

obtained. Chemical analysis shows that the TMA:PA ratio in the prisms is 14:1 (found C 50.07, H 2.73, O 45.75, N 1.32; calculated C 49.95, H 2.77, O 45.91, N 1.33 wt%). The cell dimensions, measured on precession photographs using Co $K\alpha$, are $a = 19.52$ (7), $b = 127.6$ (3), $c = 16.53$ (6) Å. The possible space groups, from systematic absences, are *Ima2* (No. 46) and *Imma* (No. 72). Density was measured by the neutral-buoyancy method in a mixture of CCl_4 and toluene and found to be 1.528 g cm^{-3} ; calculated density is 1.528 g cm^{-3} for 168 TMA + 12PA in the unit cell. The TMA $_{14}$ PA crystals show (70 $\bar{1}$), (701) and (010) faces; no twinning was encountered. The *0kl* reciprocal net shows diffuse bands joining the Bragg reflections in the c^* direction. Dimensional resemblances can be found to both α -TMA and γ -TMA but structural speculations would be premature.

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Neutron Diffraction at 15 K and *ab initio* Molecular-Orbital Studies of the Molecular Structure of Carbonohydrazide (Carbohydrazide)

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(Received 1 December 1984; accepted 13 May 1985)

Abstract

The crystal structure of carbonohydrazide, $(\text{NH}_2\text{NH})_2\text{CO}$, has been refined using single-crystal neutron diffraction data [$\lambda = 1.0470$ (3) Å] measured at 15 K. The crystal data at 15 K are $M_r = 90.1$; $P2_1/c$; $Z = 4$; $a = 3.618$ (1), $b = 8.789$ (3), $c = 12.487$ (5) Å, $\beta = 106.43$ (3)°, $V = 380.9$ (3) Å³; $D_n = 1.571 \text{ Mg m}^{-3}$; $\mu = 257.4 \text{ m}^{-1}$. The final agreement factors are $R(F) = 0.031$, $wR(F^2) = 0.046$, $S = 1.32$ for 1701 observations. The molecule has the *cis/trans/cis/trans* conformation, with significant distortions of the carbon, oxygen and nitrogen atoms from coplanarity. The structures, energies and dipole moments of the eight lowest-energy conformers with approximate C_s symmetry were calculated for the isolated molecules, at rest, by molecular-orbital theory at the HF/3-21G level, using GAUSSIAN80. The lowest-

energy conformer is that observed in the crystal structure. However, the molecular distortions in the crystal correspond to a calculated energy that is 22.8 kJ mol^{-1} above the minimum energy. These distortions arise from a complex system of intra- and intermolecular hydrogen bonds in the crystal.

Introduction

The crystal structure of carbonohydrazide, $(\text{NH}_2\text{NH})_2\text{CO}$, was determined at room temperature by Domiano, Pellinghelli & Tiripicchio (1972). They showed the molecule to have the *cis/trans/cis/trans* conformation shown in (1) in Fig. 1. The structure was re-investigated by Ottersen & Hope (1979) using X-ray data collected at 85 K. This permitted a more precise determination of the hydrogen-atom positions and an electron deformation density analysis. In addition, cell constants of a fully deuterated species have been reported by Baird & Fleming (1974).

The present work was undertaken as part of a series of neutron diffraction molecular structure refinements

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and *ab initio* molecular-orbital structure calculations. Molecules previously studied are acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980), monofluoroacetamide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981*a*), formamide oxime (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981*b*), *N,N'*-diformohydrazide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1982), glyoxime (Jeffrey, Ruble & Pople, 1982), 1,2,4-triazole (Jeffrey, Ruble & Yates, 1983), thioacetamide (Jeffrey, Ruble & Yates, 1984) and nitromethane (Jeffrey, Ruble, McMullan, Wingert & Yates, 1985).

Carbonohydrazide is the most complex of the molecules hitherto studied in this series of investigations and possesses more potential for conformational variety. Whereas the emphasis of the previous work was on how close a correspondence could be obtained between the molecular dimensions calculated by theory and observed by experiment (Jeffrey, 1984), in this work we are focusing on what structural changes can occur in a more flexible π -bonded molecule when it is subjected to crystal-field forces.

Experimental

The neutron diffraction structure analysis

The single-crystal neutron diffraction data collection at 15 K and the structure refinement followed the same procedure as described for formamide oxime

(Jeffrey *et al.*, 1981*b*) except for the information provided below.

