

$^1\text{H}/^2\text{H}$ NMR Studies of Geometric H/D Isotope Effects on the Coupled Hydrogen Bonds in Porphycene Derivatives

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Abstract: The ^1H and ^2H NMR spectra of porphycene (**1**), 2,3,6,7,12,13,16,17-octaethylporphycene (**2**), 2,7,12,17-tetra-*n*-propylporphycene (**3**), and 2,7,12,17-tetra-(*tert*-butyl)-3,6-13,16-dibenzo[*cde,mno*]porphycene (**4**) partially deuterated in the mobile proton sites are reported. These compounds exhibit two intramolecular NHN hydrogen bonds of increasing strength representing models of the concerted HH transfer in the parent compound, porphycene. The ^1H chemical shifts of the mobile protons are correlated with the difference of the energies of the amino- and imino-N1s orbitals reported by Ghosh A.; Moulder J.; Bröring M.; Vogel E. *Angew. Chem., Int. Ed.* **2001**, *113*, 445–448. The chemical shifts of **4** indicate a reduced contribution of the aromatic ring current as compared to the other compounds which is associated to the nonplanarity of this molecule. The primary H/D isotope effects on the chemical shifts give information about the *primary*, *secondary*, and *vicinal* geometric isotope effects of the two inner hydrogen bonds of porphycenes. The *vicinal* effects indicate a cooperative coupling of the two hydrogen bonds which may favor a concerted double proton-transfer mechanism.

Introduction

The measurement and interpretation of H/D isotope effects on hydrogen bond geometries has become an important tool for the characterization of proton motions in strong hydrogen bonds.^{1–3} Effects of deuteration on the heavy atoms distances of the latter have been observed a long time ago by Ubbelohde.⁴ These findings arise from anharmonic hydrogenic vibrations and can be referred to as *secondary geometric H/D isotope effects*. Recently, dipolar solid-state NMR techniques have been devised and refined in order to study not only the *secondary* but also the *primary geometric H/D isotope effects*, which refer to the different hydrogen bond positions of H and of D.^{5,6} As illustrated in Figure 1a, a general result is that in the case of asymmetric

hydrogen bonds, replacement of D by H leads to a displacement of the hydron (proton, deuteron, triton) toward the H-bond center which is accompanied by a hydrogen bond compression. By contrast, in the case of a symmetric H-bond exhibiting a single well, the deuterated bond is somewhat shorter than the protonated bond.^{5,7,8}

As hydrogen bond geometries are correlated with NMR chemical shifts,^{9,10} H/D isotope effects on the latter are very sensitive probes for obtaining information about geometric H/D isotope effects of hydrogen bonds. In principle, it is possible to calculate these effects from first principles as demonstrated recently for an intramolecular hydrogen bond¹¹ by a combination of *ab initio* calculations, calculations of multidimensional anharmonic vibrational wave functions and—for comparison with NMR chemical shifts—the calculation of the chemical shielding hypersurfaces. However, such calculations are very demanding and difficult to perform for a series of compounds. Thus, empirical hydrogen bond correlations have been proposed by some of us to correlate geometric and chemical shift isotope effects.^{1,5,6,9,10,12–15}

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- (1) Limbach, H. H.; Denisov, G. S.; Golubev, N. S. Hydrogen Bond Isotope Effects Studied by NMR. In *Isotope Effects in the Biological and Chemical Sciences*; Kohen, A., Limbach, H. H., Eds.; Taylor & Francis: Boca Raton FL, 2005; Chapter 7, pp 193–230.
- (2) Lau, J. S.; Perrin, C. Isotope Effects and Symmetry of Hydrogen Bonds in Solution: Single- and Double-Well Potential. In *Isotope Effects in the Biological and Chemical Sciences*; Kohen, A., Limbach, H. H., Eds.; Taylor & Francis: Boca Raton FL, 2005; Chapter 8, pp 230–252.
- (3) Hansen, P. E. NMR Studies of Isotope Effects of Compounds with Intramolecular Hydrogen Bonds. In *Isotope Effects in the Biological and Chemical Sciences*; Kohen, A., Limbach, H. H., Eds.; Taylor & Francis: Boca Raton FL, 2005; Chapter 9, pp 252–280.
- (4) Ubbelohde, A. R.; Gallagher, K. G. *Acta Crystallogr.* **1955**, *8*, 71–73.
- (5) Benedict, H.; Limbach, H. H.; Wehlan, M.; Fehlhammer, W. P.; Golubev, N. S.; Janoschek, R. *J. Am. Chem. Soc.* **1998**, *120*, 2939–2950.
- (6) Lorente, P.; Shenderovich, I. G.; Golubev, N. S.; Denisov, G. S.; Buntkowsky, G.; Limbach, H. H. *Magn. Reson. Chem.* **2001**, *39*, S18–S29.

(7) Almlöf, J. *Chem. Phys. Lett.* **1972**, *17*, 49–52.

- (8) Schah-Mohammed, P.; Shenderovich, I. G.; Detering, C.; Limbach, H. H.; Tolstoy, P. M.; Smirnov, S. N.; Denisov, G. S.; Golubev, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 12878–12879.
- (9) Limbach, H. H.; Pietrzak, M.; Benedict, H.; Tolstoy, P. M.; Golubev, N. S.; Denisov, G. S. *J. Mol. Struct.* **2004**, *706*, 115–119.
- (10) Limbach, H. H.; Pietrzak, M.; Sharif, S.; Tolstoy, P. M.; Shenderovich, I. G.; Smirnov, S. N.; Golubev, N. S.; Denisov, G. S. *Chem. Eur. J.* **2004**, *10*, 5195–5204.
- (11) Stare, J.; Jezierska, A.; Ambrožič, G.; Košir, I. J.; Kidrič, J.; Koll, A.; Mavri, J.; Hadži, D. *J. Am. Chem. Soc.* **2004**, *126*, 4437–4443.

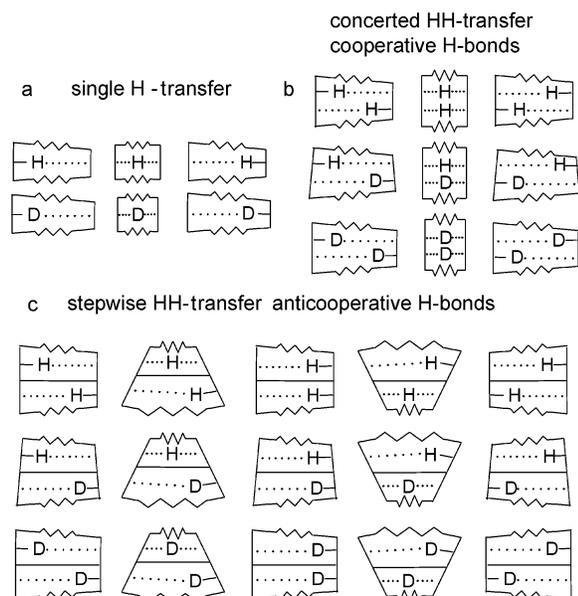


Figure 1. Simplified models of H- and D-substituted hydrogen-transfer systems. The boxes containing springs symbolize the symmetries and the compressibilities of the hydrogen bonds. (a) Geometric H/D isotope effects during compression assisted H transfer in a single hydrogen bond. The *primary* geometric isotope effect refers to a different position of H and D in the hydrogen bond. The *secondary* geometric isotope effect refers to different positions of the heavy atoms in protonated and deuterated hydrogen bonds. (b) Geometric H/D isotope effects during compression assisted concerted HH transfer in two cooperatively coupled hydrogen bonds. (c) Geometric H/D isotope effects during compression assisted stepwise HH transfer in two anti-cooperatively coupled hydrogen bonds.

