

Temperature dependence of the crystal structure of
3,5-di-*tert*-butylpyrazole from 10 KAlexandre N. Sobolev* and
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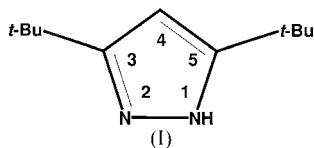
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A single crystal of 3,5-di-*tert*-butylpyrazole has been the subject of structure determinations at 10, 100, 120 and 299 K. Above ~ 110 K, the structure is *Pbca*, $a \simeq 11.3$, $b \simeq 20.6$, $c \simeq 10$ Å, $Z = 8$. Below 110 K, the c axis is doubled and the space group becomes *Pb2₁a*, $Z = 16$. Here the asymmetric unit is comprised of four molecules, arranged as a pair of overlapping hydrogen-bonded dimers, all components being ordered. In each case one methyl group of each *t*-butyl group lies coplanar with its parent pyrazole ring and, within each quasi-inversion-related dimer, one molecule has both of these methyl groups directed away from the N₂ component '*cis*', while in the other, one methyl group is toward ('*trans*'). Above 110 K the four molecules collapse into one, with one *t*-butyl group (corresponding to an overlaid '*cis/trans*' pair of the low-temperature form) modelled as disordered. The disorder has been previously described as 'temperature dependent' (Deacon *et al.*, 2001), but the present studies suggest it to be dependent on the history of the particular specimen as well.

1. Introduction

A wide range of single-crystal diffraction studies of a variety of simple azoles at diverse temperatures has been executed previously with the intent of defining and understanding the nature of their protonic hydrogen distribution, with respect to both tautomerism and hydrogen bonding. Of particular interest in these respects are the studies carried out on various 3,5-disubstituted pyrazoles where diffraction experiments have been augmented by spectroscopic and theoretical studies (Alkorta *et al.*, 1999; Baldy *et al.*, 1985; Goddard *et al.*, 1999; Llamas-Saiz *et al.*, 1995; Smith *et al.*, 1989). In particular, the same group has investigated the 3,5-di-*tert*-butyl analogue using combined room-temperature X-ray diffraction (CCD data) and variable-temperature, multi-nuclear solid-state NMR studies (Aguilar-Parrilla *et al.*, 1995). Their results are consistent with the interesting dynamic behaviour of the protonic H atoms being accompanied by rotation of the *tert*-butyl groups within the lattice. The current investigation was initiated because, during the course of studies of lanthanoid(III) complexes with the 3,5-di-*tert*-butylpyrazole anion at ~ 153 K, we revisited the structure of the parent azole at that temperature (Deacon *et al.*, 2001). It was found that at ~ 153 K, rotational disorder was seen in only one of the *tert*-butyl groups, that attached to ring position 5 (consistent with our numbering), but that at room temperature disorder became evident in both *tert*-butyl groups, 3 and 5, whose behavior is at some variance with the literature data (Aguilar-Parrilla *et al.*, 1995), wherein disorder was described only for group 5 (see schematic formula). With the local availability of a four-circle instrument operating at 10 K, we extended our

studies to that lower temperature and record the results herein.



2. Experimental

A preliminary study, in which a specimen was allowed to cool rapidly without undue precaution, showed that at low temperature a phase transition had occurred. It was found that the crystal had retained its integrity and the diffraction pattern its orthorhombic symmetry, but that doubling of an axis had occurred with a change of space group. A phase transition was subsequently determined to be ~ 110 K, with the capability to cycle reversibly through it (at the level of cell size and

