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The Crystal and Molecular Structure of 1,2-Dimethyl-1,2-diformylhydrazine at 110 K

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The crystal and molecular structure of the title compound, $C_4H_8N_2O_2$, has been determined using 2546 observed reflections collected at 110 K. The crystals are monoclinic, space group $P2_1/c$ with cell dimensions $a=7.470(2)$ Å, $b=8.936(2)$ Å, $c=11.239(2)$ Å, $\beta=131.70°(1)$. The structure model was refined to an R of 0.076. In order to reduce the influence of valence electron asphericity on the structural parameters low-angle data were excluded from the final refinement.s The heavy atom parameters converged to their final values for a minimum $\sin\theta/\lambda$ cutoff of 0.75 Å^{-1}, leaving 957 reflections, the R is 0.061. The molecule has C_2 symmetry and the torsional angle around the N – N bond is $-91.2°(2)$, with the angle between the planes of the two N – C = O fragments being 90.0°, whereas 1,2-diformylhydrazine is planar. Compared with 1,2-diformylhydrazine the loss of hydrogen bonding leads to a lengthening of the C – N bond by about 0.026 Å and a shortening of the C = O bond by about 0.021 Å, in agreement with earlier results.

The structure determination of 1,2-dimethyl-1,2-diformylhydrazine is part of a series of structure investigations of 3,6-pyridazinediones and related compounds, of which part of the purpose is to study the effect of hydrogen bonding on the N – C = O fragment. The experimental results have been complemented by a series of theoretical studies using hydrogen-bonded complexes of formamide as model systems (for a review see Ref. 1).

1,2-Diformylhydrazine is planar[2] and in the crystal the molecules are bound together by N – H···O hydrogen bonds such that each N – C = O fragment participates in two intermolecular hydrogen bonds. The structure of 1,2-diformylhydrazine has recently been reinvestigated using an extensive data set in order to study the deformation electron densities and obtain accurate hydrogen positions.[3] Recent structure investigations of hexahydro-1,2-dimethyl-3,6-pyridazinedione[4] and hexahydro-3,6-pyridazinedione[5,6] which have a hydrogen bonding corresponding to that in 1,2-diformylhydrazine, implied that the formation of the N – H···O bonds leads to a shortening of the C – N bonds by about 0.02 Å and a lengthening of the C = O bonds by about 0.02 Å. In order to get further quantitative results on the effect of hydrogen bonding on the N – C = O fragment, it was of interest to study 1,2-dimethyl-1,2-diformylhydrazine. The results from a series of structure determinations of some simple amides in the gaseous state[7 – 10] indicate that introduction of a methyl group at the nitrogen atom has little or no effect on the C – N bond, whereas a small lengthening (~0.005 Å) of the C = O bond is indicated.

The results for the hexahydro-3,6-pyridazinedione and hexahydro-1,2-dimethyl-3,6-pyridazinedione further show that the introduction of methyl groups leads to an increase in the torsional angles around the N – N bond and a larger degree of sp^3-hybridization for the nitrogen atoms. A similar introduction of methyl groups in 1,2-diformylhydrazine may give a nonplanar diformylhydrazine, as is found for tetraformylhydrazine[11] where the torsional angles around the N – N bond are 90°.

EXPERIMENTAL

Oscillation and Weissenberg photographs indicated monoclinic symmetry and the systematic absences were those characteristic of the space group $P2_1/c$. The density indicated four molecules in the unit cell.

An approximately cube-shaped crystal with edges of about 0.5 mm was used in the collection of intensity data. A computer-controlled Syntex P$\bar{1}$ four-circle diffractometer with graphite-monochromatized Mo$K\alpha$ radiation and equipped with a modified Enraf-Nonius liquid nitrogen cooling device was utilized in the determination of unit cell parameters and the recording of intensity data. Cell constants were determined by a least-squares treatment of the angular coordinates of fifteen reflections with 2θ-values between 50 and 54°. The temperature at crystal site was 110 K.