In hydrogen-bonded networks also *vicinal isotope effects* are observed where replacement of H by D does not only affect the bond in which the substitution occurs but also a neighboring hydrogen bond coupled to the first one.^{12–15} In the case of cooperative coupling the vicinal bond experiences similar geometric changes as the first one (Figure 1b). By contrast, in the case of *anti-cooperative* coupling the vicinal bond exhibits the opposite changes as compared to the bond in which the isotopic substitution occurs (Figure 1c). The comparison of both cases shows a possible impact on the mechanism of the HH transfer in coupled hydrogen bonds. Whereas cooperative coupling seems to favor a concerted transfer pathway, anti-cooperative coupling naturally explains a stepwise reaction mechanism. This idea is supported by the finding of cooperative coupling in the cyclic dimer of acetic acid,¹² which exhibits a single barrier for HH transfer as is well established for this type of systems.¹⁶

A particularly interesting system where the mechanism is still open to discussion is the tautomerism of porphycene **1** which has been synthesized by Vogel and co-workers.¹⁷ Using ¹⁵N

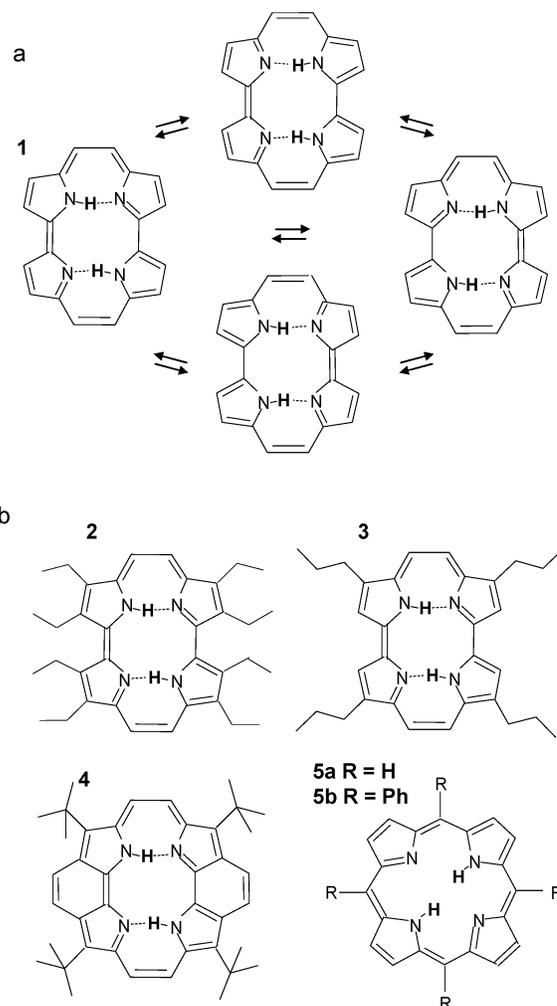


Figure 2. (a) Concerted vs stepwise HH transfer in porphycene (**1**). (b) Chemical structures of porphycenes derivatives (**2**, **3**, **4**) and of porphyrins (**5**).

NMR spectroscopy, Wehrle et al.¹⁸ have observed a fast tautomerism in the polycrystalline compound, whose rate constants were measured by ¹⁵N relaxometry.¹⁹ A barrier of about 32 kJ mol⁻¹ was observed. It could, however, not be decided whether the reaction is stepwise as in the parent compound porphyrin²⁰ or whether it is concerted as illustrated in Figure 2a. Waluk et al.²¹ have observed tunnel splittings of porphycene in the gas phase arising from a coherent concerted double proton tunnel process in the ground state and the electronic excited state. In addition, a rate process attributed to a double proton transfer in the first excited state of porphycene embedded in a polymer matrix²² was observed. Malsch and Hohlneicher²³ have performed a matrix isolation study of

- (12) Smirnov, S. N.; Golubev, N. S.; Denisov, G. S.; Benedict, H.; Schah-Mohammed, P.; Limbach, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 4094–4101.
 (13) Shenderovich, I. G.; Tolstoy, P. M.; Golubev, N. S.; Smirnov, S. N.; Denisov, G. S.; Limbach, H. H. *J. Am. Chem. Soc.* **2003**, *125*, 11710–11720.
 (14) Shenderovich, I. G.; Limbach, H. H.; Smirnov, S. N.; Tolstoy, P. M.; Denisov, G. S.; Golubev, N. S. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5488–5497.
 (15) Tolstoy, P. M.; Schah-Mohammed, P.; Smirnov, S. N.; Golubev, N. S.; Denisov, G. S.; Limbach, H. H. *J. Am. Chem. Soc.* **2004**, *126*, 5621–5634.
 (16) Meyer, R.; Ernst, R. R. *J. Chem. Phys.* **1990**, *93*, 5518–5532.
 (17) Vogel, E.; Köcher, M.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Ed.* **1986**, *26*, 257–259.

- (18) Wehrle, B.; Limbach, H. H.; Köcher, M.; Ermer, O.; Vogel, E. *Angew. Chem., Int. Ed.* **1987**, *26*, 934–936.
 (19) Langer, U.; Hoelger, Ch.; Wehrle, B.; Latanowicz, L.; Vogel, E.; Limbach, H. H. *J. Phys. Org. Chem.* **2000**, *13*, 23–34.
 (20) (a) Braun, J.; Schlabach, M.; Wehrle, B.; Köcher, M.; Vogel, E.; Limbach, H. H. *J. Am. Chem. Soc.* **1994**, *116*, 6593–6604. (b) Braun, J.; Limbach, H. H.; Williams, P.; Morimoto, H.; Wemmer, D. *J. Am. Chem. Soc.* **1996**, *118*, 7231–7232.
 (21) (a) Sepiol, J.; Stepanenko, Y.; Vdovin, A.; Mordzinski, A.; Vogel, E.; Waluk, J. *Chem. Phys. Lett.* **1998**, *296*, 549–556. (b) Galievsky, V.; Starukhin, A.; Vogel, E.; Waluk, J. *J. Phys. Chem. A* **1998**, *102*, 4966–4971. (c) Starukhin, A.; Vogel, E.; Waluk, J. *J. Phys. Chem. A* **1998**, *102*, 9999–10006. (d) Gil, M.; Jasny, J.; Vogel, E.; Waluk, J. *Chem. Phys. Lett.* **2000**, *323*, 534–541. (e) Dobkowski, J.; Galievsky, V.; Starukhin, A.; Vogel, E.; Waluk, J. *J. Phys. Chem. A* **1998**, *102*, 4966–4971.

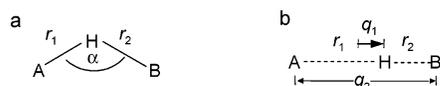


Figure 3. (a) Parameters characterizing the geometry of a hydrogen bond, i.e., the distances r_1 and r_2 and the angle (α). (b) General hydrogen bond coordinates $q_1 = 1/2(r_1 - r_2)$ and $q_2 = r_1 + r_2$ illustrated for the case of a linear hydrogen bond.

porphycene and measured IR, Raman, and UV/vis spectra, as well as site-selective fluorescence and fluorescence excitation spectra. In spite of many efforts, the NH-stretching vibrations could not be identified. Quantum-mechanical calculations indicated a border-line case between a stepwise and a concerted transfer. More recent calculations predict the trans-form to be more stable than the cis-form, as well as a stepwise pathway which is slightly favored over the concerted pathway.^{24,25} Barriers of about 20 kJ mol⁻¹ were calculated for the stepwise and those of about 26 kJ mol⁻¹ for the concerted pathway, where zero-point energy contributions were not taken into account. Ghosh et al.²⁶ have published an X-ray photoelectron study (XPS) of a series of porphycenes **1–4** (Figure 2b) in comparison with *meso*-tetraphenylporphyrin (**5b**). They observed inequivalent nitrogen nuclei which do not interconvert in the time scale of the XPS experiment. However, the energy difference between the two 1s nitrogen orbitals decreased in the series **5b**, **2**, **1**, **3**, **4**, indicating a partial symmetrization of the two hydrogen bonds with decreasing N...N distance.

