

PRECISION MOLECULAR GEOMETRY DETERMINATION: LOW TEMPERATURE NEUTRON DIFFRACTION VERSUS AB-INITIO MOLECULAR ORBITAL CALCULATIONS (*)

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ABSTRACT — Four molecules have been studied by single crystal neutron diffraction: acetamide at 23 K, fluoroacetamide at 20 K, formamide oxime at 16 K, and 1,2-diformyl hydrazine at 15 K. *Ab-initio* molecular orbital calculations were carried out using GAUSSIAN-80 at the Hartree-Fock level with a 3-21G basis set. For acetamide and 1,2-diformyl hydrazine, the conformation of the molecules in the crystal is not that of the calculated minimum energy. The observed bond lengths, when corrected for thermal motion effects, differ from those calculated by *ab-initio* geometry optimization. These differences are reduced when corrections are applied to the theoretical values for polarization, electron correlation and hydrogen bonding. Except in the case of C=N and N-O bonds, the residual discrepancies are comparable with the experimental errors (σ 's, 0.0002 to 0.0012 Å). Larger discrepancies occur in X-H bonds due to the inadequacy of thermal riding-motion corrections assuming harmonic motion.

1 — INTRODUCTION

In the past ten years, the determination of the crystal structures of organic and organometallic molecules with molecular

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weights of less than 500 daltons by X-ray diffraction has changed from an intellectually stimulating and challenging problem to a routine methodology. This is a consequence of developments in computer technology and some very clever programming of these computers by small groups of gifted crystallographers. Computer-controlled diffractometers collect the diffraction data and structure-solving and refinement packages complete the analysis. The computers provide the final numerical data and computer graphics display the results visually. Of the 800 crystal structures reported in *Acta Crystallographica Section B* for 1980, in less than one hundred was there any serious difficulty in solving the phase problem.

As a consequence, crystal structure analysis has moved out of physics to become a routine tool of analytical chemistry. Crystallographers have sought their intellectual satisfaction by applying their methodology and interests in stimulating ways in other fields of science where the geometrical arrangement of atoms in the crystalline state has relevance to the interpretation of macroscopic phenomena. Most spectacular has been the impact of crystallography on the biological sciences, leading to the birth of a new specialty in the field, molecular biology. The understanding of biological function and malfunction has moved from the microscopic scale to the atomic scale of the Angstrom unit, with important consequences in the medical sciences.

In this paper, we will be discussing an interaction between Crystallography and Quantum Chemistry. It is over 50 years since Dirac claimed quantum mechanics to be capable of explaining all of chemistry and most of physics. Since that time, both of these fields have expanded much faster than even the simpler phenomena have been explained by any solutions to the wave equations, however approximate. What quantum mechanics has provided is a convenient and generally acceptable descriptive language for explaining *qualitatively* certain chemical and physical phenomena in terms of electronic and nuclear behaviour. Despite the great growth in computing power over the past twenty years, the number of *quantitative* comparisons between the results of *ab-initio* quantum theory and experimental measurements are relatively few. The magnitude of the computing power for *ab-initio* methods has forced the use of semi-empirical

methods where quantum mechanical concepts are combined with quantities obtained from experimental observations.

In recent years, the development of the GAUSSIAN series of programs [1] has made possible the *ab-initio* nuclear geometry energy optimization of molecules containing first row elements which are large enough to form crystals at room temperatures. This interests the crystallographer who believes that crystal analysis by X-ray or neutron diffraction is the method, *par excellence*, of measuring the atomic geometry of molecules of this size. In this paper, we report the results of this comparison between theory and experiment. The molecules and crystal structures we have studied are shown in Table 1.

TABLE 1 — Molecules studied *

	Space group	Molecular symmetry	Temperature (K)	R-factor	E.s.d ($\bar{A} \times 10$)
Acetamide	R3c	1	23	0.021	10-20
Fluoroacetamide	$P\bar{1}$	m	20	0.023	4-8
Formamide oxime	$P2_12_12_1$	1	16	0.017	4-8
Diformyl hydrazine	$P2_1/c$	1	15	0.024	4-7

* The details of these results are reported elsewhere [2].

