Supporting info for:

Structures of a phosphoryl derivative of 4-allyl-2,4-dihydro-3H-1,2,4-triazole-3-thione: an illustrative example of conformational polymorphism

Ivan V. Fedyanin[a], Aida I. Samigullina[a,b], Ivan A. Krutov[c], Elena L. Gavrilova[c], Dmitry V. Zakharychev[b]

[a] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova st. 28, 119991 Moscow, Russian Federation.

[b] A. E. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Street, Kazan 420088, Russian Federation

[c] Kazan National Research Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia

E-mail: octy@xrlab.ineos.ac.ru

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1 Powder diffraction

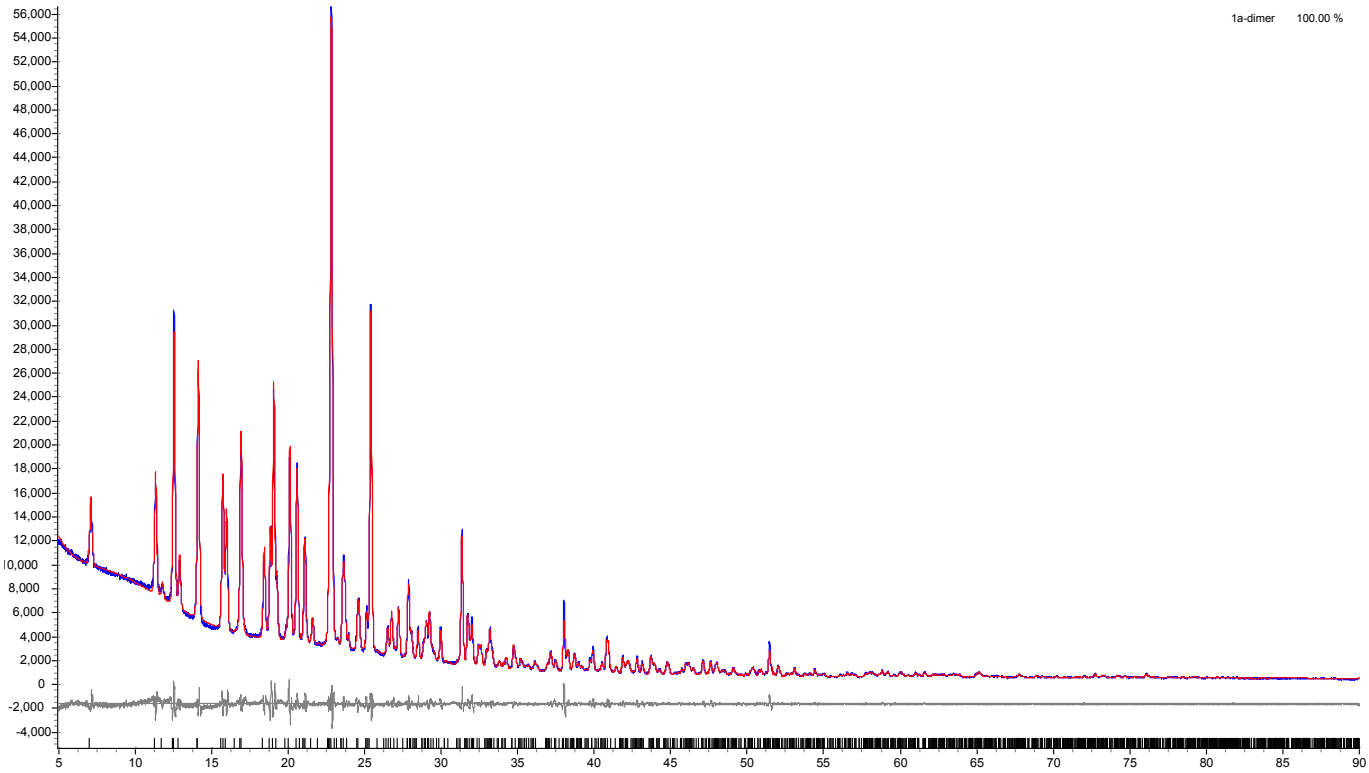


Figure S1. Experimental X-ray diffraction pattern (blue), Pawley fit (red), and difference profile (gray) for **1a** (R_{wp} = 0.046).

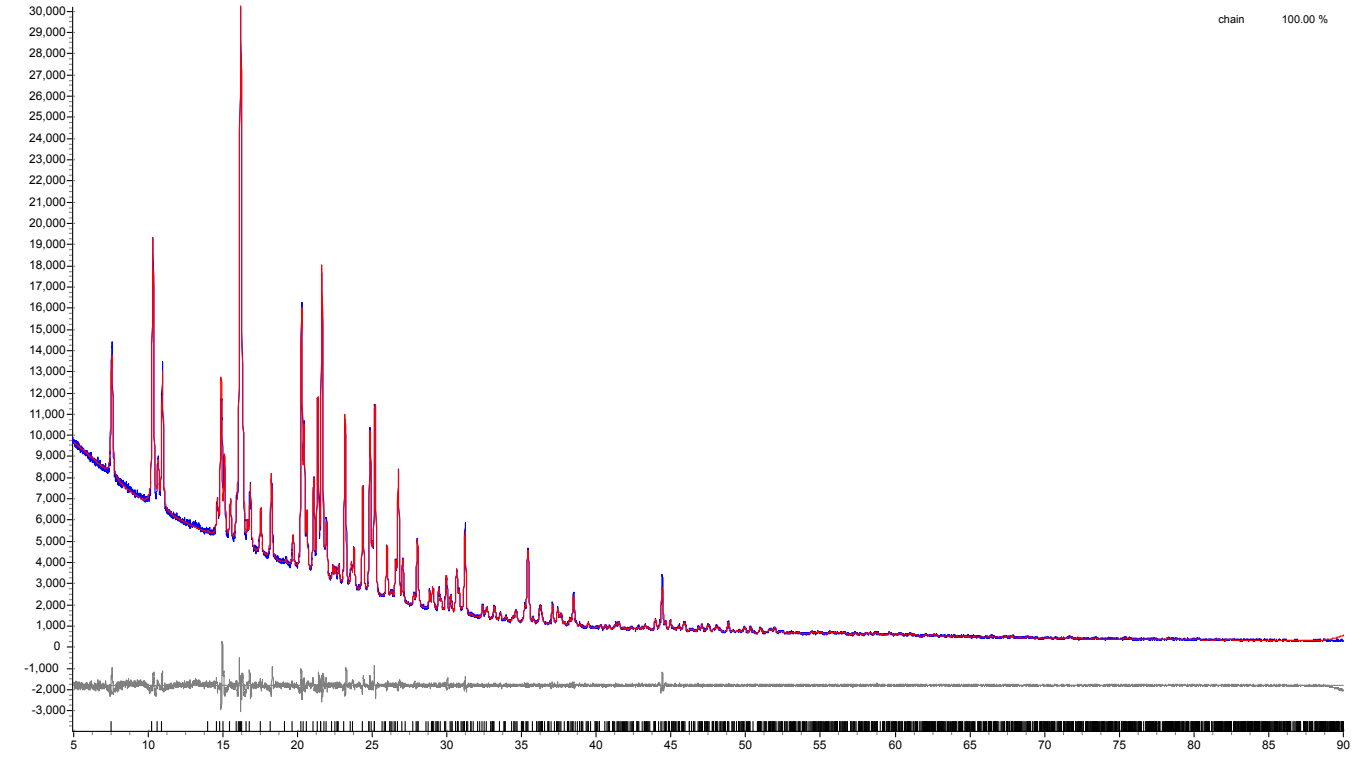


Figure S2. Experimental X-ray diffraction pattern (blue), Pawley fit (red), and difference profile (gray) for **1b** (R_{wp} = 0.037).

