The *J* Method: Application of NMR Spectroscopy to the Determination of Small Internal Rotation Barriers in Solution

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A variety of methods has been employed in the investigation of the number of rotational isomers of a molecule, their relative energies, and the heights of the potential-energy curves for internal rotation. These include thermodynamics (heat capacities), molecular orbital calculations, electron diffraction, microwave and vibrational spectroscopies, relaxation measurements, and NMR spectroscopic studies. The method of choice[1] for any particular molecule depends upon the molecular structure, the magnitude of the barrier to internal rotation, and the approximations of the model to be applied.

For barriers of <3 kcal/mol the most accurate determination of barriers to methyl group rotation is probably afforded by high-resolution microwave spectroscopy (gas phase). Even this approach contains approximations, such as semirigid Hamiltonians and ignored vibrations/torsions, which may lead to unknown errors in the final value for the barrier.[2a] The method is applied to fairly small molecules, and a molecule as large as phenylethane still presents the microwave spectroscopists with a formidable challenge. Toluene[2b,c] and phenol[3] have been studied.

For rotational barriers of larger magnitude the method of choice is probably dynamic NMR spectroscopy (DNMR). It is applicable to barriers as large as 30 kcal/mol and as small as 8–10 kcal/mol. The lowest barrier found in this way[4] is 4.2 kcal/mol. DNMR makes use of the fact that different conformers may display different chemical shifts and/or coupling constants. The conversion rate between the conformers is studied as a function of temperature. Because DNMR depends upon the dephasing of magnetization as nuclear spins are transferred between sites of different Larmor frequencies (T_2 effects), this technique becomes more difficult to apply as the magnitude of the barrier decreases. The dephasing process becomes too fast to measure accurately.

As NMR can be applied to relatively large molecules in solution, it is desirable to extend it to the measurement of barriers of less than 4 kcal/mol. Nuclear, particularly ^{13}C, spin–lattice relaxation rates are widely

used to study the dynamics of internal rotation in molecules.[5a] The sensitivity of this approach depends on the relative speeds of the internal and overall molecular motions and perhaps also on the nature of the models employed.[5b]

We here outline a recent method—the *J* method—by which rotational barriers in the range 0.2–3.0 kcal/mol, and also preferred conformations, may be determined in solution by high-resolution NMR spectroscopy. In principle, the method is applicable to all molecules containing NMR active nuclei. In practice, its application at present is restricted to benzene derivatives containing side chains whose rotation is characterized by a twofold internal barrier. The utility of the method for a range of side chains is discussed, and limitations are commented upon.

Experimentally, the *J* method requires the accurate measurement of long-range coupling constants over six bonds, ^6J, between a nucleus in the para ring position and a nucleus bonded to the carbon or heteroatom in the α position of the side chain. Such coupling constants are thought to be transmitted by the π electrons via a σ–π mechanism,[6] and as such are expected to exhibit a $\sin^2 \theta$ dependence, θ being the angle by which the α bond twists out of the plane of the aromatic ring. The couplings are likely zero for $\theta = 0°$ and at a maximum magnitude for $\theta = 90°$. INDO–FPT–MO calculations[6c] of ^6J predict a $\sin^2 \theta$ dependence and in the case of toluene, perhaps fortuitously, are in quantitive agreement with the experimental value[7] of $^6J_p^{H,H}$ of −0.62 Hz. The angular dependence can be described by eq 1, where ^6J is the observed value of the six-bond

$$^6J = {}^6J_0 + {}^6J_{90} \langle \sin^2 \theta \rangle \qquad (1)$$

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Bill Parr was born in England in 1948 and studied for his B.Sc. at Brighton Polytechnic before going to the University of York to work with R. O. C. Norman for his doctorate on the oxidation of organic compounds by gold(III) and palladium(II) salts. In 1974 he moved to the University of Manitoba, where he spent 2 years at postdoctoral work. After returning to England and a year at the University of Warwick as a postdoctoral fellow working on stopped-flow FT NMR, he joined MRPRA as project leader in charge of oxidation studies.

