

## Deformation Electron Densities. $X$ - $X_{HO}$ Fourier Synthesis vs *ab initio* Calculations

BY TOR OTTERSEN AND JAN ALMLÖF

*Department of Chemistry, University of Oslo, Oslo 3, Norway*

AND HÅKON HOPE

*Department of Chemistry, University of California, Davis, California 95616, USA*

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### Abstract

The electron density deformation in acetamide,  $C_2H_5NO$ , has been determined by  $X$ - $X_{HO}$  Fourier synthesis. The experimental results are compared with theoretical densities calculated by *ab initio* Hartree–Fock methods. In addition, theoretical densities for diformohydrazide,  $C_2H_4N_2O_2$ , and carbonohydrazide,  $CH_6N_4O$ , have also been computed, and these are compared with previously obtained experimental results. The theoretical maps have been approximately adjusted for thermal smearing in order to be more readily comparable with experimental maps. The most striking feature of the maps is the very low electron density in the N–N bonds, showing little or no increase compared to the free-atom densities.

### Introduction

Electron density deformation maps based on X-ray crystallographic data ( $X$ - $N$  and  $X$ - $X_{HO}$  maps) have become widely used in studies of density distributions in molecules and complexes (e.g. Coppens & Stevens, 1977). In order to complement information obtained by this method the results may be compared with theoretically computed deformation densities. Comparisons between experimental and thermally smeared theoretical densities may also give information on systematic differences in the two methods (Ottersen & Almlöf, 1978). Within a series of similar molecules where these differences have been mapped, one may compare theoretical densities in order to remove the effects of thermal vibrations inherent in the experimental results. The present paper will give the results from a comparative study ( $X$ - $X_{HO}$  vs *ab initio* calculations) of some closely related molecules.

In a series of low-temperature investigations the deformation density distributions in compounds containing N–C=O and N–N–C=O fragments have been studied with  $X$ - $X_{HO}$  maps [hexahydro-3,6-pyridazine-

dione (HP): Ottersen & Almlöf, 1978; diformohydrazide: Hope & Ottersen, 1978, 1979; carbonohydrazide: Ottersen & Hope, 1979; acetamide: see below]. In the recent study of HP the agreement between experimental and theoretical densities was encouragingly good, and the theoretical calculations are extended to encompass the other molecules in the series. The reinvestigations of diformohydrazide and carbonohydrazide showed that reasonably accurate nuclear positions can be found for hydrogen atoms from X-ray data alone by high-order refinements. Reliable deformation densities can thereby be obtained from  $X$ - $X_{HO}$  maps.

In view of the good experimental results obtained for these molecules and also HP where the differences follow the expected electronic variations, it was decided to include the rhombohedral structure of acetamide in the series. With the experience gained in the studies of the closely related molecules and theoretical deformation densities one should be better able to judge the results obtained in this noncentrosymmetric case. The problem of phase differences between  $F_{obs}$  and  $F_{calc}$  in the calculation of deformation densities has been discussed by Coppens (1974) and by Thomas, Tellgren & Almlöf (1975) in their study of lithium formate monohydrate by experimental ( $X$ - $N$ ) and theoretical methods. The major problem is to obtain reliable phases for  $F_{obs}$ . The structure model used to calculate these phases should ideally be such that a difference calculated in the standard way shows zero density at all points. The simple acetamide molecule is well suited both for an attempt to find such a model and for theoretical calculations.

### Crystallographic section

#### *Experimental*

Crystals of rhombohedral acetamide were grown from the melt. A crystal of dimensions  $0.35 \times 0.35 \times 0.40$  mm was mounted on a Picker automated

four-circle diffractometer equipped with an incident-beam monochromator and a modified Enraf-Nonius low-temperature device (liquid N<sub>2</sub>). The temperature was kept constant within 0.2 K at 85 K throughout the experiments. The angular coordinates ( $\chi, \phi, \omega, 2\theta$ ) of nine Mo  $K\alpha_1$  reflections ( $\lambda = 0.70926 \text{ \AA}$ ) with  $2\theta$  values between 70 and 80° were used in a least-squares calculation to determine the crystal orientation and cell dimensions. The cell dimensions were  $a = 11.504 (6)$ ,  $c = 12.986 (7) \text{ \AA}$ ,  $V = 1488.5 (5) \text{ \AA}^3$ .

The positional and thermal parameters determined in an earlier low-temperature study (Ottersen, 1975) were used together with sample scan and background measurements to predict which reflections would have measurable X-ray intensities. In order to study the electron density deformation, all reflections with  $\sin \theta/\lambda$  values less than  $0.65 \text{ \AA}^{-1}$  were recorded, whereas for reflections with  $\sin \theta/\lambda$  values above this only those were recorded which had a predicted  $I/\sigma(I) > 4.0$ .

