The Structure and Electron Deformation Density Distribution of Carbonohydrazide (Carbohydrazide) at 85 K

By Tor Ottersen

Department of Chemistry, University of Oslo, Oslo 3, Norway

and Håkon Hope

Department of Chemistry, University of California, Davis, California 95616, USA

Abstract

This investigation of carbonohydrazide [CH_6N_4O, space group $P2_1/c$, $a = 3.625$ (2), $b = 8.794$ (3), $c = 12.456$ (3) Å, $\beta = 106.17$ (2)°, $Z = 4$] indicates that good positional parameters can be obtained for H atoms by the use of high-order data, as found in the investigation of s-diformohydrazide. 3720 selected Mo $K\alpha$ reflections ($2\theta_{max} = 131°$) were measured with the crystal at 85 K; of these, 3688 with $I > \sigma(I)$ were used in the refinements. Intensities were corrected for scan-truncation errors. Full-matrix least-squares refinements were performed with minimum $\sin \theta/\lambda$ values of 0, 0·25, 0·50, 0·65, 0·75 and 0·85 Å^{-1}. H atoms were not refined for cut-offs above 0·75 Å^{-1}. The heavy-atom parameters converged to their final values for the 0·75 Å^{-1} cut-off. The maximum deviations for most parameters occurred with the 0·50 Å^{-1} cut-off. The final bond distances are: C=O 1·246 (1), C—N(1) 1·358 (1), C—N(2) 1·357 (1), N(1)—N(2) 1·410 (1), and N(3)—N(4) 1·416 (3) Å; the mean N—H is 1·019 (45) Å with a variance of 0·0049 Å^2. The configurations around N(1) and N(3) are slightly umbrella-shaped, leading to a non-planar molecule. R indices are in the range 0·025 to 0·032. The electron density deformation map, which was calculated using the structure model refined on high-order data only, implies less conjugation than that found for diformohydrazide, in keeping with the non-planarity of the carbonohydrazide molecule.

Introduction

Owing to the large electron density shift away from the nucleus in bonded H, anomalously short lengths are found for bonds involving H in X-ray structure determinations. The recent investigation of s-diformohydrazide (Hope & Ottersen, 1979) showed that good positional parameters for H atoms can be obtained by

the use of high-order data. The bond lengths found were 1·070 (18) Å for C—H and 1·021 (19) Å for N—H by refinement where data below a $\sin \theta/\lambda$ value of 0·75 Å^{-1} were excluded. The investigation further indicated a difference between H atoms bonded to different atom types, *i.e.* a higher minimum $\sin \theta/\lambda$ cut-off was necessary in order to position H atoms bonded to the more electronegative atom. Such a difference was also indicated by the study of sucrose (Hope, Poling & Ottersen, 1976).

The possibility of finding nuclear positions for H atoms solves the problem of obtaining an accurate structure model from X-ray data alone. Electron deformation densities can, therefore, be obtained from a single set of experimentl data ($X - X_{HO}$), thereby reducing possible sources of errors. The deformation density map of diformohydrazide (Hope & Ottersen, 1979), which was found in this way, indicated a highly conjugated N—C=O moiety and a remarkably small density in the N—N bond.

As part of a systematic study on the use of high-order data to position H atoms, we have investigated the structure of carbonohydrazide ('formyldihydrazine'), CH_6N_4O, which has six H atoms bonded to N atoms. It was of interest to see whether a smaller over-determination ratio would lead to nuclear positions for the H atoms. In addition, a comparison of the deformation density maps for carbonohydrazide with those for diformohydrazide might give information about the accuracy of these maps, and also give a better understanding of the bonding in the N—C=O and N—N—C=O moieties. These moieties have been studied in some detail by both experimental and theoretical means (Ottersen, 1976). The earlier structure determination of carbonohydrazide (Domiano, Pellinghelli & Tiripicchio, 1972) has shown nonplanar configurations around the N atoms bonded to the C atom, which indicates that in comparison with the planar diformohydrazide the lone-pair orbitals of these N atoms are less involved in the conjugation over the N—C=O moiety.

Experimental

Crystals of carbonohydrazide were grown from a 90% ethanol solution in a convection tube (Hope, 1971b). The earlier structure determination (Domiano et al., 1972) had been carried out at room temperature, and in order to obtain a reasonably accurate structure model on which to base the high-order data collection, a low-temperature low-order-data structure determination was first carried out. 866 Mo $K\alpha$ reflections ($2\theta_{max} = 55°$) were collected with the crystal at 85 K. Of these, 800 which had $I \geq 2\sigma(I)$ were used. Starting with the positional parameters from the room-temperature study (see Crystal data), full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for H atoms resulted in an R of 0·030 and an R_w of 0·033.

