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2020

Tan, D., Ng, Z. X., Ganguly, R., Li, Y., Soo, H. S., Sharmarke Mohamed, & García, F. (2020). Investigating the solid-state assembly of pharmaceutically-relevant N,N-dimethyl-O-thiocarbamates in the absence of labile hydrogen bonds. *CrystEngComm*, 22, 8290-8298. doi:10.1039/D0CE01336F

<https://hdl.handle.net/10356/146290>

<https://doi.org/10.1039/D0CE01336F>

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Supplementary Information

Investigating the solid-state assembly of pharmaceutically-relevant N,N-dimethyl-O-thiocarbamates in the absence of labile hydrogen bonds

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• Experimental Section:

Each mechanochemical reaction was carried out in Retsch MM400 mill at a frequency of 30 Hz using a 10 mL stainless steel milling jar and a single ball made of the same material (10 mm). ^1H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE 300 MHz with chemical shifts (δ) given in parts per million (ppm). FT-IR spectra were collected using a Fourier transform-infrared attenuated total reflectance spectrometer in the range 400 cm^{-1} to 4000 cm^{-1} .

Figure S1. General reaction scheme of the synthesis of various *N,N*-dimethyl-*O*-thiocarbamates **1-13**.

Synthesis by ball milling: Ball milling was only tested for the synthesis of **1** and **2**. A mixture of 0.50 mmol of phenol, 0.50 mmol of dimethylcarbamothioic chloride (1 equivalent), 0.55 mmol (1.1 equivalent) of DABCO, and acetonitrile as the grinding liquid ($\eta = 0.25\text{ mL mg}^{-1}$) were milled in a 10 mL stainless steel jar with one 10 mm stainless steel ball at a frequency of 30 Hz for 90 min. After the reaction, a portion of the crude mixture was used for ^1H NMR spectroscopy at this point. The ^1H NMR spectrum showed the presence of a lot of phenol starting material. Increasing the reaction duration to 2 h did not improve the conversion significantly. The crude solid was suspended in brine and extracted twice with ethyl acetate, after which the organic layers were combined and the solvent was removed *in vacuo*. The crude product was then suspended in 5 M NaOH solution and extracted with diethyl ether, after which the organic layers were combined and dried using MgSO_4 powder, and the solvent was removed *in vacuo* to afford the pure products (33% yield for **1** and 45 % yield for **2** respectively).

Synthesis in solution: Solution syntheses of the thiocarbamates were based on a previously reported protocol, with some modifications to the procedure.^[1] Each substituted phenol (10 mmol) was dissolved in 75 mL of dry acetonitrile and placed in a 250 mL round bottom flask along with a magnetic stirrer bar. DABCO (11 mmol, 1.1 equivalent) was then slowly added to the mixture with stirring until all the solids had dissolved. In some substituted phenols, a color change was observed. Subsequently, 10 mmol of dimethylcarbamothioic chloride (1 equivalent) was added to the solution and the mixture was allowed to stir at room temperature under an inert argon atmosphere for 16-18 h. For **7** and **8**, 20 mmol of NaH (2 equivalent) was used as the base instead of DABCO (excess NaH was filtered) and the reaction was refluxed overnight in toluene. During the reactions, it was observed that white precipitate started to form in the mixture. After the reaction, the solvent was removed *in vacuo* using a rotary evaporator. The remaining crude solid was extracted twice using brine and ethyl acetate, the organic layers were combined, and the solvent was removed *in vacuo*. The ^1H NMR spectrum of the crude mixture was taken at this point. For **1-6**, **9**, **10**, and **12**, the crude product was then suspended in 5 M NaOH solution and further extracted twice with diethyl ether. The organic layers were combined and dried using MgSO_4 powder and the solvent was removed *in vacuo* to afford the pure products. For **2**, **11**, and **13**, pure products were isolated after recrystallization in hot methanol.

Figure S2. Reaction scheme for the synthesis of *N,N*-diphenyl-*O*-thiocarbamate (**14**).