The intensities of 1276 symmetry-independent reflections ( $2\theta_{\max} = 134^\circ$ ) were measured using a  $\theta/2\theta$  scan, graphite-monochromatized Mo  $K\alpha$  radiation, and a scintillation detector with pulse-height analyzer. Each reflection was scanned from  $[2\theta(\alpha_1) - 0.9^\circ]$  to  $[2\theta(\alpha_2) + 0.9^\circ]$  with a scan speed of  $2.0^\circ (2\theta) \text{ min}^{-1}$ . Background counts were taken for 20 s at each end of the scan range. Coincidence losses were minimized by adding an attenuator filter when the count rate exceeded  $9500 \text{ counts s}^{-1}$ .

Two check reflections which were remeasured after every 150 reflections showed no systematic variations throughout the data collection. Each recorded number of counts,  $N$ , was assigned a standard deviation  $\sigma(N) = [N + (0.0050N)^2]^{1/2}$ ; the factor 0.0050 reproduces the observed variance in the check reflections. Based on the

values of  $\sigma(N)$  for scan and background counts, e.s.d.'s for the net intensities were calculated. Of the 1276 reflections measured, the 1261 reflections which had net intensities larger than their e.s.d.'s were used in the refinement procedure.

Lorentz and polarization corrections were applied to the net intensities. The polarization factor includes the polarization by the monochromator crystal (Hope, 1971).

The data obtained for diformohydrazide (Hope & Ottersen, 1978) and carbonohydrazide (Ottersen & Hope, 1979) showed that truncation errors had a significant effect in the refinements. The data were, therefore, corrected (Denne, 1977). Following the notation of Denne, the formula utilized was

$$I_{\text{corr}} = I/[A_1 C_1 + A_2 C_2 + \frac{1}{2}(\lambda_a - \lambda_b) \times \{A_1[I_1(\lambda_a) + I_1(\lambda_b)] + A_2[I_2(\lambda_a) + I_2(\lambda_b)]\}]$$

The line-widths [ $2.906 \times 10^{-4} \text{ \AA} (K\alpha_1)$ ,  $3.206 \times 10^{-4} \text{ \AA} (K\alpha_2)$ ] and relative intensity ( $I_2/I_1 = 0.499$ ) were taken from Compton & Allison (1935). The maximum correction applied to any intensity was  $I_{\text{corr}} = I/0.940$ .

### Refinement

The quantity  $\sum w(F_{\text{obs}} - K|F_{\text{calc}}|)^2$  was minimized in a full-matrix least-squares refinement with  $w = 1/\sigma^2(F_{\text{obs}})$ . The origin along the  $c$  axis was fixed by holding the oxygen  $z$  parameter. The atomic scattering factors used were those calculated by Doyle & Turner (1968) for carbon, nitrogen and oxygen, and the contracted spherical scattering factor calculated by Stewart, Davidson & Simpson (1965) for hydrogen. All programs subsequently used are part of an Oslo

Table 1. Results from refinements for acetamide

$R_1$  is the  $R$  factor for all data, the  $G$  factor is  $[\sum w(\Delta F)^2/(n - m)]^{1/2}$ , where  $n$  is the number of observations and  $m$  is the number of parameters.

Refinement No.	$\sin \theta/\lambda (\text{\AA}^{-1})$ cut-off	Number of reflections	Number of parameters	$R$ (%)	$R_w$ (%)	$R_1$ (%)	$G$	Scale factor ( $KF_o = F_c$ )	Comment
I	0	1261	56	3.51	3.02	3.51	2.95	0.270 (1)	
II	>0.40	1161	56	3.18	2.59	3.33	1.90	0.278 (1)	
III	>0.50	1079	56	3.02	2.27	3.31	1.37	0.278 (1)	
IV	>0.60	946	56	3.08	2.38	3.44	1.14	0.276 (1)	
V	>0.60	946	36	3.15	2.43	3.17	1.15	0.277 (1)	Hydrogen parameters from refinement I
VI	>0.75	684	36	3.52	2.99	3.22	1.04	0.278 (2)	As for V
VII	>0.75	684	36	3.53	2.99	3.65	1.04	0.276 (2)	Calculated hydrogen positions (see text)
VIII	>0.85	466	36	3.90	3.56	3.72	1.02	0.276 (3)	As for VII
IX	>0.95	261	36	4.39	4.33	3.99	1.03	0.269 (8)	As for VII
X	0	1261	81	3.37	2.74	3.37	2.69	0.270 (1)	Anisotropic thermal parameters for hydrogen
XI	<0.85	795	81	2.83	2.54	3.84	3.17	0.269 (1)	As for X
XII	<0.85	795	84	2.66	2.48	3.50	3.10	0.271 (1)	As for XI + three dummy atoms (see text)

assembly of computer programs described by Groth (1973).

The  $\sin \theta/\lambda$  cut-off value was varied systematically, refinements were performed with minimum cut-off values of 0, 0.40, 0.50, 0.60, 0.75, 0.85 and 0.95  $\text{\AA}^{-1}$ . Some data from the refinements are given in Table 1. The hydrogen atoms were refined with isotropic thermal parameters in refinements with  $\sin \theta/\lambda$  cut-off values up to 0.60  $\text{\AA}^{-1}$ . The refinements of these atoms with minimum  $\sin \theta/\lambda$  cut-off values up to 0.50  $\text{\AA}^{-1}$  showed the same trend as was found for the hydrogen atoms in the refinements of diformohydrazide (Hope & Ottersen, 1978) and carbonohydrazide (Ottersen & Hope, 1979), *i.e.* a shortening of the C–H and N–H bonds. However, the refinement with a cut-off of 0.60  $\text{\AA}^{-1}$  (No. IV) yielded unrealistic positional and thermal parameters for the hydrogen atoms. This is probably due to the relatively low overdetermination ratio of only 16.9, whereas the overdetermination ratios in the high-angle ( $>0.75 \text{\AA}^{-1}$ ) refinements of diformohydrazide and carbonohydrazide were 58.1 and 31.3, respectively.

