Supplementary information

Tailoring the Cavities of Hydrogen-bonded Amphidynamic Crystals using Weak Contacts: Towards Faster Molecular Machines

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Materials and methods

Reagents and solvents were purchased from company Sigma-Aldrich® and were used without further purification. Reactions were monitored through TLC using silica gel plates 60 F254 purchased from Merck®. Spots were detected either by UV-light absorption or by using Seebach’s TLC stain. Reactions were carried out in inert atmosphere using nitrogen (N2). Solution ¹H and ¹³C experiments were recorded at room temperature using Bruker Avance III 400 with BBO 400S1 probe or with Jeol Eclipse 300. The spectroscopic data is referenced to CDCl₃ (¹H: δ = 7.26 ppm, s; ¹³C: δ = 77.0 ppm) or DMSO-d₆ (¹H, δ = 2.5 ppm, q; ¹³C: δ = 39.52 ppm). High-Resolution Mass Spectrometry was obtained in a Jeol JMS-AccuTOF JMS-T100LC spectrometer, ionization mode: Direct Analysis in Real Time (DART). FTIR spectra experiments were recorded with Bruker ATR equipped with a diamond tip in the spectral window from 4000 to 500 cm⁻¹. Uncorrected melting points were determined in a Fisher-Johns melting point apparatus, unless otherwise noted.

Synthesis of 1,4-diazabicyclo[2.2.2]octane-d₁₀ (DABCO-d₁₀) was followed as described in a procedure already reported. M.P. 112-114 °C, MS (DART) m/z: [M+H]⁺: 121.15477 (D₈, 11.8%), 122.15622 (D₉, 35.2%), 123.16125 (D₁₀, 74.9%), 124.16953 (D₁₁, 100%), 125.17496 (D₁₂, 87.6%), which account for 93% mean content of ²H.

General procedure for the synthesis of carbazole-based stators via Suzuki coupling

Solid reagents were placed in a two-neck round-bottom flask with magnetic stirrer, connected to a reflux system, then sealed and degassed with N₂ for 20 minutes. Subsequently, solvents and solutions were poured using a syringe. In the reactions to obtain compounds 4 to 7 the system was heated to 85 °C with a heating mantle and left to react for the indicated time. The products were isolated using column chromatography with silica gel as stationary phase and hexanes to remove remaining starting materials, followed by a mixture of hexanes/ethyl acetate (97:3).

Compounds 4 to 6 were synthesized using the following quantities of reagents: 0.500 g of 3,6-diiodo-9H-carbazole (8) (1.0 eq, 1.19 mmol), 0.564 g of the corresponding difluorophenylboronic acid (3.0 eq, 3.58 mmol), 0.042 g of Pd(PPh₃)₂Cl₂ (0.05 eq, 0.06 mmol), 8 mL of toluene, 0.8 mL of ethanol and 1 mL of K₂CO₃ (2 mol L⁻¹).
3,6-bis(2,4-difluorophenyl)-9H-carbazole (4)

Reaction between 3,6-diiodo-9H-carbazole (8) and 3,5-difluorophenylboronic acid. Reaction time of 12 hours. The product was recovered as a white, granular solid (0.260 g, yield 56%, m.p. 165-167). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.29 (s, 2H, H4), 8.19 (s, 1H, H9), 7.65 (dd, 2H, $J = 8.5$, 1.8 Hz, H2), 7.51 (d, 2H, $J = 8.4$ Hz, H1), 7.23 (d, 4H, $J = 8.9$, H11), 6.78 (tt, 2H, $J = 8.9$, 2.3 Hz, H13). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 163.6 (C12, dd, $J = 246.5$, 13.6 Hz), 145.3 (C3), 140.1 (C9a), 131.2 (C10), 125.7 (C2), 124.0 (C4a), 119.1 (C4), 111.4 (C1), 110.0 (C11, d, $J = 25.2$ Hz), 101.9 (C13, t, $J = 25.5$ Hz). FTIR (ATR, cm$^{-1}$) $\nu$: 3470, 1623, 1591, 1468, 1288, 1243, 1194, 1190, 868, 848, 803, 616. HRMS (DART) m/z: [C$_{24}$H$_{14}$F$_4$N]$^+$, calculated 392.10624, found 392.10690, difference (ppm): 1.70.

3,6-bis(2,5-difluorophenyl)-9H-carbazole (5)

Reaction between 3,6-diiodo-9H-carbazole (8) and 2,5-difluorophenylboronic acid. Reaction time of 14 hours. The product was recovered as a white, fine solid (0.223 g, yield 48%, m.p. 151-153 °C). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.27 (s, 2H, H4), 8.15 (s, 1H, H9), 7.63 (d, 2H, $J = 8.4$ Hz, H2), 7.49 (d, 2H, $J = 8.4$ Hz, H1), 7.29 – 7.24 (m, 2H, H15), 7.15 (td, $J = 9.5$, 4.5 Hz, 2H, H12), 7.03 – 6.97 (m, 2H, H13). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 159.0 (C11, d, $J = 240.7$ Hz), 156.0 (C14, d, $J = 243.6$ Hz), 139.7 (C9a), 131.1 (C10, dd, $J = 24.4$, 7.7 Hz), 127.3 (C2), 126.6 (C3), 123.7 (C4a), 121.1 (C4), 117.4 (C12), 117.1 (C15), 114.6 (C13, dd, $J = 24.0$, 8.4 Hz), 110.9 (C1). FTIR (ATR, cm$^{-1}$) $\nu$: 3428, 1607, 1490, 1240, 1177, 1101, 875, 802, 761, 701, 617. HRMS (DART) m/z: [C$_{24}$H$_{14}$F$_4$N]$^+$, calculated 392.10624, found 392.10699, difference (ppm): 1.92.
3,6-bis(2,3-difluorophenyl)-9H-carbazole (6)

Reaction between 3,6-diiodo-9H-carbazole (8) and 2,3-difluorophenylboronic acid. Reaction time of 10 hours. The product was recovered as a white, fine solid (0.242 g, **yield 52%**, m.p. 144-146 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.27 (s, 2H, H4), 8.17 (s, 1H, H9), 7.64 (d, 2H, $J$ = 8.4 Hz, H2), 7.50 (d, 2H, $J$ = 8.4 Hz, H1), 7.33 – 7.30 (m, 2H, H15), 7.18 – 7.10 (m, 4H, H13, H14). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 151.9 (C12, dd, $J$ = 237.3, 12.9 Hz), 148.2 (C11, dd, $J$ = 248.2, 12.7 Hz), 139.7 (C9a), 132.1 (C10, d, $J$ = 10.2 Hz), 127.4 (C2), 126.5 (C3), 125.8 (C15), 124.2 (C14), 123.7 (C4a), 121.1 (C4), 115.5 (C13, d, $J$ = 17.4 Hz), 110.9 (C1). FTIR (ATR, cm$^{-1}$) ν: 3478, 2923, 1609, 1477, 1260, 897, 770. HRMS (DART) m/z: [C$_{24}$H$_{14}$F$_4$N]$^+$, calculated 392.10624, found 392.10818, difference (ppm): 4.95.

