

H/D Isotope Effects on ^1H NMR Chemical Shifts in Cyclic Heterodimers and Heterotrimers of Phosphinic and Phosphoric Acids

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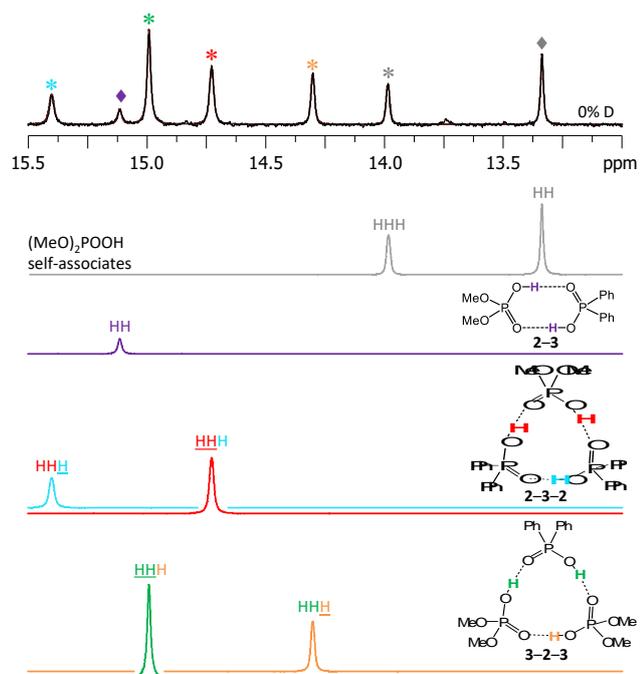


Figure S1. The low-field part of ^1H NMR spectrum of the sample containing acids **2** and **3** (1.8:1) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **2**, heterodimer **2-3** and two heterotrimers, **2-3-2** and **3-2-3**. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