The crystals were grown from an ethanol solution in a convection tube partially submersed in a water bath kept at 340 K, as described by Hope (1971). A specimen $2.2 \times 1.9 \times 1.7$ mm, weighing 0.00614 g, had eight natural faces: $\{10\bar{2}\}$, $(01\bar{2})$, $(01\bar{2})$, $(01\bar{2})$, $(01\bar{1})$, $(01\bar{1})$ and $(01\bar{1})$, and a broken face approximating (023) . It was mounted with the $[10\bar{2}]$ direction oriented 10° from the φ axis of the diffractometer and was cooled at a rate of 1° min^{-1} to 15.0 (5) K, at which it was maintained during data collection. The lattice parameters given in Table 1 were determined using 32 reflections with $43 < 2\theta < 56^\circ$. Neutron integrated intensities were measured for hkl and $hk\bar{l}$ using scan widths of $\Delta(2\theta) = 3.6^\circ$ for $\sin \theta / \lambda \leq 0.48 \text{ \AA}^{-1}$ and varied according to the dispersion formula $\Delta(2\theta) = 3.199^\circ + 2.684^\circ \tan \theta$ for $0.48 < \sin \theta / \lambda < 0.78 \text{ \AA}^{-1}$. Neutron absorption corrections were applied using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient ($\mu = 257.4 \text{ m}^{-1}$) was calculated assuming the mass absorption coefficient for chemically bonded hydrogen to be $2.835 \text{ m}^2 \text{ kg}^{-1}$ at $\lambda = 1.0470$ (McMullan & Koetzle, 1980). The resulting transmission factors ranged from 0.68 to 0.74. The data for 199 symmetry-related reflections were averaged to give an agreement factor of $\sum \langle F^2 \rangle - F^2 / \sum \langle F^2 \rangle = 0.018$. Of the 1886 reflections measured,

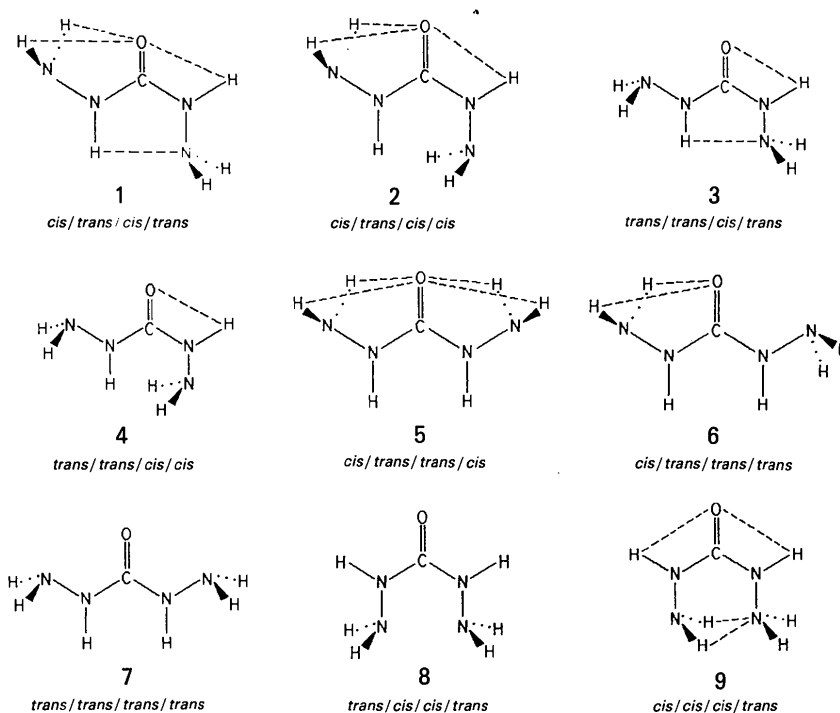


Fig. 1. Conformers considered in the theoretical calculations of carbonohydrazide. The *cis/trans* conformational notation refers to the

orientation of the $\begin{array}{c} \text{H} \\ | \\ \text{N} \cdots \cdots \\ | \\ \text{H} \end{array}$ group with respect to the C-N bond, and the N-H bond with respect to the C=O bond.

Table 1. *Crystal data for carbonohydrazide*CH₆N₄O; *P*2₁/*c*; *Z* = 4; λ = 1.0470 (3) Å.

	This work (15 K)	Ottersen & Hope (1979) (85 K)	Domiano <i>et al.</i> (1972) (room temperature)	Baird & Fleming (1974)* (room temperature)
<i>a</i> (Å)	3.618 (1)	3.625 (2)	3.728 (2)	3.71
<i>b</i> (Å)	8.789 (3)	8.794 (3)	8.841 (3)	8.82
<i>c</i> (Å)	12.487 (5)	12.456 (3)	12.659 (7)	12.39
β (°)	106.43 (3)	106.17 (2)	109.1 (1)	105.49
<i>D</i> _x (Mgm ⁻³)		1.569	1.517	1.63
<i>D</i> _n (Mgm ⁻³)	1.571			

* These results are for a completely deuterated sample of carbonohydrazide.

