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Studies in Nuclear Magnetic Resonance Spectroscopy. 17.¹ Deuteron Quadrupole Coupling Constants in Intramolecularly Hydrogen Bonded Systems

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Abstract: The ¹³C spectra of salicylaldehyde, 5-methoxysalicylaldehyde, 2-hydroxy- and 2-hydroxy-5-methoxyacetophenone, and methyl esters of anthranilic, salicylic, and 2-mercaptobenzoic acids, 1-hydroxyfluorenone, 2,3-dihydro-9-hydroxy- and 9-hydroxyphenalenone, tropolone, 1-phenylamino-7-phenylimino-1,3,5-cycloheptatriene, 6-hydroxypentafulvene-1-aldehyde, 1-benzoyl-6-phenyl-6-hydroxypentafulvene, *N,N'*-diphenyl-6-aminopentafulvene-2-alimine, and the 18-crown-6 complex of potassium hydrogen phthalate in chloroform, bromoform, or methylene dichloride solutions have been analyzed and the spin-lattice relaxation times (T_1) of the proton-bearing carbon atoms determined. The T_1 's have been used to calculate the rotational diffusion parameters assuming that the molecules diffuse as uncoupled planar rotors. It is shown that, although the anisotropies of rotational diffusion correlate well with that of the moments of inertia, the J -diffusion model overestimates the absolute magnitudes of the former. The deuteron T_1 's for the deuterium-replaced hydrogen-bonded systems have been determined and used together with the rotational diffusion parameters to evaluate the deuteron quadrupole coupling constants (DQCC). The DQCCs are shown to be linearly related to the squares of stretching frequencies for the corresponding X-H bonds. With the exception of potassium hydrogen phthalate, the last seven compounds listed above involve hydrogen bonds with double-well potentials and, in the cases of tropolone and its bisphenylaza analogue, exchange between the tautomers is shown to be slower than rotational diffusion.

The nature of the intramolecular hydrogen bond and, more specifically, the potential function for the proton continue to attract the attention of many investigators. In the past 2 decades virtually every physicochemical technique has been employed in such studies. Notable contributions to our understanding of the hydrogen bond have come from investigations involving neutron,³ electron,⁴ and X-ray diffraction,³ infrared,³ microwave,⁵ and ESCA⁶ spectroscopy (or X-ray PES), and a variety of NMR techniques³ including measurements of hydrogen-deuterium-tritium isotope effects,⁷ ¹³C relaxation times,⁸ and deuteron quadrupole coupling constants (DQCC).^{3,9,10} The values of DQCC in various hydrogen-bonding situations are particularly informative since, like stretching force constants, they probe the electrostatic environment of the deuteron in such situations.

The majority of the determinations of DQCCs have involved deuteron NMR measurements on oriented single crystals and have the advantage that they allow the evaluation of the field gradient asymmetry parameter, $\eta = (q_{xx} - q_{yy})/q_{zz}$ as well as DQCC (e^2Qq_{zz}/h). In certain circumstances, associated studies of DQCCs near the Curie point for the ferroelectric-paraelectric phase transition have provided evidence concerning the rate of exchange of the deuteron between the two donor sites. One disadvantage of the solid-state method is that it has been applicable only to molecules with very few nonexchangeable protons, although recent techniques for removal of dipolar broadening due to these protons may lift this restriction. A more serious problem arises because crystal packing forces may dictate a particular type of intermolecular

hydrogen bonding rather than the intramolecular interaction under investigation. This is true, for example, of potassium hydrogen phthalate, which is not intramolecularly hydrogen bonded in the crystalline state. Thus solution studies offer definite advantages.

There has been one investigation of the DQCC of a hydrogen-bonded deuteron in solution. Egan, Gunnarsson, Bull, and Forsén¹⁰ have determined the value of DQCC in the enol tautomer of acetylacetone-3-*O-d*₂ from measurements of deuteron relaxation times together with certain assumptions regarding rotational diffusion. They showed unequivocally that the intramolecular hydrogen bond in this molecule involves a symmetric double well potential.

We have now investigated DQCCs in systems involving intramolecular hydrogen bonds of various strengths. Because the molecules studied are more complex than acetylacetone, we have been able to use ¹³C relaxation times to take explicit account of anisotropy of rotational diffusion.

Experimental Section

Materials. Unless otherwise stated materials were obtained from commercial sources. Solids were purified by recrystallization and/or vacuum sublimation and had melting points in agreement with the literature values.

Bromoform-*d*. A 10% solution (10 mL) of NaOD in D₂O containing triethylbenzylammonium chloride (0.5 g) was shaken with bromoform (100 g) in a separating funnel. The organic layer was removed and subjected to five additional treatments under the same conditions. It was then washed twice with D₂O (10 mL), dried over Linde molecular

Table I. Carbon-13 Chemical Shifts (ppm) and Proton Chemical Shifts (ppm) and Coupling Constants (Hz) for Compounds 1-7 at 90 MHz

	R X H ^{a-c} R' O	CH ₃ ^b O	OCH ₃ O	OCH ₃ N	OCH ₃ ^{a,d} S	H ^e O 5-OCH ₃	CH ₃ ^e O 4-OCH ₃
δ_3 (C)	117.1	118.0	117.2	110.3	131.3	118.1	100.5
δ_4 (C)	136.6	136.1	135.3	134.3	132.0	124.7	
δ_5 (C)	119.5	118.6	118.8	114.4	124.2		107.2
δ_6 (C)	133.4	130.4	129.6	131.2	130.5	114.9	132.0
δ_3 (H)	6.97	6.95	6.96	6.63	7.30	6.82	6.28
δ_4 (H)	7.50	7.44	7.42	7.35	7.30	7.04	
δ_5 (H)	7.00	6.88	6.85	6.56	7.14		6.31
δ_6 (H)	7.53	7.71	7.81	7.88	8.00	6.90	7.51
$J_{3,4}$	8.39	8.50	8.40	8.42	7.94	9.08	
$J_{3,5}$	1.00	1.14	1.23	1.13	1.23		2.46
$J_{3,6}$	0.46	0.33	0.47	0.44	0.44	-0.30	0.71
$J_{4,5}$	7.23	7.21	7.27	7.03	7.40		
$J_{4,6}$	1.74	1.69	1.80	1.70	1.51	3.07	
$J_{5,6}$	7.69	8.11	7.99	8.02	7.98		9.03

^a From 360-MHz spectra. ^b $J_{4,OH} = 0.4$ Hz. ^c $J_{3,CHO} = 0.6$ Hz. ^d $J_{6,SH} = 0.4$ Hz. ^e From 60-MHz spectra.

sieve, and then distilled (bp 143.5–145 °C (724 Torr)). The isotopic purity was found to be >97% by ¹H NMR.

