Ultra-fast Rotors for Molecular Machines and
Functional Materials *via* Halogen Bonding: Crystals
of 1,4-Bis(iodoethynyl)bicyclo[2.2.2]octane with
Distinct Gigahertz Rotation at Two Sites

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Synthesis of 1,4-diethynylbicyclo[2.2.2]octane (BCO): The 9-step synthesis of BCO is shown in Scheme 1 of the main text.

a: Diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate, 1. The Dieckmann condensation of diethyl succinate was carried out following a literature procedure.¹ The product was isolated in 78 % yield. mp: 128 °C (126-127 °C Litt.); ¹H NMR (CDCl₃, 500 MHz) δ 12.20 (s, 2H), 4.24 (q, J = 7 Hz, 4H), 3.18 (s, 4H), 1.31 (t, J = 7 Hz, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 171.24, 168.39, 93.19, 60.69, 28.49, 14.18; m/z ESI(+) calcd for C₁₂H₁₆O₆ : 256.09; found 255.87; Anal. calcd for C₁₂H₁₆O₆ C, 56.24; H, 6.29. Found: C, 55.02; H, 6.19.

b: Diethyl 2,5-dioxobicyclo[2.2.2]octane-1,4-dicarboxylate, 2. The bicyclo derivative was prepared from diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate, **1**. At variance with the reported procedure,¹ the reaction mixture was heated for 96 hrs and the reaction was monitored by TLC (ethyl acetate/ petroleum ether: 1/1). The product was isolated in 85 % yield. mp: 111 °C (111-112 °C Litt.); ¹H NMR (CDCl₃, 500 MHz) δ 4.25 (q, J = 7.5 Hz, 4H), 3.07 (dd, J = 19.5 Hz, J = 3 Hz, 2H), 2.72 (d, J = 19.5 Hz, 2H), 2.51 (m, 2H), 2.11 (m, 2H), 1.29 (t, J = 7.5 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) 203.62, 168.59, 61.83, 57.25, 41.85, 24.48, 14.07; m/z ESI(+) calcd for [C₁₄H₁₈O₆ + H]⁺ : 283.11; found 282.98; Anal. calcd for C₁₄H₁₈O₆ C, 59.57 ; H, 6.43. Found: C, 59.99; H, 6.44.

c: Diethyl 2,5-diethyleneglycolbicyclo[2.2.2]octane-1,4-dicarboxylate, 3. The diketaldiester was prepared from diethyl 2,5-dioxobicyclo[2.2.2]octane-1,4-dicarboxylate, **2** via literature procedure² in 71 % yield. mp: 85 °C (85-86 °C Litt.); ¹H NMR (CDCl₃, 500 MHz) δ 4.12 (q, J = 7 Hz, 4H), 3.94 (m, 6H), 3.74 (m, 2H), 2.45 (dd, J = 14.5 Hz, J = 2.5 Hz, 2H), 2.31 (m, 2H), 1.99 (d, J = 14.5 Hz, 2H), 1.70 (m, 2H), 1.24 (t, J = 7 Hz, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 172.55, 110.11, 64.75, 60.61, 48.83, 41.72, 23.99, 14.15; m/z ESI(+) calcd for [C₁₈H₂₆O₈ + H]⁺ : 371.16; found 371.01; Anal. calcd for C₁₈H₂₆O₈ C, 58.37 ; H, 7.08. Found: C, 58.28; H, 6.95.

d: 2,5-diethyleneglycolbicyclo[2.2.2]octane-1,4-dimethanol, 4. The diketaldiol was prepared from diethyl 2,5-diethyleneglycolbicyclo[2.2.2]octane-1,4-dicarboxylate, **3**. At variance with the literature procedure,² the reaction mixture was extracted with warm ethyl acetate. After drying over MgSO₄ and evaporating the combined organic layers, one half of the target compound was isolated. Afterwards, the water layer was evaporated to dryness under low pressure and the

resulting sticky material was extracted using a soxhlet with dichloromethane to yield the remaining second half of the compound after 6 cycles. In the end, the product was isolated in 93 % yield. mp: 102 °C (100-101 °C Litt.); ¹H NMR (CDCl₃, 500 MHz) δ 4 (m, 8H), 3.66 (d, *J* = 11.25 Hz, 2H), 3.30 (d, *J* = 11.25 Hz, 2H), 2.65 (s, 2H), 2.16 (dd, *J* = 14.25 Hz, *J* = 2.5 Hz, 2H), 1.75 (m, 2H), 1.60 (d, *J* = 14.25, 2H), 1.30 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz) δ 112.29, 65.96, 63.97, 63.85, 41.34, 40.82, 23.67; DSQ (EI) *m/z* calcd for [C₁₄H₂₂O₆ + H]⁺ : 287.14; found 286.9.