3,6-diphenyl-9H-carbazole (7)

Reaction time of 24 hours. Quantities: 0.500 g of 3,6-diiodo-9H-carbazole (8) (1.0 eq, 1.19 mmol), 0.436 g of phenylboronic acid (3.0 eq, 3.58 mmol), 0.042 g of Pd(PPh$_3$)$_2$Cl$_2$ (0.05 eq, 0.06 mmol), 8 mL of toluene, 0.8 mL of ethanol and 1 mL of K$_2$CO$_3$ (2 mol L$^{-1}$). The product was recovered as a white solid (0.192 g, **yield 50%**, m.p. 204-205 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.35 (s, 2H, H4), 8.03 (s, 1H, H9), 7.75 (d, $J$ = 7.9 Hz, 4H, H11), 7.71 (d, $J$ = 8.3 Hz, 2H, H2), 7.52 (t, $J$ = 8.0 Hz, 4H, H12), 7.47 (d, $J$ = 8.6 Hz, 2H, H1), 7.38 (t, $J$ = 7.4 Hz, 2H, H13). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 142.1 (C9a), 139.5 (C3), 133.3 (C10), 128.9 (C12), 127.4 (C11), 126.7 (C13), 125.8 (C2), 124.1 (C4a), 119.0 (C4), 111.0 (C1). FTIR (ATR, cm$^{-1}$) ν: 3418, 3032, 2924, 2853, 1601, 1475, 1283, 1238, 822, 761, 697. HRMS (DART) m/z: [C$_{24}$H$_{18}$N]$^+$, calculated 320.14392, found 320.14463, difference (ppm): 2.20.
3,6-diido-9H-carbazole (8)

In a two-neck round-bottom flask attached to a condenser were placed the next quantities of reagents: 0.500 g (1.0 eq., 2.99 mmol) of carbazole, 0.650 g of KIO₃ (1.0 eq., 3.04 eq) and 0.650 g of KI (1.3 eq, 3.91 mmol). The flask was sealed and degassed with N₂ for 15 minutes, then 10 mL of glacial acetic acid were added. The mixture was heated to 85 °C and left to react for 50 minutes. Afterwards, the residue was poured into an ice-bath with Na₂SO₃ and stirred for 20 minutes. The solid formed was vacuum filtered and recrystallized from ethanol to afford a fine, gray, crystalline solid (0.952 g, yield 76%, m.p. 209-211 °C).

**¹H NMR** (300 MHz, DMSO-d₆) δ: 11.56 (s, 1H), 8.57 (s, 2H), 7.66 (dd, 2H, J = 8.5, 1.7 Hz), 7.35 (d, 2H, J = 8.5 Hz). **¹³C NMR** (75 MHz, DMSO-d₆) δ: 138.8, 134.1, 129.2, 123.9, 113.6, 81.9. **FTIR** (ATR, cm⁻¹) ν: 3410, 1867, 1736, 1560, 818, 418. **HRMS** (DART) m/z: [C₁₂H₈NI₂]⁺, calculated 419.87461, found 419.87560, difference (ppm): 2.36.

**General procedure for synthesis of single crystals of cocrystals 1-3I and 7s**

In a 6 mL capped vial were placed two equivalents of compounds 4 to 7 by one equivalent of DABCO. Afterwards, to the solution was added 3 mL of a (95:5 v/v%) hexane:ethyl acetate solvent mixture, the vial was sealed and heated for 20 minutes or until all the solids had solubilized. The vial was left to cool down to room temperature with a loose cap to allow the solvent to slowly evaporate. The vial is placed in fridge for a week to allow larger crystals to form.

**Table S1.** Melting points of cocrystals herein described

| Cocrystal  | Melting point (°C) |
|------------|--------------------|
| 1          | 157-159            |
| 2          | 156-158            |
| 3 (form I) | 149-150            |
| 7s         | 154-156            |
General procedure for obtaining of cocrystals 1 to 3I in bulk via mechanochemical synthesis

For cocrystals 1-3I, two equivalents of the corresponding carbazole moiety were placed in an agate mortar along with one equivalent of DABCO (or DABCO-d10 for deuterated rotors). Then, 4 drops of Na/benzophenone dried THF are poured into the mixture. The resulting paste was manually grinded with the agate pestle for 5 minutes, which produced an off-white pulverized solid.

Optical Microscopy

Optical microscopy images were acquired using an Olympus BX43 microscope with a QImaging MicroPublisher camera (5.0 MP RTV), using freshly grown single crystals of each rotor.

Figure S1. Optical microscopy pictures of freshly grown single crystals described in this work. In this order a) 1, b) 2, c) 3I and d) 7s.
Solution $^1$H and $^{13}$C NMR characterization of compounds

Figure S2. $^1$H solution NMR spectra of 4 (CDCl$_3$, 400 MHz)

Figure S3. $^{13}$C solution NMR spectra of 4 (CDCl$_3$, 100 MHz)
Figure S4. 2D NMR spectra of compound 4 (HSQC, up and HMBC, down).
Figure S5. $^1$H solution NMR spectra of 5 (CDCl$_3$, 400 MHz)

Figure S6. $^{13}$C solution NMR spectra of 5 (CDCl$_3$, 100 MHz)
Figure S7. 2D NMR spectra of compound 5 (HSQC, up and HMBC, down).
Figure S8. $^1$H solution NMR spectra of 6 (CDCl$_3$, 400 MHz)

Figure S9. $^{13}$C solution NMR spectra of 6 (CDCl$_3$, 100 MHz)
Figure S10. 2D NMR spectra of compound 6 (HSQC, up and HMBC, down).
Figure S11. $^1$H solution NMR spectra of 7 (CDCl$_3$, 400 MHz)

Figure S12. $^{13}$C solution NMR spectra of 7 (CDCl$_3$, 100 MHz)
Figure S13. 2D NMR spectra of compound 7 (HSQC, up and HMBC, down).
Figure S14. $^1$H solution NMR spectra of 8 (DMSO-$d_6$, 300 MHz)

Figure S15. $^{13}$C solution NMR spectra of 8 (DMSO-$d_6$, 75 MHz)
$^1$H NMR spectra. Recognition experiments

Figure S16. Stacked $^1$H solution NMR spectra (CDCl$_3$, 300 MHz, both) of pure 4 (top) and mixture 2:1 4+DABCO (bottom)

Figure S17. Stacked $^1$H solution NMR spectra (CDCl$_3$, 300 MHz, both) of pure 5 (top) and mixture 2:1 5+DABCO (bottom)
Figure S18. Stacked $^1$H solution NMR spectra (CDCl$_3$, 300 MHz, both) of pure 6 (top) and mixture 2:1 6+DABCO (bottom)

Figure S19. Stacked $^1$H solution NMR spectra (CDCl$_3$, 300 MHz, both) of pure 7 (top) and mixture 2:1 of 7+DABCO (bottom)
Figure S20. $^1$H NMR solution spectra of mixture (1:1:1) $4 + \text{DABCO} + 5$ (CDCl$_3$, 400 MHz)

