Supporting Information

Low temperature phase transition induced biaxial negative thermal expansion of 2,4-dinitroanisole

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CIFs of ordered model temperature range of 298 to 261K

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_chemical_formula_weight                198.14

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 'C'   'C'     0.0033     0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'   'H'     0.0000     0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'   'N'     0.0061     0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'   'O'     0.0106     0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_symmetry_cell_setting                  monoclinic
_symmetry_space_group_name_H-M          'P 21/n'

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 'x, y, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
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'x-1/2, -y-1/2, z-1/2'

_cell_length_a 3.980(2)
_cell_length_b 13.759(7)
_cell_length_c 15.461(8)
_cell_angle_alpha 90.00
_cell_angle_beta 90.994(8)
_cell_angle_gamma 90.00
_cell_volume 846.5(7)
_cell_formula_units_Z 4
_cell_measurement_temperature 298(2)
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_cell_measurement_theta_min 3.0
_cell_measurement_theta_max 27.5

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_exptl_crystal_density_method 'not measured'
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_diffrn_reflns_av_sigmaI/netI 0.0196
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_diffrn_reflns_limit_h_max 5
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_diffrn_reflns_limit_k_max 17
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_diffrn_reflns_limit_l_max 19
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_diffrn_reflns_theta_max 27.46
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_atom_sites_solution_secondary      difmap
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_refine_ls_extinction_coef          ?
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 _atom_site_fract_z
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 _atom_site_occupancy
 _atom_site_symmetry_multiplicity
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C2 C 0.0132(7) 0.2400(2) 0.48492(18) 0.0560(8) Uani 1 1 d . . .
C3 C -0.1243(7) 0.1517(2) 0.46236(17) 0.0562(7) Uani 1 1 d . . .
H1 H -0.2073 0.1101 0.5043 0.067 Uiso 1 1 calc R . .
C4 C -0.1361(7) 0.1264(2) 0.37577(18) 0.0593(8) Uani 1 1 d . . .
C5 C -0.0159(8) 0.1888(3) 0.31313(19) 0.0698(9) Uani 1 1 d . . .
H2 H -0.0256 0.1708 0.2552 0.084 Uiso 1 1 calc R . .
C6 C 0.1168(9) 0.2769(3) 0.3364(2) 0.0692(9) Uani 1 1 d . . .
H3 H 0.1949 0.3186 0.2939 0.083 Uiso 1 1 calc R . .
C7 C 0.3848(11) 0.4580(3) 0.3874(3) 0.0931(13) Uani 1 1 d . . .
H6 H 0.5413 0.4254 0.3508 0.140 Uiso 1 1 calc R . .
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H5 H 0.4955 0.5110 0.4164 0.140 Uiso 1 1 calc R . .
H4 H 0.2004 0.4823 0.3530 0.140 Uiso 1 1 calc R . .
N1 N 0.0207(8) 0.2632(2) 0.57758(17) 0.0744(9) Uani 1 1 d . . .
N2 N -0.2835(8) 0.0334(2) 0.35104(19) 0.0751(9) Uani 1 1 d . . .
O1 O 0.2608(7) 0.39070(18) 0.45052(16) 0.0804(8) Uani 1 1 d . . .
O4 O -0.3927(11) -0.0181(3) 0.4071(2) 0.1272(15) Uani 1 1 d . . .
O5 O -0.2937(10) 0.0114(3) 0.27530(19) 0.1184(13) Uani 1 1 d . . .
O2 O 0.167(2) 0.3269(4) 0.6045(2) 0.220(4) Uani 1 1 d . . .
O3 O -0.1103(18) 0.2138(4) 0.6260(2) 0.226(4) Uani 1 1 d . . .