The resulting model was used, together with sample scan and background measurements, to predict which reflections would have measurable X-ray intensities for a given crystal size and scan speed. A crystal of dimensions 0·45 × 0·30 × 0·20 mm was selected for data collection on a Picker automated four-circle diffractometer equipped with a modified Enraf–Nonius low-temperature device (liquid nitrogen). The temperature was kept constant within 0·2 K at 85 K throughout the experiments. The angular coordinates ($\chi,\varphi,\omega,2\theta$) of 14 Mo $K\alpha_1$ reflections with 2θ values between 70 and 110° were used in a least-squares calculation to determine the crystal orientation and cell dimensions (see Crystal data). In order to study the electron density deformation all reflections with $\sin\theta/\lambda < 0·65$ Å^{-1} were recorded, whereas for higher-order reflections only those which had a predicted $I/\sigma(I) > 15$ were measured.

The intensities of 3720 reflections ($2\theta_{max} = 131°$) were measured using a $\theta/2\theta$ scan, graphite-monochromatized Mo $K\alpha$ radiation, and a scintillation detector with pulse-height analyzer. Each reflection was scanned from $2\theta(\alpha_1) - 0·8°$ to $2\theta(\alpha_2) + 0·8°$ with a scan speed of 2·0° (2θ) min^{-1}. Background counts were measured for 20 s at each end of the scan range. Coincidence losses were minimized by adding an attenuator filter when the count rate exceeded 9500 c.p.s.

Two check reflections, which were remeasured after every 200 reflections, showed no systematic variation throughout the data collection. Each recorded number of counts, N, was assigned a standard deviation $\sigma(N) = [N + (0·0046\ N)^2]^{1/2}$, where the factor 0·0046 reproduces the observed variance in the check reflections. Based on the values of $\sigma(N)$ for scan and background counts, e.s.d.'s for the net intensities were calculated. Of the 3720 reflections measured, the 3688 which had net intensities higher than their e.s.d.'s were used in the refinement procedure.

Lorentz and polarization corrections were applied to the net intensities. The polarization factor includes the polarization by the monochromator crystal (Hope, 1971a). Initial refinements showed a systematic trend in the ratio F_o/F_c, which decreased progressively with increasing 2θ, as was found for diformohydrazide. A correction for scan-truncation errors of the form $I_{corr} = I_o/(1 - T)$ was applied to the intensities (Denne, 1977). Using the notation of Denne, $1 - T$ is given by:

$$1 - T = A_1 C_1 + A_2 C_2 + (\lambda_a - \lambda_b)\{A_1[I_1(\lambda_a)$$
$$+ I_1(\lambda_b)] + A_2[I_2(\lambda_a) + I_2(\lambda_b)]\}.$$

The line widths ($W_1 = 2·9 \times 10^{-4}$ Å and $W_2 = 3·2 \times 10^{-4}$ Å) and intensity ratio ($A_2/A_1 = 0·499$) were obtained from Compton & Allison (1935), and the wavelength values used are $\lambda_1 = 0·70926$ and $\lambda_2 = 0·71354$ Å. In view of the small absorption coefficient ($\mu = 0·143$ mm^{-1}) and the crystal shape, it was found unnecessary to correct for absorption; estimated minimum and maximum transmission factors are 0·96 and 0·98 respectively.

A later check on the data showed a small secondary-extinction effect. The data were therefore corrected for secondary extinction (Zachariasen, 1963) using the structure model refined on data with $\sin\theta/\lambda$ values > 0·75 Å^{-1}.

Crystal data (85 K)

Space group $P2_1/c$, monoclinic, $a = 3·625$ (2), $b = 8·794$ (3), $c = 12·456$ (3) Å, $\beta = 106·17$ (2)°, $V = 381·37$ (5) Å^3, $M_r = 90·09$, $Z = 4$, $D_{calc} = 1·569$ Mg m^{-3}, $F(000) = 192$. The transformation matrix for parameters reported earlier (Domiano et al., 1972) is:

$$(x, y, z)_{present} = (x,y,z)\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -2 & 0 & -1 \end{bmatrix}.$$

Refinement

The quantity $\sum w(F_{obs} - K|F_{calc}|)^2$ was minimized in full-matrix least-squares refinements with $w = 1/\sigma^2(F_{obs})$. The atomic scattering factors used were those calculated by Doyle & Turner (1968) for C, N and O; the contracted spherical scattering factor calculated by Stewart, Davidson & Simpson (1965) was used for H.

