

The Structure of Diformylhydrazine at 19 °C and –165 °C

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The crystal and molecular structure of *s*-diformylhydrazine has been refined using two X-ray data sets collected by counter methods at 19 °C (956 observed reflections) and –165 °C (1009 observed reflections). The crystals are monoclinic, space group $P2_1/c$, with cell dimensions: $a = 3.583(1)$ Å; $[3.484(1)$ Å]; $b = 6.262(1)$ Å $[6.196(2)$ Å]; $c = 8.992(1)$ Å $[8.950(4)$ Å]; $\beta = 113.04(1)^\circ$ $[112.07(3)^\circ]$, figures in brackets are cell dimensions at –165 °C. The molecule is planar and the bond lengths indicate a resonance stabilization of the molecule. The nitrogen-nitrogen bond length is found to be 1.383(2) Å, using only high-angle reflections ($\sin \theta/\lambda > 0.5$) in the refinements.

The structure investigation of *s*-diformylhydrazine is part of a series of structure studies of 3,6-pyridazindiones and related compounds.^{1–7} This structure has been reported earlier,⁸ investigated by film methods, but experience has shown that the values obtained for nitrogen-nitrogen bond lengths are often influenced by the unsymmetry of the valence electrons.^{1–5} A significant shortening of the observed length of this bond is usually found when low-angle data are excluded in the refinements.

Both experimental (Refs. 5 and 9, and references therein) and theoretical^{6,10,11} results indicate that the conjugated N–C=O-fragment is easily altered by both substitution and hydrogen bonding. A “highly” accurate structure determination of *s*-diformylhydrazine would, therefore, be of interest in order to study differences between this and similar molecules.

It was also of interest to compare results obtained by the *L*-shell¹² and extended *L*-shell¹³ methods to the electron populations found in a recent *ab initio* study.⁸ And, further,

to compare these populations to the experimental ones reported by Tomiie *et al.*⁸

In order to study the effect of different thermal vibrations on the results obtained both for populations and positional parameters, it was decided to collect data at both room- and liquid nitrogen-temperature. Corrections of positional parameters for thermal vibration effects are, for a structure like the present one, highly inaccurate.

EXPERIMENTAL

Suitable crystals of diformylhydrazine were obtained by slow evaporation of a water solution. The space group, $P2_1/a$, and the unit cell parameters reported by Tomiie *et al.*⁸ were transformed to space group $P2_1/c$.

A computer-controlled Syntex-P1 four-circle diffractometer with graphite monochromated MoK α radiation was utilized in the determination of unit cell parameters and the collection of intensity data. In the case of the low-temperature crystallographic work the diffractometer was equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope). Cell constants and their standard deviations were, in both cases, determined by a least-squares treatment of the angular coordinates of fifteen independent reflections.

The recording of the three-dimensional intensity data sets and the subsequent treatment of the data are described below. All programs utilized, when not otherwise indicated, are part of a local assembly of programs for CYBER-74 (see Ref. 14).

Room-temperature data. A redundant data set [the four octants: (hkl) , $(h\bar{k}l)$, $(\bar{h}kl)$, $(\bar{h}\bar{k}l)$] were collected using a crystal of dimensions $0.7 \times 0.4 \times 0.3$ mm, utilizing the $w-2\theta$ scanning mode with scan speed varying from 1° min^{-1} to $12^\circ \text{ min}^{-1}$ depending on the peak intensity of the reflection. Background counting time was equal to scan time. The temperature was maintained at 19 ± 1 °C. The intensities of three

standard reflections, which were remeasured for every hundred reflections, showed no systematic variations throughout the collection.

