Supporting Information

Pressure-generated hydrogen bonds and the role of subtle molecular features in tetrahydrofuran

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Experimental procedures

Loading a diamond anvil cell and crystal growth

Tetrahydrofuran (C_4H_8O; Aldrich, 99+% purity) was used without further purification. A single crystal of C_4H_8O was grown *in situ* in a modified Merrill-Bassett[1] diamond-anvil cell (DAC). The gasket was made of 0.3 mm thick steel foil and the initial diameter of the hole was 0.4 mm. Immediately after filling the chamber, DAC was closed and pressure increased in small steps. Although the compression was performed very slowly, vitrification was observed on several attempts and no crystal could be obtained, even though we tried to trigger the crystallization by cycled heating and cooling of the sample and by subjecting it to ultrasounds. Eventually, the sample at 2.52 GPa was placed in dry ice until it froze forming a polycrystalline mass. Then the DAC was heated with a hot-air gun until all the crystallites but one melted at 369 K, after which it was slowly cooled over 8 hours until the single crystal grew to entirely fill the pressure chamber at room temperature and pressure stabilized at 2.25 GPa. It is noteworthy that the crystal exhibited an unusual habit (a prism with a four-angle star-like base, see Figure 5 in the main article). This single crystal was used for the X-ray diffraction experiments. The process of obtaining single crystals at 3.3 GPa and 3.8 GPa by tightening the DAC screws and heating DAC to the equilibrium temperatures of liquid and solid phase coexistence of 383 K and 443 K, respectively proceed smoothly and took about 6 h in each case. At a still higher pressure a single crystal could not be grown due to the rapid

increase in sample viscosity.[2] We have also tried to conduct a crystallization from THF:methanol:ethanol mixture (5:4:1, v/v/v), but no sign of crystallization was observed up to 5 GPa.

Pressure and temperature determination
The temperature during the crystal growth process was controlled using a AZ Instrument 8852 thermometer equipped with a K-type (chromel-alumel) thermocouple probe, which touched a diamond anvil. Pressure was calibrated by measuring the shift of the R1 ruby fluorescence line,[3] using a BETSA PRL spectrometer with an accuracy of 0.05 GPa.

Data collection and reduction
The DAC was mounted on a KUMA KM4 diffractometer equipped with a CCD detector and a monochromated Mo sealed-tube source (Kα radiation, λ = 0.71073 Å). The alignment was performed using a gasket-shadow centering procedure.[4] Data collection was carried out using a pre-designed strategy combining ω- and ϕ-scans.[4] The overall data-collection time was 19.5 h with an exposure time of 30 s and rotation of 0.8 º per frame. The CrysAlisPro program suite was used for data collection, determination of the UB-matrices, initial data reduction, and Lp correction. Then the reflection intensities were corrected for the DAC absorption and gasket shadowing[5] and the diamond-anvil reflections were eliminated. The structure was solved straightforwardly using direct methods (SHELXS-97) and subsequently refined against F^2 with SHELXL-97[6]. The O- and C-atoms were refined with anisotropic displacement parameters, and the isotropic displacement parameters of the H-atoms were set to 1.3 times the equivalent isotropic displacement parameter of their carrier atoms. All the C-H bond lengths were restrained to be equal within a standard deviation of 0.02 Å using the SADI command of SHELXL-97. The refinement and experimental details are presented in Table S1.

References
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(3) Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A. Calibration of the pressure dependence of the R_1 ruby fluorescence line to 195 kbar. *J. Appl. Phys.* **1975**, *46*, 2774–2780.
(4) Budzianowski, A.; Katrusiak A. High-pressure crystallographic experiments with a CCD detector. In *High-Pressure Crystallography*; Katrusiak, A., McMillan, P. F., Eds.; Kluwer: Dordrecht, the Netherlands, **2004**; pp 157–168.
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Table S1. Crystal data and details of structure refinement for THF at high pressure.

