl-1,3-propanedione shows that the hydrogen bond is only slightly distorted from C_{2v} symmetry,[29] the possibility of a change in the orientation of the EFG principal axis system at deuterium must be considered.

A total of 12 different orientations of the principal axis system have been considered as shown in Figure 5. Vectors 1 and 1′

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(37) Karlstrom, G.; Wennerstrom, H.; Jonsson, B.; Forsen, S.; Almlof, J.; Roos, B. *J. Am. Chem. Soc.* **1975**, *97*, 4188.

(38) Karlstrom, G.; Jonsson, B.; Roos, B.; Wennerstrom, H. *J. Am. Chem. Soc.* **1976**, *98*, 6851.

are the O–^{2}H and O···O direction for the C_s and the C_{2v} forms, respectively. Vectors 3 and 3′ are equivalent and represent the out-of-plane direction. Vectors 2 and 2′ are normal to 1,3 and 1′,3′, respectively. With use of the values of DQCC and asymmetry parameter determined in the experiment (Table IV), rotation patterns (resonance frequencies versus the rotation angle) can be calculated from eq 2 for all of the principal axis orientations given in Figure 5. The principal axis assignment 1 > 3 > 2 gives the best fit to the experimentally determined rotation pattern. It is quite interesting to note that 1,3-diphenyl-1,3-propanedione, which has the shortest and one of the most nonlinear hydrogen bonds of the compounds listed in Table IV, nevertheless retains the same EFG principal axis system commonly found in all other hydrogen-bonded systems.[4] We may reasonably assume that the principal axis system for all the compounds listed in Table IV is invariant.

The OHO bond angles of the compounds listed in Table IV are mainly determined by the carbon–oxygen framework of the molecule. A recent theoretical study of the model hydrogen-bonding dimer, formaldehyde–water, has shown that for fixed O···^{2}H and O–^{2}H distances, the DQCC is not a strong function of the hydrogen bond angle (a maximum change of 10 kHz was observed for a deviation from linearity of 30°).[10,39]

For a given O···O distance, the sum of the O–^{2}H and ^{2}H···O distances will obviously be longer for a nonlinear than for a linear hydrogen bond. This in turn would suggest that the O–^{2}H distance will be shorter than would be predicted for a linear hydrogen bond with the same O···O distance because the attractive influence of the donor oxygen will be smaller. The effect will be most pronounced for short hydrogen bonds that differ substantially from linearity. Because of the strong relationship between DQCC and O–^{2}H distance,[10,40] the DQCC for non-linear hydrogen bonds are higher than would be expected for a linear system of the same O···O distance. The departure from the empirical relationship established for linear hydrogen bonds (Figure 4) is largest, about 75 kHz, for the case of tropolone, with a relatively short hydrogen bond and most acute bond angle. The smallest departure, no more than a few kHz, is observed for 1-hydroxy-9-fluorenone, which has a relatively long hydrogen bond.

It is interesting to compare the ^{2}H NQR data obtained in the solid state for compounds which exhibit unusual hydrogen-bonding geometries with data obtained on solutions. The hydrogen bonds of tropolone, 1-hydroxy-9-fluorenone, and 1,4-dihydroxyanthraquinone in the solid state are bifurcated (i.e., the hydrogen atom is simultaneously attracted to two hydrogen bond acceptors). Jackman et al. have recently estimated the solution state DQCC for tropolone and 1-hydroxy-9-fluorenone based upon analysis of ^{13}C and ^{2}H spin-lattice relaxation times.[41] Their values of 216 (1) and 221 (3) kHz are in good agreement with the values listed in Table IV: 211.6 (3) and 225.3 (7) kHz, respectively. Therefore, one can conclude that the effect of bifurcation of the hydrogen bond is small, at least for tropolone and 1-hydroxy-9-fluorenone. The major reason for the substantial difference in the value of the DQCC for tropolone and that found in a linear hydrogen bond having the same O···O bond distance must then be due to the nonlinearity of the relatively strong hydrogen bond.

It should be noted that the technique used by Jackman requires the assumption of a zero asymmetry parameter. It is evident from the values reported in Tables IV and V that this condition is rarely met. Tropolone and 1-hydroxy-9-fluorenone have, fortuitously, rather small asymmetry parameters, 0.08 and 0.089, respectively.