The scope of this paper was to determine the ¹H and ²H chemical shifts of **1–4** and hence the degree of cooperativity of the two hydrogen bonds in porphycenes using hydrogen bond correlation methods. A more rigorous theoretical treatment based on first principles will be published elsewhere.²⁷ In the following, we will give a short introduction into the tool of hydrogen bond correlations used to analyze the results. After an experimental section the results are reported and discussed.

Theoretical Section

In this section, we discuss various NHN hydrogen bond correlations arising from empirical data. The basic assumption is that the relations used for single hydrogen bonds can also be taken for multiple hydrogen bonds as well.

One can associate to any hydrogen-bonded system A–H...B two distances r_1 and r_2 and a hydrogen bond angle α as indicated in Figure 3a. It is convenient to define additionally the natural hydrogen bond coordinates q_1 and q_2 according to

$$q_1 = 1/2(r_1 - r_2), \quad q_2 = r_1 + r_2 \quad (1)$$

In the case of a linear hydrogen bond, q_1 corresponds directly to the distance of the proton with respect to the hydrogen bond center and q_2 to the heavy atom A...B distance as indicated in Figure 3b. According to the valence bond order concept of

Table 1. Parameters of the Anharmonic Correction in Equation 5 According to ref 9 and Corrected for Porphycene-like Systems

	$b/\text{\AA}$	$r^\circ/\text{\AA}$	f	g	c^H	d^H	c^D	d^D
ref 9	0.370	0.997	5	2	330	1.2	30	1.1
used in this paper	0.370	0.997	5	2	250	0.85	30	0.75

Pauling, Brown, and Dunitz et al.²⁸ one can associate to both bonds a valency p_i given by

$$p_i = \exp\{-(r_i - r_i^\circ)/b_i\} \quad (2)$$

where b_i is a bond decay parameter and r_i° the equilibrium distance in a fictive diatomic reference molecule where $p_i = 1$. p_i becomes zero at infinite distance. A hydrogen-bonded system A–H...B is then characterized by two bond valences p_1 and p_2 whose sum is unity, i.e.

$$p_1 + p_2 = \exp\{-(r_1 - r_1^\circ)/b_1\} + \exp\{-(r_2 - r_2^\circ)/b_2\} = 1 \quad (3)$$

Thus, both distances r_1 and r_2 depend on each other. Using eq 3, it is possible to express r_1 as a function of r_2 , or q_1 as a function of q_2 . For the case N–H...N hydrogen bonds where $b_1 = b_2 = b$ and $r_1^\circ = r_2^\circ = r^\circ$ it follows that⁵

$$q_2 = r_1 + r_2 = 2r^\circ + 2q_1 + 2b \ln[1 + \exp\{-2q_1/b\}] \quad (4)$$

Gilli and Steiner et al.²⁹ showed the validity of eq 4 on the basis of a number of neutron diffraction structures contained in the Cambridge Structural Database. The parameters of eq 4 (Table 1) depended on whether strong hydrogen bonds are included or not.^{5,29d} In fact, it was not possible to describe both strong and weak hydrogen bonds in terms of eq 4. Thus, it was shown that eq 4 is valid only in the absence of anharmonic zero-point vibrations.^{7,8} The latter requires a correction which is different for NHN and NDN systems. An empirical correction term for the isotopic sensitive valence bond orders was proposed, i.e.

$$p_1^L = p_1 - c^L(p_1 p_2)^f (p_1 - p_2) - d^L(p_1 p_2)^g; \\ p_2^L = p_2 + c^L(p_1 p_2)^f (p_1 - p_2) - d^L(p_1 p_2)^g \quad (5)$$

where c , d , f , g are isotope sensitive empirical parameters included in Table 1, and where L = H, D.

Benedict et al. have proposed to express ¹H chemical shifts as a function of the valence bond orders,^{30,31}

$$\delta(^1\text{H}) = \Delta_{\text{H}}(4p_1 p_2)^m + \delta_1^0 p_2 + \delta_2^0 p_1 \quad (6)$$

where Δ_{H} is the excess chemical shift of the quasi-symmetric complex and δ_1^0 and δ_2^0 are the limiting chemical shifts for distances r_1° and r_2° , respectively. Further, m is an empirical

(22) Waluk, J. *Acc. Chem. Res.* Published online August 25, 2006, <http://dx.doi.org/10.1021/ar0680365>.
 (23) (a) Malsch, T.; Hohlneicher, G. *J. Phys. Chem. A* **1997**, *101*, 8409–8416. (b) Malsch, T.; Roeb, M.; Karuth, V.; Hohlneicher, G. *Chem. Phys.* **1998**, *227*, 331–348.
 (24) Kozłowski, P. M.; Zgierski, M. Z.; Baker, J. J. *Chem. Phys.* **1998**, *109*, 5905–5913.
 (25) Cybulski, H.; Pecul, M.; Helgaker, T.; Jaszunski, M. *J. Phys. Chem. A* **2005**, *109*, 4162–4171.
 (26) Ghosh, A.; Moulder, J.; Bröring, M.; Vogel, E. *Angew. Chem., Int. Ed.* **2001**, *113*, 445–448.
 (27) Shibl, M. F.; Kühn, O.; Pietrzak, M.; Limbach, H. H. *ChemPhysChem*. In press.

(28) (a) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542–553. (b) Brown, I. D. *Acta Crystallogr.* **1992**, *B48*, 553–572. (c) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–161.
 (29) (a) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909–915. (b) Steiner, T.; Saenger, W. *Acta Crystallogr.* **1994**, *B50*, 348–357. (c) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1331. (d) Steiner, T. *J. Phys. Chem. A* **1998**, *102*, 7041–7052.
 (30) Smirnov, S. N.; Benedict, H.; Golubev, N. S.; Denisov, G. S.; Kreevov, M. M.; Schowen, R. L.; Limbach, H. H. *Can. J. Chem.* **1999**, *77*, 943–949.
 (31) Benedict, H.; Shenderovich, I. G.; Malkina, O. L.; Malkin, V. G.; Denisov, G. S.; Golubev, N. S.; Limbach, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 1979–1988.