Table 2. *Final atomic parameters for carbonohydrazide at 15 K*

The fractional coordinates are ×10⁵ for non-hydrogen atoms, ×10⁴ for hydrogen atoms. Anisotropic thermal parameters (Å² × 10⁴) are referred to the crystal axes and correspond to the temperature-factor expression $T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$. Estimated standard deviations given in parentheses refer to the least significant digit. Anisotropic extinction parameters *g* (rad² × 10⁸) are given.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C	98754 (15)	27939 (6)	61308 (4)	36 (2)	29 (2)	32 (2)	2 (1)	3 (2)	0 (1)
O	91513 (18)	40846 (7)	64316 (5)	72 (2)	37 (2)	51 (2)	10 (2)	15 (2)	-5 (2)
N(1)	89551 (11)	23743 (4)	50395 (3)	70 (2)	41 (1)	36 (1)	14 (1)	2 (1)	0 (1)
N(2)	64574 (11)	32908 (4)	42176 (3)	57 (2)	55 (2)	43 (1)	6 (1)	-3 (1)	9 (1)
N(3)	116103 (11)	17287 (4)	68983 (3)	71 (2)	44 (2)	37 (1)	14 (1)	1 (1)	4 (1)
N(4)	127241 (11)	3039 (4)	65552 (3)	64 (2)	44 (1)	60 (1)	10 (1)	11 (1)	4 (1)
H(1)	9123 (4)	1268 (1)	4829 (1)	261 (6)	99 (4)	170 (5)	34 (4)	32 (5)	-25 (4)
H(2)	7948 (4)	4209 (2)	4053 (1)	205 (5)	158 (5)	232 (6)	-33 (5)	36 (5)	78 (4)
H(3)	4356 (4)	3713 (2)	4528 (1)	186 (6)	311 (7)	226 (6)	123 (5)	96 (5)	46 (5)
H(4)	13056 (4)	2100 (1)	7684 (1)	227 (5)	166 (5)	106 (4)	26 (4)	-25 (4)	-33 (4)
H(5)	12275 (4)	-469 (1)	7119 (1)	272 (6)	131 (5)	220 (5)	18 (5)	11 (5)	67 (4)
H(6)	15616 (4)	327 (2)	6657 (1)	122 (5)	220 (6)	351 (7)	24 (5)	87 (5)	-11 (5)
			<i>g</i> ₁₁ 1.02 (4)	<i>g</i> ₁₂ 1.0 (1)					
			<i>g</i> ₂₂ 6.9 (4)	<i>g</i> ₁₃ 0.46 (8)					
			<i>g</i> ₃₃ 4.1 (3)	<i>g</i> ₂₃ 1.3 (2)					

1508 were symmetry independent; 28 intensities had negative values, none significantly different from zero.

The initial atomic coordinates for the refinement were from the X-ray analysis of Ottersen & Hope (1979), with isotropic thermal parameters of $U = 0.006 \text{ \AA}^2$ for non-hydrogen atoms and $U = 0.009 \text{ \AA}^2$ for hydrogen atoms. The final refinement included atomic coordinates and anisotropic thermal parameters for all atoms, anisotropic extinction parameters and a scale factor, for 115 parameters. The refinement was carried out by full-matrix least-squares procedures, minimizing the function $\sum w_i |F_o^2 - F_c^2|$, where the observational weight, w_i , was taken to be $[\sigma_{\text{counter}}^2 + (0.02 F_o^2)^2]^{-1/2}$. The scattering lengths used were those given by Koester (1977). During refinement, the 011 and 01 $\bar{1}$ intensities were found to be affected by background from the direct beam and were removed from the refinement. After the final cycle of refinement using 1701 reflections, there were no changes greater than 0.2σ in any of the parameters varied. The largest correlations (>0.5) were between the scale factor and two anisotropic extinction components, and between various anisotropic extinction components. The largest was 0.75 between *g*₂₂ and *g*₁₂. The largest feature in the final difference map corresponded to 3% of the largest hydrogen peak and was 1.6σ, where the error in ρ was estimated from σ(*F*). The final agreement factors were $R(F) =$

0.031, $R(F^2) = 0.031$, $wR(F) = 0.027$, $wR(F^2) = 0.046$, $S = 1.321$. The observation-to-parameter ratio was 14.4. Extinction was anisotropic and severe, with 33% of the reflections significantly attenuated; $F_o/F_c \leq 0.95$. The greatest was for the 022, with $F_o^2/F_c^2 = 0.35$. The final atomic parameters are given in Table 2.* The atomic notation and thermal-motion ellipsoids are shown in Fig. 2.

* Tables of observed and calculated structure factors and Cartesian coordinates for calculated conformers have been deposited with the British Library Lending Division as Supplementary Publication No. SUP42239 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

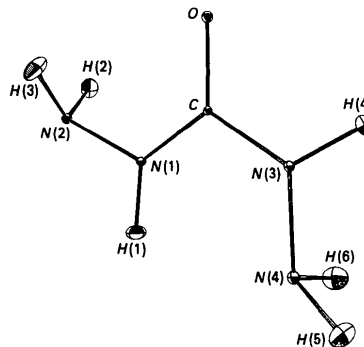


Fig. 2. Thermal ellipsoids (99% probability) and atomic notation for carbonohydrazide.

Comparison with X-ray analysis

The results of the neutron analysis agree very closely with the X-ray refinement at 85 K by Ottersen & Hope (1979) with respect to the non-hydrogen atoms. The C=O bond lengths agree exactly [1.2458 (8) Å]. In both analyses, the two C–N bonds are equal within 1σ , but the neutron values were 0.0018 Å (2.5σ) longer. The N–N bond *cis* to the C=O bond was the shorter by 0.0073 (8) and 0.0053 (8) Å for the neutron and X-ray analyses respectively. Again, the neutron distances were 0.0018 Å longer than the X-ray values. Since increased thermal libration shortens the bond lengths observed in a crystal structure analysis, these differences are in the correct direction and magnitude to be ascribed to the temperature difference of 70 K between the two experiments. The neutron N–H bond lengths agree with the X-ray values within 1.5 times their standard deviation (0.075 Å).