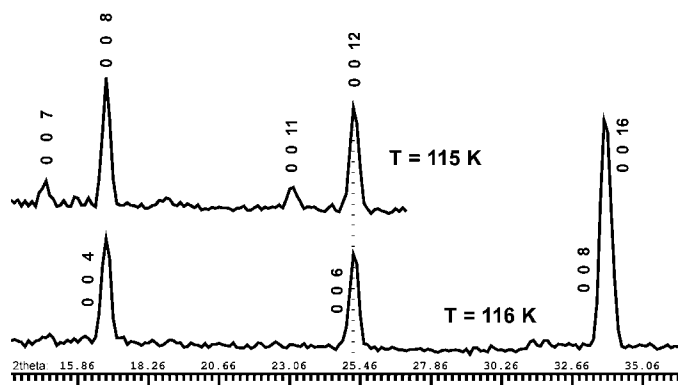


Figure 1
Representative scans along $00l$ at either side of the phase transition, '116' and '115' K in this particular experiment, the exact values somewhat dependent on the rate of cooling.

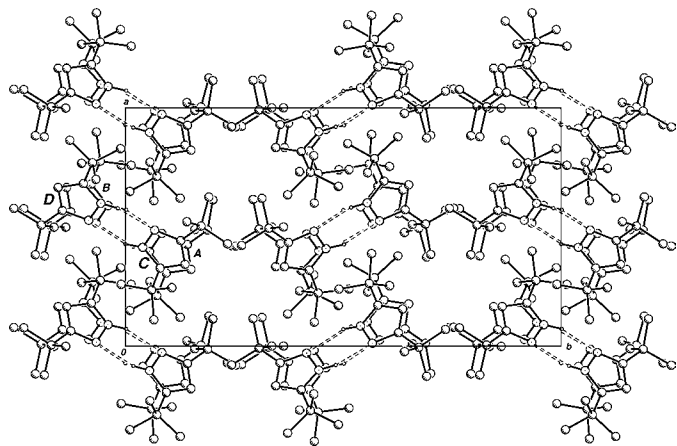


Figure 2
Unit-cell contents of the 'low-temperature' phase, projected down the (orthorhombic) c axis.

symmetry), although subsequent experiments suggested the possibility of occasional associated physical damage as a cause for care. A new specimen, $0.44 \times 0.34 \times 0.20$ mm, enclosed in a glass capillary to prevent sublimation, was mounted and cooled slowly to 10 K, while monitoring peak profiles along $00l$, to detect the axis doubling, the initial individual peak widths remaining constant (Fig. 1). A hemisphere of data was measured at 10 K, the crystal then being allowed to warm successively to 100, 120 and 299 K where unique data sets were measured; finally, an independent room-temperature data set was measured on the same specimen using a Bruker AXS CCD instrument, yielding identical refinement behavior, attempted refinement in lower symmetry proving (inherently) fruitless.

Data sets were measured with a locally assembled Huber 512 goniometer equipped with a Displex 202D cryogenic refrigerator (Henriksen *et al.*, 1986; Larsen, 1995) and using a β -filtered Mo $K\alpha$ X-ray source, by an $\omega/2\theta$ scan procedure with locally created diffractometer-control software. An absorption correction for the beryllium shield was performed using the program *PROFIT* (Streltsov & Zavodnik, 1989) and for the crystal [*Gaussian* correction, $\mu_{\text{Mo}} = 0.06 \text{ mm}^{-1}$, $T_{\text{min, max}} = 0.98, 0.99$ (all cases); Hall *et al.*, 2000]. A full-matrix least-squares refinement procedure was used (Sheldrick, 1997), minimizing $w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. Agreement factors $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and GOOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ are cited, where n is the number of reflections and p the total number of parameters refined. Anisotropic displacement parameter forms were refined for the non-H atoms; for the low-temperature (10 K) phase (x, y, z)_H were also refined, with associated isotropic displacement parameters being constrained to equivalence within each methyl group. For the 100 and 120 K studies, methyl C—H distances were allowed to vary, U_H constrained to $1.5U_{\text{eq}}$ (parent carbon). In the 299 K study, C—H distances were fixed at 0.96 Å. Table 1 summarizes the data collection and refinement details; Table 2 gives selected geometries as determined from the 10 K study. CCDC 230155–230158 contain the supplementary crystallographic data for this paper.¹