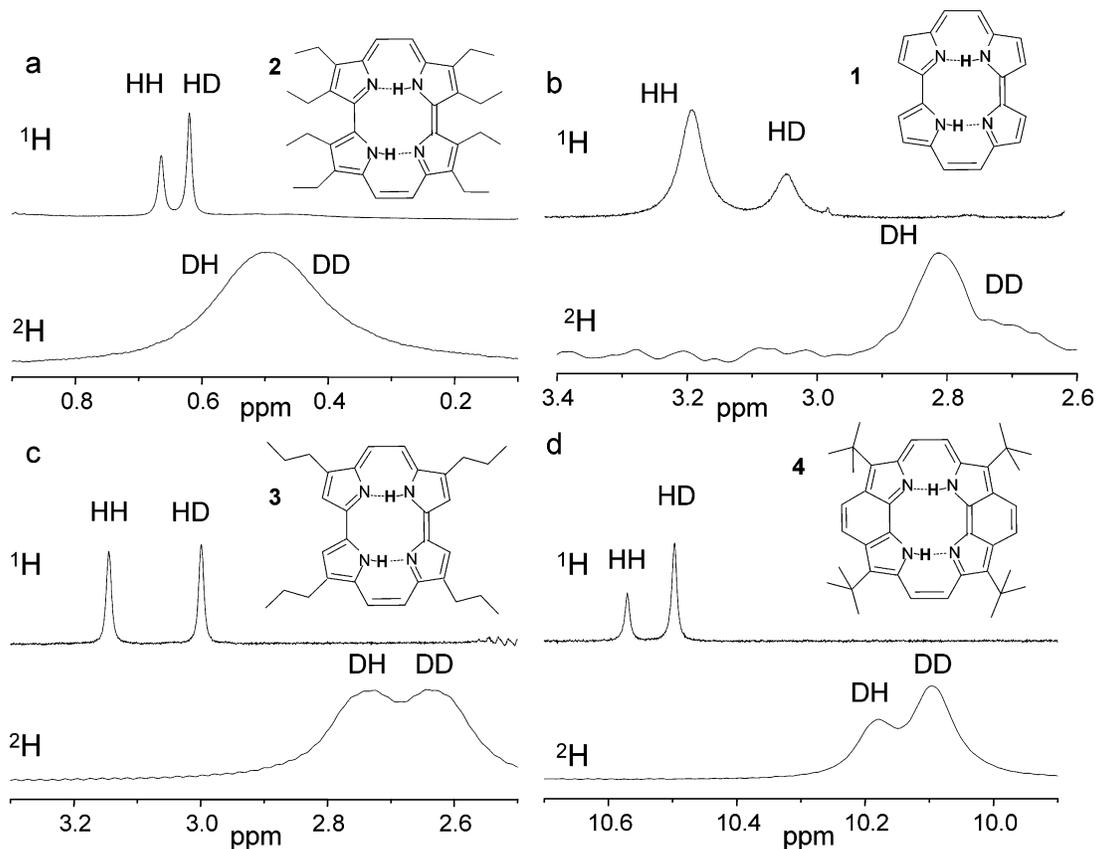


Figure 4. Inner proton and deuterium NMR signals of partially deuterated porphycenes dissolved in CDCl_3 ($T = 299 \text{ K}$). (a) **2**, $x_D = 0.6$, (b) **1**, $x_D = 0.25$. (c) **3**, $x_D = 0.5$. (d) **4**, $x_D = 0.7$ where x_D represents the deuterium fraction of the inner proton sites.

Table 2. ^1H and ^2H Chemical Shifts, NN Hydrogen Bond Distances of Porphycenes **1–4** and **5b** in CDCl_3 (0.03 M Solution) and Energy Differences Between Two $1s$ N Orbitals

	n^a	2	1	3	4	5b
$\delta(\text{NHNNHN})$ [ppm]	0	0.66 (± 0.005)	3.17 (± 0.02)	3.15 (± 0.005)	10.57 (± 0.005)	−3.60
$\delta(\text{NHNDN})$ [ppm]	1	0.62 (± 0.005)	3.03 (± 0.02)	3.00 (± 0.005)	10.50 (± 0.005)	−3.60
$\delta(\text{NDNNHN})$ [ppm]	1	0.53 (± 0.07)	2.82 (± 0.04)	2.75 (± 0.06)	10.18 (± 0.04)	−3.60
$\delta(\text{NDNDN})$ [ppm]	2	0.46 (± 0.07)	2.69 (± 0.04)	2.63 (± 0.06)	10.09 (± 0.04)	−3.60
$\Delta E(\text{N}1s)$ [eV] ²⁶		1.75	1.50	1.40	0.95	2.10
$\text{N}\cdots\text{N}$ [\AA]		2.80 ¹⁷	2.63 ³²	2.62 ³³	2.51 ³⁴	2.89 ³⁵

^a n number of deuterons. The margins of error were estimated from the line widths.

fitting parameter with value close to 1. For the $\text{N}-\text{H}\cdots\text{N}$ case, eq 6 can be simplified, because $\delta_1^\circ = \delta_2^\circ$, i.e.

$$\delta(^1\text{H}) = \Delta_{\text{H}}(4p_1p_2)^m + \delta^\circ \quad (7)$$

We propose a similar equation for the energy difference $\Delta E(\text{N}1s)$ between the two $\text{N}1s$ orbitals of porphycenes measured by XPS²⁶

$$\Delta E(\text{N}1s) = -\Delta\Delta E(4p_1p_2)^m + \Delta E^\circ \quad (8)$$

where ΔE° corresponds to the separate amino and imino nitrogens, and $\Delta\Delta E$, to the drop of the energy gap for the strongest symmetric hydrogen bond. The justification for eq 8 is based on one hand on the finding that $\Delta E(\text{N}1s)$ decreases with decreasing $\text{N}\cdots\text{N}$ distance,²⁶ and on the other hand upon the empirical finding that q_2 or q_1 are the relevant correlation parameters, and not the heavy atom distances, which are equal to q_2 only in the case of linear hydrogen bonds.

Experimental Section

The compounds studied, i.e., porphycene,¹⁷ 2,3,6,7,12,13,16,17-octaethylporphycene (**2**),³² 2,7,12,17-tetra-*n*-propylporphycene (**3**),³³ and 2,7,12,17-tetra-(*tert*-butyl)-3,6-13,16-dibenzo[*cde:mno*]porphycene (**4**)^{34,35} were synthesized as described in the literature. For the preparation of partially deuterated NMR samples the compounds were dissolved in CH_3OD , the solvent was evaporated in vacuo, and pure dry CDCl_3 was added. The sample concentrations were about 0.03 M. ^1H and ^2H NMR measurements were performed using a Bruker AMX 500 MHz spectrometer.

Results

The ^1H and ^2H NMR signals of the bridging hydrogen nuclei of **1–4** are depicted in Figure 4. Major changes of the chemical

- (32) Vogel, E.; Koch, P.; Hou, X. L.; Lex, J.; Lausmann, M.; Kisters, M.; Aukauloo, M. A.; Richard, P.; Guillard, R. *Angew. Chem., Int. Ed.* **1993**, *32*, 1600–1604.
 (33) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed.* **1987**, *26*, 928–931.
 (34) Vogel, E. *Pure Appl. Chem.* **1993**, *65*, 143–152.
 (35) (a) Webb, L. E.; Fleischer, E. B. *J. Chem. Phys.* **1965**, *43*, 3100–3111.
 (b) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144–4151.
 (c) Hennig, J.; Limbach, H. H. *J. Am. Chem. Soc.* **1984**, *106*, 292–298.