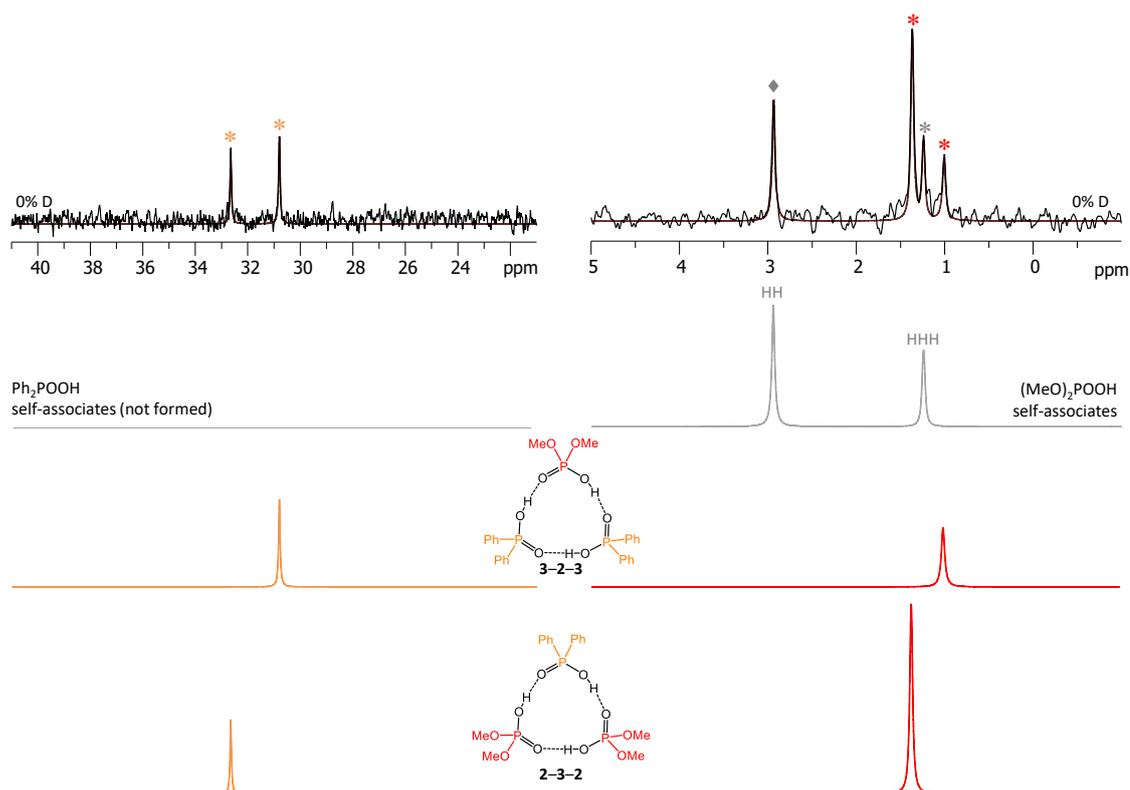


Figure S2. The parts of ^{31}P NMR spectrum of the sample containing acids **2** and **3** (1.8:1) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **2** and two heterotrimers, **2-3-2** and **3-2-3**. The self-associates of **3** are not formed, while the signals of heterodimer **2-3** are not detected due to their low intensity. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

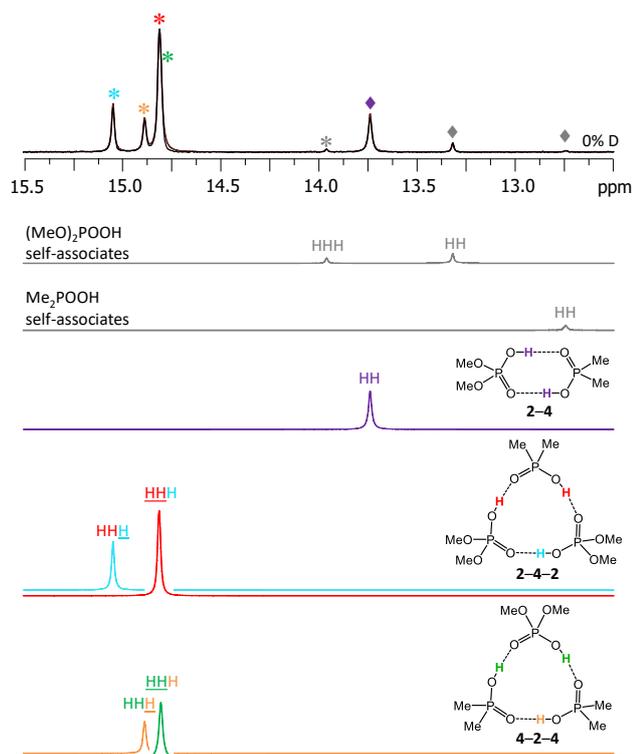


Figure S3. The low-field part of ^1H NMR spectrum of the sample containing acids **2** and **4** (1.3:1) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **2** or **4**, heterodimer **2-4** and two heterotrimers, **2-4-2** and **4-2-4**. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