Thermal-motion analysis and corrections

As for the previous analyses in this series, the thermal-motion analysis was carried out using the segmented-body method, *ORSBA* (Johnson, 1970). Preliminary testing was performed to determine the internal motion in the molecule due to the H atoms. The calculated internal-motion corrections were 0.074 Å for the radial 'stretch' motion of all H atoms, 0.107 Å for the in-plane 'half-scissors' motions of H(1) and H(4), 0.107 Å for the 'full-scissors' motions of the remaining H atoms, 0.097 Å for the out-of-plane motions of H(1) and H(4), and 0.119 Å for the out-of-plane 'wagging' motions of the remaining H atoms. These corrections for the internal motion of the H atoms were subtracted from the corresponding r.m.s. displacements before proceeding with the segmented-body analysis as described below.

The segmented-body model employed consisted of three segments and three joints. One joint connected the parent O=C–(NH)₂ segment from the center of mass of the molecule to the stationary lattice. The other two joints connected the segments N(2)H₂ and N(4)H₂ to the parent segment along the respective N–N bonds. Torsional motions about the latter two joints were the only motions considered. The overall agreement was good, with $\langle \text{r.m.s. } U_{ij}^{\text{obs}} - U_{ij}^{\text{calc}} \rangle = 0.0007 \text{ \AA}^2$, and $\sigma(U_{ij}) = 0.0009 \text{ \AA}^2$. The results are shown in Table 3. The librations about the N–N linkages are N(1)–N(2) = 8.0° (9σ) and N(3)–N(4) = 6.8° (7σ). The bond lengths corrected for thermal motion and riding motion of the H atoms (Busing & Levy, 1964) are presented in Table 4.

The theoretical calculations

The optimized molecular geometries, energies and dipole moments of the isolated carbonohydrazide

Table 3. *Thermal-motion analysis*

Principal components of translation and libration with respect to the inertial axial system (I_1 , I_2 , I_3), with I_3 normal to the molecular plane, I_1 approximately parallel to the C–N(3) bond, and origin at the center of mass of the molecule.

		I_1	I_2	I_3
T	0.072 Å	76.3°	106.5°	158.3°
	0.58	100.0	21.8	109.2
	0.56	17.0	76.2	80.2
ω	3.56°	17.0	74.2	96.1
	1.23	86.7	79.6	11.0
	1.20	73.3	160.9	80.9

conformers *at rest* were calculated at the Hartree-Fock level using the 3-21G split-valence basis set (Binkley, Pople & Hehre, 1980) incorporated in *GAUSSIAN80*. Only those conformers (1) to (9), shown in Fig. 1, that have approximate C_s symmetry were considered. The calculated energies of the fully optimized geometries, all of which except (8) corresponded to local minima in the conformational energy surface, are shown in Table 5. The results in Tables 4 and 5 are for optimizations that had no symmetry constraints imposed on them, even though all of the conformers possess approximate C_s symmetry. Since conformers (5), (7) and (8) can have C_{2v} symmetry, additional optimizations of (5) and (7) were performed with C_{2v} symmetry imposed on the molecule, yielding geometries and energies that are not significantly different from the optimizations with no imposed symmetry. Conformer (8) was not an energy minimum owing to the repulsion of the lone-pair electrons on N(2) and N(4), and the calculations were discontinued when the conformation began diverging from the approximate C_{2v} symmetry.

The optimized bond lengths and angles corresponding to each conformer calculated are given in Table 4. The Cartesian coordinates for these conformers have been deposited.* The energy and dipole moment corresponding to the experimentally observed molecular structure were also calculated and are included in Table 5.

Discussion of the theoretical results

An acyclic molecule as complex as carbonohydrazide will have a large number of local minima in the conformational potential-energy surface. We have restricted our exploration to those with m , C_s , symmetry, *i.e.* (1) to (9). Clearly the stability of a particular conformer of this molecule is mainly determined by its potential for intramolecular hydrogen-bond formation, indicated by the dashed lines in Fig. 1. The conformer (1), which is that in the crystal, can form three NH...O=C bonds and one NH...N bond, as indicated by the dashed lines in Fig. 1. However,

* See deposition footnote.

Table 4. Observed and calculated bond lengths (Å) in carbonohydrazide

The standard deviations of the observed bond lengths are 0.0008 Å for C=O, C-N and N-N bonds and 0.001 Å for N-H bonds.