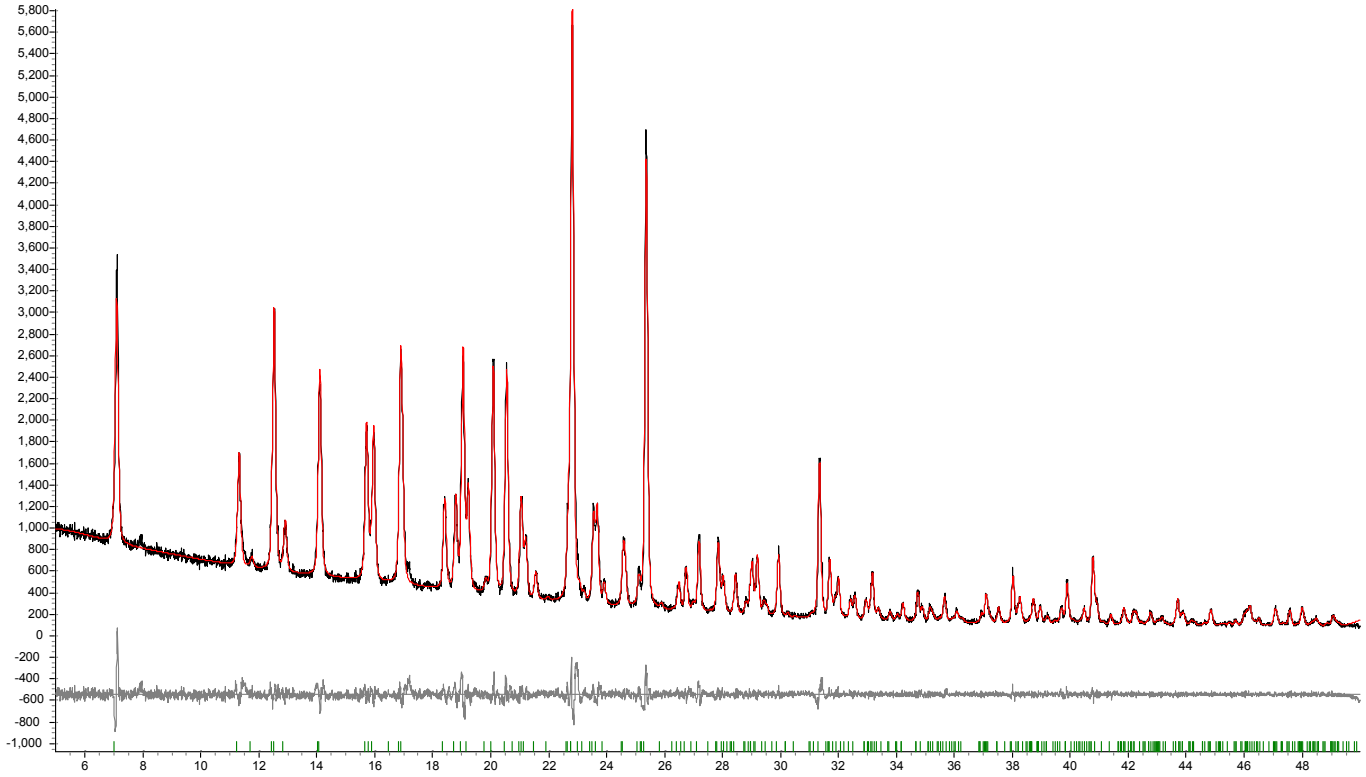


Figure S3. Experimental X-ray diffraction pattern (blue), Pawley fit (red), and difference profile (gray) for the sample **1a** heated to 170°C and cooled back to ambient conditions (R_{wp} = 0.063). The phase is the same as of the source sample. The small peak at ca. 7.6 deg. belongs to an unidentified admixture or phase.