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C2 0.0587(15) 0.0631(17) 0.0460(14) -0.0009(12) -0.0023(11) 0.0005(12)
C3 0.0612(15) 0.0629(16) 0.0447(14) 0.0018(11) 0.0060(11) 0.0000(12)
C4 0.0622(16) 0.0666(18) 0.0491(15) -0.0035(13) -0.0028(12) 0.0003(13)
C5 0.083(2) 0.085(2) 0.0420(14) 0.0027(14) -0.0019(13) 0.0033(16)
C6 0.077(2) 0.079(2) 0.0513(16) 0.0170(14) 0.0018(14) -0.0007(16)
C7 0.098(3) 0.083(2) 0.097(3) 0.034(2) -0.011(2) -0.026(2)
N1 0.098(2) 0.0762(18) 0.0492(14) -0.0069(12) 0.0026(13) -0.0215(15)
N2 0.0856(19) 0.0764(18) 0.0632(17) -0.0137(14) 0.0015(14) -0.0071(14)
O1 0.0982(18) 0.0717(15) 0.0710(15) 0.0098(11) -0.0071(13) -0.0233(12)
O4 0.189(4) 0.105(2) 0.089(2) -0.0205(17) 0.033(2) -0.069(2)
O5 0.179(3) 0.111(2) 0.0648(18) -0.0240(16) -0.0141(19) -0.027(2)
O2 0.399(9) 0.203(5) 0.0581(18) 0.006(2) -0.029(3) -0.188(6)
O3 0.352(8) 0.260(6) 0.069(2) -0.060(3) 0.086(4) -0.194(6)

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data_24dnan_283K

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_chemical_formula_weight 198.14

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 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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_symmetry_space_group_name_H-M      'P 21/n'

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 '-x, -y, -z'
 'x-1/2, -y-1/2, z-1/2'

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_cell_angle_gamma                   90.00
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_cell_formula_units_Z               4
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_exptl_crystal_density_method       'not measured'
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;Yadokari-XG 2009 (Wakita,Nemoto et al., 2009)
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  _atom_site_adp_type
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 C2 C 0.4868(8) 0.2402(2) 0.01469(18) 0.0476(8) Uani 1 1 d . A .
 C3 C 0.6241(8) 0.1513(2) 0.03742(18) 0.0473(7) Uani 1 1 d . . .
 H1 H 0.7070 0.1093 -0.0044 0.057 Uiso 1 1 calc R . .
 C4 C 0.6348(8) 0.1263(2) 0.12381(19) 0.0498(8) Uani 1 1 d . B .
25 C5 C 0.5136(9) 0.1885(3) 0.1865(2) 0.0585(9) Uani 1 1 d . . .
 H2 H 0.5223 0.1701 0.2445 0.070 Uiso 1 1 calc R . .
 C6 C 0.3812(9) 0.2768(3) 0.1633(2) 0.0584(9) Uani 1 1 d . . .
 H3 H 0.3009 0.3184 0.2057 0.070 Uiso 1 1 calc R . .
 C7 C 0.1161(11) 0.4583(3) 0.1125(3) 0.0789(12) Uani 1 1 d . . .
30 H4 H -0.0453 0.4259 0.1481 0.118 Uiso 1 1 calc R . .
 H5 H 0.0097 0.5125 0.0838 0.118 Uiso 1 1 calc R . .
 H6 H 0.3012 0.4812 0.1481 0.118 Uiso 1 1 calc R . .
 N1 N 0.4816(8) 0.2633(2) -0.07822(18) 0.0628(8) Uani 1 1 d . . .
 N2 N 0.7807(8) 0.0329(2) 0.1488(2) 0.0645(8) Uani 1 1 d . . .
35 O1 O 0.2399(7) 0.39137(18) 0.04925(15) 0.0670(8) Uani 1 1 d . . .
 O2 O 0.3354(19) 0.3276(4) -0.1050(2) 0.194(3) Uani 1 1 d . A 1
 O3 O 0.6154(17) 0.2140(4) -0.1262(3) 0.205(4) Uani 1 1 d . A 1
 O4 O 0.8906(11) -0.0189(3) 0.0927(2) 0.1125(14) Uani 1 1 d . B 1
 O5 O 0.7894(10) 0.0104(3) 0.22458(19) 0.1040(12) Uani 1 1 d . B 1
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  _atom_site_aniso_U_13
  _atom_site_aniso_U_12
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C3 0.0498(16) 0.0532(17) 0.0392(14) -0.0022(12) 0.0063(11) 0.0008(13)
C4 0.0509(16) 0.0534(17) 0.0449(16) 0.0027(13) -0.0022(12) 0.0006(14)
C5 0.070(2) 0.071(2) 0.0353(15) -0.0017(14) -0.0017(13) -0.0037(17)
C6 0.066(2) 0.065(2) 0.0445(17) -0.0145(14) 0.0031(14) 0.0023(17)
C7 0.086(3) 0.070(2) 0.081(3) -0.026(2) -0.009(2) 0.022(2)
N1 0.084(2) 0.0614(17) 0.0428(15) 0.0044(13) 0.0009(14) 0.0171(16)
N2 0.075(2) 0.0651(18) 0.0531(17) 0.0119(14) 0.0017(14) 0.0070(15)
O1 0.0836(18) 0.0572(14) 0.0601(15) -0.0082(11) -0.0053(12) 0.0214(12)
O2 0.354(8) 0.176(4) 0.0516(19) -0.004(2) -0.028(3) 0.174(5)
O3 0.322(8) 0.232(6) 0.064(2) 0.060(3) 0.082(4) 0.186(6)
O4 0.170(4) 0.090(2) 0.078(2) 0.0194(17) 0.033(2) 0.065(2)
O5 0.157(3) 0.100(2) 0.0543(17) 0.0221(16) -0.0121(18) 0.026(2)