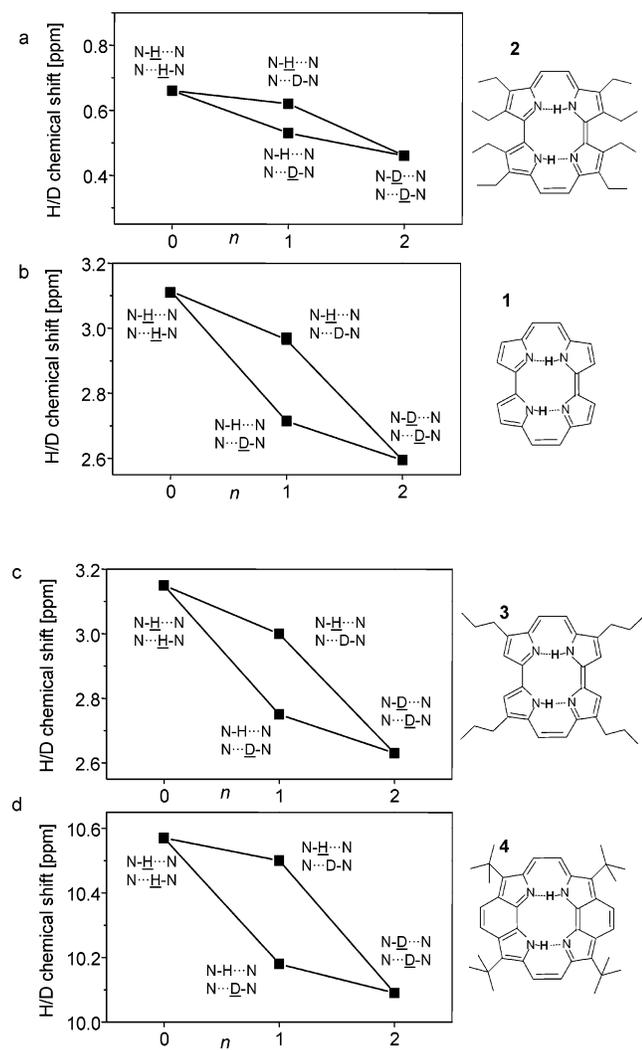


Figure 5. Chemical shifts of the inner hydrons of porphyrin **1** and its derivatives **2**, **3**, and **4** as a function of the number n of deuterons in the inner proton sites.

shifts are observed, ranging from about 0.6 ppm for **2** to about 10.5 ppm for **4**. In all cases, the deuterons of the hydrogen bonds were found to resonate at higher field as compared to the corresponding protons. Moreover, the protons in the vicinal hydrogen bonds were also shifted to high field. The ^2H signals were broad because of the quadrupole interaction of D. Their linewidths were of the order of 0.1 ppm. In the case of **1** and **2** the ^2H signals of DH and DD were not resolved; however, an estimate of the isotope shifts could be obtained by line convolution analysis. The margins of error of the chemical shifts were estimated to be about one-half of the line widths. All chemical shifts are collected in Table 2.

Discussion

The results of our measurements are depicted in Figure 5 where the chemical shifts of the protons and deuterons are plotted as a function of the number n of hydrons in the two intramolecular hydrogen bonds. Within the margin of error the primary H/D isotope effects on the hydron chemical shifts

$${}^p\Delta H(\text{D}) = \delta(\text{N}\underline{\text{D}}\text{NHN}) - \delta(\text{N}\underline{\text{H}}\text{NHN}) \cong \delta(\text{N}\underline{\text{D}}\text{NNDN}) - \delta(\text{N}\underline{\text{H}}\text{NNDN}) \quad (9)$$

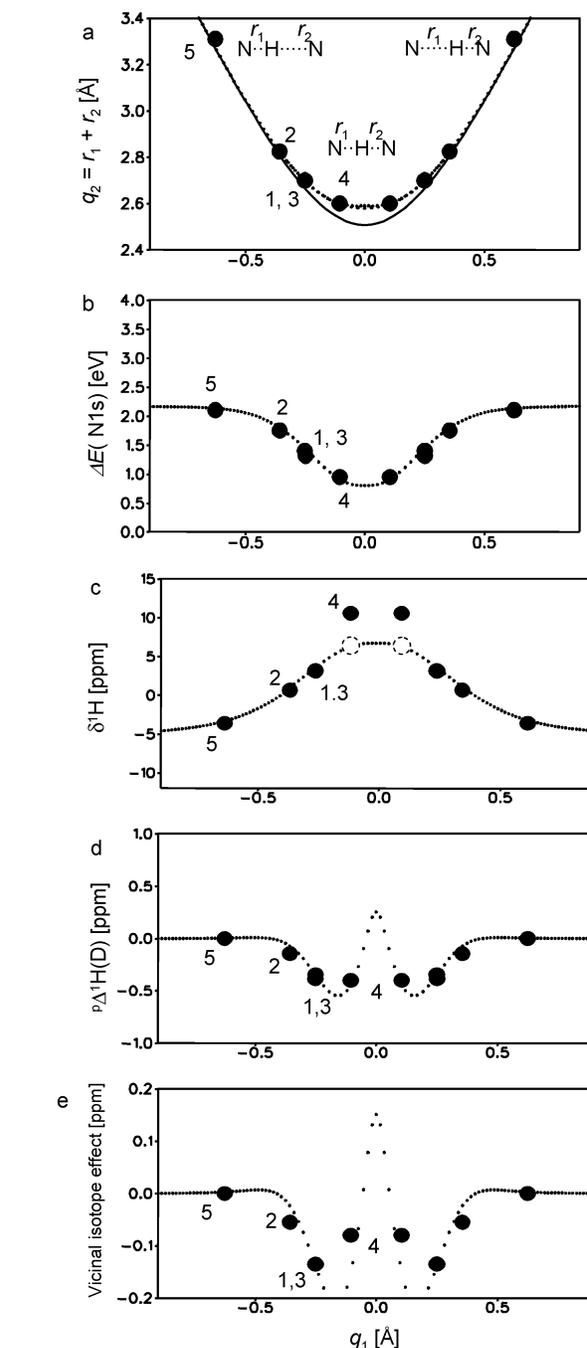


Figure 6. NHN hydrogen bond correlations of porphyrins (**5**) and porphyrines (**1–4**). The calculated solid curve represents equilibrium geometries, the dotted curves include an empirical correction for anharmonic ground-state vibrations.⁹ (a) Correlation of the NHN hydrogen bond length $q_2 = r_1 + r_2$ of porphyrin (**5a**) and porphyrines (**1–4**) with the proton-transfer coordinate $q_1 = \frac{1}{2}(r_1 - r_2)$. (b) Energy difference of the 1s nitrogen orbitals of **1** to **4** and **5b** measured by XPS²⁶ as a function of q_1 . (c) ^1H chemical shifts of the hydrogen-bonded protons as a function of q_1 . (d) Primary H/D isotope effects on the hydron chemical shifts as a function of q_1 . (e) Vicinal H/D isotope effects on the hydron chemical shifts as a function of q_1 .

are independent of whether the neighboring hydrogen bond is protonated or deuterated. In a similar way, a given H or D exhibits the same shift if in the neighboring hydrogen bond H is substituted for D, i.e.

$${}^v\Delta H(\text{D}) = \delta(\text{N}\underline{\text{H}}\text{NNDN}) - \delta(\text{N}\underline{\text{H}}\text{NHN}) \cong \delta(\text{N}\underline{\text{D}}\text{NNDN}) - \delta(\text{N}\underline{\text{D}}\text{NHN}) \quad (10)$$

Table 3. Hydrogen Bond Coordinates of the Isotopomers HH, HD, and DD for Porphycenes 1–4

	2		1		3		4	
	q_1 [Å]	q_2 [Å]	q_1 [Å]	q_2 [Å]	q_1 [Å]	q_2 [Å]	q_1 [Å]	q_2 [Å]
NHNNHN	0.3553 (± 0.0002)	2.8247 (± 0.0003)	0.2500 ^a 0.270 ^b (± 0.0008)	2.7000 ^a 2.702 ^b (± 0.0008)	0.2509 (± 0.0002)	2.7008 (± 0.0002)	0.1050 (± 0.0004)	2.6002 (± 0.0002)
NHNNDN	0.3571 (± 0.0002)	2.8271 (± 0.0003)	0.2559 (± 0.0008)	2.7059 (± 0.0008)	0.2572 (± 0.0002)	2.7072 (± 0.0002)	0.1110 (± 0.0004)	2.6023 (± 0.0002)
NDNNHN	0.3616 (± 0.0032)	2.8318 (± 0.0045)	0.2654 (± 0.0017)	2.7145 (± 0.0017)	0.2683 (± 0.0025)	2.7176 (± 0.0025)	0.1351 (± 0.0022)	2.6120 (± 0.0011)
NDNNDN	0.3647 (± 0.0032)	2.8361 (± 0.0045)	0.2708 (± 0.0017)	2.7202 (± 0.0017)	0.2733 (± 0.0025)	2.7229 (± 0.0025)	0.1408 (± 0.0022)	2.6149 (± 0.0011)

^a From the ¹⁵N NMR relaxation study (ref 19). ^b From the calculations (ref 27).