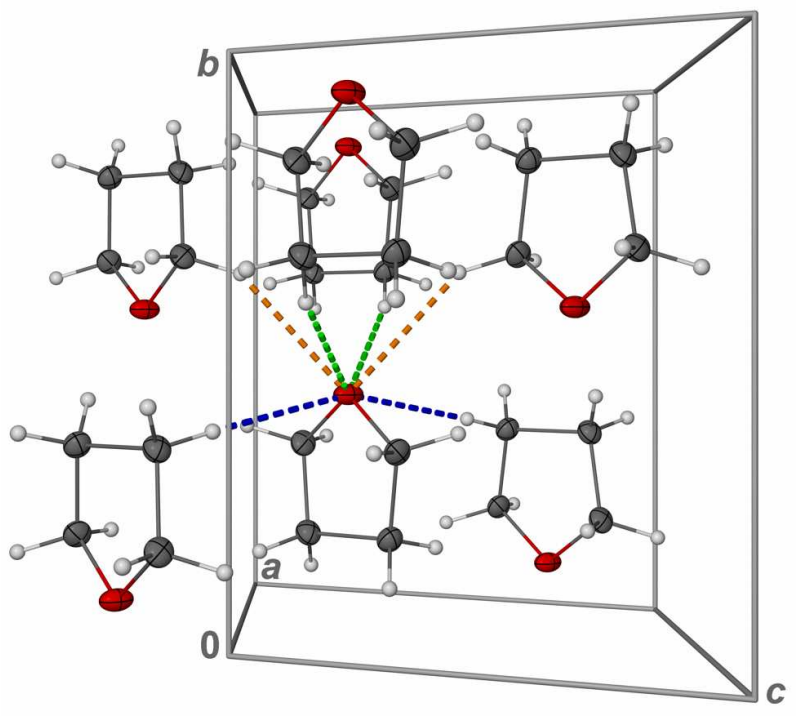
pressure	2.25(5) GPa	3.26(5) GPa	3.80(5) GPa
temperature(K)	295(2)	295(2)	295(2)
crystal size (mm)	0.40x0.43x0.20	0.41x0.41x0.20	0.41x0.41x0.20
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
unit cell dimensions (Å)	a = 5.917(2)	a = 5.840(3)	a = 5.816(3)
	b = 8.719(4)	b = 8.636(4)	b = 8.634(15)
	c = 7.411(6)	c = 7.288(7)	c = 7.237(11)
	β = 108.37(7)	β = 109.02(8)	β = 109.41(11)
volume (Å^3)	362.9(4)	347.5(4)	342.8(8)
Z	4	4	4
ρ_{calcd} (g cm^3)	1.320	1.378	1.397
μ (Mo K_α) (mm^{-1})	0.092	0.096	0.097
F(000) (e)	160	160	160
2θ max (º)	58.46	58.26	49.94
2θ range (º)	8.64-58.46	8.26-58.26	8.8-49.94
limiting indices	-6→h→6	-6→h→6	-6→h→6
	-10→k→10	-10→k→10	-8→k→8
	-6→l→6	-6→l→6	-6→l→6
reflections collected/unique	188/170	184/174	142/136
R_{int}	0.0550	0.0680	0.0537
observed reflections [$I > 4\sigma(I)$]	170	174	136
data/parameters	188/36	184/36	142/ 36
goodness of fit (F^2)	1.127	1.154	1.366
final *R* indices ($I > 4\sigma(I)$)	0.0550	0.0535	0.0513
$\Delta\sigma_{max}$, $\Delta\sigma_{min}$ (e Å^3)	0.12/ -0.12	0.11/ -0.12	0.130/-0.134
DAC transmission min/max	0.873/0.998	0.873/0.998	0.886/0.998
gasket shadowing min/max	0.607/0.966	0.615/0.965	0.633/0.968
total transmission	0.518/0.946	0.525/0.945	0.561/0.966

Table S2. Bond angles (°), torsion angles (°) and q_2 Cremer–Pople ring puckering parameters (Å) in THF crystal structure. Symmetry code: i = –x, y, –z+0.5. The structures of perdeuterated THF have been marked with asterisks.

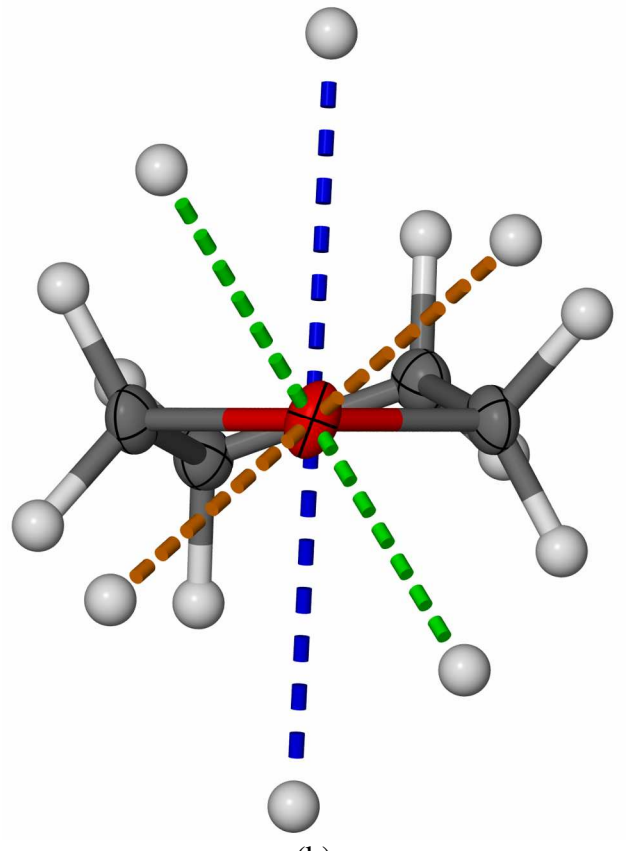
T/p	C2–O1–C2^{i}	O1–C2–C3	C2–C3–C3^{i}	C2^{i}–O1–C2–C3	O1–C2–C3–C3^{i}	C2–C3–C3^{i}–C2^{i}	q_2
5 K/ 0.1 MPa*	109.9(3)	106.4(2)	102.6(2)	–11.3(2)	28.8(2)	–34.5(2)	0.343(2)
103 K/ 0.1 MPa	108.2(4)	107.4(4)	102.0(4)	–11.5(4)	29.7(4)	–34.9(4)	0.348(5)
120 K/ 0.1MPa*	110.2(3)	106.9(3)	102.0(2)	–11.3(2)	28.4(2)	–33.7(2)	0.340(2)
148 K/ 0.1.MPa	109.8(3)	106.7(4)	101.9(3)	–11.7(3)	29.6(3)	–35.2(4)	0.355(4)
295 K/ 2.25 GPa	110.7(5)	105.7(4)	103.8(2)	–10.11(11)	26.3(3)	–31.9(3)	0.311(4)
295 K/ 3.26 GPa	110.4(4)	105.9(3)	103.80(19)	–10.15(10)	26.4(3)	–32.0(3)	0.312(4)
295 K/ 3.80 GPa	109.1(7)	106.9(4)	103.5(2)	–10.23(15)	26.4(3)	–31.7(4)	0.309(4)

