Supporting Information

for the typescript entitled “Journeys in crystal energy landscapes: actual and virtual structures in polymorphic 5-nitrobenzo[*c*][1,2,5]thiadiazole” by Francesco Silvio Gentile, Emmanuele Parisi and Roberto Centore

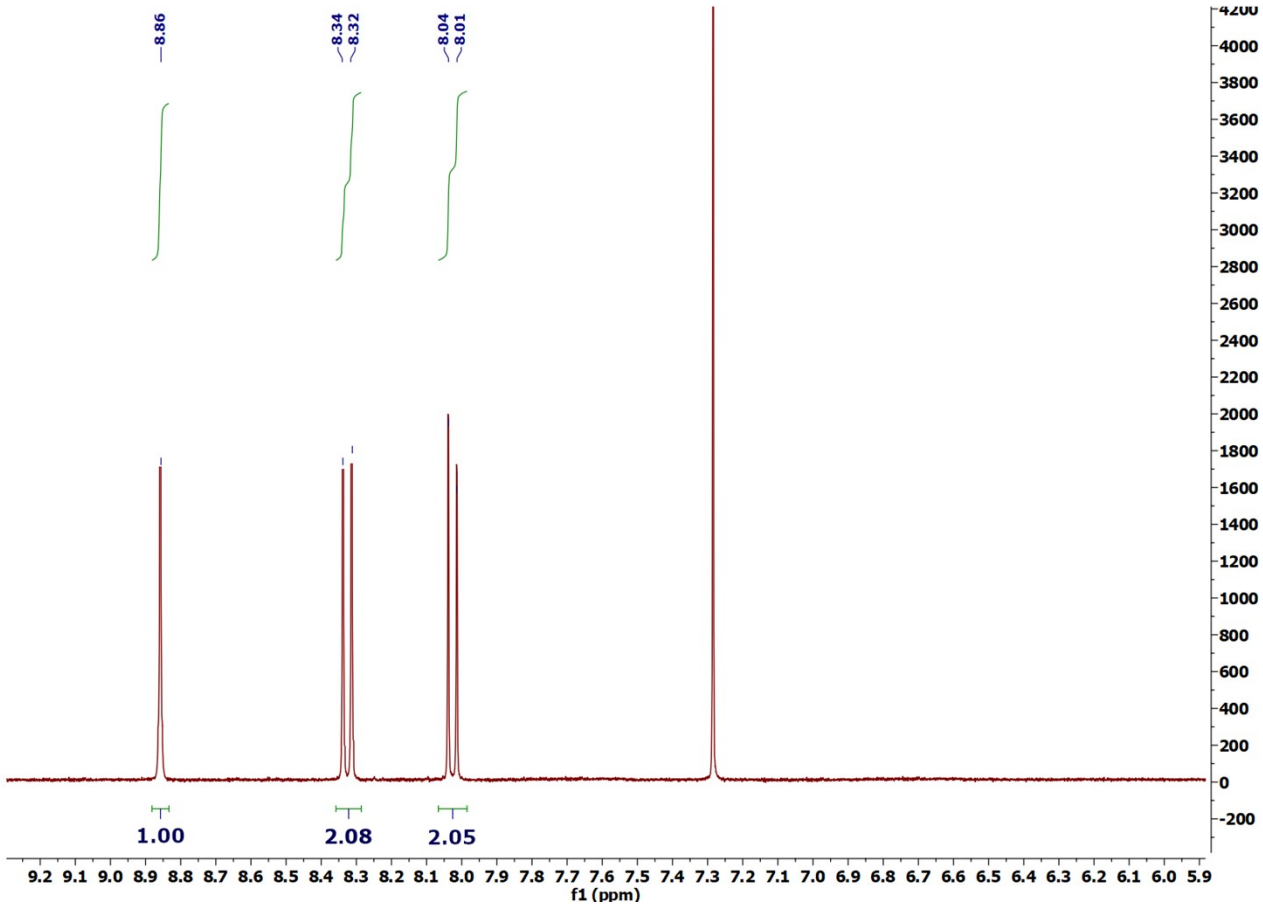

Fig. S1. ^{1}H-NMR spectrum of **1**, in $CDCl_3$ as solvent. The signal near 7.3 ppm is due to residual $CHCl_3$.