For the synthesis of **14**, 10 mmol of *N,N*-diphenylamine was dissolved in 50 mL of distilled toluene in a 100 mL Schlenk tube. Next, 20 mmol of NaH (2 equivalent) was added to the solution, and the mixture was stirred under argon for 5 h (or until no more effervescence was observed). The resulting suspension was then filtered to remove the excess unreacted NaH, and the solution was added slowly to a solution of *O*-phenyl carbonochloridothioate (10 mmol in 25 mL of dry toluene) in another 100 mL Schlenk tube. The reaction mixture was stirred and refluxed overnight (14–18 h) under argon. After the reaction, the solution was transferred to a 250 mL round bottom flask and the solvent was removed *in vacuo*. The crude mixture was dissolved in ethyl acetate, rinsed once with 5 M NaOH solution, and then rinsed twice with brine. The organic layers were combined, dried over MgSO₄, and the solvent was removed *in vacuo*. The pure product was obtained by recrystallization in warm chloroform.

Compound **15** was purchased (99% purity) from Tokyo Chemical Industries (TCI) Co. Ltd.

To obtain single crystals of all the compounds for X-ray diffraction measurements, the various products were redissolved in diethyl ether, acetone, or chloroform, and their solutions were left to evaporate over several days in small 5 mL dram vials. Polymorphism was not observed for crystals grown in diethyl ether, acetone, or chloroform, by measuring and comparing unit cell parameters of single crystals grown from each solvent. For **2–13**, diffraction quality crystals were obtained *via* slow evaporation from their respective solutions. For **14**, the thin needle-like crystals were obtained by dissolving the product in a 2:1 mixture of acetone and DMSO and the resulting solution was left to slowly evaporate. Very thin hair-like needles started to form after two days and diffraction quality crystals were only obtained after one month. For **15**, very brittle plate-like crystals were formed *via* slow evaporation of a solution using a 1:1 mixture of acetone and chloroform. After 3 days, diffraction quality crystals were obtained.

- **Spectroscopic Data for Compounds**

***O*-phenyl dimethylcarbamothioate 1**

Yellow solid (88% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.36 (s, 3 H), δ 3.47 (s, 3 H), δ 7.09 (d, *J* = 8.01 Hz, 2 H), δ 7.24-7.31 (m, 1 H) δ 7.36-7.45 (m, 2 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.7, 43.2, 122.9, 125.8, 129.1, 154.1, 187.4; **HRMS**: Calculated for C₉H₁₂NOS [M+H]: 182.0640; measured: 182.0712.

***O*-4-fluorophenyl dimethylcarbamothioate 2**

White powder (72% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.36 (s, 3 H), δ 3.47 (s, 3 H), δ 7.00-7.12 (m, 4 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.7, 43.3, 116.2, 124.2, 149.9, 160.3 (d, *J* = 13.2 Hz), 187.9; **¹⁹F-NMR** (282 MHz, CDCl₃) δ -116.9; **HRMS**: Calculated for C₉H₁₁NOSF [M+H]: 200.0581; measured: 200.0545.

***O*-4-chlorophenyl dimethylcarbamothioate 3**

White powder (91% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.32 (s, 3 H), δ 3.44 (s, 3 H), δ 7.02 (d, *J* = 7.83 Hz, 2 H), δ 7.35 (d, *J* = 8.01 Hz, 2 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.8, 43.4, 124.1, 129.1, 132.2, 152.6, 188.4; **HRMS**: Calculated for C₉H₁₁ONSCl [M+H]: 216.0301; measured: 216.0250.

***O*-p-tolyl dimethylcarbamothioate 4**

White powder (90% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 2.36 (s, 3 H), δ 3.34 (s, 3 H), δ 3.47 (s, 3 H), δ 6.97 (d, *J* = 7.86 Hz, 2 H), δ 7.20 (d, *J* = 8.05 Hz, 2 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 21.0, 38.7, 43.2, 122.4, 129.6, 135.5, 152.0, 188.0; **HRMS**: Calculated for C₁₀H₁₄ONS [M+H]: 196.0831; measured: 196.0796.

O-4-methoxyphenyl dimethylcarbamothioate 5

Yellow powder (95% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.33 (s, 3 H), δ 3.45 (s, 3 H), δ 3.80 (s, 3 H), δ 6.87-6.99 (m, 4 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.7, 43.3, 55.6, 114.2, 125.5, 147.7, 157.3, 188.5; **HRMS**: Calculated for C₁₀H₁₄O₂NS [M+H]: 212.0724; measured: 212.0745.

O-perfluorophenyl dimethylcarbamothioate 6

White powder (98% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.40 (s, 3 H), δ 3.49 (s, 3 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 39.0, 43.4, 118.4, 124.2, 133.4, 157.1, 186.2; **¹⁹F-NMR** (282 MHz, CDCl₃) δ -162.9, -158.2, -152.2; **HRMS**: Calculated for C₉H₇ONSF₅ [M+H]: 272.0172; measured: 272.0169.