data_24dnan_273K

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_chemical_formula_weight 198.14
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'H' 'H' 0.0000 0.0000
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'N' 'N' 0.0061 0.0033
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'O' 'O' 0.0106 0.0060
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_symmetry_space_group_name_H-M 'P 21/n'
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'x, y, z'
'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x-1/2, -y-1/2, z-1/2'
_cell_length_a 3.957(2)
_cell_length_b 13.735(7)
_cell_length_c 15.454(8)
_cell_angle_alpha 90.00
_cell_angle_beta 91.156(8)

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_diffrn_reflns_limit_h_max              5
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loop_
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 _atom_site_type_symbol
 _atom_site_fract_x
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 _atom_site_fract_z
 _atom_site_U_iso_or_equiv
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 _atom_site_occupancy
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 _atom_site_calc_flag
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C1 C 0.3651(8) 0.3053(2) 0.0763(2) 0.0516(8) Uani 1 1 d . . .
C2 C 0.4868(8) 0.2402(2) 0.01469(18) 0.0476(8) Uani 1 1 d . A .
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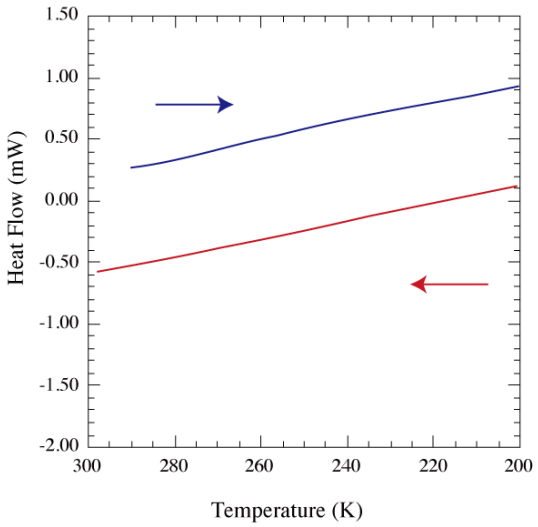
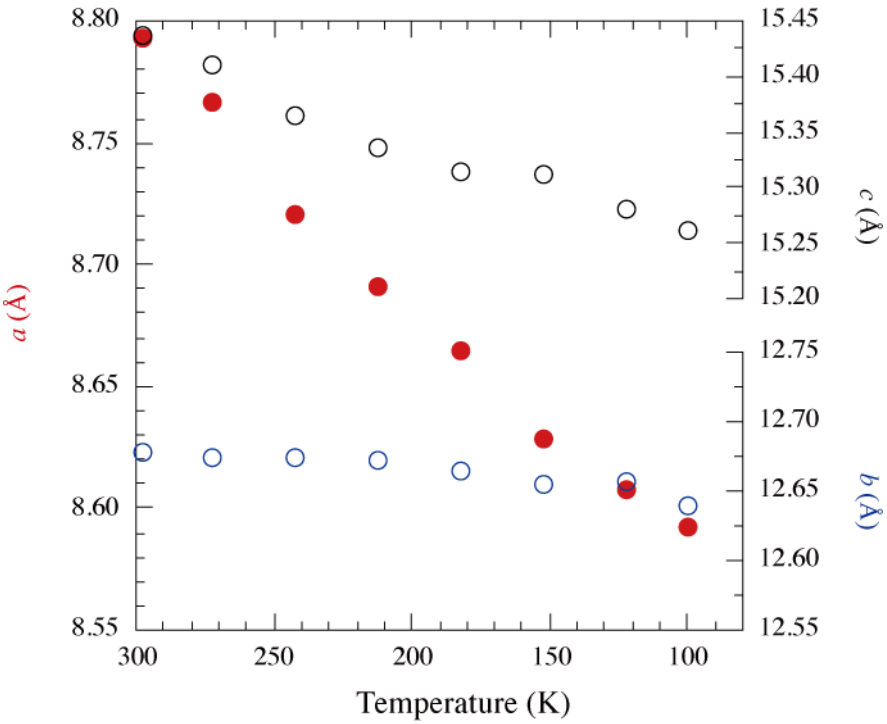