The Laue symmetry-related reflections were compared and merged.¹⁵ The s -factor, defined as:

$$s = \frac{\sum_{\text{all pairs}} \{I(hkl) - I(\bar{h}\bar{k}\bar{l})\}}{\sum_{\text{all pairs}} \{I(hkl) + I(\bar{h}\bar{k}\bar{l})\}}$$

is 0.026. The estimated standard deviations were taken as the square root of the total counts with a 2% addition (p) for experimental uncertainties. The mean p , calculated on the basis of the intensity variation of each check reflection, was 1.3%.

Of the 1959 reflection pairs measured ($2\theta_{\text{max}} = 100^\circ$), 956 merged reflections had intensities larger than three times their standard deviations, the remainder being excluded from further calculations. The intensities were corrected¹⁵ for Lorentz and polarization effects.

Low-temperature data. The $w-2\theta$ scanning mode with scan speed varying from 2° min^{-1} to $12^\circ \text{ min}^{-1}$ was utilized, using a crystal of dimensions $0.2 \times 0.4 \times 0.4$ mm. Background counting time was equal to scan time. The temperature at crystal site was -165°C . Reflections which had integrated counts of less than 8, determined in a $2s$ scan over the peak, were not measured. The intensities of three standard reflections which were remeasured for every fifty reflections showed no systematic variations throughout the collection.

The estimated standard deviations were taken as the square root of the total counts with a 2% addition (p) for experimental uncertainties. The mean p , calculated on the basis of the intensity variation of each check reflection, was 1.4%. Of the 1086 unique reflections measured ($2\theta_{\text{max}} = 90^\circ$) 1009 had intensities larger than twice their standard deviations, the remainder being excluded from further calculations. The intensities were corrected for Lorentz and polarization effects.

The atomic scattering factors used were those of Doyle and Turner¹⁶ for oxygen, nitrogen, and carbon, and of Stewart *et al.*¹⁷ for hydrogen. Core and valence electron scattering factors used in the L -shell and extended L -shell refinements were those given by Stewart.¹²

CRYSTAL DATA

Diformylhydrazine, $\text{C}_2\text{H}_4\text{N}_2\text{O}_2$, crystal system: monoclinic; absent reflections: $(h0l)$ for l odd; $(0k0)$ for k odd; space group $P2_1/c$. $M = 88.1$ amu; $Z = 2$; $F(000) = 92$. Cell dimensions at 19°C : $a = 3.583(.001)$ Å; $b = 6.262(.001)$ Å; $c = 8.992(.001)$ Å; $\beta = 113.04(.01)^\circ$; $V = 185.66(.08)$ Å³, $D_{\text{calc}} = 1.576$ g/cm³. Cell di-

mensions at -165°C : $a = 3.484(.001)$ Å; $b = 6.196(.002)$ Å; $c = 8.950(.004)$ Å; $\beta = 112.07(0.3)^\circ$; $V = 179.0(1)$ Å³; $D_{\text{calc}} = 1.634$ g/cm³. Figures in parentheses are estimated standard deviations.

REFINEMENTS

Least-squares refinements of all positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms proceeded smoothly, yielding a conventional R -factor of 0.079 and a weighted R_w of 0.091 for the room-temperature dataset. The corresponding values for the low-temperature dataset were $R = 0.069$ and $R_w = 0.080$. No explanation can be furthered for these relatively large R -factors. There were no indications of secondary extinction, difference fourier calculations showed only spurious peaks (< 0.3 e/Å³), and there is no indication of disorder in the structures. Also crystals from different batches and different diffractometers were used in the two data collections (at 19°C and -165°C), and the crystals were mounted generally.