Figure S21. $^1$H NMR solution spectra of mixture (1:1:1) $4 + \text{DABCO} + 6$ (CDCl$_3$, 400 MHz)
Figure S22. $^1$H NMR solution spectra of mixture (1:1:1) 5+DABCO+6 (CDCl$_3$, 400 MHz)

Table S2. Chemical shifts of $^1$H in solution NMR for the recognition experiments with DABCO

| Compound | 4 | 5   | 6   | 7    |
|----------|---|-----|-----|------|
| 4        | 8.33 |     |     |      |
| 5        | 8.39, 8.37 | 8.29 |     |      |
| 6        | 8.40 | 8.37 | 8.49 |      |
| 7        | -   | -   | -   | 8.33 |
Crystallographic information tables and X-Ray diffraction studies

X-Ray diffraction data were obtained at variable temperature either from Bruker D8 diffractometer equipped with a PHOTON II CPAD detector with synchrotron radiation ($\lambda = 0.7288$ Å) on beamline 12.2.1 at Advanced Light Source, or from Bruker Smart APEX II CCD$^{52}$ with graphite monochromatic MoKα radiation ($\lambda = 0.71073$ Å), as noted in the following tables. Cell refinement was carried out using SAINT V8.38A.$^{53}$ Structure solution, final refinement and data output was carried out using SHELX-2014$^{54}$ through direct methods. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions using a riding model, with isotropic thermal parameters $U_{iso}(H) = 1.2U_{eq}(C)$. Crystal structures were generated with Mercury 4.3.1.$^{55}$

Powder X-Ray diffraction data were collected at room temperature in a Bruker D2 PHASER diffractometer, using CuKα radiation ($\lambda = 1.5406$ Å), operating at 30 kV and 10 mA with a $\theta-\theta$ configuration in a $2\theta$ interval of 5-45°, step of 0.02°, time 0.250 s.

Figure S23. Asymmetric unit for cocrystal 1 at a) 100, 150 and 200 K (LT), and b) at 300 K (HT). Ellipsoids are drawn at 50% probability level. Colors used account for symmetry equivalent components.
**Table S3.** Crystallographic parameters for 1

| Formula | \(2(C_{24}H_{12}F_3N)_2\) | \(2(C_{24}H_{12}F_3N)_2\) | \(2(C_{24}H_{12}F_3N)_2\) | \(2(C_{24}H_{12}F_3N)_2\) | \(2(C_{24}H_{12}F_3N)_2\) |
|----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Formula weight | 894.88 | 894.88 | 894.88 | 894.88 | 894.88 |
| Temperature (K) | 100(2) | 150(2) | 200(2) | 250(2) | 300(2) |
| System | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space Group | \(P_2_1\) | \(P_2_1\) | \(P_2_1\) | \(P_2_1\) | \(Cc\) |
| \(a\) (Å) | 14.0179(5) | 14.0331(4) | 14.0444(4) | 14.0592(6) | 13.9524(6) |
| \(b\) (Å) | 13.6325(5) | 13.6998(4) | 13.7744(4) | 13.8649(6) | 14.0942(5) |
| \(c\) (Å) | 22.7651(7) | 22.8049(7) | 22.8418(7) | 22.8854(9) | 22.7794(8) |
| \(\alpha\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(\beta\) (°) | 107.5360(10) | 107.5550(10) | 107.5900(10) | 107.6288(14) | 106.4326(15) |
| \(\gamma\) (°) | 90 | 90 | 90 | 90 | 90 |
| \(\rho\) (g/cm\(^3\)) | 1.433 | 1.422 | 1.411 | 1.398 | 1.383 |
| \(V\) (Å\(^3\)) | 4148.2(2) | 4180.1(2) | 4212.2(2) | 4251.5(3) | 4296.5(3) |
| \(Z\) | 4 | 4 | 4 | 4 | 4 |
| Absorption coefficient (mm\(^{-1}\)) | 0.114 | 0.114 | 0.113 | 0.112 | 0.110 |
| \(F(000)\) | 1848 | 1848 | 1848 | 1848 | 1848 |
| Crystal size (mm) | 0.100 x 0.090 x 0.030 | 0.100 x 0.090 x 0.030 | 0.100 x 0.090 x 0.030 | 0.100 x 0.090 x 0.030 | 0.100 x 0.090 x 0.030 |
| Radiation \([\lambda\) (Å)] | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) |
| Collected reflections | 148821 | 145863 | 144945 | * | 20394 |
| Independent reflections | 23303 | 22549 | 22733 | * | 5794 |
| Data/rest/param | 23303/1/1201 | 22549/1/1201 | 22733/1/1201 | * | 5794/2/602 |
| GooF | 1.029 | 1.037 | 1.025 | * | 1.047 |
| Final R indexes \([I_o>2\sigma(I_o)]\) | \(R_1=0.0337\) | \(R_1=0.0355\) | \(R_1=0.0412\) | * | \(R_1=0.0372\) |
| \(wR_2=0.0884\) | \(wR_2=0.0945\) | \(wR_2=0.1098\) | \(wR_2=0.0936\) |
| Final R indexes \([all\ data]\) | \(R_1=0.0348\) | \(R_1=0.0372\) | \(R_1=0.0439\) | * | \(R_1=0.0471\) |
| \(wR_2=0.0896\) | \(wR_2=0.0965\) | \(wR_2=0.1134\) | \(wR_2=0.0993\) |
| Largest diff. peak/hole \((eA^-3)\) | 0.317/-0.299 | 0.332/-0.237 | 0.341/-0.309 | * | 0.140/-0.165 |
| CCDC number | 2022170 | 2022171 | 2022172 | * | 2022173 |

