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A helical structure with $Z' = 10$

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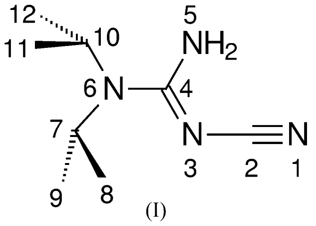
The structure of *N*″-cyano-*N*,*N*-diisopropylguanidine, a push–pull nitrile that includes the $H_2N-C{=}N-CN$ fragment, has been determined. Although the number of molecules in the asymmetric unit is exceptionally high ($Z' = 10$), there were no special crystallographic difficulties associated with data collection, structure solution or structure refinement because the individual molecules are small (12 non-H atoms) and because there is no important crystallographic pseudosymmetry. A complete set of N—H⋯N bonds is formed. Pairs of molecules form dimers, which associate to form ribbons that twist into a helix having five dimers per turn. The helices lie parallel to [101] and fit together with close contacts in three different directions perpendicular to that axis. The problems with optimizing so many different intermolecular contacts lead to a loosely packed structure.

1. Introduction

The structure of *N*″-cyano-*N*,*N*-diisopropylguanidine, a synthetic precursor to the corresponding guanidinobenzimidazole derivative, was undertaken as part of a project on the competition between intra- and intermolecular hydrogen bonding in guanidinobenzimidazole (Chen *et al.*, 2005). The structure turned out to be so unusual that it warranted a careful look.



(I)

The space group ($P2_1/c$) is unremarkable, but the number of molecules in the asymmetric unit ($Z' = 10$) is exceptionally high (Brock & Dunitz, 1994; Steed, 2003). In past studies of high-Z' structures (Koutentis *et al.*, 2001; Duncan *et al.*, 2002; Lehmler *et al.*, 2002, 2004) we have always been able to uncover a good reason for the large size of the asymmetric unit. We have found that large values of Z' are usually associated with an identifiable packing problem or conflict.

The structure of the isomer related by exchange of one H atom on N5 and one isopropyl group on N6, *i.e.* *N*″-cyano-*N*,*N*′-diisopropylguanidine (hereafter the *N*,*N*′ isomer), is known [Chen *et al.*, 2005; refcode MAFZUP in the Cambridge Structural Database (Allen, 2002; hereafter the CSD)]. The *N*,*N*′ isomer has a similar but not identical pattern of N—

H···N bonds as the *N*,*N* isomer, but crystallizes in $P2_1/c$ with $Z' = 1$.

2. Crystal structure determination

Crystals (m.p. 410 K) grow from chloroform at room temperature as rectangular parallelepipeds; they are longest along [101] and the normal to the largest face is ($\bar{1}$01). Crystals were also grown from ethyl acetate at room temperature and from 1:1 hexane/ethyl acetate solutions at *ca* 253 K. All crystals were either rectangular parallelepipeds or smaller needles. Several of each habit were indexed; all gave the same unit cell.

Despite the large value of Z' there were no special problems associated with data collection or processing, or with structure solution, because the total number of non-H atoms (12 × 10 = 120) is moderate and because there is no important crystallographic pseudosymmetry. The refinement (see Table 1 and the deposited material[1]) was also straightforward. The atoms of each molecule are numbered as shown in (I); the different molecules are labeled according to the residue-numbering scheme available in *SHELXL*97 (Sheldrick, 1997*b*). Under that scheme the N3 atom of molecule 5 has the label N3_5. The molecules are numbered sequentially as they occur in the helix of dimers (see Fig. 1).

The only disordered atoms are those of the second isopropyl group of molecule 3, although the ellipsoids for some of the other isopropyl groups are relatively large. Refinement of two sets of atoms for molecule 3 (C10_3 and C10′_3, C11_3 and C11′_3, and C12_3 and C12′_3) with the restraint SAME gave acceptable bond lengths and angles,

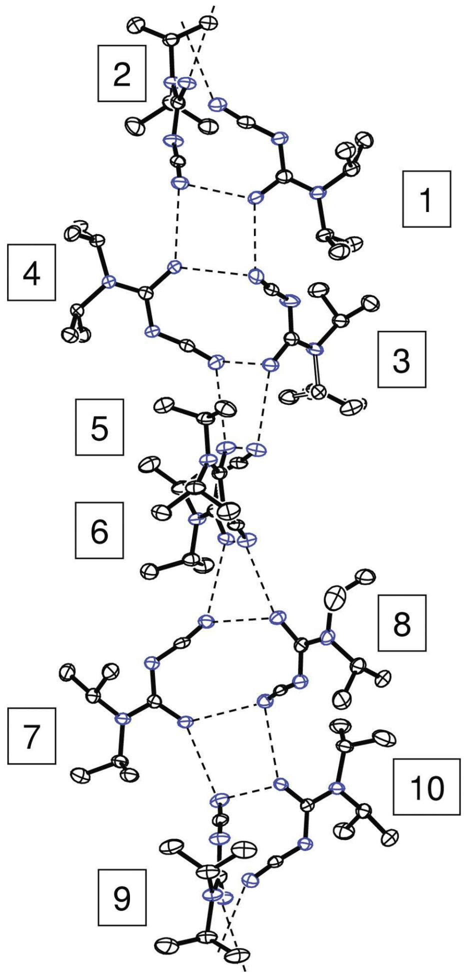


Figure 1
Perspective drawing of the asymmetric unit. Ellipsoids have been drawn at the 50% probability level and H atoms have been omitted. The residue number for each molecule is shown; the numbers of the individual atoms can be worked out by referring to the chemical line drawing. One of the pseudo-twofold axes lies horizontally in the plane of the drawing between molecules 5 and 6.

