Non-planar structures of $\mathrm{Et_3N}$ and $\mathrm{Pr^i{}_3N}$: a contradiction between the X-ray, and NMR and electron diffraction data for $\mathrm{Pr^i{}_3N}$

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The crystal structures of $\mathrm{Et_3N}$ and $\mathrm{Pr^i{}_3N}$ were determined by X-ray analysis using the *in situ* crystallization technique for single crystal growth on the diffractometer; both have a pyramidal configuration of the nitrogen atom, even $\mathrm{Pr^i{}_3N}$, which was considered to be planar in accord with electron diffraction and NMR data.

Aliphatic amines represent an important class of compounds widely used in organic chemistry. One of the dominant characteristics of saturated amines is that in the absence of steric congestion their ground state is pyramidal, whereas the exited state is planar. Sterically hindered tertiary amines are particularly interesting in this respect because strong steric effects of substituents can be used to change the geometry around the nitrogen atom. The stereodynamics of simple tertiary amines has been the subject of a few reviews[1] and original publications.[2–9] Most of these studies dealt with investigations into the dynamics of the inversion-rotation processes in amines and/or energetic molecular mechanics and quantum calculations.[9b]

The molecular structures of $\mathrm{MeNH_2}$, $\mathrm{Me_2NH}$, $\mathrm{Me_3N}$ and $\mathrm{Me_2EtN}$ were studied by the gas electron diffraction (GED) and microwave techniques,[10] $\mathrm{Me_3N}$ was also studied in the solid state.[11] All compounds have pyramidal configuration around the nitrogen, with C–N–C angles of 110.4–111.8° and C–N lengths of 1.451–1.471 Å $\mathrm{(CF_3)_3N}$.[12] has a larger C–N–C angle [117.9(4)°] and a shorter C–N length [1.426(6) Å]. The GED and theoretical studies of $\mathrm{Et_3N}$ showed[13] that it exists as a mixture of three conformers with C_3, C_s and C_1 symmetry having very similar energies [angle around N = 112.6(26)°, N–C = 1.466(1) Å]. The structure of the partially fluorinated analogue, $\mathrm{(CH_2CF_3)_3N}$, was studied *via* GED and X-ray analysis.[14] The GED investigation[15] of $\mathrm{(CF_2CF_3)_3N}$ detected only one conformer having C_3 symmetry with almost planar configuration around the nitrogen atom (C–N–C = 119.3°) and rather a long C–N bond length [1.482(7) Å].

Amongst all known structures of noncyclic trialkylamines there is only one other example where a planar configuration around nitrogen was assumed. This is a GED study of $\mathrm{Pr^i{}_3N}$ by Bock *et al.*[16] [C–N–C = 119.2(3)°, C–N = 1.460(5) Å, C_3 symmetry with C–N–C′–H′ = 5.0(18)°.] Although these data are mostly in line with NMR studies of this compound in solution and in the solid state,[2,7] there are some contradictions with the results of quantum chemical calculations of its molecular structure.[9] Thus, AM1 and PM3 methods predict a nonplanar structure (C–N–C = *ca.* 116.3°) with rather small inversion barriers. In contrast, STO-3G, 3-21G and 6-31G calculations predict a planar structure, while a 6-31G** calculation yields a nearly planar structure (bond angle at N = 119.01°).

Here we compare the X-ray crystal structure of $\mathrm{Me_3N}$ **1**[11] with those of $\mathrm{Et_3N}$ **2** and $\mathrm{Pr^i{}_3N}$ **3**, the latter two being reported here for the first time; for **1** we present a redetermination based on data which covers a wider 2θ range and twice as many unique reflections.§

In the crystal structure of **1**, the pyramidal molecules have effective $C_{3\mathrm{v}}$ symmetry.[11] Those C–H bonds which have an *anti* orientation with respect to the N atom lone pair have a slightly longer bond length [0.997(10) Å] in comparison with the two others [0.959(18) and 0.957(11) Å], which may be attributed to the hyperconjugation effect. Geometrical parameters around the N atom in the crystal [C–N–C = 110.7(1)°, height of N pyramid = 0.450 Å and C–N = 1.448(1) Å] almost coincide with those in the gas phase (110.6° and 1.451 Å)[9] and the previous X-ray determination (110.4° and 1.454 Å). The charge density distribution (Fig. 1), using a quasi-high-order refinement with the Seiler and Dunitz weight scheme,[17] contains the DED maximum at the nitrogen lone pair position at a distance about 0.58 Å from its nuclei, as well as DED peaks at the N–C and C–H bonds. The DED maximum at the N–C bond is slightly shifted from the N–C line inside the $\mathrm{NC_3}$ tetrahedron, which may reflect bending of this bond due to repulsion between the electron density of the lone pair and the covalent N–C bond. Very similar bond bending was found in crystals of $\mathrm{NH_3}$.[18]

