

of aminoperylene's fluorescence intensity on the pulsed excitation energy in the high-intensity region of 50–150 mJ/pulse; comparison of photoionization quantum efficiencies measured at high (laser) and low (sunlight) intensities; and determination of the intensity dependence of the photoionization yield at intensities considerably below those already studied. Until such results are available, the most cautious interpretation of the data is that the photoionization of aminoperylene at 530 nm is biphotonic.

Acknowledgment. The advice of Dr. G. A. Kenney-Wallace is gratefully acknowledged.

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Proton, Deuterium, and Tritium Nuclear Magnetic Resonance of Intramolecular Hydrogen Bonds. Isotope Effects and the Shape of the Potential Energy Function

Sir:

The difference in chemical behavior of the three isotopes of hydrogen is mainly caused by the difference in their masses, which in turn influences the vibrational motions and the zero-point vibrational energies. Thus, from a measurement of an isotope effect in some property, one can make deductions about the shape of potential energy surfaces. This has been extensively exploited for elucidating chemical reaction paths from kinetic data.¹ Here we report the usefulness of ¹H, ²H, and ³H NMR as a means of studying the shape of the potential energy surface in the vicinity of the equilibrium position.

Primary isotope effects² of the NMR chemical shifts of ²H and ³H in organic compounds are usually very small, in the case of ³H usually <0.03 ppm for tritium bound to sp²- or sp³-type carbons.^{3,4} Exceptions to this general rule are systems with relatively strong hydrogen bonds, for which deuterium isotope effects, Δδ(¹H, ²H), as large as 0.6 ppm have been found.^{5–7} We have previously reported the results of a systematic NMR study of the deuterium isotope effect, Δδ(¹H, ²H), in a series of systems all containing hydrogen bonds of the type O—H—O.⁶ A correlation between the isotope effect and the value of the chemical shift, δ(¹H), was observed for the hydrogen-bonded nucleus.

The only conceivable source of isotope effects on chemical shifts within the Born–Oppenheimer approximation lies in the isotopes mass dependence of vibrational motion. The quantities that determine the magnitude are the vibrational wave functions, ψ, for the ground state (and possibly low-lying excited vibrational states) and the variation of the chemical shift, δ, with the nuclear configuration. Neglecting thermal averaging we have

$$\Delta\delta(^1\text{H}, ^k\text{H}) = \int |\psi(^1\text{H})|^2 \delta \, d\tau - \int |\psi(^k\text{H})|^2 \delta \, d\tau \quad (k = 2 \text{ or } 3) \quad (1)$$

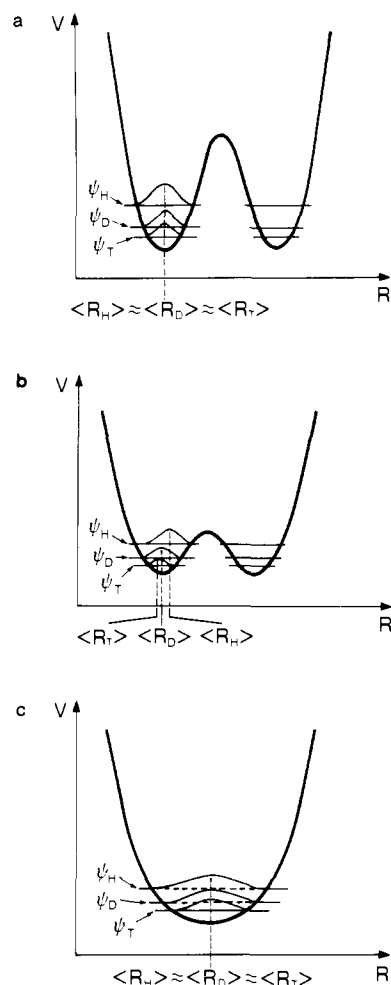


Figure 1. Schematic illustration of the position of the hydrogen isotopes, in the zero point vibrational levels, for different types of hydrogen bond potential functions: (a) a double minimum potential with a high central barrier and low anharmonicity at the potential minima; (b) a double minimum potential with a low central barrier and high anharmonicity at the potential minima; (c) a single minimum potential.

The variation of the proton chemical shift with nuclear distance in hydrogen-bonded systems is such that the proton is deshielded as the proton moves toward the midpoint between the heavy atoms (O, N, or F) of the bond.^{8,9} This fact can be used to correlate the chemical shift with the shape of the hydrogen bond potential. In Figure 1 we have schematically illustrated three types of potentials that may be encountered in hydrogen-bonded systems.

