

Karplus-Type Relationship for Quadrupole Coupling Constants and Asymmetry Parameters for Substituted Acetic Acids[†]

Margo A. Jackisch, William L. Jarrett, Kermin Guo, Frank R. Fronczek, and Leslie G. Butler*

Contribution from the Macromolecular Studies Group, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. Received April 13, 1987

Abstract: The deuterium quadrupole coupling constant for the methyl group in acetic acid dimer was calculated as a function of the torsion angle about the carbon-carbon bond. The results show that when a deuteron approaches either of the negatively charged oxygen atoms, the quadrupole coupling constant for the deuteron is reduced by as much as 4.2 kHz. Both the calculated quadrupole coupling constant, $e^2q_{zz}Q/h$, and asymmetry parameter, η , are fitted with a Karplus-type equation: $e^2q_{zz}Q/h = A - 0.5491 \cos \theta - 1.7859 \cos 2\theta$; $\eta = 0.0491 + 0.0058 \cos \theta - 0.0081 \cos 2\theta$. Adiabatic demagnetization in the laboratory frame spectroscopy at 77 K for (4-chlorophenyl)[2,2-²H₂]acetic acid showed two inequivalent deuteron sites that, on the basis of deuterium double transitions, are demonstrated to be due to two deuteron sites bound to the same carbon atom. The solid-state structure of (4-chlorophenyl)acetic acid was determined by single-crystal X-ray diffraction. The ADLF and structural data for (4-chlorophenyl)[2,2-²H₂]acetic acid were used to obtain a preliminary value for the A parameter as 170.767 kHz.

Solid-state deuterium NMR spectroscopy is mainly used to study molecular motions¹⁻⁷ but rarely to determine solid-state structures. There are relatively few methods for utilizing solid-state deuterium NMR spectra to measure structural parameters. In 1964, Chiba reported a correlation between deuterium quadrupole coupling constants and hydrogen bond lengths between oxygen donors and acceptors.⁸ The deuterium asymmetry parameter has also been used to assign distances in hydrogen bonds.^{9,10} This work has been extended to include nitrogen donors and acceptors.¹¹ However, there are no reported correlations between carbon-bound deuterium quadrupole coupling constants and solid-state structural features. Herein, we report preliminary results for a Karplus-type relationship^{12,13} for measuring torsion angles involving C-²H sites α to a carboxyl group. This is the first report of an expression that allows one to convert solid-state deuterium NMR data into structural information for a C-²H bond adjacent to some functional group. The possible areas of application are as varied as the current use of solid-state deuterium NMR, ranging from polymers to biomaterials to surface-adsorbed species.

It is generally assumed that, in the aliphatic C-²H bond, there is a characteristic value for the static deuterium quadrupole coupling constant. Furthermore, in the high-field solid-state deuterium NMR experiment, all observed reductions in the apparent quadrupole coupling constant have been attributed to molecular motions that reorient the C-²H bond with respect to the applied magnetic field. However, Hiyama et al. found that in thymine-*methyl-d*₃ the methyl group deuteron resonances are affected by an adjacent exocyclic oxygen atom.¹⁴ Also of note, the C²H₂ units in succinic acid,¹⁵ α -glycine,¹⁶ and DL-serine¹⁷ have at least two distinct values for the deuterium quadrupole coupling constant. In this work, we report the high-resolution adiabatic demagnetization in the laboratory frame (ADLF) spectrum of (4-chlorophenyl)[2,2-²H₂]acetic acid, which reveals inequivalent deuterium sites. The origin of the inequivalency is traced to the carboxylic oxygen atoms adjacent to the C²H₂ unit.

In solid-state deuterium NMR spectroscopy, structural information comes about from the fact that the deuterium NMR spectrum is determined by the electric field gradient at the deuterium nuclear site. The electric field gradient is a tensor quantity with a trace of zero.¹⁸ In reports of solid-state deuterium NMR data, the common convention is to refer to an axis system that diagonalizes the electric field gradient tensor; the largest diagonal element of the tensor, eq_{zz} , gives the quadrupole coupling constant, $e^2q_{zz}Q/h$.¹⁹ The quadrupole coupling constant is a direct function of the charge distribution in the close vicinity of the deuterium

nucleus, as shown in eq 1. Note that only occupied molecular

$$eq_{zz} = \sum_n K_n \frac{3z_n^2 - r_n^2}{r_n^5} - e \left\langle \Psi^* \left| \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} \right| \Psi \right\rangle \quad (1)$$

orbitals, ignoring electron correlation, contribute to the electric field gradient; the absence of contributions from excited states greatly simplifies the calculations required to compute quadrupole coupling constants. This is in contrast to the situation for chemical shift calculations. The other major elements of the electric field gradient tensor, eq_{xx} and eq_{yy} , are obtained by a similar summation of neighboring charge with a $1/r^3$ distance dependence. Also specified in reports of solid-state deuterium NMR spectra is the asymmetry parameter, η , of the electric field gradient tensor (eq 2). We note that C-²H bonds, with local axial symmetry, should

$$\eta = (eq_{xx} - eq_{yy})/eq_{zz} \quad (2)$$

have asymmetry parameters close to zero.

