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Crystal and Molecular Structure of Carbohydrazide

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The crystal structure of carbohydrazide, $OC(NH{-}NH_2)_2$, has been determined from X-ray intensity data (Cu $K\alpha$ radiation) measured with an automatic diffractometer. The space group is $P2_1/c$ with unit-cell dimensions $a=3{\cdot}728$ (2), $b=8{\cdot}841$ (3), $c=12{\cdot}659$ (7) Å; $\beta=109{\cdot}1$ (1)°, $V=394{\cdot}3$ Å^3, $Z=4$. The structure was solved by the symbolic addition procedure and refined by the full-matrix least-squares method to $R=4\%$. The molecule, depending upon rotations around the bonds C–N and N–N, has one $-NH{-}NH_2-$ group in *cis,gauche* position (*cis* position with respect to C–O, with $-NH_2$ in *gauche* position with respect to C–N) and the second group $-NH{-}NH_2$ in *trans,antigauche* position. The different conformational orientations do not alter appreciably bond distances and angles. The group of atoms N–CO–N is planar, with bond distances and angles practically equal to those in urea. One hydrogen bond $-NH\cdots NH_2-=2{\cdot}950$ Å joins the molecules in chains parallel to [001] and weak hydrogen bonds, both N···O and N···N, connect the chains.

Introduction

Several investigations of the properties of thiocarbohydrazide, $SC(NH{-}NH_2)_2$ (hereafter tcaz), and its derivatives both in the crystal state and in solution have been undertaken in this laboratory. The tcaz molecule can assume, by rotation around the bond C–N, two different conformations of the hydrazinic radicals with respect to the bond C–S; one with both groups rotated in such a way as to bring $-NH_2$ toward C–S, *i.e.* in *cis,cis* conformation, and the other with one $-NH{-}NH_2$ group rotated in *cis* position and the second in *trans* position, *i.e.* in *cis,trans* conformation. The first conformation is found in the neutral molecule (Braibanti, Tiripicchio & Tiripicchio Camellini, 1969), in the monoprotonated cation (to be published) and in the chelate molecule (Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1971); the second type is found in biprotonated tcaz (Braibanti, Pellinghelli, Tiripicchio & Tiripicchio Camellini, 1971). We have now undertaken the study of carbohydrazide, $OC(NH{-}NH_2)_2$ (hereafter caz) and its derivatives to define the differences between tcaz and caz, in structure and in chemical behaviour. The results of the structural determination of the neutral caz molecule are presented here.

Experimental

Preparation

Prismatic colourless crystals of the commercial product were chosen for the X-ray analysis.

Crystal data

Compound: carbohydrazide, $OC(NH{-}NH_2)_2$
Formula weight 90·09
Crystal class: monoclinic prismatic
Unit-cell parameters (determined from rotation and Weissenberg photographs and refined from the least-squares fit to $(\theta, \chi, \varphi)_{hkl}$ values of 13 reflexions measured on a Siemens single crystal diffractometer, Cu $K\alpha$ radiation, $\lambda=1{\cdot}54178$ Å):
$a=3{\cdot}728$ (2), $b=8{\cdot}841$ (3), $c=12{\cdot}659$ (7) Å
$\beta=109{\cdot}1$ (1)°, $V=394{\cdot}3$ Å^3; $Z=4$
$D_x=1{\cdot}517$, $D_m=1{\cdot}525$ g.cm^{-3}
$\mu(\text{Cu } K\alpha)=11{\cdot}17$ cm^{-1}; F(000) = 192
Space group: $P2_1/c$ [C_{2h} (5), No. 14] from systematic absences.

Intensity data

The intensity data were collected on a single-crystal automated Siemens diffractometer on line with a Siemens 304/P computer using Ni-filtered Cu $K\alpha$ radiation and the ω–2θ scan technique. A prismatic crystal of approximate dimensions $0{\cdot}070\times0{\cdot}080\times0{\cdot}200$ mm was aligned with its [100] axis along the φ axis of the diffractometer. With the maximum value of $2\theta=140°$ the number of collected independent reflexions was 755. Of these, 652 were used in the crystal analysis, taking as unobserved the reflexions whose intensities were less than twice their standard deviations [$\sigma^2(I)=$ total counts$+(0{\cdot}005I)^2$]. Corrections for Lorentz and polarization factors were made in the usual way, but no correction was made for absorption.