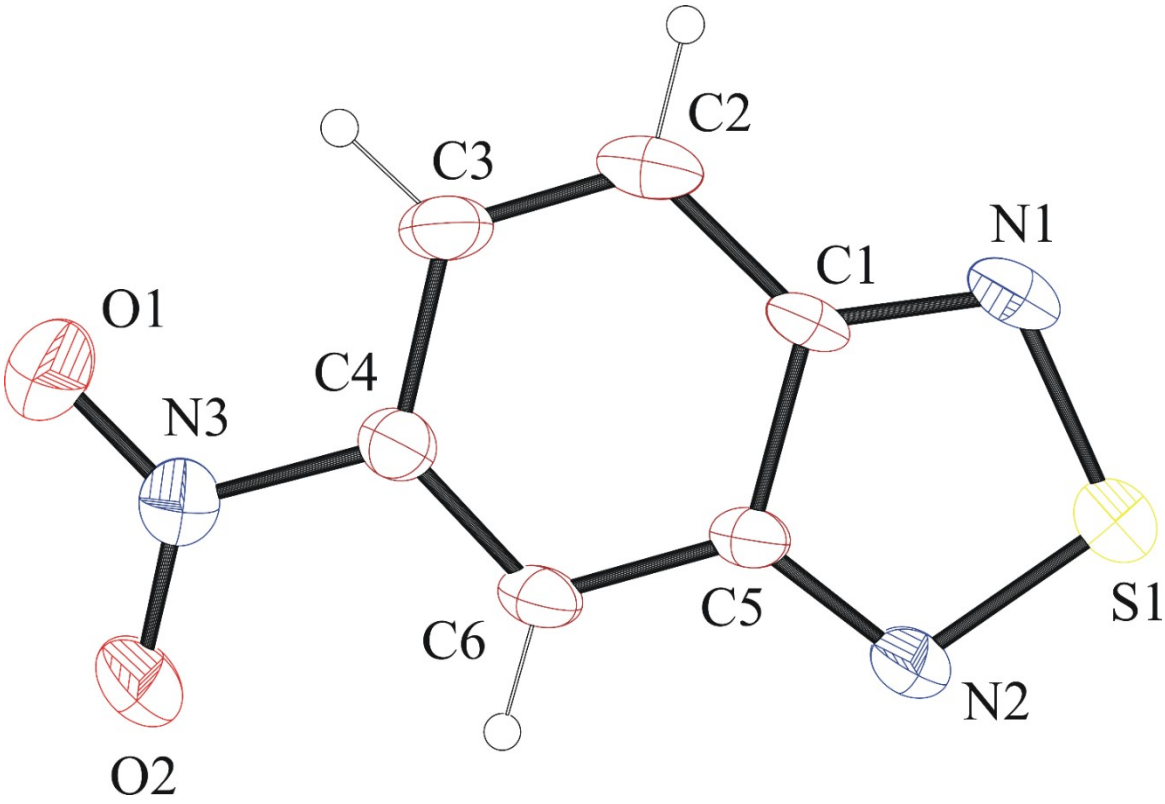

Fig. S2. ORTEP diagram of the molecular structure of **1** in polymorph II at 293 K. Thermal ellipsoids are drawn at 30 % probability level.