3. Results and discussion

The high-temperature form of 3,5-di-*tert*-butylpyrazole packs in the centrosymmetric orthorhombic space group *Pbca* (No. 61) with an asymmetric unit composed of one formula unit, devoid of crystallographic symmetry, and with disordered *tert*-butyl and protonic hydrogen functions. Dimers in which the molecules are linked *via* N—H...N hydrogen bonds and related by crystallographic inversion centres stack obliquely up the c axis (~ 10 Å). In the low-temperature form the c axis

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA5008). Services for accessing these data are described at the back of the journal. These data can also be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1
Experimental table.

	10 K	100 K	120 K	299 K
Crystal data				
Chemical formula	C ₁₁ H ₂₀ N ₂	C ₁₁ H ₂₀ N ₂	C ₁₁ H ₂₀ N ₂	C ₁₁ H ₂₀ N ₂
<i>M_r</i>	180.29	180.29	180.29	180.29
Cell setting, space group	Orthorhombic, <i>Pb2₁a</i>	Orthorhombic, <i>Pb2₁a</i>	Orthorhombic, <i>Pbca</i>	Orthorhombic, <i>Pbca</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.279 (2), 20.634 (4), 19.542 (4)	11.366 (2), 20.654 (5), 19.723 (4)	11.356 (2), 20.637 (4), 9.850 (2)	11.482 (1), 21.130 (2), 9.992 (1)
<i>V</i> (Å ³)	4548.0 (15)	4630.0 (17)	2308.4 (8)	2424.2 (4)
<i>Z</i>	16	16	8	8
<i>D_x</i> (Mg m ⁻³)	1.053	1.035	1.038	0.988
(sin θ/λ) _{max}	0.594 ₆	0.594 ₆	0.594 ₆	0.705 ₀
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	14	14	14	24
θ range (°)	16.0–20.1	16.0–16.6	16.0–16.8	12.8–13.8
μ (mm ⁻¹)	0.06	0.06	0.06	0.06
Temperature (K)	10 (2)	100 (2)	120 (2)	299 (2)
Crystal form, colour	Prism, colourless	Prism, colourless	Prism, colourless	Prism, colourless
Crystal size (mm)	0.44 × 0.34 × 0.20	0.44 × 0.34 × 0.20	0.44 × 0.34 × 0.20	0.44 × 0.34 × 0.20
Data collection				
Diffractometer	Huber 512 goniometer	Huber 512 goniometer	Huber 512 goniometer	Huber 512 goniometer
Data collection method	ω -2 θ scan	ω -2 θ scan	ω -2 θ scan	ω -2 θ scan
Absorption correction	Gaussian	Gaussian	Gaussian	Gaussian
<i>T_{min}</i>	0.980	0.980	0.979	0.979
<i>T_{max}</i>	0.988	0.988	0.987	0.988
No. of measured, independent and observed reflections	15 825, 4162, 3744	4203, 4203, 3456	2043, 2043, 1419	3550, 3550, 1686
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.070	–	–	–
θ_{max} (°)	25.0	25.1	25.1	30.1
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 ⇒ <i>h</i> ⇒ 13 –24 ⇒ <i>k</i> ⇒ 24 –23 ⇒ <i>l</i> ⇒ 23	0 ⇒ <i>h</i> ⇒ 13 0 ⇒ <i>k</i> ⇒ 24 0 ⇒ <i>l</i> ⇒ 23	0 ⇒ <i>h</i> ⇒ 13 0 ⇒ <i>k</i> ⇒ 24 0 ⇒ <i>l</i> ⇒ 11	0 ⇒ <i>h</i> ⇒ 16 0 ⇒ <i>k</i> ⇒ 29 0 ⇒ <i>l</i> ⇒ 14
No. and frequency of standard reflections	3 every 100 reflections	3 every 100 reflections	3 every 100 reflections	3 every 100 reflections
Intensity decay (%)	2	2	2	2
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.040, 0.102, 1.07	0.079, 0.226, 1.15	0.063, 0.162, 1.08	0.090, 0.335, 0.99
Weighting coefficient (<i>A</i>)	0.0639	0.1043	0.0721	0.1631
Weighting coefficient (<i>B</i>)	0.7985	4.3675	0.8688	0.6552
No. of reflections	4162	4203	2043	3550
No. of parameters	742	524	164	175
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.7985P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1043P)^2 + 4.3675P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.8688P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1631P)^2 + 0.6552P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.044	0.003	<0.0001	0.009
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.28, –0.21	0.45, –0.31	0.23, –0.19	0.20, –0.21
Extinction method	<i>SHELXL</i>	None	<i>SHELXL</i>	<i>SHELXL</i>
Extinction coefficient	0.0012 (4)	–	0.0044 (18)	0.034 (7)