Structure determination and refinement

The structure was solved by symbolic addition procedure (Germain & Woolfson, 1968). An absolute scale factor and the mean isotropic temperature factor were obtained by Wilson's (1942) method. The normalized structure factors, E_h's, were computed from the equation

$$E_h^2=F_h^2/\varepsilon\sum_{j=1}^{N}f_{jh}^2\,,$$

where ε is unity for all reflexions other than $h0l$ and $0k0$ for which $\varepsilon=2{\cdot}0$. N is the number of atoms in the unit cell and F_h is on an absolute scale and corrected for thermal motion. Only normalized structure factors greater than 1·5 were used in the phase determination. Reflexions 110 ($|E|=2{\cdot}67$), 145 ($|E|=2{\cdot}77$) and $2,1,\overline{12}$ ($|E|=3{\cdot}06$) were chosen to define the origin. Symbols a, b, c and d were assigned to the phases of the reflexions $17\overline{8}$ ($|E|=3{\cdot}61$), 068 ($|E|=3{\cdot}01$), $12\overline{5}$ ($|E|=2{\cdot}30$)

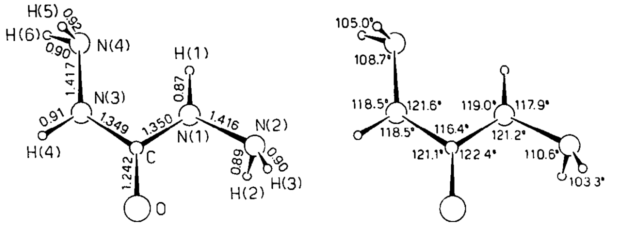

Fig. 1. Bond lengths and angles in the carbohydrazide molecule.

and 0,2,10 ($|E|=2·83$) respectively. From inspection of the interactions among the signs and symbols, it was decided that all the symbols were probably minus. With these assignments, the signs of 130 reflexions with $E \geq 1·30$ were determined and used to compute an E map which revealed the whole structure except for the hydrogen atoms. A structure-factor calculation using atomic parameters obtained from this E map gave an R value of 0·52. This value decreased to 0·14 after six cycles of full-matrix least-squares refinement with isotropic temperature factors. Anisotropic temperature factors were then introduced and the R value decreased to 0·071 after six cycles. At this stage an (F_o-F_c) synthesis was computed and the positions of the hydrogen atoms were found. The six hydrogen atoms were included in the subsequent refinement with isotropic temperature factors. R dropped to 0·042, excluding non-observed reflexions. Unit weights were used up to this point, then the scheme $1/w=(A+BF_o+CF_o^2)$ was assumed; $A=0·06003$, $B=0·08085$ and $C=0·00027225$ were determined by plotting ΔF against $|\bar{F}_o|$. The final value of R was 0·040.

The final atomic coordinates are given in Table 1 and the thermal parameters in Table 2. A list of observed and calculated structure factors is available either from the authors on request or as supplementary publication number 30007*

The atomic scattering factors of Cromer & Mann (1968) were used for O, N and C and those of Stewart, Davidson & Simpson (1965) for H.

Table 1. *Final fractional atomic coordinates* (× 10⁴) *with e.s.d.'s*

	x	*y*	*z*
O	6522 (3)	4132 (1)	3582 (1)
N(1)	8560 (4)	2340 (2)	4934 (1)
N(2)	7828 (5)	3243 (2)	5765 (1)
N(3)	8081 (5)	1817 (2)	3118 (1)
N(4)	9539 (5)	0347 (2)	3443 (1)
C	7665 (4)	2827 (2)	3868 (1)
N(1)	9036 (57)	1383 (26)	5077 (18)
H(2)	9163 (67)	4099 (29)	5867 (19)
H(3)	5396 (74)	3567 (27)	5502 (20)
H(4)	7920 (59)	2153 (24)	2422 (19)
H(5)	8049 (60)	−0304 (24)	2916 (18)
H(6)	11846 (70)	0281 (27)	3371 (18)

All the calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programs written by Immirzi (1967).