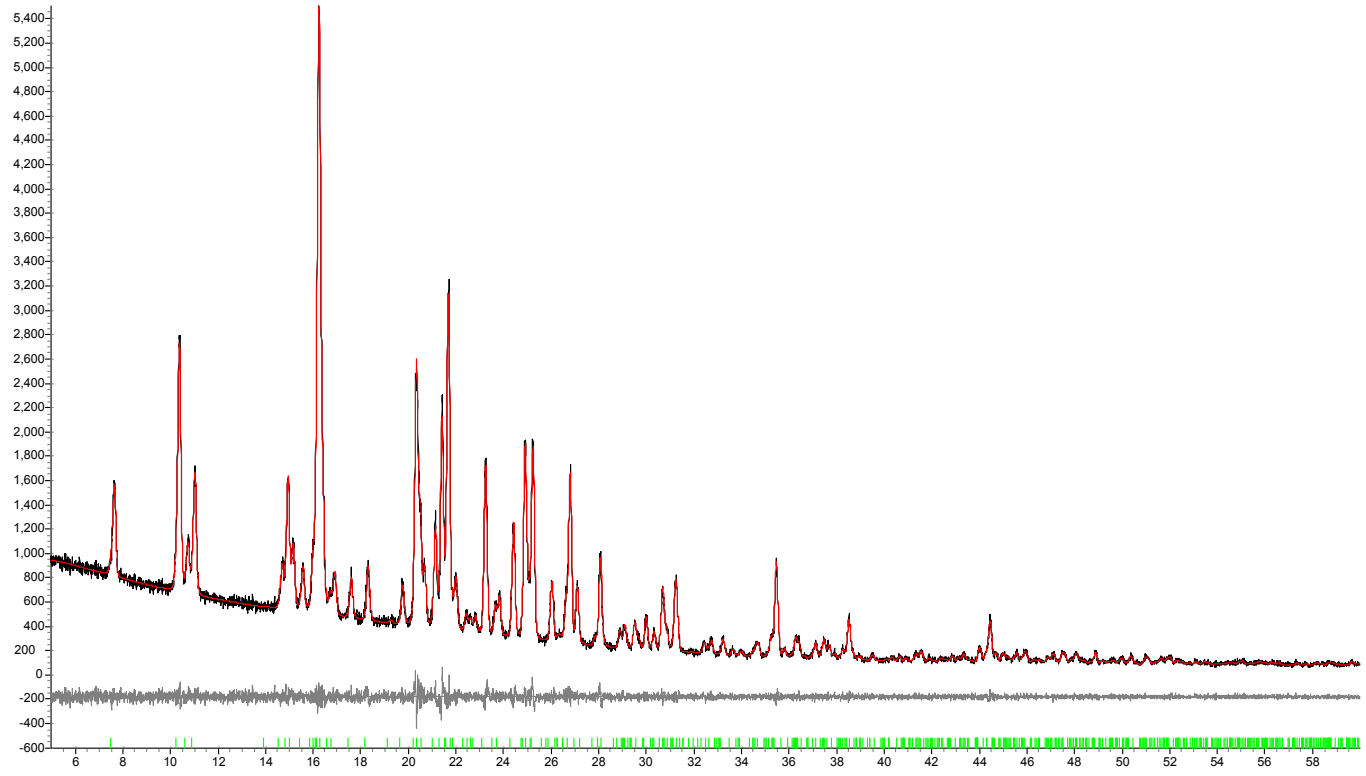


Figure S4. Experimental X-ray diffraction pattern (blue), Pawley fit (red), and difference profile (gray) for the sample **1a** heated to 200°C and cooled back to ambient conditions (R_{wp} = 0.051). The irreversible phase transition to **1b** was observed.

2 Molecular geometry

2.1 Molecular projections along rotable bonds

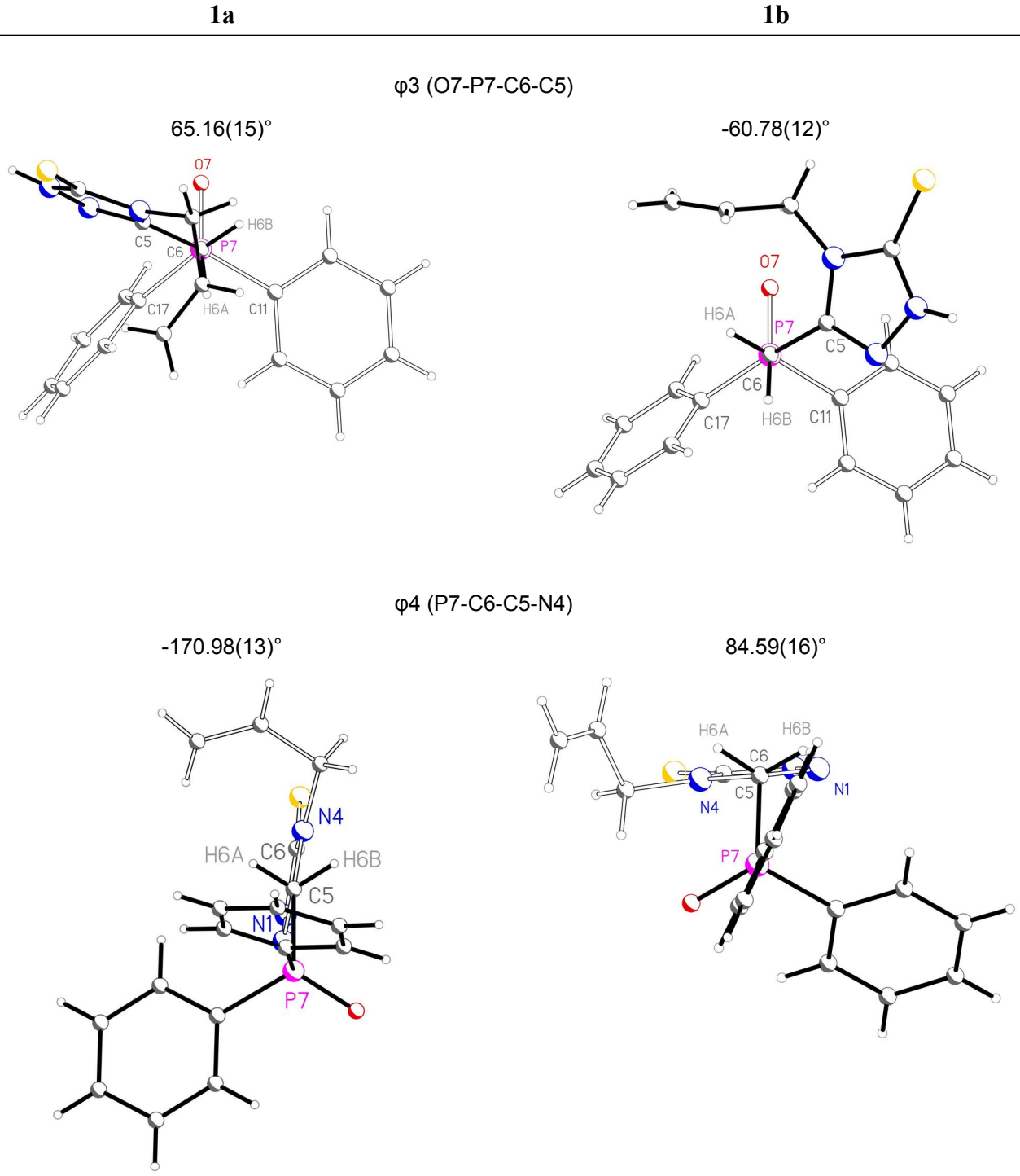
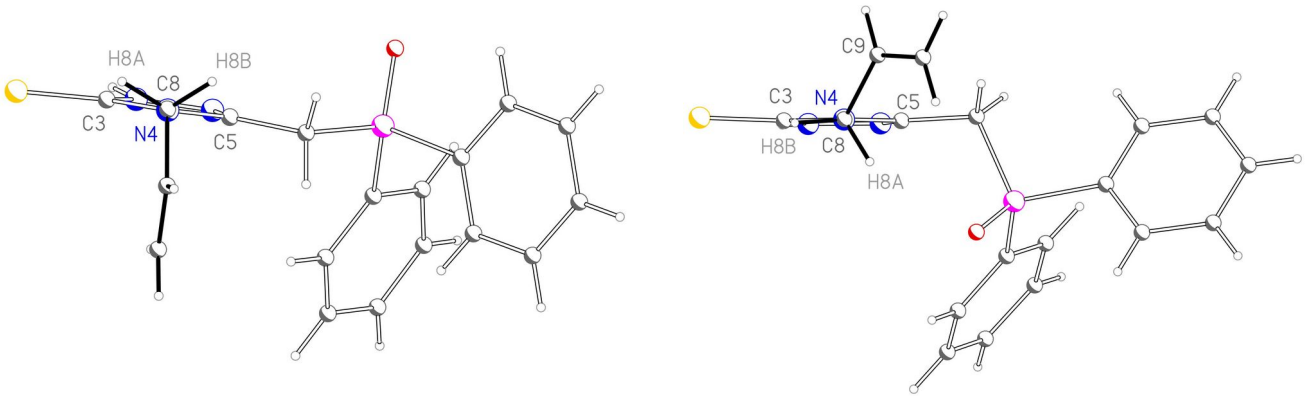


Figure S5. Molecular projections along rotable bonds. Bonds of molecular fragments connected to the front atom are drawn with soling line and those connected to the back atoms are drawn with open line. The corresponding torsion angles ant their values are given above each projection.