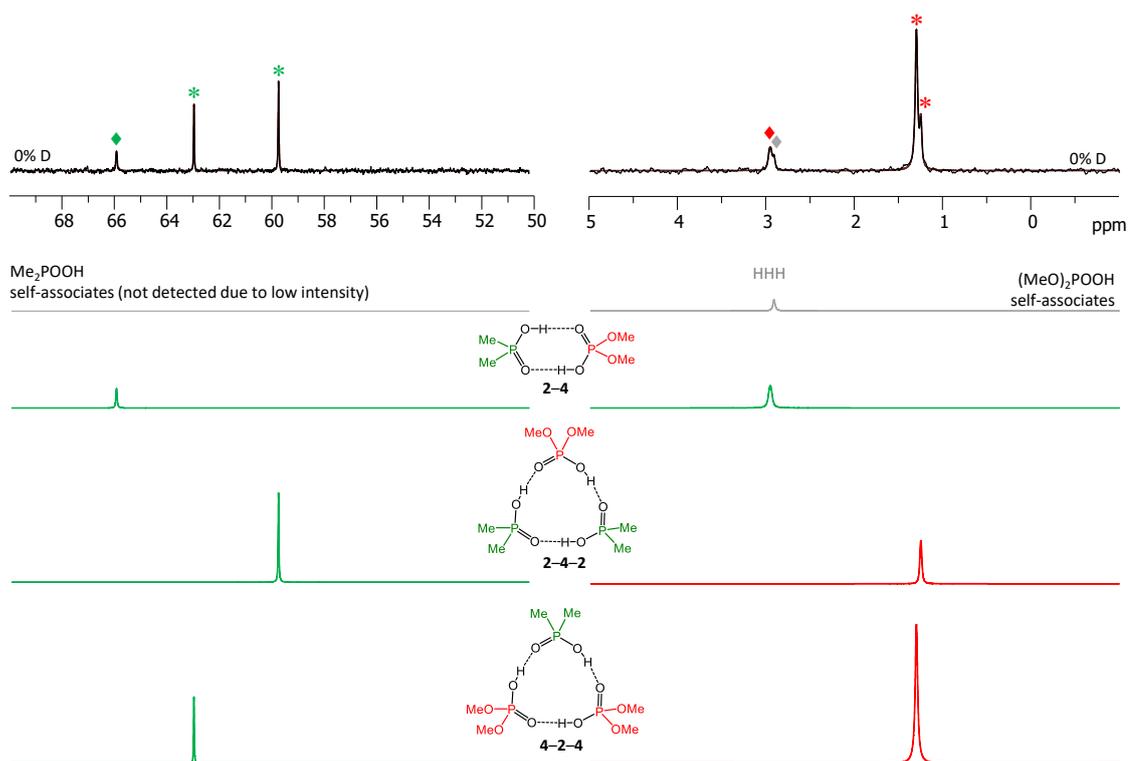


Figure S4. The parts of ^{31}P NMR spectrum of the sample containing acids **2** and **4** (1.3:1) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **2**, heterodimer **2-4** and two heterotrimers, **2-4-2** and **4-2-4**. The self-associates of **4** are not detected due to the low intensity of their signals. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

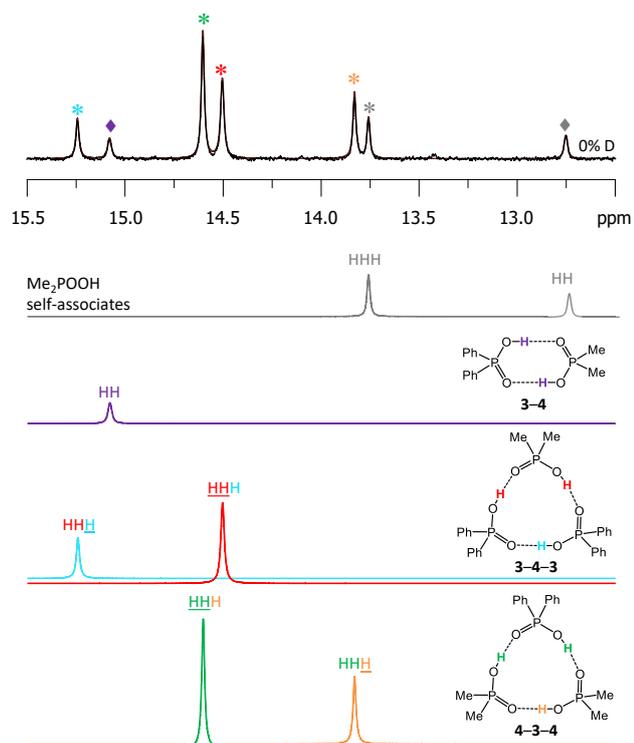


Figure S5. The low-field part of ^1H NMR spectrum of the sample containing acids **3** and **4** (1:1.4) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **4**, heterodimer **3-4** and two heterotrimers, **3-4-3** and **4-3-4**. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