In the case of weak hydrogen bonds (Figure 1a) the potential minima should be deep with a low anharmonicity approaching that of an ordinary covalent O–H bond. The effective equilibrium positions of the hydrogen isotopes, $\langle R \rangle$, will then be closely similar for ¹H, ²H, and ³H. In this case the isotope effect on the chemical shift is expected to be zero in the first approximation. Experimentally this situation should be encountered in, for example, water or alcohols. For stronger and shorter hydrogen bonds (Figure 1b) the potential minima draw closer together with an accompanying decrease of the central barrier and increase in the anharmonicity of the potential. The equilibrium positions will now be different—we expect $\langle R_H \rangle > \langle R_D \rangle > \langle R_T \rangle$ (assuming R to be measured from the nearest heavy atom of the hydrogen bond). In this case we will observe positive isotope effects in the chemical shift—larger for ³H than for ²H.

In the case of extremely strong and short hydrogen bonds we may encounter the situation shown in Figure 1c.¹⁰ Here the potential is symmetrical and the equilibrium distances $\langle R_H \rangle$,

Table I. Deuterium and Tritium Isotope Effects on Chemical Shifts^a

compd	$\delta(^1\text{H})$, ppm	$\Delta\delta(^1\text{H}, ^2\text{H})$, ^b ppm (± 0.03)	$\Delta\delta(^1\text{H}, ^3\text{H})$, ^b ppm (± 0.01)	$\frac{\Delta\delta(^1\text{H}, ^3\text{H})}{\Delta\delta(^1\text{H}, ^2\text{H})}$
benzyl alcohol	2.00	-0.02 ^c	-0.016 ^e	
O-hydroxyacetophenone	12.28 ^d	0.10 ^d	0.074 ^e	
salicylaldehyde	11.02	0.06 ^d	0.008 ^e	
acetoacetic ethyl ester	12.70	0.16 ^f	0.214 ^g	1.34 (± 0.28)
acetylacetone	16.11	0.61 ^f	0.830 ^g	1.36 (± 0.07)
benzoylacetone	16.59	0.67 ^f	0.932 ^g	1.39 (± 0.07)
dibenzoylmethane	17.61	0.72 ^f	1.011 ^g	1.40 (± 0.07)
1-dimethylamine-8-dimethylammonium naphthalene cation ^h	18.46	0.66 ^c	0.915 ^e	1.39 (± 0.07)
hydrogen maleate anion ⁱ	20.5	-0.03 ^d	-0.07 ^{e,j}	
hydrogen phthalate anion ⁱ	21.0	-0.15 ^d	-0.25 ^{e,j}	1.66 (± 0.33)

^a Measurements were performed at 31.5 °C, unless otherwise stated. ^b Measurements were performed on Varian XL-100 NMR spectrometers operating at a ¹H frequency of 100.1 MHz, ²H frequency of 15.4 MHz, and ³H frequency of 106.7 MHz. ^c CH₃CN and CD₃CN were used as internal standards in CH₂Cl₂ solution. ^d From ref 6. ^e CH₃CN and CH₂TCN were used as internal standards in CD₂Cl₂ solution. ^f Measured relative to the olefinic hydrogens in an ~0.25 M C₆H₆ solution, containing approximately equivalent amounts of proton and deuterium compounds. ^g Measured relative to the olefinic hydrogen in an ~0.25 M C₆D₆ solution, containing ~25 mCi of activity. ^h Tetraphenylboron as counterion. ⁱ Tetrabutylammonium counterion. ^j Extrapolated to -55 °C from measurement at -16.2, -24.8, and -38 °C.

(R_D), and (R_T) become equal. However, the differences in vibrational amplitudes between ¹H, ²H, and ³H tend to make the chemical shifts of the isotopes increase with their mass since a hydrogen nucleus is deshielded as the hydrogen approaches a heavier atom⁸ and because the heavier nuclei have lower vibrational amplitudes. This effect thus gives rise to negative isotope effects.¹¹

From a more quantitative treatment of the effect of the vibrational motion on the NMR chemical shift,¹² it follows that, for the case of an anharmonic cubic term in the potential as in Figure 1b, the deuterium and tritium isotope effects are related by

$$\Delta\delta(^1\text{H}, ^3\text{H}) = 1.44 \Delta\delta(^1\text{H}, ^2\text{H}) \quad (2)$$

when the reduced mass determining the vibrational motion in the mode considered is taken as the mass of the hydrogen isotope. For the symmetric case of Figure 1c the relation between the isotope effects is as given in eq 2, when the potential is harmonic. However, in symmetrical hydrogen bonds the quartic term is often very strong¹³ and this could lead to larger ratio between the isotope effects.