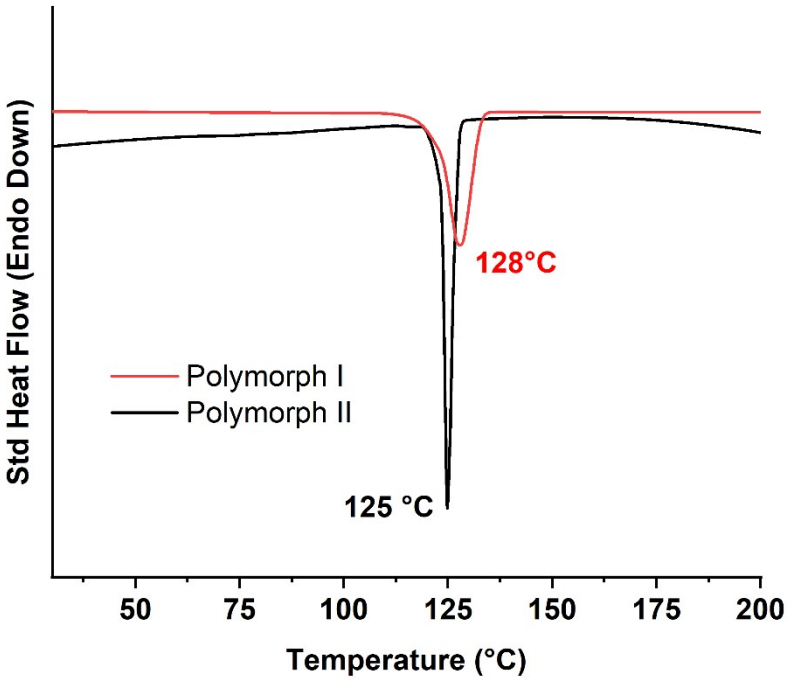

Fig. S3. DSC thermograms, on heating, of samples of polymorphs I and II of compound **1**. Heating rate is 10 °C/min, under flowing N_2.

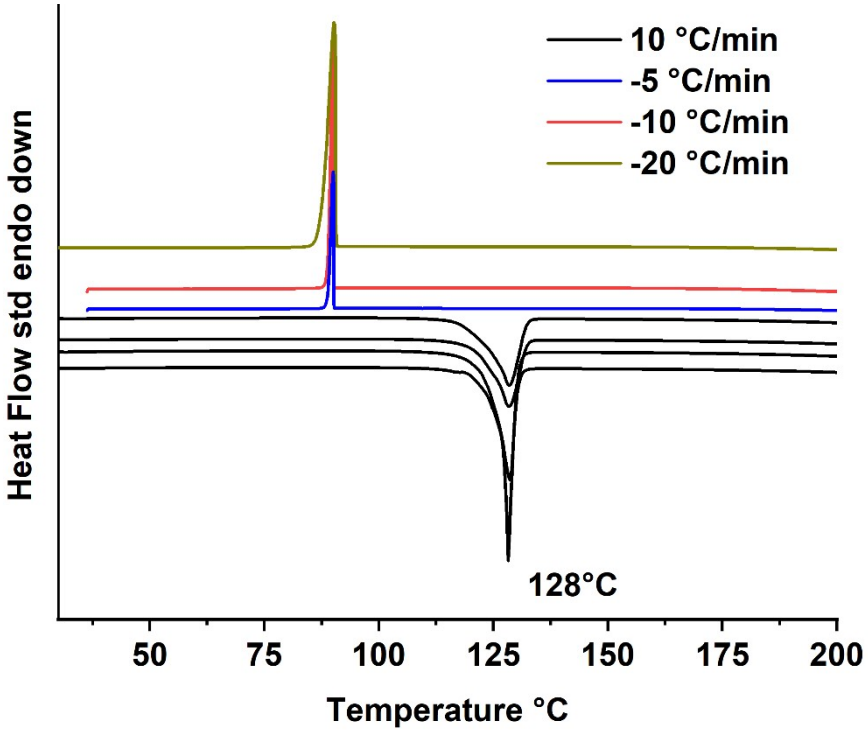

Fig. S4. DSC thermograms, on heating (black curves), of samples of compound **1** obtained by cooling the liquid phase at different cooling rates (5 °C/min blue curve, 10 °C/min red curve, and 20 °C/min brown curve). Heating rate is 10 °C/min in all cases. Measurements performed under flowing N_2.