Table 1
Experimental data.

Crystal data	
Chemical formula	$C_8H_{16}N_4$
M_r	168.25
Cell setting, space group	Monoclinic, $P2_1/c$
a, b, c (Å)	20.247 (2), 18.212 (2), 27.665 (3)
β (°)	102.94 (4)
V (Å^3)	9942.30 (18)
Z	40
D_x (Mg m^{-3})	1.124
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	40 263
θ range (°)	1.0–27.5
μ (mm^{-1})	0.07
Temperature (K)	90.0 (2)
Crystal form, color	Thick plate, colorless
Crystal size (mm)	0.40 × 0.30 × 0.20
Data collection	
Diffractometer	Nonius KappaCCD
Data collection method	1.2° ω scans at fixed χ = 55°
Absorption correction	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.972
$T_{\max}$	0.986
No. of measured, independent and observed reflections	60 120, 17 510, 10 748
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.073
$\theta_{\max}$ (°)	25.0
Range of *h, k, l*	$-24 \Rightarrow h \Rightarrow 24$ $-21 \Rightarrow k \Rightarrow 21$ $-32 \Rightarrow l \Rightarrow 32$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.131, 1.00
No. of reflections	17 510
No. of parameters	1206
H-atom treatment	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.29, −0.21

Computer programs used: *COLLECT* (Nonius, 1999), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *XP* in Siemens *SHELXTL* (Sheldrick, 1994), *Mercury* (Bruno *et al.*, 2002) and local procedures.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM5021). Services for accessing these data are described at the back of the journal.

Table 2
Distances (Å) and angles (°) averaged over the ten independent molecules.

The penultimate column gives the average uncertainty for an individual value; the last column gives the maximum deviations from the average value.

Atom 1	Atom 2	Average distance	Average s.u.	Range w.r.t. average
N1	C2	1.165 (1)	0.002	+0.005, −0.005
C2	N3	1.309 (1)	0.003	+0.004, −0.007
N3	C4	1.341 (1)	0.002	+0.004, −0.002
C4	N5	1.341 (1)	0.002	+0.006, −0.008
C4	N6	1.344 (1)	0.002	+0.007, −0.005
N6	C7	1.488 (1)	0.002	+0.005, −0.008
N6	C10†	1.484 (1)	0.002	+0.004, −0.006
C7	C8	1.522 (2)	0.003	+0.009, −0.008
C7	C9	1.522 (1)	0.003	+0.004, −0.006
C10	C11†	1.522 (2)	0.003	+0.007, −0.008
C10	C12†	1.516 (3)	0.003	+0.006, −0.016

Atom 1	Atom 2	Atom 3	Average angle	Average s.u.	Range w.r.t. average
N1	C2	N3	173.2 (2)	0.2	+1.1, −0.8
C2	N3	C4	120.2 (3)	0.2	+2.1, −0.9
N3	C4	N5	121.9 (2)	0.2	+1.1, −0.6
N3	C4	N6	117.1 (1)	0.2	+0.7, −0.7
N5	C4	N6	121.0 (1)	0.2	+0.6, −0.7
C4	N6	C7	121.2 (1)	0.2	+0.4, −0.9
C4	N6	C10†	122.0 (2)	0.2	+0.5, −0.9
N6	C7	C8	113.3 (3)	0.2	+0.8, −1.4
N6	C7	C9	112.6 (2)	0.2	+0.7, −0.8
C7	N6	C10†	116.5 (1)	0.2	+0.6, −0.5
N6	C10	C11†	111.2 (2)	0.2	+0.7, −0.8
N6	C10	C12†	111.3 (2)	0.2	+0.7, −0.7
C8	C7	C9	112.9 (1)	0.2	+0.6, −0.7
C11	C10	C12†	111.7 (2)	0.2	+0.6, −1.7

† Value(s) for molecule 3 omitted.

tolerable ellipsoids and an occupancy factor for C10_3 of 0.598 (7). The ellipsoid for N6_3 is elongated in a way that suggests that the position of N6_3 depends on the orientation of the attached isopropyl group.

Initially the H atoms were all placed in calculated positions (AFIX 13, 137 and 93 for the CH, CH_3 and NH_2 groups); the U values were set to the $U_{\rm iso}$ for the attached atom times 1.5 (for the methyl groups) or 1.2 (for the $-CHMe_2$ and $-NH_2$ groups). The positions calculated for the H atoms attached to the amino group (N5_*n*) cannot be quite correct because all the H10_*n*···H5*A*_*n* distances (1.71–1.93 Å) are short and some are very short. In the final cycles the coordinates of the H5*A*_*n* and H5*B*_*n* atoms were varied under restraints (FLAT and SADI) designed to keep the CNH_2 fragment planar and to keep all N—H distances and all H—N—H angles the same. The final N—H distances are all 0.88 or 0.89 Å, and the C—N—H angles are in the range 117–127°. Ten of the H10_*n*···H5*A*_*n* distances are reasonably satisfactory (1.84–1.97 Å), but the distance for the minor component of disordered molecule 3 is still short (1.74 Å). Refinements with fewer restraints gave results we considered less acceptable.