Table I lists the deuterium and tritium isotope effects on the hydrogen chemical shift measured under similar conditions for a number of systems with strong intramolecular hydrogen bonds. It is seen that the explanation of the deuterium isotope effects in terms of a correlation between the hydrogen-bond potential and the sign of the isotope effect⁶ is substantiated by the ³H measurements. For all the cases where the sign of the isotope effect indicates a double minimum potential, the ratio $\Delta\delta(^1\text{H}, ^3\text{H})/\Delta\delta(^1\text{H}, ^2\text{H})$ is close to the value of 1.44 predicted in eq 2. For the hydrogen phthalate anion the isotope effect is negative, indicating a single minimum potential, and the ratio between the isotope effects appears to be larger than 1.44, although the experimental accuracy does not allow a definite conclusion on this point.

The observed tritium and deuterium shift isotope effects in hydrogen-bonded systems are thus consistent with the simple theoretical model. Conversely, measurement of isotope effects should be an experimental method of assessing the shape of hydrogen-bond potential-energy functions—in particular the discrimination between double and single minimum potentials. We have recently measured the isotope effect $\Delta\delta(^1\text{H}, ^2\text{H})$ of the enolic hydrogen in malondialdehyde to be $+0.42 \pm 0.03$ ppm ($\delta(^1\text{H})$ 13.99 ppm),¹⁴ clearly pointing to a double minimum potential in the hydrogen bond. This result is in complete agreement with recent quantum chemical,¹⁵ microwave spectroscopic,¹⁶ and X-ray photoelectron spectroscopic¹⁷ findings.

Positive deuterium and tritium isotope shift effects are also observed for the hydrogen bond in protonated "proton sponge" (1-dimethylamine-8-dimethylammonium naphthalene cation) which places this bond in the double minimum category. This finding is in agreement with N_{1s} X-ray photoelectron spectroscopic results.¹⁸

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$$\Delta\delta(^1\text{H}, ^k\text{H}) = \delta(^1\text{H}) - \delta(^k\text{H}) \quad (k = 2 \text{ or } 3)$$
 where the ¹H chemical shifts are measured relative to tetramethylsilane and the ²H and ³H chemical shifts are given relative to ²H and ³H labeled Me₄Si, respectively. This implies that the measured isotope effects will contain a contribution from the isotope effect of the reference. The latter should, however, be constant and in all likelihood much smaller than those reported in this communication. For practical reasons the isotope effects reported here have been measured relative to some convenient standard, for example, the solvent NMR signals. The small additional isotope effects so introduced are neglected.
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- (10) When the central barrier in the double minimum case decreases well below the lowest zero-point vibrational levels we will have a situation similar to that for a true single minimum case.
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describing the potential energy function, but it can be estimated that the bond length in a symmetrical single minimum O—O potential will decrease by a few thousands of an ångström when deuterium is substituted for protium. Thus this effect would also give rise to negative isotope effects, although seemingly smaller than the values actually observed in the hydrogen maleate and hydrogen phthalate anions (Table I).

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Characterization and Molecular Structure of [(PPh₃)RhC₂B₉H₁₁]₂, a Phosphinorhodacarborane Dimer Containing Rh–H–B Bridges

Sir:

We have recently shown that a number of B–H-containing substrates undergo catalytic isotopic exchange of terminal hydrogen with deuterium gas¹ in the presence of the hydrido-rhodacarborane [3,3-(PPh₃)₂-3-H-3,1,2-RhC₂B₉H₁₁] (I) and a mechanism was postulated which involved the oxidative addition of boron–hydrogen bonds to the catalytic species. The complex I is also an efficient homogeneous catalyst for the hydrogenation of terminal olefins² and it was observed during hydrogenation studies³ that exposure of a yellow solution of I and substrate olefin to air produced a purple product.⁴ We report the complete characterization of the purple complex II,⁵ which can be viewed as a model intermediate in the oxidative addition of a terminal boron–hydrogen bond to rhodium.

The complex II was prepared by heating a solution of I in benzene with 2 equiv of benzoyl peroxide. The reaction mixture was purified by column chromatography (silica gel, 2:1 heptane–benzene) and the complex was obtained in 40% yield as dark purple microcrystals.⁶

The infrared spectrum of II (Nujol) showed a band characteristic of terminal B–H bonds at 2600 cm⁻¹ and peaks due to the coordinated dicarbollide and triphenylphosphine ligands. The visible spectrum in benzene exhibited peaks at 570 nm (log ϵ 3.76) and 390 (3.76) and the elemental analysis supported the formulation of II as [(Ph₃P)RhC₂B₉H₁₁]_n which resembled a partially characterized compound previously reported in the literature.⁷ Calcd for C₂₀H₂₆PRhB₉: C, 48.28; H, 5.27; B, 19.55; P, 6.22; Rh, 20.68. (Anal. Found: C, 48.27; H, 5.21; B, 19.76; P, 5.72; Rh, 20.01.) Osmometric molecular weight studies in benzene gave mol wt 965 ± 32 (three determinations). Calcd for [C₂₀H₂₆PRhB₉]₂: mol wt 995.22. The 200-MHz ¹H NMR spectrum in CD₂Cl₂ showed a complex multiplet centered at δ 7.33 due to the PPh₃ ligands, three carborene C–H resonances⁸ at 3.52 (area 2), 2.57 (1) and 1.62 (1) and a complex multiplet at 1.23 due to B–H resonances. A broad resonance at δ -18.5 due to the hydrogen atoms of the inequivalent Rh–H–B bridges sharpens to two resonances at 233 K (δ -18.0 and -19.0). The 80.5-MHz ¹¹B{¹H} NMR spectrum in CD₂Cl₂⁹ exhibited peaks at -26.2, -16.3, -4.8, 3.5, and 24.2 ppm in a ratio of 1:8:7:1:1. The 81.02-MHz ³¹P{¹H} NMR spectrum in C₆D₆¹⁰ gave two doublets of equal