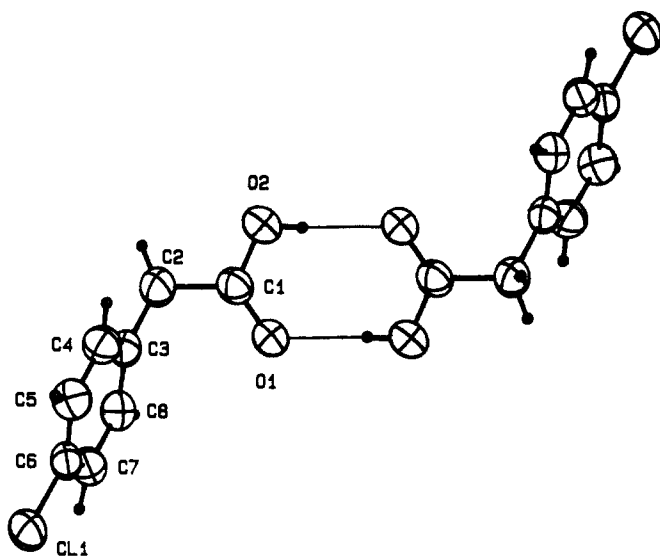
This report consists of four components: (1) The results of an ab initio molecular orbital calculation of acetic acid dimer, in which

- (1) Spiess, H. W. *Adv. Polym. Sci.* **1985**, *66*, 23-56.
- (2) Jelinski, L. W. *Annu. Rev. Mater. Sci.* **1985**, *15*, 359-377.
- (3) Vold, R. R.; Brandes, R.; Tsang, P.; Kearns, D. R.; Vold, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 302-303.
- (4) Torchia, D. A. *Annu. Rev. Biophys. Bioeng.* **1984**, *13*, 125-144.
- (5) Frey, M. H.; DiVerdi, J. A.; Opella, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 7311-7315.
- (6) Eckman, R.; Vega, A. J. *J. Phys. Chem.* **1986**, *90*, 4679-4683.
- (7) Major, P. D.; Raidy, T. E.; Ellis, P. R. *J. Am. Chem. Soc.* **1986**, *108*, 8123-8129.
- (8) Chiba, T. *J. Chem. Phys.* **1964**, *41*, 1352-1358.
- (9) Butler, L. G.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6541-6549.
- (10) Brown, T. L.; Butler, L. G.; Curtin, D. Y.; Hiyama, Y.; Paul, I. C.; Wilson, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 1172-1177.
- (11) Keiter, E. A. Ph.D. Dissertation, University of Illinois, 1986.
- (12) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11-15.
- (13) Colucci, W. J.; Gandour, R. D.; Mooberry, E. A. *J. Am. Chem. Soc.* **1986**, *108*, 7141-7147.
- (14) Hiyama, Y.; Roy, S.; Guo, K.; Butler, L. G.; Torchia, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 2525-2526.
- (15) Boroske, E.; Mayas, L.; Mobius, K. *J. Magn. Reson.* **1979**, *35*, 231-246.
- (16) Weeding, T.; Kwiram, A. L.; Rawling, D. C.; Davidson, E. R. *J. Chem. Phys.* **1985**, *82*, 3516-3526.
- (17) Hartzell, C. J.; Kwiram, A. L. *J. Magn. Reson.* **1987**, *73*, 315-322.
- (18) Flygare, W. H. *Molecular Structure and Dynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1978.
- (19) Poole, C. P., Jr.; Farach, H. A. *The Theory of Magnetic Resonance*; Wiley-Interscience: New York, 1972.

[†] A portion of this work has been presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 5-10, 1987.

Table I. Crystal and Refinement Data for (4-Chlorophenyl)acetic Acid

mol formula	C ₉ H ₇ ClO ₂
MW	170.5
a, Å	15.627 (2)
b, Å	4.6182 (4)
c, Å	11.579 (3)
β, deg	108.60 (2)
V, Å ³	792.0 (4)
Z	4
D _{calcd} , g cm ⁻³	1.430
λ, Å	1.54184
cryst syst	monoclinic
space gp	P2 ₁ /c
μ, cm ⁻¹	38.85
min rel transmissn, %	46.88
intens decay, %	13.8
cryst dimens, mm	0.08 × 0.40 × 0.44
temp., °C	24
scan type	ω-2θ
2θ _{max} , deg	150
no. of reflns	1632
no. of obsd reflns	1345
observn criterion	I > 3σ(I)
no. of parameters refined	129
R (=Σ ΔF /ΣF _o)	0.055
R _w (=Σw(ΔF) ² /ΣwF _o ²) ^{1/2}	0.086
max resid density, e Å ⁻³	0.28
min resid density, e Å ⁻³	-0.34
extinction coeff	1.5 (10) × 10 ⁻⁶

**Figure 1.** ORTEP drawing of the (4-chlorophenyl)acetic acid dimer showing the atom-labeling scheme.

the methyl group orientation is varied with respect to the oxygen atoms of the carboxylic group, are fitted to Karplus-type equations. (2) A single-crystal X-ray diffraction experiment of (4-chlorophenyl)acetic acid shows two distinct C-H sites α to the carboxylic group. (3) The ADLF spectrum of (4-chlorophenyl)[2,2-²H₂]-acetic acid shows two inequivalent deuterium sites. (4) Analysis of the ADLF double transitions proves that the two inequivalent deuterium sites are bound to the same carbon atom.