The absolute values of the correlation coefficients for the final cycle are all below 0.35 except for those coefficients involving the H atoms attached to N5_*n* (values as high as 0.64) and the atoms of the disordered isopropyl group (values as high as 0.84).

The average values of the bond lengths and angles are given in Table 2. The excellent agreement between the ten (or, in some cases, nine) independent values is noteworthy.

The data are generally weak [only 62% of the reflections measured to $\sin\theta/\lambda = 0.595$ Å^{-1} at 90 (2) K have $I > 2\sigma(I)$], but there is no simple class of weak reflections because there is no important crystallographic pseudosymmetry.

3. Results

3.1. Molecular geometry

The ten molecules are very similar except for the torsion angles involving the isopropyl groups. The ten molecules were overlaid at six match points (all non-H atoms except those in the two isopropyl groups) using Version 2.1 of the program *CrystMol* (Duchamp, 2004). The fit (see Fig. 2) for those six points is excellent (r.m.s. deviation 0.057 Å). The torsion angles N3—C4—N6—C7 or N5—C4—N6—C7 look (see Fig. 2) as if they form a regular progression [from −18 (1) to +11 (1)°] that might be associated with a structural modulation, but the order of the molecules (7, 2, 6, 1, 4, 5, 9, 10, 3, 8) shows no obvious pattern. In any event the r.m.s. deviation for a fit of eight points (C7 and C10 included) is 0.105 Å and for all 12 non-H atoms (minor component of disordered molecule 3 omitted) is 0.179 Å.

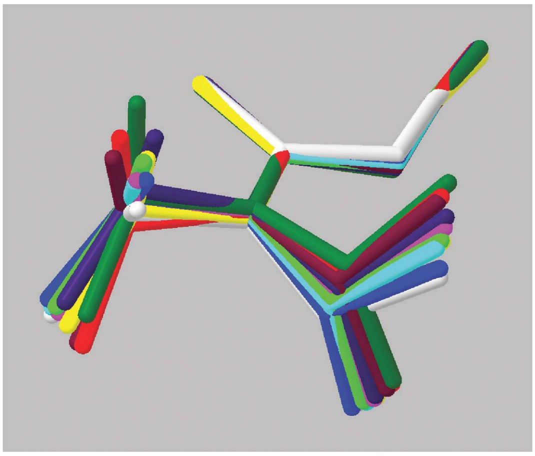
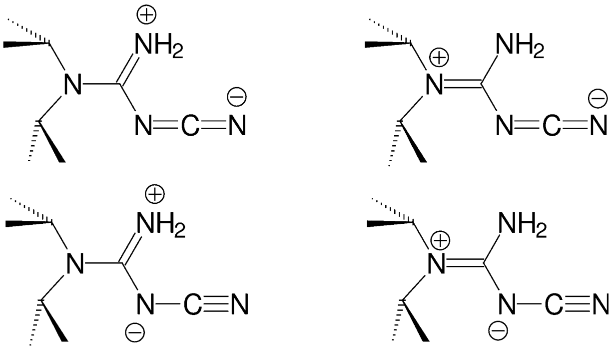


Figure 2
Superposition of the ten independent molecules calculated and drawn using Version 2.1 of the program *CrystMol* (Duchamp, 2004). The color codes are the same as in Fig. 3. The minor component of disordered molecule 3 has been omitted.



(II)

The essential equality of the three distances around C4 (see Table 2) shows that the resonance forms with C4—N5 and C4—N6 as double bonds [see (II)] are important. The N—H···N bonding pattern (discussed below) indicates that the resonance forms with charge localized on N3 [see lower two resonance forms in (III)] are unimportant, as was expected. The N1—C2 bond is slightly elongated as is typical in push–pull nitriles (Ziao *et al.*, 2001).

There are no important differences between the bond lengths and angles in this compound and in its *N*,*N*′ isomer (Chen *et al.*, 2005).

The N3—C2—N1 angle differs from 180° by nearly 7°; a similar distortion (7.9°) is found in the *N*,*N*′ isomer. The bending of the N—CN group allows the two N1 atoms in the dimer to be farther apart than they would be if this angle were not distorted. It is also possible, however, that the angular distortions are associated with the hydrogen bonding because the N1_*n*···N1_*n*′ distances (3.374–3.574 Å) are substantially longer than twice the van der Waals radius of an N atom (2 × 1.55 = 3.10 Å; Bondi, 1964).