Methyl *N*-Methylantranilate. This ester was prepared in 75% yield by passing anhydrous HCl through a 0.65 M solution of the corresponding acid in methanol. The solvent was removed and the residue distilled (bp 73 °C (0.05 mm)).

Methyl *o*-Mercaptobenzoate. This compound (bp 91 °C (0.5 mm)) was prepared by the same method.

Phenylamino-7-phenylimino-1,3,5-cycloheptatriene (11). This was prepared by the method of Brasen, Holmquist, and Benson.¹¹ Recrystallization of the crude product from aqueous methanol afforded the pure compound as yellow crystals (mp 82–84 °C). **2,3-Dihydro-9-hydroxyphenalenone (9),¹² 9-hydroxyphenalenone (12),¹² 6-hydroxypentafulvene-1-aldehyde (13),¹³ 1-benzoyl-6-phenyl-6-hydroxypentafulvene (14),¹⁴ and *N,N'*-diphenyl-6-aminopentafulvene-2-alimine (15)¹⁵** were prepared by the methods described in the literature.

Deuteration. The liquid compounds 1–7 were shaken twice with D₂O, dried over Linde 4 Å molecular sieve, and distilled under reduced pressure through a Vigreux column.

Solids were dissolved in chloroform or ether and shaken twice with D₂O. After removal of the solvent the products were purified by vacuum sublimation. In the cases of 6-hydroxyfulvene-1-aldehyde (13) and its diphenyl analogue (14), deuteration was effected by conversion to the anions in alkaline D₂O followed by neutralization with 1.25 M phosphoric acid-*d*₃.

Sample Preparation. The samples for NMR spectroscopy were prepared as solutions (0.35–1.2 M) in chloroform containing 5% hexafluorobenzene and a capillary filled with acetone-*d*₆. For compounds 1–7, the solutions were degassed by four freeze-pump-thaw cycles. For the remaining compounds the solvent was degassed first and then line transferred into the NMR tube containing the acetone capillary and the solid sample.

A solution of potassium hydrogen phthalate was prepared by transferring degassed methylene chloride onto an equimolar mixture of carefully dried 18-crown-6 and the phthalate salt. The solvent was then removed and the residue heated overnight at 52 °C and a pressure of 0.001 Torr to ensure complete drying. Fresh, degassed methylene chloride containing hexafluorobenzene (4% v/v) was line transferred onto the residue.

NMR Spectroscopy. Unless otherwise mentioned, all spectra were obtained with a JEOL PS-100-FT interfaced with a Nicolet 1080 computer and operating in the quadrature phase detection mode. The ¹³C probe utilized a deuteron field frequency lock provided by capillary samples of acetone-*d*₆. The ²H probe was operated with a fluorine lock using hexafluorobenzene as the lock reference. All measurements were made at 26 ± 0.5 °C.

The relaxation measurements were made using the standard inversion-recovery sequence. The H₁ homogeneity of both probes is excellent and no correction was needed. Usually about 16 τ values arranged in random order were used with a recovery time of 5T₁. The values of T₁'s and their precision indices were obtained by a two-parameter least-squares analysis of peak heights vs. τ values. Occa-

sionally one or two points were rejected on an approximate χ^2 basis.

Infrared Spectroscopy. Spectra were obtained using a PE580 IR spectrophotometer and were calibrated against polystyrene. The measurements were made over a concentration range of 0.01–0.1 M in spectrograde carbon tetrachloride.

Results

¹³C Spectral Assignments. The method for determining the deuteron quadrupole coupling constants discussed below requires the unambiguous assignments of the ¹³C resonances of all proton-bearing carbon atoms for each molecule investigated. These assignments have been made using decoupling techniques, as well as the values of long-range coupling constants ($J_{C,H}$). In many cases it is first necessary to analyze and assign the proton spectrum. The bases for assignments are now briefly summarized.

Carbonyl Derivatives of Benzene. The seven derivatives listed in Table I were investigated. The assignments of the proton spectra are based on complete analysis using LAOCN3 and the assumption that H(6) which is ortho to the carbonyl substituent is deshielded with respect to H(3). The assignments of the proton-bearing carbon atoms followed from a series of single-frequency off-resonance decoupling (SFORD) experiments. The resonances of C(3) and C(4) of methyl *o*-mercaptobenzoate (5) could not be assigned by this technique owing to the near degeneracy of the absorptions of the corresponding protons. However, full analysis of the multiplets in the fully coupled ¹³C spectrum permitted unequivocal assignments.

The long-range couplings of the labile proton to the ring protons merit comment. Values of 0.6 and 0.4 Hz were found for $^5J_{3,CH=O}$ and $^5J_{4,OH}$ in salicylaldehyde which agree well with previously published values¹⁶ where both interactions involve a planar zigzag pathway. $^5J_{4,OH} = 0.4$ Hz was also observed for *o*-hydroxyacetophenone. Splittings of this type were absent in spectra of methyl salicylate and methyl *N*-methylantranilate, presumably because of rapid exchange. In contrast, methyl *o*-mercaptobenzoate has $^5J_{6,SH} = 0.4$ Hz whereas $^5J_{4,SH} < 0.2$ Hz. On the basis of the correlations established by Schaefer and Parr,¹⁷ it would seem that the molecule does not have an intramolecular hydrogen bond, the SH group adopting the conformation *s-trans* to the ortho substituent. Salicylaldehyde and *o*-hydroxyacetophenone (and presumably the esters 3 and 4) have the *s-cis* conformation in keeping with the presence of reasonably strong intramolecular hydrogen bonds.^{18,19}

Compounds 8–16.²⁰ We have previously assigned the ¹³C

spectrum of 1-hydroxyfluorenone (**8**).⁸ The aromatic region of the 360-MHz ¹H spectrum²¹ of 2,3-dihydro-9-hydroxyphenalenone (**9**) was fully analyzed. The only ambiguity was the assignment to H(4) and H(6), which was resolved through the observation that the absorption of the former exhibited coupling to the 3-methylene protons which could be removed by selective decoupling. SFORD experiments then furnished the ¹³C assignments. Similar experiments lead to the ¹³C assignments for 9-hydroxyphenalenone (**12**) itself, apart from a possible ambiguity in the assignment to H(3), H(7), and H(2), H(8). Distinction between these two was possible because the absorption of C(3), but not of C(2), exhibited splitting due to a three-bond coupling (³J_{13C,H} = 5 Hz) in the gated fully coupled spectrum.