Three-dimensional intensity data were recorded using the $\omega-2\theta$ scanning mode with scan speed variable from 2.0 to 6.0° min^{-1}, depending on the peak intensity of the reflection. Background counting time was equal to 0.7 × scan time and the scan area was from $2\theta(\alpha_1)-0.8°$ to $2\theta(\alpha_2)+0.8°$. All reflections with 2θ-values less than 50° were recorded, whereas for reflections above this limit only those which had intensities larger than 5 cps determined in a 2 s scan were recorded. There was some accumulation of ice on the crystal during the data collection. However, the intensities of three standard reflections which were remeasured after every sixty reflections were essentially constant throughout the recording run.

The estimated standard deviations were taken as the square-root of the total counts with a 2 % addition for experimental uncertainties. Of the 3033 reflections measured ($2\theta_{max}=80°$), the 2546 which had intensities larger than twice their standard deviations were used in the refinements. 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 which is described in Ref. 12.

The atomic scattering factors used were those calculated by Doyle and Turner[13] for oxygen, nitrogen and carbon, and of Stewart *et al.*[14] for hydrogen.

CRYSTAL DATA

1,2-Dimethyl-1,2-diformylhydrazine, $C_4H_8N_2O_2$, $M=116.12$ amu. Space group $P2_1/c$, cell dimensions at 110 K: $a=7.470(2)$ Å, $b=8.936(2)$ Å, $c=11.239(2)$ Å, $\beta=131.70°(1)$, $V=560.2(2)$ Å^3. D_{obs} (flotation, 19 °C) $=1.36$ g cm^{-3}, $Z=4$, $D_{calc}=1.376$ g cm^{-3}, $F(000)=248$.

STRUCTURE DETERMINATION AND REFINEMENTS

The phase problem was solved by the MULTAN program assembly.[15] The heavy atom structure model was refined with anisotropic temperature factors to a conventional R of 0.10. The eight hydrogen atoms were found among the ten largest peaks in a difference Fourier synthesis calculated using this structure model. These were included in the refinement with isotropic thermal parameters. Full-matrix least-squares refinement of all positional and thermal parameters converged to an R of 0.076 and an R_W of 0.096. The "goodness of fit", $\{[\Sigma w(F_o-|F_c|)^2]/(m-s)\}^{\frac{1}{2}}$, (G) is 4.73.

In order to remove the influence of the valence electron asphericity on the heavy atom parameters the minimum $\sin\theta/\lambda$ cutoff value for data used in the refinements was increased systematically. The heavy atom parameters converged to their final values for a minimum $\sin\theta/\lambda$ cutoff of 0.75 Å^{-1}, in agreement with earlier structure refinements.[3,16] The hydrogen parameters were not refined. The refinement using the 957 F_o's with $\sin\theta/\lambda$-values larger than 0.75 Å^{-1} converged to an R of 0.061, an R_w of 0.075 and a G of 2.31. These relatively large R-factors may be caused both by the accumulation of ice on the crystal during the data collection and the relatively large crystal size. Although this did not affect the intensities of the check reflection, it may have caused errors in other reflections, and part of the large crystal may have moved outside the homogenous part of the X-ray beam for certain diffractometer settings. A final difference Fourier synthesis showed only spurious peaks of maximum density 0.3 e Å^{-3} apart from the accumulation of density in bond and lone-pair regions. The final heavy atom parameters are listed in Table 1, together with the hydrogen parameters obtained in the refinement using all data. A list of observed and calculated structure factors is available from the author upon request. Standard deviations in molecular parameters were calculated from the correlation matrix.