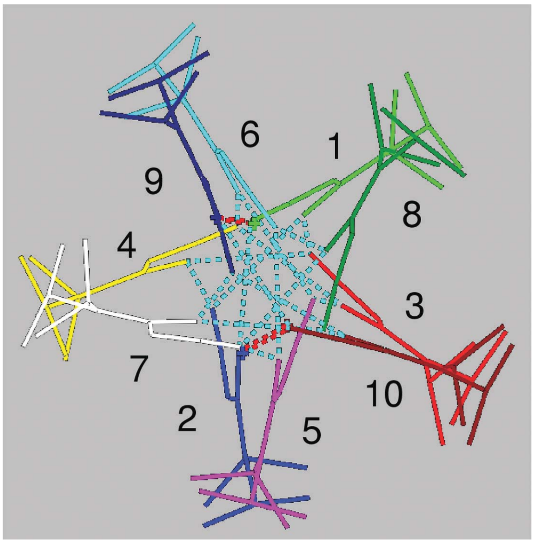


Figure 3
A projection of the asymmetric unit as viewed along [101]. The residue numbers of the individual molecules are shown. The axes are the same as in Fig. 4. The colors are the defaults assigned by the program *Mercury* (Bruno *et al.*, 2002).

3.2. Hydrogen bonding

The Z' value of ten occurs because pairs of molecules form dimers that are linked together to form ribbons, which twist to form helices with five dimers per turn (see Figs. 1 and 3). The approximate symmetry of the helices is that of the rod groups $p5_122$ and $p5_422$; the approximate twofold axes pass through the centers of the N—H···N-bonded dimers. The helix axes are parallel to [101] (see Fig. 4), which explains why this direction of the crystal grows fastest. If the transformation (101/010/$\bar{1}$00) is applied to the $P2_1/c$ cell then the helices are parallel to the new vector **a** and the space group becomes $P2_1/n$.

3.2.1. N···N distances. The N···N distances found in this study are typical of the hydrogen bonds found in push–pull nitriles (Ziao *et al.*, 2001). The two kinds of N—H···N bonds (those within and those between dimers) seem to be equally strong. For the $R_2^2(10)$ dimers (notation as in Bernstein *et al.*, 1995) the range of N···N distances is 2.942–3.072 Å, with an average of 3.018 (15) Å; for the $R_4^4(8)$ rings between dimers the range and average are 2.911–3.064 and 3.005 (15) Å.

Dimers are also formed in the *N*,*N*′ isomer (refcode MAJZUP); the N···N distance (2.986 Å) in the *N*,*N*′ isomer is not significantly different from that in the *N*,*N* isomer. The length of the other short N···N distance (3.021 Å) in the *N*,*N*′ isomer is also similar. The dimers in the structures of the two isomers are linked together in different ways, however, because in the *N*,*N* isomer each of the four N atoms in the $R_2^2(10)$ ring is involved in two N—H···N bonds, while in the *N*,*N*′ isomer each of the amino N atoms of the dimer is involved in only one N—H···N bond. In the *N*,*N*′ isomer the second amino donor is not part of the dimer, but does link to an $R_2^2(10)$ ring in an adjacent molecule. The overall structure

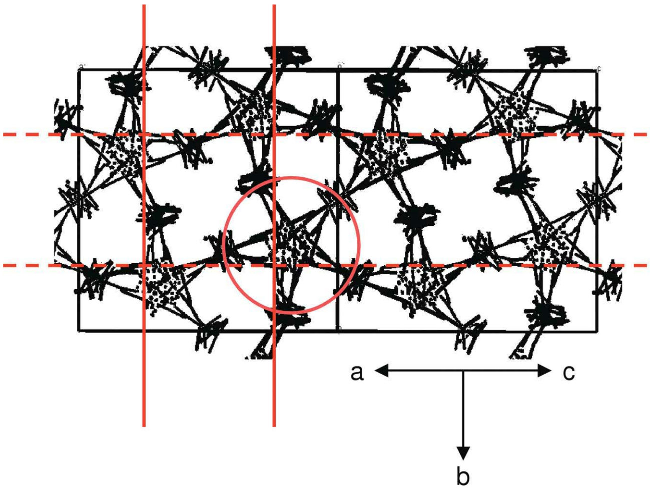


Figure 4
Crystal packing as viewed along [101]. The H atoms have been omitted. The asymmetric unit is marked by a circle. The traces of the glide planes (horizonal) and the positions of the 2_1 axes (vertical) are shown.

of the N,N' isomer has a two-dimensional network of linked dimers, but has no direct dimer$\cdots$dimer link.

3.2.2. Hydrogen bonding in other push–pull nitriles. A search of the CSD [Allen, 2002; version 5.25 (November 2003) plus updates of January, April and July 2004] for structures containing an $H_2N—C{=}N/C—CN$ [where N/C means that either an N or C atom may be present] fragment gave over 250 hits, which were examined with the program *Mercury* (Bruno *et al.*, 2002). A full set of N—H$\cdots$N bonds was found in only one hit[2] (TADHUB; Dyachenko *et al.*, 1989) and several of the bonds in TADHUB are long [N$\cdots$N distances 2.991 and 3.113 Å in $R_2^2(10)$ rings, and 3.185 and 3.245 Å in $R_4^4(8)$ rings]. The full set of N—H$\cdots$N bonds found in the $Z' = 10$ structure reported here (and in the N,N' isomer MAFZUP, which was not entered into the CSD until 2005) is very unusual for the fragment $H_2N—C{=}N/C—CN$.