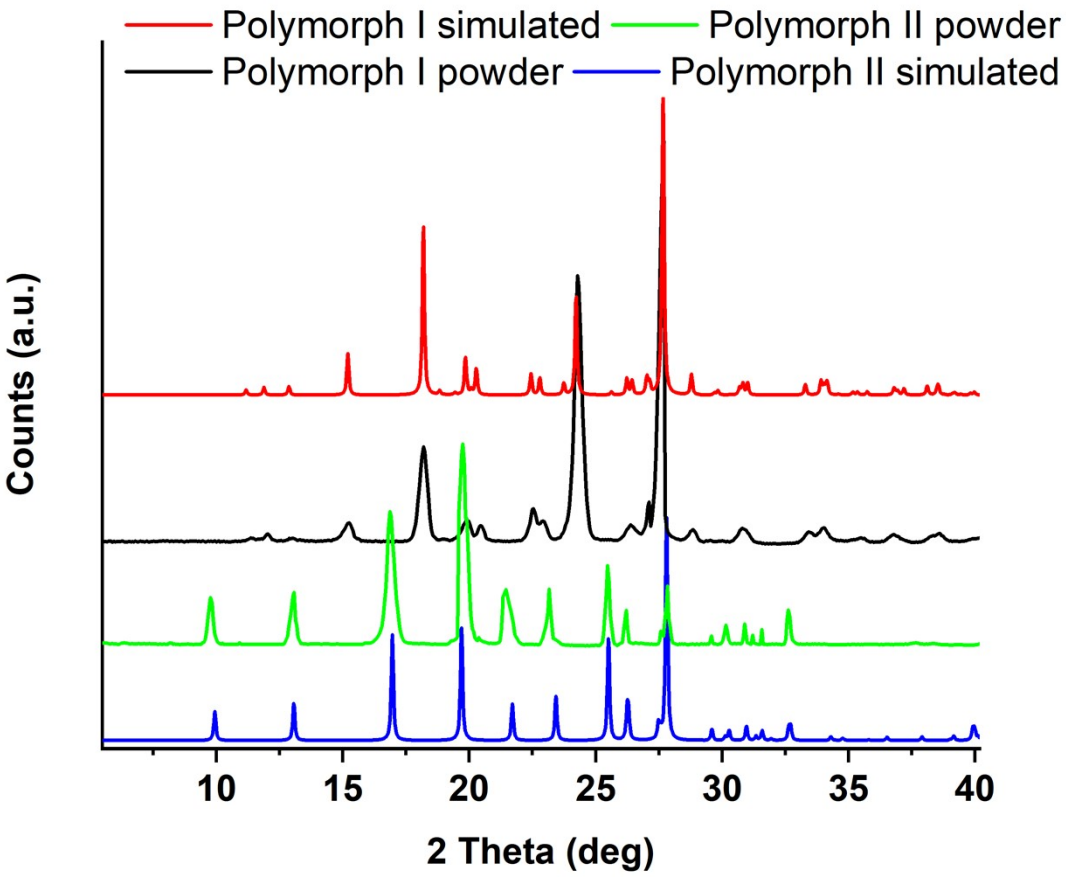

Fig. S5. Experimental and simulated powder diffraction patterns of polymorphs I and II of **1**. CuKα radiation was used in all cases.

Table S1. Initial and final optimized cell parameters for actual and virtual crystal structures of **1**, at 0 K.