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Table I
Sample Values of $\langle \sin^2 \theta \rangle$ for Selected Temperatures, Twofold Barriers,[a] and Reduced Moments of Inertia[b]

T, K	V_2					
	0.5	1.5	2.5	0.5	1.5	2.5
200	0.427 (8)	0.334 (5)	0.298	0.354 (6)	0.167 (71)	0.096 (9)
250	0.441 (2)	0.354 (5)	0.312 (3)	0.382 (3)	0.208 (11)	0.124 (6)
300	0.450 (1)	0.371 (2)	0.326 (7)	0.401 (2)	0.242 (4)	0.151 (4)
350	0.457 (8)	0.385 (6)	0.339 (40)	0.415 (6)	0.271 (2)	0.177 (80)
400	0.463 (3)	0.397 (8)	0.351 (2)	0.425 (2)	0.294 (6)	0.202 (4)

[a] In kcal/mol, the first set of three columns referring to a low-energy conformation, A, the second set to a low-energy conformation, D. [b] The numbers refer to a reduced moment of inertia of 1.0×10^{-38} g cm². The numbers in parentheses show how the number changes in the last (or last two) places when the reduced moment of inertia is 5.0×10^{-38} g cm².

coupling, $^6J_0$ and $^6J_{90}$ are the values at $\theta = 0$ and 90°, and $\langle \sin^2 \theta \rangle$ represents the value of $\sin^2 \theta$ averaged over the hindered rotor states. Use of a hindered rotor treatment affords $\langle \sin^2 \theta \rangle$ as a function of the barrier height, V_2. Thus, if $^6J_{90}$ is known, the ratio $^6J/^6J_{90}$ may be used to arrive at the barrier height.

The Model

Equation 1 has a well-known counterpart in ESR spectroscopy,[8] eq 2, used to account for the angular

$$a_\beta = B + A \cos^2 \theta \qquad (2)$$

dependence of β-hyperfine coupling constants, a_β, in alkyl radicals. It has been applied by Stone and Maki[9] using both classical and quantum mechanical approximations. Fessenden[10] employed a more rigorous solution using Mathieu functions, but tabulations of such functions are only available for low reduced moments of inertia. Kochi[11] overcame this limitation by a numerical approximation.

A useful quantum mechanical solution to the hindered rotor problem[13] was outlined by Ayscough, Brice and McClung.[12] Their method involves the solution of the eigenvalue problem in eq 3. The principle pa-

$$-(\hbar^2/2I)(d^2\psi_m/d\alpha^2) + (V_0/2)(1 - \cos 2\alpha)\psi_m = E_m\psi_m \qquad (3)$$

rameters there are I, the reduced moment of inertia about the aryl side chain bond, and V_0, the magnitude of the twofold barrier to internal rotation. In terms of the free rotor basis, one obtains the hindered rotor states, ψ_m, and their energies, E_m. The value of $\langle \sin^2 \alpha \rangle$ is then obtained by weighting its expectation value for each state with a Boltzmann factor in the normal way. Tables of T, I, and $\langle \sin^2 \alpha \rangle$ as a function of V_2 can be drawn up by computer. At near ambient temperatures, the first 21 free rotor states provide an adequate basis, but it can be easily extended. In terms of conformations A, B, it is convenient to specify that $\alpha = 0$ when $\theta = 30°$ or 60° and for C, D that $\alpha = 0$ when $\theta = 90°$ or 0°. The calculated values of $\langle \sin^2 \alpha \rangle$ can then be converted to $\langle \sin^2 \theta \rangle$, directly useful in relating ^6J to V_2. Table I illustrates the values of $\langle \sin^2 \theta \rangle$ obtained for a selection of temperatures, twofold barriers,

and reduced moments of inertia in situations in which A or D are the low-energy conformations (details of the algebraic procedure as well as extensive tables of $\langle \sin^2 \theta \rangle$ are available from the authors upon request).

Application to Benzene Derivatives

Consider conformers A to D, representing benzyl or benzal compounds. In terms of the indicated angle θ
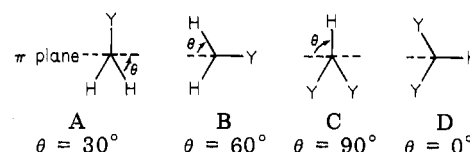
it follows that if conformers A or B represent the stable high barrier form, $\langle \sin^2 \theta \rangle$ is 0.5 at $V_2 = 0$ and $\langle \sin^2 \theta \rangle = 0.25$ or 0.75 at $V_2 = \infty$. For C and D, $\langle \sin^2 \theta \rangle$ varies between unity and zero. Furthermore, $\langle \sin^2 \theta \rangle$ is relatively insensitive to the value of the reduced moment of inertia, I, at least for the range 0.1×10^{-38} to 10.0×10^{-38} g cm². It is also evident that the intrinsic accuracy of the method is better for molecules possessing C, D conformations in the side chain than for those with A, B conformations, an increasingly relevant consideration for higher V_0 values, say 2.5–4.0 kcal/mol.