The $\sin\theta/\lambda$ cut-off value was varied systematically; refinements were performed with minimum cut-offs of 0, 0·25, 0·50, 0·65, 0·75 and 0·85 Å^{-1}. Some data from the refinements are given in Table 1. H parameters were not refined for the 0·85 Å^{-1} cut-off.

Table 1. *Results from refinements on subsets of data*

The G factor is the goodness-of-fit parameter $\{[\Sigma w(F)^2/(n - m)]^{1/2}$, where n is the number of observations and m is the number of parameters$\}$. The standard deviations given in parentheses are the mean e.s.d.'s for the averaged parameters.

$(\sin \theta/\lambda)_{min}$ (Å^{-1})	Number of reflections	Number of parameters	R (%)	R_w (%)	G	Scale factor $(KF_o = F_c)$	Mean N–H (Å)
0	3688	79	3·23	3·58	3·29	0·0989 (1)	0·878 (9)
0·25	3641	79	3·13	3·34	2·89	0·0992 (1)	0·866 (9)
0·50	3295	79	2·70	2·52	1·62	0·1011 (1)	0·801 (13)
0·65	2844	79	2·37	2·14	1·15	0·0997 (1)	0·893 (40)
0·75	2471	79	2·39	2·15	1·02	0·1001 (2)	1·019 (45)
0·85	2053	55	2·54	2·37	0·99	0·1001 (2)	

The heavy-atom parameters converged to their final values for the 0·75 Å^{-1} cut-off in agreement with the results for diformohydrazide (Hope & Ottersen, 1978). The correlation coefficients between the scale factor and the thermal parameters (B_{ii}'s) of the heavy atoms in this refinement were in the range -0.30 to -0.38. The absolute values of other correlation coefficients were all less than 0·3. Final atomic parameters are listed in Table 2.* The estimated standard deviations in molecular parameters were calculated from the full correlation matrix.

Discussion

As was found for diformohydrazide (Hope & Ottersen, 1979), the O and H atomic parameters have their maximum deviations for the 0·50 Å^{-1} cut-off, where the positional deviation of the O atom is 0·0022 Å and the mean deviation of the H atoms is 0·229 Å. The positional shifts of the N atoms were small; N(1) and N(3) (see Fig. 1 for the numbering of the atoms) had

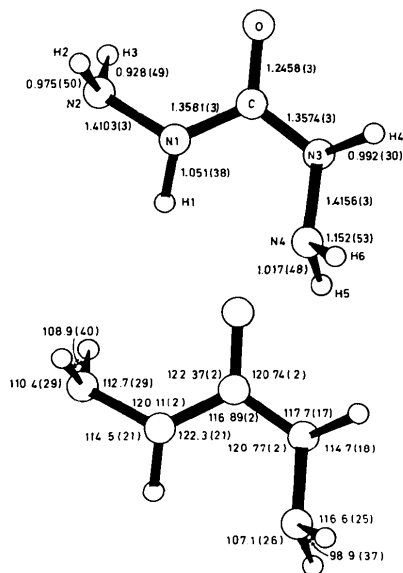maximum deviations of 0·006 Å, and N(2) and N(4) of 0·009 Å, in the refinement using all data. Maximum deviations in bond lengths are: C=O +0·001 Å, N–H

Fig. 1. Bond lengths (Å) and bond angles (°) with e.s.d.'s Results are from the refinement using only data with $\sin \theta/\lambda$ values >0.75 Å^{-1}. The e.s.d.'s are calculated from the full correlation matrix.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33978 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and thermal parameters* (Å^2) *with estimated standard deviations from refinement on data with* $\sin \theta/\lambda$ *values* >0.75 Å^{-1}

The anisotropic temperature factors are given as $\exp\{-\frac{1}{4}[B_{11}(a^*h)^2 + B_{22}(b^*k)^2 + B_{33}(c^*l)^2 + 2B_{12}(a^*b^*)hk + 2B_{13}(a^*c^*)hl + 2B_{23}(b^*c^*)kl]\}$.