Computer programs used: *Local diffractometer control software*, *PROFIT* (Streltsov & Zavodnik, 1989).

is doubled to ~ 19.5 Å (Table 1), with the lattice symmetry degraded to non-centrosymmetric *Pb2₁a*, a non-standard setting of No. 29, which preserves the relationship of the cell axes between the two forms. Four independent molecules comprise the asymmetric unit and are arranged as a pair of (previously centrosymmetric) dimers. In superposition down the *c* axis (Fig. 2), the originally coincident dimers are now displaced by ~ 0.2 Å. The constitution of this cluster of four

molecules is quite remarkable. No disorder is found within either the protonic hydrogen or *tert*-butyl components, *i.e.* the structure is now fully ordered. Noting the pairing as (*AB*) overlaid above (*CD*), we find that the *tert*-butyl groups are all disposed with one of the methyl groups, denoted (3/5)2, quasi-coplanar with the parent pyrazole ring. In molecules *A* and *C* these methyl groups are both directed away from the N₂ components of their molecules ('*cis*'), but in molecules *B* and

Table 2
Bond lengths (Å) and angles (°) for 3,5-di-*tert*-butylpyrazole (10 K).

Parameter/ molecule	<i>A(cis)</i>	<i>B(trans)</i>	<i>C(cis)</i>	<i>D(trans)</i>	Average
N1—H1	0.83 (4)	0.91 (4)	0.86 (5)	0.86 (5)	0.87 (3)
N1...H1'	2.10 (4)	2.05 (4)	2.06 (5)	2.09 (5)	2.08 (2)
N1...N2'	2.862 (4)	2.865 (4)	2.845 (4)	2.866 (4)	2.860 (9)
N1—N2	1.372 (4)	1.364 (4)	1.361 (4)	1.359 (4)	1.364 (4)
N1—C5	1.341 (4)	1.343 (4)	1.345 (4)	1.345 (4)	1.344 (2)
N2—C3	1.335 (4)	1.345 (4)	1.345 (4)	1.341 (4)	1.342 (4)
C3—C4	1.411 (4)	1.403 (4)	1.409 (4)	1.405 (4)	1.407 (3)
C3—C31	1.519 (4)	1.518 (4)	1.521 (4)	1.517 (4)	1.519 (2)
C31—C32	1.534 (4)	1.535 (4)	1.529 (4)	1.527 (4)	1.533 (3)
C31—C33	1.531 (4)	1.541 (4)	1.535 (4)	1.546 (4)	1.538 (6)
C31—C34	1.552 (4)	1.536 (4)	1.536 (4)	1.540 (4)	1.541 (7)
C4—C5	1.377 (4)	1.391 (4)	1.381 (4)	1.383 (4)	1.383 (5)
C5—C51	1.516 (4)	1.518 (4)	1.519 (4)	1.514 (4)	1.517 (2)
C51—C52	1.528 (4)	1.528 (4)	1.531 (4)	1.536 (4)	1.531 (3)
C51—C53	1.548 (4)	1.533 (4)	1.538 (4)	1.542 (4)	1.540 (6)
C51—C54	1.534 (4)	1.535 (4)	1.538 (4)	1.541 (4)	1.537 (3)
N1—H1—N2'	152 (3)	149 (3)	152 (4)	149 (4)	151 (2)
C5—N1—N2	113.2 (3)	113.0 (3)	113.2 (3)	113.3 (3)	113.2 (1)
C3—N2—N1	104.3 (2)	104.7 (2)	104.5 (2)	104.5 (2)	104.5 (1)
