Nitrogen Inversion in the Solid State: Characterization of a Conformational Process in Crystalline 1,3,5-Tribenzyl-1,3,5-triazacyclohexane by *X*-Ray Analysis at Several Temperatures

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The occupation of the axial and equatorial sites at the N atoms of crystalline 1,3,5-tribenzyl-1,3,5-triazacyclohexane changes with temperature, consistent with dynamic nitrogen inversion in the solid, below *ca.* 250 K the molecules adopting a single conformation, *eaa* (*e* = equatorial, *a* = axial), but at higher temperatures the equatorial component increasing markedly; from the *X*-ray results, ΔH° for the $a \rightleftharpoons e$ process is -54 kJ mol^{-1} for N(1) and 36 and 37 kJ mol^{-1} for N(3) and N(5), while ΔS° is -173 J K^{-1} mol^{-1} for N(1) and 121 and 118 J K^{-1} mol^{-1} for N(3) and N(5).

The crystalline state is generally considered to provide a rather rigid environment and there has been little investigation of conformational processes in single crystals. Barriers associated with conformational processes in the solid are expected to be substantially higher than in solution and only processes that have low barriers in liquids are likely candidates for investigation in solids. Among possible choices, inversion of configuration at tertiary nitrogen atoms has been extensively studied in the liquid phase; barriers to nitrogen inversion in saturated six-membered rings are small and it has been estimated that the upper temperature limit at which nitrogen inversion might be frozen out in the liquid is as low as *ca.* −150 °C.[1]

We chose to study 1,3,5-tribenzyl-1,3,5-triazacyclohexane (1,3,5-tribenzylhexahydro-1,3,5-triazine) in the solid state because (i) it has three nitrogen atoms at which inversion can occur, (ii) it is a low-melting solid (m.p. 50 °C),[2] suggesting that lattice forces are not particularly strong, and (iii) the planar phenyl groups are ideally suited for constrained refinement as rigid groups in crystal-structure analysis.[3] At room temperature (293 K) the crystal structure proved to be disordered with partial occupation of the equatorial and axial

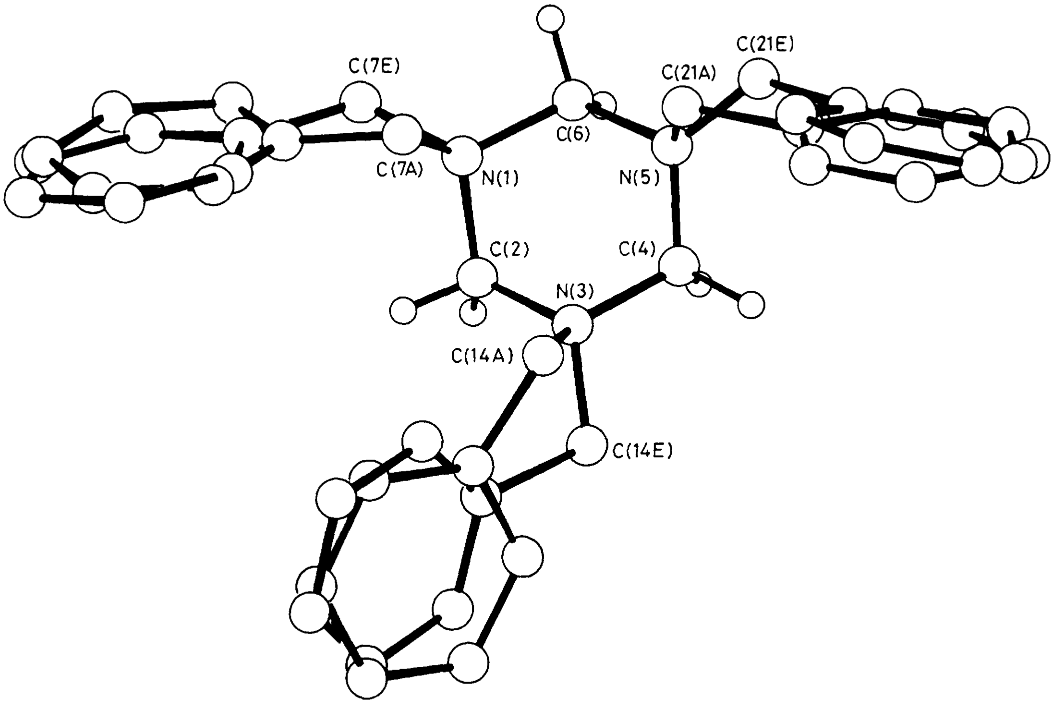

Figure 1. The conformationally disordered structure of 1,3,5-tribenzyl-1,3,5-triazacyclohexane at 293 K. The C and N atoms are represented by spheres of radius 0.15 Å and the H atoms of the central ring by spheres of radius 0.1 Å. The H atoms of the disordered benzyl groups are omitted.

