

The Crystal and Molecular Structure of Hexahydro-3,6-pyridazinedione at -165°C

T. OTTERSEN

Department of Pharmacy, University of Oslo, Oslo 3, Norway

The crystal and molecular structure of the title compound, $\text{C}_4\text{H}_6\text{N}_2\text{O}_2$, has been determined by X-ray methods using 732 reflections above background level collected by counter methods at -165°C . The crystals are orthorhombic, space group $Ibca$, with cell dimensions: $a=9.112(2)$ Å, $b=17.063(3)$ Å, $c=6.175(1)$ Å, with eight molecules in the unit cell. The structure model was refined to an R -factor of 0.039. In order to reduce the influence of the valence electrons all reflections with $\sin \theta/\lambda < 0.5$ Å $^{-1}$ were excluded in the last stages of the refinement procedure (leaving 489 F_o 's, $R=0.031$). The molecule has a "twisted boat" conformation with C_2 symmetry. It is found that substitution at C1 has a significant effect on the molecular parameters.

The structure determination of hexahydro-3,6-pyridazinedione (cyclic succinhydrazide) is part of a series of structure investigations of 3,6-pyridazinediones and related compounds (see Ref. 1 and references therein).

s-Diformylhydrazine has been found² to have a planar S-shape (excluding the hydrogen atoms) in the crystal state, and the bond lengths indicate a high degree of conjugation over the entire molecule. Both experimental³⁻⁵ and theoretical^{6,7} results imply that the $\text{N}-\text{C}=\text{O}$ fragment is easily altered by both substitution and hydrogen bonding. A study of how changes in conformation and substitution will affect the conjugation in the *s*-diformylhydrazine ($\text{O}=\text{C}-\text{N}-\text{N}-\text{C}=\text{O}$) fragment is therefore of interest. A structure determination of cyclic succinhydrazide was consequently carried out. This molecule was expected to have a "twisted boat" conformation close to that found for 1,4-cyclohexanedione⁸ which gives a nonplanar diformylhydrazine fragment.

EXPERIMENTAL

Cyclic succinhydrazide was synthesized by reduction of 3,6-pyridazinedione (maleic hydrazide) with aluminium amalgam.⁹ The crude product was recrystallized in ethyl alcohol. Rhomb-shaped platy crystals were formed.

Oscillation, Weissenberg and precession photographs indicated orthorhombic symmetry. The systematically absent reflections were those characteristic of the space group $Ibca$ and the observed density indicated eight molecules in the unit cell (*i.e.* $\frac{1}{2}$ molecule per asymmetric unit).

A computer-controlled Syntex P1 four-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope), was utilized in the determination of unit cell parameters and the collection of intensity data. The work was carried out using a crystal of dimensions $0.3 \times 0.2 \times 0.05$ mm. Cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of fifteen symmetry-independent reflections with 2θ -values between 42 and 50° . The temperature at crystal site was -165°C .

Three-dimensional intensity data were recorded using the $\omega-2\theta$ scanning mode with scan speed variable from 2 to 8°min^{-1} , depending on the peak intensity of the reflection. Background counting time was equal to $0.7 \times$ scan time. Reflections with 2θ -values larger than 50° which had integrated counts of less than 5 cps, determined in a 2 s scan over the reflection, were not measured. The variations in the intensities of three standard reflections which were remeasured after every fifty reflections were random. Accordingly no corrections were applied to the intensity data for these variations.

The estimated standard deviations were taken as the square root of the total counts with a 2% addition for experimental uncertainties. Of the 787 symmetry-independent

reflections measured ($2\theta_{\max}=70^\circ$), 732 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections, and the remaining were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 and is described in Ref. 10.

The atomic scattering factors used were those of Doyle and Turner¹¹ for oxygen, nitrogen, and carbon, and of Stewart *et al.*¹² for hydrogen.

CRYSTAL DATA

Hexahydro-3,6-pyridazinedione (cyclic succinhydrazide), $C_4H_6N_2O_2$, orthorhombic. Cell dimensions at -165°C : $a=9.112(2)$ Å, $b=17.063(3)$ Å, $c=6.175(1)$ Å. Figures in parentheses are estimated standard deviations. $V=960.1$ Å³; $M=114.1$ amu; $D_{\text{obs}}(19^\circ\text{C})=1.57$ g/cm³; $Z=8$; $D_{\text{calc}}=1.579$ g/cm³; $F(000)=480$. Absent reflections: (hkl) for $h+k+l$ odd; $(0kl)$ for k odd and l odd; $(h0l)$ for h odd and l odd; $(hk0)$ for h odd and k odd; space group *Ibca*.

STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by a computer procedure¹³ based on direct methods utilizing tangent refinement.