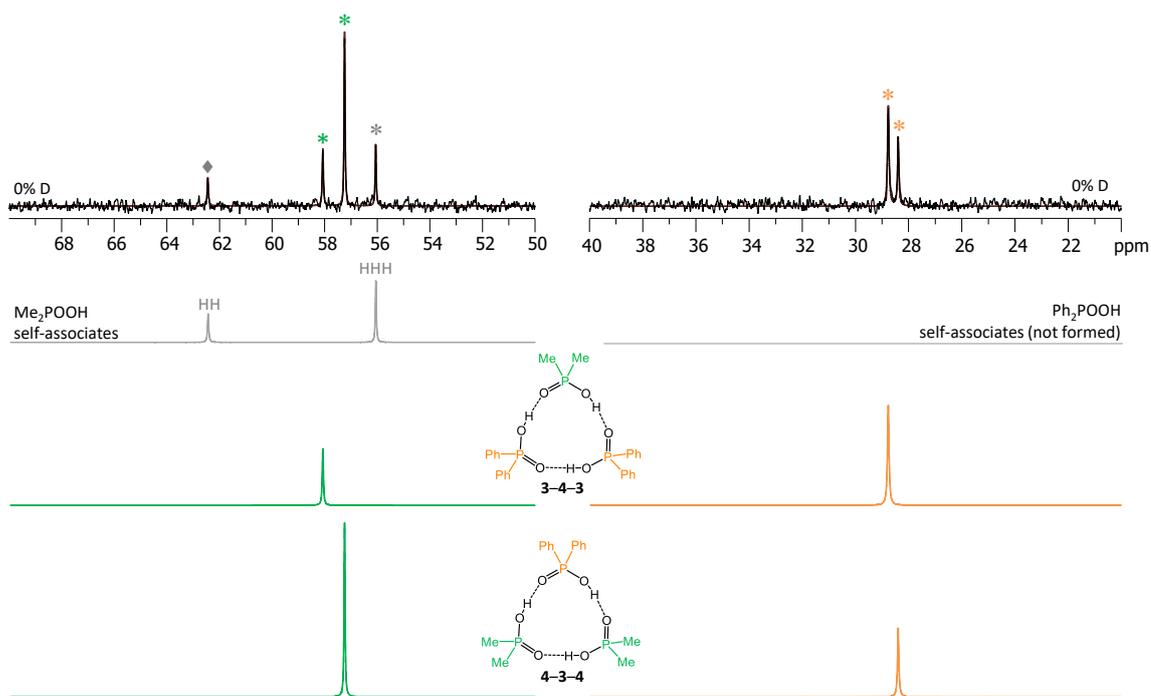


Figure S6. The parts of ^{31}P NMR spectrum of the sample containing acids **3** and **4** (1:1.4) in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from self-associated of **4**, heterodimer **3-4** and two heterotrimers, **3-4-3** and **4-3-4**. The self-associates of **3** are not formed, while the signals of heterodimer **3-4** are not detected due to their low intensity. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