The theory of σ–π coupling mechanisms implies that if J_0 is negligible, $^6J_p^{H,CH_3}$ in toluene should equal $-^7J^{CH_3CH_3}$ in *p*-xylene. This is observed experimentally for *p*-xylene and its ring-substituted derivatives.[6d,e] Ring substituents such as chlorine and bromine do not dramatically alter the *total* π population of the benzene ring, although there may be a redistribution of this population, especially since the substituent will polarize the σ framework. Because ^6J is probably determined by *net* π electron distribution (multiple coupling paths), the redistribution of π density within the ring need not significantly affect the magnitude of ^6J. Observations[14] support the argument that ^6J is in general little affected by the presence of halogen substituents at the meta position.

Having taken $^6J_0$ as zero, it is necessary to arrive at an estimate for $^6J_{90}$. The simplest approach uses the fact that the sixfold barrier to methyl group rotation in toluene,[2] 0.014 kcal/mol, is effectively zero and therefore $\langle \sin^2 \theta \rangle = 0.5$; an experimental value[7] for ^6J of -0.62 Hz leads to a $^6J_{90}$ value of -1.24 Hz (as long as ^6J depends on $\sin^2 \theta$, any preferred conformation of the CH$_3$ group about the exocyclic C–C bond in toluene will yield, by trigonometric averaging over three C–H bonds, $\langle \sin^2 \theta \rangle = 0.5$). Of course, this will require modification

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in some cases because side-chain substituents may alter bond angles and thereby change $^6J_{90}$ or may polarize the C–X bonds and thereby alter the σ–π overlap integrals. In practice such problems are sometimes found to be of minor importance.

Although the magnitudes of six-bond couplings, $^6J^{H,H}$, are generally <1 Hz, this does not preclude the accurate estimation of barrier heights because the precision of spectral analysis can be high (<0.01 Hz standard deviation in a least-squares fit), so that the accuracy in ^6J is perhaps 0.02 Hz.[15]

Some Examples

As a first example, consider phenylethane. The presence of a methyl group in the side chain is not expected to perturb the σ–π parameters appreciably. Therefore $^6J_{90}$ should be close to the value, –1.24 Hz, in toluene. Arguments based upon an electronegativity relationship (see below) suggest a value for $^6J_{90}$ of –1.20 Hz. The 100-MHz spectrum of phenylethane is too tightly coupled to permit analysis, but use can be made of the fact that halogens at the meta ring positions should not influence the magnitude of ^6J. The $^6J^{H,H}$ value in 3,5-dibromophenylethane is -0.47_7 Hz and hence $\langle \sin^2 \theta \rangle$ is $0.47_7/1.20$ or 0.39_8. Using this value and a table of $\langle \sin^2 \theta \rangle$ vs. V_2, constructed with the appropriate values of temperature (305 K) and reduced moment of inertia (0.6×10^{-38} g cm^2), a barrier height of 1.15 ± 0.20 kcal/mol is deduced[16] (the error being based solely upon measurement errors) for rotation about the exocyclic C–C bond. There are four conceivable low-energy conformations for the CH$_2$X (X = Me) group, E, F, G, and H. All four give $\langle \sin^2 \theta \rangle = 0.5$

| E | F | G | H |
| $\theta = 30°$ | $\theta = 60°$ | $\theta = 60°$ | $\theta = 30°$ |
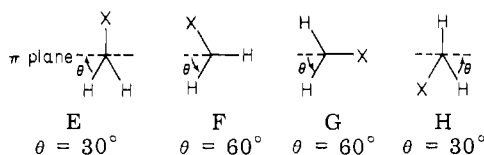
in the free rotation limit. In the high barrier limit E, F, G, and H yield $\langle \sin^2 \theta \rangle$ values of 0.25, 0.375, 0.75, and 0.625, respectively. For barriers of <3 kcal/mol, $\langle \sin^2 \theta \rangle$ will take values within the ranges 0.25–0.5 or 0.75–0.5 depending upon the low-energy conformation. The value of $\langle \sin^2 \theta \rangle$ obtained above for 3,5-dibromophenylethane, 0.39_8, allows G and H to be discounted, and conformer F could only be the preferred conformer if the barrier were >3 kcal/mol. The J method therefore predicts E to be the preferred conformer, and the barrier to be 1.15 kcal/mol. We are assuming, of course, that there is one preferred conformer, governed by a twofold barrier.

These findings are in quite good agreement with a later heat capacity determination[17] of the barrier, which yielded 1.16 kcal/mol, and with low-resolution microwave deductions[18] that conformer E represents the low-energy form; the latter is also in accord with STO-3G calculations.[19] A check on the angular dependence of $^6J_p^{H,H}$ in phenylethanes is furnished by the value of

–0.29 Hz observed in 2,6-dichlorophenylethane.[14b] In this molecule, V_2 is much greater than 3 kcal/mol and E is the preferred conformation, leading to a prediction that ^6J is –1.20 (sin^2 30°) or –0.30 Hz.