3.2.3. Comparisons with *vic*-diols. Hydrogen-bond patterns for the fragments $H_2N—C{=}N/C—CN$ might be expected to be similar to those for HO—C—C—OH (Brock, 2002), HO—C=C—OH and $HO—C_{ar}—C_{ar}—OH$, because both sets of fragments have two hydrogen-bond donors and two acceptors in close proximity and pointing in similar directions. The ribbon, or ladder, pattern of N—H$\cdots$N bonding found in the title compound is indeed similar to an O—H$\cdots$O pattern that is quite common for *vic*-diols that are not sterically hindered. There are, however, important differences between the two kinds of patterns (see Fig. 5). In the *vic*-diols each O atom in the dimer donates a proton and accepts a proton, while in $H_2N—C{=}N/C—CN$ compounds each N atom of the dimer either donates two or accepts two protons. The locations of the lone pairs differ as well. If the $N/C—C{\equiv}N$ moiety is described at least to some extent by the resonance form $N/C{=}C{=}N$, then the lone pairs on the terminal N atom are located above and below the fragment plane, as is shown in Fig. 5. No lone pair points to the side of the dimers, as is the case in the diols.

3.2.4. Arrangement of molecules in the dimer. If both of the lone pairs on the cyano N atom accept protons, then the two hydrogen-bond donors should approach the cyano N atom from opposite sides of the $N_2C{=}N—CN$ plane (see Fig. 5). This preference is obvious, for example, in the structure of the N,N' isomer. The cyano acceptors, however, must approach the $—NH_2$ group, from directions coplanar with the $N_2C{=}N—CN$ plane because rotation of the amino group out of that plane would decrease the resonance stabilization energy of the molecule.

The molecules in the *vic*-diol dimers are most often related by a real or approximate inversion center (Brock, 2002), but inversion symmetry is less favorable in $H_2N—C{=}N/C—CN$ dimer ribbons because the preferred directions of approach of amino dimers discussed above require a large N$\cdots$HNH$\cdots$N$\cdots$HN torsion angle for the donors and acceptors that are part of an $R_4^4(8)$ ring. If that torsion angle is large then the distance between the extra-dimer donor and acceptor must also be too large for the formation of a dimer ribbon.

In a few *vic*-diol structures the two molecules of the dimer are related by a twofold axis within the $R_2^2(10)$ ring or perpendicular to it. The perpendicular arrangement, which is seen here (approximately), is favorable for the $H_2N—C{=}N/C—CN$ structures because it allows the N$\cdots$HNH$\cdots$N$\cdots$HN torsion angle discussed in the previous paragraph to be much smaller than if the two molecules were related by an inversion center. In this structure the range of the ten N$\cdots$HNH$\cdots$N$\cdots$HN torsion angles is 18–41°.

3.2.5. Role of the isopropyl substituents. If the dimer ribbons in this structure were flat, as they often are in the *vic*-diol structures, then the isopropyl substituents in adjacent dimers would interfere. Rotations around the C4—N6 bonds might relieve the steric crowding, but only at the expense of resonance stabilization energy.

3.2.6. Caveat. The lone-pair positions shown in Fig. 5 are only an approximation. In the *vic*-diols the proton often approaches what would seem to be the region between the two lone pairs, which is possible because the two lone pairs need accept only one proton. In the compound reported here, however, the nitrile N atom must accept two protons. Doing so would seem impossible if the resonance form shown at the top

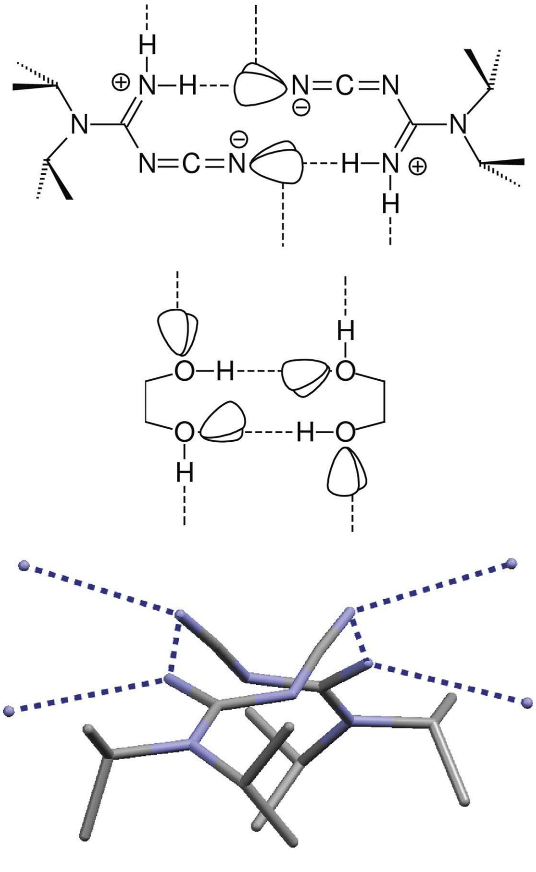


Figure 5
Diagrams of the dimers formed in this structure and of a typical dimer formed by a *vic*-diol. A drawing of the dimer formed by molecules 1 (on top) and 2 is also shown.

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[2] The structure of the N,N' isomer, which also has a full set of N—H(N bonds, has not yet been archived in the CSD.

Table 3
$Z' \geq 10$ structures found in the CSD that seem to be reliable.