N2—C3—C4	110.5 (3)	110.5 (3)	110.4 (3)	110.5 (3)	110.48 (4)
N2—C3—C31	120.0 (3)	119.5 (3)	120.0 (3)	119.9 (3)	119.9 (2)
C4—C3—C31	129.5 (3)	129.9 (3)	129.5 (3)	129.6 (3)	129.6 (2)
C3—C31—C32	110.3 (2)	109.6 (3)	109.9 (2)	109.9 (3)	109.9 (3)
C3—C31—C33	109.8 (2)	109.4 (2)	109.7 (2)	108.5 (2)	109.4 (5)
C3—C31—C34	109.5 (2)	109.7 (2)	109.2 (2)	110.0 (3)	109.6 (3)
C32—C31—C33	109.4 (3)	109.2 (3)	109.7 (3)	109.7 (3)	109.5 (2)
C32—C31—C34	109.0 (2)	109.8 (3)	109.0 (3)	109.6 (3)	109.4 (4)
C33—C31—C34	108.8 (3)	109.1 (3)	109.3 (3)	109.0 (3)	109.1 (2)
C3—C4—C5	106.2 (3)	105.9 (3)	106.0 (3)	106.1 (3)	106.1 (1)
N1—C5—C4	105.8 (3)	105.9 (3)	106.0 (3)	105.6 (3)	105.8 (2)
N1—C5—C51	121.6 (3)	122.5 (3)	121.7 (3)	122.7 (3)	122.1 (5)
C4—C5—C51	132.6 (3)	131.6 (3)	132.3 (3)	131.7 (3)	132.1 (4)
C5—C51—C52	109.6 (2)	110.4 (2)	109.3 (2)	110.4 (2)	109.9 (5)
C5—C51—C53	109.8 (2)	109.3 (2)	109.0 (2)	108.8 (2)	109.2 (4)
C5—C51—C54	109.7 (2)	109.1 (2)	110.1 (2)	109.4 (2)	109.6 (4)
C52—C51—C53	109.3 (2)	109.4 (3)	109.0 (2)	109.4 (2)	109.3 (2)
C52—C51—C54	109.6 (2)	109.6 (2)	109.5 (2)	109.9 (2)	109.57 (5)
C53—C51—C54	108.8 (2)	108.9 (3)	109.9 (2)	108.9 (2)	109.1 (5)

Average distances and angles for <i>tert</i> -butyl groups			
C31—C3 _x	1.537 (7)	C3,5—C31,51	1.518 (2)
C51—C5 _x	1.536 (6)	C31,51—C31 _x ,51 _x	1.536 (6)
C3—C31—C3 _x	109.6 (4)	C31 _x —C31—C31 _x '	109.3 (3)
C5—C51—C5 _x	109.6 (5)	C51 _x —C51—C51 _x '	109.4 (4)
Average	109.6 (5)	Average	109.3 (3)

D only the methyl in position 3 points away, the other, 5, being directed toward N2 ('*trans*'). The protonic H atoms are all located on N1 atoms, arguably the less crowded site in the *trans* form (Fig. 3). As superposed in the cluster, *tert*-butyl groups 3 are similar, but groups 5 are different within each pair *A/D*, *B/C*. Comparison of the non-H atom geometries in the four molecules (Table 2) shows that, whereas N—C distances are similar about N1,2, there is, unsurprisingly, a considerable difference in the angles subtended at these atoms, those at protonated N1 being greater than those at N2 by almost 10°. These differences are propagated to the angles at C(3,5), which are independent of the *tert*-butyl dispositions. Also, the *tert*-butyl substituents have little impact on the magnitudes of the exocyclic angles, but it was observed that for all rings the exocyclic angles at C3,5 toward C4 are larger