2 — THE THEORETICAL METHOD

The nuclear geometry minimization was carried out with *ab-initio* molecular orbital (LCAO) theory at the Hartree-Fock level using the 3-21G split-valence basis set incorporated in the GAUSSIAN-78 and -80 programs. All geometrical parameters were minimized. In appropriate cases, the final minimization was preceded by global searches of minimized energy conformations using the smaller STO-3G basis set. Comparison with spectroscopic microwave data on simpler molecules gives good reason to believe that at the HF/3-21G level of approximation,

the agreement in bond lengths with experimental values is within 0.05 Å. Table 2 gives the differences between theory and experiment for these simpler molecules at different levels

TABLE 2 — Molecular geometry from quantum mechanics: $\Delta_{\text{theory-exp.}}$ (Å)

Ab-initio M.O. calculations using Pople methodology [3]

Basis sets	Electronic Correlations				
	Hartree-Fock	Moller Plesset Perturbations			
		MP1	MP2	MP3	∞
STO-3G	0.010 <i>d</i>				
3-21G 4-31G	0.000 <i>a</i> 0.033 <i>b</i> 0.006 <i>c</i> 0.039 <i>d</i>				
6-31G *	0.018 <i>a</i> 0.014 <i>b</i> 0.009 <i>c</i> 0.029 <i>d</i>		0.006 <i>a</i> 0.012 <i>b</i> 0.008 <i>c</i>	0.005 <i>a</i> 0.012 <i>b</i> 0.008 <i>c</i>	
6-31G **					
\downarrow ∞				Schrödinger Equation	

a C-N in methylamine
b C-H in formaldehyde
c N-H in methylamine
d N-O in formaldoxime

} vs microwave spectroscopy

of approximation. Table 3 shows a similar comparison in a different form.

These results show that in certain cases, i.e. for the C-N bond in methylamine, there is a cancellation of errors in the

TABLE 3—Effects of level of approximation on bond lengths in some small molecules

Bond	Molecule	HF/3-21G [4]	HF/6-31G * [4]	MP3/6-31G * [5]	Spectroscopy [6] ± (0.005-0.010)
C-C	Ethane	1.542	1.528	1.526	1.526
C=O	Formaldehyde	1.207	1.184	1.210	1.208
C-N	Methylamine	1.472	1.453	1.466	1.471
N-O	Hydroxylamine	1.469	1.403	1.444	1.453
C=N	Methylenimine	1.256	1.250	1.275	1.273
C-H	Methane	1.083	1.084	1.091	1.094
	Formaldehyde	1.083	1.092	1.104	1.116
N-H	Ammonia	1.002	1.002	1.017	1.012
O-H	Methanol	0.946	0.946	0.967	0.956

lower level approximations. The poorer agreement is observed for multiple bonds, as in C=O, and for bonds between electro-negative atoms, as in N-O, as shown in Table 4. This suggests that the calculated theoretical bond lengths are sensitive to the effects of electron correlation. The molecules shown in Table 1 contain between 32 and 46 electrons. Extension to molecules with more than 50 electrons involves excessive computing, which increases approximately as the fourth power of the number of electrons. Calculations at higher levels for molecules of this size is also not feasible, since each advance to a higher level in Table 2, involves a factor of about ten in computing.

3 — THE EXPERIMENTAL METHOD

All the crystal structures shown in Table 1 have been determined previously by X-ray diffraction. The experimental data for this work was collected at the Brookhaven High Flux Reactor using monochromated neutrons. The crystals were maintained at the temperatures indicated in Table 1, using a DISPLEX (CS-202) closed-cycle refrigerator. The intensities were corrected for absorption and extinction. The nuclear parameters were refined by full-matrix least-squares [7], using an anisotropic extinction parameter [8] where necessary. The thermal motion was analyzed by the segmented-body analysis method, ORSBA [9]. The bond lengths were corrected for the libration effect and for riding-motion [10] in the case of those involving hydrogen atoms.

The use of neutron diffraction permits the direct comparison with the theoretically calculated nuclear geometries. With present low-temperature technology, lower temperatures can be obtained on neutron diffractometers than on X-ray instruments.