In order to reduce the effects of the unsymmetry of the valence electrons on the refined parameters, low-angle data were excluded from the refinements. By a systematic variation of the lower $\sin \theta/\lambda$ cut value for the data, it was found for both data sets that this unsymmetry had no effect on structural parameters when all reflections with $\sin \theta/\lambda < 0.5$ Å⁻¹ were excluded. This value for the "cut" has been found earlier.^{4,5} The refinement of positional and anisotropic thermal parameters for non-hydrogen atoms using the 830 reflections with $\sin \theta/\lambda \geq 0.5$ Å⁻¹ collected at 19°C , resulted in an R of 0.078, R_w of 0.082 and an R factor for the total data set, R_t , of 0.079. The corresponding parameters using the data collected at -165°C are: number of reflections 828, $R = 0.069$, $R_w = 0.069$, and $R_t = 0.073$. Atomic parameters obtained in these two latter refinements, *i.e.* for non-hydrogen atoms, and final parameters for hydrogen atoms from the refinements using the total data sets are listed in Table 1. A list of observed and calculated structure factors is available from the author upon request. Standard deviations in molecular dimensions

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. (All parameters for non-hydrogen atoms: $\times 10^4$; coordinates for hydrogen: $\times 10^3$.) The temperature factor for non-hydrogen atoms is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Parameters for non-hydrogen atoms are from refinements using high-angle data only.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
A. Refinement using data collected at 19 °C.										
O	38022(41)	14623(18)	26196(12)		7347(99)	1428(23)	640(10)	-351(67)	-715(46)	-245(21)
N	-6283(34)	10405(16)	301(11)		5358(82)	1105(18)	491(9)	375(58)	-92(38)	-55(18)
C	11038(38)	21644(18)	13828(12)		5738(92)	1083(21)	570(10)	-229(63)	348(47)	-212(21)
HC	18(16)	349(10)	125(6)	4.2(9)						
HN	-247(12)	148(8)	-79(6)	3.1(6)						
B. Refinement using data collected at -165 °C										
O	38075(34)	14601(16)	26231(12)		3330(76)	678(18)	371(10)	-86(53)	321(37)	-39(19)
N	-6493(34)	10473(15)	327(12)		2923(77)	504(17)	336(9)	217(54)	534(39)	-52(19)
C	10786(37)	21810(17)	13866(13)		2869(80)	520(19)	377(10)	-107(58)	701(42)	-84(21)
HC	0(7)	363(3)	131(2)	1.3(4)						
HN	-274(8)	160(5)	-84(3)	3.1(5)						

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

L-shell¹² and extended *L*-shell¹³ refinements were then performed, using in all cases only reflections with $\sin \theta/\lambda$ values less than 0.65 \AA^{-1} . *R*-factors obtained are as follows: Data set collected at 19°C : *L*-shell refinement yielded an *R* of .070 and R_w of 0.088, and the extended *L*-shell refinement resulted in $R=0.066$, $R_w=0.084$ for the 280 reflections used. A usual least-square refinement using the same part of the data set gave the values $R=0.070$, $R_w=0.089$. Data set collected at -165°C : *L*-shell refinement yielded an *R* of 0.062 and R_w of 0.073, and the extended *L*-shell refinement resulted in $R=0.058$, $R_w=0.069$ for the 380 reflections used. A usual least-squares refinement using the same part of the data set gave the values $R=0.059$, $R_w=0.070$.

The adjusted¹² gross atomic populations found by these four refinements are listed in Table 2, together with results from *ab initio* calculations.⁶

DISCUSSION

Bond lengths and bond angles are listed in Fig. 1, where the numbering of the atoms is indicated. Differences between the two structure models, excluding parameters involving hydrogen atoms, are small, within three times the standard deviations, and are probably due to differences in thermal vibrations. Corrections of the positional parameters for librational motion of the structure model refined using the room-temperature data set, yielded unsatisfactory results only, *i.e.* negative libration axes. The structure model obtained using the low-temperature dataset will, therefore, be used in the discussion.

Table 2. Gross atomic populations. T. Results from *ab initio* calculations (Ref. 6). A. Data collected at 19°C used in refinements. B. Data collected at -165°C used in refinements. C. Results from Fourier methods (Ref. 8). LS. *L*-shell refinement. ELS. Extended *L*-shell refinement. Estimated standard deviations are in the last digit of the corresponding parameter and are given in parentheses.