Molecular Orbital Calculations

The electric field gradient tensors at the methyl hydrogen sites in acetic acid were obtained from ab initio molecular orbital calculations with the GAUSSIAN 82 program and a 6-31G** basis set.^{20,21} In this work, we have taken the deuterium nuclear quadrupole moment as 2.86×10^{-27} cm².²² The convention used

(20) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whitesides, R. A.; Schelgel, H. B.; Fluder, E. M.; Pople, J. A. *GAUSSIAN 82*; Carnegie-Mellon University: Pittsburgh, PA, 1984.

(21) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for (4-Chlorophenyl)acetic Acid^a

atom	x	y	z	B _e ^b , Å ²
Cl(1)	0.55733 (4)	0.0711 (2)	0.18353 (5)	6.82 (2)
O1	0.8933 (1)	0.4782 (5)	-0.0019 (2)	6.67 (4)
O2	0.9965 (1)	0.7827 (5)	0.1057 (2)	7.75 (5)
C1	0.9157 (1)	0.6790 (5)	0.0697 (2)	4.90 (4)
C2	0.8507 (2)	0.8338 (6)	0.1201 (2)	6.06 (6)
C3	0.7765 (1)	0.6444 (5)	0.1336 (2)	4.67 (4)
C4	0.7851 (2)	0.5110 (6)	0.2444 (2)	5.41 (5)
C5	0.7190 (2)	0.3370 (6)	0.2604 (2)	5.54 (5)
C6	0.6416 (1)	0.2891 (5)	0.1628 (2)	4.69 (4)
C7	0.6311 (2)	0.4184 (6)	0.0515 (2)	5.21 (5)
C8	0.6980 (2)	0.5938 (5)	0.0378 (2)	5.11 (5)
H(O2)	1.028 (2)	0.70 (1)	0.069 (3)	8 (1)
H1(C2)	0.827 (3)	0.984 (8)	0.061 (3)	10 (1)
H2(C2)	0.884 (2)	0.926 (6)	0.191 (2)	4.4 (6)
H4	0.837 (2)	0.550 (6)	0.308 (2)	5.1 (7)
H5	0.725 (2)	0.264 (7)	0.334 (2)	4.2 (6)
H7	0.574 (2)	0.390 (6)	-0.008 (2)	4.1 (6)
H8	0.690 (2)	0.685 (7)	-0.041 (2)	4.0 (6)

^aHydrogen atoms refined isotropically. ^bThe equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation $\frac{1}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12} \cos \gamma + acB_{13} \cos \beta + bcB_{23} \cos \alpha]$.

Table III. Bond Distances and Angles in (4-Chlorophenyl)acetic Acid

Distances (Å)			
Cl(1)-C6	1.734 (1)	C3-C8	1.387 (2)
O1-C1	1.218 (2)	C4-C5	1.368 (2)
O2-C1	1.289 (2)	C4-H4	0.92 (2)
O2-H(O2)	0.84 (3)	C5-C6	1.384 (2)
C1-C2	1.504 (2)	C5-H5	0.89 (2)
C2-C3	1.499 (2)	C6-C7	1.382 (2)
C2-H1(C2)	0.96 (3)	C7-C8	1.372 (2)
C2-H2(C2)	0.92 (2)	C7-H7	0.94 (2)
C3-C4	1.391 (2)	C8-H8	0.98 (2)
Angles (deg)			
C1-O2-H(O2)	110 (2)	C3-C4-H4	117 (1)
O1-C1-O2	122.8 (1)	C5-C4-H4	121 (1)
O1-C1-C2	122.9 (1)	C4-C5-C6	118.9 (1)
O2-C1-C2	114.3 (2)	C4-C5-H5	120 (1)
C1-C2-C3	113.8 (2)	C6-C5-H5	121 (1)
C1-C2-H1(C2)	103 (2)	C1-C6-C5	118.9 (2)
C1-C2-H2(C2)	107 (1)	C1-C6-C7	120.7 (1)
C3-C2-H1(C2)	111 (2)	C5-C6-C7	120.4 (2)
C3-C2-H2(C2)	115 (1)	C6-C7-C8	119.6 (1)
H1(C2)-C2-H2(C2)	106 (2)	C6-C7-H7	115 (1)
C2-C3-C4	120.3 (2)	C8-C7-H7	125 (1)
C2-C3-C8	122.1 (1)	C3-C8-C7	121.3 (1)
C4-C3-C8	117.6 (1)	C3-C8-H8	119 (1)
C3-C4-C5	122.0 (2)	C7-C8-H8	120 (1)