4 — COMPARISON BETWEEN THEORY AND EXPERIMENT

Agreement between the theoretical and experimental molecular geometries is not expected for the following reasons:

- 1 — Molecule at rest versus molecule undergoing thermal and zero point motion.

TABLE 4 — Experimental and theoretical molecular dimensions (\AA) of acetamide at 23 K and fluoro-acetamide at 20 K
 The σ values in parentheses refer to the last significant figure

Bond	CH_3CONH_2			$\text{FCH}_2\text{CONH}_2$			
	Experimental at 23 K		Theoretical	E.D.	Experimental at 20 K		Theoretical
	Observed	Corrected			Observed	Corrected	
C—C	1.5094(10)	1.513	1.516	1.519(6)	1.5109(5)	1.512	1.517
C=O	1.2468(12)	1.250	1.216	1.220(3)	1.2437(5)	1.246	1.216
C—N	1.3351(11)	1.337	1.358	1.380(4)	1.3242(2)	1.327	1.341
C—F					1.3906(5)	1.391	1.405
C—H(1)	1.085(2)	1.125	1.085				
C—H(2)	1.076(2)	1.119	1.082	1.124(10)	1.0942(7)	1.112	1.078
C—H(2')	1.076(2)	1.119	1.079		1.0937(8)	1.112	1.078
N—H(3)	1.023(2)	1.036	0.998		1.0227(8)	1.037	0.997
N—H(4)	1.023(2)	1.037	0.994	1.022(11)	1.0138(7)	1.037	0.994

- 2 — Isolated molecule versus molecule in the crystal field. Distortion of molecules due to hydrogen bonds, polar interactions, and van der Waals' forces.
- 3 — Approximations in the *ab-initio* theory due to deficiencies in basis set and electron correlation.

Of these, thermal motion, hydrogen-bonding, and approximations in the theory were expected to be significant in terms of the experimental errors of the neutron diffraction measurements. All these crystals contain hydrogen-bonded molecules. They would not be crystals at room temperature otherwise. The necessity to use crystals which have melting points above room temperature is a technicality concerned with the efficient utilization of a scarce neutron facility. Procedures are being developed at Brookhaven National Laboratory to grow and examine low-melting crystals outside the neutron beam and transfer them to the cryostat without melting. This would permit similar studies of simple molecules where higher level theory can be applied.

At the start of these experiments, we were by no means certain that we could unscramble these three effects, which are likely to be all of the same order of magnitude; that is, between 0.01 and 0.05 Å. However, we were sure we would learn something new in trying to do so. Unsuccessful experiments are frequently more informative than successful ones.

The first interesting result that we obtained was that for two of these molecules, acetamide and diformyl hydrazine, the conformation of the molecules in the crystal is not that of the calculated minimum energy for the isolated molecules at rest. The molecule of acetamide is shown in Fig. 1. The thermal ellipsoids are at 75 % probability instead of the more usual 50 %. The relatively large thermal ellipsoids of the C-H bonds at 23 K were unexpected. Acetamide is an asymmetric molecule in an asymmetric crystal structure, space group R3c. In contrast, the theoretical minimum energy conformation of acetamide has *m* symmetry with one of the C-H bonds in the plane of the molecule. At the HF/3-21G level, the observed asymmetric conformation is calculated to be 1.5 kJ/mol higher than the symmetrical molecule. We can speculate that this is due to better van der Waals' packing

of the methyl groups on adjacent molecules, but we have no proof of this and the reason may, in fact, be more subtle.