Parameter	Obs.	Obs.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(9)
		corr.								
C=O	1.2458	1.247	1.223	1.222	1.215	1.213	1.222	1.213	1.204	1.226
C-N(1)	1.3592	1.362	1.350	1.360	1.357	1.367	1.361	1.371	1.381	1.358
C-N(3)	1.3597	1.360	1.369	1.366	1.381	1.378				1.370
N(1)-N(2)	1.4121	1.413	1.421	1.433	1.406	1.404	1.422	1.422	1.402	1.427
N(3)-N(4)	1.4184	1.420	1.415	1.406	1.417	1.402				1.404
N(1)-H(1)	1.0135	1.027	0.992	0.990	0.996	0.994	0.993	0.993	0.997	0.995
N(3)-H(4)	1.0259	1.045	0.997	0.995	0.997	0.995				0.997
N(2)-H(2)	1.0229	1.043	1.006	1.006	1.001	1.000	1.006	1.006	1.000	1.003
N(2)-H(3)	1.0160	1.039								
N(4)-H(5)	1.0242	1.043	1.004	1.000	1.004	0.998	1.006	1.000	1.000	1.005
N(4)-H(6)	1.0177	1.040								

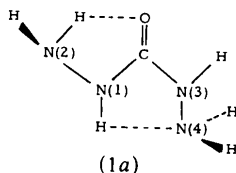
Table 5. Calculated energies

Conformer	Dipole moment ($\times 10^{-30}$ Cm)	Energy (hartrees)*	$\text{kJ mol}^{-1}\dagger$
(1)	14.28	-332.10401	0.00
(2)	10.94	-332.09706	18.25
(3)	19.95	-332.09444	25.12
(4)	20.21	-332.08591	47.51
(5)	6.10	-332.10006	10.38
(6)	15.54	-332.08986	37.13
(7)	22.45	-332.07856	66.85
(9)	18.11	-332.08905	39.31
Crystal	14.51	-332.09533	22.8

* 1 hartree = 4.35916 aJ.

† Relative to conformer (1).

in the crystal, the N(2)H₂ group is twisted about the N-N bond, so that H(3) is closer to the carbonyl oxygen (2.537 Å) than H(2) (2.880 Å).



We therefore explored the question whether conformer (1a) would have lower energy, since it would replace one more favorable hydrogen-bond geometry for two less favorable geometries. The calculation indicated that (1a) was in fact not an energy minimum and the structure optimized back to (1). At the temperature of crystallization, 340 K, the population of conformer (1), based on these calculations, which exclude any solvent effects, is over 97%.

The next highest-energy conformer, (5), also has four hydrogen bonds, but this energetic advantage is partially offset by the parallel alignment of the N-H bond dipoles. The sequence of energies of the other conformers is predictable on this basis. Thus (2) has three NH...O=C bonds, (3) has one NH...O=C and one NH...N bond, (6) has two NH...O=C bonds offset by parallel N-H bond dipoles. It is interesting to note that the extended, all-*trans*, conformer (7) was the least stable of those calculated, having no

intramolecular hydrogen bonds, and both parallel N-H bond dipoles and parallel C=O and N lone-pair dipoles. It is also interesting that in the structure of thiocarbonylhydrazide (Braibanti, Tiripicchio & Camellini, 1969), the molecule was observed to have a conformation analogous to (3) of this paper.

The Cartesian coordinates of the calculated minimum-energy structures for the conformers (1) to (7) and (9) are given in the supplementary data.* Table 4 shows the changes in calculated bond lengths that accompany the differences in conformations.

Comparison of the theoretical and experimental results

The C=O bonds

The calculated carbonyl bond lengths for the isolated molecule are relatively insensitive to conformation. Where the carbonyl oxygens accept three or four hydrogen bonds, as in (1), (2) and (5), the calculated length is 1.222-1.223 Å; where they accept one or two bonds, as in (3), (4) and (6), it is 1.213-1.215 Å. The exception is (9), where the syndiaxial orientation of the N-N bonds opens the C-N-N angles to 114 and 131° and brings H(1) and H(4) closer to the carbonyl oxygen, thereby forming a stronger hydrogen bond and consequently a longer C=O distance of 1.226 Å. It is interesting to note that the theory predicts a lengthening of the C=O acceptor bonds, even when the hydrogen-bond direction is close to 90° to the direction of the covalent bond. The atomic overlap, which is indicative of the bonding character, for these intramolecular bonds is greater for N(1)H...N(4), 0.0206, than for N(2)H...O, 0.0025 or N(3)H...O, 0.0026.

In the crystal structure, the intramolecular hydrogen bonding is retained and three intermolecular hydrogen bonds to the carbonyl oxygen are added, with H-O distances of 2.019, 2.055 and 2.436 Å. The C=O bond length in the crystal is correspondingly further lengthened to the observed corrected value of 1.247 Å. This is consistent with the effects of hydrogen

* See deposition footnote.

bonding on C=O bond lengths in the crystal structures of acetamide (Jeffrey *et al.*, 1980) and fluoroacetamide and calculated theoretically for the formamide dimer (Jeffrey *et al.*, 1981*a, b*).