herein for reporting the electric field gradient is $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$.¹⁹ The acetic acid dimer geometry was taken from the literature,²³ all conformations of the dimer had at least a center of symmetry. As a brief check of superposition error, some conformations of the dimer were studied with a 6-31G basis set,²⁴ while some monomer conformations were examined with both 6-31G and 6-31G** basis sets. Minor changes in the deuterium quadrupole coupling constant and asymmetry parameter were found with the smaller basis set, but, most importantly, the orientation of the electric field gradient tensor was not affected. No corrections were made for vibrational effects that are expected to slightly reduce the magnitude of the electric field gradient tensor elements.²⁵

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

(23) (a) Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 6572-6575. (b) Nagaoka, S.-I.; Hirota, N.; Matsushita, T.; Nishimoto, K. *Chem. Phys. Lett.* **1982**, *92*, 498-502.

(24) Hehre, W. J.; Ditchfield, D.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261.

(25) Kern, C. W.; Matcha, R. L. *J. Chem. Phys.* **1968**, *49*, 2081-91.

Experimental Section

Sample Preparation. (4-Chlorophenyl)acetic acid (Aldrich, recrystallized from ethanol/water) was deuteriated at the methylene site by refluxing in $\text{LiO}^2\text{H}^2/\text{H}_2\text{O}$ for 6 days; the product was isolated by neutralization with H_2SO_4 and recrystallization from 10% ethanol in water. Integration of the solution ^1H NMR spectra showed $\sim 90\%$ deuteriation at the methylene site; no other sites were deuteriated.

Crystallographic Work. Crystals for X-ray crystallography were grown from a 1:1 mixture of ethanol/water held at 5°C for 2 weeks. Diffraction data were obtained on an Enraf-Nonius CAD4 diffractometer equipped with $\text{Cu K}\alpha$ radiation and a graphite monochromator. Experimental parameters are given in Table I. Data reduction included corrections for Lorentz, polarization, background, and absorption effects. Absorption corrections were based on Ψ scans. The structure was solved by heavy-atom methods and refined by full-matrix least squares based on F with weight $w = \sigma^{-2}(F_o)$ using the Enraf-Nonius SDP programs.²⁶ Non-hydrogen atoms were treated anisotropically; hydrogen atoms were located in difference maps and refined isotropically. Final R factors are given in Table I; atomic positions are listed in Table II. Figure 1 shows the atom-labeling scheme. Bond distances and angles are listed in Table III.

ADLF Spectroscopy. The ADLF spectra of (4-chlorophenyl)[2,2- $^2\text{H}_2$]acetic acid were obtained on a home-built spectrometer.²⁷ The instrument consists of an IBM 9000 computer (68 000 CPU, 1-Mbyte RAM), a CAMAC crate holding 12 CAMAC modules, and a Novex wide-band transceiver, preamplifier, and 15-MHz 400-W power amplifier. The computer controls the CAMAC crate via an IEEE-488 bus using custom software composed of approximately 5000 lines written in Pascal. Special CAMAC modules include dual 20-MHz 8-bit digitizers coupled to 24-bit by 8K signal averagers, a home-made pulse programmer with 100-ns resolution and 1024 steps, and several interface boards that allow the computer to control the amplitude and frequency of the zero-field rf irradiation.²⁸ The high-field magnet is a Varian XL100 electromagnet with a 0–120 A power supply. Both the high-field and zero-field rf coils along with the sample transport tube are mounted in a liquid nitrogen Dewar. A region of zero-field or small applied magnetic field is maintained by a Helmholtz coil. The zero-field is calibrated with a gaussmeter and checked against the deuterium ADLF spectrum of acetamide.²⁹

All spectra were obtained at 77 K. The high-field strength was 0.3 T, corresponding to a frequency of 15 MHz (^1H). The 90° pulse length for ^1H was $4\ \mu\text{s}$ with a probe ringdown time of approximately $10\ \mu\text{s}$. The signal was acquired with an Ostroff-Waugh pulse sequence set to generate 128 spin echoes;³⁰ each echo is individually digitized. The zero-field rf amplitude was 0.034 G peak for single quantum spectra and 1.9 G peak for the double-transition spectra.

The deuterium fine structure^{29,31–36} in the ADLF spectrum was analyzed with Ragle's program.³⁶ The electric field gradient tensor orientation with respect to the molecular coordinate system was taken from an acetic acid dimer calculation with a conformation set to yield the same torsion angles as found in the crystal structure of (4-chlorophenyl)acetic acid. The calculated electric field gradient tensor orientations were adjusted to give a right-handed coordinate system prior to using the Ragle program.