1a **1b**

φ5 (C5-N4-C8-C9)

-84.0(2)° 63.7(2)°



φ6 (N4-C8-C9-C10)

-8.8(3)° -134.75(18)°

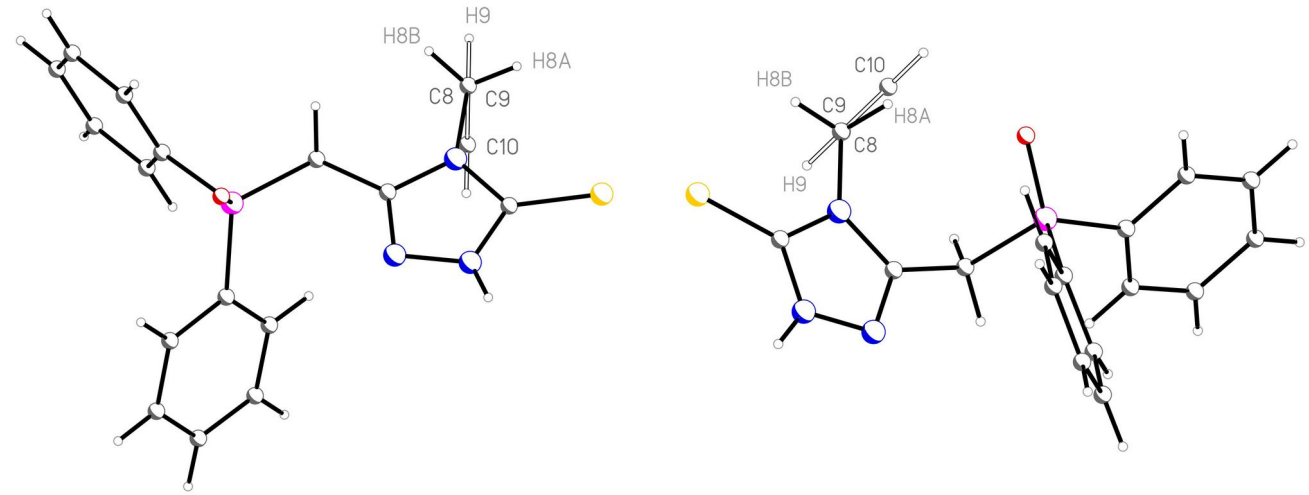


Figure S5 (continued)

2.2 Intramolecular bonding interactions

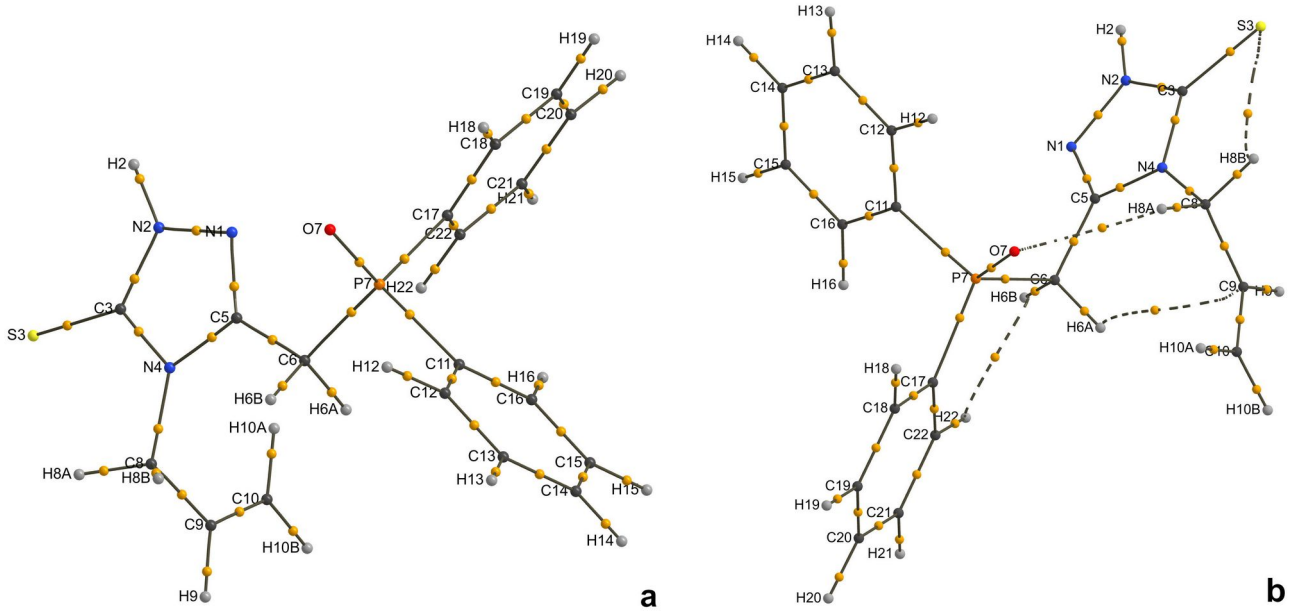


Figure S6. Molecular graphs of the compound 1 in polymorphs **1a** (a) and **1b** (b), based on PBE0-D3/POB-TZVP-rev2 electron density of the optimized crystal structures. Bond critical points are drawn as orange spheres, non-covalent interactions shown with dashed lines.

3 DFT calculations (PBE0-D3/POB-TZVP-rev2)

3.1 General information

All calculations were performed with CRYSTAL17 software package version 1.0.2. The combination of PBE0-D3 density functional and POB-TZVP-rev2 basis set was used. The structures of polymorphs were optimized using experimental unit cell parameters.

3.2 Calculated energies

Table S1. Calculated energies (Hartree). All values are given per one molecule (i.e., for crystal structures they are divided by Z).