The ¹³C resonances of tropolone (**10**) have been assigned previously on the basis of calculated charge densities.²² We have confirmed these results by SFORD experiments using the results of a fully analyzed proton spectrum.²³ The protons of the seven-membered ring of 1-phenylamino-7-phenylimino-1,3,5-cycloheptatriene (**11**) exhibit a readily analyzed absorption pattern which is at higher fields than those of the phenyl rings so that the corresponding ¹³C resonances could be assigned by SFORD experiments. The ¹³C resonance of the para carbon atoms of the phenyl rings, which was included in the determination of the rotational diffusion parameters, was assigned on the basis of its intensity relative to those of the ortho and meta positions.

Considerations of intensities and SFORD experiments lead to unequivocal assignments of the ¹³C spectrum of 6-hydroxyfulvene-1-aldehyde (**13**), the proton spectrum of which has been previously reported.²⁴ The assignments of the analogous diphenyl derivative (**14**) and of *N,N'*-diphenyl-6-aminofulvene-2-aldimine (**15**) follow from similar arguments. SFORD experiments were necessary to distinguish the resonances of 3- and 5-carbon atoms of the five-membered ring from that of the para carbon atoms of the phenyl substituents.

The proton spectrum of the 18-crown-6 complex of potassium hydrogen phthalate was analyzed and provided the basis of the SFORD experiments used for the ¹³C assignments.

Determination of Deuteron Quadrupole Coupling Constants.

All the systems studied here are assumed to undergo rotational diffusion as planar asymmetric rotors, at least as far as the nuclei involved in the relaxation processes investigated. For such systems, the relation between the deuteron spin-lattice relaxation time, T_1^Q , and the quadrupole coupling constant with its associated asymmetry parameter, η , is given by the equation derived by Huntress for a planar, uncoupled rotor,^{25,26}

$$1/T_1^Q = [3(2I + 3)/40I^2(2I - 1)] (1 + \eta^2/3) \times (e^2Qq_{zz}/h)^2 (A \cos^2 \Psi + B \sin^2 \Psi) \quad (1)$$

where Ψ is the angle which the principal electric field gradient subtends with one of the principal in-plane axes of rotational diffusion. $A = [3(D_x + D_z)]^{-1}$ and $B = [3(D_x - D_z)]^{-1}$ in which D_x , D_y , and D_z are the elements of the diagonalized diffusion tensor.

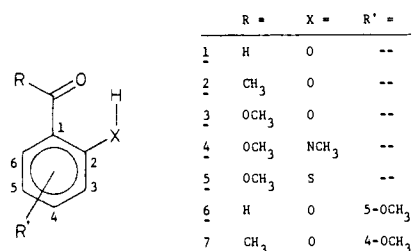
The required values of A and B are obtained from the values of the spin-lattice relaxation time, T_1^{DD} , of the ¹³C nuclei which have directly bonded protons. These relaxation times, which are dominated by dipole-dipole interactions, are given by the equation

$$1/T_1^{DD}(j) = \gamma_H^2 \gamma_C^2 \hbar^2 \left[A \sum_i r_{ij}^{-6} \cos^2 \Psi_{ij} + B \sum_i r_{ij}^{-6} \sin^2 \Psi_{ij} \right] \quad (2)$$

where r_{ij} is the length of the internuclear vector involving the i th proton and the j th carbon atom and Ψ_{ij} is the angle which

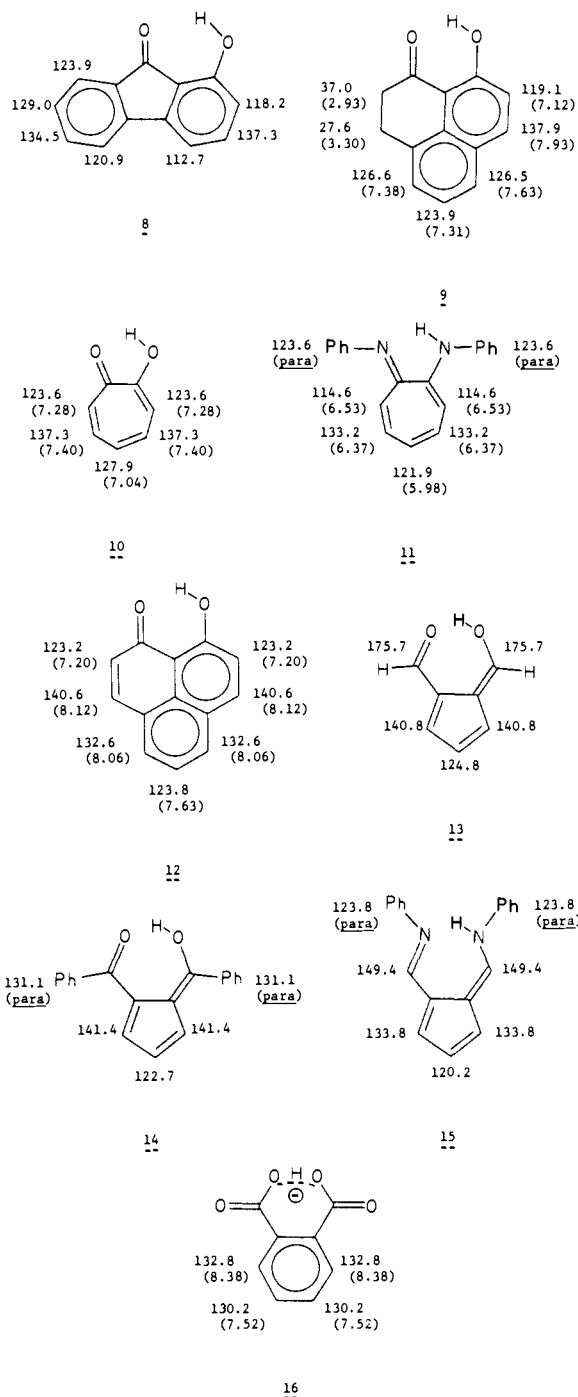
this vector subtends with the appropriate, principal in-plane diffusion axis. For the molecules **10–16**, we assume that the position of the deuteron has a negligible effect on rotational diffusion²⁷ and that the principal in-plane diffusion axes are determined by symmetry. Only two ¹³C relaxation times are then needed to solve eq 2 for A and B . In those cases where more than two relaxation times are available, A and B have been found by the method of nonlinear least squares.²⁸ Only the contributions of directly attached and vicinal protons have been included. For compounds **1–9** the principal axes are not uniquely determined by symmetry. In these cases, the substitution $\Psi_{ij} = \phi_{ij} + \theta$ can be made in eq 2, where ϕ_{ij} is now the angle subtended with some arbitrarily chosen in-plane axis and θ is the angle through which this axis must be rotated to make it coincident with one of the principal in-plane axes. The modified equation is then solved for A , B , and θ , using the nonlinear least-squares method in the overdetermined cases.