**Table S4.** Hydrogen bond parameters in the two crystal phases of the supramolecular rotor 1

| Distance D-A (Å) | Angle N-H···N (°) | Distance D-A (Å) | Angle N-H···N (°) |
|-----------------|-----------------|-----------------|-----------------|
| **100 K (P2_1)** | **300 K (Cc)** | **100 K (P2_1)** | **300 K (Cc)** |
| 2.840(2) | 177(2) | 2.884(3) | 164(4) |
| 2.876(2) | 176(2) | 2.875(3) | 166(4) |
| 2.826(2) | 175(2) | 2.875(3) | 166(4) |
| 2.847(2) | 174(2) | 2.875(3) | 166(4) |
| Crystallographic parameters for 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ |
|-----------------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Formula weight                             | 894.88                 | 894.88                 | 894.88                 | 894.88                 | 894.88                 |
| Temperature (K)                             | 100(2)                 | 150(2)                 | 200(2)                 | 250(2)                 | 302(2)                 |
| System                                      | monoclinic             | monoclinic             | monoclinic             | monoclinic             | monoclinic             |
| Space Group                                 | P2₁/n                  | P2₁/n                  | P2₁/n                  | P2₁/n                  | P2₁/n                  |
| a (Å)                                       | 6.6570(3)              | 6.6613(3)              | 6.6696(2)              | 6.6803(2)              | 6.6761(5)              |
| b (Å)                                       | 14.8520(6)             | 14.8875(6)             | 14.9431(5)             | 15.0128(5)             | 15.0587(11)            |
| c (Å)                                       | 21.2537(8)             | 21.2797(8)             | 21.3309(7)             | 21.3972(7)             | 21.4293(14)            |
| α (°)                                       | 90                     | 90                     | 90                     | 90                     | 90                     |
| β (°)                                       | 95.7210(10)            | 95.554(2)              | 95.362(2)              | 95.1430(10)            | 94.9412(17)            |
| γ (°)                                       | 90                     | 90                     | 90                     | 90                     | 90                     |
| ρ (g/cm³)                                   | 1.420                  | 1.415                  | 1.404                  | 1.391                  | 1.385                  |
| V (Å³)                                      | 2090.88(15)            | 2100.40(15)            | 2116.63(12)            | 2137.29(12)            | 2146.43(1)             |
| Z                                           | 2                      | 2                      | 2                      | 2                      | 2                      |
| Absorption coefficient (mm⁻¹)               | 0.113                  | 0.113                  | 0.112                  | 0.111                  | 0.106                  |
| F(000)                                      | 922                    | 924                    | 924                    | 924                    | 924                    |
| Crystal size (mm)                           | 0.340 x 0.120 x 0.100  | 0.340 x 0.120 x 0.100  | 0.340 x 0.120 x 0.100  | 0.340 x 0.120 x 0.100  | 0.413 x 0.368 x 0.298  |
| Radiation                                   | Synchrotron            | Synchrotron            | Synchrotron            | Synchrotron            | MoKα                   |
| [λ (Å)]                                     | (0.7288)               | (0.7288)               | (0.7288)               | (0.7288)               | (0.71073)              |
| Collected reflections                       | 73120                  | 60836                  | 58731                  | 60892                  | 27821                  |
| Independent reflections                     | 7264                   | 6418                   | 5448                   | 5759                   | 4923                   |
| Data/rest/param                             | 7264/0/338             | 6418/0/338             | 5448/0/338             | 5759/0/338             | 4923/0/338             |
| GoF                                         | 1.066                  | 1.063                  | 1.067                  | 1.068                  | 0.988                  |
| Final R indexes [I>2σ(I)]                   | R₁=0.0474              | R₁=0.0526              | R₁=0.0492              | R₁=0.0588              | R₁=0.0542              |
|                                               | wR₂=0.1231             | wR₂=0.1318             | wR₂=0.1218             | wR₂=0.1355             | wR₂=0.0895             |
| Final R indexes [all data]                  | R₁=0.0507              | R₁=0.0566              | R₁=0.0530              | R₁=0.0652              | R₁=0.1814              |
|                                               | wR₂=0.1276             | wR₂=0.1376             | wR₂=0.1266             | wR₂=0.1439             | wR₂=0.1229             |
| Largest diff. peak/hole (eA⁻³)              | 0.558/-0.421           | 0.518/-0.340           | 0.372/-0.277           | 0.530/-0.409           | 0.187/-0.179           |
| CCDC number                                 | 2022174                | 2022175                | 2022176                | 2022177                | 2022178                |
Table S6. Crystallographic parameters for 3I

| Formula | 2(C_{24}H_{13}F_{4}N)·C_{6}H_{12}N_{2} | 2(C_{24}H_{13}F_{4}N)·C_{6}H_{12}N_{2} | 2(C_{24}H_{13}F_{4}N)·C_{6}H_{12}N_{2} |
|---------|----------------------------------------|----------------------------------------|----------------------------------------|
| Formula weight | 894.88 | 894.88 | 894.88 |
| Temperature (K) | 100(2) | 200(2) | 299(2) |
| System | monoclinic | monoclinic | monoclinic |
| Space Group | P2_1/n | P2_1/n | P2_1/n |
| a (Å) | 6.7657(3) | 6.7928(4) | 6.8192(8) |
| b (Å) | 14.4934(9) | 14.5649(8) | 14.6728(18) |
| c (Å) | 21.3307(10) | 21.3902(12) | 21.461(3) |
| α (°) | 90 | 90 | 90 |
| β (°) | 96.1667(13) | 95.7754(16) | 95.452(4) |
| γ (°) | 90 | 90 | 90 |
| ρ (g/cm³) | 1.429 | 1.412 | 1.390 |
| V (Å³) | 2079.54(16) | 2105.5(2) | 2137.7(5) |
| Z | 2 | 2 | 2 |
| Absorption coefficient (mm⁻¹) | 0.109 | 0.108 | 0.106 |
| F(000) | 924 | 924 | 924 |
| Crystal size (mm) | 0.393 x 0.372 x 0.198 | 0.386 x 0.267 x 0.208 | 0.393 x 0.372 x 0.198 |
| Radiation | MoKα | MoKα | MoKα |
| [λ (Å)] | (0.71073) | (0.71073) | (0.71073) |
| Collected reflections | 49708 | 29489 | 28587 |
| Independent reflections | 6833 | 6161 | 5098 |
| Data/rest/param | 6833/15/356 | 6161/342/356 | 5098/15/356 |
| Goof | 1.131 | 1.017 | 1.009 |
| Final R indexes | R₁=0.0613 | R₁=0.0596 | R₁=0.0572 |
| [I>2σ(Io)] | wR₂=0.1430 | wR₂=0.1075 | wR₂=0.1092 |
| Final R indexes | R₁=0.0755 | R₁=0.1748 | R₁=0.1583 |
| [all data] | wR₂=0.1503 | wR₂=0.1391 | wR₂=0.1405 |
| Largest diff. peak/hole (eÅ⁻³) | 0.435/-0.314 | 0.199/-0.247 | 0.158/-0.163 |
| CCDC number | 2022179 | 2022180 | 2022181 |
**Table S7. Crystallographic parameters for 3II**