	Space group	Initial lattice parameters[(a)]	Optimized lattice parameters at 0 K
A1	$P\bar{1}$	a=5.7385(4) Å α=112.262(2)° b=7.8571(5) Å β=93.986(2)° c=8.3539(5) Å γ=91.902(2)°	a=5.4402 Å α=113.029° b=7.4196 Å β=93.3165° c=8.2797 Å γ=96.122°
A2	Pc	a=3.812(3) Å α=90° b=8.905(4) Å β=95.02(4)° c=10.498(5) Å γ=90°	a=3.6099 Å α=90° b=8.7323 Å β=89.48° c=9.7339 Å γ=90°
V1	$P2_1/c$	a=9.8560(11) Å α=90° b=3.8407(4) Å β=102.777(4) ° c=18.626(2) Å γ=90°	a=10.0709 Å α=90° b=3.4310 Å β=101.261 ° c=18.4084 Å γ=90°
V2	$P2_1/c$	a=10.1467(13) Å α=90° b=4.8078(6) Å β=97.320(3)° c=13.8542(17) Å γ=90°	a=8.9824 Å α=90° b=5.2876 Å β=89.773° c=13.1096 Å γ=90°
V3	$P2_12_12_1$	a=3.9535(3) Å α=90° b=11.7197(10) Å β= 90° c=13.7875(12) Å γ=90°	a=3.4480 Å α=90° b=13.7005 Å β=90° c=13.29205 Å γ=90°
V4	$P2_1/c$	a=13.2549(6) Å α=90° b=3.8667(2) Å β=109.309(2)° c=13.0731(6) Å γ=90	a=15.6219 Å α=90° b=3.5893 Å β=113.141° c=12.3234 Å γ=90
V5	$P\bar{1}$	a=8.4896(5) Å α=70.833(2)° b= 9.8602(6) Å β= 83.675(2)° c= 10.0057(6) Å γ= 84.293(2)°	a=7.7295 Å α= 74.458° b=9.4201 Å β= 86.354° c=9.1012 Å γ= 88.015°
V6	$P2_1/c$	a=7.3545(6) Å α=90° b=15.0337(12) Å β=104.4670(10)° c= 8.7923(7) Å γ=90°	a= 5.7593 Å α=90° b= 14.8756 Å β= 88.0002 ° c= 7.4178 Å γ=90°
V7	$P2_1/c$	a= 16.3500(7) Å α=90° b= 4.6387(2) Å β= 102.521(4)° c= 14.6202(6) Å γ=90°	a= 10.1515 Å α=90° b= 5.9762 Å β= 114.049° c= 11.5446 Å γ=90°

(a)In the case of A1 and A2 the initial lattice parameters are those of the corresponding room temperature crystal structures of polymorphs I and II respectively. For V1, V2, V3, V4, V5, V6 and V7 the initial lattice parameters are those of the experimental structures with CSD refcodes JIWVAP, JIWWEU, JIWWUK, DOLROO, JIXFII, REBHIQ and GASFAK respectively (see Chart 2 of the typescript).

In the case of actual crystal structures, A1 and A2, the agreement between optimized and experimental lattice parameters is within 7%, with optimized unit cell lengths systematically lower than experimental ones, because optimization is at 0 K, while experimental lattice parameters are measured at room temperature. As we have shown in previous papers (see ESI of reference 1 and SI file of reference 2), a better agreement, within 3%, is obtained if experimental lattice parameters are determined at 173 K.

Reference

1 R. Centore, M. Causà, F. Cerciello, F. Capone, and S. Fusco, *CrystEngComm* 2014, **16**, 9168-9175.

2 R. Centore, S. Fusco, F. Capone, and M. Causà, *Cryst. Growth Des.* 2016, **16**, 2260−2265.

Crystal structure, in CIF format, for the optimized actual and virtual structures at 0 K