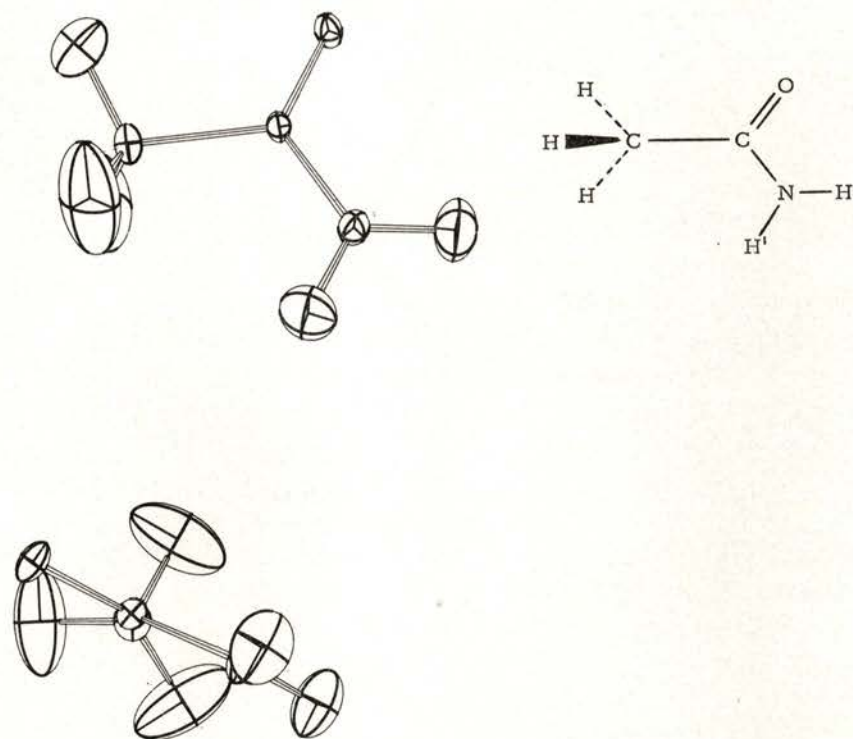


Fig. 1 — Thermal ellipsoids for acetamide (hexagonal form) at 23 K, shown at 75% probability. Top: atomic notation and view perpendicular to C, N, O plane. Bottom: view in direction of C(2)-C(1) bond.

In monofluoroacetamide, shown in Fig. 2, both the observed and calculated molecules have the same *m* conformation, with the C-F bond in the plane of the molecule. The bond lengths for these two molecules are shown in Table 4. For the bonds not involving hydrogens, the thermal motion corrections are $\approx 0.002 \text{ \AA}$. The uncertainty in these corrections, due to the assumption in the models used and of harmonic motion, is likely to be about

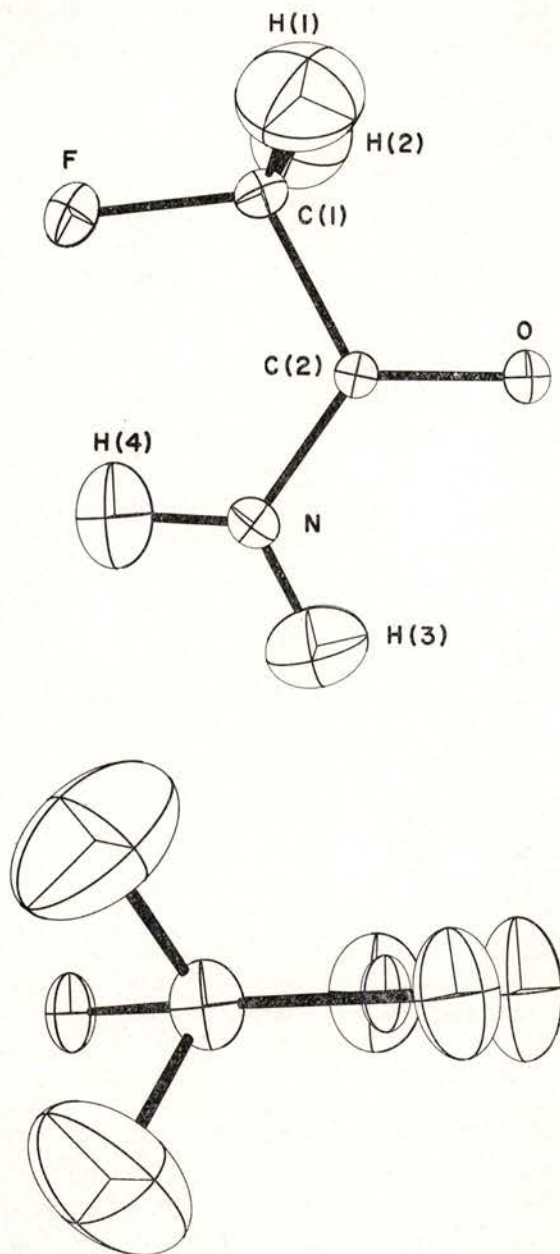


Fig. 2 — Atomic notation and thermal ellipsoids (75%) for monofluoroacetamide at 20 K, viewed normal to and in the plane of the molecule.