	Total energy[#1]	Grimme (D3) dispersion energy part (E_{3part})	BSSE-corrected energy[#2] (E_{cp})
	Optimized crystal structures (E_{cryst})		
1a	-1674.701837	-0.123714	
1b	-1674.694842	-0.117937	
	Isolated molecules in crystal geometry (E_{mol})		
1a	-1674.579396	-0.057210	-1674.548351
1b	-1674.589500	-0.057363	-1674.556240
	Optimized conformer (E_{molopt})		
1a	-1674.586882	-0.058954	
1b	-1674.595937	-0.060805	
min. [#3]	-1674.596465	-0.058287	
	Isolated supramolecular synthon in crystal geometry ($E_{synthon}$)		
1a	-1674.579347	-0.057217	
1b	-1674.589505	-0.057366	
	Isolated molecules in crystal geometry (E_{mol}) used for synthon BSSE correction		
	-1674.579396	-0.057210	-1674.525308
	-1674.589500	-0.057363	-1674.538433

Notes:

[#1] Total energy includes -D3 Grimme dispersion energy.

[#2] BSSE-corrected DFT energy is calculated by the counterpoise approach (MOLEBSSE or GHOSTS keywords of CRYSTAL17) and does not include Grimme dispersion energy.

[#2] Energy of the conformer obtained by an exhaustive search of low-energy conformers

Formulas used to calculate energetic characteristics:

$$BSSE = (E_{mol} - E_{mol,d3part}) - E_{cp,crystal}$$

$$E_{latt} = E_{mol} - E_{cryst} - BSSE$$

$$E_{cog} = E_{molopt}(min) - E_{cryst} - BSSE$$

3.3 Atomic coordinates of the DFT-optimized structures

1a crystal (CIF format)

```
data_dimer
_symmetry_space_group_name_H-M   'P 21/c'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   12.9204
_cell_length_b                   9.3989
_cell_length_c                   14.3269
_cell_angle_alpha                90.000
_cell_angle_beta                 103.436
_cell_angle_gamma                90.000
_cell_volume                     1692.2
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
S3 S 0.32126 0.07958 0.07865
P7 P 0.75257 0.4957 0.15264
O7 O 0.69718 0.63953 0.14762
N1 N 0.54076 0.34845 0.04277
N2 N 0.44541 0.27578 0.01407
H2 H 0.3935 0.30046 -0.05102
C3 C 0.42503 0.19151 0.08339
N4 N 0.50972 0.21428 0.16003
C5 C 0.5776 0.30844 0.13111
C6 C 0.67955 0.35228 0.19484
H6B H 0.66631 0.39537 0.26272
H6A H 0.73204 0.25992 0.21443
C8 C 0.52235 0.15598 0.25591
H8B H 0.55096 0.24141 0.3075
H8A H 0.4425 0.12927 0.26445
C9 C 0.59514 0.03064 0.27578
H9 H 0.61549 -0.0016 0.35085
C10 C 0.63432 -0.03894 0.21127
H10A H 0.61565 -0.00904 0.13578
H10B H 0.68552 -0.13076 0.23065
C11 C 0.87683 0.49495 0.24349
C12 C 0.89001 0.59208 0.3187
H12 H 0.82632 0.66602 0.32143
C13 C 0.9828 0.58985 0.39075
H13 H 0.99275 0.66411 0.4501
C14 C 1.06268 0.4924 0.38745
H14 H 1.1354 0.48953 0.44349
C15 C 1.04947 0.39537 0.31246
H15 H 1.11201 0.31919 0.31037
C16 C 0.95658 0.39632 0.24062
H16 H 0.94641 0.32025 0.18221
C17 C 0.78937 0.44707 0.04284
C18 C 0.82906 0.55708 -0.00438
H18 H 0.8267 0.66613 0.02009
C19 C 0.86981 0.52643 -0.08325
H19 H 0.90107 0.61123 -0.11992
C20 C 0.87155 0.38739 -0.11525
H20 H 0.90546 0.36451 -0.17618
C21 C 0.82987 0.27844 -0.06975
H21 H 0.83043 0.16991 -0.09552
C22 C 0.78848 0.30791 0.00933
H22 H 0.75498 0.22205 0.04363
```

1b crystal (CIF format)

```
data_chain
_symmetry_space_group_name_H-M   'P 21/c'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   12.9164
_cell_length_b                   12.6337
_cell_length_c                   12.0704
_cell_angle_alpha                90.000
_cell_angle_beta                 116.155
_cell_angle_gamma                90.000
_cell_volume                     1767.99
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
S3 S 1.29886 0.06553 0.40715
P7 P 0.78592 0.17872 0.2399
O7 O 0.85081 0.27077 0.21868
N1 N 0.98918 -0.03592 0.33331
N2 N 1.09902 -0.04479 0.34152
H2 H 1.12582 -0.11626 0.31937
C3 C 1.16085 0.04423 0.3813
N4 N 1.08618 0.11389 0.39773
C5 C 0.98401 0.06086 0.36811
C6 C 0.88145 0.10344 0.37669
H6A H 0.90601 0.15584 0.45644
H6B H 0.83333 0.03632 0.38749
C8 C 1.11477 0.22407 0.43613
H8A H 1.05846 0.27568 0.36109
H8B H 1.20348 0.23349 0.44813
C9 C 1.10716 0.24908 0.55316
H9 H 1.14785 0.19376 0.62922
C10 C 1.05649 0.33568 0.56738
H10A H 1.0149 0.39148 0.49197
H10B H 1.05604 0.3546 0.65469
C11 C 0.73567 0.08737 0.11189
C12 C 0.78012 0.09845 0.02628
H12 H 0.83761 0.16391 0.03561
C13 C 0.74972 0.02666 -0.06971
H13 H 0.78255 0.03497 -0.13791
C14 C 0.67489 -0.05571 -0.0805
H14 H 0.6518 -0.11167 -0.15573
C15 C 0.62878 -0.06576 0.00339
H15 H 0.56793 -0.12885 -0.00768
C16 C 0.65888 0.00577 0.09989
H16 H 0.62054 -0.00086 0.16357
C17 C 0.66563 0.21742 0.26889
C18 C 0.60196 0.3052 0.20474
H18 H 0.62942 0.35088 0.14622
C19 C 0.50558 0.33607 0.21904
H19 H 0.4553 0.40327 0.16708
C20 C 0.47337 0.28019 0.29796
H20 H 0.39673 0.30243 0.30774
C21 C 0.53833 0.19439 0.36414
H21 H 0.51352 0.15125 0.42625
C22 C 0.63425 0.16233 0.34965
H22 H 0.68294 0.09489 0.40281
```