The C–N bonds

These bonds have characteristic 'peptide bond' lengths of 1.35 to 1.38 Å; they are more sensitive to conformational change than are the C=O bonds. In all conformers, the calculations predict that the *trans* C–N(1) bond is shorter than the *cis* C–N(3) bond, by amounts ranging from 0.006 Å in (2) to 0.019 Å in (1). The longest C–N bonds are in the all-*trans* conformer, (7). In the crystal structure, the two C–N bonds are equal, within 0.6σ ; the difference of 0.002 Å arising from the thermal-motion corrections is probably not significant. Compared with the theoretical calculations, C–N(1) is longer in the crystal by 0.012 Å and C–N(3) is shorter by 0.009 Å. The hydrogen-bonding environments of N(1) and N(3) are not markedly different, as shown in Fig. 3(b), and the reason for these differences is to be found in the molecular distortions. The planar N–N–C=O conformation permits maximum π bonding. For N(2)–N(1)–C=O, the distortion from planarity is 12.6°. For N(4)–N(3)–C=O, it is only 5.3°.

The N–N bonds

The calculated N–N bond lengths for the isolated molecule vary from 1.402 Å in (4) and (7) to 1.433 Å in (2). Two factors are involved. One is the hydrogen bonding. The N–N bond is short if neither the N–H nor the NH₂ group is involved in hydrogen bonding, as in (7) and in the N(1)–N(2) bond in (4) and the N(3)–N(4) bond in (6). Conversely it is long if the NH₂ group is involved in bonding, as in N(1)–N(2) in (1), (2) and (9) and both N–N bonds in (5).

The second factor is the conformation. Where *trans* and *cis* H₂N–NH orientations occur in the same conformer, the *trans* is longer by 0.006 Å in (1), 0.018 Å in (6), 0.010 Å in (9). In (4) however, this trend is overridden by the hydrogen-bonding effect, which shortens N(3)–N(4) relative to N(1)–N(2).

In the crystal, the difference in the two bonds is the reverse of that calculated for conformer (1), which again must be ascribed to differences in the hydrogen-bonding environment.

The N–H bonds

The calculations predict that in all conformers >N–H bonds are 0.003 to 0.013 Å shorter than NH₂ bonds. Hydrogen-bond formation is predicted to lengthen the N–H bonds involved. This is found in the calculated values, although the differences are small, <0.006 Å. This is because the directions of the intramolecular hydrogen bonds are such that polariz-

ation occurs almost normal to the direction of the covalent N–H bond. Differences in the N–N–H valence angles are more pronounced; *cf.* N(1)–N(2)–H 109.5° *vs* N(3)–N(4)–H 111.7° in (1), 109.3° *vs* 113.4° in (6).

Comparison with the experimental values is complicated by the effect of the anharmonic thermal motion of the hydrogen atoms, which tends to have an equal and opposite effect to riding motion at 15 K for small first-row element molecules that are hydrogen bonded in the crystal (Jeffrey & Ruble, 1984; Craven & Swaminathan, 1984). Since the hydrogen bonding affects the observed bond lengths both by inducing changes in electronic structure and in the riding motion and anharmonicity through changes in the bending and stretching force constants, it is impossible to deconvolute these effects at this time. Only for C–H bonds, which are not, or only very weakly, hydrogen bonded can the effects of riding motion and anharmonicity be balanced in a reasonable way to give agreement with the theoretical values.

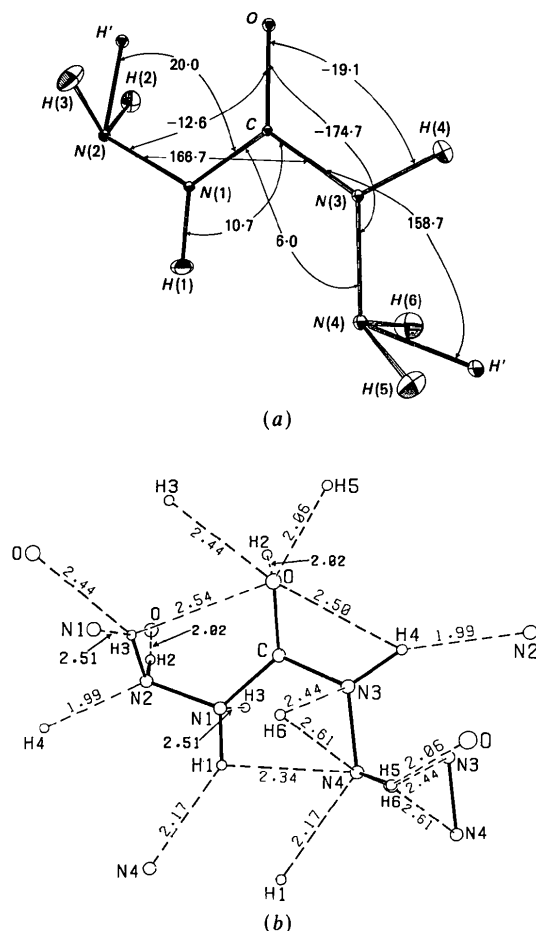


Fig. 3. (a) Torsion angles for carbonohyazide. E.s.d.'s are 0.1°. H' are dummy atoms that bisect the NH₂ group to show the orientation. (b) The hydrogen-bonding environment about a typical carbonohyazide molecule, showing the 19 hydrogen bonds in which each molecule participates.