The structure model was refined to a conventional R of 0.07. At this point the hydrogen atoms were placed in calculated positions and anisotropic thermal parameters for all nonhydrogen atoms were introduced. Full matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms and isotropic

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms. Results from the refinement using all observed data.

Atom	x	y	z	B
H1	-127(1)	493(1)	-18(2)	2.1(3)
H2	-115(1)	723(1)	54(2)	1.5(3)
H3	-215(1)	679(1)	226(1)	1.3(3)

thermal parameters for hydrogen atoms using all observed reflections converged to a weighted R_w of 0.046 and a conventional R of 0.039.

Earlier structure determinations^{1,2,4,5,14} have indicated that structural parameters found for molecular systems like the present one are significantly influenced by the asphericity of the valence electrons. In order to reduce this influence all reflections with $\sin \theta/\lambda < 0.5$ Å⁻¹ were excluded from the refinement [leaving 489 F_o 's (m)]. Earlier work^{2,5,14} has shown that this asphericity has little or no effect when this cutoff value in $\sin \theta/\lambda$ is used. Least-squares refinement of all parameters ($s=37$) involving nonhydrogen atoms resulted in a conventional R of 0.031, an R_w of 0.034, and an R -factor for the total data-set of 0.042. The "goodness of fit" ($\{(\sum W(F_o - |F_c|)^2)/(m-s)\}^{1/2}$) is 1.51. Atomic parameters for nonhydrogen atoms, obtained in this refinement are listed in Table 1, and parameters for hydrogen atoms, from the refinement using all observed reflections, are given in Table 2. A list of observed and calculated structure factors is available from the author upon request. (May also be obtained from: Department of Chemistry, University of Oslo, Oslo 3, Norway.)

Standard deviations in molecular parameters

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\text{all} \times 10^5$) for nonhydrogen atoms. The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Results from the refinement using high-angle data only.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	4255(7)	60422(4)	4536(13)	182(6)	84(2)	924(19)	11(4)	-50(14)	-42(9)
N	-17311(7)	54095(4)	2(14)	180(6)	60(2)	865(17)	4(5)	56(13)	-56(9)
C1	-9418(8)	60567(5)	4046(16)	216(7)	59(2)	620(21)	11(5)	8(15)	-29(9)
C2	-18329(8)	67886(5)	7566(17)	234(7)	60(2)	1017(21)	20(5)	-114(17)	-88(10)

were calculated from the correlation matrix ignoring standard deviations in cell parameters.

The r.m.s. difference between the observed U_{ij} 's (high-angle data refinement) and those calculated from the "rigid body" model¹⁵ is 0.0004 Å², which indicates that the molecule may be regarded as a rigid body. The atomic positions were accordingly corrected for the librational motion. The eigenvalues of T are 0.10, 0.09 and 0.09 Å², and the r.m.s. librational amplitudes are 4.3, 1.9 and 1.3°. The major axis is nearly parallel with a line through O-O'.

DISCUSSION

A view of the molecular packing in the crystal is given in Fig. 1. Hydrogen bonding across the centres of symmetry forms chains along the (101) and $(\bar{1}01)$ directions. The N-C=O fragments form hydrogen bonded "dimers" similar to those found for formamide.¹⁶ The length of the hydrogen bonds (2.762 Å) is equal to that found for diformylhydrazine.² Overlapping molecules in two chains [one along (101) and one along $(\bar{1}01)$] are separated by $c/2$ (3.088 Å). Between the chains there are only van der Waals contacts in the (010) direction. The closest nonbonding contact (excluding hydrogen atoms) is 3.465 Å [C2...C2 (-0.5-x, 1.5-y, 0.5-z)].

Bond lengths and bond angles are listed in Table 3 and some also in Fig. 2, where the

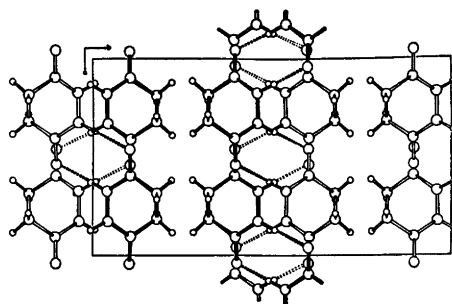


Fig. 1. The crystal structure as seen along the c -axis.

numbering of the atoms is indicated. All three bonds O-C1, C1-N and N-N are significantly longer than the corresponding bonds of, respectively, 1.234(1), 1.333(1) and 1.383(2) Å found for diformylhydrazine.² The results from a series of structure investigations of formamide and substituted formamides in the gas state (see Refs. 3 and 17, and references therein) indicate that both the C1-O and C1-N bonds are lengthened by approximately 0.01 Å when a methyl group is introduced at C1. The differences between the results obtained in this investigation and those found for diformylhydrazine are of the same magnitude. The lengthening of the N-N bond may be caused by the twist of 25.5° (see Table 4) around this bond. Also, the configuration around N is slightly nonplanar. This bond length is close

Table 3. Bond lengths (Å) and bond angles (°). The estimated standard deviations are given in the last digit of the corresponding number and are in parentheses. For nonhydrogen atoms are the parameters obtained in the refinement based only on high-angle data, used in the calculations.