The hydrogen atomic parameters found in the refinement using all data (No. I) were included in the structure factor calculations and only the heavy-atom parameters refined for cut-off values of 0.60 and 0.75  $\text{\AA}^{-1}$ . In order to obtain electron deformation densities

Table 2. Fractional atomic coordinates and thermal parameters for acetamide with estimated standard deviations

The numbering of the atoms may be found in Fig. 4. Parameters used for hydrogen atoms in refinement No. VII are calculated positional parameters (see text) and the isotropic thermal parameters obtained in refinement No. I. HCN, HCO and HCC are the three dummy hydrogens used in refinement XII (see text).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq.</sub> or <i>B</i> ( $\text{\AA}^2$ )
Refinement No. VII				
O	0.24058 (8)	−0.00181 (9)	−0.00140	1.23 (3)
N	0.33303 (10)	−0.10053 (8)	0.09196 (9)	1.09 (2)
C	0.34035 (7)	0.00280 (9)	0.04042 (11)	0.93 (2)
C(1)	0.47593 (8)	0.12870 (8)	0.03599 (11)	1.13 (2)
H(1)	0.241	−0.183	0.104	2.01 (27)
H(2)	0.415	−0.096	0.126	1.02 (22)
H(3)	0.488	0.186	0.107	3.10 (32)
H(4)	0.557	0.105	0.033	2.53 (28)
H(5)	0.480	0.195	−0.027	3.74 (38)
Refinement No. XII				
O	0.2405 (1)	−0.0017 (1)	−0.0014 (0)	1.31 (4)
N	0.3333 (1)	−0.1002 (2)	0.0918 (1)	1.12 (5)
C	0.3404 (1)	0.0030 (1)	0.0400 (1)	1.05 (5)
C(1)	0.4759 (1)	0.1285 (1)	0.0359 (1)	1.27 (5)
H(1)	0.258 (2)	−0.167 (2)	0.101 (1)	2.3 (8)
H(2)	0.400 (1)	−0.096 (1)	0.117 (1)	2.0 (11)
H(3)	0.486 (2)	0.178 (2)	0.102 (2)	3.2 (13)
H(4)	0.544 (2)	0.108 (2)	0.034 (2)	1.9 (12)
H(5)	0.483 (2)	0.188 (3)	−0.020 (2)	4.0 (12)
HCO	0.290	0.001	0.019	2.0
HCN	0.330	−0.049	0.066	2.0
HCC	0.408	0.066	0.038	2.0

the hydrogen atoms were placed in new positions calculated by increasing the C–H and N–H lengths to 1.10 and 1.02  $\text{\AA}$ , respectively, in refinements with cut-off values of 0.75  $\text{\AA}^{-1}$  and above, *i.e.* all bond angles involving hydrogens were kept at the values obtained in refinement I, and the isotropic thermal parameter as found for the hydrogens in that refinement were retained. The different treatment of hydrogen atoms in the refinements was found, by comparison of refinements IV and V and VI and VII, to have no significant influence on the heavy-atom parameters obtained.

The heavy-atom parameters converged to their final values for the 0.75  $\text{\AA}^{-1}$  cut-off in agreement with the studies of diformohydrazide and carbonohydrazide. Correlation factors in this refinement (No. VII) between the scale factor and the  $B_{ii}$ 's were of the order of −0.3 to −0.6, and between  $x$ ,  $y$ ,  $B_{11}$ ,  $B_{22}$  and  $B_{12}$  parameters of the order of 0.3 to 0.7. Final atomic parameters obtained in refinement VII are listed in Table 2, together with the parameters used for hydrogen atoms.\*

#### Calculation of electron density deformations

The deformation electron density,  $\rho_{x-x^h}$ , at a point  $\mathbf{r}$  in the unit cell is given, following the notation of Coppens (1974), by the expression

$$\rho_{x-x^h}(\mathbf{r}) = (1/V) \sum_{\mathbf{H}} \Delta F \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}),$$

where  $\Delta F$  is the difference between the scaled observed structure factors,  $KF_{\text{obs}}$ , and the structure factor,  $F_{\text{calc, VII}}$ , calculated using the atomic parameters obtained in the high-angle data refinement (No. VII, see Table 2) and free-atom form factors. In the non-centrosymmetric cases the assumption that the phase angle of  $F_{\text{obs}}$  is the same as that of  $F_{\text{calc, VII}}$  may lead to considerable errors in the Fourier summation. In addition to errors in the phase angles, the  $|\Delta F|$ 's will always be too small, see the discussion by Coppens (1974), and the results obtained by Thomas, Tellgren & Almlöf (1975). Ideally, the phase angles accompanying the observed structure factors should be calculated in such a way that the total electron density distribution is accounted for, *i.e.* the structure model used in the calculation of phase angles should give zero standard difference electron density at all points.