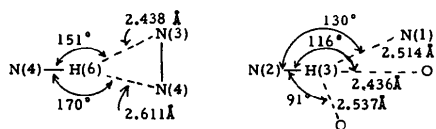
The molecular distortions

The molecule is distorted in the crystal, to the extent of 22.8 kJ mol^{-1} from the theoretical calculations. These distortions are shown by the torsion angles given in Fig. 3(a). In addition to the distortions of the non-hydrogen framework from the minimum-energy torsion-angle values of 0 or 180° , the NH_2 groups are rotated out of the mirror-plane orientation. This is shown by the torsion angles to the dummy atoms, H' , which lie on the bisectors of the NH_2 angle. The complex hydrogen-bonding environment of the molecule, which is responsible for these distortions, is shown in Fig. 3(b). Of the four intramolecular hydrogen bonds in the isolated molecule, three are retained. Owing to the rotation of the $\text{N}(2)\text{H}$ group, the intramolecular $\text{H}(3)\cdots\text{O}$ distance becomes shorter at 2.54 \AA , while $\text{H}(2)\cdots\text{O}$ becomes longer at 2.88 \AA . In addition, the molecule is a donor for eight intermolecular hydrogen bonds and accepts eight intermolecular bonds. The geometry of these bonds is given in Table 6.

The hydrogen bonding and molecular packing

In this crystal structure, all the first non-covalently bonded neighbors to the hydrogen atoms are the electronegative oxygens or nitrogens. We define these as hydrogen bonds. All the hydrogen atoms are involved in hydrogen bonding and all the oxygen and nitrogen atoms accept one or more bonds. The carbonyl oxygen has three intermolecular and two intramolecular bonds. The secondary nitrogens both accept one bond. One of the primary nitrogens accepts one bond, $\text{N}(1)$, while the other accepts two intermolecular and one intramolecular bond.

There are two two-center $\text{NH}\cdots\text{O}=\text{C}$ bonds, from $\text{N}(2)\text{H}(2)$ and $\text{N}(4)\text{H}(5)$. The bond lengths of 2.019 and 2.055 \AA are in excellent agreement with the mean value of 2.047 \AA for 36 $\text{N}(\text{H})\text{H}\cdots\text{O}$ bonds in the crystal structures of nucleosides and nucleotides (Jeffrey, Maluszynska & Mitra, 1985). The $\text{N}(4)\text{H}(6)$ and $\text{N}(2)\text{H}(3)$ are involved in three- and four-center hydrogen bonds with the geometry shown below. The secondary $>\text{N}-\text{H}$ groups are involved in unsymmetrical three-center bonds in which the weaker component is intramolecular.



The dominant features of the molecular packing are the presence of three distinct types of dimers, and the stacking of these dimers parallel to the a axis. In Fig. 4, molecules E through J and K through N are shown forming chains, with each maintaining a constant z value. As these chains are stacked along the

Table 6. *Hydrogen-bond geometry in the crystal structure of carbonohydrazide*

Bond	$\text{H}\cdots\text{A}$ (\AA)	$\text{N}-\text{H}\cdots\text{A}$ ($^\circ$)	ORTEP symmetry operation codes for A
$\text{N}(2)-\text{H}(2)\cdots\text{O}$	2.019 \AA	173.8°	76 602
$\text{N}(4)-\text{H}(5)\cdots\text{O}$	2.055	149.4	74 603
$\text{N}(1)-\text{H}(1)\cdots\text{N}(4)$	2.165	142.3	75 602
$\text{N}(3)-\text{H}(4)\cdots\text{N}(4)$	2.340	99.6	55 501
$\text{N}(3)-\text{H}(4)\cdots\text{N}(2)$	1.992	150.9	65 501
$\text{N}(3)-\text{H}(4)\cdots\text{O}$	2.497	65.0	55 501
$\text{N}(4)-\text{H}(6)\cdots\text{N}(3)$	2.438	150.8	65 501
$\text{N}(4)-\text{H}(6)\cdots\text{N}(4)$	2.611	170.3	65 501
$\text{N}(4)-\text{H}(6)\cdots\text{N}(1)$	2.514	130.2	45 501
$\text{N}(2)-\text{H}(3)\cdots\text{O}$	2.436	116.4	66 602
$\text{N}(2)-\text{H}(3)\cdots\text{O}$	2.537	91.0	55 501

Symmetry code: 01 = x, y, z ; 02 = $\bar{x}, \bar{y}, \bar{z}$; 03 = $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; 04 = $x, \frac{1}{2} - y, \frac{1}{2} + z$. E.s.d.'s for bond lengths are 0.002 \AA , for angles 0.1° .

c axis, they alternate direction in a criss-cross fashion. Within each chain, each molecule forms a dimer with each of two adjacent molecules. One of these dimers is linked by $\text{H}(3)\cdots\text{O}$ intermolecular hydrogen bonds, while the other dimer is formed through $\text{H}(1)\cdots\text{N}(4)$ intermolecular hydrogen bonds. (In Fig. 4, dimer $G\cdots H$ is of the former type, while dimer $G\cdots F$ is of the latter.) Each chain is bound to the chains immediately above and below it by two types of hydrogen bonds. At $y=0$ and $y=\frac{1}{2}$, there exists a series of $\text{H}(5)\cdots\text{O}$ hydrogen bonds and, within a given series, each such hydrogen bond is related by a centre of symmetry to the $\text{H}(5)\cdots\text{O}$ bonds above and below it. In addition, at $y=\frac{1}{4}$ and $y=\frac{3}{4}$, there are series of $\text{H}(4)\cdots\text{N}(2)$ hydrogen bonds and the hydrogen bonds within each series are related by the c -glide plane.