1a isolated conformer (XYZ format)

```
42

P          2.82429       -4.84541        2.30634
O          2.33531       -6.25591        2.11948
C          3.50500       -4.07138        0.81994
C          4.09220       -4.73393        3.60492
C          1.56011       -3.65650        2.93098
C          3.64866       -2.69332        0.68178
C          3.88310       -4.91943       -0.21372
C          4.17085       -5.80672        4.48639
C          4.94834       -3.64647        3.75068
H          2.07631       -2.76909        3.31534
H          1.10232       -4.15548        3.79416
C          0.53424       -3.25116        1.94723
H          3.32800       -2.02046        1.47094
C          4.18186       -2.16858       -0.48318
H          3.73296       -5.98734       -0.09608
C          4.41797       -4.38878       -1.37656
H          3.51137       -6.65483        4.33405
C          5.09271       -5.78215        5.52103
H          4.91562       -2.82353        3.04375
C          5.86907       -3.62838        4.78480
N          0.26697       -3.85250        0.82741
N         -0.27077       -2.14640        2.13045
H          4.28724       -1.09471       -0.59343
C          4.56930       -3.01696       -1.51036
H          4.71032       -5.04864       -2.18600
H          5.15593       -6.61885        6.20829
C          5.93768       -4.69344        5.67179
H          6.54208       -2.78506        4.89472
N         -0.75307       -3.08645        0.28175
C         -1.11416       -2.02735        1.04103
C         -0.23737       -1.21638        3.23464
H          4.98400       -2.60511       -2.42399
H          6.66173       -4.67767        6.47929
H         -1.15951       -3.33613       -0.60440
S         -2.27493       -0.86295        0.75629
H         -0.18542       -1.78080        4.17146
H         -1.20255       -0.69415        3.21254
C          0.88256       -0.22788        3.14966
H          1.04318        0.35116        4.05671
C          1.62120       -0.00220        2.07546
H          2.39746        0.75445        2.07767
H          1.45971       -0.54283        1.14773
```

1b isolated conformer (XYZ format)

```
42

S          2.59125       -6.07275        2.08676
C          4.22650       -6.09406        1.74590
N          5.06518       -7.15234        1.69748
N          5.06236       -5.03311        1.44855
H          4.80382       -8.10918        1.86503
N          6.37784       -6.81835        1.39722
C          6.33255       -5.52469        1.25547
C          4.61569       -3.64667        1.34288
C          7.53111       -4.69467        1.03620
H          5.20993       -3.02612        2.01854
H          3.57377       -3.67185        1.68153
C          4.71853       -3.13815       -0.05710
H          8.34161       -5.35246        0.71791
H          7.36413       -3.92803        0.27382
P          8.02291       -3.78792        2.57725
H          4.15420       -3.68458       -0.81054
C          5.43498       -2.07195       -0.37931
O          7.27472       -2.48446        2.74423
C          9.81485       -3.56326        2.44826
C          7.67609       -4.97524        3.90059
H          5.47403       -1.69906       -1.39732
H          6.00218       -1.53521        0.37752
C         10.30676       -2.32706        2.85514
C         10.68931       -4.54178        1.98058
C          6.41877       -4.88988        4.49435
C          8.54936       -5.99510        4.26140
H          9.60436       -1.57384        3.19678
C         11.66830       -2.07663        2.80478
H         10.31772       -5.50642        1.64900
C         12.04973       -4.28608        1.93459
H          5.75806       -4.07174        4.22925
C          6.02756       -5.84145        5.42097
H          9.53958       -6.05093        3.82279
C          8.15723       -6.93640        5.19862
H         12.05160       -1.11243        3.12010
C         12.53817       -3.05511        2.34801
H         12.73042       -5.04771        1.57064
H          5.04311       -5.78094        5.87109
C          6.89490       -6.86621        5.76884
H          8.83973       -7.72934        5.48414
H         13.60371       -2.85678        2.30799
H          6.58827       -7.61101        6.49527
```

