

The Crystal Structure and Electron Density Distribution of Tetraformohydrazide at 110 K

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The deformation electron density in tetraformohydrazide (TFH) has been determined by $X-X_{HO}$ Fourier synthesis and by *ab initio* Hartree-Fock calculations. The structure has been refined to a final R_w of 3.8%. The general features of the difference maps are the same with both methods. The most striking feature of the maps is the low electron density in the N–N bond, showing little or no increase compared to the free-atom densities.

The present work is part of a series of investigations on bonding and electron density distributions in molecules containing the N–C=O and N–N moieties. The effect of hydrogen bonding has been studied in some detail both by experimental and theoretical methods.^{1–3} Changes introduced by various substitutions have also been systematically investigated. The X-ray study of 1,2-diformohydrazide³ showed that even for H-atoms realistic nuclear positions can be obtained, and this opens a possibility to obtain accurate experimental deformation densities from X-ray data alone. Deformation density distributions in a series of related molecules have been investigated and compared with theoretical distributions.^{4–6} Within this series the effect of basis set changes in the theoretical investigations has also been investigated.⁶

An earlier X-ray study of TFH⁷ showed a molecular configuration with torsional angles about the N–N bond of 90° in agreement with the structure of 1,2-dimethyl-1,2-diformohydrazide,² whereas 1,2-diformohydrazide is planar.³ The N–N bond should be affected by this non-planarity, and the conjugation over the N–C=O moieties should also be influenced by the competition of two such groups for the N lone-pair.

In order to study these effects and also to get more information about the deformation density distribution in the N–C=O and N–N moieties, the present investigation was undertaken. TFH crystallizes in a non-centrosymmetric space group, which introduces some complications to the calculation of difference Fourier syntheses. By this study one would therefore gain experience concerning the calculation of deformation densities for such space groups.

EXPERIMENTAL

19.0 g (0.20 mol) sodium diformamide⁸ was ground together with 4.4 g (0.05 mol) 1,2-diformohydrazide⁹ and the mixture suspended in 55 ml anhydrous CH_2Cl_2 . 22.9 g (0.20 mol) methanesulfonyl chloride dissolved in 16 ml anhydrous CH_2Cl_2 was added in one portion while stirring, and the heterogeneous reaction mixture was refluxed with stirring for 12 h. The white solid material was filtered off and extracted with acetone for 7 h in a Soxhlet apparatus. By concentrating the acetone extract to ca. 50 ml, the TFH precipitated as a white solid. Further concentration of the acetone extract gave only very minor amounts of TFH. Recrystallization from acetone gave 2.6 g (36% yield based on 1,2-diformohydrazide) of pure TFH as white cubic crystals applicable for X-ray crystallography.

NMR spectra were obtained on Varian T-60A (¹H) and Bruker WH90 FT (¹³C) instruments, and data are given in ppm measured relative to TMS. The mass spectrum was recorded on an AEI-MS902 instrument with ion source temperature 100°C (70 eV, direct sample insertion). ¹H NMR (4% in DMSO-*d*₆): δ 9.27 (4H, s). ¹³C NMR (9% in DMSO-*d*₆): δ 161.6. Mass spectrum *m/e*, (%): 116(2), 88(45), 70(9), 60(48), 46(11), 45(18), 44(100),

42(22), 40(36). The spectrum showed no molecular ion. The m/e 116, 88 and 60 were shown by high resolution to have the composition $C_3H_4N_2O_3$, $C_2H_4N_2O_2$ and CH_4N_2O , respectively.

Data collection and reduction. A crystal of dimensions $0.20 \times 0.20 \times 0.35$ mm was selected for data collection on a Syntex-P1 four-circle diffractometer equipped with a modified Enraf-Nonius low-temperature device (liquid nitrogen). The temperature at the crystal site was 110 ± 1 K. The angular coordinates of 15 reflections with 2θ values between 40 and 70° were used in a least-squares calculation to determine the crystal orientation and cell dimensions (see Crystal data).