DISCUSSION

Mean bond lengths and bond angles are listed in Fig. 1 where also the numbering of the atoms is indicated. The values of corresponding bonds and angles in the two N-methylformamide fragments are equal, the maximum deviations being 0.003(4) Å

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations. The anisotropic temperature factor is given by: $\exp\{-2\pi^2[U_{11}(a^*h)^2+\ldots+2U_{23}(b^*c^*kl)]\}$. The parameters given for nonhydrogen atoms are those obtained in the refinement using only data with $\sin\theta/\lambda > 0.75$ Å^{-1}.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	.1307(4)	.4555(2)	.9166(3)	.0237(7)	.0137(6)	.0312(8)	−.0047(4)	.0176(6)	−.0042(4)
C2	.2136(3)	.5728(2)	.9906(2)	.0181(7)	.0133(6)	.0222(7)	−.0016(4)	.0139(6)	−.0003(4)
N3	.2871(3)	.6868(2)	.9524(2)	.0182(6)	.0120(5)	.0184(6)	−.0028(3)	.0130(5)	−.0025(4)
N4	.3828(2)	.8132(2)	1.0481(2)	.0138(6)	.0126(5)	.0167(6)	−.0008(3)	.0090(5)	−.0027(4)
C5	.2327(3)	.9272(2)	1.0098(2)	.0184(7)	.0142(6)	.0209(7)	.0009(4)	.0134(6)	−.0003(4)
O6	.2985(4)	1.0445(2)	1.0846(3)	.0299(8)	.0137(6)	.0305(8)	−.0007(4)	.0222(7)	−.0041(4)
C7	.2876(3)	.6787(2)	.8229(2)	.0208(7)	.0201(7)	.0189(7)	−.0008(5)	.0141(5)	−.0019(5)
C8	.6423(3)	.8213(2)	1.1779(2)	.0152(6)	.0201(7)	.0175(6)	−.0013(4)	.0091(5)	−.0015(4)

Atom	x	y	z	B	Atom	x	y	z	B
H2	.243(6)	.588(3)	1.089(4)	3.4(6)	H5	.075(4)	.911(3)	.917(3)	1.5(4)
H71	.429(6)	.709(3)	.859(4)	2.9(6)	H72	.148(5)	.723(3)	.732(3)	2.7(6)
H73	.270(5)	.577(3)	.783(3)	2.2(5)	H81	.717(5)	.780(3)	1.141(3)	1.9(5)
H82	.685(5)	.767(3)	1.265(3)	2.8(6)	H83	.697(5)	.928(3)	1.218(3)	2.3(6)

Table 2. Torsional angles (°), the angles are positive in a right-hand screw.

Angle			
O1−C2−N3−N4	−178.7(2)	O6−C5−N4−N3	−178.9(2)
O1−C2−N3−C7	−3.5(3)	O6−C5−N4−C8	−3.6(3)
C7−N3−N4−C5	93.4(2)	C2−N3−N4−C8	93.3(2)
C2−N3−N4−C5	−91.2(2)	C7−N3−N4−C8	−82.1(2)

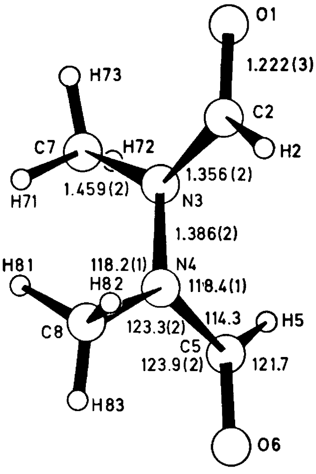

Fig. 1. Mean bond lengths (Å) and bond angles (°). The C−H lengths are in the range 0.89−1.02 Å.

between the two C=O bonds and 0.2°(2) between the angles C2−N3−N4 and C5−N4−N3.