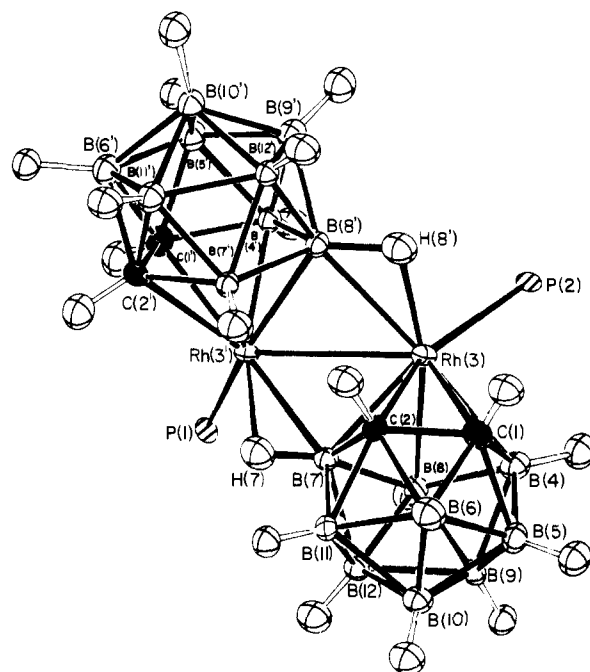


Figure 1. Molecular structure of II (CH₂Cl₂ solvate molecules and phenyl rings on phosphorus atoms are omitted for clarity).

Table I

cell data	298 K	113 K
cell dimensions		
<i>a</i> , Å	11.202 (2)	11.118 (2)
<i>b</i> , Å	13.660 (3)	13.456 (3)
<i>c</i> , Å	18.565 (3)	18.390 (3)
α , deg	93.48 (2)	93.09 (2)
β , deg	76.44 (1)	76.22 (1)
γ , deg	76.80 (2)	76.90 (2)
cell volume, <i>V</i> , Å ³	2669.1 (1.0)	2585.7 (9)
X-ray density, ρ , g cm ⁻³	1.350 (<i>Z</i> = 2)	1.362
floatation density, $KI_{(aq)}$, g cm ⁻³	1.32 (5)	

Table II. Selected Bond Distances and Angles

dis- tances, Å	Rh(3)		angles, deg		Rh(3')	
	Rh(3)	Rh(3')	Rh–H–B _σ	Rh–B _σ –Rh ^a	Rh(3)	Rh(3')
Rh–H	1.78 (6)	1.77 (6)	97 (4)	102 (5)		
Rh–B _σ	2.327 (8)	2.238 (8)	Rh–B _σ –Rh ^a	75.7 (2)	77.2 (2)	
Rh–C	2.251 (6)	2.214 (7)	B _σ –Rh–P	101.1 (2)	96.2 (2)	
	2.280 (7)	2.269 (7)				
Rh–B	2.190 (8)	2.173 (8)	Rh–Rh ^a –B _σ	50.6 (2)	49.7 (2)	
	2.211 (8)	2.190 (8)				
	2.220 (8)	2.221 (8)	P–Rh–H	85 (2)	89 (2)	
Rh–P	2.338	2.360 (2)				
Rh–Rh	2.7628 (9)					

^a Refers to Rh atom not indicated by column heading.

intensity centered at 36.7 (*J*_{P–Rh} = 172 Hz)¹¹ and 29.7 ppm (*J*_{P–Rh} = 135 Hz).

Suitable crystals for X-ray diffraction studies were obtained by layering a CH₂Cl₂ solution of II with heptane.¹² The dark purple crystals of II are triclinic, *P* $\bar{1}$. Cell data are presented in Table I.¹³ The molecular structure of II is shown in Figure 1; significant bond distances and angles are presented in Table II.

As can be seen from Figure 1, each rhodium atom is symmetrically bound to the pentagonal face of the dicarbollide ligand and interacts with the other dicarbollide ligand via a