Description of the structure

The structure of the caz molecule (Fig. 1) is similar to tcaz, *i.e.* it is of type *cis,trans*. The bond lengths and angles in the molecule are given in Table 3. The distances C–O = 1·242 (2) Å and C–N = 1·349 (2), 1·350 (2) Å are equal to those found by neutron diffraction in urea [1·243 (6) and 1·351 (7) Å, respectively: Worsham, Levy & Peterson, 1957]. The values 1·298 (2) Å for C–O and 1·315 (1), 1·312 (1) Å for C–N, determined by neutron diffraction in uronium nitrate (Worsham & Busing, 1969) indicate that in caz the increase of double bond character of C–O is paralleled by an increase in single bond character of C–N. The relation between lengthening of C=O, or C=S, and shortening of C–N is a general property of ureide, N–CO–N, and thioureide, N–CS–N, groups, which confirms conjugation in them. This is also confirmed by the planarity of N–CO–N, again in accordance with urea. The best plane through N(1), C, O, N(3) is $-0·9351X -0·3039Y -0·1822Z=-2·7770$, where X, Y, Z are coordinates in Å referred to a system with $X\equiv x$, $Y\equiv y$ and $Z \perp (X, Y)$. Deviations from the plane (with e.s.d.'s in parentheses) are: Δ[N(1)] = −0·0002 (16), Δ[C] = 0·0005 (16), Δ[O] = −0·0001 (12), Δ[N(3)] = −0·0002 (19) Å. Atoms H(1) and H(4) deviate

Table 2. *Thermal parameters with e.s.d.'s*

The anisotropic thermal parameters are in the form $\exp[-0·25(h^2a^{*2}B_{11}+\cdots 2klb^*c^*B_{23})]$.

	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	4·18 (5)	1·81 (4)	2·18 (4)	0·52 (4)	0·91 (4)	0·25 (3)
N(1)	4·62 (7)	1·96 (5)	1·44 (5)	0·74 (5)	1·18 (5)	−0·04 (4)
N(2)	4·13 (7)	2·37 (5)	1·69 (5)	0·23 (5)	1·42 (5)	−0·43 (4)
N(3)	5·23 (8)	1·89 (5)	1·64 (5)	0·53 (5)	1·33 (5)	0·01 (4)
N(4)	3·81 (7)	1·74 (5)	2·26 (5)	0·27 (4)	1·16 (5)	−0·21 (4)
C	2·56 (6)	1·86 (5)	1·60 (5)	−0·19 (4)	0·65 (5)	−0·11 (4)
H(1)	3·30 (42)					
H(2)	4·19 (49)					
H(3)	4·26 (48)					
H(4)	3·53 (42)					
H(5)	3·28 (39)					
H(6)	4·02 (48)					

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* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. 30007. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

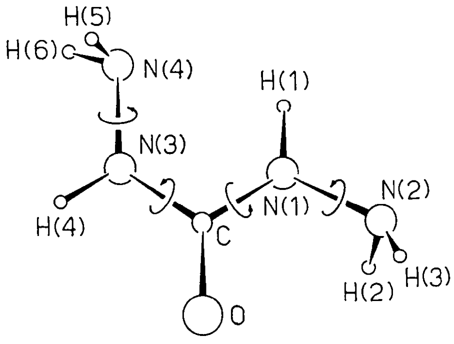

Fig. 2. Conformation of the carbohydrazide molecule: group $N(1)H-N(2)H_2$ is in *cis,gauche* position and group $N(3)H-N(4)H_2$ in *trans,antigauche* position.