In order to get a better determination of the phase angles of the low-angle data, the hydrogen atoms were refined with anisotropic temperature factors in a

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35039 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

least-squares refinement using all data (No. X, Table 1). A difference electron density map calculated in the standard fashion using the parameters obtained in this refinement showed relatively large, ellipsoid-shaped densities in the C–N, C–C(1) and C=O bonds, maximum peak heights of  $0.25 \text{ e } \text{Å}^{-3}$ , and small densities ( $\sim 0.10 \text{ e } \text{Å}^{-3}$ ) in the positions of the oxygen lone pairs. A refinement was then performed using only the 795 observed reflections with  $\sin \theta/\lambda \leq 0.85 \text{ Å}^{-1}$  (No. XI). The deformation map calculated using this subset of data and the parameters obtained from this refinement showed only minor changes from the earlier map.

In order to account for this density, three dummy atoms placed at the midpoints of the C=O, C–N and C–C(1) bonds were included in the structure model and their occupancy parameters refined (using  $f_{\text{H}}$ 's) together with the positional and anisotropic thermal parameters of the other atoms (refinement No. XII). Attempts to refine thermal parameters for these three dummy hydrogens resulted in unrealistic values for scale and temperature factors. The atomic parameters obtained in refinement No. XII are listed in Table 2, and the scale factor is given in Table 1 together with other results from this refinement. The difference electron density map calculated using these parameters and the subset of data with  $(\sin \theta/\lambda)_{\text{max}} = 0.85 \text{ Å}^{-1}$  is presented in Fig. 1(a). Compared with the results from the map

calculated using the parameters obtained in refinement No. X, the densities in bonds and oxygen lone pairs have been reduced to about 50%, whereas there are only minor changes in the negative areas.

The deformation electron densities were calculated using the subset of data with  $(\sin \theta/\lambda)_{\text{max}} = 0.85 \text{ Å}^{-1}$ . The scaling and phase angles of the observed structure factors were determined by the parameters obtained in refinement No. XII, whereas the  $F_{\text{calc}}$ 's were calculated using the atomic parameters obtained in refinement No. VII. The resulting  $\rho_{X-X'}$  map in the molecular plane is shown in Fig. 1(b), and the deformation densities in the C=O, C–N and C–C(1) bonds normal to the molecular plane are shown in Fig. 2. The mean difference in phase angles between  $F_{\text{obs}}$  and  $F_{\text{calc}}$  ( $\overline{|\Delta\phi|}$ ) taken over the 795 observed reflections in the subset is  $2.34^\circ$ , whereas the corresponding r.m.s. phase difference,  $(\overline{\Delta\phi^2})^{1/2}$ , is  $3.72^\circ$ . These values are much smaller than the corresponding values of  $3.3$  and  $7.2^\circ$  found for lithium formate monohydrate (Thomas, Tellgren & Almlöf, 1975). However, it is interesting to note that the corresponding differences in phase angles between the  $F_{\text{obs}}$ 's calculated using the parameters obtained in refinement No. X, and the same  $F_{\text{calc}}$ 's are  $2.36$  and  $3.60^\circ$ , respectively. The inclusion of the three dummy atoms, which reduce the difference densities in bonds and lone pairs by about 50%, has very little effect on the mean  $\Delta\phi$ 's. On the other hand, changes in  $\Delta\phi$ 's for individual reflections of  $3$  to  $5^\circ$  are not uncommon.

In order to compare the deformation densities calculated by use of vectorial differences, *i.e.* where

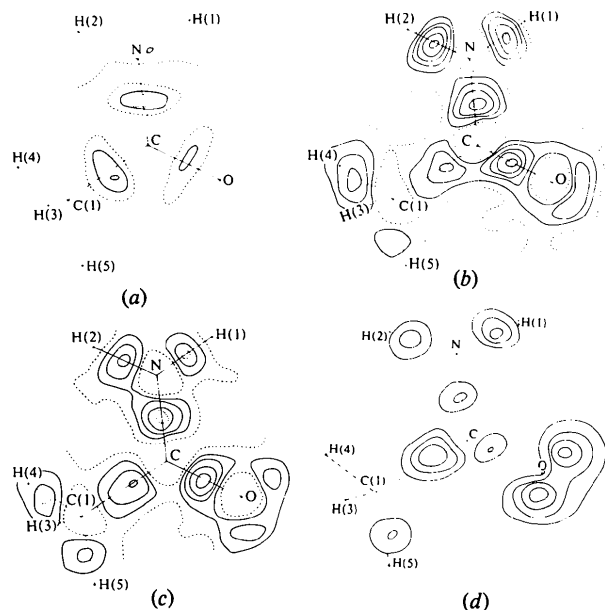


Fig. 1. Deformation densities in the molecular plane of acetamide. The contours are given at levels of  $0.1 \text{ e } \text{Å}^{-3}$ . The zero level is dashed, the dotted line indicates an extra height of  $0.05 \text{ e } \text{Å}^{-3}$ . (a) Standard difference Fourier synthesis using low-order model, (b) vectorial difference synthesis, (c) standard difference synthesis, high-order model, (d) theoretical difference synthesis. The basis set *A* has been used (see text). An isotropic temperature factor  $B = 2.0 \text{ Å}^2$  has been applied.