Application of eq 2 requires a knowledge of the geometries of the molecules studied. The skeletal geometries of the series **1–7** were based on salicylic acid, for which both X-ray^{29,30,31}



and neutron³¹ diffraction structures have been published, although the results are little changed if standard bond lengths and angles are employed. The geometry of 1-hydroxyfluorenone (**8**) was assumed to be the same as that of fluorenone³² with a C(1)–O bond length of 1.37 Å with the bond bisecting the exterior angle of the ring. Standard bond lengths and regular hexagonal aromatic rings were assumed to be present in 2,3-dihydro-9-hydroxyphenalenone (**9**). X-ray structures are available for tropolone (**10**),^{33,34} 9-hydroxyphenalenone (**12**),³⁵ 6-hydroxyfulvene-1-aldehyde (**13**),³⁶ *N,N'*-diphenyl-6-aminofulvene-1-aldimine (**15**),³⁷ and potassium hydrogen phthalate (**16**).³⁸ The structure of *N,N'*-diphenylaminotropolonimine (**11**) was based on the known structure³⁹ of the *N,N'*-dimethyl analogue and that of 1-benzoyl-6-phenyl-6-hydroxyfulvene (**14**) was assumed to be similar to that of **13** with standard geometries for the phenyl substituents. In all molecules, each aromatic hydrogen atom was then located at the vibrationally averaged distance (1.107 Å) from the carbon atom as found for benzene⁸ and at a position corresponding to the bisection of the exterior angle involved. Justification for the use of a single value of r_{ij} throughout is provided by the observation that, for all overdetermined cases, eq 2 reproduces the individual values of T_1 to within their standard deviations.

The data for the diffusion constants and the directions of their principal diffusion axes (where not determined by symmetry) are given in Table II. On the basis of the J -diffusion model of McClung,⁴⁰ the rotational diffusion constants are expected to be linearly related to the reciprocals of the corresponding moments of inertia and the anisotropy parameter A/B should be equal to $(I_x^{-1} + I_z^{-1})/(I_y^{-1} + I_z^{-1})$. These ratios are also recorded in Table II, together with θ' , the angle which diagonalizes the moments of inertia tensor. In the cases of the methyl esters **3–5** it has been assumed that the methyl group adopts the coplanar Z conformation. There is indeed a good correlation ($r = 0.966$) between the two anisotropies (eq 3) but the J -diffusion model evidently overestimates the anisotropy of rotational diffusion. Nevertheless, the empirical eq 3, which reproduces the A/B values in Table II with a standard deviation



of better than 4%, can probably be used together with a single relaxation time to provide fairly accurate estimates of DQCC at least for planar molecules of the types considered here in solvents which are reasonably symmetric and inert.

$$(I_x^{-1} + I_z^{-1}) / (I_y^{-1} + I_z^{-1}) = 1.9(A/B) - 1.0 \quad (3)$$

The extraction of DQCC from eq 1 requires, in addition to A and B , a knowledge of the asymmetry parameter, η , and the direction of the principal field gradient at the deuteron (q_{zz}). For the relatively weak hydrogen bonds found in compounds 1–11 the asymmetry parameter has been presumed to be less than 0.1 and its neglect in the calculation of DQCC is therefore less than 0.3%. This assumption is supported by the results of ab initio MO calculations⁴¹ for various hydrogen-bond geometries of the enol of malondialdehyde. These same calculations indicate that much stronger hydrogen bonds may be associated with appreciable asymmetry parameters and much smaller DQCCs. Using the MO calculation of the enol of

malondialdehyde as a guide, it may be concluded that η for 12 is less than 0.25, which would still only introduce an error of <2%. For the remaining compounds (13–16), the contribution of the asymmetry parameter could be significant (for $\eta = 1$, DQCC calculated by eq 1 is reduced by 13.4% from the value for $\eta = 0$) and we shall return to this problem in the Discussion section.

The choice of the direction of the principal field gradient requires careful consideration. For the weaker hydrogen bonds (1–11), the direction is essentially that of the X–D bond and it is then only necessary to know the C–X–D bond angle in order to calculate the angle Ψ used in eq 1. Indeed, even for methyl salicylate, which has the largest anisotropy of rotational diffusion of the compounds in this group, an error of 10° in this angle would only result in a 4% error in DQCC. The problem is more severe for very strong hydrogen bonds and the MO calculations for the symmetric (C_{2v}) geometry of the enol of malondialdehyde find the principal field gradient to be perpendicular to the molecular plane.

The angles between q_{zz} and the principal axis of rotational diffusion are recorded together with T_1^Q and DQCC in Table III. The angles in compounds 1–4, 6, and 7 are based on the neutron diffraction structure of salicylic acid.³¹ In the case of 5, a similar geometry was adopted except that the other planar, nonbonded conformation of the S–H group was assumed (see above). The position of the deuteron in 1-hydroxyfluorenone has been previously determined from ¹³C relaxation times⁸ and that for the aminotroponimine (11) from ¹³C and ¹⁵N relaxation times.⁴² The X-ray data for 9-hydroxyphenalenone³⁵ does not allow an accurate position of the hydrogen-bonded proton; the angles for this compound, as well as for its 2,3-dihydro derivative (9), are assumed to be the same as in 5,8-dihydroxy-1,4-naphthoquinone.⁴³ The X-ray diffraction structures for tropolone³³ and *N,N'*-diphenyl-6-aminopentafulvene-1-aldehyde (15)³⁷ provide sufficiently accurate positions for the bridging proton. The neutron diffraction structure was used for 6-hydroxyfulvene-1-aldehyde (13) and, by analogy, for its diphenyl derivative (14). The principal field gradient axis for the hydrogen phthalate ion has been assumed to be collinear with the O–D–O bridge since this is what was found by Chiba⁴⁴ for the deuterium maleate ion in crystalline potassium hydrogen maleate.