10 %, i.e. of the same magnitude as the experimental standard deviations. In other words, the application of thermal motion corrections approximately doubles the uncertainty of the experimental results.

The significant result is for the observed and calculated C-N and C=O distances. The C-N bonds are observed 0.021 Å shorter than those calculated, and the C=O bonds are observed 0.034 Å longer. This we interpreted as due to hydrogen-bonding in the crystal. To verify this, a HF/3-21G calculation was carried out on the formamide closed hydrogen-bonded dimer. These results are shown in Fig. 3. The values in parentheses are for the monomer. At this level of theory, the hydrogen-bonding diminishes the C-N bonds by 0.023 Å and lengthens the C=O bonds by 0.018 Å. In view of the disparity between the dimer model and the acetamide crystal structure, this agreement is very satisfactory. The theory also predicts a lengthening of the N-H bonds by 0.018 Å when involved in hydrogen-bonding.

The comparison of the experimental and observed X-H bond lengths is obscured by the large thermal riding-motion corrections shown in Table 3. Clearly, the agreement between experiment and theory for X-H bonds is better if the thermal motion effect is ignored. The reason for that, we believe, is because the effect of the riding-motion, which leads to a shortening of the observed bond lengths, is compensated for by the anharmonicity of the internal stretching motion, which increases the bond length to that of a bond in a molecule *at rest*. At these low temperatures, these two effects appear to almost cancel.

Another significant source of discrepancy between theory and experiment is the level of approximation in the theory. This can be estimated from the results of the higher order calculations on simple molecules containing the same bonds, shown in Tables 1 and 2.

Both corrections for hydrogen-bonding and basis set and electron correlation deficiencies can be applied to give residual discrepancies shown in Table 5. These residuals are less than 0.010 Å, except for the C-N bond in fluoroacetamide and the C-H bond lengths. This is better agreement than we anticipated, in view of the approximation of the simple hydrogen-bonding model and deficiencies in the thermal motion and *ab-initio*