O-2,6-dimethylphenyl dimethylcarbamothioate 7

Yellow powder (73% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 2.20 (s, 6 H), δ 3.40 (s, 3 H), δ 3.50 (s, 3 H), δ 7.08 (m, 3 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 16.8, 38.5, 43.4, 125.8, 128.3, 131.0, 151.2, 186.1; **HRMS**: Calculated for C₁₁H₁₆ONS [M+H]: 210.0995; measured: 210.0953.

O-2,6-dichlorophenyl dimethylcarbamothioate 8

Yellow powder (81% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.43 (s, 3 H), δ 3.51 (s, 3 H), δ 7.16 (t, *J* = 8.10 Hz, 1 H), δ 7.38 (d, *J* = 7.98 Hz, 2 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.9, 43.6, 126.8, 128.3, 129.8, 146.8, 184.4; **HRMS**: Calculated for C₉H₁₀ONSCl₂ [M+H]: 249.9869; measured: 249.9860.

***O*-3,4,5-trimethoxyphenyl dimethylcarbamothioate 9**

White powder (98% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.31 (s, 3 H), δ 3.42 (s, 3 H), δ 3.81 (s, 6 H), δ 3.82 (s, 3 H), δ 6.31 (s, 2 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.7, 43.0, 55.9, 60.9, 100.4, 135.9, 150.0, 153.2, 187.3; **HRMS**: Calculated for C₁₂H₁₈O₄NS [M+H]: 272.0957; measured: 272.0974.

***O*-3,5-bis(trifluoromethyl)phenyl dimethylcarbamothioate 10**

White powder (97% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.38 (s, 3 H), 3.47 (s, 3 H), δ 7.57 (s, 2 H), δ 7.77 (s, 1 H); **¹³C-NMR** (75 MHz, CDCl₃) δ 38.9, 43.4, 119.7 (m), 123.9 (m), 124.6, 132.4 (q, ¹*J*_{C-F} = 34.5 Hz), 154.2, 186.4; **¹⁹F-NMR** (282 MHz, CDCl₃) δ -62.9; **HRMS**: Calculated for C₁₁H₁₀ONSF₆ [M+H]: 318.0420; measured: 318.0387.

***O*-4-cyanophenyl dimethylcarbamothioate 11**

Yellow powder (78% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.37 (s, 3 H), 3.47 (s, 3 H), δ 7.21 (d, *J* = 8.00 Hz, 2 H), δ 7.71 (d, *J* = 7.98 Hz, 2 H); **¹³C-NMR** (300 MHz, CDCl₃) δ 38.7, 43.6, 109.4, 118.6, 124.1, 133.6, 157.2, 186.3; **HRMS**: Calculated for C₁₀H₁₁ON₂S [M+H]: 207.0660; measured: 207.0592.

***O*-4-nitrophenyl dimethylcarbamothioate 12**

White powder (98% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.39 (s, 3 H), 3.48 (s, 3 H), δ 7.26 (d, *J* = 8.05 Hz, 2H), δ 8.29 (d, *J* = 8.12 Hz, 2H); **¹³C-NMR** (300 MHz, CDCl₃) δ 39.1, 43.4, 123.9, 124.8, 145.2, 158.5, 186.1 ; **HRMS**: Calculated for C₉H₁₁O₃N₂S [M+H]: 227.0479; measured: 227.0490.

***O*-naphthalen-2-yl dimethylcarbamothioate 13**

Yellow powder (70% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 3.43 (s, 3 H), δ 3.50 (s, 3 H), δ 7.23-7.29 (m, 1 H), δ 7.44-7.54 (m, 3 H), δ 7.79-7.90 (m, 3 H); **¹³C-NMR** (300 MHz, CDCl₃) δ 38.8, 43.4, 119.8, 124.1, 126.4, 127.2, 128.5, 128.9 129.3, 132.2, 133.4 152.6, 187.1; **HRMS**: Calculated for C₁₃H₁₄ONS [M+H]: 232.0837; measured: 232.0796.