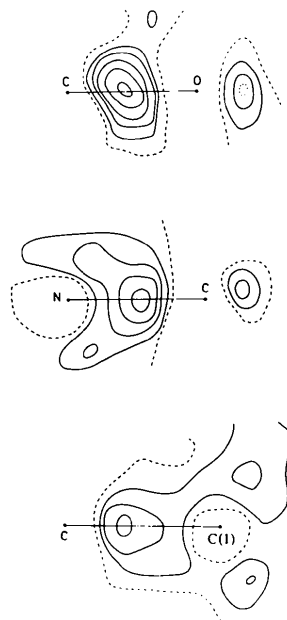


Fig. 2. Experimental deformation densities normal to the molecular plane in the bonds of acetamide. Contour levels of  $0.1 \text{ e } \text{Å}^{-3}$ ; the zero level is dotted.

phase difference has been taken into account, to the standard difference densities, a density map in the molecular plane was calculated using the parameters obtained in refinement No. VII and the same scale factor which was used for the other maps. This difference map is shown in Fig. 1(c).

### Theoretical investigations

In order to calculate theoretically the deformation densities, *ab initio* calculations were performed for the three molecules. The program system *MOLECULE* (Almlöf, 1974) was used to solve the Hartree–Fock equations within a basis spanned by contracted Gaussian basis functions.

The influence on the results by the choice of basis set was investigated in some detail by using four different basis sets in the calculations on diformohydrazide. The smallest one consisted of a  $7s3p$  basis for C, N and O and  $3s$  for H, contracted to  $4s2p$  and  $2s$ , respectively. In a more extended basis,  $9s5p$  and  $5s$  were contracted to  $5s3p$  and  $3s$ . These basis sets are denoted *A* and *B* in the following. Both these basis sets were then augmented by a set of  $3d$  functions on C, N and O and a  $2p$  set on H. The *d* exponents used were 0.63, 0.95 and 1.33, respectively, as suggested by Roos & Siegbahn (1970). For H, a *p* exponent of 0.8 was employed. In this way, two new basis sets denoted *A\** and *B\** were generated.

No geometry optimization was performed for the systems under consideration. All calculations were done with geometries deduced from the X-ray investigations.

From the wavefunctions obtained, the total electron densities were computed. The deformation densities were then calculated as differences between these distributions and corresponding densities for the non-interacting, neutral atoms in their ground states. In order to minimize systematic errors, the atomic densities used were computed with exactly the same basis sets as those used for the molecular calculations.

One could argue that the subtraction of densities for *ground-state* atoms might not give the most informative picture of the charge deformation in the molecule. ‘Valence-state’ atomic densities would presumably be more suitable in a study of density deformations relevant to the chemical bonding in the molecule. However, the experimental  $\Delta\rho$  maps were obtained using conventional atomic scattering factors. These are computed from *ground-state* atomic Hartree–Fock wavefunctions. Accordingly, it was decided to use the same approach for the theoretical maps in order to facilitate a comparison between the two methods.

Even though this is accounted for, a direct comparison between experimental and theoretical maps shows substantial dissimilarities. These are partly due to the fact that the former maps have been ‘smeared’

out as a result of thermal vibration. It is not trivial to apply the experimental temperature factors to the theoretical densities, since these cannot be uniquely decomposed into atomic contributions. A temperature correction of the theoretical results can only be strictly applied when a TLS analysis of the experimental data is performed, allowing a unique assignment of a thermal ellipsoid to every point in space. Since we lack such information, the thermal effects have been approximately accounted for by applying an overall temperature factor according to the formula

$$\rho(\mathbf{r}) = (4\pi/B)^{3/2} \int \rho_0(\mathbf{r}') \exp[-4\pi^2(\mathbf{r}' - \mathbf{r})^2/B] dv'.$$

In this expression,  $\rho_0$  and  $\rho$  are the densities before and after the correction is applied, and *B* is a conventional, overall isotropic Debye–Waller factor.

The influence of basis-set truncation was studied in some detail for diformohydrazide. Deformation density maps obtained with the four basis sets *A*, *B*, *A\** and *B\** are shown in Fig. 3.