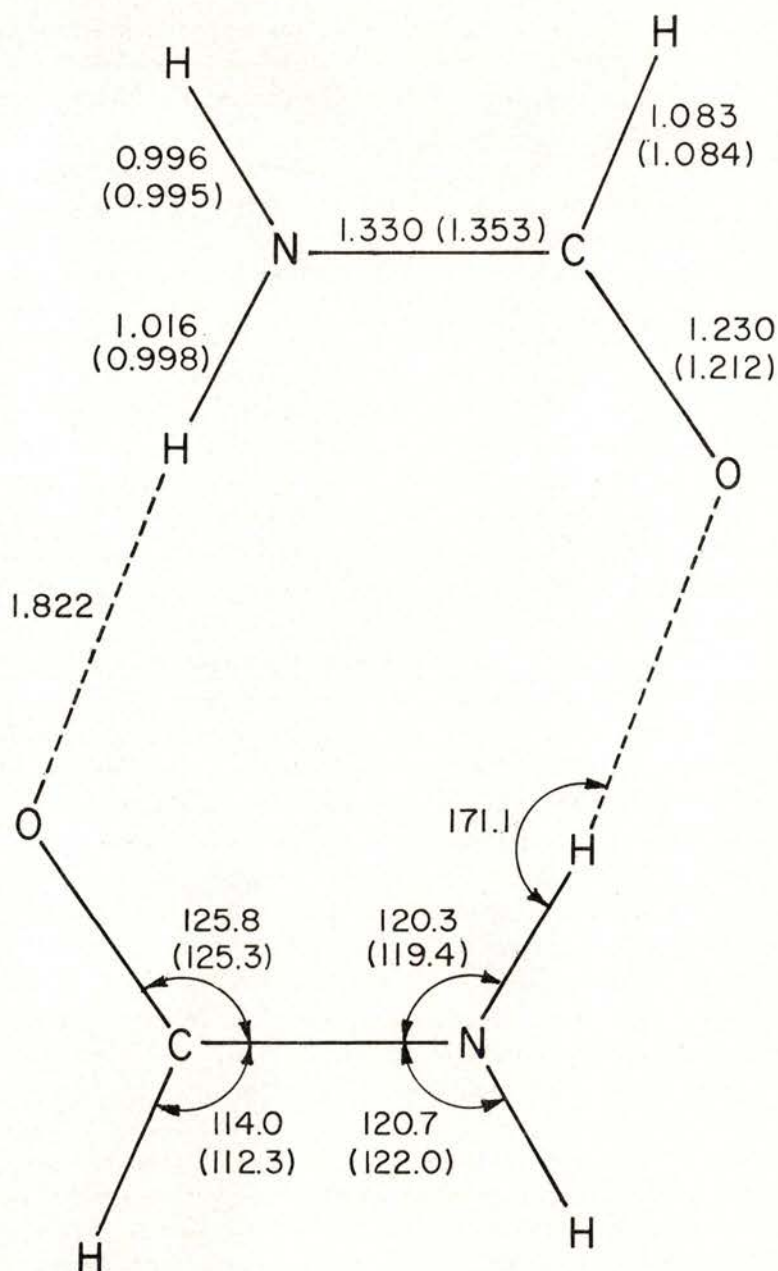


Fig. 3 — Theoretical geometry optimization of formamide and the hydrogen-bonded formamide dimer with HF/3-21G, using GAUSSIAN 80. The values in parentheses refer to the monomer.

TABLE 5— Analysis of bond length discrepancies in acetamide and fluoroacetamide

Upper values are for acetamide, lower values for fluoroacetamide

Bond	Δ Theory-Experiment	Higher Level Extrapolation	H-bonding Extrapolation	Residual Δ
C=O	-0.034 -0.030	+0.014 <i>a</i>	+0.018	-0.002 +0.002
C-N	+0.021 +0.015	-0.006 <i>b</i>	-0.023	-0.008 -0.014
N-H	-0.041 -0.041	+0.015 <i>c</i>	+0.020	-0.006 -0.006
C-C	+0.003 +0.005	-0.003 <i>d</i>		0.000 +0.002
C-H	-0.037 -0.034	+0.011 <i>e</i>		-0.026 -0.023

a MP2/6-31G * formaldehyde*b* MP2/6-31G * methylamine*c* MP2/6-31G * ammonia*d* HF/6-31G * acetaldehyde*e* MP2/6-31G * methane

theories used. Very similar results were obtained for formamide oxime, as shown in Table 6.