REFCODE	Z'	Space group	T (K)	R
ASAPEP[a]	10	$P2_1/a$	93	0.058
BIPCOS01[b]	16	$P1$	RT	0.070
CHOEST21[c]	16	$P1$	310	0.064
HEYHUO02[d]	12	$P\overline{1}$	140	0.118
HUVLAL[e]	18	$P\overline{1}$	155	0.067
IDOSID[f]	24	$P1$	110	0.052
NIKZUC10[g]	16	$P3_2$	173	0.072
TRIMES10[h]	12	$P1$	RT	0.112
WODCOH[i]	11	$P2_1/a$	193	0.042

References: (*a*) Osako *et al.* (2004); (*b*) Brückner (1982); (*c*) Hsu *et al.* (2002); (*d*) Kumar *et al.* (2002); (*e*) Fujdala *et al.* (2003); (*f*) Hou *et al.* (2001); (*g*) Hassaballa *et al.* (1998); (*h*) Herbstein & Marsh (1977); (*i*) Jacobsen *et al.* (2000).

of Fig. 5 were not important. This structure is a good example of resonance-assisted hydrogen bonding (Gilli *et al.*, 1989).

The N—H···N bonds within the dimer have directions that are reasonably consistent with a classical description of the lone-pair orbitals (see Fig. 5), but the inter-dimer N—H···N bonds, which are equally short, would seem to require that at least one of the lone pairs be shifted to the side.

3.2.7. Formation of helices. If there is an approximate twofold axis through the middle of the dimer and if the two hydrogen bonds to the adjacent dimer are not parallel (as they are not; see Fig. 5), then the dimers within the ribbon cannot be related by any improper symmetry operation. The ribbon must be helical. The remaining question concerns the number of dimers per turn of the helix. A larger number of dimers per turn means a smaller twist between dimers, but usually also means a larger number of independent molecules in the asymmetric unit. It is unlikely that the compromise observed, which is also influenced by inter-helix interactions, could have been predicted.

3.3. Helix geometry and packing

Fig. 4 shows that adjacent helices are in contact in the regions of the isopropyl groups. There are three different sets of important contacts to other helices. The isopropyl groups from molecules 3 and 10 (see Fig. 3) from one helix are in contact with isopropyl groups from molecules 4 and 7 in the adjacent helix that is related to the first helix by the *c* glide (see Fig. 6); the pattern of the molecule numbers at this interface is 3, 4′, 10, 7′, 3, 4′, ..., where primed and unprimed molecules are in different helices. Around the 2_1 axes the corresponding pattern, which is very similar to that shown in Fig. 6, is 2, 9′, 5, 6′, 2, 9′, ... Across the inversion centers the pattern, which is very similar to the other two, is 1, 1′, 8, 8′, 1, 1′, ...

The dimers are tilted within the helices so that the angles between the vectors C4_(2$n - 1$)–C4_2n and [101] (the helix axis) are 67.1, 70.6, 73.0, 70.5 and 71.8° (all s.u.s 0.2°) for n = 1–5. The combination of this angle and the rotation around the helix axis guarantees that the sets of isopropyl groups pointing in a specific direction will be approximately evenly spaced (see Fig. 6), even though the number of dimers that separates those isopropyl groups alternates between one and two. Two adjacent helices then fit together quite neatly (see Fig. 6).

The approximate twofold axes of the helices generate no crystallographic pseudosymmetry. These twofold axes are approximately perpendicular to the helix axis [101], as is **b**, but none of the approximate twofold axes is closely aligned with **b** (see Fig. 4).

The Kitaigorodskii (1961) packing coefficient (with the minor component of the disorder removed and the occupancy of the major component set to 1) as calculated by *PLATON* (Spek, 2003) is 0.66 at 90 K. Even if the temperature were 300 K rather than 90 K, this value would be at the low end of the expected range (0.65–0.80; Kitaigorodskii, 1961; Dunitz *et al.*, 2000); at 300 K, where the density can be expected to be several per cent lower than at 90 K, the packing coefficient would be even smaller. The N—H···N bonding and the difficulty of arranging fivefold helices in a two-dimensional pattern probably account for the relatively loose packing. When the view shown in Fig. 4 is drawn with space-filling surfaces there are obvious small channels in the centers of the 'square' and 'triangular' polygons that have helices at their

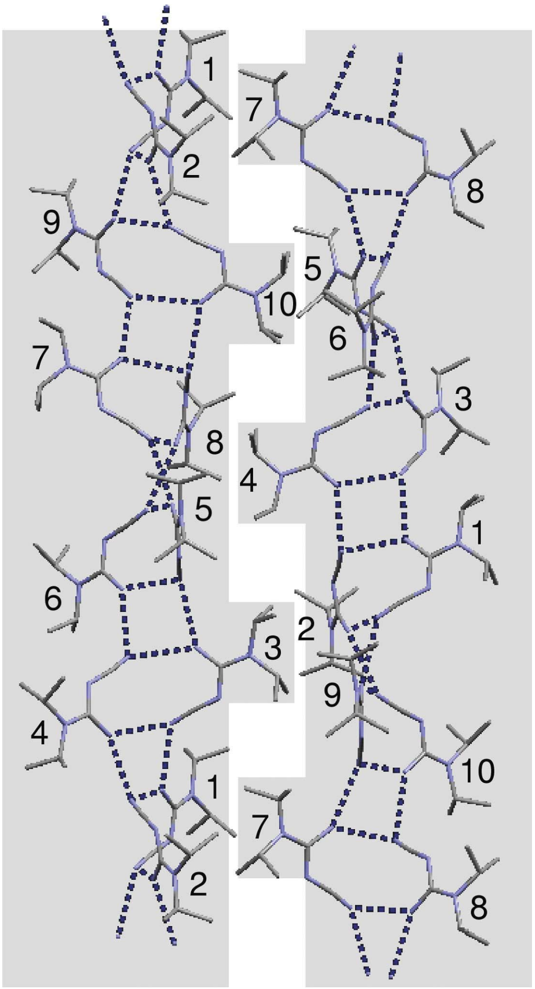
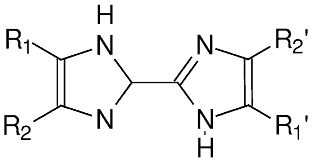