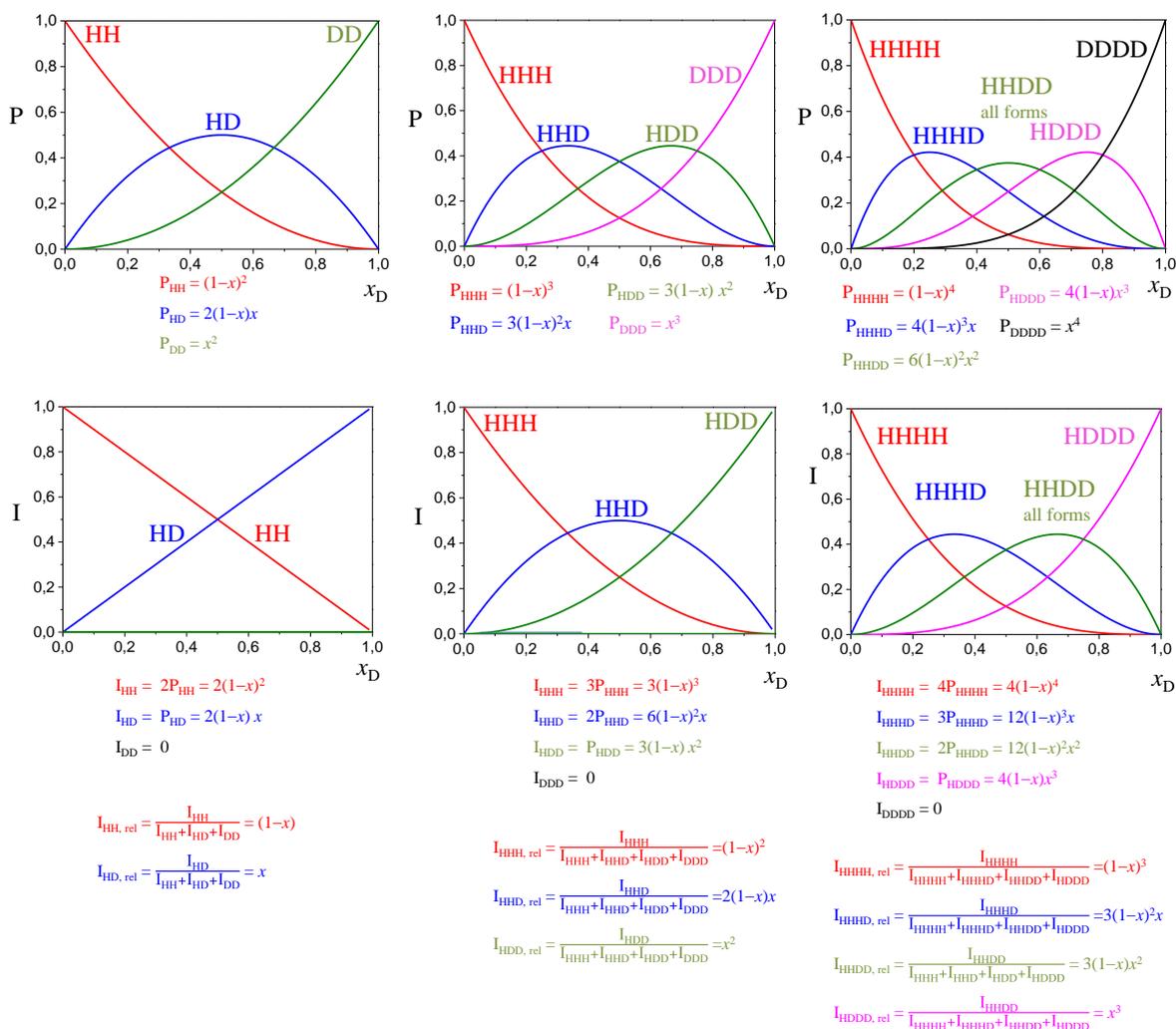


Figure S7. The probabilities of various isotopologs (top) and the relative integrated intensities of their ^1H NMR signals (bottom) calculated for cyclic dimers (left) and cyclic trimers (center) and cyclic tetramers of the **X-Y-X-Y** type (right) as a function of the deuterium ratio x_D .