The intensities of 874 reflections ($2\theta_{\max} = 136^\circ$) were recorded using a $\theta/2\theta$ scan, graphite monochromatized MoK_α radiation, and a scintillation detector. Since the number of symmetry-independent reflections is small, no attempts were made to exclude low-intensity reflections from the measurements, as was done in similar studies.^{3,10} Each reflection was scanned from $2\theta(\alpha_1) - 1.4^\circ$ to $2\theta(\alpha_2) + 1.9^\circ$ for reflections with $2\theta \leq 50^\circ$, and from $2\theta(\alpha_1) - 1.0^\circ$ to $2\theta(\alpha_2) + 1.1^\circ$ for reflections with $2\theta \geq 50^\circ$, with a scan speed variable from $1.0^\circ/\text{min}$ to $2.0^\circ/\text{min}$ (2θ) depending on the intensity of the reflection as measured in a 3 s preliminary scan.

Three check reflections, measured after every sixty reflections, showed no systematic variations throughout the data collection. Estimated standard deviations of the net intensities were calculated as:

$$\sigma(I) = [(B_1 + B_2) \times \left(\frac{\text{scan time}}{2 \text{ background time}} \right)^2 + I_s + 10^{-4} \times I_s^2]^{\frac{1}{2}}$$

where B_1 and B_2 are the two background counts and I_s is the integrated intensity. The factor 10^{-4} accounts for the observed mean-square deviation of the check reflections. Of the 874 reflections measured, the 730 having net intensities $> 2\sigma(I)$ were used in the refinement.

Lorentz and polarization corrections were applied to the net intensities. The polarization factor includes polarization by the monochromator crystal.¹¹ The intensity data were corrected for truncation errors.¹² Using the notation of Ref. 12, the correction is given by:

$$I_{\text{corr}} = I/[A_1 C_1 + A_2 C_2 + (\lambda_a - \lambda_b)\{A_1 [I_1(\lambda_a) + I_1(\lambda_b)] + A_2 [I_2(\lambda_a) + I_2(\lambda_b)]\}]$$

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 and Allison,¹³ and the wavelength values used are $\lambda_1 = 0.70926$ and $\lambda_2 = 0.71354$ Å. The maximum correction is $I_{\text{corr}} = I/0.935$.

The estimated errors in intensities due to absorption were all in the range 3–5%, and it was therefore regarded unnecessary to apply absorption corrections. Checks on the data during the refinement procedure indicated no effects from secondary extinction.

CRYSTAL DATA (at 110 K)

Space group $I4\bar{2}m$, $a = 6.443(1)$ [6.492(4)], $c = 7.475(1)$ [7.545(4)], $V = 310.36(9)$ Å³ [318.0], $M = 144.06$, $Z = 2$, $D_{\text{calc}} = 1.541$ g cm⁻³, $F(000) = 148$, $\mu = 1.509$ cm⁻¹. The numbers in brackets are results from the earlier room-temperature study.

REFINEMENT

The quantity $\sum w(F_{\text{obs}} - K|F_{\text{calc}}|)^2$ was minimized in full-matrix least-squares refinements with $w = 1/\sigma^2(F_{\text{obs}})$. Starting positional parameters were obtained from the earlier study.⁷ The atomic scattering factors used were those calculated by Doyle and Turner¹⁴ for C, N and O; the contracted spherical scattering factor calculated by Stewart, Davidson and Simpson¹⁵ was used for H.

The $\sin \theta/\lambda$ cut-off value was varied systematically, refinements were performed with minimum cut-off values of 0.0, 0.50, 0.65, 0.75 and 0.85 Å⁻¹. Hydrogen parameters were not refined for cut-off limits above 0.65 Å⁻¹. In some of the refinements with low-order data the hydrogens were refined with anisotropic temperature factors in order to obtain a better agreement between F_{obs} and F_{calc} . A refinement was also performed with a maximum cut-off of 0.85 Å⁻¹. Some data from the refinements are given in Table 1.

The heavy-atom parameters converged to their final values for the 0.75 Å⁻¹ cut-off in agreement with the results for previous investigations.^{3,10}

As found earlier, the maximum deviation from the "true" nuclear position occurred for the 0.50 Å⁻¹ cut-off. This behaviour is now rather well established and seems to reflect real features of the electron density distribution in the X–H bond. For cut-off values above 0.50 Å⁻¹ the refined H position shifts towards a more reasonable value. In the present case the C–H bond lengthens to $1.02(5)$ Å for the 0.65 Å⁻¹ cut-off. This is still too short, but the low scattering power of H at high angles increases the standard deviation of the H parameters to the extent that the use of higher cut-off values is fairly meaningless.