Table S3. Angles (°) between the H···O contact directions and the putative lone pair direction (LP), as calculated for a tetrahedral sp^3 configuration, with the oxygen atom in the center, and the hydrogen atoms and the lone pairs in the corners. Symmetry codes: ii = x–0.5, 0.5+y, z; iii = –x, –2–y, 1–z; iv = 0.5–x, –1.5–y, 1–z. The structures of perdeuterated THF have been marked with asterisks.

T/p	∠(H31···O1^{ii}, LP)	∠(H22···O1^{iii}, LP)	∠(H32···O1^{iv}, LP)
5 K/0.1 MPa*	24	36	46
103 K/0.1 MPa	23	35	46
120 K/0.1MPa*	24	36	46
148 K/0.1.MPa	24	35	46
295 K/2.25 GPa	25	36	46
295 K/3.26 GPa	24	37	47
295 K/3.80 GPa	24	38	47



(a)



(b)

Figure S1. Three symmetry-related pairs of short H···O contacts (dashed lines) in the THF crystal structure at 3.80 GPa shown along [100] (a); and one THF molecule viewed along its C_2 axis with six H atoms coordinating the oxygen atom (b). The color code corresponds to that in Figure 1 in the main article.

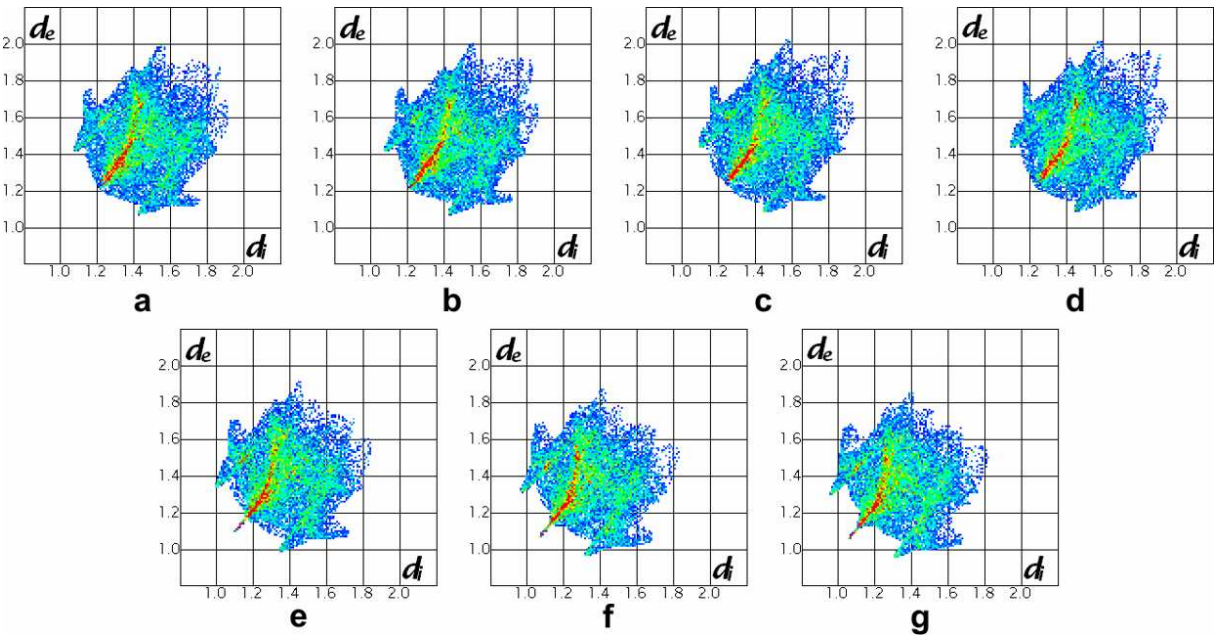


Figure S2. Hirshfeld fingerprints plots of the THF structures at (a) 0.1 MPa/5 K; (b) 0.1MPa/103K; (c) 0.1 MPa/120K; (d) 0.1 MPa/148K; (e) 2.25 GPa/295 K; (f) 3.26 GPa/295 K and (g) 3.80 GPa/295 K.