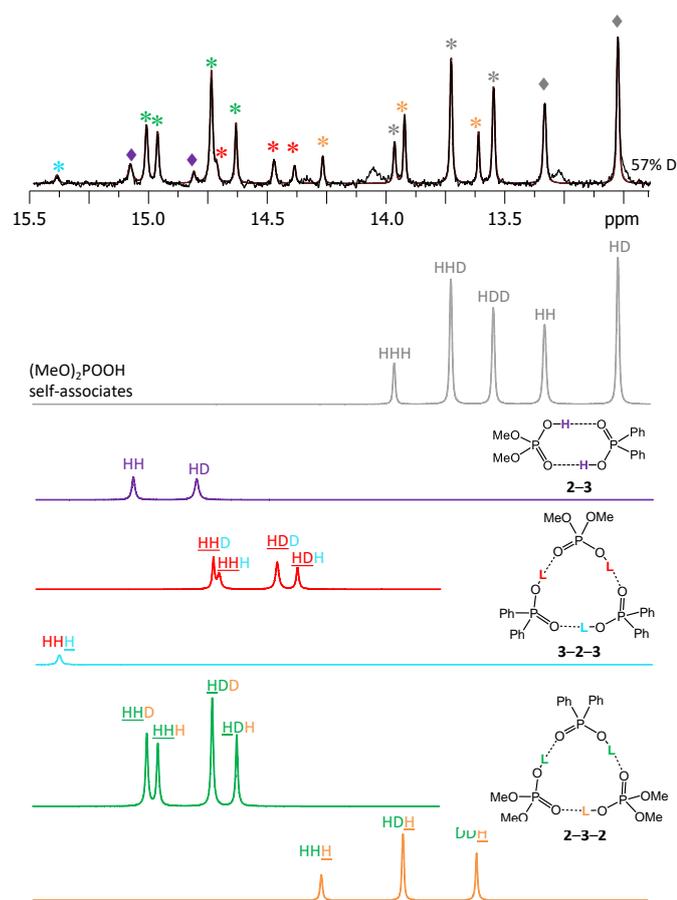


Figure S8. The low-field part of ^1H NMR spectrum of the sample containing partially deuterated (OH/OD , 57% D) acids **2** and **3** (4:1) in solution in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The experimental spectrum is deconvoluted into the sub-spectra arising from various isotopologs of self-associates, heterodimer and heterotrimer. For visual clarify the signals in the experimental spectrum and the computed sub-spectra are color coded.

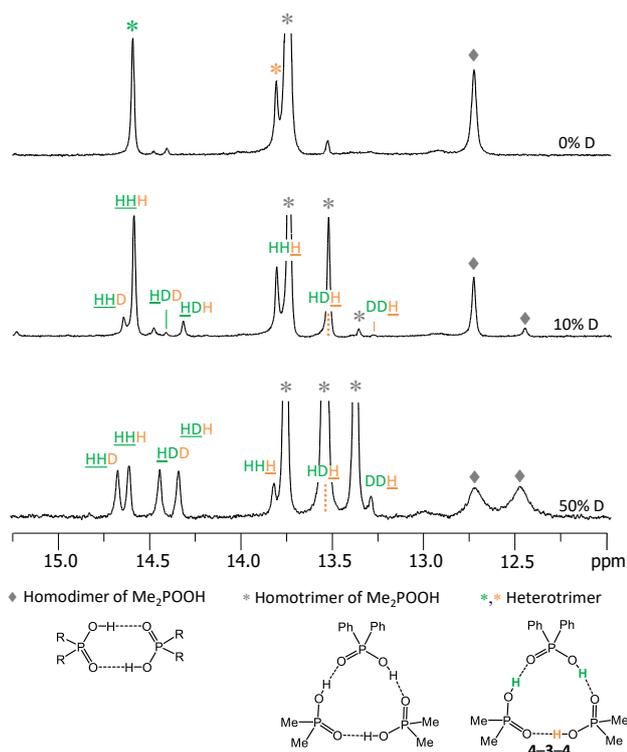


Figure S9. The low-field part of ^1H NMR spectra of the sample containing partially deuterated (OH/OD, from top to bottom: 0% D, 10% D, 50% D) acids **3** and **4** (1:22) in solution in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. Due to the large excess of acid **3** only one type of hetero-complex is formed, namely, a heterotrimer **4-3-4**. The evolution of the relative intensities of signals as a function of the deuteration ratio was used to assign the signals to particular isotopologs. For visual clarify the signals in the experimental spectrum and in the computed sub-spectra are color coded.