	x	y	z	$B_{11}(B)$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	0·91784 (8)	0·40923 (2)	0·64304 (2)	1·111 (6)	0·541 (4)	0·664 (4)	0·136 (4)	0·193 (4)	−0·071 (3)
N(1)	0·89251 (8)	0·23715 (2)	0·50403 (2)	1·049 (6)	0·559 (4)	0·428 (4)	0·180 (4)	0·028 (3)	0·008 (3)
N(2)	0·64397 (8)	0·32846 (3)	0·42194 (2)	0·877 (5)	0·698 (4)	0·532 (4)	0·104 (4)	−0·014 (3)	0·109 (3)
N(3)	1·16345 (8)	0·17395 (3)	0·68966 (2)	1·105 (6)	0·583 (4)	0·456 (4)	0·144 (4)	−0·022 (4)	0·027 (3)
N(4)	1·27130 (8)	0·03114 (3)	0·65547 (2)	0·898 (6)	0·566 (4)	0·690 (4)	0·118 (4)	0·127 (4)	0·074 (3)
C	0·98837 (8)	0·27985 (2)	0·61310 (2)	0·649 (5)	0·494 (4)	0·463 (4)	0·023 (4)	0·092 (3)	0·009 (3)
H(1)	0·9167 (113)	0·1241 (43)	0·4794 (32)	1·57 (32)					
H(2)	0·7845 (146)	0·4133 (56)	0·4017 (39)	1·89 (43)					
H(3)	0·4392 (142)	0·3664 (53)	0·4448 (40)	1·77 (40)					
H(4)	1·3281 (91)	0·2106 (34)	0·7626 (25)	1·24 (27)					
H(5)	1·2281 (139)	−0·0476 (52)	0·7106 (39)	1·77 (43)					
H(6)	1·5948 (151)	0·0119 (56)	0·6675 (43)	1·89 (44)					

(mean) -0.217 Å, found with the 0.50 Å^{-1} cut-off; C—N -0.002 Å, for all data, and also for the 0.50 Å^{-1} cut-off; N(1)—N(2) $+0.004$ Å and N(3)—N(4) $+0.005$ Å, from the refinement using all data.

The mean N—H bond length for the various sin θ/λ cut-offs is given in Table 1. The length decreases with increasing sin θ/λ cut-offs up to the 0.50 Å^{-1} cut-off where the shortest bonds are found (mean 0.799 Å). The N—H distances increase for the 0.65 Å^{-1} cut-off, but are still too short. The lengths obtained for the 0.75 Å^{-1} cut-off give a reasonable mean N—H bond of 1.019 Å with a variance of 0.005 Å^2. The final bond lengths are given in Fig. 1. The variations with increasing (sin $\theta/\lambda)_{min}$ cut-offs and the final mean N—H bond length are in good agreement with the results found for diformohydrazide. However, the e.s.d.'s are two to three times larger than those found for the N—H and C—H bonds in that investigation. The over-determination ratio for the 0.75 Å^{-1} cut-off in the present case is 31, whereas for diformohydrazide it is 58. This may explain the better refinement behavior of the H atoms in diformohydrazide, although the exclusion of data above a sin θ/λ value of 1.28 Å^{-1} in the present case may also be of significance.

Bond lengths and bond angles obtained with a minimum sin θ/λ cut-off of 0.75 Å^{-1} are given in Fig. 1. Both C—N bonds are significantly longer (by about 0.008 Å) than those found in the room-temperature low-order-data investigation (Domiano *et al.*, 1972), whereas the N(1)—N(2) bond is significantly shorter (~0.006 Å). The C—N—N angles are about $1.1°$ smaller in the present study.

The molecule is not planar; deviations from a least-squares plane through O, C, N(1) and N(3) are (Å × 10^{-3}): O -1, N(1) -1, N(2) -267, N(3) -1, N(4) 112, C 3, H(1) -134, H(4) 359. The configurations around both N(1) and N(3) are slightly umbrella-shaped.

The distances between the heavy atoms, where even the N—N lengths indicate some double-bond character, imply that the extensive hydrogen bonding affects the bonding in the entire molecule. (Hydrogen-bond parameters are given in Table 3.) Studies of similar molecules (Ottersen, 1976, and references therein) have shown that the conjugation in N—C=O fragments increases with hydrogen bonding.