$\Delta[H(1)] = 0{\cdot}1152$ (225) and $\Delta[H(4)] = -0{\cdot}1522$ (232) Å from the plane. The atoms N(2) and N(4) are $+0{\cdot}1532$ (19) and $-0{\cdot}0585$ (19) Å out of this plane, respectively; they are displaced on opposite sides of the plane, thus differing from the tcaz molecule in which both atoms are on the same side. The angles O–C–N(1), O–C–N(2) and N(1)–C–N(3), of 122·4, 121·1 and 116·4°, are equal to those found in urea (121·5, 121·5 and 117° respectively). These angles and the planarity of the ureide group are consistent with the assignment of sp^2 hybridization to the bonds around carbon, whereas the sums of the angles around N(1) and N(3) indicate that these two nitrogen atoms are not in purely sp^2 hybridization. This situation is the same as that of tcaz and differs from that in urea. The angles around the N(2) and N(4) atoms are in good agreement with the expected sp^3 hybridization.

Table 3. *Bond distances and angles in the molecule*

C—O	1·242 (2) Å	O—C—N(1)	122·4 (1)°
C– N(1)	1·350 (2)	O– C—N(3)	121·1 (1)
C—N(3)	1·349 (2)	N(1)–C—N(3)	116·4 (2)
N(1)–N(2)	1·416 (2)	C—N(1)—N(2)	121·2 (2)
N(3)–N(4)	1·417 (3)	C—N(1)–H(1)	119·0 (14)
N(1)–H(1)	0·87 (2)	H(1)–N(1)–N(2)	117·9 (14)
N(2)–H(2)	0·89 (3)	N(1)–N(2)–H(2)	110·6 (16)
N(2)–H(3)	0·90 (3)	N(1)–N(2)–H(3)	108·6 (15)
N(3)–H(4)	0·91 (2)	H(2)–N(2)–H(3)	103·3 (23)
N(4)–H(5)	0·92 (2)	C—N(3)–N(4)	121·6 (1)
N(4)–H(6)	0·90 (3)	C—N(3)–H(4)	118·5 (14)
		H(4)–N(3)–N(4)	118·5 (14)
		N(3)–N(4)–H(5)	106·3 (14)
		N(3)–N(4)–H(6)	108·7 (15)
		H(5)–N(4)–H(6)	105·0 (21)

The rotation angles of hydrazinic groups (Table 4) show that they undergo double conformational rotations, one around the line C–N and another around the line N–N (Fig. 2). Therefore the group $-N(1)H-N(2)H_2$ can be said to be in *cis* position with respect to C=O, to specify the rotation around C–N(1) and in *gauche* position with respect to C–N(1), to specify the rotation around N(1)–N(2). The group $-N(3)H-N(4)H_2$ can be said to be in *trans* position with respect to C=O and *antigauche* (*gauche* + 180°) position with respect to C–N(3). Deviations of hydrogen atoms from perfectly symmetric *gauche* or *antigauche* positions are in the range 3 to 17°.

The nitrogen–nitrogen bonds in the two hydrazinic groups are equal [N–N = 1·416 (2) and 1·417 (3) Å]. These values agree well with those found for the same bonds in hydrazine derivatives (Braibanti, Manotti Lanfredi, Tiripicchio & Bigoli, 1970) and in thiosemicarbazide (Andreetti, Domiano, Fava Gasparri, Nardelli & Sgarabotto, 1970).

The packing of caz molecules in the crystal structure is determined by several hydrogen bonds (Table 5). A clinographic projection of the structure with the network of hydrogen bonds is shown in Fig. 3. The hydrogen bond between N(2) and N(3) [2·950 (3) Å] joins caz molecules in chains parallel to [001]. Weaker N···O and N···N hydrogen bonds hold together the chains.