Results and Discussion

On the basis of the significant difference between the C1-O1 and C1-O2 bond distances (Table III) and on the correlation noted by Dieterich et al.,³⁷ there appears to be little crystallographic

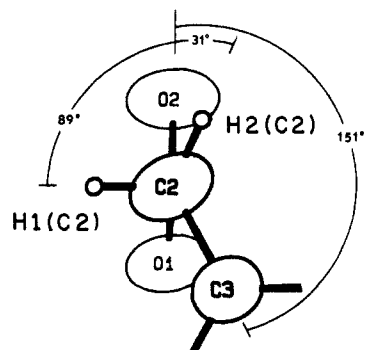


Figure 2. Relative orientation of the carboxyl acid group and the CH_2 unit of (4-chlorophenyl)acetic acid. Viewed along the C2-C1 bond. The acid carbon, C1 , is hidden from view by C2 .

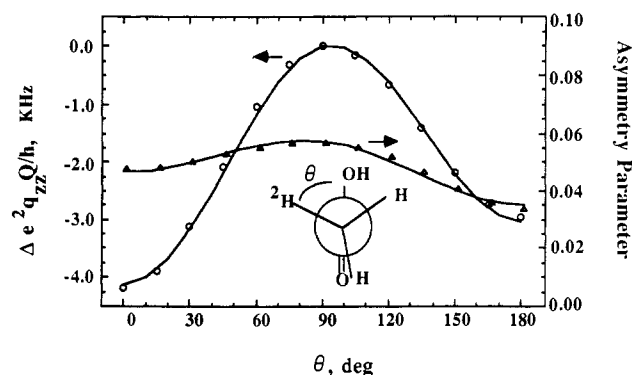


Figure 3. Calculated deuterium quadrupole coupling constants and asymmetry parameters for the acetic acid dimer as a function of the $^2\text{H-C-C-OH}$ dihedral angle: \circ , $\Delta e^2q_{zz}Q/h$; Δ , asymmetry parameter. The solid lines are based on the Karplus-type equations, eq 3 and 4, given in the text.

disorder of the type that would result in an interchange of C-OH and C=O sites in the carboxyl group in (4-chlorophenyl)acetic acid. Thus, we conclude that O2 is the hydroxyl oxygen site and O1 the carbonyl. This assignment is supported by the location and refinement of the acid H atom. When we assume tetrahedral geometry at C2 , the torsion angles shown in Figure 2 are related by an angle of 120° to the O2-C1-C2-C3 torsion angle, $150.6(2)^\circ$. Figure 2 shows a portion of the $\text{CH}_2(\text{C}_6\text{H}_4\text{Cl})$ unit viewed along the C2-C1 bond and the torsion angles for the two inequivalent methylene hydrogen atoms.

The calculated deuterium quadrupole coupling constant and asymmetry parameters for an acetic acid dimer are shown in Figure 3. To minimize the basis set dependence, the acetic acid results are plotted as the change in the deuterium quadrupole coupling constant. The reference value ($e^2q_{zz}Q/h = 218.2\ \text{kHz}$) is for a deuterium site rotated so as to give maximum distance from the oxygen atoms to the deuterium site and corresponds to a torsion angle, θ , of 90° . We note that there is a large variation in $\Delta e^2q_{zz}Q/h$ with rotation angle; it reaches a maximum of $-4.2\ \text{kHz}$ for a deuterium at closest approach to the hydroxyl oxygen site, $\theta = 0^\circ$. The points shown in Figure 3 were fitted by Karplus-type equations to give eq 3 and 4. Because of the tendency

$$e^2q_{zz}Q/h = A - 0.5491 \cos \theta - 1.7859 \cos 2\theta \quad (3)$$

$$\eta = 0.0491 + 0.0058 \cos \theta - 0.0081 \cos 2\theta \quad (4)$$

for calculated deuterium quadrupole coupling constants to be larger than experimental values,^{9,38,39} the A parameter of eq 3 will be determined by use of experimentally derived deuterium quadrupole coupling constants.

(26) Frenz, B. A. *Enraf Nonius Structure Determination Package SDP/VAX V3.0*; Enraf-Nonius: Delft, Holland, copyright 1985.

(27) A similar, but non-computer-controlled instrument is described in: Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 2327–2334.

(28) Butler, L. G.; Reiner, C. A.; Brown, T. L. *Rev. Sci. Instrum.* **1982**, *53*, 984–988.

(29) Edmonds, D. T.; Hunt, M. J.; MacKay, A. L. *J. Magn. Reson.* **1973**, *11*, 77–82.

(30) Ostroff, E. D.; Waugh, J. S. *Phys. Rev. Lett.* **1966**, *16*, 1097–1098.

(31) Edmonds, D. T.; Hunt, M. J.; MacKay, A. L. *J. Magn. Reson.* **1975**, *20*, 505–514.

(32) Edmonds, D. T.; White, A. A. L. *J. Magn. Reson.* **1978**, *31*, 149–159.