***O*-phenyl diphenylcarbamothioate 14**

White powder (73% yield); **¹H-NMR** (300 MHz, CDCl₃) δ 7.07-7.25 (m, 6 H), δ 7.29-7.50 (m, 9 H); **¹³C-NMR** (300 MHz, CDCl₃) δ 122.6, 122.7, 126.2, 127.6, 127.9, 129.3, 129.5, 130.0, 138.0, 153.9, 189.2; **HRMS**: Calculated for C₁₄H₁₈O₃N₃S [M+H]: 306.0960; measured: 306.0953.

- Infrared Spectra of Compounds**

Figure S3. FTIR of 1.

Figure S4. FTIR of 2.

Figure S5. FTIR of 3.

Figure S6. FTIR of 4.

Figure S7. FTIR of 5.

Figure S8. FTIR of 6.

Figure S9. FTIR of 7 .

Figure S10. FTIR of 8 .

Figure S11. FTIR of 9.

Figure S12. FTIR of 10.

Figure S13. FTIR of 11.

Figure S14. FTIR of 12.

Figure S15. FTIR of 13.

Figure S16. FTIR of 14.

• **Single Crystal X-ray Data and Description**

Table S1. Crystallographic data for compounds

Compound	2	3	4	5
Formula	C ₉ H ₁₀ FNOS	C ₉ H ₁₀ ClNOS	C ₁₀ H ₁₃ NOS	C ₁₀ H ₁₃ NO ₂ S
MW	199.24 g/mol	215.69 g/mol	195.27 g/mol	211.27 g/mol
Temperature	301(2) K	100(2) K	138(2) K	123(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell	a = 7.3327(6) Å b = 10.8014(9) Å c = 12.9437(11) Å α = 88.123(3)° β = 86.737(3)° γ = 76.071(3)°	a = 8.1419(2) Å b = 9.5362(3) Å c = 13.6861(4) Å α = 90° β = 105.4170(10)° γ = 90°	a = 8.0113(3) Å b = 9.6951(3) Å c = 13.9342(4) Å α = 90° β = 106.6239(13)° γ = 90°	a = 8.7175(4) Å b = 9.9546(4) Å c = 12.4668(5) Å α = 90° β = 99.0234(16)° γ = 90°
Volume	993.23(14) Å ³	1024.39(5) Å ³	1037.04(6) Å ³	1068.47(8) Å ³
Z	4	4	4	4
Density	1.332 g/cm ³	1.399 g/cm ³	1.251 g/cm ³	1.313 g/cm ³
Abs. coeff.	0.300 mm ⁻¹	0.536 mm ⁻¹	0.273 mm ⁻¹	0.277 mm ⁻¹
F(000)	416	448	416	448

6	7	8	9	10
C ₉ H ₆ F ₅ NOS	C ₁₁ H ₁₅ NOS	C ₉ H ₉ Cl ₂ NOS	C ₁₂ H ₁₇ NO ₄ S	C ₁₁ H ₉ F ₆ NOS
271.21 g/mol	209.30 g/mol	250.13 g/mol	271.32 g/mol	317.25 g/mol
301(2) K	100(2) K	100(2) K	100(2) K	298(2) K
0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
triclinic	triclinic	monoclinic	monoclinic	orthorhombic
<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>c a</i> 2 ₁
a = 6.358(2) Å b = 7.684(3) Å c = 11.573(4) Å α = 91.215(13)° β = 104.219(11)° γ = 94.232(12)°	a = 7.3200(3) Å b = 11.5744(5) Å c = 13.5992(5) Å α = 80.8887(15)° β = 80.9328(14)° γ = 80.5041(17)°	a = 7.2726(2) Å b = 7.4019(2) Å c = 19.9994(4) Å α = 90° β = 97.9720(10)° γ = 90°	a = 37.1149(9) Å b = 5.54430(10) Å c = 12.8872(3) Å α = 90° β = 95.9708(10)° γ = 90°	a = 10.683(5) Å b = 15.115(7) Å c = 8.801(4) Å α = 90° β = 90° γ = 90°
546.1(3) Å ³	1111.79(8) Å ³	1066.18(5) Å ³	2637.49(10) Å ³	1421.1(12) Å ³
2	4	4	8	4
1.649 g/cm ³	1.250 g/cm ³	1.558 g/cm ³	1.367 g/cm ³	1.483 g/cm ³
0.347 mm ⁻¹	0.259 mm ⁻¹	0.769 mm ⁻¹	0.252 mm ⁻¹	0.289 mm ⁻¹
272	448	512	1152	640

