

Table S1. Comparison of solvent properties and their deuterated equivalents. The values given in bold were selected for the analyses described in the manuscript.

	Solvent	Molar volume	Boiling point	Refractive index	Dielectric constant	Electric dipole moment		Volume magnetic susceptibility in air at normal pressure	Volume magnetic susceptibility
		MV	t _{BP}	n _D ²⁰	ε	ρ		χ _{sol}	χ _{sol}
		cm ³ /mol	°C			Cm	Debye	ppm	ppm
aromatic	benzene	89.4	80.1	1.5011	2.27	0.0 x10 ⁻³⁰	0.000		
	benzene- <i>d</i> ₆	88.6	79.1	1.4986	2.3			-7.37	-7.56
	toluene	106.8	110.6	1.4969	2.38	1.0 x10 ⁻³⁰	0.300		
	toluene- <i>d</i> ₈	106.6	109.0	1.493	2.4			-7.90	-8.01
protic	acetic acid	57.1	117.9	1.3719	6.17	5.6 x10 ⁻³⁰	1.679		-6.66
	acetic acid- <i>d</i> ₄	57.3	115.5	1.368	6.1				
	methanol	40.7	64.5	1.3284	32.66	5.9 x10 ⁻³⁰	1.769		
	methanol- <i>d</i> ₄	40.5	65.0	1.3256	32.7			-6.69	-6.79
	ethanol	58.5	78.3	1.3614	24.55	5.8 x10 ⁻³⁰	1.739		
	ethanol- <i>d</i> ₆	58.7	78.0	1.358	24.5				-7.29
aprotic	dimethyl sulfoxide	71.3	189.0	1.4793	46.45	13.5 x10 ⁻³⁰	4.047		
	dimethyl sulfoxide- <i>d</i> ₆	70.7	190.0	1.4758	46.7			-7.80	-7.83
	acetone	74.0	56.1	1.3587	20.56	9.0 x10 ⁻³⁰	2.698		
	acetone- <i>d</i> ₆	73.5	55.5	1.3554	20.7			-5.70	-5.78
	tetrahydrofuran	81.7	66.0	1.4072	7.58	5.8 x10 ⁻³⁰	1.739		
	tetrahydrofuran- <i>d</i> ₈	81.0	64.0	1.4035	7.6			-7.96	-8.08
	acetonitrile	52.6	81.6	1.3441	35.94	13.0 x10 ⁻³⁰	3.897		
	acetonitrile- <i>d</i> ₃	52.2	80.7	1.3406	37.5			-6.65	-6.76
	chloroform	80.7	61.2	1.4459	4.89	3.8 x10 ⁻³⁰	1.466		
	chloroform- <i>d</i>	80.3	60.9	1.4445	4.8			-9.24	-9.07
	Data references:	protonated solvents - [48]; deuterated solvents - [63]	protonated solvents - [62]; deuterated solvents - [63]				deuterated solvents - [38]; acetic acid - [59, 60]; ethanol - [61]		

Units conversion for Electric dipole moment: ρ [C m] = 3.336x10⁻³⁰ * ρ [Debye]

Table S2. Comparison of both experimental and estimated values of cohesive energy density (ced) from various literature sources. The values given in bold were selected for the analyses described in the manuscript.

		experimental		experimental		experimental		experimental		literature average		empirical estimated with some experimental confirmation			
Reference		[33]		[39]		[44]		[45]		[43]		[48]			
												Total	Polar	Dispersion	Hydrogen Bond
		cal cm ⁻³	J cm ⁻³	cal cm ⁻³	J cm ⁻³	cal cm ⁻³	J cm ⁻³	kBar	J cm ⁻³	cal cm ⁻³	J cm ⁻³	J cm ⁻³	J cm ⁻³	J cm ⁻³	J cm ⁻³
aromatic	benzene	83.7	350	85.0	356					83.7	350	343	0	339	4
	toluene	79.4	332	79.2	331	78.9	330			79.9	334	330	2	324	4
protic	acetic acid			102.0	427					107.1	448	457	64	210	182
	methanol	208.8	874	210.3	880	211.7	886			204.5	856	877	151	228	497
	ethanol	161.3	675	161.3	675					166.9	698	703	77	250	376
aprotic	dimethyl sulfoxide	168.6	705	144.0	603					210.3	880	712	269	339	104
	acetone	94.3	395	98.0	410	95.8	401			95.5	399	397	108	240	49
	tetrahydrofuran	86.9	364	82.8	346	87.4	366			82.8	347	379	282	32	64
	acetonitrile	139.2	582	141.6	593					142.1	595	595	324	234	37
	chloroform	85.4	357	86.5	362			3.61	361			359	10	317	32