| Formula | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ | 2(C₂₄H₁₃F₄N)·C₆H₁₂N₂ |
|---------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| **Formula weight** | 894.88 | 894.88 | 894.88 | 894.88 | 447.44 |
| **Temperature (K)** | 100(2) | 150(2) | 200(2) | 250(2) | 300(2) |
| **System** | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| **Space Group** | Pc | P2/c | P2/c | P2/c | P2/c |
| **a (Å)** | 19.0865(8) | 19.1368(8) | 19.1580(7) | 19.2225(9) | 19.2767(6) |
| **b (Å)** | 6.7670(3) | 6.7789(3) | 6.7794(3) | 6.7835(3) | 6.7799(2) |
| **c (Å)** | 17.3518(7) | 17.4066(8) | 17.4666(6) | 17.5663(8) | 17.6615(6) |
| **α (°)** | 90 | 90 | 90 | 90 | 90 |
| **β (°)** | 109.3540(10) | 109.3730(10) | 109.3620(10) | 109.337(2) | 109.2900(10) |
| **γ (°)** | 90 | 90 | 90 | 90 | 90 |
| **ρ (g/cm³)** | 1.406 | 1.395 | 1.389 | 1.375 | 1.364 |
| **ν (Å³)** | 2114.48(16) | 2130.24(16) | 2140.25(14) | 2161.35(17) | 2178.66(12) |
| **Z** | 2 | 2 | 2 | 2 | 4 |
| **Absorption coefficient (mm⁻¹)** | 0.112 | 0.111 | 0.111 | 0.110 | 0.109 |
| **F(000)** | 924 | 924 | 924 | 924 | 924 |
| **Crystal size (mm) x x x** | 0.300 x 0.300 x 0.030 | 0.300 x 0.300 x 0.030 | 0.300 x 0.300 x 0.030 | 0.300 x 0.300 x 0.030 | 0.300 x 0.300 x 0.030 |
| **Radiation** | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) | Synchrotron (0.7288) |
| **Collected reflections** | 71153 | 73488 | 65803 | 69239 | 67379 |
| **Independent reflections** | 12908 | 6498 | 6030 | 5831 | 5405 |
| **Data/rest/param** | 12908/2/601 | 6498/75/338 | 6030/75/338 | 5831/75/338 | 5405/75/338 |
| **GooF** | 1.045 | 1.045 | 1.034 | 1.049 | 1.048 |
| **Final R indexes [I₀>2σ(I₀)]** | R₁=0.0381 | R₁=0.0585 | R₁=0.0542 | R₁=0.0572 | R₁=0.0580 |
| | wR₂=0.0991 | wR₂=0.1458 | wR₂=0.1407 | wR₂=0.1497 | wR₂=0.1585 |
| **Final R indexes [all data]** | R₁=0.0391 | R₁=0.0606 | R₁=0.0585 | R₁=0.0609 | R₁=0.0629 |
| | wR₂=0.1005 | wR₂=0.1484 | wR₂=0.1462 | wR₂=0.1549 | wR₂=0.1661 |
| **Largest diff. peak/hole (eÅ⁻³)** | 0.498/-0.417 | 0.863/-0.532 | 0.666/-0.313 | 0.462/-0.419 | 0.375/-0.377 |
| **CCDC number** | 2022182 | 2022183 | 2022184 | 2022185 | 2022186 |
Table S8. Crystallographic parameters for 7s

| Formula | \( \text{C}_{24}\text{H}_{17}\text{N} \cdot \text{C}_{6}\text{H}_{12}\text{N}_2 \) |
|---------|--------------------------------------------------|
| Formula weight | 431.56 |
| Temperature (K) | 100(2) |
| System | monoclinic |
| Space Group | \( P2_1/c \) |
| \( a \) (Å) | 9.1480(4) |
| \( b \) (Å) | 22.6374(10) |
| \( c \) (Å) | 11.7158(5) |
| \( \alpha \) (°) | 90 |
| \( \beta \) (°) | 105.813(2) |
| \( \gamma \) (°) | 90 |
| \( \rho \) (g/cm\(^3\)) | 1.228 |
| \( V \) (Å\(^3\)) | 2334.37(10) |
| \( Z \) | 4 |
| Absorption coefficient (mm\(^{-1}\)) | 0.075 |
| F(000) | 920 |
| Crystal size (mm) | 0.250 x 0.110 x 0.005 |
| Radiation | Synchrotron |
| \( [\lambda \text{ (Å)}] \) | (0.7288) |
| Collected reflections | 66651 |
| Independent reflections | 7141 |
| Data/rest/param | 7141/0/301 |
| GooF | 1.027 |
| Final R indexes | \( R_1=0.0409 \) |
| \( [I_0>2\sigma(I_0)] \) | \( wR_2=0.1089 \) |
| Final R indexes | \( R_1=0.0470 \) |
| [all data] | \( wR_2=0.1144 \) |
| Largest diff. peak/hole (eÅ\(^{-3}\)) | 0.323/-0.265 |
| CCDC number | 2022187 |
**Figure S24.** Interactions C-H···F-C around DABCO in rotor 1 at different temperatures (ORTEP diagram, 50% level probability). For structures at 100 and 200 K (1-LT) are shown both DABCO fragments in the asymmetric unit, the hydrogen bonded carbazole units were omitted.

**Figure S25.** Crystal arrangement of cocrystal 3I (ORTEP diagram, 50% level probability). Close interactions C-F···H-C around DABCO are highlighted with blue dotted lines.
Table S9. Close contacts C-H⋯F-C present around DABCO in rotor 1 at several temperatures per unit cell.

| Rotor 1 | Experimental (100K) | Optimization (100 K) | Experimental (300 K) |
|---------|---------------------|----------------------|---------------------|
| F1-H31A | 2.814               | F1-H                 | 2.467               | F1-H31A | 2.855 |
| F1-H31B | 2.664               | F1-H                 | 2.667               | F1-31B | 2.667 |
| F41-H34A | 2.597               | F2-H                 | 2.881               | F41-34A | 2.665 |
| F41-H36B | 2.849               | F3-H                 | 2.930               | F41-H36B | 2.909 |
| F72-H34A | 2.604               | F3-H                 | 2.930               | F72-H34A | 2.612 |
| F72-H34B | 2.94                | F4-H                 | 2.713               | F72-H34B | 2.969 |
| F73-H33A | 2.991               | F4-H                 | 2.602               | F74-H36A | 2.657 |
| F73-H34B | 2.955               | F5-H                 | 2.578               | F112-H31B | 2.766 |
| F74-H36A | 2.622               | F5-H                 | 2.734               | F112-H33B | 2.892 |
| F113-H33A | 2.977              | F6-H                 | 2.899               | F114-H35B | 2.98 |
| F112-H31B | 2.742               | F7-H                 | 2.667               | F4-H109 | 2.801 |
| F112-H33A | 2.868               | F7-H                 | 2.467               | F2-H101 | 2.663 |
| F114-H35B | 2.958               | F8-H                 | 2.489               | F4-H112 | 2.936 |
| F4-H109 | 2.737               | F9-H                 | 2.734               | F4-H106 | 2.981 |
| F2-H101 | 2.613               | F9-H                 | 2.578               | F4-H107 | 2.687 |
| F44-H112 | 2.898               | F10-H                | 2.61                | F4-H107 | 2.881 |
| F43-H106 | 2.848               | F11-H                | 2.92                | F4-H108 | 2.649 |
| F43-H107 | 2.621               | F11-H                | 2.93                | F71-H101 | 2.685 |
| F42-H107 | 2.836               | F12-H                | 2.518               | F71-H102 | 2.688 |
| F42-H108 | 2.642               | F12-H                | 2.902               | F111-H108 | 2.892 |
| F71-H101 | 2.698               | F13-H                | 2.701               | F1-H31A | 2.855 |
| F71-H102 | 2.637               | F13-H                | 2.862               | F1-31B | 2.667 |
| F111-H108 | 2.857               | F14-H                | 2.548               | F41-34A | 2.665 |
| F1-H31A | 2.814               | F14-H                | 2.763               | F41-H36B | 2.909 |
| F1-H31B | 2.664               | F15-H                | 2.518               | F72-H34A | 2.612 |
| F41-H34A | 2.597               | F15-H                | 2.746               | F72-H34B | 2.969 |
| F41-H36B | 2.849               | F16-H                | 2.714               | F74-H36A | 2.657 |
| F72-H34A | 2.604               | F16-H                | 2.59               | F112-H31B | 2.766 |
| F72-H34B | 2.94                | F17-H                | 2.794               | F112-H33B | 2.892 |
| F73-H33A | 2.991               | F18-H                | 2.63                | F114-H35B | 2.98 |
| F73-H34B | 2.955               | F19-H                | 2.59                | F4-H109 | 2.801 |
| F74-H36A | 2.622               | F19-H                | 2.71                | F2-H101 | 2.663 |
| F113-H33A | 2.977               | F20-H                | 2.79                | F4-H112 | 2.936 |
| F112-H31B | 2.742               | F21-H                | 2.63                | F4-H106 | 2.981 |
| F112-H33A | 2.868               | F22-H                | 2.862               | F4-H107 | 2.687 |
| F114-H35B | 2.958               | F22-H                | 2.701               | F4-H107 | 2.881 |
| F4-H109 | 2.737               | F23-H                | 2.549               | F4-H108 | 2.649 |
| F2-H101 | 2.613               | F23-H                | 2.770               | F71-H101 | 2.685 |
| F44-H112 | 2.898               | F24-H                | 2.755               | F71-H102 | 2.688 |
| F43-H106 | 2.848               | F24-H                | 2.51               | F111-H108 | 2.892 |
| F43-H107 | 2.621               |                      |                    |            |
| F42-H107 | 2.836               |                      |                    |            |
| F42-H108 | 2.642               |                      |                    |            |
| F71-H101 | 2.698               |                      |                    |            |
| F71-H102 | 2.637               |                      |                    |            |
| F111-H108 | 2.857               |                      |                    |            |
Figure S26. Comparative between contacts showed by a) XRD data and b) optimized structures in rotor 1, both at 100 K. For a) the two DABCO units showed are present in the asymmetric unit at that temperature.