substituent sites at all three nitrogen atoms (see Figure 1) and satisfactory convergence of the *X*-ray analysis was achieved with constrained refinement of the disordered phenyl groups.† The equatorial/axial populations at the N atoms, derived from the least-squares analysis, are shown in Table 1. The disorder can be attributed either to a static mixture of various conformers [N(1*a*)N(3*a*)N(5*e*); N(1*e*)N(3*e*)N(5*a*); N(1*e*)N(3*a*)N(5*a*); *etc.*; *e* = equatorial, *a* = axial] or to dynamic nitrogen inversion at each N atom. To discriminate between these possibilities we carried out *X*-ray studies of the compound at other temperatures.

On lowering the temperature of the crystal the cell dimensions and cell volume changed smoothly with no indication of a phase change; the β angle of the monoclinic cell, for example, increased from 109.0° at 293 K to 116.5° at 127 K. The crystal structure at 127 K, the lowest temperature investigated, proved to be ordered with a single conformer N(1*e*)N(3*a*)N(5*a*) present (Figure 2). At 250 K only traces of other conformations were present whereas at 268 K the disorder was pronounced with significant populations of the axial and equatorial sites at each nitrogen atom (see Table 1). The changes in the occupation of the axial and equatorial sites as the temperature is altered establish that nitrogen inversion is occurring in the solid at room temperature and immediately below.

The axial/equatorial populations in Table 1 yield equilibrium constants for the axial $\rightleftharpoons$ equatorial processes and knowledge of these at two or more temperatures allows values of ΔH° and ΔS° for the inversion process at each N atom to be calculated. The results are included in Table 1. The ΔH° and ΔS° values for N(3) and N(5) are similar but differ appreciably from the values for N(1). The differences presumably reflect the different crystal environments around the three nitrogen atoms.

At low temperatures a unique *eaa* conformer has been characterized and at higher temperatures there is an overall increase in the equatorial component. It is not possible to specify the precise mixture of molecular conformers (*eee, eea, eaa, aaa*) present at higher temperatures, but if it is assumed that *eee* and *aaa* can be disregarded because of repulsion between axial substituents in the latter and lone pairs of electrons in the former,[1] the temperature-dependent molecular process is *eaa* $\rightleftharpoons$ *eea* and the conformational composition is 100% *eaa* at 127 K, 92% *eaa* and 8% *eea* at 250 K, 74% *eaa*

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† *Crystal data:* $C_{24}H_{27}N_3$; $M = 357.53$, monoclinic, space group $P2_1/n$, $Z = 4$, Cu-K_α radiation, $\lambda = 1.5418$ Å. At 293 K, $a = 19.799(2)$, $b = 6.108(1)$, $c = 18.035(2)$ Å, $\beta = 109.01(2)°$, $U = 2062$ Å^3, 2229 reflections with $I > 2.5\sigma(I)$. At 268 K, $a = 19.982(4)$, $b = 6.034(1)$, $c = 18.039(3)$ Å, $\beta = 112.40(2)°$, $U = 2011$ Å^3, 2848 reflections with $I > 2.5\sigma(I)$. At 250 K, $a = 20.120(3)$, $b = 5.991(2)$, $c = 18.051(3)$ Å, $\beta = 114.71(2)°$, $U = 1977$ Å^3, 3172 reflections with $I > 2.5\sigma(I)$. At 127 K, $a = 20.181(3)$, $b = 5.926(2)$, $c = 17.930(3)$ Å, $\beta = 116.51(2)°$, $U = 1919$ Å^3, 3374 reflections with $I > 2.5\sigma(I)$.

At 127 K, direct phasing procedure (MITHRIL)[5] for structure solution, followed by least-squares refinement, $R = 0.037$, $R_w = 0.067$, with $w = \sigma^2(|F|)^{-1}$.

At 293 K, direct phasing for partial structure solution. Subsequent electron density calculations showed considerable disorder in the phenyl groups. Peaks for both *a* and *e* methylene C atoms at each N atom indicated that the phenyl disorder is caused by partial occupation of axial and equatorial sites. The three major phenyl groups were treated as rigid hexagons with C–C 1.38 Å, C–H 1.00 Å, ∠C–C–C 120°, and after least-squares refinement the major peaks in the residual electron density were assigned to the minor phenyl groups. In subsequent least-squares calculations all six phenyl groups were treated as rigid groups with ideal geometry as defined above and with the sum of the axial and equatorial occupations at each N atom constrained to unity. At convergence $R = 0.076$, $R_w = 0.062$, with $w = 1$. The disordered component of the crystal structure comprises 78% of the scattering matter.