11	12	13	14	15
C ₁₀ H ₁₀ N ₂ OS	C ₉ H ₁₀ N ₂ O ₃ S	C ₁₃ H ₁₃ NOS	C ₁₉ H ₁₅ NOS	C ₁₉ H ₁₇ NOS
206.26 g/mol	226.25 g/mol	231.30 g/mol	305.38 g/mol	307.39 g/mol
100(2) K	100(2) K	100(2) K	100(2) K	100(2) K
0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
monoclinic	orthorhombic	monoclinic	orthorhombic	Monoclinic
<i>P</i> 2 ₁ / <i>n</i>	<i>P n a</i> 2 ₁	<i>P c</i>	<i>P c a</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
a = 8.4215(3) Å b = 14.1614(7) Å c = 8.8819(4) Å α = 90° β = 108.134(2)° γ = 90°	a = 7.0984(2) Å b = 21.9932(6) Å c = 6.5396(2) Å α = 90° β = 90° γ = 90°	a = 11.9751(10) Å b = 5.8514(5) Å c = 8.4304(6) Å α = 90° β = 103.293(3)° γ = 90°	a = 34.1190(14) Å b = 5.5552(3) Å c = 32.3777(13) Å α = 90° β = 90° γ = 90°	a = 17.044(2) Å b = 5.7630(7) Å c = 18.072(2) Å α = 90° β = 117.231(4)° γ = 90°
1006.65(8) Å ³	1020.94(5) Å ³	574.90(8) Å ³	6136.8(5) Å ³	1578.4(3) Å ³
4	4	2	16	4
1.361 g/cm ³	1.472 g/cm ³	1.336 g/cm ³	1.322 g/cm ³	1.294 g/cm ³
0.288 mm ⁻¹	0.305 mm ⁻¹	0.258 mm ⁻¹	0.212 mm ⁻¹	0.206 mm ⁻¹
432	472	244	2560	648

Figure S17. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **2** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831302

Figure S18. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **3** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831300

Figure S19. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **4** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831294

Figure S20. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **5** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831297

Figure S21. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **6** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831296

Figure S22. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **7** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831301

Figure S23. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **8** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831304

Figure S24. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **9** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831298

Figure S25. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **10** as determined by single-crystal X-ray diffraction (see Table S1). Both CF₃ groups are disordered over two positions. CCDC deposit code: 1831299

Figure S26. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **11** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831307

Figure S27. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **12** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831295

Figure S28. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **13** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831305

Figure S29. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **14** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831306

Figure S30. Molecular structure visualized using ORTEP-3 with thermal ellipsoids at 50% probability of **15** as determined by single-crystal X-ray diffraction (see Table S1). CCDC deposit code: 1831303

Figure S31. Section of the crystal structure of **5**, illustrating the alternating inter-locked layers (blue and yellow).

Figure S32. Section of the crystal structure of **12**, illustrating alternating opposite layers.

Figure S33. Capped stick representation of crystal structure of Tolnaftate **15**, denoting **Type III** and **IV** interactions between adjacent naphthyl (in yellow) and phenyl (in blue) rings.

- **Computational Calculations**

Methodology

Periodic DFT-D optimization and estimate of mechanical properties of crystals

The equilibrium geometry for each crystal structures **2-15** was calculated using a periodic dispersion-corrected density functional theory (DFT-D) model as implemented in VASP,^[2-4] which uses the projector-augmented wave (PAW)^[5] method with plane-wave basis sets and PAW pseudo-potentials. In all cases, the Perdew-Burcke-Ernzerhof (PBE)^[6] generalized gradient approximation (GGA) was used for the exchange-correlational functional coupled with the D3 dispersion-correction.^[7] VASP input files were generated using the cif2cell^[8] program. In order to aid rapid convergence, a two-stage geometry optimization protocol was employed: initially a fixed-cell geometry optimization was performed, after which the converged structure was used as input for a full geometry optimization of both the atom positions and cell parameters. In all cases, a Γ -centered Monkhorst-Pack scheme was used to generate a tight K-point mesh with maximum K-point distance set to $2\pi \times 0.032 \text{ \AA}^{-1}$. In all calculations, the cut-off energy for the planewave basis was set to 500 eV. Within each self-consistent field cycle, the convergence threshold was set at 1×10^{-4} eV and the geometry was considered converged when all forces were below $0.03 \text{ eV \AA}^{-1}$. Second-order elastic constants for each crystal were computed using ElasTool,^[9] which interfaces with VASP and operates under the stress-strain method. In all cases, the input structure for mechanical properties calculations was the equilibrium structure following full geometry optimization of the atom positions and lattice parameters. ElasTool uses optimized high efficiency strain-matrix sets (OHESS)^[10] to compute elastic constants. Values of -0.03 , 0.0 and 0.03 were used to define the strains acting on the crystal. The relaxed structure following full geometry optimization of the atom positions and lattice parameters was used to define the crystal under zero strain. The OHESS generated crystals under strain were then relaxed at fixed volume using VASP, leading to a set of elastic constants produced by ElasTool. For each crystal, ELATE^[11] was used to compute the mechanical properties using the elastic constants generated by ElasTool.