Table S10. Close contacts C-H⋯F-C present around DABCO in rotor 2 at several temperatures per unit cell

| Rotor 2 | Experimental (100 K) | Optimization (100 K) | Experimental (300 K) |
|---------|----------------------|----------------------|----------------------|
| F2-H27B | 2.824                | F1-H                 | F2-H29A              | 2.968                |
| F2-H30A | 2.723                | F2-H                 | F2-H29B              | 2.678                |
| F2-H27B | 2.824                | F2-H                 | F2-H30A              | 2.861                |
| F2-H30A | 2.723                | F2-H                 | F2-H30B              | 2.993                |
| F4-H25B | 2.793                | F2-H                 | F3-H27B              | 2.859                |
| F4-H26A | 2.853                | F2-H                 | F2-H25A              | 2.756                |
| F4-H29B | 2.92                 | F3-H                 | F2-H28B              | 2.645                |
| F4-H29A | 2.612                | F4-H                 | F3-H30B              | 2.988                |
| F4-H26B | 2.646                | F4-H                 | F2-H26A              | 2.945                |
| F4-H27A | 2.858                | F4-H                 | F2-H29A              | 2.968                |
| F4-H27B | 2.64                 | F4-H                 | F2-H29B              | 2.678                |
| F4-H28A | 2.704                | F4-H                 | F2-H30A              | 2.861                |
| F4-H28B | 2.818                | F5-H                 | F2-H30B              | 2.993                |
| F4-H25B | 2.793                | F5-H                 | F3-H27B              | 2.859                |
| F4-H26A | 2.853                | F5-H                 | F2-H25A              | 2.756                |
| F4-H29B | 2.92                 | F5-H                 | F2-H28B              | 2.645                |
| F4-H29A | 2.612                | F5-H                 | F3-H30B              | 2.988                |
| F4-H26B | 2.646                | F6-H                 | F2-H26A              | 2.945                |
| F4-H27A | 2.858                | F6-H                 | 2.469                |
| F4-H27B | 2.64                 | F6-H                 | 2.605                |
| F4-H28A | 2.704                |                      |                      |
| F4-H28B | 2.818                |                      |                      |
Figure S27. Comparative between contacts showed by a) XRD data and b) optimized structures in rotor 2, both at 100 K.

Table S11. Close contacts C-H⋯F-C present around DABCO in rotor 3I at several temperatures per unit cell

|                  | Experimental (100 K) | Optimization (100 K) | Experimental (300 K) |
|------------------|----------------------|----------------------|----------------------|
| F4-H27A          | 2.671                | F1-H                 | F4-H27A              | 2.823                |
| F4-H27B          | 2.735                | F1-H                 | F4-H27B              | 2.749                |
| F4-H28A          | 2.619                | F1-H                 | F4-H28A              | 2.598                |
| F4-H28B          | 2.524                | F1-H                 | F4-H28B              | 2.804                |
| F4-H25A          | 2.676                | F2-H                 | F4-H29B              | 2.78                 |
| F4-H30A          | 2.628                | F3-H                 | F4-H26B              | 2.725                |
| F4-H25B          | 2.816                | F4-H                 | F4-H29A              | 2.918                |
| F4-H26A          | 2.863                | F4-H                 | F4-H30A              | 2.959                |
| F4-H27A          | 2.671                | F4-H                 | F4-H27A              | 2.823                |
| F4-H27B          | 2.735                | F5-H                 | F4-H27B              | 2.749                |
| F4-H28A          | 2.619                | F6-H                 | F4-H28A              | 2.598                |
| F4-H28B          | 2.524                | F7-H                 | F4-H28B              | 2.804                |
| F4-H25A          | 2.676                | F8-H                 | F4-H29B              | 2.78                 |
| F4-H30A          | 2.628                | F8-H                 | F4-H26B              | 2.725                |
| F4-H25B          | 2.816                | F8-H                 | F4-H29A              | 2.918                |
| F4-H26A          | 2.863                | F8-H                 | F4-H30A              | 2.959                |
| F9-H             | 2.679                |                      |                      |                      |
| F10-H            | 2.225                |                      |                      |                      |
| F11-H            | 2.630                |                      |                      |                      |
|                  |                      |                      |                      | 2.724                |

Figure S28. Comparative between contacts showed by a) XRD data and b) optimized structures in rotor 3I, both at 100 K.
Figure S29. Comparison of Powder X-Ray diffraction patterns: a) 1-\(d_{10}\) experimental, b) 1 experimental and c) Calculated from 1

Figure S30. Comparison of Powder X-Ray diffraction patterns: a) 2-\(d_{10}\) experimental, b) 2 experimental and c) Calculated from 2
Figure S31. Comparison of Powder X-Ray diffraction patterns. a) Calculated from 3II, b) 3I-\(d_{10}\) experimental, c) 3I experimental and d) calculated from 3I.
**Solid-state $^{13}$C CPMAS**

$^{13}$C NMR CPMAS spectra was recorded according with conditions described using polycrystalline samples of cocrystals in a Bruker Avance 500 with a PH MAS DVT 500S1 BL3.2 probe at spectrometer frequency of 125.78 MHz and room temperature (300 K) for all experiments. In following figures, signals marked “*” are assigned for carbon atoms of DABCO.