Units conversion for ced: $\text{ced} [\text{J cm}^{-3}] = \text{ced} [\text{MPa}] = 4.1840 * \text{ced} [\text{cal cm}^{-3}] = 4.1840 * \delta^2 [\text{cal}^{0.5} \text{cm}^{-1.5}] = 100 * \text{ced} [\text{kBar}]$

$$\text{ced} [\text{MPa}] = (\delta_D^2 [\text{MPa}^{0.5}] + \delta_P^2 [\text{MPa}^{0.5}] + \delta_H^2 [\text{MPa}^{0.5}])$$

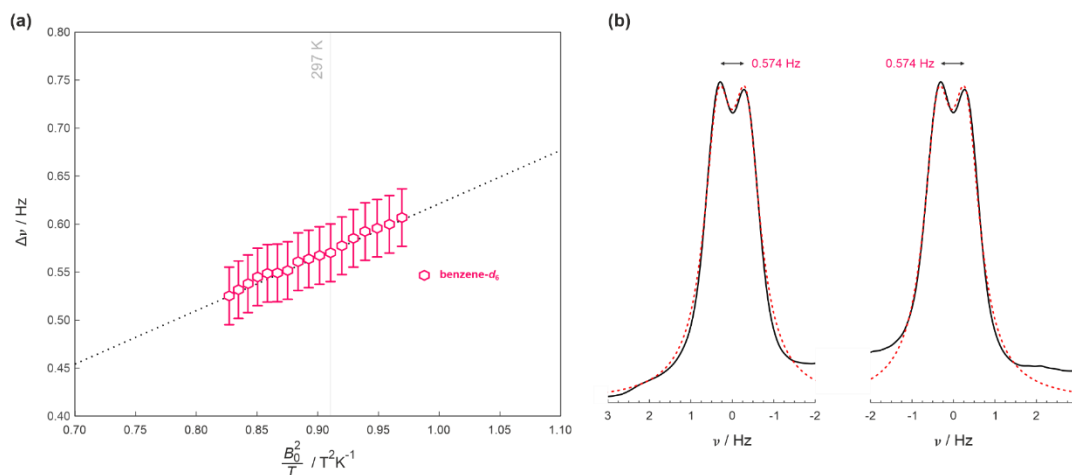
Table S3. The values of ced for acetic acid from various sources.

	ced	ced	technique	enthalpy	process	Reference
	cal cm ⁻³	J cm ⁻³		kJ/mol		
experimental	102.0	427	vapor pressure			[39]
literature average	107.1	448				[43]
empirical estimate		457				[48]
from experimental enthalpy of vaporization	165.2	691	vapor pressure	42.0		[47]
	87.2	365	calorimetric measurements	23.4	liquid to gas at equilibrium	[46]
	205.1	858	calorimetric measurements	51.6	liquid to monomer gas	[46]

Estimate of ced from enthalpy of vaporization:

$$\text{ced} [\text{J cm}^{-3}] = 4.1840 * \text{ced} [\text{cal cm}^{-3}] = (\Delta H_{\text{vap}} [\text{J mol}^{-1}] - R [\text{J mol}^{-1} \text{K}^{-1}] T [\text{K}]) * MV^{-1} [\text{cm}^{-3} \text{mol}^{-1}]$$

Figure S1. (a) Temperature dependence of the quadrupolar splitting in the deuterium spectrum of benzene- d_6 . (b) The ^{13}C satellite signals in the deuterium spectrum of benzene- d_6 used to estimate quadrupolar splitting in (a). Red dotted lines represent simulations.



The detailed step-by-step description of the procedure to estimate energy barrier:

Step 1. From the magnetic field dependence (equation (2) in the manuscript) at constant room temperature (i.e., 297K), the value of the magnetic anisotropy $\Delta\chi_{\text{ax}}$ for each solvent is known (listed in Table 1 of the manuscript). Therefore, at a constant magnetic field of 16.445 T (700 MHz NMR spectrometer), the “predicted” splitting $\Delta\nu$ can be calculated for other temperatures at that magnetic field from the same equation (2).

Step 2. The natural logarithm of “predicted” splitting $\ln(\Delta\nu)$ as function of the inverse of temperature (T^{-1}) can be fitted to the Arrhenius equation (dotted lines in Figure 5(b) in the manuscript). From the fit the energy required for the reorientation in the given solvent can be extracted.

Step 3. The natural logarithm of the experimentally measured (at 700 MHz) splitting $\ln(\Delta\nu)$ as function of the inverse of temperature (T^{-1}) can be fitted to the Arrhenius equation (experimental points in Figure 5(b) in the manuscript). From the fit the additional energy required for reorientation can be extracted.

Step 4. The difference in the energies above is called the energy barrier ΔE .

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