The third type of dimer is linked by a pair of $\text{H}(2)\cdots\text{O}$ intermolecular hydrogen bonds; this is demonstrated in Fig. 5 by molecules A and B . The $\text{H}(2)\cdots\text{O}$ and $\text{H}(3)\cdots\text{O}$ type dimers help to maintain the stacks along the a axis. Fig. 5 shows the six intermolecular hydrogen bonds, along with the

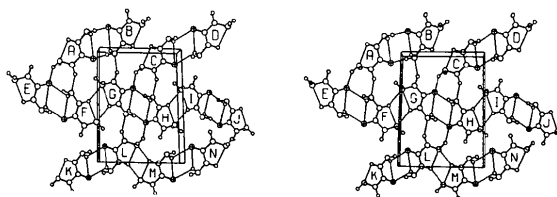


Fig. 4. Stereoview of the packing arrangement viewed down the a axis. The molecules are $A = 84 603$, $B = 65 504$, $C = 75 603$, $D = 66 504$, $E = 64 501$, $F = 75 602$, $G = 55 501$, $H = 66 602$, $I = 46 501$, $J = 57 602$, $K = 54 503$, $L = 45 404$, $M = 65 503$, $N = 56 404$, with the symmetry codes as given in Table 6.

Table 7. Observed and calculated valence angles ($^{\circ}$) and pyramidalization of the NH_2 groups

Pyramidalization (θ) in degrees is defined by V_1 [$\text{N}(2) \rightarrow \text{N}(1)$], V_2 [$\text{N}(2) \rightarrow \text{H}(2)$], V_3 [$\text{N}(2) \rightarrow \text{H}(3)$], $V_4 = V_2 \times V_3$, $\theta = \cos^{-1} [V_1 \times V_4 / |V_1| |V_4|]$.

Valence angles	Observed	Calculated for (1)
N(1)-N(2)-H(2)	109.3 (1)	109.5
N(1)-N(2)-H(3)	109.0 (1)	109.5
H(2)-N(2)-H(3)	106.4 (1)	109.9
N(3)-N(4)-H(5)	105.3 (1)	111.7
N(3)-N(4)-H(6)	108.3 (1)	111.7
H(5)-N(4)-H(6)	106.5 (1)	112.9
Pyramidalization		
N(2) from N(1), H(2), H(3)	57.7 (1)	54.5
N(4) from N(3), H(5), H(6)	61.1	47.6

H(2)---O and H(3)---O dimeric hydrogen bonds, in which a typical molecule participates to strengthen these stacks. Apparently, these stacks are much stronger than the criss-crossing dimer chains that are held together only by the dimeric hydrogen bonds.

The pyramidal N-NH₂ groups

Table 7 shows the observed and calculated pyramidal character of the NH_2 groups. The agreement between the observed and calculated valence angles is extraordinary, indicating that the N-NH₂ group is sig-

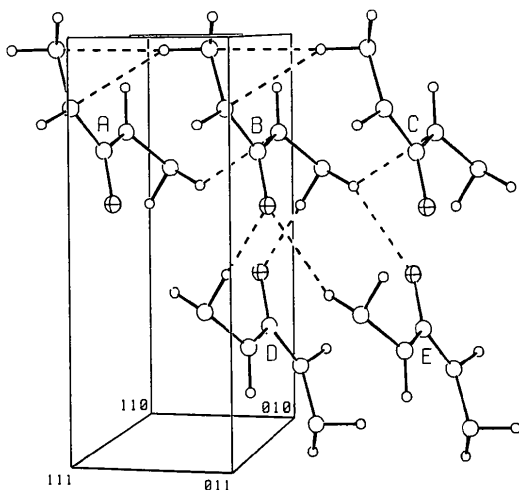


Fig. 5. View showing the ten hydrogen bonds in which each molecule participates for strengthening of the dimer stacks along the a axis. The molecules are $A = 55\ 501$, $B = 45\ 501$, $C = 35\ 501$, $D = 66\ 602$, $E = 56\ 602$, with the symmetry codes as given in Table 6.

nificantly less deformable by crystal-field forces than

is the $\begin{array}{c} \text{C} \\ \diagdown \\ \text{N} \\ \diagup \\ \text{N}-\text{H} \end{array}$ group.

This research is supported by the National Science Foundation through Grant Nos. CHE-8117260 and CHE-8316882. The neutron diffraction measurements were carried out at the High Flux Beam Reactor at Brookhaven National Laboratory, which is operated under contract DE-AC-02-CH00016 with the US Department of Energy. The authors are grateful to Dr R. K. McMullan for his assistance with the neutron data collection.

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