The molecule has very close to C_2 symmetry with the twofold axis passing through the midpoint of the N−N bond (see Fig. 1). The *N*-methylformamide fragments are essentially planar, the mean deviations from least-squares planes through the two O=C−N fragments being: N4/N3 −0.026 Å, C7/C8 −0.076 H2/H5 −0.059 Å, respectively. This implies that the nitrogen atoms are sp^2-hybridized in agreement with the results found for amides.[17] The dihedral angle between these two planes are 90.0°, as was found for tetraformylhydrazine,[11] and the torsional angle C2−N3−N4−C5 is −91.2°(2). (Torsional angles are listed in Table 2.) 1,2-Diformylhydrazine was found to be planar,[2,3] and the large twist around the N−N bond in 1,2-dimethyl-1,2-diformylhydrazine must be caused by the introduction of the two bulky methyl groups and the decreased participation of the two nitrogen lone pairs in the conjugation over the N−C=O fragment caused by the lack of hydrogen bonding. Evidence for the influence of the methyl groups on the twist around the N – N bond is found in hexahydro-1,2-dimethyl-3,6-pyridazinedione where this twist is restrained by the ring formation and the two methyl groups are bent out of the planes of the O = C – N fragments by −0.78 Å and 1.05 Å, respectively. On the other hand the torsional angle C7 – N3 – N4 – C8 is only −82.1°(2), and the more localized (than in 1,2-diformylhydrazine) nitrogen lone pairs must also have an influence on the twist around the N – N bond. Theoretical calculations[1] imply that the formation of N – H···O hydrogen bonds as found in 1,2-diformylhydrazine leads to a loss of σ-electron density from the oxygen *via* the hydrogen bond.[1] This is countered by a larger increase in the π-electron population on the oxygen, which in turn leads to a larger participation of the nitrogen lone pair in the conjugation over the N – C = O fragment, *i.e.* delocalized lone pairs. This leads to a planar 1,2-diformylhydrazine molecule.

The decreased participation of the nitrogen lone pairs in the conjugation caused by the lack of hydrogen bonding in 1,2-dimethyl-1,2-diformylhydrazine is evident in the C = O and C – N bond lengths when compared with those found in 1,2-diformylhydrazine[3] [1.2380(2) and 1.3316(2) Å, respectively]. Taking into consideration the lengthening of about 0.005 Å of the C = O bond induced by the introduction of a methyl group at the nitrogen atom (see Ref. 1 for a discussion of this), the formation of one intermolecular N – H···O hydrogen bond such that both the nitrogen and oxygen atom in the N – C = O fragment participates in the hydrogen bonding, leads to a lengthening of the C = O bond by about 0.021 Å and a shortening of the C – N bond by about 0.026 Å. These values are in good agreement with those found for the hexahydro-3,6-pyridazinediones[4,6] (0.019 and 0.020 Å, respectively) and for the unreduced 3,6-pyridazinediones[1] (0.015 and 0.025 Å, respectively).

The introduction of methyl groups and the lack of hydrogen bonding leads to a lengthening of the N – N bond from 1.3797(2) Å in 1,2-diformylhydrazine to 1.386(2) Å in 1,2-dimethyl-1,2-diformylhydrazine. A similar difference was found for the two hexahydro-3,6-pyridazinediones [1.398(1) and 1.406(1) Å, respectively]. The N – C_{Me} bond lengths found in the present structure are equal to those found in hexahydro-1,2-dimethyl-3,6-pyridazinedione[4] and in the gas phase structure investigation of *N*-methylformamide.[10]

A comparison of the structures obtained for 1,2-dimethyl-1,2-diformylhydrazine and hexahydro-1,2-dimethyl-3,6-pyridazinedione,[4] and 1,2-diformylhydrazine[3] and hexahydro-3,6-pyridazinedione[6] reveals that the introduction of $-CH_2-$ groups at the carbon atoms leads to significant lengthenings of the bonds. The increases are about: C = O 0.008 Å, C – N 0.012 Å and N – N 0.019 Å. The changes in the C = O and C – N bonds are the same as those found between formamide[9] and acetamide,[7] and between *N*-methylformamide[10] and *N*-methylacetamide[8] in the gas phase. These results imply that restraints induced by the ring formation in the hexahydro-3,6-pyridazinediones have no effect, and that these lengthenings of the bonds are coupled to the inductive effect of the methyl groups. Theoretical calculations on formamide and acetamide[17] show that the overlap populations are significantly larger in acetamide than in formamide, although the gross population of the central carbon atom has decreased.

The shortest intermolecular contacts in the present structure are consistent with normal van der Waals-type contacts.

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