**Figure S32.** $^{13}$C CPMAS spectra of a) rotor 1 ($d_1 = 20$ s, $p_{15} = 2.5$ ms, 15 kHz spinning) and b) rotor 1 ($d_1 = 20$ s, $p_{15} = 0.1$ ms, 15 kHz spinning).
Figure S33. $^{13}$C CPMAS spectra of a) compound 5 ($d_1 = 20$ s, $p_{15} = 2.5$ ms, 15 kHz spinning), b) rotor 2 ($d_1 = 20$ s, $p_{15} = 2.5$ ms, 15 kHz spinning) and c) rotor 2 ($d_1 = 20$ s, $p_{15} = 0.1$ ms, 15 kHz spinning).

Figure S34. $^{13}$C CPMAS spectra of a) compound 6 ($d_1 = 20$ s, $p_{15} = 2.5$ ms, 15 kHz spinning), b) rotor 3I ($d_1 = 20$ s, $p_{15} = 2.5$ ms, 15 kHz spinning) and c) rotor 3I ($d_1 = 20$ s, $p_{15} = 0.1$ ms, 15 kHz spinning).
VT $^2$H Echo-spin experiments

Solid-state $^2$H echo-spin experiments were performed on a Bruker AV600 instrument at 92.1 MHz (deuteron resonance frequency) with a 5 mm wideline probe and 90-degree pulse of 2.9 $\mu$s. To suppress the undesired artifacts, a quadrupolar-echo sequence with phase recycling was used. An echo delay of 50 $\mu$s was used after the refocusing delay of 46 $\mu$s, and the recycle delay between pulses was 5 s. In the experiment, about 50 mg of sample was placed in a short borosilicate glass NMR tube. 256 scans were acquired for all temperatures explored. All spectra in this work were obtained using a line broadening of 3.0 kHz in data processing.

Figure S35. Variable temperature $^2$H quadrupolar echo-spin spectra of rotor 1-$d_{10}$. In this order: a) 350 K, b) 325 K, c) 300 K, d) 250 K, e) 200 K, f) 175 K and g) 150 K. Experimental data is shown in black and simulated in red dotted lines. For simulated data were used a QCC of 170 kHz, cone angle of 70° and line-broadening of 6 kHz. “*” shows the signal assigned for isotropic motion of free DABCO.
Figure S36. Variable temperature $^2$H quadrupolar echo-spin spectra of rotor 2-$d_{10}$. In this order: a) 300 K, b) 250 K, c) 200 K, d) 175 K, e) 150 K. Experimental data is shown in black and simulated in red dotted lines. For simulated data were used a QCC of 170 kHz, cone angle of 70° and line-broadening of 6 kHz.

Figure S37. Variable temperature $^2$H quadrupolar echo-spin spectra of rotor 3I-$d_{10}$. In this order: a) 300 K, b) 250 K, c) 200 K, d) 175 K, e) 150 K. Experimental data is shown in black and simulated in red dotted lines. For simulated data were used a QCC of 170 kHz, cone angle of 70° and line-broadening of 6 kHz. "*" shows the signal assigned for isotropic motion of free DABCO.
Computational section

DFT periodic computations were carried out by using the Vienna ab initio simulation package (VASP 5.4.4)\textsuperscript{8, 9} with the projector augmented wave (PAW) potentials to describe the interaction between ions and electrons.\textsuperscript{10} The generalized gradient approximation, as proposed by Perdew-Burke-Ernzerhof (PBE-GGA),\textsuperscript{11} is used for the exchange and correlation potential in conjunction with the Grimme’s D3-dispersion correction approach.\textsuperscript{12} The plane-wave kinetic-energy cutoff is set at 600 eV. The first Brillouin zone was sampling using Monkhorst-Pack k-grids of $4 \times 2 \times 1$ and $2 \times 2 \times 1$ k-points. The lattice parameters of each system were obtained by direct minimization of the total energy, with the atomic positions fully optimized until the interatomic forces were less than 0.001 eV/Å. Energy barriers were calculated using the Nudged Elastic Band (NEB)\textsuperscript{13} method implemented in VASP. The calculation was initialized using by seven intermediate images on each path segment, obtained by cubic spline interpolation. All NEB calculations were done for a fixed cell shape and volume.

Structural parameters

![Structural parameters](image)

**Figure S38.** Atomic representation of optimized rotors a) 1, b) 2 and c) 3I. For the modelling of these structures, single crystal data at 100 K was used.
Table S12. Comparative table of calculated and experimental cell parameters for cocrystals.

| Lattice parameter | Method     | 1-LT (100 K) | 1-LT (200 K) | 1-HT (300 K) | 2 (100 K) | 3I (100 K) |
|-------------------|------------|-------------|-------------|-------------|---------|----------|
| a (Å)             | Experimental | 14.018      | 14.044      | 13.952      | 6.657   | 6.766    |
|                   | Calculated  | 14.013      | 14.001      | 13.630      | 6.605   | 6.748    |
|                   | % Error    | (0.04 %)    | (0.31 %)    | (2.31 %)    | (0.78 %)| (0.27 %) |
| b (Å)             | Experimental | 13.633      | 13.774      | 14.094      | 14.852  | 14.493   |
|                   | Calculated  | 13.733      | 13.732      | 14.052      | 14.904  | 14.441   |
|                   | % Error    | (0.73 %)    | (0.30 %)    | (0.30 %)    | (0.35 %)| (0.36 %) |
| c (Å)             | Experimental | 22.765      | 22.842      | 22.779      | 21.254  | 21.331   |
|                   | Calculated  | 22.479      | 22.480      | 22.489      | 20.869  | 21.059   |
|                   | % Error    | (1.26 %)    | (1.58 %)    | (1.27 %)    | (1.81 %)| (1.28 %) |
| α (°)             | Experimental | 90.0        | 90.0        | 90.0        | 90.0    | 90.0     |
|                   | Calculated  | 90.0        | 90.0        | 90.0        | 90.0    | 90.0     |
|                   | % Error    | (0.0 %)     | (0.0 %)     | (0.0 %)     | (0.0 %)| (0.0 %)  |
| β (°)             | Experimental | 107.54      | 107.6       | 106.4       | 95.72   | 96.2     |
|                   | Calculated  | 107.70      | 107.7       | 106.4       | 96.96   | 97.1     |
|                   | % Error    | (0.15 %)    | (0.1 %)     | (0.0 %)     | (1.30 %)| (0.94 %) |
| γ (°)             | Experimental | 90.0        | 90.0        | 90.0        | 90.0    | 90.0     |
|                   | Calculated  | 90.0        | 90.0        | 90.0        | 90.0    | 90.0     |
|                   | % Error    | (0.0 %)     | (0.0 %)     | (0.0 %)     | (0.0 %)| (0.0 %)  |
| Volume (Å³)       | Experimental | 4148.216    | 4212.210    | 4296.547    | 2090.882| 2079.542 |
|                   | Calculated  | 4121.157    | 4117.928    | 4133.111    | 2030.241| 2036.345 |
|                   | % Error    | (0.65 %)    | (2.24 %)    | (3.80 %)    | (2.90 %)| (2.08 %) |
Rotational barriers

Figure S39. Calculated rotational barriers for rotor 1 at a) 100 K, b) 200 K and c) 300 K. Maximum at 2.5, 2.4 and 2.3 kcal/mol, respectively.