3.4 Lowest energy conformer found by an exhaustive search

Coordinates (XYZ format)

```
42

P1          -0.04690         0.14820         0.22280
O2           -0.76040        -1.17650          0.37590
S2          -5.91990         1.49590        -0.60100
C3           0.24710         0.61220        -1.49850
C4           1.55240         0.15520         1.07480
C5          -0.93200         1.57030         0.99490
H6          -1.11890         1.26200         2.02880
C8           0.44070         1.92690        -1.91500
H9           0.36040         2.75030        -1.21420
C10          0.54830        -0.15270        -3.75570
H11          0.58040        -0.96140        -4.47750
C12          0.29160        -0.42740        -2.42310
H13          0.10790        -1.44110        -2.08320
C14          0.69780         2.19380        -3.24960
H15          0.84100         3.21780        -3.57590
C16          0.75620         1.15550        -4.16700
H17          0.95450         1.36910        -5.21180
C18          1.82560        -0.92330         1.90830
H19          1.09170        -1.71820         1.98960
C20          3.67720         1.13030         1.62060
H21          4.40520         1.92580         1.50420
C22          3.02600        -0.96920         2.60000
H23          3.24420        -1.81120         3.24790
C24          3.94740         0.05680         2.45880
H25          4.88690         0.01850         2.99940
C26          2.48170         1.18060         0.92510
H27          2.28350         2.00780         0.24990
H28         -0.26630         2.43620         1.01080
C29         -3.61190         0.00100         1.12560
H30         -2.86600        -0.74120         0.83200
H31         -4.60570        -0.31780         0.79270
C32         -3.59000         0.23340         2.60060
H33         -4.29810         0.96730         2.98130
C34         -2.77750        -0.41730         3.42040
H35         -2.07010        -1.14760         3.03540
H36         -2.79840        -0.25400         4.49260
C37         -2.18940         1.95270         0.32470
N38         -3.35990         1.23490         0.38560
N39         -2.31590         3.02580        -0.40420
N40         -3.63820         2.97390        -0.82090
C41         -4.31950         1.90230        -0.35430
H42         -4.02290         3.69720        -1.40530
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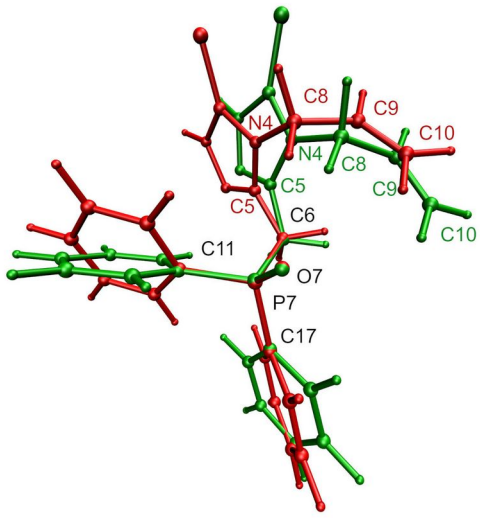

Figure S7. Overlay of the lowest-energy conformer generated by the exhaustive search (green) and the conformer taken from the polymorph **1b** (red). Coordinates of both conformers are taken from PBE0-D3/POB-TZVP-rev2 geometry optimization. The atom P7 and four connected atoms are superimposed.

4 Bonding interactions

4.1 Intermolecular bonding interactions

Table S2. Intermolecular bonding interactions in 1a (based on PBE0-D3/POB-TZVP-rev2 data)

N	A1	A2	*r*(A1-A2), exp Å	*r*(A1-A2), DFT Å	$\rho(\mathbf{r})$ e Å^{-3}	$\nabla^2\rho(\mathbf{r})$ e Å^{-5}	ε	E_{EML} kcal/mol
1	O7	H2	1.727	1.689	0.307	3.33	0.01	15.15
2	S3	H12	2.855	2.759	0.075	0.77	0.09	1.65
3	H8A	O7	2.454	2.431	0.065	0.87	0.05	1.56
4	H10B	O7	2.441	2.486	0.056	0.79	0.06	1.44
5	H16	C13	2.635	2.658	0.052	0.52	0.29	1.13
6	C21	H13	2.785	2.742	0.047	0.48	0.52	1.10
7	N1	N1	3.230	3.182	0.044	0.57	0.07	1.08
8	C16	H19	2.854	2.803	0.043	0.48	1.12	1.04
9	S3	H6B	3.009	2.832	0.059	0.56	0.08	0.99
10	H13	C14	3.028	2.978	0.039	0.42	0.64	0.99