Table S1. The ^{31}P NMR chemical shifts of various isotopologs of homodimers and heterodimers of POOH-containing acids **1–4** in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The corresponding spectra are shown in Figures 4, 6, 8 and Figures S2, S4, S6.

| Complex | $(\text{PhO})_2\text{POOH}$ | $(\text{MeO})_2\text{POOH}$ | Ph_2POOH | Me_2POOH |
|-------------------------|-----------------------------|-----------------------------|--------------------------|--------------------------|
| 1-1 ^a | -8.09 | - | - | - |
| 2-2 ^b | - | 2.91 | - | - |
| 3-3 ^c | - | - | n.d. ^d | - |
| 4-4 ^a | - | - | - | 62.46 |
| 1-2 | -7.88 | 2.64 | - | - |
| 1-3 | n.m. ^e | - | - | n.m. |
| 1-4 | -8.17 | - | - | 72.99 |
| 2-3 | - | n.d. | n.d. | - |
| 2-4 | - | 2.96 | - | 65.92 |
| 3-4 | - | - | n.d. | n.d. |

^a – chemical shifts found in this work coincide with those reported previously in [Mulloyarova, V.V.; Giba, I.S.; Kostin, M.A.; Denisov, G.S.; Shenderovich, I.G.; Tolstoy, P.M. Cyclic trimers of phosphinic acids in polar aprotic solvent: symmetry, chirality and H/D isotope effects on NMR chemical shifts. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4901–4910.].

^b – chemical shifts match reasonably well those reported previously in Ref. [Detering, C.; Tolstoy, P.M.; Golubev, N.S.; Denisov, G.S.; Limbach, H.H. Vicinal H/D isotope effects in NMR spectra of complexes with coupled hydrogen bonds: phosphoric acids. *Dokl. Phys. Chem.* **2001**, *379*, 191–193.].

^c – the diphenylphosphinic acid **3** is poorly soluble in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ and does not form self-associates in a detectable amount

^d – n.d. – not detected.

^e – n.m. – not measured.

Table S2. The ^{31}P NMR chemical shifts of various isotopologs of homotrimers and heterotrimers of POOH-containing acids **1–4** in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ at 100 K. The corresponding spectra are shown in Figures 4, 6, 8 and Figures S2, S4, S6.

| Complex | $(\text{PhO})_2^{31}\text{POOH}$ | $(\text{MeO})_2^{31}\text{POOH}$ | $\text{Ph}_2^{31}\text{POOH}$ | $\text{Me}_2^{31}\text{POOH}$ |
|---------------------------|----------------------------------|----------------------------------|-------------------------------|-------------------------------|
| 1-1-1 ^a | -11.56 | - | - | - |
| 2-2-2 ^b | - | 1.22 | - | - |
| 3-3-3 ^c | - | - | n.d. ^d | - |
| 4-4-4 ^a | - | - | - | 56.07 |
| 1-2-1 | -11.43 | 1.15 | - | - |
| 2-1-2 | -11.62 | 1.20 | - | - |
| 1-3-1 | -11.65 | - | 37.85 | - |
| 3-1-3 | -12.25 | - | 33.68 | - |
| 1-4-1 | -11.46 | - | - | 71.55 |
| 4-1-4 | -11.50 | - | - | 63.86 |
| 2-3-2 | - | 1.37 | 32.65 | - |
| 3-2-3 | - | 1.00 | 30.79 | - |
| 2-4-2 | - | 1.30 | - | 62.93 |
| 4-2-4 | - | 1.25 | - | 59.66 |
| 3-4-3 | - | - | 28.76 | 58.07 |
| 4-3-4 | - | - | 28.39 | 57.24 |

^a – chemical shifts found in this work coincide with those reported previously in [Mulloyarova, V.V.; Giba, I.S.; Kostin, M.A.; Denisov, G.S.; Shenderovich, I.G.; Tolstoy, P.M. Cyclic trimers of phosphinic acids in polar aprotic solvent: symmetry, chirality and H/D isotope effects on NMR chemical shifts. *Phys. Chem. Chem. Phys.* **2018**, *20*, 4901–4910.].