The lengthening of the C=O bond in carbonohydrazide compared with that in diformohydrazide (Hope & Ottersen, 1978) [1.246 (1) and 1.239 (1) Å

respectively] is probably caused by the difference in hydrogen bonding. The O atom in carbonohydrazide participates in three relatively weak hydrogen bonds; the single hydrogen bond in diformohydrazide is relatively strong. [See Ottersen & Heiberg (1976) for a discussion of the additivity of the effect of hydrogen bonding.] However, the participation of the orbitals of two N lone pairs in the conjugation over the N—C(O)—N fragment may lead to less participation of the O π orbitals, *i.e.* the O π electron is pushed toward the O atom.

The lengths of the C—N bonds [1.358 (1) and 1.357 (1) Å], compared with that in diformohydrazide [1.331 (1) Å], together with the nonplanar configurations around N(1) and N(3) clearly show that the N(1) and N(3) lone-pair orbitals are less involved in the conjugation than are those in diformohydrazide. Evidence for this is also found in the electron density deformations (see below). The two N lone pairs in carbonohydrazide must compete in the conjugation, *i.e.* the participation of two lone pairs would lead to a too-electron-rich system.

The difference between the lengths of the N(1)—N(2) [1.410 (1) Å] and N(3)—N(4) bonds [1.416 (1) Å] may be caused by the difference in the hydrogen-bonding environment (see Table 3). The hydrogen bonding involving N(1) and N(3) is similar, whereas N(2) participates in one more hydrogen bond than does N(4). However, the difference in the positions of N(2) and N(4) relative to the C=O bond [N(2) *cis*, N(4) *trans*] and the positions of the H atoms may also affect the N—N lengths. The N(2) lone pair is *cis* to H(1), whereas the N(4) lone pair is *trans* to H(4) (see Fig. 3).

Electron density deformation

Electron density difference maps through various sections in the molecule are plotted in Figs. 2–5. The F_c's are calculated using the structure model obtained in the refinement with a minimum sin θ/λ cut-off value of 0.75 Å^{-1}. The 1636 F_o's which have sin $\theta/\lambda \leq 0.85$ Å^{-1} were used in the Fourier summation. The scale factor, 0.0991 (1), was obtained by refinement using this subset of data and structure model; $R = 0.038$, $R_w = 0.053$.

The general shape and peak heights of the deformation densities found in carbonohydrazide are in

Table 3. *Hydrogen-bond parameters*

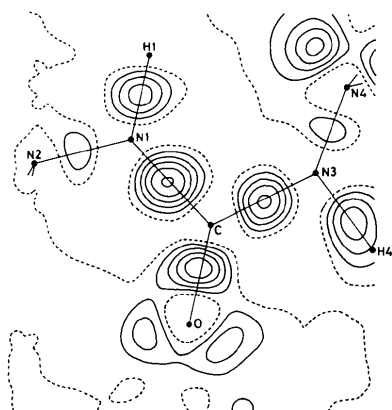| D	A	In position	$D \cdots A$ (Å)	$H \cdots A$ (Å)	$\angle DHA$ (°)
N(3)—H(4)	N(2)	$(1 + x, 0.5 - y, 0.5 + z)$	2.9323 (3)	2.017 (30)	151.2 (24)
N(1)—H(1)	N(4)	$(2 - x, -y, 1 - z)$	3.0347 (3)	2.126 (39)	143.6 (31)
N(4)—H(5)	O	$(2 - x, -0.5 + y, 1.5 - z)$	2.9794 (3)	2.076 (52)	144.7 (41)
N(2)—H(3)	O	$(1 - x, 1 - y, 1 - z)$	3.0341 (3)	2.446 (46)	122.1 (36)
N(2)—H(2)	O	$(2 - x, 1 - y, 1 - z)$	3.0356 (4)	2.023 (48)	178.6 (41)

Fig. 2. Deformation density in the least-squares plane through O, N(1), N(3) and C. The contours are at intervals of 0·1 e Å⁻³. The zero-line is broken.