e: 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane-2,5-dione, 5. The diketodiol was prepared from 2,5-diethyleneglycolbicyclo[2.2.2]octane-1,4-dimethanol, **4** via literature procedure² in quantitative yields. The compound is a sticky oil engaged as such in the next step: ¹H NMR (acetone-*d*₆, 500 MHz) δ 4.26 (m, 4H), 3.13 (m, 2H), 2.98 (m, 2H), 1.50 (m, 2H), 1.26 (m, 2H); DSQ (EI) *m/z* calcd for [C₁₀H₁₄O₄ + H]⁺: 199.09; found 198.9.

f: Bicyclo[2.2.2]octane-1,4-diyldimethanol, 6. The diol was prepared from 1,4-bis(hydroxymethyl)bicyclo[2.2.2]octane-2,5-dione, **5** via literature procedure² in 41 % yield. mp: 106 °C (107-108 °C Litt.); ¹H NMR (CDCl₃, 500 MHz) δ 3.27 (s, 4H), 1.42 (s, 12H); ¹³C NMR (CDCl₃, 125 MHz) δ 71.48, 33.59, 27.64; *m/z* ESI(+) calcd for [C₁₀H₁₈O₂+H]⁺ – H₂O : 153.13; found 153.13. Anal. calcd for C₁₀H₁₈O₂ C, 70.55 ; H, 10.66. Found: C, 70.79 ; H, 10.70.

g: Bicyclo[2.2.2]octane-1,4-dicarbaldehyde, 7. The dicarbaldehyde was prepared from a Swern oxidation of the bicyclo[2.2.2]octane-1,4-diyldimethanol, **6** via literature procedure^{3,4} in 65 % yield. It was engaged immediately in the next step to prevent degradation. DSQ (EI) *m/z* calcd for [C₁₀H₁₄O₂ + H]⁺: 167.10; found 166.9.

h: 1,4-bis(2,2-dibromovinyl)bicyclo[2.2.2]octane, 8. Using the Corey-Fuchs methodology and following the literature procedure,^{5,6} at 0 °C, triphenylphosphine (76 g, 289.77 mmol) was added in small portions to a CBr₄ solution (46 g, 138.7 mmol) in CH₂Cl₂ (250 mL). The mixture was warmed up at room temperature and stirred for 30 minutes before adding dropwise and slowly a solution of freshly prepared bicyclo[2.2.2]octane-1,4-dicarbaldehyde, **7** (5 g, 30.10 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred at room temperature for 5 h and monitored by TLC (eluent: CH₂Cl₂). Finally, the mixture was quenched with H₂O (200 mL) and extracted with dichloromethane. The organic layer was dried over MgSO₄. The crude material was purified by

silica gel column chromatography with 100 % *n*-hexane. The tetrabromine derivative was isolated as a white crystalline powder (9 g) with 65 % yield. mp : 109 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 6.41 (s, 2H), 1.82 (s, 12H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 145.49, 85.64, 35.77, 29.75; DSQ (EI) m/z calcd for $[\text{C}_{12}\text{H}_{14}\text{Br}_4 + \text{H}]^+$: 474.78; found 474.9; Anal. calcd for $\text{C}_{12}\text{H}_{14}\text{Br}_4$ C, 30.16 ; H, 2.95. Found: C, 30.25; H, 2.91.

i: 1,4-diethynylbicyclo[2.2.2]octane, 9. Using the Corey-Fuchs methodology and following the literature procedure,^{5,6} to a solution of 1,4-bis(2,2-dibromovinyl)bicyclo[2.2.2]octane, **8** (6 g, 12,66 mmol) in THF (50 mL) under argon, *n*-butyllithium (22 mL of 2.5 M soln. in hexane, 55 mmol) was slowly added at -78°C. The reaction mixture was stirred at -78°C for 1 h, then warmed slowly to room temperature, and the reaction was monitored with TLC (eluent: CS_2). At the end, the reaction mixture was quenched with an aqueous saturated ammonium chloride solution. The mixture was extracted with dichloromethane, and dried over MgSO_4 . The crude material was purified by silica gel column chromatography with 100% *n*-hexane. The final compound was isolated as a white crystalline powder (1.9 g) with 95 % yield. mp: 166 °C; ^1H NMR (CDCl_3 , 500 MHz) δ 2.08 (s, 2H), 1.78 (s, 12H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 90.99, 68.13, 31.57, 26.00; Anal. calcd for $\text{C}_{12}\text{H}_{14}$ C, 91.08 ; H, 8.92. Found: C, 90.12; H, 9.04.