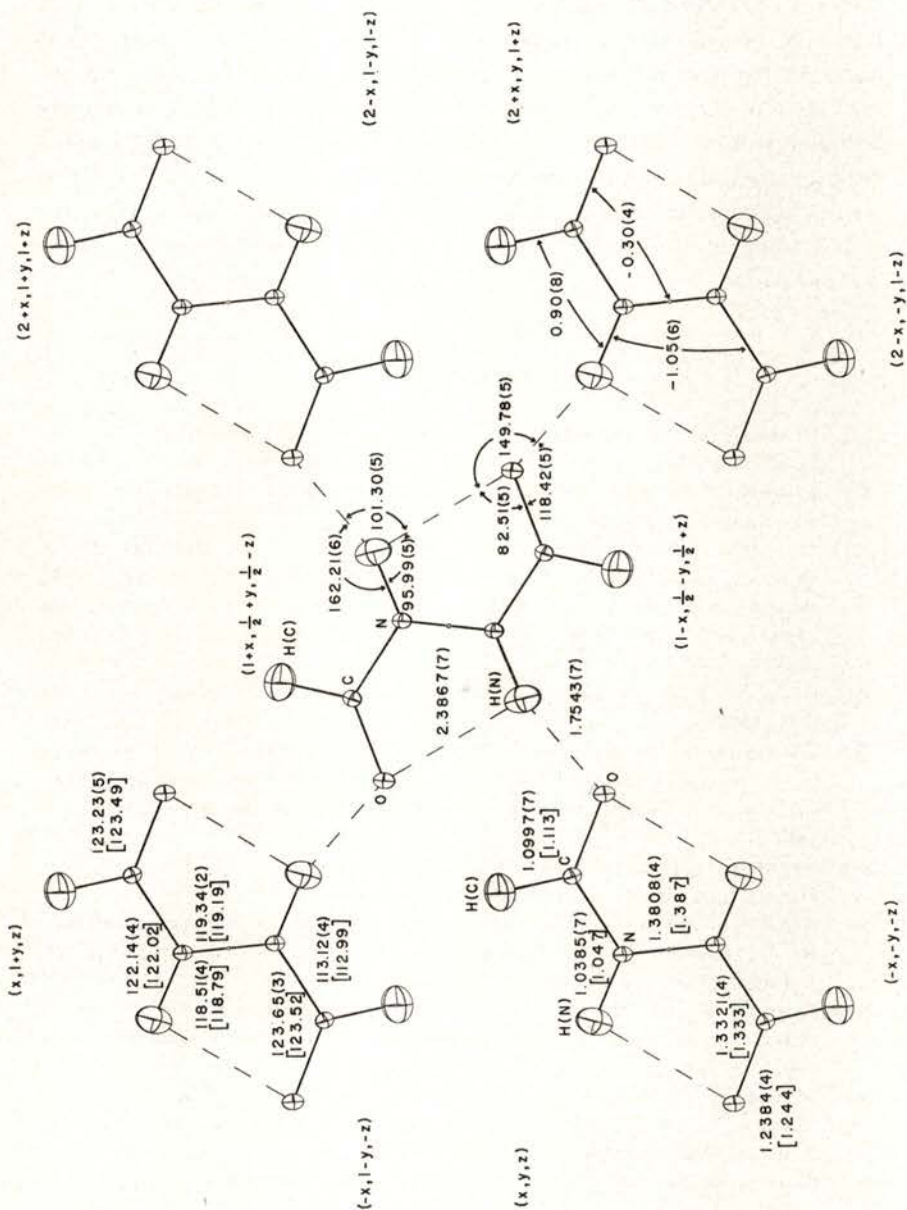
In diformyl hydrazine, the theoretical minimum energy conformation for the isolated molecule has symmetry 2. As with hydrazine itself, the >N-N< bonds are not coplanar. In the crystal structure, the molecules are planar with *m* symmetry. This is certainly due to the strong hydrogen-bonded layer arrangement in the crystals, shown in Fig. 4. The energy difference between the calculated non-planar conformation and the observed planar conformation is small, 5.4 kJ/mol. This is much smaller than the 108 kJ/mol difference between the non-planar and planar conformation for hydrazine [4].

TABLE 6 — Analysis of bond length discrepancies in formamide oxime

Bond	Neutron diffraction, 16 K		Δ Theory-experiment	H-bonding	Δ HF/3-21G \rightarrow MP3/6-31G *	Residual
	Observed	Corrected				
C-N(1)	1.3347(4)	1.351	+0.002		-0.006 ^a	-0.004
C-N(2)	1.2959(4)	1.299	-0.030		+0.019 ^b	-0.011
N(2)-O	1.4283(4)	1.435	+0.034		-0.025 ^c	+0.009
N-H	1.0120(8)	1.026	-0.036	+0.020	+0.015 ^a	-0.001
C-H	1.0899(8)	1.101	-0.040		+0.020 ^d	-0.020
O-H	0.9906(8)	1.002	-0.037	+0.005	+0.011 ^e	-0.021

^a methanimine ^b methylenimine ^c hydroxylamine ^d formaldehyde ^e methanol

Fig. 4 (facing page) — Hydrogen bonding in the crystal structure of 1,2-diformyl hydrazine. Values in [] are bond lengths (Å) and bond angles (°) corrected for thermal motion. The plane of the diagram is (102).



In summary, the agreement in bond lengths between *ab-initio* M.O. theory at the HF/3-21G level of approximation and neutron diffraction structure analyses at <25 K, is generally better than 0.015 Å, as shown in Table 6. A notable exception is the N-O bond in formamide oxime. The predominance of negative values in Table 6 suggests that the corrections for thermal motion are being systematically over-estimated and that better and possibly simpler methods should be sought. The X-H bond lengths show better agreement between theory and experiment, if it is assumed that riding-motion and anharmonicity effects cancel at these temperatures.

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