Figure S40. Calculated rotational barrier for rotor 2 at 100 K. Maximum at 1.3 kcal/mol.

Figure S41. Calculated rotational barrier for rotor 3I at 100 K. Maximum at 1.4 kcal/mol.
Non-covalent interactions

Figure S42. Non-covalent interactions (NCIs) analyses. Plots in pairs found in 1-LT.
Figure S43. Non-covalent interactions (NCIs) analyses. Plots in pairs found in 1-HT.

Figure S44. Non-covalent interactions (NCIs) analyses. Plots in pairs found in 2.
Non-covalent interactions (NCIs) analyses. Plots in pairs found in 3I.

VT $^1$H and $T_1$ spin-lattice relaxation experiments

$T_1$ experiments were performed on a Bruker AV600 instrument set at 600 MHz with a saturation-recovery pulse sequence featuring a delay time $t$ between two 90° pulses. The intensity of wideline $^1$H NMR spectrum was monitored, and a set of delay time was used for each sample at different temperatures to ensure the sufficient recovery of spectrum intensity (approximately $5 \times T_1$). Crystalline powder of the samples was placed in a short borosilicate tube (cut from a regular 5-mm NMR tube) capped with Teflon plugs at both ends. $T_1$ data was obtained from exponential fitting of the spectrum intensity change as a function of $t$.

$$I(t) = I_0 \left[ 1 - e^{-\frac{t}{T_1}} \right]$$

Table S13. Summarized $T_1$ data for rotors

|   | $1000/T$ | $\ln(T_1^{-1})$ | $1000/T$ | $\ln(T_1^{-1})$ | $1000/T$ | $\ln(T_1^{-1})$ |
|---|---------|----------------|---------|----------------|---------|----------------|
| 1 | 2.86    | -0.774036      | 3.33333 | -2.27187       | 3.33333 | -1.75279       |
| 2 | 3.08    | -0.601416      | 3.63636 | -2.27869       | 3.63636 | -1.66055       |
| 3 | 3.33    | -0.499259      | 4       | -2.18619       | 4       | -1.48256       |
| 4 | 3.63636 | -0.413962      | 4       | -2.0408        | 4       | -1.26805       |
| 5 | 4.44444 | -0.937191      | 5       | -1.51978       | 5       | -0.750756      |
| 6 | 4.44444 | -1.40984       | 6.66667 | -1.07179       | 6.66667 | -0.512464      |
Figure S46. Fitting of saturation recovery data for 1 at a) 350, b) 325, c) 300, d) 275, e) 250 and f) 225 K.
**Figure S47.** Fitting of saturation recovery data for 1 at a) 200 and b) 175 K

**Figure S48.** Fitting of saturation recovery data for 2 at a) 300, b) 275, c) 250 and d) 225 K
Figure S49. Fitting of saturation recovery data for 2 at a) 200 and b) 175 K

Figure S50. Fitting of saturation recovery data for 3I at a) 300, b) 275, c) 250 and d) 225 K
Figure S51. Fitting of saturation recovery data for 3I at a) 200, b) 175 and c) 150 K
Voids and Hirshfeld surface analysis

Voids were generated with tool integrated in Mercury 4.3.1, according with description in figures. Hirshfeld and shape index surfaces were calculated using TONTO,\textsuperscript{14} integrated in the software CrystalExplorer 17.\textsuperscript{15}

![Hirshfeld surface analysis](image)

**Figure S52.** Contributions of intermolecular interactions onto the DABCO Hirshfeld Surface mapped for rotors herein reported.

### Table S14. Numerical values for main intermolecular contributions on DABCO surface mapped

| Cocrystal | 1 | 2 | 3I |
|-----------|---|---|----|
| Temperature | 100 K | 300 K | 100 K | 300 K | 100 K | 300 K |
| N···H | 6.1% | 5.9% | 5.6% | 5.9% | 5.6% | 5.6% |
| H···F | 29.1% | 29.1% | 24.4% | 25.3% | 31.1% | 30.0% |
| H···H | 40.7% | 40.9% | 64.6% | 63.9% | 56.5% | 58.4% |
| H···C | 24.1% | 24.1% | 5.3% | 4.9% | 6.8% | 6.0% |
**Figure S53.** Shape index surfaces for cocrystal 1, mapped from -1.0 to 1.0 at a) 100 K (both symmetrically inequivalent DABCO mapped), with mean value of 0.2746, accounting both surfaces and b) 300 K, 0.2781.

**Figure S54.** Voids in lattice of rotor 1 (300 K) with 0.6 Å probe radius and 0.7 Å grid spacing. The void volume accounts for 5.3%, 229.4 Å³. Ellipsoids plotted at 50% probability level. Hydrogen atoms omitted for better visualization.
**Figure S55.** Hirshfeld fingerplots for DABCO in cocrystal 1-HT. Blue colored surfaces showed account for contributions of 24.1 (up, left), 29.1 (up, right), 40.9 (down, left) and 5.9% (down, right) of the total mapped surface.

**Figure S56.** Shape index surfaces for cocrystal 2, mapped from -1.0 to 1.0 at a) 100 K, with mean values of 0.2310, and b) 300 K, 0.2228.
Figure S57. Voids in lattice of rotor 2 (300 K) with 0.6 Å probe radius and 0.7 Å grid spacing. The void volume is 3.3%, 71.13 Å³. Ellipsoids plotted at 50% probability level. Hydrogen atoms omitted for better visualization.

Figure S58. Hirshfeld fingerplots for DABCO in cocrystal 2 at 300 K. Blue colored surfaces showed account for contributions of 4.9 (up, left), 25.3 (up, right), 63.9 (down, left) and 5.9% (down, right) of the total mapped surface.
**Figure S59.** Shape index surfaces for cocrystal 3I, mapped from -1.0 to 1.0 at a) 100 K, with mean values of 0.2114, and b) 300 K, 0.2172.

**Figure S60.** Voids in lattice of rotor 3I with 0.6 Å probe radius and 0.7 Å grid spacing. The void volume is 2.1%, 44.0 Å³. Ellipsoids plotted at 50% probability level. Hydrogen atoms omitted for better visualization.
Figure S61. Hirshfeld fingerplots for DABCO in cocrystal 3I at 300 K. Blue colored surfaces showed account for contributions of 6.0 (up, left), 30.0 (up, right), 58.4 (down, left) and 5.6% (down, right) of the total mapped surface.
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