Fig. S1 DSC plot of the α—form crystal.

Table S1 Crystal and experimental data for the α—form

Compound reference	298	273	243	213	183	153	123	100
Chemical formula	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$	$C_7H_6N_2O_5$
Formula Mass	198.14	198.14	198.14	198.14	198.14	198.14	198.14	198.14
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	8.794(3)	8.767(3)	8.721(3)	8.691(3)	8.665(3)	8.629(4)	8.608(2)	8.593(2)
b/Å	12.678(3)	12.675(4)	12.675(4)	12.673(4)	12.666(4)	12.656(5)	12.658(3)	12.641(3)
c/Å	15.437(5)	15.411(5)	15.366(5)	15.336(5)	15.316(5)	15.314(7)	15.282(4)	15.263(4)
α/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β/°	98.052(4)	97.912(5)	97.580(4)	97.417(4)	97.277(3)	97.292(6)	97.022(3)	97.065(4)
γ/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	1704.1(9)	1696.2(10)	1683.7(10)	1675.0(10)	1667.4(10)	1658.9(13)	1652.6(7)	1645.3(7)
Temperature/K	298	273	243	213	183	153	123	100
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
No. of formula units per unit cell, *Z*	8	8	8	8	8	8	8	8
Absorption coefficient, μ/mm^{-1}	0.134	0.135	0.136	0.137	0.137	0.138	0.138	0.139
No. of reflections measured	13575	13531	13438	13317	13280	13236	13148	12659
No. of independent reflections	3895	3877	3841	3824	3798	3797	3767	3767
R_{int}	0.0345	0.0323	0.0330	0.0314	0.0291	0.0302	0.0300	0.0381
Final R_1 values ($I > 2\sigma(I)$)	0.0594	0.0578	0.0524	0.0503	0.0482	0.0442	0.0405	0.0354
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1274	0.1265	0.1096	0.1096	0.1049	0.0954	0.0910	0.0670
Final R_1 values (all data)	0.1067	0.0985	0.0837	0.0749	0.0692	0.0644	0.0565	0.0587
Final $wR(F^2)$ values (all data)	0.1483	0.1466	0.1239	0.1211	0.1150	0.1074	0.0984	0.0730
Goodness of fit on F^2	1.093	1.046	1.057	1.071	1.067	1.050	1.054	0.879

(a)



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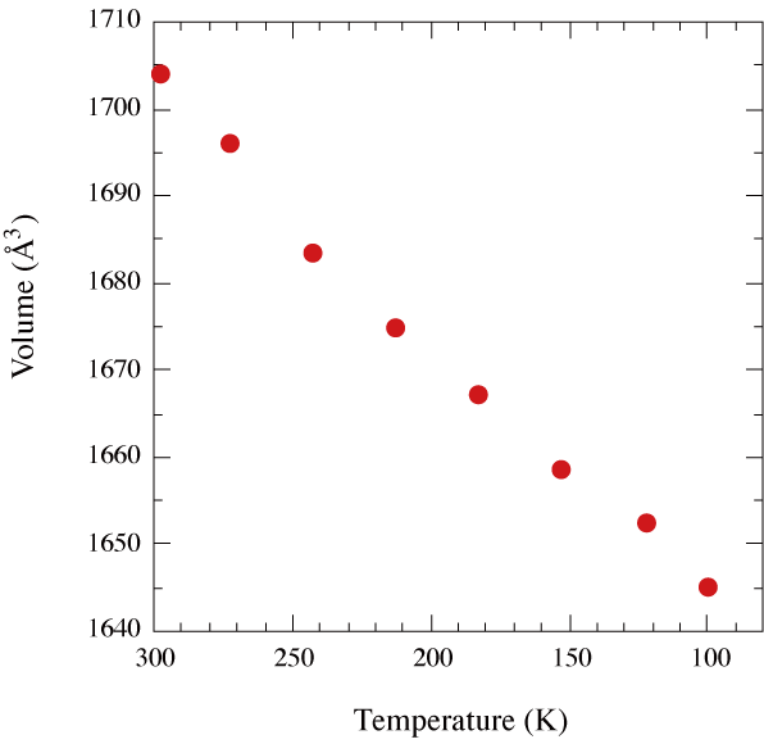