1,4-bis(iodoethynyl)bicyclo[2.2.2]octane (BIBCO). A solution of 1,4-diethynylbicyclo[2.2.2]octane, **9** (250 mg, 1.58 mmol) in methanol (40 mL) was cooled at 0°C and treated with KOH (461 mg, 8.22 mmol). After 20 min. of stirring at 0°C, *N*-iodosuccinimide (850 mg, 3.78 mmol) was added and the mixture stirred at 0°C for another 20 min. The reaction mixture was then warmed slowly to room temperature and the stirring was maintained for 2hrs. 50 mL of water and 100 mL of dichloromethane were added and the organic layer was separated, dried over MgSO_4 , and evaporated to dryness. The crude material was purified by chromatography on silicagel with CS_2 as the eluent. The product was isolated in 76% yield as a white crystalline powder, which was crystallized in hot ethanol as colorless thin plates. DSC decomp.: 261.6 °C. ^1H NMR (500 MHz, acetone- d_6) δ = 1,74. ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 100.7, 31.4, 28.4, -6.3. DSQ (EI): m/z $[\text{M}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{I}_2$: 409.9; found 409.6. Anal. Calcd for: C, 35.15; H, 2.95. Found: C, 35.02; H, 2.99.

Table S1. Crystal data, data collection and refinement details for a BIBCO single crystal at 295 K, 130 K and 90 K ($C_{12}H_{12}I_2$, $M = 410$, $F(000) = 1520$)

Temperature / K	295(2)	130(2)	90(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
$a / \text{\AA}$	31.576(2)	31.769(3)	13.913(1)
$b / \text{\AA}$	7.1977(5)	7.0328(8)	13.913(1)
$c / \text{\AA}$	12.2949(7)	12.0594(4)	16.236(2)
$\alpha / ^\circ$	90	90	79.081(7)
$\beta / ^\circ$	111.674(6)	110.900(6)	65.960(7)
$\gamma / ^\circ$	90	90	60.573(6)
$V / \text{\AA}^3$	2596.7(3)	2517.1(4)	2499.7(4)
Space group, Z	$C2/c$, 8	$C2/c$, 8	$P-1$, 8
$\rho_{\text{calc.}} / \text{g}\cdot\text{cm}^{-3}$	2.098	2.164	2.179
μ / cm^{-1}	48.08	49.60	49.94
$T_{\text{min}}, T_{\text{max}}$	0.212, 0.648	0.320, 0.664	0.441, 0.662
$2\theta_{\text{max}} / ^\circ$	61.0	76.0	70.2
Range of data	$-44 \leq h \leq 36$ $-10 \leq k \leq 10$ $-13 \leq l \leq 17$	$-54 \leq h \leq 54$ $-12 \leq k \leq 12$ $-20 \leq l \leq 20$	$-22 \leq h \leq 22$ $-22 \leq k \leq 22$ $-26 \leq l \leq 26$
Reflections collected	29119	42868	78664
Independent reflections	3954	6807	-
R_{int}	0.0338	0.0346	-
No. of parameters	155	154	506
GooF on F^2	1.007	1.026	1.060
$R_1 [I > 2\sigma(I)]$	0.0364	0.0316	0.0519
$wR_2 [I > 2\sigma(I)]$	0.0945	0.0667	0.1297

Figure SI-1. Temperature dependences of the unit cell parameters of a BIBCO single crystal have monotonic character (blue squares - cooling, red circles - heating). A reversible phase transition, from monoclinic $C2/c$ to triclinic $P\bar{1}$ symmetry, occurs at 110K. For clear representation of the relative changes, lattice parameters in a whole temperature range are reduced to primitive triclinic cell of the high-temperature monoclinic phase. Doubling of a and b parameters of the primitive lattice, which appears below 110K, is not considered here.

Figure SI-2 (a): ^{13}C CP/MAS spectra of polycrystalline BIBCO (75 MHz, room temperature, recycle delay time = 10 s, contact time = 5 ms) at MAS = 4 kHz, 5 kHz, and 10 kHz. Asterisks denote spinning side bands.