The two methoxy derivatives 6 and 7 present a special problem in that, while the methoxyl group is probably coplanar with the aromatic ring,⁴⁵ it can still populate two conformations. Since the relaxation times are not linearly related to A and B in eq 2, solution of eq 1 requires data for at least seven protonated carbon atoms in order to evaluate A , B , and θ for each conformation and their relative populations. In the case of 6, a reasonable approximation is available through the assumption that the C(4)–H(4) internuclear vector is parallel to that of the O–H. DQCC (kHz) is then given by eq 4⁴⁵ in which r_{CH} is again the vibrationally averaged C–H bond length.

$$\text{DQCC} = 49.3r_{CH}^{-3} (T_1^{DD}/T_1^Q)^{1/2} \quad (4)$$

This approximation is also valid for compounds 1–4, and indeed the values of DQCC so calculated agree within $\pm 1\%$ with those given in Table III.

Equation 4 cannot be applied to 7. We have calculated DQCC using anisotropies based on eq 3 and the assumption that the conformations are equally populated. This leads to a value of 184 kHz. The difficulty of dealing with this quite simple molecule demonstrates that the methods described above are not readily applicable to flexible systems except in those fortunate instances for which the approximation embodied in eq 4 can be made.

Table II. Anisotropies of Rotational Diffusion (from ^{13}C T_1 Data) and of Moments of Inertia

compd	$A, \times 10^{-11}$ s	$B, \times 10^{-11}$ s	θ , deg	A/B	$((I_x)^{-1} + (I_z)^{-1}) / ((I_y)^{-1} + (I_z)^{-1})$	θ' , deg
1	0.768 ± 0.001	0.567 ± 0.001	-16.0 ± 0.2 ^a	1.35 ± 0.00	1.69	-19.9
2	1.057 ± 0.005	0.815 ± 0.004	3.7 ± 0.1 ^a	1.30 ± 0.01	1.52	0.6
3	1.193 ± 0.002	0.746 ± 0.002	6.1 ± 0.2 ^a	1.60 ± 0.01	1.99	9.7
4	1.776 ± 0.072	1.509 ± 0.093	44.9 ± 15.8 ^a	1.18 ± 0.09	1.49	26.0
5	1.538 ± 0.034	1.285 ± 0.035	21.9 ± 5.5 ^a	1.20 ± 0.04	1.47	13.5
8	1.561 ± 0.036	2.063 ± 0.042	5.0 ± 3.9 ^b	0.76 ± 0.02	0.49	0.0
9	1.790 ± 0.123	1.664 ± 0.123	<i>c</i>	1.08 ± 0.11	1.30	-0.3 ^d
10	0.810 ± 0.013	0.622 ± 0.009	<i>e</i>	1.30 ± 0.03	1.40	<i>e</i>
11	3.742 ± 0.204	4.861 ± 0.108	<i>e</i>	0.77 ± 0.05	0.46	<i>e</i>
12	4.326 ± 0.069	3.760 ± 0.044	<i>e</i>	1.15 ± 0.02	1.32	<i>e</i>
13	0.576 ± 0.013	0.479 ± 0.007	<i>e</i>	1.20 ± 0.03	1.54	<i>e</i>
14	3.314 ± 0.209	5.022 ± 0.113	<i>e</i>	0.66 ± 0.04	0.25	<i>e</i>
15	4.363 ± 0.163	4.419 ± 0.133	<i>e</i>	0.99 ± 0.05	0.81	<i>e</i>
16	3.271	2.774	<i>e</i>	1.18	1.10	<i>e</i>

^a Relative to axis through C(1), C(4). ^b Relative to axis through carboxyl group. ^c Assumed to be C_{2v} . ^d Relative to axis through C(1a), C(6). ^e C_{2v} .

Table III. Deuteron Spin-Lattice Relaxation Times and Quadrupole Coupling Constants for Some Intramolecularly Hydrogen Bonded Systems in CHCl_3 at 26 °C

compd	T_1, Qs	$-\Psi q_{zz}$, deg	DQCC, kHz ^e
1	0.230 ± 0.001	-6.1	196 ± 0.4
2	0.184 ± 0.003	13.6	186 ± 2
3	0.133 ± 0.001	16.0	206 ± 1
4	0.097 ± 0.001	54.8	209 ± 5
5	0.299 ± 0.002	-88.2	133 ± 2
6	0.139 ± 0.001	<i>a</i>	201 ^b
7	0.104 ± 0.002	<i>a</i>	184 ^a
8	0.072 ± 0.000	60.4	221 ± 3
9	0.112 ± 0.004	76.0	190 ± 7
10	0.203 ± 0.001	46.2	216 ± 1
11	0.038 ± 0.001	46.2	203 ± 3
12 ^c	0.090 ± 0.001	76.0	141 ± 1
13	0.913 ± 0.030	82.8	124 ± 2
14	0.131 ± 0.002	82.8	102 ± 1
15	0.096 ± 0.001	74.4	127 ± 2
16 ^d	0.476 ± 0.026	90.0	72 ± 2

^a See text. ^b Calculated with eq 4. ^c In CDBr_3 . ^d In CH_2Cl_2 . ^e The errors are the propagated errors in the measurements of the ^2H and ^{13}C relaxation times and do not, of course, include the uncertainties in the choices of direction of q_{zz} .

Discussion

The quadrupole coupling constant of deuterium in hydrogen-bonding situations is expected to provide at least a qualitative indication of the strength of "hydrogen bond", since, as the deuteron moves toward positions midway between the acceptor and donor atoms, the electric field gradient is reduced. Approximate linear relations between DQCC and the length of the bond H- - O in O-H- - O systems have been found by Soda and Chiba⁴⁷ and more recently by Hunt and Mackay.⁴⁸ The latter workers, using values determined by double resonance NMR experiments on solids, established the relation

$$\text{DQCC (kHz)} = 328 - 643/R^3 \quad (5)$$

where R is the distance O- - H in Å. The value (328 kHz) in the absence of hydrogen bonding is in reasonably close agreement with that of 318.6 ± 2.4 kHz found⁴⁹ by beam maser experiments for gaseous HDO. Equation 5 predicts DQCC = 0 at about $R = 1.25$ Å. This equation, which is double valued in R , is clearly invalid for the more symmetrical situations, i.e., for really strong hydrogen bonds. Ab initio MO calculations⁴⁰ for the enol tautomer of malondialdehyde lead to a value of 56 kHz ($\eta = 0.33$) for the hypothetical symmetrical hydrogen bond with the principal component q_{zz} being