(33) d'Avignon, D. A.; Brown, T. L. *J. Phys. Chem.* **1981**, *85*, 4073–4079.

(34) Day, R. O.; Hadipour, N.; Ragle, J. L. *J. Magn. Reson.* **1984**, *57*, 369–384.

(35) Day, R. O.; Hadipour, N.; Ragle, J. L. *J. Magn. Reson.* **1984**, *59*, 373–380.

(36) Hadipour, N.; Ragle, J. L. *Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys.* **1985**, *40A*, 355–360.

(37) Dieterich, D. A.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1974**, *96*, 6372–6380.

(38) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977.

(39) Zamani-Khamiri, O.; Hameka, H. F. *J. Chem. Phys.* **1981**, *75*, 781–786.

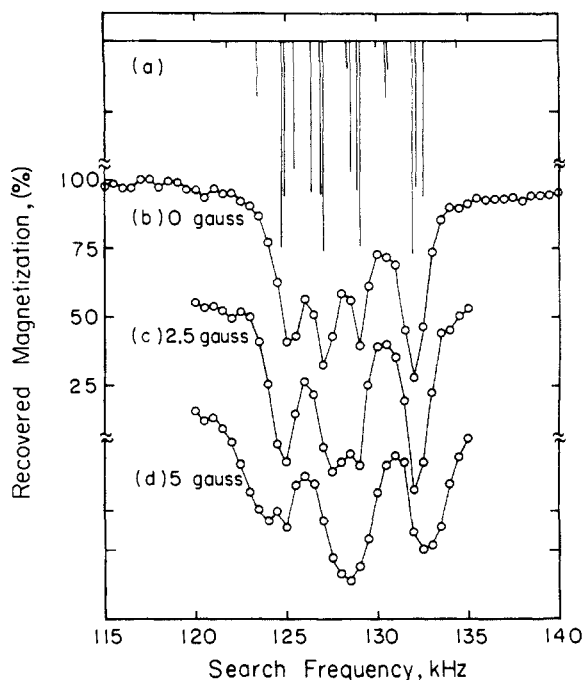


Figure 4. Deuterium ADLF spectra of (4-chlorophenyl)[2,2- $^2\text{H}_2$]acetic acid taken at 77 K with 0.5-kHz search frequency increments. (a) The calculated fine structure for a C^2H_2 unit. Initial assignment of transitions based upon frequency shifts caused by a small applied magnetic field: (b) 0 G; (c) 2.5 G, (d) 5 G.

On the basis of the torsion angles shown in Figure 2 and on the Karplus-type equation, eq 3, for predicting the deuterium quadrupole coupling constant, the high-resolution, zero-field ADLF spectrum of (4-chlorophenyl)[2,2- $^2\text{H}_2$]acetic acid should show two different sets of deuterium ν_- and ν_+ transitions. While four transitions are indeed observed, as shown in Figure 4, the assignment is not straightforward. The methods used for spectral interpretation are similar to those applied to other coupled deuterium spin systems: (1) Zeeman-perturbed ADLF spectroscopy and (2) analysis of the deuterium–deuterium induced fine structure and double transitions. Application of small magnetic fields causes the ν_- and ν_+ transitions to be asymmetrically broadened in a characteristic fashion; the ν_- transition is broadened to lower frequency, the ν_+ to higher frequency.⁴⁰ By this technique, the peaks at 125.0 (7) and 129.0 (7) kHz are identified as the ν_- transitions and the ones at 127.0 (7) and 132.0 (7) kHz as the ν_+ transitions.

Observation of deuterium–deuterium dipolar coupling induced fine structure and double transitions were used to assign the ν_- transition of a deuteron to its corresponding ν_+ transition. Figure 5 shows the observed double-transition spectrum together with the calculated transition frequencies and relative intensities.^{29,31–36} The fine structure shown in Figure 4 (top trace) contributes to the rather large line width, $\Delta\nu \sim 1.5$ kHz, in the 0-G spectrum. The observation of double transitions conclusively shows that the two deuterium sites are in close proximity, less than several angstroms from each other. Also, the form of the double-transition spectrum is incompatible with other possible explanations for two distinct deuterium sites, for instance, two crystallographic modifications of (4-chlorophenyl)acetic acid.