Fig. S2 Variation of the unit cell parameters of the α—form as a function of temperature; (a) cell lengths, and (b) volume.

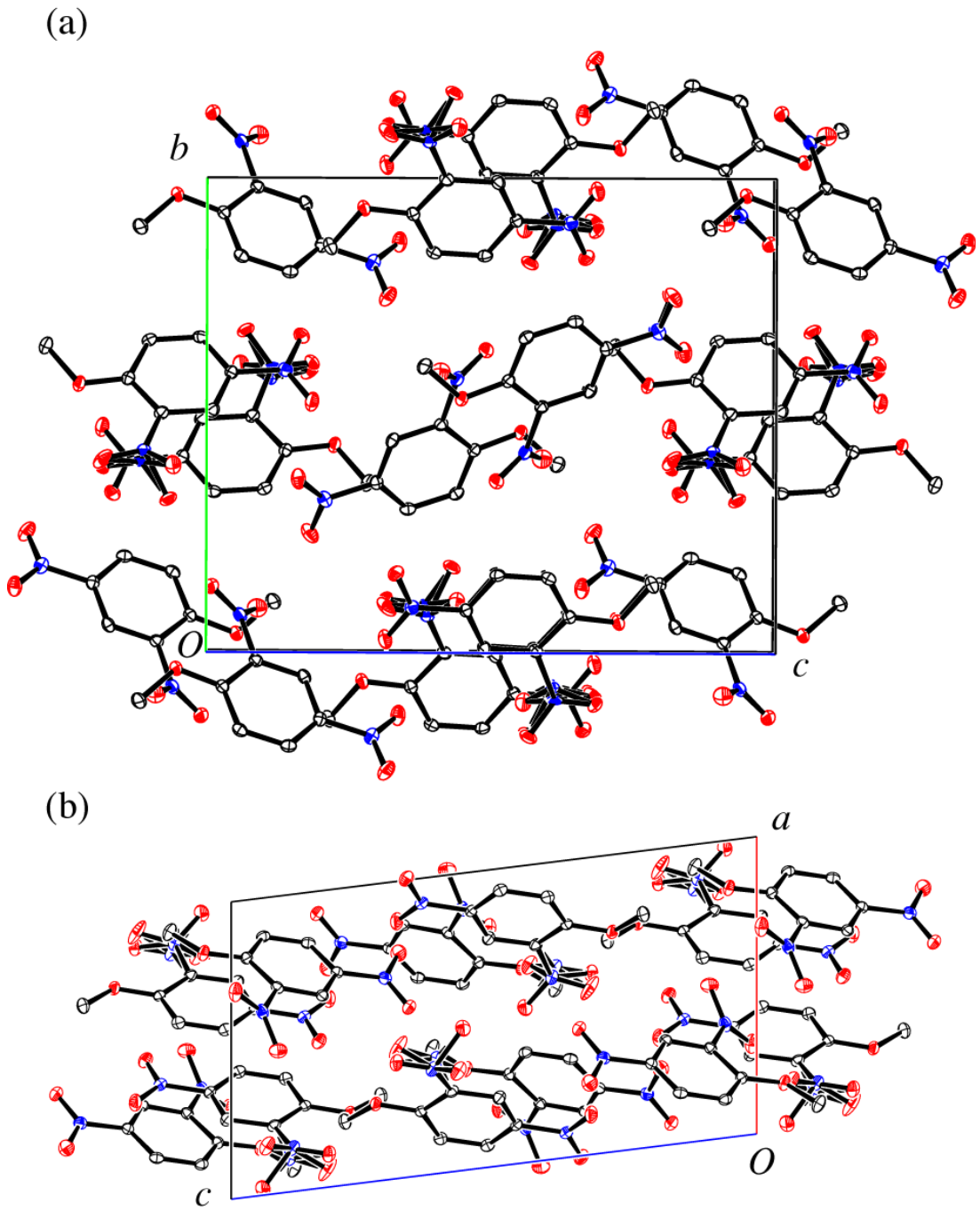

Fig. S3 Crystal structure of the α—form at 100 K (a) viewed down the *a* axis (b) viewed down the *b* axis. The hydrogen atoms have been omitted for clarity.