(a)   (b)
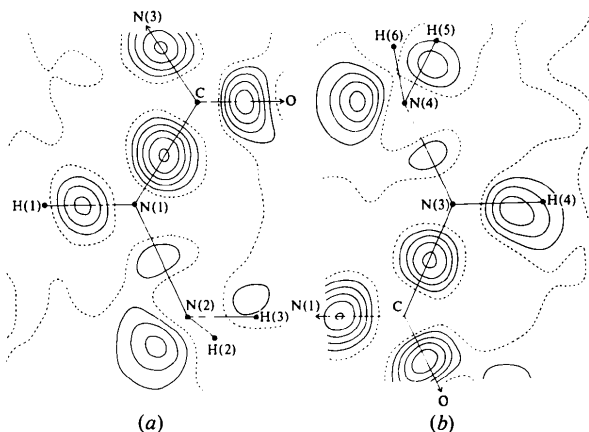
Fig. 3. Deformation densities in the planes defined by (a) N(1), N(2) and C [distances of other atoms from this plane are O 0·221, H(1) −0·315, H(2) 0·901, H(3) −0·569 Å]; and (b) N(3), N(4) and C [O 0·095, H(4) 0·445, H(5) −0·577, H(6) 0·986 Å]. The contours are at intervals of 0·1 e Å⁻³. The zero-line is broken.
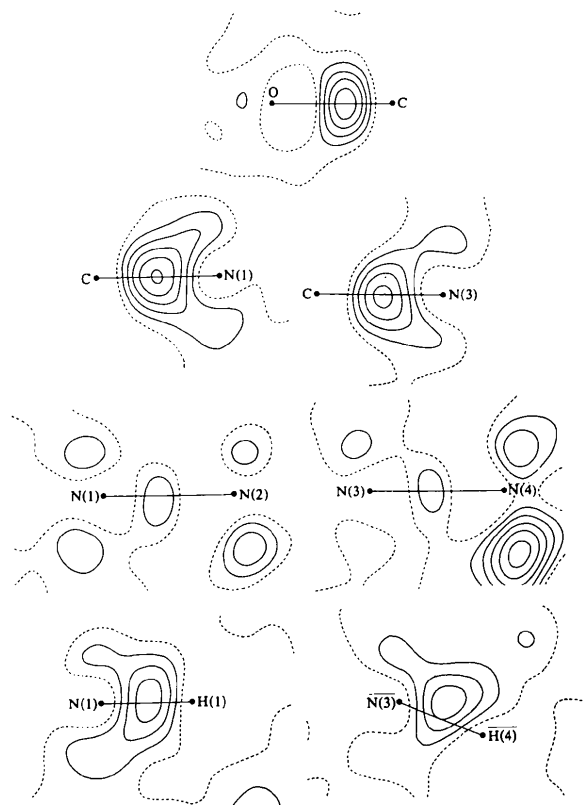

Fig. 4. Deformation densities in the bonds normal to the plane defined by O, N(1), N(3) and C. The densities given for N(1)—N(2) and N(3)—N(4) are in the planes normal to N(1), N(2) and C, and N(3), N(4) and C respectively. The contours are at intervals of 0·1 e Å⁻³. The zero-line is broken.
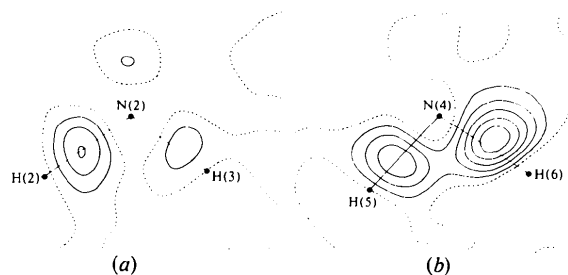

(a)   (b)

Fig. 5. Deformation densities in the planes defined by (a) N(2), H(2) and H(3); and (b) N(4), H(5) and H(6). The contours are at intervals of 0·1 e Å⁻³. The zero-line is broken.

excellent agreement with the corresponding results for diformohydrazide (Hope & Ottersen, 1979). The deformation densities around N(1) or N(3) and in the N—C bonds (Figs. 2, 3 and 4) imply that the N lone pairs, although clearly participating in the conjugation over the N—C(O)—N fragment, are more localized than in diformohydrazide and less involved in the conjugation; this is in agreement with the N—C lengths obtained and with the nonplanarity of carbono-hydrazide.

The deformation density in the N—N bonds (Figs. 3 and 4) is remarkably low with maximum peak heights of 0·18 e Å⁻³, in agreement with that found in diformo-hydrazide and in theoretical deformation maps (Ottersen, Almlöf & Hope, 1979). The N(2) and N(4) lone pairs are located close to the molecular plane, giving a minimum possible overlap with the N(1) and

N(3) lone pairs respectively. Both the N(2) and N(4) lone pairs are acceptors in hydrogen bonds, and this use of the lone pairs together with the participation of the N(1) and N(3) lone pairs in the conjugation over the N—C(O)—N fragment is probably one of the reasons for the short N—N bonds [apparent double-bond characters on the basis of the lengths are: N(1)—N(2) 0·24, N(3)—N(4) 0·21]. The utilization of the lone pairs and the dihedral angle of ~90° leads to a

minimization of lone-pair–lone-pair interactions, which gives a shortened N—N bond.