Packing index and cohesive energy densities of crystals

Packing indices for the experimental structures were computed using PLATON.^[12-13] The cohesive energy density (CED) for each crystal structure was computed using the Forcite module of BIOVIA Materials Studio 8.0.^[14] In all cases, the input structure was the relaxed structure produced following full geometry optimization of the atom positions and lattice parameters in VASP. Prior to calculation of the CED, the geometry of the atoms and lattice parameters were relaxed in Forcite using the COMPASSII^[15] force field and its associated charges for the atoms. Convergence thresholds used were an energy of $1 \times 10^{-4} \text{ kcal mol}^{-1}$, force of $5 \times 10^{-3} \text{ kcal mol}^{-1} \text{ \AA}^{-1}$, stress of $5 \times 10^{-3} \text{ GPa}$ and displacement of $5 \times 10^{-5} \text{ \AA}$. Following geometry optimization, Forcite was used once again to compute the CED using the same force field and convergence thresholds.

• Hirshfeld Surface Analysis

Hirshfeld surface mapping and analyses were performed on all 14 crystal structures as well as selected *O*-thiocarbamate compounds in the Cambridge Structural Database for further analysis. These include the following compounds with CSD codes ERIWEH,^[16] GIQDES,^[17] JELTUQ,^[18] JELVAY,^[19] VIVVUU,^[20] and ZAHHUO^[21]. The Hirshfeld surfaces were modelled using CrystalExplorer^[7]. Percentage contributions of the interatomic interactions are shown. Any interactions that have < 0.1% contribution or are undetected are omitted for emphasis purposes, unless otherwise described.

Figure S34. (A) Hirshfeld surface mapped with d_{norm} of 2 and (B-L) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S35. (A) Hirshfeld surface mapped with d_{norm} of **3** and (B-N) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S36. (A) Hirshfeld surface mapped with d_{norm} of **4** and (B-H) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S37. (A) Hirshfeld surface mapped with d_{norm} of 5 and (B-J) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S38. (A) Hirshfeld surface mapped with d_{norm} of **6** and (B-L) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S39. (A) Hirshfeld surface mapped with d_{norm} of 7 and (B-J) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S40. (A) Hirshfeld surface mapped with d_{norm} of **8** and (B-M) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S41. (A) Hirshfeld surface mapped with d_{norm} of **9** and (B-H) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S42. (A) Hirshfeld surface mapped with d_{norm} of 10 and (B-O) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S43. (A) Hirshfeld surface mapped with d_{norm} of **11** and (B-M) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S44. (A) Hirshfeld surface mapped with d_{norm} of **12** and (B-M) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S45. (A) Hirshfeld surface mapped with d_{norm} of **13** and (B-I) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S46. (A) Hirshfeld surface mapped with d_{norm} of **14** and (B-G) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules. C-C contributions, though < 0.1%, are specifically noted here to emphasize the lack of any $\pi \cdots \pi$ stacking interactions between the phenyl rings.

Figure S47. (A) Hirshfeld surface mapped with d_{norm} of **15** and (B-H) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S48. (A) Hirshfeld surface mapped with d_{norm} of ERIWEH and (B-K) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S49. (A) Hirshfeld surface mapped with d_{norm} of GIQDES and (B-K) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S50. (A) Hirshfeld surface mapped with d_{norm} of JELTUQ and (B-H) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S51. (A) Hirshfeld surface mapped with d_{norm} of JELVAY and (B-F) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S52. (A) Hirshfeld surface mapped with d_{norm} of VIVVUU and (B-H) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

Figure S53. (A) Hirshfeld surface mapped with d_{norm} of ZAHHUO and (B-I) fingerprint plots resolved into various interatomic contacts with respective percentages of contact contributing to the total Hirshfeld surface area of the molecules.

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