The authors thank Professor A. Braibanti for helpful discussions. They are also grateful to Professor

Table 4. *Rotation angles of hydrazinic groups around* N–N

	$N(1)H-N(2)H_2$ (*cis*)			$N(3)H-N(4)H_2$ (*trans*)	
	Plane	φ		Plane	φ
a	C, N(1), N(2)	0°	*a*	C, N(3), N(4)	0°
b	N(1), N(2). H(3)	49·72	*b*	N(3), N(4), H(5)	137·03
c	H(1), N(1), N(2)	164·15	*c*	H(4), N(3), N(4)	193·65
d	N(1), N(2), H(2)	297·08	*d*	N(3), N(4), H(6)	249·52
e	N(1), N(2), bisector $\widehat{bd}$	173·40	*e*	N(3), N(4), bisector $\widehat{bd}$	13·27

Rotation from *gauche* conformation

φ_b–60°	10·28°	$\varphi_b - 300°(+360°)$	180° + 17·03°
φ_d–300°	2·92	φ_d–60°	180 + 9·52
$\Delta\varphi_{av}$	6·60	$\Delta\varphi_{av}$	180 + 13·27

Interplanar angles

$\widehat{bd}$	112·64°	$\widehat{bd}$	112·49°
$\widehat{ab}$	49·72	$\widehat{ab}$	137·03
$\widehat{ad}$	62·92	$\widehat{ad}$	110·48

Table 5. *Hydrogen bonds*

N(1)-H(1)···N(4^{i})	3·068 (3) Å	N(1)-H(1)···N(4^{i})	141·1 (19)°
H(1)···N(4^{i})	2·34 (2)	H(1)-N(1)···N(4^{i})	28·6 (14)
N(2)-H(2)···O^{ii}	3·061 (2)	N(2)-H(2)···O^{ii}	166·0 (22)
H(2)···O^{ii}	2·19 (2)	H(2)-N(2)···O^{ii}	10·0 (16)
N(2)-H(3)···O^{iii}	3·095 (2)	N(2)-H(3)···O^{iii}	118·7 (19)
H(3)···O^{iii}	2·56 (3)	H(3)-N(2)···O^{iii}	46·4 (15)
N(3)-H(4)···N(2^{iv})	2·950 (3)	N(3)-H(4)···N(2^{iv})	151·3 (19)
H(4)···N(2^{iv})	2·12 (3)	H(4)-N(3)···N(2^{iv})	20·1 (13)
N(4)-H(5)···O^{v}	3·007 (4)	N(4)-H(5)···O^{v}	154·4 (19)
H(5)···O^{v}	2·15 (2)	H(5)-N(4)···O^{v}	18·0 (14)

Asymmetric units

No label	x,	y,	z
i	$2-x$,	$-y$,	$1-z$
ii	$2-x$,	$1-y$,	$1-z$
iii	$1-x$,	$1-y$,	$1-z$
iv	x,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$
v	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$

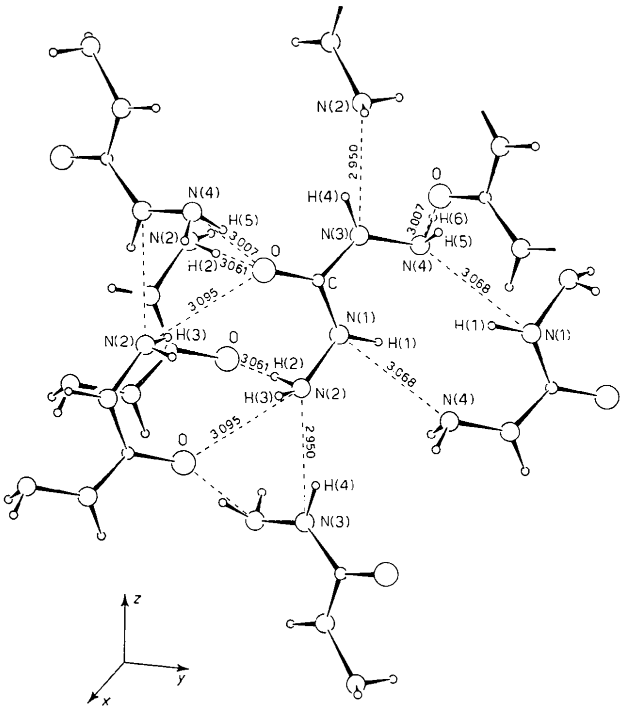

Fig. 3. Clinographic projection of the structure with network of hydrogen bonds.

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