Conclusion

The least-squares refinement of H parameters on high-order X-ray data shows that the data do contain information about the H atoms, but in this study the amount of data seems to be less than that needed for satisfactory refinement. The variation in the N—H bond lengths with the various minimum sin θ/λ cut-off values follows the same trend as that seen in diformo-hydrazide: the N—H distances decrease with increasing (sin $\theta/\lambda)_{min}$ up to about 0·50 Å^{-1}, where the shortest bond lengths are found; a minimum cut-off of 0·75 Å^{-1} is necessary in order to obtain a reasonable mean N—H bond length.

The excellent agreement between the difference electron densities obtained for carbonohydrazide and diformohydrazide, where the differences follow the expected electronic variations, further support the usefulness of the $X - X_{HO}$ method for obtaining information about electron density deformations.

References

COMPTON, A. H. & ALLISON, S. K. (1935). X-rays in Theory and Experiment. London: Macmillan.
DENNE, W. A. (1977). Acta Cryst. A33, 438–440.
DOMIANO, P., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1972). Acta Cryst. B28, 2495–2498.
DOYLE, P. A. & TURNER, P. S. (1968). Acta Cryst. A24, 390–397.
HOPE, H. (1971a). Acta Cryst. A27, 392–393.
HOPE, H. (1971b). J. Appl. Cryst. 4, 333.
HOPE, H. & OTTERSEN, T. (1978). Acta Cryst. B34, 3623–3626.
HOPE, H. & OTTERSEN, T. (1979). Acta Cryst. B35, 370–372.
HOPE, H., POLING, M. A. & OTTERSEN, T. (1976). Abstr. Am. Crystallogr. Assoc. Summer Meeting, p. 55, D7.
OTTERSEN, T. (1976). Adv. Mol. Relaxation Processes, 9, 105–128.
OTTERSEN, T., ALMLÖF, J. & HOPE, H. (1979). To be published.
OTTERSEN, T. & HEIBERG, A. (1976). Adv. Mol. Relaxation Processes, 8, 305–311.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). J. Chem. Phys. 42, 3175–3187.
ZACHARIASEN, W. H. (1963). Acta Cryst. 16, 1139–1144.

Structural Studies of *O*-Cyclocytidine Derivatives. I. The Crystal and Molecular Structure of 6,2'-Anhydro-1-β-D-arabinofuranosyl-6-hydroxycytosine

By Yuriko Yamagata, Satoshi Fujii, Tadashi Kanai,* Keizo Ogawa and Ken-ichi Tomita

Faculty of Pharmaceutical Sciences, Osaka University, Yamadakami, Suita, Osaka 565, Japan

Abstract

The title compound, $C_9H_{11}N_3O_5$, crystallizes in the monoclinic system with space group $P2_1$, $Z = 2$ and unit-cell dimensions $a = 10\cdot491$ (10), $b = 7\cdot255$ (7), $c = 6\cdot858$ (14) Å and $\beta = 103\cdot55$ (10)°. The structure was solved by the direct interpretation of the three-dimensional Patterson function and refined by full-matrix and block-diagonal least-squares methods. The final R value was 0·051 for 740 independent reflections. The glycosyl torsion angle, χ_{CN}, is 111·4° (*high anti*) and the arabinose conformation is unusual C(4')- exo. The orientation of the C(5')—O(5') bond is *gauche–gauche* as found frequently in many nucleosides.

* Present address: Tokyo Research Laboratories, Kohjin Co., Komiya-cho, Hachioji, Tokyo 105, Japan.

Introduction

The compound 1-β-D-arabinofuranosylcytosine (Ara-C) has been known to be effective as an inhibitor of DNA synthesis (Talley & Vaitkevicius, 1963) and it has been used for the medical treatment of leukemia and lymphoma. Furthermore, the Ara-C cyclo-derivative, 2,2'-anhydro-1-β-D-arabinofuranosylcyto-sine (2,2'-CC), possesses biological activity (Hoshi, Kanzawa, Kuretani, Saneyoshi & Arai, 1971) as a