Figure SI-2(b): ^{13}C CP/MAS spectrum (MAS = 10 kHz, recycle delay time = 30 s, contact time = 5 ms) of polycrystalline BIBCO at $T = 267\text{ K}$.

Figure SI-3. ^{13}C NMR spectra for BIBCO recorded in a CD_2Cl_2 solution at 125 MHz

Figure SI-4(a): Representative ^1H wideline spin-lattice relaxation (T_1) measurement via the saturation-recovery method at $T = 50\text{K}$.

Figure SI-4(b): Mono-exponential fit to representative ^1H wideline spin-lattice relaxation (T_1) inversion recovery data at $T = 50\text{ K}$ ($T_1 = 1.1\text{ s}$).

^{13}C CP/MAS NMR Experimental Details: The ^{13}C CPMAS spectra were acquired on a polycrystalline BIBCO sample at a ^{13}C frequency of 75 MHz and a ^1H frequency of 300 MHz using a ^1H ninety degree ($\pi/2$) pulse width of 4.00 microseconds (μs), a Hartmann-Hahn contact time of 5 milliseconds (ms), a data acquisition time of 66 ms, and a recycle delay of greater than five times the spin-lattice relaxation time of the protons. The sample was spun at a MAS rate of 10 kHz in a 4 millimeter (outside diameter) rotor, and the thermocouple was calibrated using the chemical shift of ^{207}Pb in $\text{Pb}(\text{NO}_3)_2$ as previously described elsewhere.⁷

Figure SI-5(a): Representative ^1H spin-lattice relaxation (T_1) measurement via the inversion-recovery method by detection through ^{13}C CP/MAS (MAS= 10 kHz) at $T = 290\text{ K}$.

Figure SI-5(b): Mono-exponential fit to ^1H spin-lattice relaxation (T_1) data measured via the inversion-recovery method by detection through ^{13}C CP/MAS (MAS= 10 kHz) at $T= 290\text{ K}$ ($T_1 = 5.33\text{ s}$).

Figure SI-6. The structure of 1,4-bis(iodoethynyl)benzene² is strikingly similar to that of BIBCO. It is directed by the same set of halogen bond interactions, $\text{C}-\text{I}\cdots\pi$, $3.427\text{ \AA}$ and $\text{C}-\text{I}\cdots\text{I}-\text{C}$, $4.101\text{ \AA}$. $\text{C}-\text{I}$, $2.006\text{ \AA}$.

Figure SI-7. The layered structure of 1,4-diiodobicyclo[2.2.2]octane, with a loose, single $\text{C}_{\text{sp}3}-\text{I}\cdots\text{I}$ interaction, $4.309\text{ \AA}$, and $\text{C}_{\text{sp}3}-\text{I}$, $2.163\text{ \AA}$.

Figure SI-8. (a-h) 2D-Fourier maps reconstructed at different temperatures on F_{obs} (experimental electron density scale is in $\text{e}\text{\AA}^{-3}$, x and y axes are in $\text{\AA}$) in the planes of the rotor atoms. Left pictures are for the initially ordered BIBCO layer; right pictures are for the initially disordered layer. Note that the relative orientations of the molecules are not correlated in the patterns at different temperatures and, therefore, could not be directly compared.

(a)

(b)

Figure SI-9. The pattern of intermolecular interactions within layer A'B' (a) and C'D' (b). The layers are projected along the rotor axes.

(a) Within layer A'B' the gyroscope axes are essentially parallel, a checkerboard pattern of equal numbers of δ and λ conformers is identified. Once the rotor fragments are inscribed into triangles, a dual pattern of side-by-side and apex-to-apex tiling of the triangles is identified, the former being associated with shorter intermolecular contacts. Double ribbons of side-by-side closed packed rotors are segregated along the $[110]$ direction also showing a loosening of the packing in between the ribbons. Note in addition that the molecules are bent inwards the ribbon which makes for shorter C-H $\cdots$ I intermolecular contacts. As a result, most of the hydrogen bond contacts with H $\cdots$ I distances of 3.27-3.36 Å (dashed lines) are concentrated within the ribbon. There are only two such contacts in between the ribbons with H $\cdots$ I distances of 3.36 Å.