The deuterium ADLF spectroscopy and structural data for (4-chlorophenyl)[2,2- $^2\text{H}_2$]acetic acid are summarized in Table IV. The assignment of the site with the larger value of the deuterium quadrupole coupling constant to the deuteron with a torsion angle of 89° is based upon the Karplus-type relationship given in eq 3. The “ C^2H distant” from an oxygen atom site has a value of the deuterium quadrupole coupling constant that is similar to values found in simple hydrocarbons. For comparison, the C^2H_2 unit in [9,9- $^2\text{H}_2$]fluorene has a deuterium quadrupole

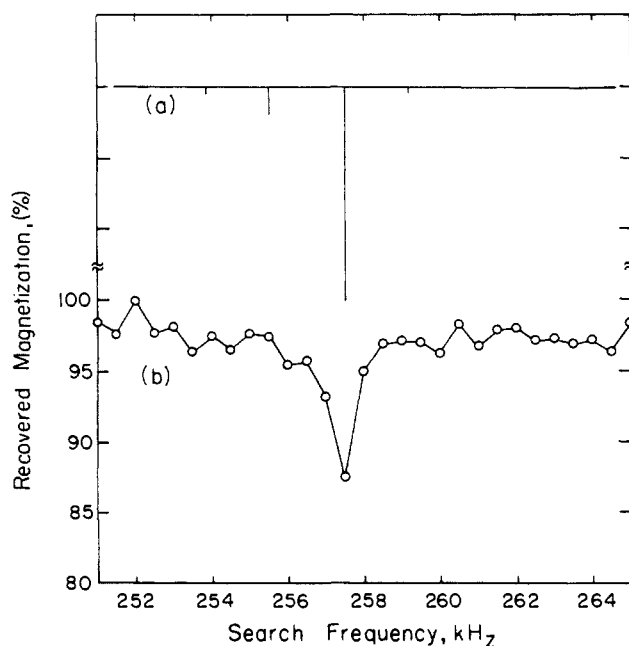


Figure 5. Deuterium double-transition ADLF spectra: (a) calculated double-transition spectrum for a C^2H_2 unit; (b) experimental spectrum taken at 77 K with 0.5-kHz search frequency increments.

Table IV. Deuterium Quadrupole Coupling Constants, Asymmetry Parameters, and Structural Data for (4-Chlorophenyl)[2,2- $^2\text{H}_2$]acetic Acid

	C^2H distant	C^2H near
$d(\text{O} \cdots ^2\text{H})$, ^a Å	2.70 (3)	2.36 (2)
θ , ^b deg	89	31
ν_+	132.0 (7)	127.0 (7)
ν_-	129.0 (7)	125.0 (7)
$e^2q_{zz}Q/h$, kHz	174.0 (9)	168.0 (9)
η	0.034 (16)	0.024 (17)

^aDistance from deuteron to nearest oxygen atom. ^b θ is the torsion angle between the hydroxyl oxygen and the deuteron as defined in Figures 2 and 3.

coupling constant of 173 (1) kHz.⁴¹

In the foregoing analysis, the effect of the phenyl substituent on the C^2H_2 unit has been ignored. This approach is justified on two counts: First, molecular orbital calculations of toluene have shown that there is only a small perturbation of the aliphatic C^2H bonds that is caused by the aromatic π -electrons or the ortho hydrogens.¹⁴ Second, in (4-chlorophenyl)acetic acid, the $\text{C}1\text{--C}2\text{--C}3\text{--C}4$ torsion angle is $94.8 (3)^\circ$. This angle is very close to 90° , an orientation that places both methylene hydrogens in equivalent positions with respect to the phenyl ring.

The ADLF and structural data for (4-chlorophenyl)[2,2- $^2\text{H}_2$]acetic acid were used to obtain a preliminary value for the A parameter of eq 3 as 170.767 kHz. All values of the parameters obtained from the acetic acid calculations should be regarded as preliminary until confirmed by experiment as inductive effects from substituents and steric effects may modify the results.

Conclusions

Neighboring oxygen atoms can affect the deuterium quadrupole coupling constant of C^2H bonds. In acetic acid and substituted acetic acids, the magnitude of the effect is related to the $^2\text{H}\text{--C}\text{--C}\text{--OH}$ torsion angle. A Karplus-type equation fits the calculated values well.

In summary, the oxygen-perturbed C^2H site has a substantially different quadrupole coupling constant than do unperturbed C^2H sites. As noted by Hiyama et al.¹⁴ neighboring oxygen atoms have an unexpected effect on the solid-state deuterium NMR spectrum

(40) Edmonds, D. T. *Phys. Rep.* 1977, 29C, 233–290.

(41) Altbach, M. I.; Hiyama, Y.; Gerson, D. J.; Butler, L. G. *J. Am. Chem. Soc.* 1987, 109, 5529–5531.

of deuteriated methyl groups. This work provides further confirmation of their report.

The fact that the calculated deuterium quadrupole coupling constants and asymmetry parameters of acetic acid dimer can be fitted by a Karplus-type equation is very interesting. Heretofore, there were no reported methods for correlating deuterium quadrupole coupling constants with solid-state structural features. Further work is now in progress to refine experimental values for the parameters *A*, *B*, and *C*. It should be straightforward to extend the method to other functional groups, for example, esters, ketones, and sulfones.

Acknowledgment. The support of the Research Corp., the Petroleum Research Fund, administered by the American

Chemical Society, and the LSU Center for Energy Studies is gratefully acknowledged. Purchase of 100- and 400-MHz NMR spectrometers was made possible by an NIH shared instrumentation grant (1 S10 RR02459-01). The purchase of the Enraf-Nonius CAD4 diffractometer was made possible by an NSF instrumentation grant (CHE-8500781). We thank Drs. Dennis A. Torchia and Yukio Hiyama for their encouragement with this work and Dr. John L Ragle for his spectral simulation program.