Atom/ atom group	T	A LS	ELS	B LS	ELS	C
O	8.56	8.34(10)	8.27(21)	8.30(7)	8.26(16)	8.61
NH	8.20	7.88(12)	7.69(21)	8.10(8)	7.96(16)	7.72
CH	6.24	6.78(16)	7.04(25)	6.60(11)	6.78(16)	6.60

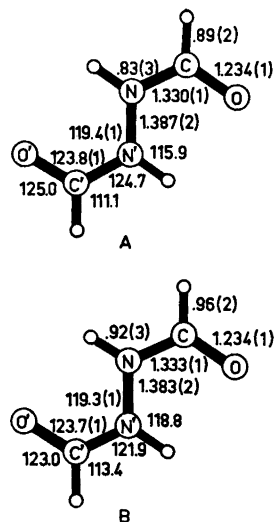


Fig. 1. Bond lengths and bond angles with estimated standard deviations in parentheses. Structure models from refinements using high-angle data only. A, results from refinements using the data set collected at 19°C ; B, results from refinements using the data set collected at -165°C (the e.s.d.'s for bond angles involving hydrogen are about 1.2°).

The length of the N-N bond and the planarity of the molecule (see Table 3) indicates a high degree of conjugation in the molecule, with sp^2 -hybridization of the nitrogen atoms. This hybridization of nitrogen atoms bonded to formyl groups is usually found.^{7,9} The N-N bond length of 1.383 \AA is significantly shorter than those of 1.409 and 1.411 \AA found in formyl dihydrazine⁷ and also to that of 1.406 \AA in 1,2-dimethyl-3,6-pyridazinedione.² It is, on the other hand, significantly longer than the N-N bond lengths found in the

Table 3. Deviations of the hydrogen atoms from a least squares plane through O, C and N.

A, at 19 °C; plane equation:
 $(-0.2099 x - 0.0523 y + 0.0388 z)R - 0.004 = 0$.
 B, at -165 °C; plane equation:
 $(0.2177 x + 0.0529 y - 0.0387 z)R - 0.007 = 0$.

Atom	Deviation ($\text{\AA} \times 10^3$)	
	A	B
HC	-52	3
HN	18	-44

monolactim 3,6-pyridazinediones^{1,2-5} (1.353 - 1.371 Å).

Both experimental^{1,4,5} (see also Ref. 9 and references therein) and theoretical^{6,10,11} results indicate that hydrogen bonding has a marked effect on the conjugation in the N-C=O fragment. A hydrogen bond from nitrogen to oxygen, as in the present structure [N...O distance 2.763(1) Å], will increase the conjugation, *i.e.* give a shorter C-N bond and a longer C-O bond. The bond lengths found here are, respectively, 1.333 and 1.234 Å, while the corresponding bonds reported for formamide in the gas state¹⁸ are 1.368 and 1.212 Å. These differences in the two molecules again indicate the effect of hydrogen bonding on a conjugated system like formyl.

A series of *ab initio* calculations⁶ indicated that "dimerization" of formamide *via* a N-N bond will give a shortened C-N bond. The lengths found for the C-N bonds in formyl dihydrazine are 1.350 and 1.354 Å, which are significantly longer than in the present structure. However, this bond of 1.333 Å is also significantly shorter than the corresponding bond length of 1.345 Å found for 4,5-dichloro-3,6-pyridazindione¹ where a similar N-N bond and hydrogen bond system is present.

Results from theoretical and experimental electron population analyses are listed in Table 2. The gross atomic populations yielded by the extended *L*-shell refinement using the low-temperature data set are probably the "best". Although, theoretical and experimental results are not directly comparable (both because of the difference in dividing the electrons between the centers in the two methods, and because hydrogen bonding and other

short contacts alter the electron cloud), it is interesting to note that in all cases is a large concentration of electron density centered on the oxygen atom, while the CH-group is electron deficient.

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