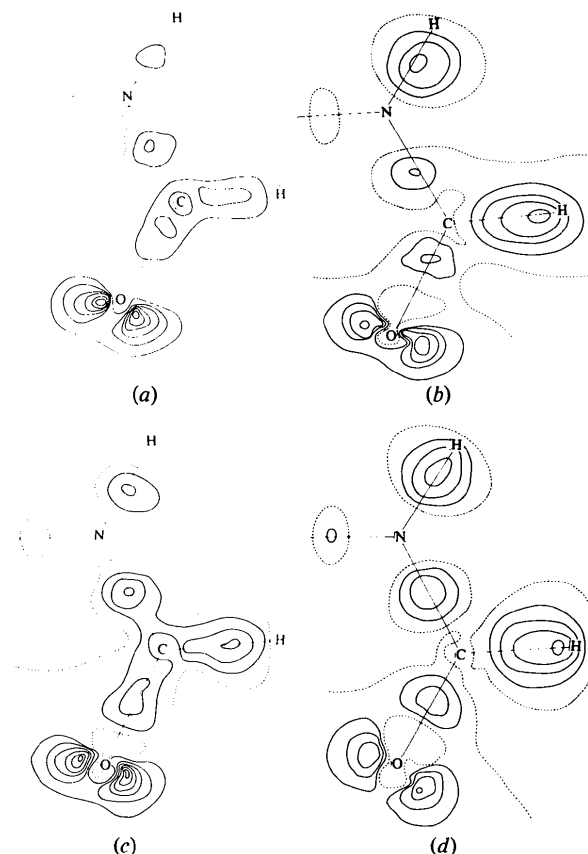


Fig. 3. Theoretical deformation densities for diformohydrazide using four different basis sets. No thermal smearing has been applied. The contour interval is  $0.2 \text{ e } \text{Å}^{-3}$ , the zero level is dotted. The basis sets used in (a)–(d) are labelled *A*, *B*, *A\** and *B\** as described in the text.

Significant effects can be observed from truncation of the basis set, although the main features of the maps remain qualitatively the same. In particular, the peak heights of lone-pair-like regions around oxygen are seen to decrease when the basis set increases, whereas bond density peaks are generally more pronounced when a larger basis is used. Although these effects are by no means negligible they seem to appear in a quite systematic and predictable way, a fact known also from other, similar investigations. Relevant information about deformation densities can therefore often be obtained from calculations with relatively small basis sets, if these characteristic shortcomings are borne in mind. Accordingly, it was decided to use basis set *A* for the calculations on carbonohydrazide and acetamide, this being more feasible from a computational point of view.

### Results and discussion

Bond lengths and bond angles for acetamide obtained in the high-angle data refinement (No. VII) are given in Fig. 4. The values found for the molecular parameters involving only heavy atoms change very little with variations in the  $(\sin \theta/\lambda)_{\min}$  cut-off, in agreement with the results obtained for diformohydrazide (Hope & Ottersen, 1978) and carbonohydrazide (Ottersen & Hope, 1979). The maximum change is in the C–N bond which lengthens from 1.3265 (15) Å in the refinement using all data (No. I) to 1.3296 (15) Å in the high-angle data refinement (No. VII). There are no significant differences between the heavy-atom molecular parameters obtained in the earlier high-angle (cut-off 0.50 Å<sup>-1</sup>), low-temperature investigation (Ottersen, 1975) and those obtained in the present study. The largest differences are for the C–N bond which earlier was found to be 1.336 (4) Å and, for the C–O bond, the value obtained in the earlier study was 1.243 (4) compared to 1.2467 (13) Å in the present work.

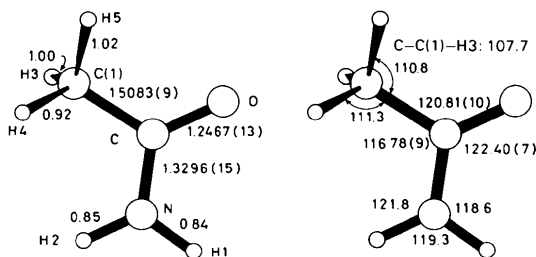


Fig. 4. Bond lengths (Å) and bond angles (°) for acetamide with estimated standard deviations. These values have been calculated using the heavy-atom positional parameters obtained in the high-angle data refinement (No. VIII) and the hydrogen positional parameters found in the refinement using all data (No. I).

Table 3. Parameters for the hydrogen bonds in acetamide

	N...O (Å)	
N–H(1)...O	2.904 (1)	$\frac{1}{3} - x + y, -\frac{1}{3} + y, \frac{1}{6} + z$
N–H(2)...O	2.880 (1)	$\frac{1}{3} + x, -\frac{1}{3} - x + y, \frac{1}{6} + z$

The molecule, apart from the methyl hydrogens, is planar. Deviations from a least-squares plane through the four heavy atoms are: O –0.001 (1); N –0.002 (1); C 0.005 (1); C(1) –0.002 (1); H(1) –0.11 (2); H(2) 0.01 (2) Å. The oxygens which are acceptors in the two N–H...O hydrogen bonds lie relatively close to this plane, deviations are –0.648 (1) and 0.326 (1) Å. Parameters for the hydrogen bonds are shown in Table 3. These hydrogen bonds have a significant influence on the conjugation over the N–C=O fragment, as has been discussed earlier (Ottersen, 1975, 1976).