A similar observation had been made previously for the two coupled hydrogen bonds in FHFHF⁻.¹⁴ This finding allows us to separate the discussion in two parts. In the first part, we will concentrate on the effects of H/D substitution on a given hydrogen bond, and in the second part we will discuss the coupling between both bonds.

Chemical Shift: NHN Hydrogen Bond Correlation of Porphycenes. The observed primary HD isotope shifts are in all cases negative and relatively large, i.e., up to 0.5 ppm. As has been discussed previously,^{1,2,8} this finding is in agreement with the presence of strong low-barrier hydrogen bonds, which exhibit a shortening of the covalent and a lengthening of the hydrogen bond upon deuteration as was illustrated for a single, strong hydrogen bond in Figure 1a. The observed low-field shifts between **1** and **4** indicate a compression of the hydrogen bonds. In the following, we would like, however, to give a more quantitative description of the findings, and correlate them with the findings of the XPS spectra.²⁶

In Figure 6a is depicted the geometric correlation of the hydrogen bond coordinates of NHN hydrogen bonds calculated as described in the theoretical section, using the parameters of Table 1. The solid line was calculated for a series of classical equilibrium geometries, and the dotted line using the empirical parameters for anharmonic zero-point vibrations. As neutron structures which give information about the positions of the hydrogen atoms were not available for porphycenes, we proceeded as follows.

Using ¹⁵N NMR solid-state relaxometry¹⁹ it had been possible to obtain an approximate NH distance for porphycene **1** of about $r_{\text{NH}} = 1.10$ Å, which is correlated with a hydrogen bond distance of $r_{\text{H}\cdots\text{N}} = 1.60$ Å. The corresponding value of $q_1 = \pm 0.25$ Å and $q_2 = 2.70$ Å is labeled as **1** in Figure 6a. q_2 is slightly larger than the N \cdots N distance $R_{\text{NN}} = 2.63$ Å obtained by crystallography,¹⁷ which also gave a hydrogen bond angle of $\alpha_{\text{NH}\cdots\text{N}} = 152^\circ$. As shown in Figure 6a, the anharmonic correction is relatively small. A second point on the correlation curve of Figure 6a was porphyrin **5a**, whose geometry has been calculated recently.³⁶ In the next step, we plotted the values of $\Delta E(\text{N1s})$ ²⁶ for **1** and **5b** in the diagram of Figure 6b and adapted the parameters ΔE^0 and $\Delta\Delta E$ in eq 8 in such a way that the calculated dotted line in Figure 6b reproduced the experimental values of **1** and **5b**.

Using the values of $\Delta E(\text{N1s})$ for the other porphycenes we determined their hydrogen bond coordinates q_1 from the

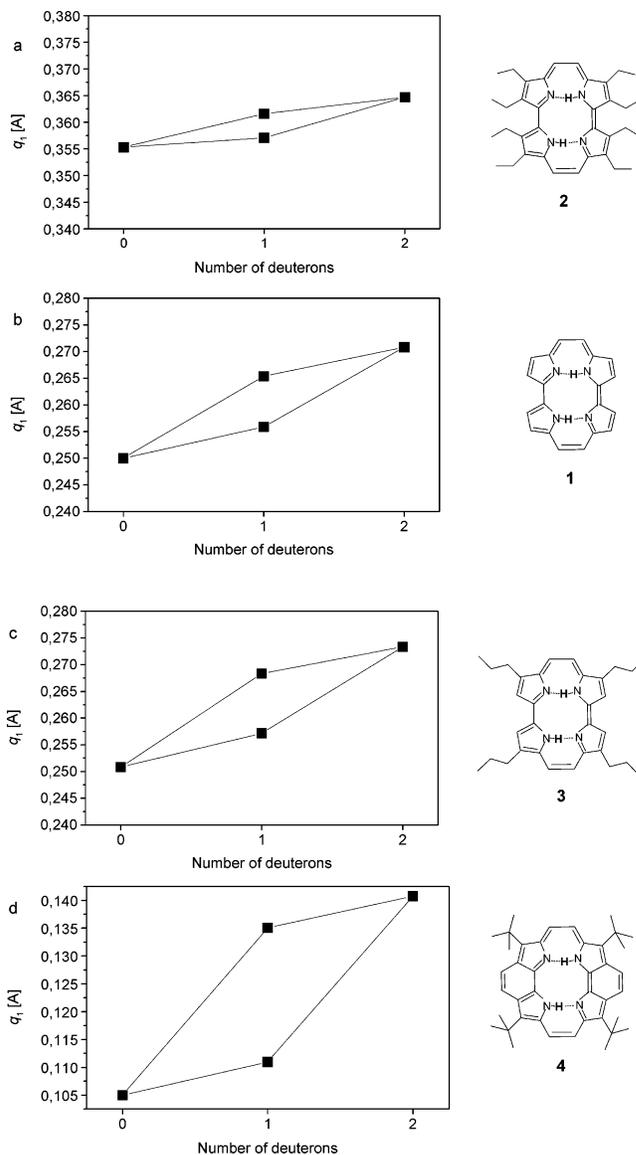


Figure 7. Proton-transfer coordinate $q_1 = 1/2(r_1 - r_2)$ of porphycenes **1–4** as a function of the number n of deuterons in the inner proton sites.

calculated line in Figure 6b, and finally q_2 , from the correlation line of Figure 6a. These values are included in Table 3.

The ¹H chemical shifts of the inner protons of **1–5** as a function of q_1 are depicted in Figure 6c. We found that **1**, **2**, **3**, and **5a** were well reproduced by the dotted correlation line calculated using eq 7, by using the parameters $\Delta_{\text{H}} = 14$ ppm and $\delta^0 = -5$ ppm. We note that the data points of **4** cannot be

(36) Maity, D. K.; Bell, R. L.; Truong, T. N. *J. Am. Chem. Soc.* **2000**, *122*, 897–906.

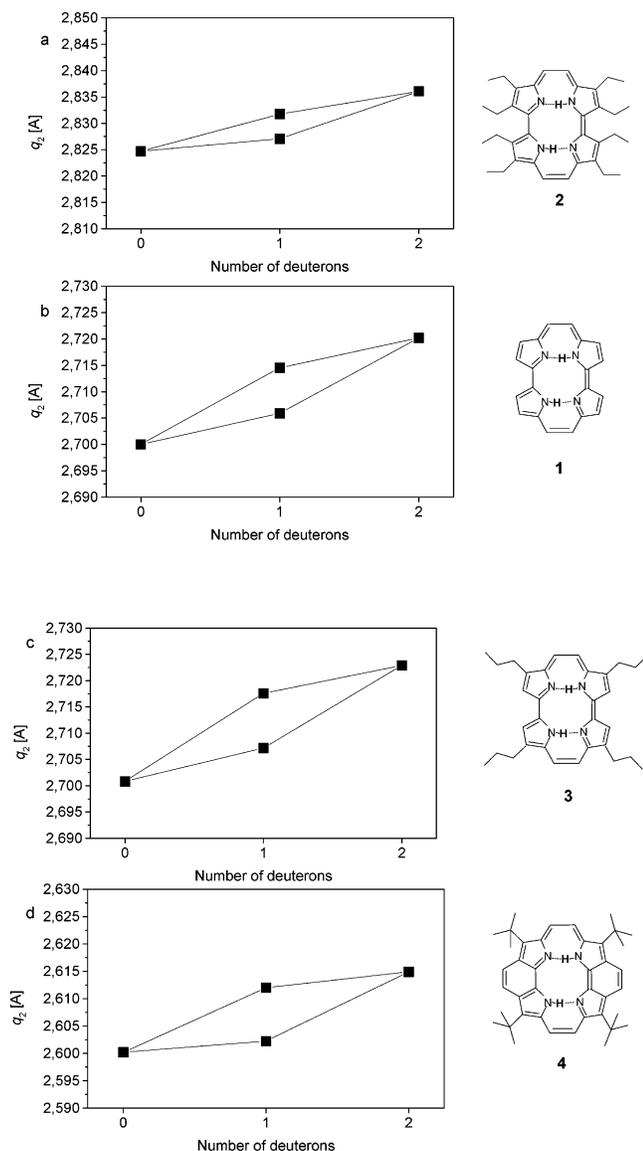


Figure 8. Hydrogen bond length $q_2 = r_1 + r_2$ of porphycenes **1–4** as a function of the number n of deuterons in the inner proton sites.