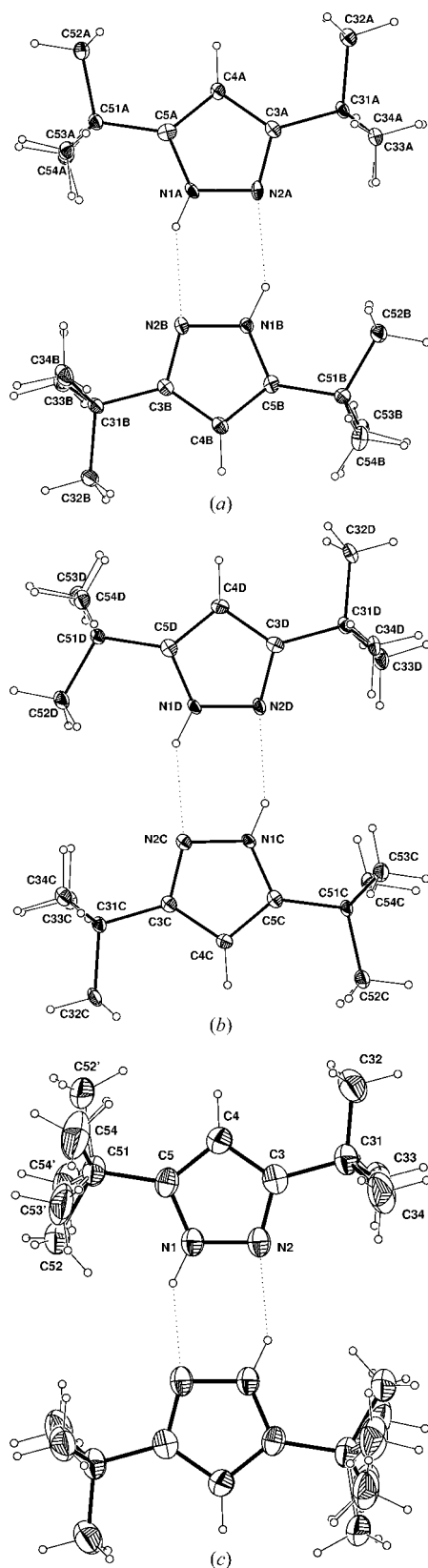


Figure 3
(*a*, *b*) The two pairs of molecules comprising the asymmetric unit of the low-temperature form at 10 K; 50% probability amplitude displacement ellipsoids being shown for the non-H atoms here and elsewhere; H atoms, where shown, have an arbitrary radius of 0.08 Å. (*c*) The asymmetric unit with its inversion image at 120 K.

than those towards nitrogen. The results of the determination carried out at 100 K essentially replicate these at 10 K after due allowance for the influence of temperature increase, although the displacement of the *AB/DC* pairs in superposition is slightly reduced to ~ 0.14 Å. At 120 K, the structure has converted to *Pbca*, requiring only one molecule per asymmetric unit. Only one protonic hydrogen site is observed, still in association with N1, with disorder being observed only at *tert*-butyl 5, which may be envisaged as a coalescence of the contributions of superimposed constituent pairs. Interestingly, site-occupancy refinement for the two components does not converge to 0.5:0.5 but, rather, 0.663 (5):0.337 (5) in favour of the '*trans*' component and was constrained ultimately to 2:1. However, whether this ratio implies any deeper significance is doubtful since at 299 K this occupancy became 0.52 (1) and was constrained at 0.5 in the final refinement. No disorder was observed in *tert*-butyl 3 and only one protonic hydrogen site was observed. These latter observations are of interest as they are at variance with the two previous room-temperature studies, which are, in turn, at variance with each other, suggesting that the history of the individual specimen may be of significance in determining its behavior in this regard.

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