The deformation densities for diformohydrazide, acetamide and carbonohydrazide are shown in Figs. 1, 2, 3, 5, 6. The qualitative agreement between theoretical and experimental maps is considered satisfactorily good, although far from perfect. Peaks in covalent bonds and in lone-pair regions around N and O are consistent with an intuitive picture of the charge distribution, and are obtained with both methods. The overall features of the maps are very similar to those obtained from X-ray investigations on formamide (Stevens, 1978) and allenedicarboxylic acid–acetamide (Berkovitch-Yellin & Leiserowitz, 1977), and from quantum-mechanical calculations on *N*-methylacetamide (Hagler & Lapicciarella, 1976*a,b*). It is noted that the theoretical densities generally have lower peaks in the covalent-bond regions than the experimental maps, whereas the situation is reversed for the lone-pair peaks. As discussed previously for diformohydrazide, this difference can be rationalized as a basis-set effect. In diformohydrazide, it is of particular interest to note the very low peak in the N–N bond, a feature common to the experimental and the theoretical maps.

Similar, unusually low deformation densities in the N–N bond were also found in HP (Ottersen & Almlöf, 1978), and in tetraformohydrazide (Ottersen & Almlöf, 1980). With the exception of carbonohydrazide, these N–N bonds are all situated on symmetry elements. One might suspect, therefore, that the above effect is simply an artifact, due to the well known accumulation of systematic errors in such positions. However, similar low N–N bond densities were found in the theoretical investigations as well, where no such systematic effects are likely to occur. The reasons for this rather peculiar property of N–N single bonds must therefore be sought in the detailed electronic structure of the bond. A more detailed analysis and discussion of this

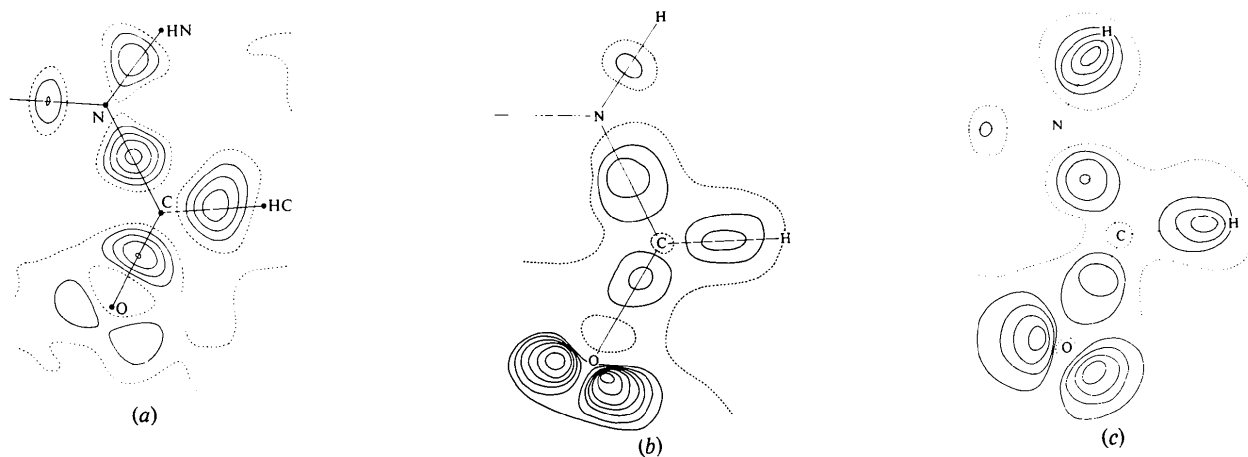


Fig. 5. Deformation densities in the molecular plane of diformohydrazide. (a) Experimental results, (b) theoretical results with basis set  $A$ , assuming  $B = 1.0 \text{ \AA}^2$ , (c) theoretical results, basis set  $B^*$ ,  $B = 1.0 \text{ \AA}^2$ . Contour levels of  $0.1 \text{ e \AA}^{-3}$ ; the zero level is dotted.