Supplementary Material Available: Listings of anisotropic thermal parameters and torsion angles for (4-chlorophenyl)acetic acid (3 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Dynamics of H₂ Elimination from the Methaniminium Cation, [CH₂NH₂]⁺. Isotope Effects, Translational Energy Release, and Molecular Orbital Calculations

Kevin F. Donchi,[†] Bruce A. Rumpf,[†] Gary D. Willett,^{*†} John R. Christie,[‡] and Peter J. Derrick^{*†}

Contribution from the School of Chemistry, University of New South Wales, Kensington, 2033, New South Wales, Australia, and Department of Chemistry, La Trobe University, Bundoora, 3083, Victoria, Australia. Received May 1, 1987

Abstract: Various molecular orbital methods have been used to examine possible reaction mechanisms for the unimolecular decomposition [CH₂NH₂]⁺ → [HCNH]⁺ + H₂. Measurements of deuterium isotope effects on the translational energy release indicate the nonequivalence of the two departing hydrogen atoms, as does the reported absence of hydrogen scrambling in the products of this decomposition. The semiempirical calculations and the ab initio calculations up to and including the 6-31G** level predict that the departing hydrogen atoms do become equivalent and indistinguishable and that there will be significant hydrogen scrambling. This paradox is resolved on the grounds that geometries corresponding to stationary points in these calculations would not be stationary were a degree of configuration interaction to be included. The overall conclusion reached is that the transition state for elimination for H₂ from [CH₂NH₂]⁺ is an asymmetric nonplanar structure with a geometry not far distant from [CH₃NH]⁺, which is not a stable minimum on the potential surface.

The power of molecular orbital calculations in the determination of stable structures of small gaseous organic ions is now well established.¹⁻³ Procedures for identifying cols on the potential energy surfaces are established,⁴ but the significance of the findings is not always clear-cut.⁵ A particular challenge arises when the results of molecular orbital calculations are to be used to elucidate reaction dynamics. In this paper, we present results of extensive ab initio and semiempirical methods of calculation pertaining to the [CH₂NH₂]⁺ potential energy surface, which suggest that the loss of H₂ from the methaniminium ion, [CH₂NH₂]⁺, proceeds via a symmetrical 1,1-elimination transition structure. Experimental results concerning the reaction dynamics indicate unequivocally that the transition structure for this elimination of H₂ is asymmetric. The paradox is explored and resolved on the grounds that cols located using the GAUSSIAN 82 ab initio molecular orbital package with the 6-31G** basis set would not be features of a more accurate potential energy surface.

Interest in H₂ eliminations from small organic ions was stimulated by the proposal of Williams and Hvistendahl⁶ that the large translational energy releases observed for many such reactions could be accounted for in terms of molecular orbital symmetry arguments. The elimination of H₂ was proposed to be a sym-

metry-forbidden synchronous⁷ 1,2-elimination. Supporting the proposals were the observation that [CH₂ND₂]⁺ ions eliminated only HD and certain measurements of isotope effects on ion abundances.^{6,8} A col corresponding to a planar and almost symmetric 1,2-elimination transition structure was located in an ab initio molecular orbital study.⁹ However, this result is of questionable validity as the search considered only a restricted subset of planar geometries. The proposals put forward by Williams and Hvistendahl⁶ can be separated into two parts. First, there is the argument that orbital symmetry creates a hump along the reaction pathway, so that there is a reverse critical energy

(1) Baer, T. In *Mass Spectrometry* (A Specialist Periodical Report); Johnstone, R. A. W., Ed.; Royal Society of Chemistry: London, 1981; Vol. 6; pp 1-56.

(2) Pople, J. A. *Int. J. Mass Spectrom. Ion Phys.* 1976, 19, 89-106.

(3) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(4) (a) Pulay, P. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977, Vol. 4. (b) Kato, S.; Morokuma, K. *Chem. Phys. Lett.* 1979, 65, 19-25.

(5) Lorquet, J. C. In *Mass Spectrometry*, (A Specialist Periodical Report); Johnstone, R. A. W., Ed.; Royal Society of Chemistry: London, 1984, Vol. 7, pp 63-78.

(6) Williams, D. H.; Hvistendahl, G. *J. Am. Chem. Soc.* 1974, 96, 6753-6755.

(7) Dewar, M. J. S. *J. Am. Chem. Soc.* 1984, 106, 209-219.

(8) Williams, D. H. *Acc. Chem. Res.* 1977, 9, 7432.

(9) Saebo, S. *Chem. Phys. Lett.* 1977, 47, 564-568.

[†]University of New South Wales.

[‡]La Trobe University.

*Address correspondence to: Department of Chemistry, University of Warwick, Coventry CV4 7AL, England.