Next, consider application of the J method to isopropylbenzene derivatives, in which the CHX$_2$ (X = Me) side chain may adopt conformations K, L, M, or N, although the assumption is usually made that K and

| K | L | M | N |
| $\theta = 0°$ | $\theta = 90°$ | $\theta = 60°$ | $\theta = 30°$ |
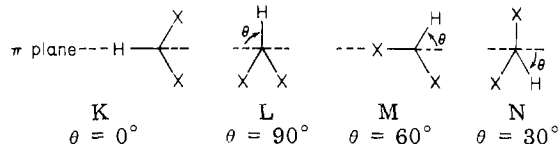
L represent the low- and high-energy conformations, respectively. The presence of two methyl groups within the side chain is assumed to reduce $^6J_{90}$ by at most 0.08 Hz from the –1.24 Hz value in toluene. Experimentally $^6J^{H,H}$ in 3,5-dibromoisopropylbenzene[20] is -0.25_3 Hz; using eq 1, $\langle \sin^2 \theta \rangle$ is 0.204 if $^6J_{90}$ is taken as –1.24 Hz or 0.218 if $^6J_{90}$ is –1.16 Hz. This corresponds to barrier values of 1.95 ± 0.2 or 1.77 ± 0.2 kcal/mol, quite close to the value of 2.13 kcal/mol measured for the neutral trityl radical.[21] For low barriers, adoption of K, L, M, or N as the low-energy conformation would give $\langle \sin^2 \theta \rangle$ values in the range 0.5–0.0, 0.5–1.0, 0.5–0.75, or 0.5–0.25. Because $\langle \sin^2 \theta \rangle = 0.21$, conformation K is chosen as the ground-state conformation for the CHMe$_2$ side chain. The absence of angle-independent contributions to $^6J_p^{H,H}$ in benzalic derivatives is confirmed by the observation of "zero" values for this coupling in the 2,6-dichloro derivatives of benzal chloride[22] and iodide,[23] in which the barriers are high (15 and 21 kcal/mol) and the side chains are effectively locked into conformation K ($\theta = 0°$).

Provided the assumption is made that the barrier in phenylcyclopropane is primarily twofold in nature, the J method becomes applicable. The proton spectrum[24] proved amenable to analysis and gave a value of –0.23 $\pm$ 0.02 Hz for $^6J_p^{H,H}$. Electron diffraction[25] indicates the C_{ring}–C_α–H angle to be larger than in toluene, and on the basis that this will reduce overlap with the aromatic π orbitals somewhat, it is reasonable to anticipate a change in the value of $^6J_{90}$. INDO–FPT–MO calculations,[24] which give the correct magnitude of $^6J_{90}$ for toluene, predict $^6J_{90}$ in phenylcyclopropane to be –1.11 Hz. When this value is used, $\langle \sin^2 \theta \rangle$ is 0.21 $\pm$ 0.02 and the barrier is then 1.9 $\pm$ 0.3 kcal/mol[24] (the increased error limit arises from an allowance of a 0.1 Hz error in $^6J_{90}$). The conformer in which the C_α–H band prefers the plane of the aromatic ring is the low-energy form, a preference in agreement with the results of INDO and STO-3G calculations.[24]

When an experimental ^6J value of –0.23 Hz and a $^6J_{90}$ value of –1.24 Hz ($\langle \sin^2 \theta \rangle = 0.18_8$) are used, the J method yields a barrier of 2.1 kcal/mol for the barrier

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Table II
J Method Values for the Barrier to Side-Chain Rotation in $ArCH_2X$ Compounds at 305 K

X	E_x	$^4J^{H,H}$, Hz	$^6J^{H,H}$, Hz	$^6J_{90}^{H,H}$, Hz	$\langle \sin^2 \theta \rangle$	barrier, kcal/mol alternatives	barrier, kcal/mol preferred	low-energy conformer
Me	2.5	−0.64	−0.477	−1.24	0.385	1.33	1.2 ± 0.2	E
				−1.20	0.398			
Ph		−0.64	−0.498	−1.24	0.402		1.1 ± 0.2	E
$CH=CH_2$		−0.65	−0.87	−1.24	0.393	1.21	1.1 ± 0.2	E
				−1.20	0.406	1.03		
CN		−0.76	−0.60	−1.24	0.48	0.20	0.25 ± 0.2	
				−1.32	0.455	0.45		
NH_2	2.75	−0.73	−0.579	−1.24	0.467	0.33	0.3 ± 0.3	
				−1.17	0.495	0.05		E or F
NMe_2	2.75	−0.73	−0.512	−1.24	0.413	0.95	0.8 ± 0.2	E
				−1.17	0.438	0.66		
$AsMe_2$	2.1	−0.49	−0.39	−1.24	0.315	2.93	3.0 ± 0.5	E
OH	3.5	−0.77	−0.59	−1.24	0.476	0.24		
				−1.13	0.52	0.20	0.30 ± 0.2	
				−1.085	0.54	0.40		
SH	2.5	−0.56	−0.42	−1.24	0.34	2.15	2.0 ± 0.2	E
				−1.20	0.35	1.92		
SeH	2.4	−0.49	−0.37	−1.24	0.297	3.53	3.3 ± 0.7	E
				−1.21	0.304	3.30		
Cl	3.0	−0.52	−0.40	−1.14	0.35	1.92	2.0 ± 0.2	E
Br	2.8	−0.44	−0.32	−1.16	0.28	>4	3.7[a]	E
I	2.55	−0.40	−0.31	−1.195	0.26	>4	4.2[a]	E