Table IV. Comparison of OH Stretching Frequencies and Deuteron Quadrupole Coupling Constants for Intramolecularly Hydrogen Bonded Phenols

compd	$\nu_{\text{OH}}, \text{cm}^{-1}$	DQCC, kHz
8	3404	221 ± 3
6	3202	201 ^a
3	3196	206 ± 1
1	3185	196 ± 4
9	3055	190 ± 7
7	3055	184 ^a
2	3026	186 ± 2

^a See text.

out of plane. Similarly, a calculated value of 52 ($\eta = 0.24$)⁵⁰ and an observed one of 56 kHz ($\eta = 0.53$)⁴⁴ are obtained for potassium hydrogen maleate which, by analogy with the neutron diffraction structure of potassium chloromaleate, is believed to have a symmetric hydrogen bond.⁵¹ Thus, we believe that values in the range 50–60 kHz are evidence for a symmetric bond. It must be realized, of course, that, because of the difference in zero-point energies for hydrogen and deuterium bonds, it is possible for the former to involve a symmetric single well potential even though that of the latter may correspond to a symmetric double well. Nevertheless, the DQCCs clearly provide a useful criterion of the strengths of intramolecular hydrogen bonds.

Unsymmetrical Systems. Compounds 1–9 constitute systems in which only one tautomer is present and, with the possible exception of methyl *o*-mercaptobenzoate, involve highly unsymmetrical hydrogen bonds of modest strength. Their DQCCs nevertheless exhibit significant variations.

A direct relation between the field gradient q_{zz} (and hence DQCC) and the force constant for the stretching vibration has been established for diatomic molecules.⁵² Chiba⁴⁴ and Blinc and Hadži⁹ have shown that, for hydrogen bonds of the type O-H- - O, there is a good correlation between the square of the O-H stretching frequency and the DQCC of the deuterium analogue. These studies involved investigation of crystalline materials and, except for very strong hydrogen bonds, both the square of ν_{OH} ⁵³ and DQCC⁵⁴ were shown to depend on the O- - O internuclear distance. We have determined ν_{OH} for compounds 1–3 and 6–9 (Table IV) and there is the expected linear correlation of DQCC with ν_{OH}^2 (DQCC = $(1.4 \times 10^{-5})\nu_{\text{OH}}^2 + 57$; $r = 0.973$).

The value of DQCC for methyl *N*-methylantranilate is nearly the same as for methyl salicylate. This probably indicates a weaker hydrogen bond in the former since for equal strengths the DQCCs would be expected to parallel the values

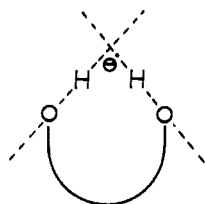


Figure 1.

found for gaseous NH_2D (282 ± 12 kHz)⁵⁵ and HDO (318.6 ± 2.4 kHz).⁴⁹

The value found for methyl *o*-mercaptobenzoate is smaller than that found in HDS (154.7 ± 1.6 kHz)⁴⁹ or thiophenol-*S-d* (146 ± 3 kHz).⁵⁶ As discussed above, long-range proton-proton coupling constant data are consistent with the absence of intramolecular hydrogen bonding in this molecule. Whether the small decrease in the DQCC relative to thiophenol is due to some population of the H-bonded conformation for **5** or whether it merely reflects a change in ionicity of the SH bond due to the electron-withdrawing effect of the ortho carbonyl group cannot be ascertained from the present study.

Potentially Symmetric Hydrogen Bonded Systems. Each of the molecules **10**–**16** exhibits ^1H and ^{13}C NMR spectra which are consistent with either C_{2v} symmetry or with existence of rapidly equilibrating C_s tautomers. The latter situation poses a special problem with respect to the calculation of the DQCC from ^2H relaxation data because of the way in which the components of the electric field gradient tensor average when the chemical exchange is comparable to or faster than rotational diffusion. This problem has been treated by Wennerström,⁵⁷ who has shown that, if the asymmetry parameter is assumed to be zero, then in the limit of fast exchange (relative to rotational diffusion) eq 1 must be replaced by

$$1/T^Q = [3(2I + 3)/40I^2(2I - 1)](e^2q_{zz}/h)^2 \times (A \cos^2 \Psi + B \sin^2 \Psi) (2 + 3 \cos^2 \beta - 1)/4 \quad (6)$$

where β is the angle defined in Figure 1. Thus, in the absence of prior knowledge concerning the rate of exchange, two values of DQCC must be considered⁵⁸ and these are presented in Table V.

Tropolone (**10**) is of particular interest. X-ray photoelectron spectroscopy (X-ray PES) has shown^{6a} that in the gas phase this molecule is unsymmetrical, the two oxygen atoms differing by 2.3 eV in their 1s binding energies. In the solid state, tropolone has C_s symmetry and the hydroxylic protons are implicated in bifurcated hydrogen bonding involving both intra- and intermolecular interactions.³³ Both the magnitude and the anisotropy of rotational diffusion leave no doubt that tropolone is monomeric in solution and presumably has a geometry similar to that found in the crystalline state. Of the two values calculated for DQCC, that corresponding to the fast exchange is unacceptable, being some 110 kHz greater than found for gaseous water. We therefore conclude that the rate of intramolecular deuteron exchange in tropolone-*O-d* is less than 10^{10} s^{-1} , the approximate rate of rotational diffusion under our experimental conditions. The DQCC for the slow exchange limit is approximately the same as observed for compounds **1**–**3** and **6**–**9**, thus establishing the asymmetry of the hydrogen bond in this molecule in solution.

A similar situation exists for 1-phenylamino-7-phenylimino-1,3,5-cycloheptatriene (**11**). The X-ray diffraction structure of the analogous *N,N'*-dimethyl compound has been reported by Goldstein and Trueblood.³⁹ It is consistent with C_{2v} molecular symmetry, although the possibility of statistical disordering resulting from random distribution of the two individual C_s tautomers was acknowledged. Location of the exchangeable proton from studies⁴² of ^{13}C and ^{15}N spin-lattice relaxation times has shown that the C_s geometry prevails in

Table V. Effect of Rapid Chemical Exchange on Deuteron Quadrupole Coupling Constants Calculated from Deuteron Spin-Lattice Relaxation Times for Some Potentially Symmetric Intramolecularly Hydrogen Bonded Systems

compd	β , deg	DQCC _(slow) , kHz	DQCC _(fast) , kHz
10	95.9	216	426
11	100.7	203	386
12	144.8	140	161
13	172.7	124	125
14	172.7	102	103
15	169.8	127	128
16	180.0	72	72

solution. As with tropolone, the value of DQCC calculated for the fast exchange limit is clearly far too high, being about 100 kHz greater than that for gaseous NH_2D ,⁵⁵ so that exchange must be slow on the rotational diffusion time scale. The value calculated for slow exchange clearly confirms that the deuteron bridge involves a symmetric double well potential.