The analyses at 250 K and 268 K used atomic co-ordinates from the 293 K and 127 K analyses as starting points and subsequent calculations were similar to those for the 293 K analysis. At convergence $R = 0.051$, $R_w = 0.051$, with $w = 1$ (250 K) and $R = 0.059$, $R_w = 0.045$, with $w = 1$ (268 K).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Axial/equatorial occupations and ΔH°, ΔS° for the axial (a) $\rightleftharpoons$ equatorial (e) process at each N site.

	N(1)		N(3)		N(5)	
Temp./K	*e*	*a*	*e*	*a*	*e*	*a*
293	0.769(6)	0.231	0.423(8)	0.577	0.271(12)	0.729
268	0.963(4)	0.037	0.199(5)	0.801	0.096(6)	0.904
250	1.000	0.000	0.052(4)	0.948	0.031(7)	0.969
127	1.000	0.000	0.000	1.000	0.000	1.000
ΔH°/k J mol^{-1}	−54(5)		36(3)		37(3)	
ΔS°/J K^{-1} mol^{-}	−173(18)		121(12)		118(12)	

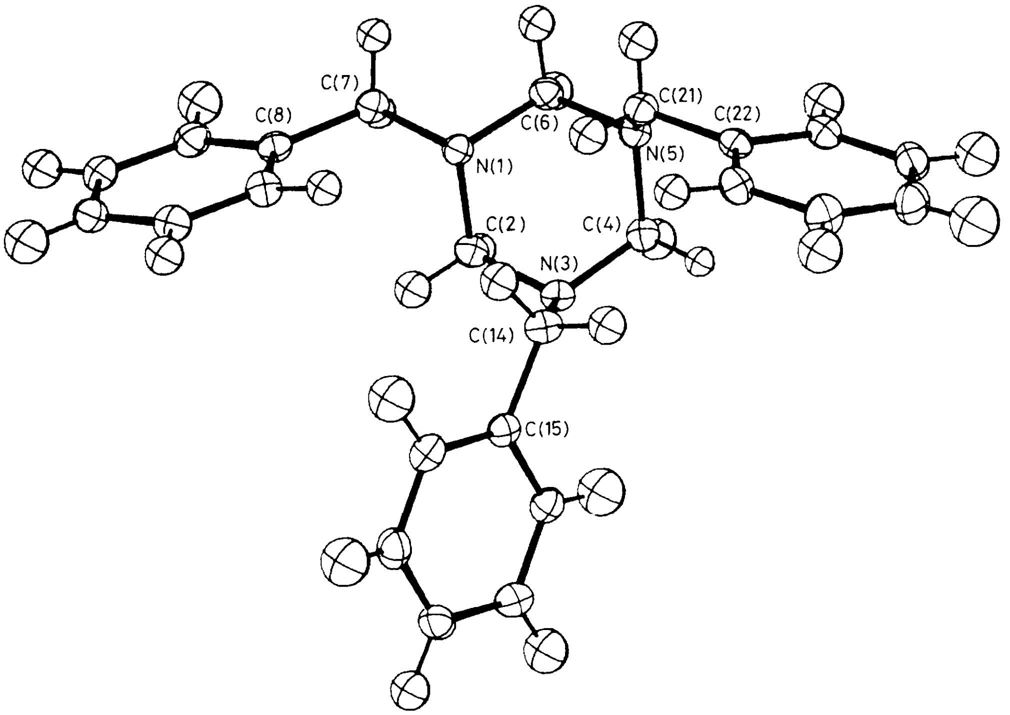

Figure 2. The ordered structure of 1,3,5-tribenzyl-1,3,5-triazacyclohexane at 127 K. The thermal ellipsoids of the C, N, and H atoms are drawn at the 50% probability level.

and 26% *eea* at 268 K, and 54% *eaa* and 46% *eea* at 293 K. At the m.p. (50 °C), the conformational composition is calculated to be 34% *eaa* and 66% *eea*.

In the axial $\rightleftharpoons$ equatorial interchange seen at higher temperatures, the methylene C atoms of the benzyl groups move *ca.* 1.4 Å. The phenyl group at each methylene C, on the other hand, is dragged a smaller distance, the C(8*e*) $\rightleftharpoons$ C(8*a*), C(15*e*) $\rightleftharpoons$ C(15*a*), and C(22*e*) $\rightleftharpoons$ C(22*a*) separations being *ca.* 0.6 Å.

Several *X*-ray studies have dealt with the re-orientation of molecules in single crystals[4] but there does not appear to be a previous *X*-ray investigation of an axial $\rightleftharpoons$ equatorial conformational process in the solid state. Additional 1,3,5-triazacyclohexane derivatives are being examined for comparison with the tribenzyl compound.

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