[a] Lower limit.

to rotation of the cyclohexane ring in 3,5-dichlorophenylcyclohexane.[26] If the C_{ring}–C_α–H angle is increased by 2° from tetrahedral, then $^6J_{90}$ may decrease to −1.14 Hz, which would give a barrier of 1.9_5 kcal/mol. In either event the same low-energy conformation is preferred as deduced for phenylcyclopropane.

The similarity of the values for the barriers in phenylcyclopropane and phenylcyclohexane could be advanced as evidence that the barriers in these compounds arise mainly as a result of steric hindrance between C–H bonds, expected to be at a minimum when the C_α–H bond is in the plane of the aromatic ring.

In 3-bromo- and 3,5-dibromostyrenes, $\langle \sin^2 \theta \rangle$ has an average value of $0.22_5 \pm 0.04$, leading to a barrier estimate of 1.7 ± 0.3 kcal/mol for rotation of the vinylic fragment.[27]

Benzylic Compounds

The previous examples demonstrate that the J method gives realistic barrier values and conformation preferences for hydrocarbon side chains. We now examine the applicability of the method to benzylic side chains, CH_2X, containing various substituents, X. The assessment of the correct value of $^6J_{90}$ to be used for a particular substituent, X, touched upon above, presents the most problematical aspect. This is particularly so if the substituent is a very polar one (F, OH). It seems reasonable to expect a sizeable reduction in $^6J_{90}$ because of polarization of the π-type molecular orbitals of the CH_2X group. It was suggested that a linear relationship exists between $^6J_{90}$ and E_x, the electronegativity of X.[28-30] For X = F a value of −1.02 Hz was taken, yielding an empirical relationship predicting

(26) T. Schaefer, W. Niemczura, and W. Danchura, *Can. J. Chem.*, 57, 355 (1979).

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suitable values for $^6J_{90}$ for different substituents. The results of the application of the J method to benzylic compounds are set out in Table II, the effect of a variation in $^6J_{90}$ being included in several cases.

Some general points can be made from the data in Table II. First, the magnitude of the barriers increases down groups for side chains bonded via group 5, 6, and 7 heteroatoms, as might be anticipated from the increasing size of the heteroatom: thus $AsMe_2 > NMe_2$; SeH > SH > OH; I ≥ Br > Cl. Second, the barriers fall into two main groups. Where the substituent X represents an entity containing an heteroatom from the first row of the periodic table (X = NH_2, OH), the barrier to rotation of CH_2X is small (<0.5 kcal/mol). When X represents entities bonded via second, third, and fourth row elements, the rotational barriers are >1.5 kcal/mol and the ground-state conformation is invariably of type E. Note also that for very bulky substituents (X = SeH, Br) the accuracy of the barriers derived by the J method decreases as a consequence of the shape of the $\langle \sin^2 \theta \rangle$ vs. V_2 curve at V_2 > 2.5 kcal/mol, and it may be best to take barriers so deduced as representing lower limits. None of this vitiates the use of $\langle \sin^2 \theta \rangle$ as an indicator of ground-state conformation in such compounds. The notion of a classical angel θ is strictly valid only for a rigid molecule.

Benzalic Compounds

Applications of the J method to benzalic side chains, CHX_2, are fewer; available data are summarized in Table III, the results for isopropylbenzene,[20] phenylcyclopropane,[24] and phenylcyclohexane[26] having been discussed above. Replacement of the cyclohexane ring by a 1,3-dithiane ring is found to affect the barrier height only slightly[26] if the same value of $^6J_{90}$ is used for both compounds (reasonable because $E_C = E_S$). Apparently the CH_2 groups and S atoms have similar steric requirements in their interaction with the C_o–H bonds of the aromatic ring. The much smaller barrier, 0.4 ± 0.2 kcal/mol, for rotation of a 1,3-dioxane ring[26] is derived using a $^6J_{90}$ value of −0.96 Hz (reduced as a