reproduced in this way. This can be rationalized as follows. The value of δ^0 is mainly determined by the ring current of the aromatic $(4n + 2)$ Hückel- π -electron system of porphyrin which is planar. However, the crystal structure of **4** indicates a nonplanar porphycene skeleton, in which the aromatic ring current is partially suppressed. Therefore, we estimate that the reference value for a system such as **4** must be around $\delta^0 \approx 0$ ppm. By correcting for this difference, one obtains the dotted data points in Figure 6c. This result indicates that other phenomena than hydrogen bond geometries can determine the ^1H chemical shifts and that caution is needed when using equations such as eq 7.

In Figure 6d were then plotted the primary H/D isotope effects on the chemical shifts as a function of the hydrogen bond coordinate q_1 . For the calculation of the dotted line a combination of the all equations listed in the theoretical section and the parameters determined above were used which reproduced well the experimental data. We note that these isotope effects are much less sensitive to the above-mentioned partial suppression of the aromatic ring current in **4** as the terms δ^0 cancel.

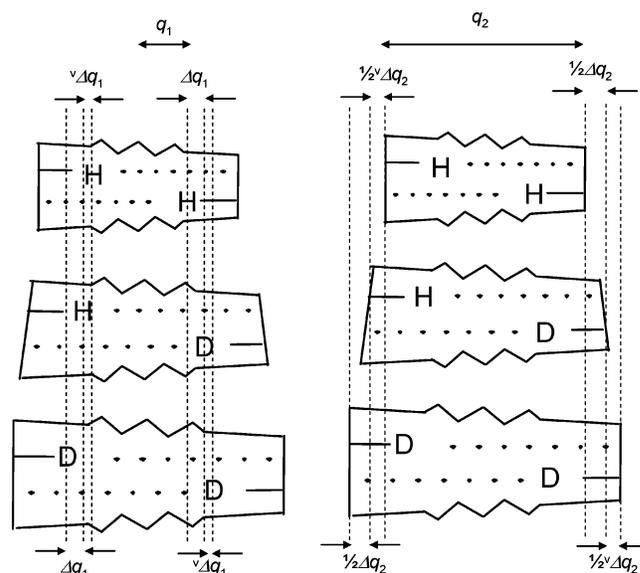


Figure 9. Visualization of H/D isotope effects on cooperatively coupled hydrogen bonds.

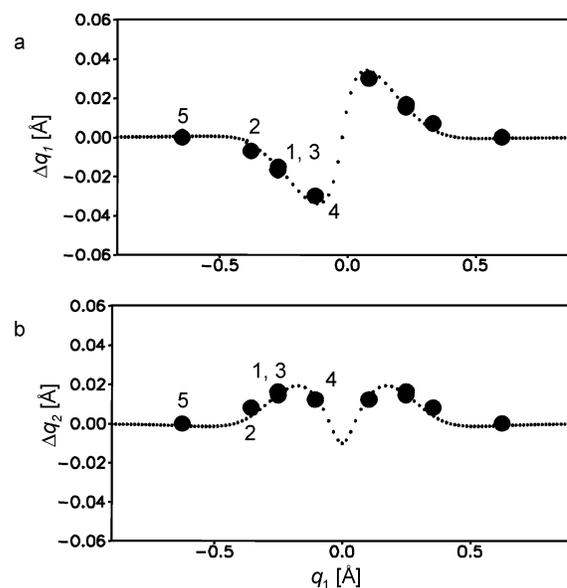


Figure 10. (a) Primary $\Delta q_1 = q_1(\text{NDNNLN}) - q_1(\text{NHNNLN})$ and (b) secondary $\Delta q_2 = q_2(\text{NDNNLN}) - q_2(\text{NHNNLN})$, $L = \text{H, D}$ geometric H/D isotope effects of porphycenes as a function of q_1 .

Additionally, we plot in Figure 6e the vicinal H/D isotope effects on the chemical shifts as a function of the hydrogen bond coordinate, q_1 . Qualitatively, they behave in a way similar to that of the primary effects. However, as no equations for the vicinal isotope effects are available, the dashed line was added only as a guide for the eye.

For the remaining discussion we convert the chemical shift data into geometric effects as illustrated in Figures 7 and 8. The larger effects refer to the geometric changes of a given hydrogen bond after isotopic substitution, the smaller *vicinal* effects from isotopic substitution in vicinal bonds. All effects used in the following discussion are visualized in Figure 9. The *primary* geometric H/D isotope effects represent the changes of the hydron positions

$$\Delta q_1 = q_1(\text{NDNNLN}) - q_1(\text{NHNNLN}), \quad L = \text{H, D} \quad (11)$$

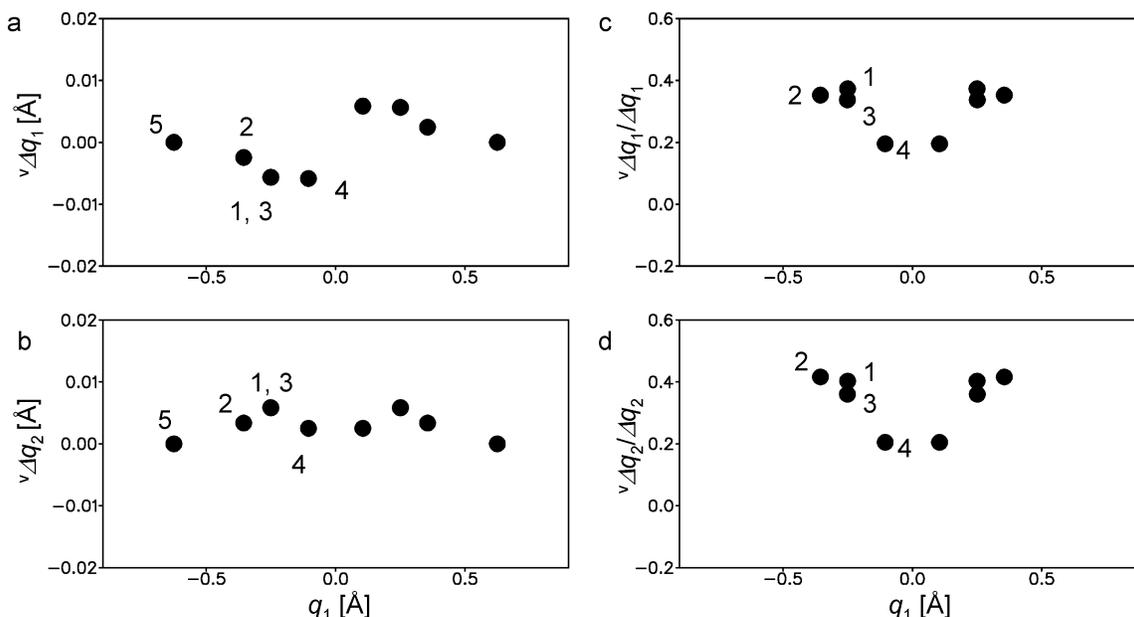


Figure 11. (a) Vicinal primary geometric H/D isotope effects $\Delta q_1 = q_1(\underline{\text{NLNNDN}}) - q_1(\underline{\text{NLNNHN}})$ and (b) vicinal secondary geometric H/D isotope effects $\Delta q_2 = q_2(\underline{\text{NLNNDN}}) - q_2(\underline{\text{NLNNHN}})$ of porphycene as a function of q_1 . (c) and (d) Geometric coupling ratios $\Delta q_1/\Delta q_1$ and $\Delta q_2/\Delta q_2$ as a function of q_1 .