^b – chemical shifts match reasonably well those reported previously in Ref. [Detering, C.; Tolstoy, P.M.; Golubev, N.S.; Denisov, G.S.; Limbach, H.H. Vicinal H/D isotope effects in NMR spectra of complexes with coupled hydrogen bonds: phosphoric acids. *Dokl. Phys. Chem.* **2001**, *379*, 191–193.].

^c – the diphenylphosphinic acid **3** is poorly soluble in $\text{CDF}_3/\text{CDF}_2\text{Cl}$ and does not form self-associates in a detectable amount

^d – n.d. – not detected.



$$\text{fractionation factor } \varphi_{1-2} = \frac{([D]/[H])_{\text{complex-1}}}{([D]/[H])_{\text{complex-2}}}$$

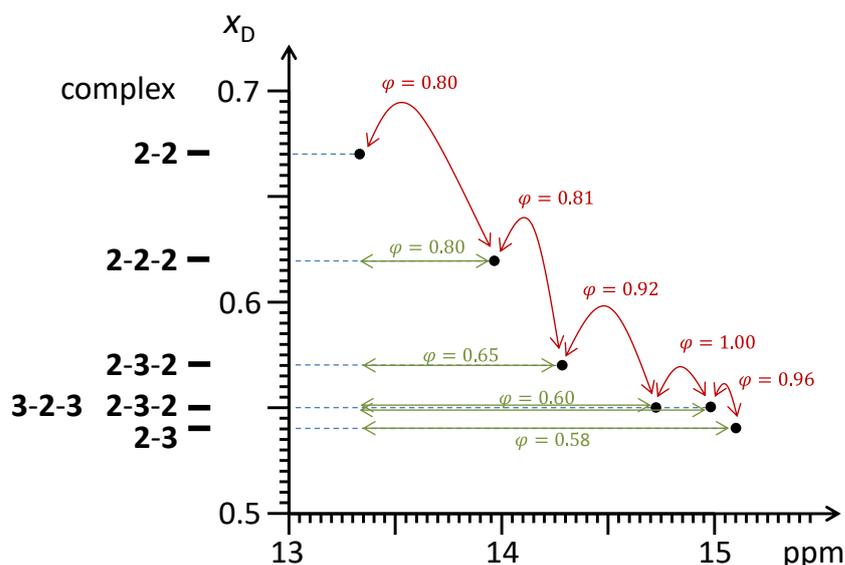


Figure S10. The analysis of H/D fractionation factors for a mixture of partially deuterated acids **2** and **3**, based on the ^1H NMR spectrum shown in Figure S8 and the individual deuteration ratios listed in Table S3.

Note: the H/D fractionation factors are defined with respect to a standard/reference, which is usually water. In our case the fractionation factors were calculated either with respect to one of the complexes (green labels in Figure S10) or within a selected pair of complexes (red labels). It has to be mentioned that for many other samples the changes of deuteration ratios x_D between individual complexes are either too small or lie within the experimental error.

Table S3. The deuteration ratios of individual hydrogen bonds for the sample of a mixture of partially deuterated acids **2** and **3** (see ^1H NMR spectrum in Figure S8). Note that intensities of some isotopologs are too small to reliably measure the deuteration ratio (this is why only one signal of heterotrimer **3-2-3** was analyzed).

| Complex | 2-2 | 2-2-2 | 2-3-2 | 3-2-3 | 2-3-2 | 2-3 |
|-----------------------|-------|-------|-------|-------|-------|-------|
| $\delta\text{H, ppm}$ | 13.33 | 13.96 | 14.29 | 14.72 | 14.98 | 15.10 |
| x_D | 0.67 | 0.62 | 0.57 | 0.55 | 0.55 | 0.54 |