Table 1. Some results from refinements using various parts of the data set. Estimated standard deviations are given in parentheses.

sin θ/λ cut-off (\AA^{-1})	reflections	parameters	R (%)	R_w (%)	R_i (%) ^a	Goodness of fit	Scale for F_o	C–H(\AA)
<0.85	259	23	2.80	3.63	4.81	4.25	0.06502(1)	0.986(15)
–	730	23	3.81	3.98	3.81	2.88	0.06582(1)	0.977(11)
–	730	20	3.79	4.00	3.79	2.89	0.06583(1)	0.973(11)
>0.50	668	20	3.54	2.72	2.88	1.56	0.06782(1)	0.781(20)
>0.65	604	20	3.76	2.75	3.80	1.30	0.06764(1)	1.023(51)
>0.75	544	17	4.22	3.13	3.66	1.22	0.06707(1)	
>0.85	471	17	4.57	3.61	3.60	1.17	0.06568(2)	

^a R_i is the R -factor for the whole data set.

Final atomic parameters from some of the refinements are given in Table 2. The estimated standard deviations in the molecular parameters were calculated from the full correlation matrix. The values of the correlation coefficients involving H were all less than 0.30.

THE STRUCTURE

Molecular parameters are given in Fig. 1. The torsional angle around the N–N bond is crystallographically determined to 90° , with planar configurations around the N atoms. The configuration around the C–N bond is similar to that in diformohydrazide,³ with the oxygen atoms *cis*-planar relative

to the N–N bond. The introduction of two new formyl groups leads to decrease in the N–N–C angle of 1.0° . The angles around N are equivalent to those found in 1,2-dimethyl-1,2-diformohydrazide,² which has a similar configuration as TFH with torsional angles around the N–N bond close to 90° , but with the oxygens anti-planar to the N–N bond.

In Table 3 the bond lengths are compared with those obtained in similar structures. The values differ widely from those reported earlier for TFH.⁷ Some reasons for these discrepancies may be found in the low overdetermination ratio and the refinement technique used in the earlier investigation.

The C–N and C=O bond lengths obtained in the present study imply a low degree of conjugation

Table 2. Parameters from some of the refinements. S is the cut-off value for $\sin \theta/\lambda$ in \AA^{-1} . The anisotropic temperature factor is given by $\exp(-[B_{11}h^2 + \dots + B_{23}kl])$. E.s.d.'s (in parentheses) are in units of the last digits given.

	S	X	Z	$B_{11}(B)$	B_{33}	B_{12}	B_{13}
O	>0.75	0.24913(7)	0.10071(8)	0.01396(10)	0.00576(5)	–0.01652(20)	–0.00041(8)
	>0.65	0.24923(6)	0.10076(7)	0.01387(8)	0.00576(4)	–0.01637(16)	–0.00034(7)
	<0.85	0.24914(12)	0.10079(11)	0.01442(17)	0.00608(13)	–0.01548(38)	–0.00078(22)
N	>0.75	0.0	0.09208(7)	0.00598(5)	0.00270(4)	–0.00098(14)	0.0
	>0.65	0.0	0.09207(6)	0.00597(5)	0.00258(4)	–0.00104(13)	0.0
	<0.85	0.0	0.09244(16)	0.00673(15)	0.00234(14)	–0.00102(53)	0.0
C	>0.75	0.13412(6)	0.18042(6)	0.00787(6)	0.00355(4)	–0.00319(13)	–0.00113(6)
	>0.65	0.13415(5)	0.18039(5)	0.00780(5)	0.00354(4)	–0.00325(12)	–0.00117(6)
	<0.85	0.13423(13)	0.17987(14)	0.00822(14)	0.00441(14)	–0.00204(41)	–0.00159(23)
H	>0.65	0.1253(59)	0.3168(69)	2.06(47)			
	>0.50	0.1198(25)	0.2834(27)	2.01(26)			
	<0.85	0.1213(20)	0.3108(21)	0.0119(33)	0.0018(25)	–0.0107(107)	0.0035(47)

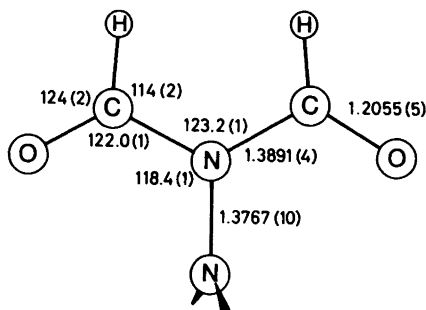


Fig. 1. Bond distances and angles in tetraformohydrazide.

over the $N-C=O$ fragment. The reason for this must be twofold; the lack of hydrogen bonding in the present case and the two formyl groups competing for the nitrogen lone-pair. Earlier studies have shown that hydrogen bonding has a marked effect on the conjugation of $N-C=O$ groups; for a review see Refs. 1 and 2. The reduced participation of the N lone-pair in the conjugation is evidenced by the differences between the bond lengths in TFH and in dimethyl-diformohydrazide.