The crystal structure of $\mathrm{Et_3N}$ **2** is characterized by a rather complicated disorder phenomenon related with the crystallographic m-plane passing through the nitrogen and Me C(1) atoms, such that each $\mathrm{CH_2}$ group has two distinguishable orientations in the crystal, while the carbon atoms of the Me groups have only one position with differing orientations of their hydrogens. The nitrogen has the usual pyramidal configuration [C–N–C = 107.9–112.1(1)°, height of N pyramid = 0.467 Å, and C–N = 1.422–1.497(2) Å; their relatively large scatter is related to the disordering]. As expected, the orientation of all Me groups with respect to the N atom lone pair was found to be *gauche*. We cannot exclude, however, the possibility that the complicated crystal disordering in **2** may be a result of some crystal twinning that was not resolved.

X-Ray diffraction data for $\mathrm{Pr^i{}_3N}$ **3** were collected at 203, 168, 118 and 84 K in order to reveal the nature of the structural disordering. The crystals are hexagonal, space group $P6_3/m$, Z = 3, and no indication of a phase transition was found in the temperature interval studied. The structure was solved and refined first at 203 K in this space group with the strictly planar

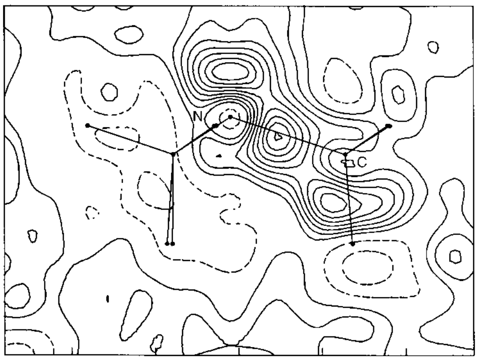

Fig. 1 Deformation electron density in the plane of the three-fold axis and N–C bond. Positive and negative contours are given through 0.025 and −0.05 e Å^{-3}, negative contours dashed.

configuration around the N atom in the special position $\bar{6}$ (2/3, 1/3, 1/4). In accord with this symmetry, the central C and methine H atoms of the Pr^{i} groups must be in the crystallographic m-plane together with nitrogen, while two Me groups of each Pr^{i} substituent are above and below this plane and perpendicular to it. The refinement of this model, however, resulted in an unreasonably large U_{33} component of the nitrogen thermal ellipsoid, indicating some kind of disordering, therefore its position was split into two 'halves' below and above the m-plane with a distance of 0.529(8) Å between them. This model was found to be more significant than the previous one and resulted in 'normal' thermal ellipsoids of all atoms and a nonplanar geometry around nitrogen (Table 1). Because these data alone could not give an answer about the nature of the crystal disordering (whether it is dynamic and related to the inversion of the N atom in the crystal, or it is static and the crystal structure represents a superposition of two pyramidal molecules having so-called 'crystal-imposed' symmetry), additional diffraction data at 168, 118 and 84 K were analyzed. We expected that in the case of a dynamic disorder a lowering of the temperature would result in a proportional decrease of the nitrogen thermal ellipsoid (mostly of its U_{33} component), but even at 84 K this ellipsoid still was very large (Fig. 2) and the split model with two 'halves' of the nitrogen atom was found to be significant. These additional data therefore give a definite proof of the pyramidal structure of Pr$^{i}_{3}$N in the crystal and the static nature of the disordering.

Our X-ray data for Pr$^{i}_{3}$N to a certain extent contradict earlier GED and NMR measurements[2,7,16] but they agree well with AM1, PM3 and *ab initio* calculations[9] giving a nonplanar structure for this molecule. However, we cannot totally exclude the possibility that the nonplanar structure of **3** may be enhanced by the crystal field effect. On the other hand, for tricyclopropylamine[19] which has the same spatial requirements as Pr$^{i}_{3}$N, effective C_s symmetry was found, it was not planar (height of N pyramid = 0.467 Å with C–N–C = 110°) and it is not disordered,[20] thus being very similar to Me$_3$N. In all three structures the intermolecular contacts are significantly larger than the sum of van der Waals radii (H···H > 2.75 Å). In comparison with the structures of **1** and **2**, the height of the N atom pyramid in **3** is the smallest (0.27–0.29 Å) and the inversion barrier is probably not very high.