Table III
Barriers to Rotation of Benzalic and Other Side Chains in Compounds of Type ArCHX or ArCHX$_2$

X or X$_2$	$^4J^{H,H}$, Hz	$^6J^{H,H}$, Hz	$^6J_{90}^{H,H}$, Hz	$\langle \sin^2 \theta \rangle$	barrier, kcal/mol	low-energy conformer
Me$_2$	-0.56_8	-0.25_3	-1.24	0.204	1.95 ± 0.2	K
			-1.16	0.218	1.77 ± 0.2	
F$_2$	-0.46_5	-0.26^a	-0.87	0.30	1.1 ± 0.2	K
Cl$_2$	-0.43	-0.21	-1.05	0.20	2.0 ± 0.3	K
Br$_2$	-0.38	-0.12	-1.09	0.11	3.5 ± 0.6	K
▷	-0.47	-0.23	-1.11	0.21	1.9 ± 0.3	K
(structure)	-0.57_6	-0.23_3	-1.24	0.18_8	2.1 ± 0.3	K
			-1.14	0.20	1.95 ± 0.3	
(structure O)	-0.73	-0.40	-0.96	0.41_7	0.4 ± 0.2	K
(structure S)	-0.48	-0.21_8	-1.24	0.17	2.25 ± 0.3	
			-1.14	0.19	2.1 ± 0.3	K
=CH$_2$		-0.25	-1.05	0.225^b	1.7 ± 0.3	K

^{a} Average of value in 3,5-dichloro derivative and parent compound. ^{b} Average of value in 3,5-dibromo derivative and 3-bromo derivative.

result of the presence to two electronegative oxygen atoms). The J method agrees with X-ray,[31] molecular mechanics,[32] and calorimetric data.[33] The foregoing discussion includes the assumption that the three compounds exist predominantly in equatorial forms, reasonable because the free energies of these isomers are 3.1, 3.1, and 1.7 kcal/mol lower than those of the axial isomers in phenylcyclohexane, 2-phenyl-1,3-dioxane,[33] and 2-(p-chlorophenyl)-1,3-dithiane,[34] respectively. Inversion of the alicyclic rings has also been ignored, as this is anticipated to be much slower than is the internal rotation.

Extension to Use of $^6J^{H,F}$

Having demonstrated the application of the J method using $^6J^{H,H}$ it is of interest to consider whether the analogous six-bond proton–fluorine coupling constants may also be useful in this context. INDO–FPT–MO calculations[6c,28] predict a $\sin^2 \theta$ dependence. Such coupling constants offer practical advantages because they are, in general, about double the magnitude of the corresponding $^6J^{H,H}$ values ($^6J^{H,H}$ in toluene is -0.62 Hz and $^6J^{H,F}$ is -1.12 Hz in p-fluorotoluene) and are also accessible from the ^{19}F spectrum in cases where the proton spectrum may be too tightly coupled or too complex to permit analysis.

The detailed studies suggest that the attitude toward use of such six-bond proton–fluorine coupling constants in the J method must be that, while such couplings are reliable indicators of conformational preferences and of the *relative* magnitudes of the rotational barriers, the accuracy of barriers obtained by their use is open to question.[35]

Side Chains Bonded to the Ring by Heteroatoms

The barrier to rotation of the $-SiH_3$ group in phenylsilane[36] in the gas phase is 0.018 kcal/mol, similar

to the value of 0.014 kcal/mol for toluene. This, together with the work of Rastelli and Pozzoli[37] indicating that the bond angles within the side chains of phenylsilanes and phenylmethylsilanes do not depart from the tetrahedral value by more than 1°, invited the application of the J method to phenylsilanes of type PhSiH$_2$X and PhSiHX$_2$ (X = Me or Cl). The value of ^6J, -0.343 Hz, measured in phenylsilane,[38] provides an estimate of -0.686 Hz for $^6J_{90}$; the smaller value for the six-bond coupling compared to toluene is attributable to reduced orbital overlap caused by the length of the C–Si bond (1.84 Å).

For phenyldimethyl- and phenyldichlorosilanes[38] the observed ^6J values give barrier estimates of 1.0 ± 0.2 kcal/mol. In both cases the low-energy conformation is given as that in which the Si–H bond prefers the plane of the aromatic ring. The choice of ground-state conformation is therefore the same as for isopropylbenzene and benzal chloride, but the barriers derived are substantially lower, not unreasonable in view of the greater distance between side-chain atoms and the ortho C–H bonds in the silanes.