In conclusion, the molecular parameters obtained in the present study are found to confirm and enhance the conclusions drawn from earlier investigations.

Deformation electron density. TFH crystallizes in a non-centrosymmetric space group. A difference density map calculated in the standard way, assuming the same phases for F_{obs} and F_{calc} , will therefore suffer from considerable errors.^{6,16} The difference densities were therefore calculated in the same way as for acetamide.⁶ A low-order refinement ($<0.85 \text{ \AA}^{-1}$) with 259 observed reflections was performed in order to obtain atomic parameters for comput-

ing the scale and phases of F_{obs} . For this purpose, a good fit between observed and calculated intensities is more important than the physical significance of the parameters, and anisotropic temperature factors were therefore refined for the hydrogen atoms. The final F_{calc} , on the contrary, were computed from atomic parameters refined with high-order data ($>0.75 \text{ \AA}^{-1}$ for the heavy atoms, $>0.65 \text{ \AA}^{-1}$ for hydrogen). The low-order subset of data was used in all calculations of deformation densities.

The mean difference in phase angles between F_{obs} and F_{calc} is 1.16° , and the corresponding r.m.s. phase difference is 2.55° . These values are small compared with those found for acetamide,⁶ 2.3 and 3.7° , respectively, and for lithium formate monohydrate,¹⁷ 3.3 and 7.2° . However, results from other, similar investigations indicate that the absolute values of these phase differences do not necessarily reflect the effect their omission would have on the densities.

The resulting $X-X_{HO}$ map is shown in Fig. 2. The densities in bonds and lone-pairs increased with 10–40% compared to the map calculated with the standard method.

A difference map based on the low-order parameters showed densities in the bond and lone-pair regions of up to 50% of those shown in Fig. 2. Ideally for the purpose of this parameter set this difference should show zero value at all points, since the parameters are used to calculate the phases of F_{obs} . However, since all interesting regions in TFH are situated on symmetry elements where the e.s.d. of the density is relatively high, no attempts were made to obtain a better fit for the low-order refinement, as was done for acetamide.

Deformation electron densities are often readily accessible to theoretical calculations. Systems of the size of TFH may easily be treated with compa-

Table 3. Some bond lengths obtained in a series of related molecules.

	C=O	C-N	N-N
TFH (present work)	1.2055(5)	1.3891(4)	1.3767(10)
TFH (previous work ⁷)	1.214(5)	1.325(4)	1.346(6)
Diformohydrazide ³	1.2380(2)	1.3316(2)	1.3797(2)
Dimethyldiformohydrazide ²	1.222(3)	1.356(2)	1.386(2)
Hexahydropyridazinedione ⁴	1.245(1)	1.346(1)	1.398(1)
Carbonohydrazide ¹⁰	1.2458(3)	1.3581(3)	1.4103(3)
		1.3574(3)	1.4156(3)
Hexahydro-dimethylpyridazinedione ¹⁸	1.230(1)	1.366(1)	1.406(1)
	1.232(1)	1.366(1)	