DQCC calculated for 9-hydroxyphenalenone undergoing slow exchange is similar to that found for the enol of acetylacetone¹⁰ in which the hydrogen bond presumably has a similar geometry. The X-ray PES results^{6a} for both compounds and for the enol of malondialdehyde indicate that the hydrogen bond involves a double well potential. This conclusion is substantiated by microwave studies in the case of malondialdehyde⁵ and hydrogen-deuterium-tritium chemical shift isotope effect in the case of acetylacetone.⁷ An X-ray diffraction study is consistent with a C_{2v} structure for 9-hydroxyphenalenone but, as with the *N,N'*-dimethyl analogue of compound **11**, this could be due to disordering through rapid proton transfer.³⁵ The geometries of these systems are such that there is only a small difference between the values of DQCC calculated on the basis of fast and slow exchange. In their microwave spectroscopic study of malondialdehyde, Rowe, Duerst, and Wilson⁵ observed a low vibrational frequency ($16 \pm 14 \text{ cm}^{-1}$) which they assigned to proton tunnelling between the two tautomers. Fluder and de la Vega⁵⁹ have calculated the reaction profile for this exchange using the 4-31G basis set and found a barrier of 8.5 kcal mol⁻¹ and an exchange rate of $0.8 \times 10^{11} \text{ s}^{-1}$. Although this rate will be slower for deuterium, it is clear that, in the absence of further experiments, it is not possible to decide on the relative rates of exchange and rotational diffusion and consequently between the two values for 9-hydroxyphenalenone given in Table IV.

The remaining systems in Table IV have geometries such that the deuteron relaxation times, and the values of DQCC calculated therefrom, are unaffected by the exchange process.

6-Hydroxyfulvene-1-aldehyde (**13**) has been extensively studied. Both neutron diffraction³⁶ and X-ray PES⁶ indicate the existence of a symmetric double well potential and the infrared spectrum has also been interpreted as supporting the C_s structure.²⁴ On the other hand, the microwave spectrum⁶⁰ is consistent with either C_{2v} symmetry or with a pair of C_s tautomers undergoing equilibration at a rate of $2 \times 10^{12} \text{ s}^{-1}$. The DQCC in Table IV shows that the deuteron bond is asymmetric, although the value is significantly lower than that found in 9-hydroxyphenalenone, suggesting that the double well profile is flatter in the former. It is noteworthy that DQCC for the 1,6-diphenyl derivative (**14**) is some 20 kHz lower than found for the parent compound (**13**).

The X-ray structure of *N,N'*-diphenyl-6-aminopentafulvene-2-aldimine (**15**)³⁷ exhibits an interesting distortion relative to **13**. In the latter the O-H...O' distance is 2.51 Å³⁶ compared to 2.79 Å for the analogous N-H...N' separation in **15**. The compound **15** is nearly planar and this results in a close approach (2.40 Å) of ortho hydrogen atoms of the phenyl

substituents. Evidently the increase in the N-H - -N' distances occurs so as to allow greater planarity of the whole system. In any event, there is a significant increase in DQCC for this system as a result of the lengthening of the internuclear distance between the two nitrogen atoms. The hydrogen bond is nevertheless substantially stronger than that in the aminotroponimine (**11**) in which the internuclear separation in the N,N'-dimethyl analogue is 2.51 Å. This is because the hydrogen bond in **15** is much more nearly linear. There is abundant evidence that the linear arrangement is to be preferred.⁶¹

Potassium deuterium phthalate was examined as its 18-crown-6 complex in order to minimize contributions of the counterion to the field gradient tensor for the deuteron. The X-ray structure for the uncomplexed salt reveals inter- rather than intramolecular hydrogen bonding, although the closely related chloromaleate ion possesses a strong symmetric intramolecular hydrogen bond.⁵¹ The evidence⁷ based on proton-deuteron-tritium chemical shift isotope effects is, however, convincing for the existence of a symmetric hydrogen bond in solution. Certainly the value of DQCC is consistent with this interpretation. Actually, the value of 72 kHz in Table IV assumes $\eta = 0$. If the value of $\eta = 0.53$ found for potassium maleate⁴⁴ is included, DQCC is reduced to 69 kHz.

Conclusion

The combined use of ¹³C and ²H spin-lattice relaxation times provides a convenient means of determining quadrupole coupling constants of intramolecularly "hydrogen bonded" deuterons in planar molecules in the liquid phase.

In systems of the type X-D - -Y, the strength of the "hydrogen bond" is related to the position of the deuteron relative to X and Y which, in turn, controls the magnitude of the quadrupole coupling constant. Thus, values of this coupling constant provide a qualitative criterion of the strengths of hydrogen bonds in series in which X and Y are held constant. The compounds surveyed in this paper are seen to provide series in which the hydrogen bonds vary from weak (highly unsymmetrical) to very strong (symmetrical) hydrogen bonds.

The relation between deuteron quadrupole coupling constants and deuteron spin-lattice relaxation times offers the exciting prospect of studying certain intramolecular deuteron transfers which might have rates comparable to that of rotational diffusion.