On the basis of the above results it is concluded that the J method can be used to deduce ground-state conformations, and for SiHX$_2$ side chains, reasonably reliable estimates of the rotational barriers about C–Si bonds; but the small experimental values of the six-bond coupling constants introduce larger errors than for barriers about C–C bonds. For SiH$_2$X side chains, for which the $\langle \sin^2 \theta \rangle$ vs. V_2 plots cover narrower ranges, the errors may be large enough to preclude use of the J method to determine barriers.[38]

The J method has been shown to be inapplicable to the study of phenylphosphine derivatives[39] as a consequence of the severe departure from tetrahedral geometry about the phosphorus atom in such compounds.

Experimental values of V_2 for the sulfhydryl group in benzenethiol are various.[40,41] Combined far-infrared and microwave data in the gas phase[42] gave 0.76

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kcal/mol for V_2. The six-bond coupling in benzenethiol is -0.33 Hz.[43] STO-3G calculations predict[43] a CSH angle of 95.8°. Increased orbital overlap due to such a bond angle is more than offset by the greater length of the C–S bond. It was argued[43] that $\langle \sin^2 \theta \rangle$ is 0.31, making the in-plane conformer the low-energy form and yielding a barrier of 1.1 ± 0.2 kcal/mol, in rough agreement with data from a dielectric relaxation study.[44]

The C–Se bond length in benzeneselenol is greater than the C–S bond length in benzenethiol, so $^6J_{90}$ for the selenol may be taken[45] to have a maximum magnitude of 1.05 Hz, while its minimum, 0.90 Hz, can be derived from the observed ^6J value of -0.45 Hz in the event that $\langle \sin^2 \theta \rangle$ is 0.5 (if the barrier is zero). The upper limit to the barrier to rotation of the SeH group is then 0.35 ± 0.25 kcal/mol. The substituents in phenol, benzenethiol, and benzeneselenol prefer a planar conformation, but the barriers to rotation about C–O, C–S, and C–Se bonds are 3.4 ± 0.2, 1.1 ± 0.2, and 0.35 ± 0.25 kcal/mol, respectively. The decrease is presumably a result of the progressive loss of lone-pair–π-electron conjugation.

The barrier to hydroxyl group rotation in para-substituted phenols is known to depend on the substituent, and a similar dependence is therefore expected in para-substituted benzenethiols. The presence of a substituent in the para position renders $^6J^{H,H}$ unobtainable, but on the basis of $^4J^{H,SH}$ numbers, the barriers vary from near zero for p-aminobenzenethiol to about 2.7 kcal/mol for p-nitrobenzenethiol.[46]

The long-range couplings in 2-hydroxythiophenol demonstrated[47] that the S–H bond lies in a plane approximately perpendicular to the rest of the molecule. The polar O–H bond hydrogen bonds to the mainly 3p lone pair on the sulfur, forcing the S–H bond out of plane.

Temperature Effects and the *J* Method

All of the foregoing examples have related to measurements performed at 305 K. But $\langle \sin^2 \theta \rangle$, and therefore ^6J_p, will be temperature dependent as a consequence of population redistribution among the hindered rotor energy levels. In practice dJ/dT is very small and is difficult to measure experimentally. Thus $^6J^{H,F}$ in 4,4'-difluorodiphenylmethane changes by only 0.07 Hz for a 120° temperature change[48] ($dJ/dT \simeq 7 \times 10^{-4}$ Hz/K), the rotational barrier being estimated at 1.5 ± 0.25 kcal/mol, with E as the low-energy conformer.

Solvent Perturbations of Conformational Energies and Barriers

The relative conformational energies, particularly of polar molecules whose polarity has a marked dependence on conformation, can be solvent dependent. A striking example is furfuraldehyde, in which the stability of the two planar conformers is reversed by going from the vapor phase to a solution in dimethyl ether.[49]

Of course, in the molecules to which the *J* method has been applied, the two conformers have the same energy. Therefore the problem becomes one of deciding how the barrier itself is changed by the presence of solvent molecules. For dimethylamide derivatives the solvent dependence of the internal rotational barrier is ~10% of the mean barrier.[50] The latter is large, about 20 kcal/mol, and it does not follow that the solvent dependence of smaller barriers, ca. 2 kcal/mol, is also relatively small.

In this connection, T_1 measurements of internal motion in molecules in solution become of interest. For example, the temperature dependence of the internal reorientation rate in perfluorotoluene,[51] extracted by the application of a classical model, yields an internal barrier of about 1.4 kcal/mol. The gas-phase value of this sixfold barrier does not exceed 0.1 kcal/mol. The difference is attributed to solvent effects. Similar results are found for toluene. It is interesting, therefore, that a quantum mechanical approach[52] to the internal rotational contribution to T_1 in mesitylene yields a result consistent with an internal barrier of 0.014 kcal/mol in both liquid and gas whereas the "activation energy" treatment yields ~1 kcal/mol in liquid toluene.