Table 1 Geometry of Pr$^{i}_{3}$N in the crystal at different temperatures

Parameter	203 K	168 K	118 K	84 K
Bond length/Å				
N–C(1)	1.461(2)	1.468(1)	1.469(1)	1.469(1)
C(1)–C(2)	1.511(2)	1.519(1)	1.520(1)	1.522(1)
N–N′	0.529(8)	0.543(4)	0.564(3)	0.583(3)
Bond angle (°)				
C(1)–N–C(1′)	116.8(1)	116.7(1)	116.4(1)	116.2(1)
N–C(1)–C(2)	122.3(2)	122.5(1)	122.8(1)	123.0(1)
N–C(1)–C(2A)	103.8(2)	103.6(1)	103.2(1)	102.7(1)
C(2)–C(1)–C(2A)	109.8(2)	109.8(1)	109.7(1)	109.8(1)

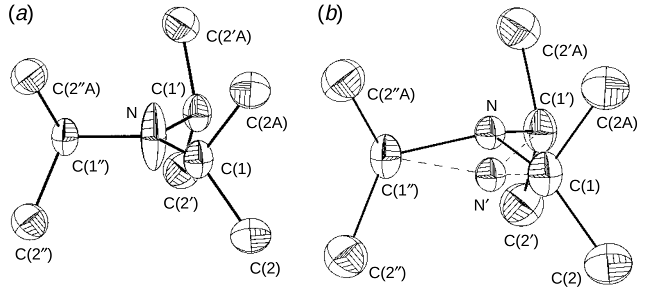

Fig. 2 View of Pr$^{i}_{3}$N in the crystal at 84 K (H atoms are not shown): (*a*) N atom in the special position $\bar{6}$ (2/3, 1/3, 1/4) and (*b*) split model with two 'halves' of the pyramidal N below and above the m-plane

Notes and References

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§ *Crystal data* for **1**: C$_3$H$_9$N, trigonal, space group $P\bar{3}$, T = 143 K, a = 6.143(1), c = 6.979(2) Å, V = 228.10 Å^3, Z = 3, 2767 measured reflections $2\theta_{\max}$ = 80°, 944 unique and 570 observed unique reflections with $F_o > 4.0\ \sigma(F)$, 25 parameters, R = 0.0454, Rw = 0.0687.

For **2**: C$_6$H$_{15}$N, orthorhombic, space group *Pnma* ($Pna2_1$ was excluded by parallel refinements, giving the same type of disorder) T = 138 K, a = 7.337(1), b = 11.797(2), c = 8.470(2) Å, V = 733.1(3) Å^3, Z = 4, 1958 measured reflections $2\theta_{\max}$ = 60°, 757 observed unique reflections with $F_o > 4.0\ \sigma(F)$, 56 parameters, R = 0.0506, Rw = 0.0534.

For **3** (ref. 19): C$_9$H$_{21}$N, hexagonal, space group $P6_3/m$ (removing the mirror plane and refinement at all temperatures with a fully occupied N atom in $P6_3$, starting at a position of the split atoms, resulted in the same picture as for $P6_3/m$), Z = 3, data collection at T = 203 K, 168, 118 and 84 K with the total number of the collected reflections = 1786, 2253, 4217 and 3269, respectively, up to $2\theta_{\max}$ = 50, 60 and 80° (at 118 and 84 K), the number of unique observable reflections with $F_o > 4.0\ \sigma(F)$ = 270, 422, 640 and 769, 35 refined parameters, refinement at 203 and 84 K to R = 0.037 and 0.042, Rw = 0.087 and 0.060. At 203 and 84 K, a = 7.200(1) and 7.138(2), c = 11.460(2) and 11.365(2) Å, V = 514.5(1) and 501.5(2) Å^3. All single crystals were grown *in situ* on the diffractometer using a zone-melting crystallization technique (ref. 21). Measurements were performed on a Nicolet R3m/V diffractometer using Mo-Kα-radiation, graphite monochromator and the Wyckoff scan method. All calculations were made with the SHELX program package. CCDC 182/762.

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Received in Cambridge, UK, 21st November 1997; 7/08399H