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_symmetry_equiv_pos_as_xyz
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_cell_length_b                  7.4196
_cell_length_c                  8.2797
_cell_angle_alpha               113.029
_cell_angle_beta                 93.3165
_cell_angle_gamma                96.122
_cell_volume                    303.9986
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_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
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N1 N    0.341937763  0.186341421  0.207399679
O2 O   -0.296764468  0.162818002 -0.453973841
S1 S    0.229135566  0.318088357  0.397591857
N2 N   -0.309563045  0.262134534 -0.295117948
N3 N   -0.011769266  0.385451455  0.308994501
C1 C   -0.007342488  0.306840060  0.133924037
C2 C   -0.177568332  0.330148761  0.009264883
H1 H   -0.328269233  0.416272044  0.051593025
C3 C   -0.136931322  0.242487056 -0.165017295
C4 C    0.064093496  0.133227625 -0.225319179
H2 H    0.085834551  0.072711054 -0.364753545
C5 C    0.227673251  0.105914748 -0.107799466
H3 H    0.377822633  0.018302558 -0.151678583
C6 C    0.196154505  0.193845484  0.075489200
```

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_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
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_cell_length_b                  8.7323
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_cell_angle_alpha                 90
_cell_angle_beta                 89.480
_cell_angle_gamma                 90
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_atom_site_label
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_atom_site_fract_x
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_atom_site_fract_z
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  C2 C    -0.290636397  0.266217595 -0.119491927
  H1 H    -0.453006936  0.242394310 -0.210496559
  C3 C    -0.146318627  0.150595081 -0.041407789
  H2 H    -0.184795987  0.031920780 -0.070562174
  C4 C     0.053413652  0.184828790  0.081298096
  C5 C    -0.041945485  0.451374136  0.051681468
  C6 C     0.112921553  0.330333403  0.129018645
  H2 H     0.280124852  0.355529616  0.218120164
  N1 N    -0.366559054 -0.452579347 -0.134635871
  N2 N    -0.018028096 -0.400471975  0.085262866
  N3 N     0.208095781  0.059962562  0.160123305
  O1 O     0.147527548 -0.073478128  0.122923501
  O2 O     0.398861138  0.090758250  0.262828312
  S1 S    -0.236511730 -0.302404155 -0.037072502
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_symmetry_equiv_pos_as_xyz
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3 -x,-y,-z
4 x,1/2-y,1/2+z
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_cell_length_c                  18.4084
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C2 C    -0.315812871 -0.316047319 -0.439760789
C3 C    -0.159571625  0.381362268 -0.333215019
H1 H    -0.064560792  0.243203270 -0.309025988
C4 C    -0.389239956 -0.392228915 -0.324453609
H2 H    -0.463732600 -0.359941685 -0.289678467
C5 C    -0.418412028 -0.275360098 -0.396831666
H3 H     0.485265160 -0.142258646 -0.421140209
C6 C    -0.185789416 -0.486600422 -0.407658917
S1 S    -0.176002829 -0.303469171  0.465566059
N1 N    -0.324683329 -0.202929560  0.489931195
N2 N    -0.098248770 -0.497703954 -0.453813197
N3 N    -0.234441799  0.332717713 -0.216293336
N4 O    -0.127120289  0.160142121 -0.190126041
O1 O    -0.320180664  0.421325296 -0.178759643
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3 -x,-y,-z
4 x,1/2-y,1/2+z
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_atom_site_fract_z
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O1 O    -0.488117928  0.173974719 -0.138734788
O2 O     0.358848453  0.238912835 -0.264591116
N1 N     0.070879199  0.271845765 -0.079386440
N2 N     0.290548269  0.405761561  0.029874631
N3 N     0.406183858  0.107299102 -0.193405013
C1 C     0.148206427  0.466415757 -0.117767675
C2 C     0.121503310 -0.403919783 -0.211807903
H1 H     0.033504529 -0.464558598 -0.262750749
C3 C     0.211460414 -0.204947107 -0.237375996
H2 H     0.197850798 -0.104979832 -0.309003409
C4 C     0.328220870 -0.126045975 -0.170511597
C5 C     0.364966144 -0.249727120 -0.082647199
H3 H     0.456567455 -0.192184890 -0.034634084
C6 C     0.273143317 -0.457328308 -0.054639887
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3 -x,1/2+y,1/2-z
4 1/2-x,-y,1/2+z
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S1 S     -0.121198672   0.359896925  -0.434913624
O1 O      0.346290074  -0.223428882   0.375726035