In 3,5-dibromoisopropylbenzene we have found no dependence of V_2 on the polarity of solvent, within experimental error, by the *J* method. However, much more work on solvent effects is needed, particularly for highly polar side chains.

Conclusions

The *J* method appears to give reasonable estimates of internal rotation barriers about the C–C, C–Si, and C–S bonds attaching side chains to benzene rings and often allows the low-energy conformation to be deduced. The major difficulty is the determination of suitable maximum values of the long-range coupling constants, i.e., of $^6J_{90}$. Barriers derived using $^6J^{H,F}$ values are less accurate, but the correct choice of the low conformation may be made. The *J* method becomes inaccurate for barriers of >3 kcal/mol. It is also clear that microwave or other determinations of the barriers for several of the compounds discussed here would be useful in assessing the accuracy of the *J* method more rigorously.

Extension of the method to include the use of couplings other than $^6J^{H,H}$ and $^6J^{H,F}$ should be possible if couplings can be found which display a known angular dependence and are insensitive to substituent effects. Interesting examples worthy of investigation are the couplings $^5J^{H,C}$ and $^5J^{F,C}$ between side-chain nuclei[53] and the para ring carbon atom, for which INDO–FPT–MO calculations predict a $\sin^2 \theta$ dependence.[39]

It is interesting that the newer NMR spectrometers, operating at 400 or 500 MHz for protons, would yield the V_2 in phenylethane in solution in about 24 h, given the procedure discussed in this account. With such instruments many of the experimental and model problems, discussed above, could be circumvented.

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Surface Structure Determinations with Ion Beams

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During the last decade, the research objectives of most surface chemists have turned from an interest in macroscopic aspects of interfacial chemical reactions to the development of atomic descriptions of the surface chemical bond. This more advanced understanding now seems feasible, since many spectroscopic methods have entered the scene that can provide the same type of information which has been available on bulk phase systems since the 1930s. Most of the present effort is directed at determining either atomic positions of atoms or small molecules adsorbed on metal single-crystal surfaces or the detailed nature of the molecular orbitals which participate in the bond.

The question of atomic structure seems most crucial since correct nuclear coordinates facilitate electronic structure calculations. The battery of techniques presently available may well be adequate to solve the structure problem, although uncertainties in how to interpret the spectroscopic results have restricted most work to fairly simple, model-type systems. For example, the location of a sulfur atom on a Ni(001) surface has just recently been determined to be 1.3 Å above the surface Ni plane and presumably in a fourfold coordination site. The same value has been obtained using low-energy electron diffraction (LEED),[1] photoelectron diffraction (PhD),[2] and other photoemission techniques.[3] The bond distance is not found to be much different than that obtained for bulk NiS. A few other isolated surface bond distances have been determined using a surface EXAFS method[4a] and an ion backscattering technique.[4b] As far as we know, however, the NiS case is the only example where the same result has been obtained by three different methods. And, although many LEED structure determinations have been published,[5] in the absence of supporting data from other methods the reliability of the results is still usually open to discussion.

Ion Bombardment Methods

Here we wish to focus on the question of the atomic structure of surfaces utilizing ion beams of sufficient

energy to induce nuclear rearrangements which are controlled by the original configuration of atoms. With this approach, the incident ion, usually an inert gas such as He^+, Ne^+, or Ar^+, is accelerated to a kinetic energy of 200–5000 eV and focused onto the sample surface. The momentum exchange between the primary ion and the atoms of the lattice is sufficient to initiate some atomic motion which has a component of momentum moving out into the vacuum. If this component is sufficient to overcome the surface binding forces, then some secondary particles may be found to eject from the solid.[6] A fraction of these particles are ionized as they leave the surface and can, therefore, be detected directly with a mass spectrometer (i.e., as in secondary ion mass spectrometry or SIMS). The SIMS technique has been of considerable recent interest to the surface analyst, since for elements with low ionization potentials or high electron affinities (e.g., H^+, Na^+, K^+, O^-, Cl^-, Br^-, F^-) the limit of detection can approach 10^{-14} g.[7] Furthermore, the primary ion can be focused to a diameter of 100 nm, allowing high spatial resolution. The ion microprobe has found numerous applications in the fields of geology, biology, semiconductor technology, and metallurgy.[8] It is also possible, although generally with a large loss in sensitivity, to utilize some sort of post-ionization of the neutral species.[9] This approach eliminates the large variations of the ion yield with the surface electronic properties, making the technique more quantitative.

To utilize SIMS for examination of surface structure, at least two major problems have to be solved. First, the primary ion beam is known to induce a great deal of damage which can alter the chemical nature of the sample. In 1970, Benninghoven proposed that if the total primary dose (the number of ions/cm² to strike

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