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References and Notes

- Part 16: L. M. Jackman and J. C. Trewella, *J. Am. Chem. Soc.*, **101**, 6428 (1979).
- Bell Laboratories.
- "The Hydrogen Bond. Recent Developments in Theory and Experiments", P. Schuster, G. Zundel, and C. Sandorfy, Eds., North-Holland Publishing Co., Amsterdam, 1976. This work, in three volumes, summarizes most of the recent work in these areas.
- A. L. Andreassen and S. H. Bauer, *J. Mol. Struct.*, **12**, 381 (1972).
- W. F. Rowe, R. W. Duerst, and E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 4021 (1976).
- (a) R. S. Brown, *J. Am. Chem. Soc.*, **99**, 5479 (1977); (b) R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *ibid.*, **101**, 3157 (1979).
- L. J. Altman, D. Laungani, G. Gunnarsson, H. Wennerström, and S. Forsén, *J. Am. Chem. Soc.*, **100**, 8264 (1978).
- L. M. Jackman and J. C. Trewella, *J. Am. Chem. Soc.*, **98**, 5712 (1976).
- R. Blinc and D. Hadži, *Nature (London)*, **212**, 1307 (1966).
- W. Egan, G. Gunnarsson, T. W. Bull, and S. Forsén, *J. Am. Chem. Soc.*, **99**, 4568 (1977).
- W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).
- K. Hafner, K. H. Vöpel, G. Ploss, and C. König, *Justus Liebigs Ann. Chem.*, **661**, 52 (1963).
- R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, R. E. Cais, and F. B. Bramwell, *J. Am. Chem. Soc.*, **100**, 7629 (1978).
- W. J. Linn and W. H. Sharkey, *J. Am. Chem. Soc.*, **79**, 4970 (1957).
- U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, **92**, 4849 (1970).
- D. G. Kowalewski and S. Castellano, *Mol. Phys.*, **16**, 567 (1969).
- T. Schaefer and W. J. E. Parr, *Can. J. Chem.*, **55**, 3752 (1977).
- (a) I. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **34**, 353 (1961); (b) S. Forsén and B. Åkermark, *Acta Chem. Scand.*, **17**, 1907 (1963); (c) D. C. Nonhebel, *Tetrahedron*, **24**, 1869 (1968).
- M. Kondo, *Bull. Chem. Soc. Jpn.*, **45**, 2790 (1972).
- Chemical shifts accompany the structural formulas, the proton values being in parentheses.
- The 360-MHz spectrum of this compound was provided by G. G. McDonald, University of Pennsylvania School of Medicine, Department of Biochemistry and Biophysics, Philadelphia, Pa.
- L. Weiler, *Can. J. Chem.*, **50**, 1975 (1972).
- (a) H. Sugiyama, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A*, **20**, 34 (1968); (b) D. J. Bertelli, T. G. Andrews, and P. O. Crews, *J. Am. Chem. Soc.*, **91**, 5286 (1969). The values used in the present work are our own.
- K. Hafner, H. E. A. Kramer, H. Musso, G. Ploss, and G. Schulz, *Chem. Ber.*, **97**, 2066 (1964).
- W. T. Huntress, *Adv. Magn. Reson.*, **4**, 1 (1970).
- W. T. Huntress, *J. Chem. Phys.*, **48**, 3524 (1968).
- In 1-hydroxyfluorenone, for example, the relaxation times of the proton-bearing carbon atoms for the normal and *O-d* species are identical within experimental error.⁸
- Calculations were performed using the program NLIN2 from the IBM SHARE library.
- W. Cochran, *Acta Crystallogr.*, **6**, 260 (1953).
- M. Sundaralingam and L. H. Jensen, *Acta Crystallogr.*, **18**, 1053 (1965).
- G. E. Bacon and R. J. Jude, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **138**, 19 (1973).
- H. R. Luss and D. L. Smith, *Acta Crystallogr., Sect. B*, **28**, 884 (1972).
- H. Shimanouchi and Y. Sasada, *Acta Crystallogr., Sect. B*, **29**, 81 (1973).
- T. A. Hamor and J. E. Derry, *Acta Crystallogr., Sect. B*, **29**, 2649 (1973).
- C. Svenson, S. C. Abrahams, J. L. Bennstein, and R. C. Haddon, *J. Am. Chem. Soc.*, in press.
- H. Fuess and H. J. Linder, *Chem. Ber.*, **108**, 3096 (1975).
- H. L. Ammon and U. Mueller-Westerhoff, *Tetrahedron*, **30**, 1437 (1974).
- Y. Okaya, *Acta Crystallogr.*, **19**, 879 (1965).
- P. Goldstein and K. N. Trueblood, *Acta Crystallogr.*, **23**, 148 (1967).
- R. E. D. McClung, *J. Chem. Phys.*, **57**, 5478 (1972).
- G. Karlström, H. Wennerström, B. Jönsson, S. Forsén, J. Almlöf, and B. Roos, *J. Am. Chem. Soc.*, **97**, 4188 (1975).
- L. M. Jackman and J. C. Trewella, unpublished results.
- P. D. Cradwick and D. Hall, *Acta Crystallogr., Sect. B*, **27**, 1990 (1971). The C-O-H bond angle in this molecule is $104 \pm 2^\circ$. This value, and the skeletal geometry of **9**, was used to derive ψ .
- T. Chiba, *J. Chem. Phys.*, **41**, 1352 (1964).
- B. W. Liebich, *Acta Crystallogr., Sect. B*, **32**, 431 (1976).
- L. M. Jackman, E. S. Greenberg, N. M. Szeverenyi, and G. K. Schnorr, *J. Chem. Soc., Chem. Commun.*, 141 (1974).
- G. Soda and T. Chiba, *J. Chem. Phys.*, **50**, 439 (1969).
- M. J. Hunt and A. L. Mackay, *J. Magn. Reson.*, **15**, 402 (1974).
- P. Thaddeus, L. C. Krishner, and P. Cahill, *J. Chem. Phys.*, **41**, 1542 (1964).
- M. Žaucer, E. Zakrajšek, J. Koller, D. Hadži, and A. Azman, *Mol. Phys.*, **21**, 461 (1971).
- R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965).
- L. Salem, *J. Chem. Phys.*, **38**, 1227 (1963).
- R. Blinc, D. Hadži, and A. Novak, *Z. Electrochem.*, **64**, 567 (1960).
- D. Hadži and B. Orel, *J. Mol. Struct.*, **18**, 227 (1973).
- P. Thaddeus, L. C. Krisher, and J. H. N. Loubser, *J. Chem. Phys.*, **40**, 257 (1964).
- B. M. Fung and I. Y. Wei, *J. Am. Chem. Soc.*, **92**, 1497 (1970).
- H. Wennerström, *Mol. Phys.*, **24**, 69 (1972).
- If the rates of exchange are approximately equal to rotational diffusion, the calculated values of DQCC will be intermediate between those calculated for the fast and slow exchange limits.
- E. M. Fluder and J. R. de la Vega, *J. Am. Chem. Soc.*, **100**, 5265 (1978).
- H. M. Pickett, *J. Am. Chem. Soc.*, **95**, 1770 (1973).
- W. A. P. Luck in ref 3.