Table S2 Principal coefficients of thermal expansion and corresponding principal axes determined for the α—form temperature range of 293—100 K.

		Component of $\mathbf{x}_i$ along the crystallographic axes			
Principal axis, *i*	α_i (MK^{-1})	*a*	*b*	*c*	Approximate axis
1	13.7(19)	0	-1	0	[010]
2	26.6 (13)	0.6188	0	0.7855	[101]
3	136(7)	-0.9823	0	0.1875	[100]

Table S3 Short ring-interactions with Cg-Cg distances for the β—form [a]

Temp. (K)	Cg1-Cg2 distance (Å)	β (°)[b]	plane	slippage (Å) distance (Å)	θ (°)[c]
298	3.980(3)	25.4	3.5937(12)	1.710	65.2
283	3.962(3)	25.2	3.5822(13)	1.692	65.4
273	3.957(3)	25.2	3.5781(13)	1.690	65.4
261	3.929(2)	23.4	3.6051(9)	1.562	67.9
236	3.908(3)	23.4	3.5841(7)	1.558	68.5
226	3.897(2)	23.4	3.5753(7)	1.550	69.0
208	3.880(2)	23.3	3.5614(6)	1.540	69.2
198	3.876(2)	23.4	3.5557(6)	1.543	69.4
173	3.854(2)	23.5	3.5342(6)	1.536	69.4
128	3.828(2)	23.5	3.5102(5)	1.527	69.8
100	3.814(1)	23.5	3.4966(5)	1.523	70.0

[a]Distances between center of gravity of phenyl ring (Cg1: *x*, *y*, *z*) and (Cg2: -1 + *x*, *y*, *z*) within 6.0 Å and b angle < 60 °. [b]Angle between Cg1 -> Cg2 vector and normal to plane 2 as shown Fig. S4. [c]This angle is defined in the main text.

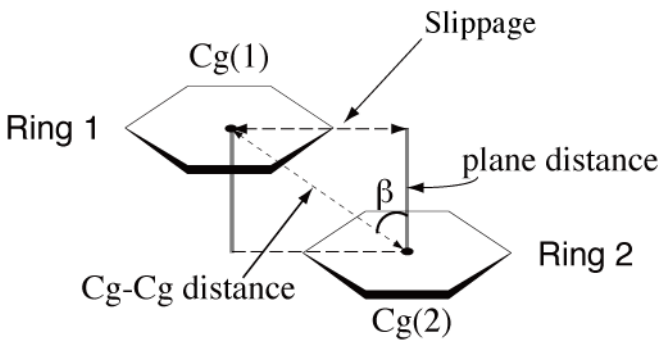

Fig. S4 Definition of parameters in Table S3.

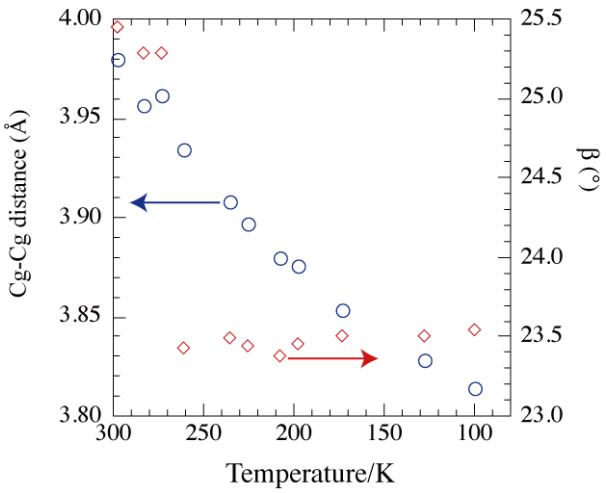

Fig. S5 Variation of the π-π interactions parameters in the β—form crystal as a function of temperature. The blue open circles and red open diamonds represent the Cg1-Cg2 distance and the β angle from Table S3, respectively.