Figure 6
Diagram showing how two adjacent helices related by the *c* glide fit together.

corners. The channels in the 'square' polygons are a little larger than the channels in the 'triangular' polygons, but are still much too small to accomodate any molecule. The loose packing also explains the larger than average displacements of the atoms of the isopropyl groups.

3.4. Several related structures

In the structure reported here there are five dimers per turn. Helical ribbons very reminiscent of Fig. 3 are also seen in several 2,2′-biimidazole fragments substituted in the 4, 4′, 5 and 5′ positions. The covalent bond between the two rings takes the place of the N—H···N-bonded dimer; steric crowding favors a small twist around that covalent bond. In QENYAJ and QENYEN (Allen *et al.*, 2001) there are two and three symmetrically substituted molecules per turn (approximate 90 and 120° rotations between adjacent molecules), while in QENYIR (Allen *et al.*, 2001) there are six asymmetrically substituted molecules per turn (approximate 60° rotations between molecules). This packing pattern also occurs in the *vic*-diol BUHDAJ (Fronczek *et al.*, 1982), where a 4_2 axis guarantees that there are two symmetrically substituted, chiral molecules per turn.



(III)

3.5. Other structures with $Z' \geq 10$

A search of the CSD for error-free structures with $Z' \geq 10$ and archived coordinates located 14 different structures, of which two (NABUOX and GAVPEY) have been shown (Nekola *et al.*, 2002; Hao *et al.*, 2005) to have higher symmetry (and thus a lower Z') than originally reported. Of the remaining 12 structures one is a polymeric structure (WIMTOB) of uncertain precision. Another (GEKLOX01) is a disordered structure of a channel-inclusion complex that has $Z' = 12$ in the space group Pc and an R factor of 0.15. The structure QAJDAG (Wingerter *et al.*, 2000) was reported as being in $P2_1$ with $Z' = 12$, but is found by *PLATON* (Spek, 2003) to be in $Pn2_1a$ (standard setting $Pna2_1$) with $Z' = 6$; after looking at the structure and reading the original paper we concluded that the higher-symmetry space group is almost certainly a better description. The other nine structures (see Table 3) seem to be reliable.

Most of these structures can be described as modulated, which is to say that quite small displacements and/or rotations of molecules (or ions) would lead to a simpler structure with a smaller unit cell. Two of the structures in Table 3 have molecules in two or more hydrogen-bonding environments and are modulated as well. Hydrated trimesic acid (TRIMES10; Herbstein & Marsh, 1977) is a sort of channel inclusion 'complex' in which trimesic acid molecules, rather than a different guest, are included in the channels. No $Z' \geq 10$ structure was found of the type reported here, in which each of the many independent molecules is in a different crystallographic environment and in which there is no important crystallographic pseudosymmetry.

The CSD was also scanned for error-free structures with $10 > Z' \geq 5$ and archived coordinates in order to check for the possibile existence of a structure with ≥ 10 independent molecules, each located on a symmetry element.

4. Discussion

4.1. High Z' structures

The Z' value in this structure is exceptional; we find only nine reliable structures with the same or higher Z' values are archived in the CSD (see Table 3), which means that the frequency of occurrence of $Z' \geq 10$ is *ca* 30 p.p.m. The scarcity of such structures may be partly a result of the crystallographic difficulties associated with data collection (large unit cells; weak scattering; classes of reflections with very low intensity) and with structure solution and refinement (pseudosymmetry; correlation). It is probably no accident that seven of the nine $Z' \geq 10$ structures were published after 1997, *i.e.* after CCD diffractometers and restrained refinements had become common. Still, the number of $Z' \geq 10$ structures is so low that they must be considered to be anomalies.

The infrequent occurrence of high Z' structures suggests they are associated with packing problems. No structure is found unless it is favorable either energetically or kinetically, and there are reasons to believe that simpler structures are better than high Z' structures on both counts.

Analyses of entries in the CSD show (Brock & Dunitz, 1994) that the asymmetric unit is usually as small as possible. The independent part of the cell normally contains one formula unit, but if that unit can conform to inversion symmetry then Z' is nearly always $\frac{1}{2}$ (Pidcock *et al.*, 2003). Certain other kinds of symmetry are nearly always retained ($\overline{4}$ and $\overline{6}$ axes) or sometimes retained (twofold axis; Pidcock *et al.*, 2003). Symmetry elements that are seldom retained, like mirror planes, are usually associated with poor crystal packing.