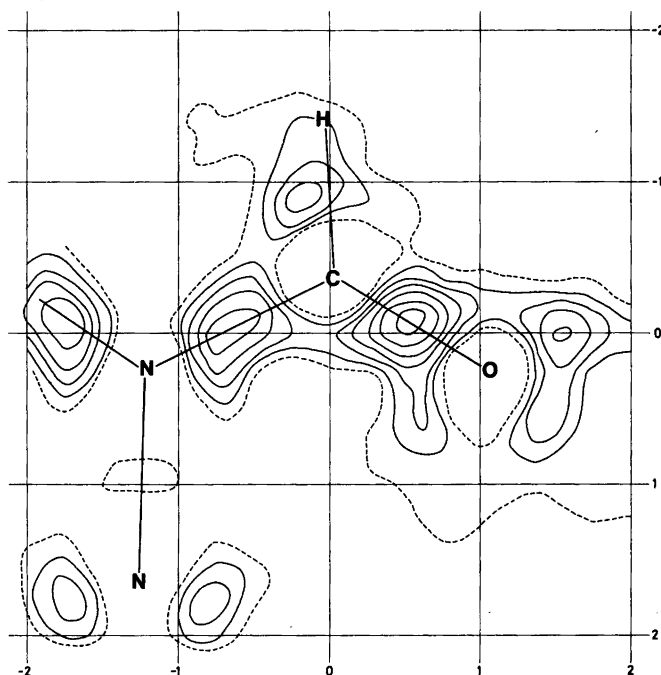


Fig. 2. Experimental deformation density in the symmetry plane of the molecule.

ratively accurate calculations on the Hartree-Fock level of approximation. The question then arises whether that approximation is applicable for the study of problems related to electron density distributions.

Defining a fluctuation potential as the difference between the exact Hamiltonian and the sum of Hartree-Fock operators for the electrons of a system

$$H' = H - \sum_i F(i)$$

it may be shown that, in a perturbational approach, the Hartree-Fock electron density is correct up to the second order in the fluctuation potential. The Hartree-Fock method should therefore be rather well suited for the present type of investigation.

In a previous study on diformohydrazide, it was found that a polarized basis of roughly triple-zeta quality produced rather reliable deformation densities. The same basis set was therefore used in the present investigation (*i.e.* $9s5p1d$ contracted to $5s3p1d$ for C, N and O, and $5slp$ contracted to $3slp$ for H). The entire basis set for the calculation thus comprised 224 contracted basis functions. From the calculated wavefunctions the electron density

$$\rho(r_1) = \int \psi^*(r_1, r_2 \dots r_n) \psi(r_1, r_2 \dots r_n) dv_2 dv_3 \dots dv_n$$

was evaluated. The deformation density was obtained by subtracting densities for the atoms, calculated in the same way and with the same basis set. This procedure ensures a close cancellation of errors introduced by the different approximations used in the calculations. The resulting theoretical deformation density is shown in Fig. 3. Both the experimental and the theoretical deformation densities conform well with those obtained earlier for similar structures.^{4-6,10} The peak heights in the C=O bonds vary from 0.4 to 0.6 $e \text{ \AA}^{-3}$, and in the C-N bonds from 0.4 to 0.55 $e \text{ \AA}^{-3}$. The largest difference between the experimental and theoretical densities is found in the oxygen lone-pair region, where the theoretical densities are significantly higher than the experimental ones. Similar discrepancies have been noted in previous studies on related compounds.^{4,6} The basis set used in the present calculations probably gives somewhat overestimated lone-pair densities (*cf.* Ref. 6 for a systematic investigation of this effect), but this does not seem to explain the whole discrepancy. According to the theoretical maps, the oxygen lone-pairs are very

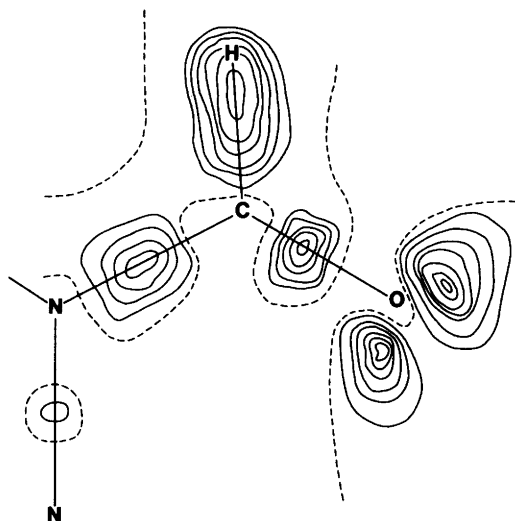


Fig. 3. Theoretical deformation density in the symmetry plane of the molecule.

contracted and close to the nucleus. It seems likely, therefore, that the high-order atomic parameters are still affected by these density distributions, which accordingly will appear with reduced amplitude in the difference maps.

When comparing the present results with those obtained earlier, the differences are rather small and probably insignificant, in particular when diformohydrazide is concerned. The particularly low densities previously found in the N-N bonds are observed in the present case also. A detailed discussion of the deformation density in TFH in relation to the previous findings is therefore considered superfluous.

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