O2 O      0.024660612  -0.286603432   0.249942304
N1 N     -0.286373362   0.337277133   0.448160546
N2 N     -0.209824216   0.480037270  -0.431924450
N3 N      0.231919142  -0.294688835   0.325907617
C1 C      0.402332441   0.436183880   0.315497805
H1 H      0.356246773   0.374717327   0.265285301
C2 C      0.347126912  -0.391947092   0.357185202
C3 C      0.281327054  -0.471853882   0.290128821
H2 H      0.127362750  -0.459564365   0.220152842
C4 C     -0.416893436   0.421879566   0.411000329
C5 C     -0.370547138  -0.496407305   0.479573897
C6 C     -0.485825840  -0.401313614   0.450457058
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4 x,1/2-y,1/2+z
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loop_
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C2 C    -0.326326258  0.324781089 -0.435344581
C3 C    -0.256603649  0.334649352 -0.318927984
H1 H    -0.269267408  0.208169623 -0.246660260
C4 C    -0.173864657 -0.497599639 -0.305158064
C5 C    -0.156261290 -0.325700970 -0.398972610
H2 H    -0.090482153 -0.185343283 -0.380107721
C6 C    -0.222805661 -0.333343210  0.488646197
H3 H    -0.211301246 -0.196162088  0.417345851
N1 N    -0.379168355  0.441327453  0.362345798
N2 N    -0.410351477  0.168577715 -0.467174509
N3 N    -0.098742186 -0.496880343 -0.187890888
O1 O    -0.109358783  0.318144492 -0.108887004
O2 O    -0.028144472 -0.312492144 -0.173457162
S1 S    -0.4654444320  0.219616008  0.385922802
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N2 N 0.445847011 0.870645193 -0.195806184
C1 C 0.249969481 0.937430939  0.207843761
N3 N 0.181261614 0.960893168  0.352113197
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O2 O 0.165974907 0.849711016  0.462051098
C2 C 0.256117494 0.996040645 -0.062187915
C3 C 0.390115105 0.883209645 -0.057970967
C4 C 0.376515935 0.821994350  0.215460631
H1 H 0.415244567 0.757762051  0.326478834
C5 C 0.188126087 1.025357605  0.075945256
H2 H 0.093420201 1.113009857  0.077975709
C6 C 0.450390513 0.796959112  0.083986508
H3 H 0.548499358 0.710594665  0.087849266
S2 S  0.172724206 0.626788549 -0.206211620
N4 N 0.289626615 0.498483493 -0.085934494
N5 N 0.064018823 0.697016214 -0.074942877
C7 C 0.247193081 0.510189366  0.055545215
C8 C 0.135148347 0.568525580  0.334107612
H4 H 0.101832930 0.589002099  0.444183036
C9 C 0.117621877 0.623702475  0.062299260
C10 C 0.32045854 0.425106349  0.191259372
H5 H 0.415452250 0.337405574  0.191505187
C11 C 0.05985078 0.649518327  0.205067970
H6 H -0.03718830 0.734766780  0.209974770
C12 C 0.265313461 0.45971300  0.324158205
N6 N 0.351818728 0.384915239  0.461429743
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O4 O 0.308541585 0.417644669 0.582633636

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2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
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H2 H 0.749496768 0.534034539  0.556079489
H3 H 0.752815002 0.477492540 -0.114646134
C1 C 0.743739369 0.573935157  0.102440280
C2 C 0.743128215 0.591371001  0.291842321
C3 C 0.749983118 0.521160406  0.411975682
C4 C 0.756577295 0.431117525  0.344858989
C5 C 0.756978916 0.416330053  0.151999776
C6 C 0.750924410 0.488944943  0.029684011
N1 N 0.763702155 0.329839458  0.104394210
N2 N 0.762310513 0.354906258  0.440832646
N3 N 0.737863708 0.648213279 -0.023632289
O1 O 0.738678568 0.630199549 -0.187830835
O2 O 0.732532634 0.725729206  0.037052343
S1 S 0.7679393166 0.268740375 0.291747964
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_space_group_name_Hall          '-P 2ybc'
loop_
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_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                  10.1515
_cell_length_b                  5.9762
_cell_length_c                  11.5446
_cell_angle_alpha                90
_cell_angle_beta                114.049
_cell_angle_gamma                90
_cell_volume                    639.589
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
H1 H 0.272930609  0.636694618 -0.088709674
H2 H 0.408419688  0.275206617 -0.015728514
H3 H 0.241519744  0.188500491  0.270675496
C1 C 0.177726953  0.615118450  0.049612233
C2 C 0.265474933  0.537644823 -0.012637766
C3 C 0.338886937  0.340389335  0.027095556
C4 C 0.326130338  0.215789655  0.128161795
C5 C 0.247624923  0.285352196  0.193807553
C6 C 0.173042541  0.490839044  0.155893500
N1 N 0.400547098  0.003674008  0.165065881
N2 N 0.096716819  0.799710079  0.022154964
N3 N 0.092425965  0.584995901  0.209373738
O1 O 0.386747824 -0.106580185  0.251202278
O2 O 0.473535873 -0.062737524  0.108112482
S1 S  0.021511004  0.819474157  0.128558907
```