	Bond length	E.s.d.	Corrected bond length		Bond angle	E.s.d.
O-C1	1.247	(1)	1.248	O-C1-N	121.61	(8)
N-C1	1.341	(1)	1.344	O-C1-C2	123.51	(8)
N-N'	1.401	(1)	1.402	C1-N-N'	122.43	(5)
C1-C2	1.506	(1)	1.509	N'-C1-C2	114.88	(6)
C2-C2'	1.533	(2)	1.535	C1-C2-C2'	109.85	(6)
N-H1	0.93	(2)		C1-N-H1	121	(1)
C2-H2	0.98	(2)		N'-N-H1	116	(1)
C2-H3	0.98	(2)		C1-C2-H2	107	(1)
				C1-C2-H3	107	(1)
Hydrogen bond length				C2'-C2-H2	114	(1)
N-O(-x, 1-y, -z)	2.762(1)			C2'-C2-H3	110	(1)
				H2-C2-H3	109	(2)

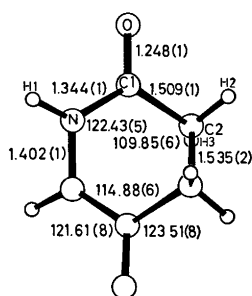


Fig. 2. Bond lengths (Å) (corrected for thermal vibration effects) and bond angles (°) with estimated standard deviations. Structure model obtained using high-angle data only in the refinement.

to that found for 1,2-dimethyl-3,6-pyridazinedione¹⁸ [1.406(1) Å], where the configuration around the N-atoms is about the same as in the present structure. However, a lengthening of this bond caused by the substitution at C1 is indicated by the difference in the N—C (methyl) bonds found in *N*-methylformamide³ and *N*-methylacetamide.¹⁷ The C2—C2' bond has a normal $C(sp^3)$ — $C(sp^3)$ bond length,¹⁹ while the C1—C2 bond is about 0.01 Å shorter than the corresponding lengths for *N*-methylacetamide and acetamide.²⁰ This shortening is probably a result of the increased conjugation over the N—C=O fragment which is caused by the hydrogen bonding. There is a significant lengthening of the C—O bonds and a corresponding shortening of the C—N bonds in the present structure compared with similar non-hydrogen bonded molecules, as has been found earlier (see Refs. 2, 3, and 7 and references therein).

The bond angles around C1 are similar to

Table 4. Dihedral angles (°) with estimated standard deviations. The angles are positive in a right-hand screw.

Dihedral angle	(°)
O—C1—N—N'	178.1(1)
O—C1—C2—C2'	142.2(1)
C2—C1—N—N'	-2.7(2)
N—C1—C2—C2'	-37.0(1)
C1—N—N'—C1'	25.5(2)
C1—C2—C2'—C1'	56.2(1)

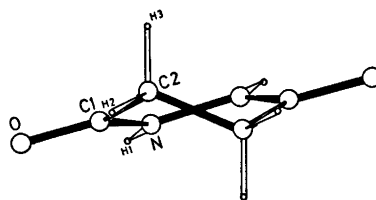


Fig. 3. The molecular conformation as seen along the *b*-axis.

Table 5. Deviations (Å × 10³) from a least-squares plane through O, N, C1, and C2.

Atom	Deviations	Atom	Deviations
O	1	O'	379
N	1	N'	-43
C1	-4	C1'	394
C2	1	C2'	878
H1	-31	H1'	-335

those found for the corresponding angles in other 3,6-pyridazinediones.^{4,5,18} The ∠C1—N—N' is opened by about 3° compared with diformylhydrazine³ and is close to the ones found for 1,2-dimethyl-3,6-pyridazinedione.¹⁸

A drawing of the molecular conformation is given in Fig. 3. The molecule has a "twisted boat" conformation, as has been found for 1,4-cyclohexanedione,⁹ with C_2 symmetry. The four atoms O, N, C1, and C2 are planar (see Table 5). The values of the dihedral angles around the C1—N and N—N' bonds are much smaller than those found around the C1—C2 and C2—C2' bonds. This is probably caused by conjugation over the entire diformylhydrazine fragment.

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Received March 21, 1975.