Deuterium T_{1d} Behavior. The ability to obtain ^{2}H NQR spectra via the ADLF experiment was limited by the short (<1 s) ^{2}H T_{1d} (spin–lattice relaxation time in zero applied magnetic field) observed in several samples at various temperatures, as shown in Tables IV and V. For nuclei having an electric quadrupole moment, modulation of the electric field gradient at the S spin site provides an effective coupling mechanism between the S spin system and the lattice.[42,43] Because the deuterium quadrupole transitions occur in the range of 10–200 kHz, the ^{2}H T_{1d} will be reduced by molecular motions occurring in the frequency range of 10^4–10^7 s^{-1}.

In all of the samples for which ^{2}H NQR transitions could not be observed, there is evidence for the presence of motion in the solid state that could modulate the EFG at the deuterium site. In 1,3-diphenyl-1,3-propanedione, neutron diffraction results suggest a large thermal motion of the hydrogen atom in the hydrogen bond.[29] Tropolone, which exists as hydrogen-bonded dimers in the solid state, exhibits librational motion about the center of the dimer.[44]

It has been postulated, on the basis of the degree of crystallographic twofold disorder in the hydrogen bond, that aromatic carboxylic acids may exhibit a wide range of proton-transfer rates,[38] depending in part on the substitution of the benzene ring. (Here, proton transfer is used to describe the motion of either ^{1}H or ^{2}H). Of the compounds listed in Table V, the expected order of proton transfer rates is 4-chlorobenzoic acid > benzoic acid > 2-bromobenzoic acid. It is noteworthy that ^{2}H NQR transitions were observed at 77 K for 2-bromobenzoic acid but not for the other two acids. Presumably for 2-bromobenzoic acid proton transfer is in the slow exchange region.[40] At 300 K ^{2}H NQR transitions were not observed for 2-bromobenzoic acid, presumably because proton-exchange rates are not favorable. On the other hand, spectra are seen for the other compounds, in which proton-exchange rates may be in the fast exchange limit.

Note that the small differences in the ^{2}H NQR frequencies determined for the carboxylic acids provide no information about the dynamics of the hydrogen bond. The slightly smaller value of the DQCC found for 4-chlorobenzoic acid is readily explained by the slightly shorter O···O bond distance of this compound (see Table V).

By way of summary, the ^{2}H NQR data for a number of O–H···O hydrogen-bonded systems have been obtained. We have shown that, in nonlinear hydrogen bonds, for a given O···O distance the DQCC is higher than expected from the empirical correlations established for linear systems. The effect can be accounted for in terms of a shorter O–H bond for a given O···O distance as compared with a linear system. Further, temperature dependence studies have yielded understandable patterns of the ^{2}H T_{1d} values in relation to expected rates of deuterium transfer in the hydrogen bond.

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Registry No. 1,3-Diphenyl-1,3-propanedione, 120-46-7; salicylamide, 65-45-2; 1,4-dihydroxyanthraquinone, 81-64-1; tropolone, 533-75-5; salicyclic acid, 69-72-7; *o*-nitrophenol, 88-75-5; 1-hydroxy-9-fluorenone, 6344-60-1; 3-hydroxy-2-naphthoic acid, 92-70-6; 1-hydroxy-2-naphthoic acid, 86-48-6; potassium acid phthalate, 877-24-7; 4-chlorobenzoic acid, 74-11-3; benzoic acid, 65-85-0; 2-bromobenzoic acid, 88-65-3; 3-hydroxybenzaldehyde, 100-83-4.

Supplementary Material Available: Tables of anisotropic thermal parameters and of structure factors (6 pages). Ordering information is available on any masthead page.

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(39) It should be noted that the labeling system employed in ref 10 differs from that employed in describing the crystal structure of 1-hydroxy-9-fluorenone. To avoid confusion, we have represented the covalent deuterium–oxygen bond as O–^{2}H and the deuterium–donor oxygen bond as O···^{2}H.

(40) Dixon, M.; Claxton, T. A.; Smith, J. A. S. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 2158.

(41) Jackman, L. M.; Trewella, J. C.; Haddon, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 2519.

(42) Abragam, A. "The Principles of Nuclear Magnetism"; Oxford University Press: Oxford, 1978.

(43) Hubbard, P. S. *J. Chem. Phys.* **1970**, *53*, 985.

(44) Shimanouchi, H.; Sasada, Y. *Acta Crystallogr., Sect. B* **1973**, *B29*, 81.

(45) Dieterich, D. A.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1974**, *96*, 9372.

(46) Slichter, C. P. "Principles of Magnetic Resonance", 2nd ed., Springer-Verlag: New York, 1978; p 167.