(b) Within layer C'D', in contrast to layer A'B', the gyroscope axes of molecules C' and D' are orthogonal. The layer consists of segregated $\cdots C'C'C' \cdots$ and $\cdots D'D'D' \cdots$ rows parallel to $[-110]$ with alternating side-by-side and apex-to-apex interactions between adjacent δ and λ conformers (like $\cdots A'A'A' \cdots$ and $\cdots B'B'B' \cdots$ rows along b in layer A'B'). Side-by-side C-H $\cdots$ I contacts of 3.31 and 3.36 Å and apex-to-apex contacts of 3.30 and 3.24 Å are observed inside C' and D' rows, respectively, while there is only one C-H $\cdots$ I contact (3.35 Å) between orthogonal C' and D' molecules.

Figure SI-10. A principal difference in interlayer interactions: C' and D' molecules in the surroundings of A' (or B') have mutually perpendicular rotor axes (a) while A' and B' molecules in the surroundings of C' (or D') have parallel rotor axes (b). C–I $\cdots\pi$, C–I $\cdots$ I–C and C–H $\cdots$ I contacts are drawn in red, purple and black dashed lines, respectively. Contact distances at different temperatures are given in Table S2.

Table S2. C–I $\cdots\pi$ and I $\cdots$ I contact distances (Å) in the monoclinic structure at 295 and 130 K and triclinic structure at 90 K

C–I $\cdots\pi$ (Å)					
295 K	130 K	90 K			
I _A $\cdots$ C _B		I1A $\cdots$ C _{D'}	I2A $\cdots$ C _{C'}	I1B $\cdots$ C _{C'}	I2B $\cdots$ C _{D'}
3.427	3.330	3.324	3.309	3.314	3.285
3.583	3.469	3.461	3.449	3.450	3.402
I _B $\cdots$ C _A		I1C $\cdots$ C _{A'}	I2C $\cdots$ C _{B'}	I1D $\cdots$ C _{B'}	I2D $\cdots$ C _{A'}
3.499	3.425	3.426	3.403	3.412	3.391
3.721	3.666	3.681	3.628	3.652	3.637

C–I $\cdots$ I (Å)				
C–I _A $\cdots$ I _B	C–I1A $\cdots$ I1D	C–I2A $\cdots$ I1C	C–I1B $\cdots$ I2C	C–I2B $\cdots$ I1D
4.005	3.948	3.952	3.973	3.933
C–I _B $\cdots$ I _A	C–I1C $\cdots$ I1A	C–I2C $\cdots$ I2B	C–I1D $\cdots$ I1B	C–I2D $\cdots$ I2A
4.062	4.003	3.967	3.996	4.008

(a)

(b)

Figure SI-11. (a) Hexagonal network formed in the crystal by I-atoms of BIBCO molecules located in two adjacent A'B' and C'D' layers. Successive I $\cdots$ I distances along [110] at 90 K are (starting from I2D): 3.9373(4) – 3.9962(6) – 3.9329(4) – 4.0083(6) – 3.9524(4) – 3.9670(6) – 3.9726(4) – 3.9839(5) Å. Between the [110] chains the I $\cdots$ I distances are 4.2463(6) – 4.4585(6) Å in excess of the sum of van der Waals radii for iodine, 4.20 Å. (b) Structure projection along c^* showing that the iodine atoms from successive sheets stand almost one above the other. Hence, the gyroscopes appear to be located within the hexagonal cavities of honeycomb iodine sheets serving as rigid lamellar templates.

Figure SI-12: Temperature dependence of the ^1H spin-lattice relaxation time (T_1) in BIBCO displaying two minima, observed at 26.4 MHz (yellow squares) and 300 MHz (green circles). The heavy blue and red lines correspond to a Kubo-Tomita fit at 26.4 MHz, assuming **Eyring-type processes**. The dotted black line corresponds to the weighted sum of these two processes observed at 26.4 MHz, and displays an excellent fit to the data. The light blue and light red dotted lines correspond to a Kubo-Tomita fit at 300 MHz, assuming Eyring-type processes. The dotted gray line corresponds to the weighted sum of the two processes observed at 300 MHz. For the low energy process, $\Delta H^\ddagger = 1.48$ kcal/mol and $\Delta S^\ddagger = 2.50$ J/K·mol. For the higher energy process, $\Delta H^\ddagger = 2.47$ kcal/mol and $\Delta S^\ddagger = -0.45$ J/K·mol.

Figure SI-13: Representative ^1H wide line spectra (26.4 MHz) for $T= 40$ K (blue) and $T= 220$ K (red).

Figure SI-14: Room temperature solid-state FT-IR of BIBCO. IR(cm^{-1}): 2948.41, 2865.07, 2904.76, 2173.12, 2164.71, 1450.88, 1159.47, 951.32.

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