The secondary geometric H/D isotope effects represent the changes of the hydrogen bond lengths

$$\Delta q_2 = q_2(\underline{\text{NDNNLN}}) - q_2(\underline{\text{NHNNLN}}), \quad \text{L} = \text{H, D} \quad (12)$$

The primary vicinal effects represent the changes of the hydron position of a given bond by H/D substitution in a vicinal bond

$$\Delta q_1 = q_1(\underline{\text{NLNNDN}}) - q_1(\underline{\text{NLNNHN}}), \quad \text{L} = \text{H, D} \quad (13)$$

whereas the secondary vicinal geometric H/D isotope effects

$$\Delta q_2 = q_2(\underline{\text{NLNNDN}}) - q_2(\underline{\text{NLNNHN}}) \quad (14)$$

represent the changes of the length of a given hydrogen bond induced by H/D substitution in a vicinal bond. Figures 7 and 8 indicate that within the margin of error the values of eqs 11–14 are independent of whether $\text{L} = \text{H}$ or D which simplifies considerably the following discussion.

In Figure 10 we have plotted the primary and secondary single hydrogen bond isotope effects as a function of the H position q_1 . The dotted lines reproduced very well the data points. Whereas porphyrin **5a** does not exhibit geometric H/D isotope effects as the NH vibrations are quasi-harmonic, the primary geometric H/D isotope effects increase in the series **2**, **1**, **3**, **4**. The latter is expected to exhibit the largest effect. By contrast, the secondary geometric isotope effect is similar for **3** and **4**. A situation of a quasi-symmetric hydrogen bond as found previously for $[(\text{CO})_5\text{C}\equiv\text{N}\cdots\text{H}\cdots\text{N}\equiv\text{C}(\text{CO})_5]^- [\text{AsPh}_4]^{+5}$ is, however, not observed in this series.

Coupling of the Two NHN Hydrogen Bonds in Porphycenes. Finally, we come to the discussion of the coupling of the two hydrogen bonds in porphycene derivatives. In Figure 11 we have plotted the vicinal isotope effects on the hydrogen bond geometries as a function of the H position q_1 .

The vicinal effects observed clearly indicate the presence of cooperative hydrogen bonds. Substitution of H by D in a vicinal hydrogen bond increases the NHN bond length (Figure 11b)

and shifts a given hydron away from the hydrogen bond center (Figure 11a). In weak, i.e. long, hydrogen bonds the effects are small but increase when the hydrogen bonds becomes stronger, i.e. shorter. It is worth noticing that Figure 11a,b looks very similar to Figure 10a,b, which concerns primary and secondary isotope effects.

As the values of the vicinal effects depend on the size of the single hydrogen bond effects, it is interesting to discuss the ratios

$$R_2 = \Delta q_2/\Delta q_2 = [q_2(\underline{\text{NLNNDN}}) - q_2(\underline{\text{NLNNHN}})]/[q_2(\underline{\text{NDNNLN}}) - q_2(\underline{\text{NHNNLN}})] \quad (15)$$

and

$$R_1 = \Delta q_1/\Delta q_1 = [q_1(\underline{\text{NLNNDN}}) - q_1(\underline{\text{NLNNHN}})]/[q_1(\underline{\text{NDNNLN}}) - q_1(\underline{\text{NHNNLN}})] \quad (16)$$

in order to obtain a measure of the geometric coupling of the two hydrogen bonds. R_2 is the bond length change of a given hydrogen bond in the presence of a unit change of the length of the vicinal hydrogen bond. R_1 is the change of the hydron position of a given hydrogen bond in the presence of a unit change of the position of the hydron in a vicinal hydrogen bond.

The results which are depicted in c and d of Figure 11 indicate the following. When a given hydrogen bond is compressed, the vicinal hydrogen bond is also compressed. The effect depends on the hydrogen bond geometry. The maximum compression of the vicinal H-bond is about 40%. In the quasi-symmetric region the effect is still around 20%. Similar effects are observed for the hydron coordinate q_1 . Moving a hydron in one hydrogen bond toward the H-bond center leads to a displacement of the vicinal hydron toward the H-bond center as well, where the displacement of the latter is about 40–20% of the former. Both vicinal effects seem to be correlated with each other; thus, there is some coupling through the skeleton. The behavior of the two graphs in c and d of Figure 11 around $q_1 = 0$ suggests this skeleton coupling vanishes. In this case a direct interaction of

the two protons in the quasi-symmetric hydrogen bond regime may become possible.

Conclusions

We have measured the NMR spectra of partially deuterated porphycenes and analyzed the chemical shifts of the hydrogen-bonded protons and deuterons. With the use of the tool of hydrogen bond correlations these parameters provide interesting information about the average hydrogen bond geometries. Generally, substitution of D by H leads to a compression of a given hydrogen bond and a shift of H toward the hydrogen bond center, as indicated in Figure 1a. Moreover, the two hydrogen bonds of porphycene exhibit a cooperative coupling according to Figure 1b. Thus, compression of one hydrogen bond by isotopic substitution leads to a similar effect in the vicinal hydrogen bond. These effects increase when the hydrogen bonds become shorter until the point of maximum hydrogen bond compression. By contrast, in the structural isomer porphyrin the NHN hydrogen bonds are very weak. Geometric isotope effects are absent as the hydrogenic vibrations are quasi-harmonic.³⁷ Although the two NH-stretching vibrations of porphyrin are coupled,³⁸ compression of one hydrogen bond does not seem to affect the other. Thus, in the transition state of the porphyrin

tautomerism only one NHN hydrogen bond is compressed, whereas the other does not exhibit major changes.³⁶ In other words, the two weak hydrogen bonds of porphyrins are not coupled. This is consistent with a stepwise reaction pathway which has been established experimentally²⁰ and theoretically,^{24,36} as illustrated schematically in Figure 1c.

It would be tempting to conclude that the tautomerism of porphycene is concerted; however, further experimental and theoretical studies will be necessary to support such a conclusion. A further challenge is the theoretical description of geometric isotope effects. For this purpose the calculation of multidimensional vibrational wave functions of the electronic ground-state potential energy surface is necessary. Preliminary results for the HH and DD cases of porphycene **1** have been reported recently.³⁹ A more detailed study that also includes the HD isotopologue and gives an almost quantitative agreement with the data shown in Figures 7b and 8b will be reported elsewhere.²⁷

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(37) Schlabach, M.; Wehrle, B.; Rumpel, H.; Braun, J.; Scherer, G.; Limbach, H. H. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 821–833.

(38) Limbach, H. H.; Hennig, J.; Stulz, J. *J. Chem. Phys.* **1983**, *78*, 5432–5436.

(39) Shibl, M. F.; Tachikawa, M.; Kühn, O. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1368–1373.