11	S3	H14	2.815	2.789	0.055	0.59	0.09	0.98
12	H15	C12	2.847	2.820	0.040	0.42	0.31	0.93
13	H12	H19	2.368	2.376	0.038	0.44	0.42	0.87
14	H20	C16	2.860	2.869	0.038	0.38	0.55	0.85
15	C9	N4	3.485	3.479	0.033	0.44	0.52	0.83
16	C6	C21	3.653	3.689	0.031	0.37	8.11	0.79
17	C11	H21	2.930	2.954	0.036	0.39	1.57	0.78
18	H22	H14	2.514	2.587	0.030	0.36	0.43	0.76
19	H19	H13	2.468	2.513	0.031	0.39	2.16	0.75
20	C9	C20	3.665	3.632	0.031	0.35	0.12	0.74
21	C10	H8B	3.224	3.125	0.030	0.33	0.22	0.70
22	H20	C16	3.168	3.138	0.028	0.33	0.53	0.68
23	H18	S3	3.205	3.180	0.034	0.31	0.11	0.64
24	H21	S3	3.115	3.101	0.028	0.32	0.06	0.60
25	C19	C19	3.725	3.678	0.024	0.28	3.91	0.54
26	O7	H15	3.040	2.933	0.024	0.28	0.15	0.48
27	H22	S3	3.303	3.358	0.022	0.22	0.20	0.45
28	S3	H10A	3.272	3.421	0.021	0.18	0.05	0.36
29	H10A	N2	3.209	3.275	0.015	0.23	1.73	0.34
30	H18	H15	2.766	2.775	0.016	0.19	0.50	0.33
31	H10B	H15	2.828	2.850	0.013	0.17	0.77	0.27
32	N1	H9	3.160	3.435	0.011	0.13	0.07	0.20
33	N1	H8B	3.497	3.507	0.009	0.13	0.58	0.19

Note: Experimental N-H distances set to 1.085 Å for aromatic carbon atoms and 1.095 Å for other atoms; N-H set to 1.040 Å

Table S3. Intermolecular bonding interactions in 1b (based on PBE0-D3/POB-TZVP-rev2 data)

N	A1	A2	*r*(A1-A2), exp Å	*r*(A1-A2), DFT Å	$\rho(\mathbf{r})$ e Å^{-3}	$\nabla^2\rho(\mathbf{r})$ e Å^{-5}	ε	E_{EML} kcal/mol
1	H2	O7	1.634	1.569	0.393	4.09	0.01	20.99
2	H6A	N1	2.723	2.746	0.050	0.70	0.37	1.47
3	C10	H12	2.722	2.680	0.049	0.54	0.30	1.21
4	C13	C18	3.336	3.314	0.043	0.45	0.96	1.09
5	H19	S3	3.020	2.914	0.052	0.50	0.18	1.00
6	C20	H14	2.680	2.765	0.047	0.47	0.80	0.99
7	H20	H15	2.420	2.411	0.040	0.46	0.41	0.97
8	C16	C15	3.639	3.442	0.037	0.41	0.09	0.95
9	N1	H9	2.881	2.832	0.041	0.47	0.23	0.93
10	H21	S3	2.788	2.890	0.040	0.46	0.09	0.84
11	H16	H20	2.613	2.533	0.033	0.40	1.26	0.84
12	C13	C10	3.561	3.468	0.033	0.36	1.35	0.83
13	S3	H22	2.982	2.992	0.045	0.43	0.09	0.80
14	H21	H18	2.361	2.406	0.036	0.40	0.04	0.79
15	H10B	C3	2.728	2.772	0.037	0.45	2.16	0.79
16	H18	S3	3.255	3.025	0.043	0.38	0.09	0.72
17	H13	S3	3.240	3.204	0.031	0.29	0.02	0.58
18	C14	H8B	3.109	3.147	0.024	0.27	1.17	0.56
19	H14	S3	3.262	3.415	0.021	0.21	0.63	0.43
20	C18	H15	3.181	3.292	0.017	0.19	1.24	0.33
21	H10A	H10A	2.850	2.787	0.014	0.16	0.09	0.28
22	H8A	N1	3.173	3.206	0.014	0.17	0.42	0.25
23	H20	H9	2.959	2.979	0.010	0.13	0.22	0.21

Note: Experimental N-H distances set to 1.085 Å for aromatic carbon atoms and 1.095 Å for other atoms; N-H set to 1.043 Å

4.2 Connectivity graphs of H-bonded synthons

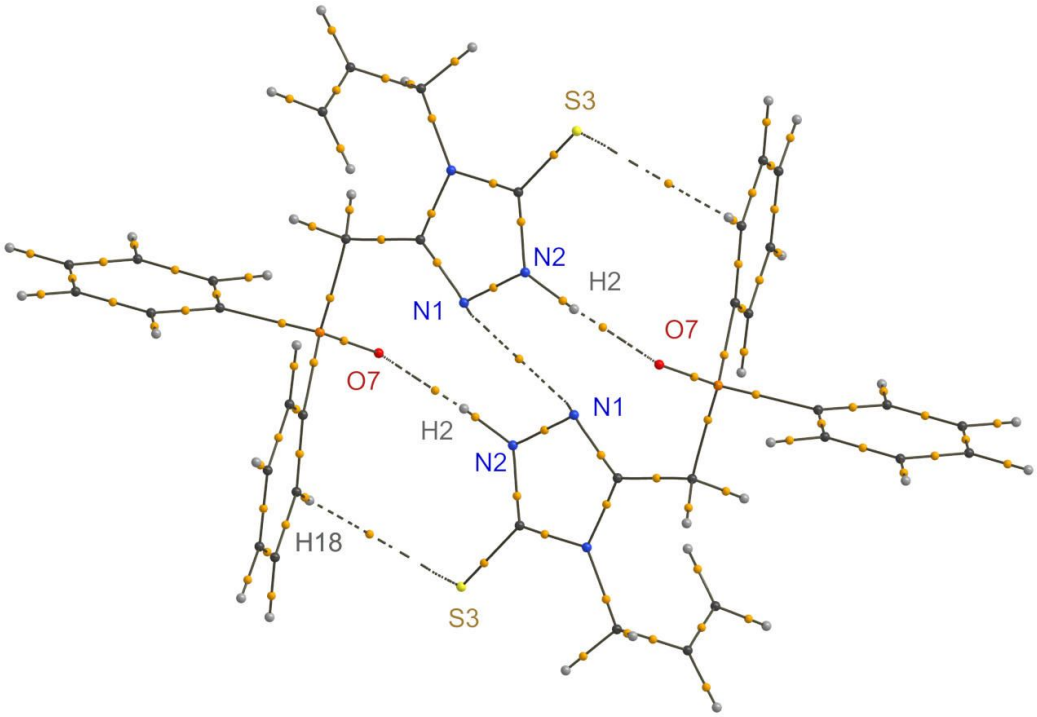

Figure S8. Connectivity graph of the H-bonded dimer in the polymorph **1a**, calculated from $\rho(\mathbf{r})$ distribution of the optimized crystal structure at PBE0-D3/POB-TZVP-rev2 level. Non-covalent bonded interactions are drawn with dashed lines; only atoms participating in intermolecular bonding interactions are labeled.

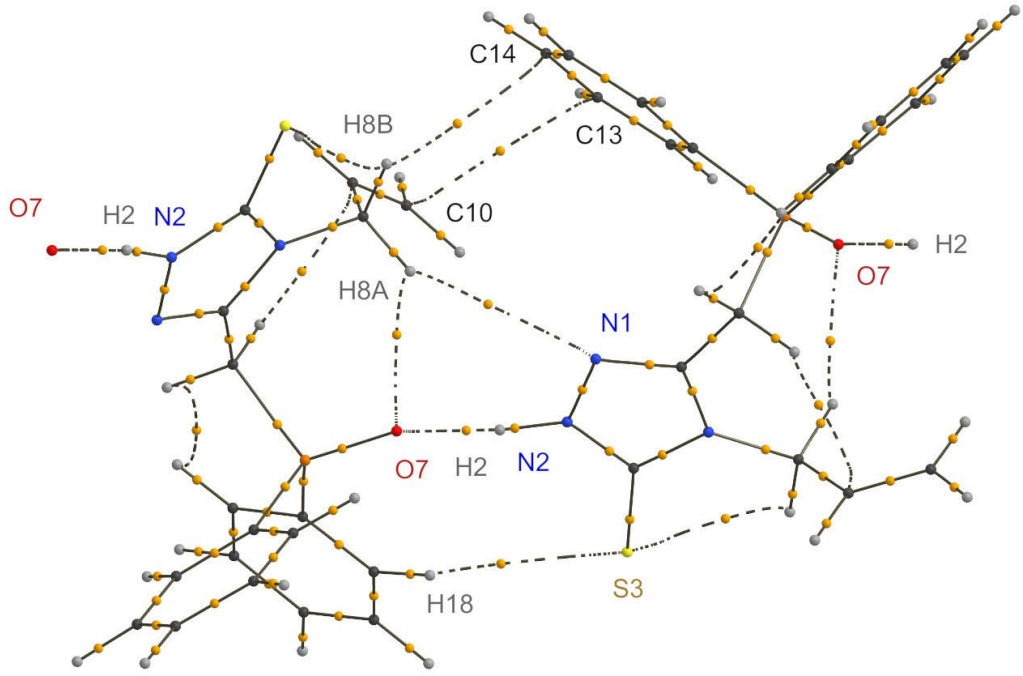

Figure S9. Connectivity graph of the H-bonded chain in the polymorph **1b**, calculated from $\rho(\mathbf{r})$ distribution of the optimized crystal structure at PBE0-D3/POB-TZVP-rev2 level. Only two molecules and atoms O7 and H2 extending the chain are shown. Non-covalent bonded interactions are drawn with dashed lines; only atoms participating in intermolecular bonding interactions are labeled.

5 Hirshfeld fingerprint plots

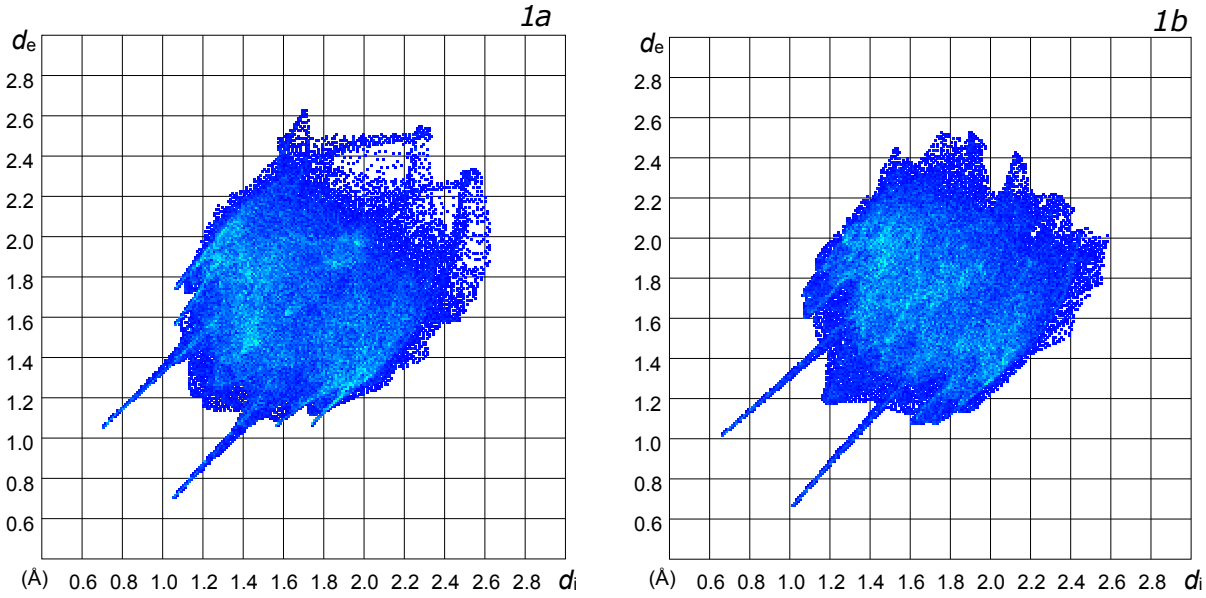

Figure S10. Fingerprint plots for polymorphs **1a** and **1b**.