If the asymmetric unit has $Z' > 1$, then the packing density seems likely to be lower than average, and a lower packing density usually means a higher packing energy. If the chemically equivalent units are in significantly different orientations or have different conformations, then there must be at least one direction in the crystal in which the spacings (or repeat distances) appropriate for independent units are different. The high probability (*ca* 99%) that inversion symmetry will be retained (Pidcock *et al.*, 2003) supports this explanation, because the imposed symmetry means that the two halves of the molecule (or ion) will be in the same environment; the imposed symmetry reduces the number of different kinds of intermolecular (or interionic) contacts by a factor of about two. If the number of contacts is reduced, so is the problem of matching the spacings.

The argument in the previous paragraph suggests that high Z' structures should usually be modulated, as they usually are, because the smaller the displacements and rotations the fewer the problems there are with matching the spacings. The $Z' = 10$ structure reported here is exceptional because it is not modulated. There are three different sets of van der Waals contacts between isopropyl groups (two sets of four molecules and one of two; see Fig. 4) that must be optimized in directions perpendicular to [101]. It is therefore no surprise that the packing is relatively loose.

Structures with a very high Z' sometimes have a hydrogen-bonded (or packing) unit composed of several independent molecules in a structure that is modulated so that there are several independent packing units. The combination of a packing unit of several molecules and a two- or threefold modulation may result in a high value of Z'. The structures BIPCOS01 and CHOEST21 (see Table 3) are examples of this structure type. The structure reported here can also be viewed as a relatively simple, two-dimensional packing (see Fig. 4) of hydrogen-bonded aggregates that are infinitely long.

Many $Z' > 1$ structures may occur for kinetic rather than thermodynamic reasons. Modulated structures are often found when crystals grown at one temperature are cooled to a much lower temperature before data collection. The small changes in relative position or orientation of the independent molecules (or ions) can often be understood as a response to the decrease with temperature in amplitudes of low-frequency vibrations. An intermolecular contact that may be acceptable when amplitudes are large (because the average interatomic distance is large) may become too repulsive when the amplitudes become smaller (biphenyl is a classic example; see Busing, 1983). Perhaps a different, lower Z', structure would be more stable at the low temperature and might be found if crystals could be grown at that low temperature (consider the example of ferrocene; Seiler & Dunitz, 1982). A crystal being cooled, however, and especially a crystal that is cooled rapidly (as is usually the case), is unlikely to transform into a very different structure. Small changes in the higher temperature structure are much more likely.

Consider the high-Z' crystals that are found without any cooling having taken place. Structures that are not modulated seem more likely to occur if the multi-molecule packing unit (*e.g.* a hydrogen-bonded aggregate) exists in the solution (or melt) from which the crystal is grown. It is certainly easy to believe that fragments of the hydrogen-bonded helices found in this structure exist in the chloroform solutions from which crystals were obtained. The needle-like habit of smaller crystals supports that suggestion.

4.2. Helix formation

The loosely packed structure that is observed for this molecule probably can only exist because of the $N-H\cdots N$ bonds that are formed. A typical structure of a molecule of this type would have a smaller Z' value, would be more tightly packed, and would be held together by a smaller number of $N-H\cdots N$ bonds.

That said, there is sufficient precedent for hydrogen-bonded helices that the structure 'looks' quite normal, especially since the helical aggegate is a consequence of the hydrogen-bonding requirements of the molecule.

4.3. Role of molecule size

Structures with larger values of Z' are often composed of molecules that are relatively small and rigid. Structures of smaller, more rigid molecules are easier to solve and refine, and a smaller number of independent atoms means a stronger diffraction pattern.

That said, it is also possible that smaller, more rigid molecules are more likely than larger, less rigid molecules to crystallize with high values of Z'. If there are only a few low-energy modes by which an individual molecule can adjust to optimize the packing, then packing problems may have to be resolved by an increase in the number of independent molecules. In the structure reported here the only low-energy distortions possible involve the torsion angles of the isopropyl groups.

5. Summary

The packing units in crystals of *N''*-cyano-*N*,*N*-diisopropylguanidine are $N-H\cdots N$ bonded helices formed from $N-H\cdots N$ bonded dimers. The number of molecules in the asymmetric unit ($Z' = 10$) is exceptionally high because there are five dimers per turn of the helix. Most high Z' structures are modulated, but this one is not. The structure is also very unusual in that the $H_2N-C{=}N-CN$ fragment forms a complete set of hydrogen bonds. It seems likely that the energy advantage of forming the $N-H\cdots N$ bonds offsets the energy disadvantage (*i.e.* low-density packing) of the existence of a very large number of independent molecules in quite different crystallographic environments. The very high Z' value in this structure is the cost of the formation of a full set of hydrogen bonds.

The problems associated with fitting the helices together to fill space mean that the sizes and conformational preferences of the specific substituents attached to the $H_2N-C{=}N-CN$ fragment determine whether the helical assembly can exist in the solid state. Hydrogen-bonded helices could almost certainly exist in solution for other substituents, but it seems likely that the energy balance necessary for acceptable packing of helices in a crystal would be too fine to be achieved if the -N(isopropyl)$_2$ fragment were replaced. The formation of this interesting and rather beautiful structure would then have to be viewed as fortuitous.

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