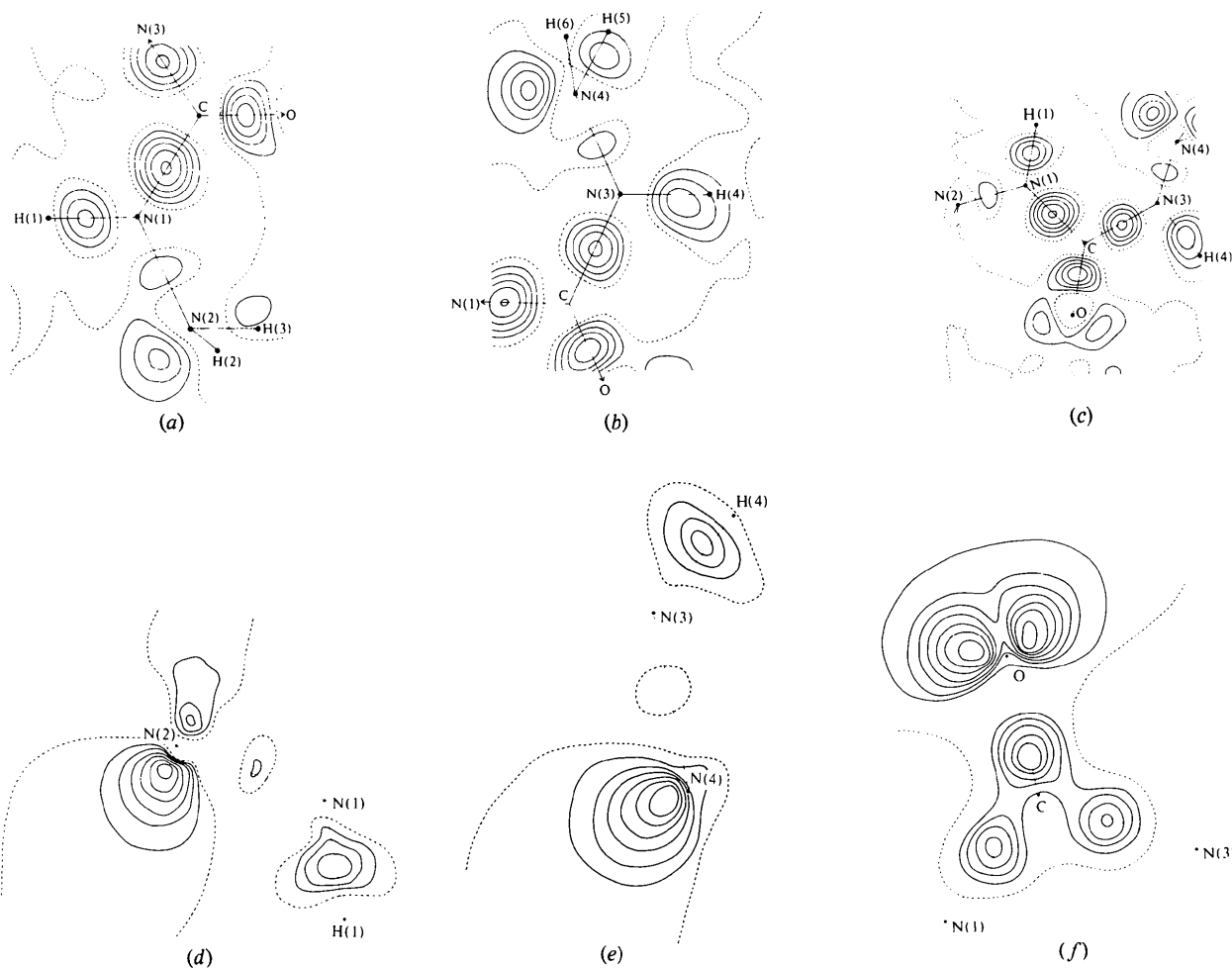


Fig. 6. Deformation density for carbohydrazide, (a)–(c) experimental results, (d)–(f) theoretical results, basis set  $A$ ,  $B = 1.0 \text{ \AA}^2$ . Contour levels of  $0.1 \text{ e \AA}^{-3}$ ; the zero level is dotted.

particular phenomenon will be given in a forthcoming paper (Ottersen & Almlöf, 1980).

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## Topography of Cyclodextrin Inclusion Complexes.

### XII.\* Hydrogen Bonding in the Crystal Structure of $\alpha$ -Cyclodextrin Hexahydrate: The Use of a Multicounter Detector in Neutron Diffraction

BY B. KLAR†

*Institut Max von Laue–Paul Langevin, avenue des Martyrs, 38 Grenoble, France*

AND B. HINGERTY AND W. SAENGER

*Abteilung Chemie, Max-Planck-Institut für experimentelle Medizin, Hermann-Rein-Strasse 3, 3400 Göttingen, Federal Republic of Germany*

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#### Abstract

In the crystalline complex  $\alpha$ -cyclodextrin hexahydrate,  $C_{36}H_{60}O_{30} \cdot 6H_2O$ , orthorhombic, space group  $P2_12_12_1$ ,  $Z = 4$ ,  $a = 14.858$  (3),  $b = 34.038$  (7),  $c = 9.529$  (2) Å, thirty hydroxyl hydrogen atoms are present, including one which is disordered (occupancies 0.92:0.08) and could not be located with certainty from X-ray counter data. 851 low-angle neutron data

were measured using a conventional four-circle diffractometer with a graphite monochromator ( $\lambda = 2.384$  Å) and a neutron flux rate of  $6.4 \times 10^4$  n mm<sup>-2</sup> s<sup>-1</sup>. Further, 1957 high-angle neutron data were collected by means of the multicounter device 'hedgehog'. This instrument contains 100 BF<sub>3</sub> counters mounted on rotatable and extendable arms on the inside of a sphere, at the centre of which is installed a conventional Eulerian cradle holding the sample crystal. With the application of a modified Laue method, integration is over wavelength rather than over crystal rocking motion; a wavelength band of  $1.275 < \lambda < 1.31$  Å, a Cu-crystal monochromator, and a neutron flux of  $2.4 \times 10^4$  n mm<sup>-2</sup> s<sup>-1</sup> were used. Details of the measurement and of the data reduction are given, and the refinement process, including combined neutron and a new set of 4268 X-ray data, is described. *R* factors are

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† Present address: SCS Scientific Control Systems GmbH, Oehleckerling 40, D-2000 Hamburg 62, Federal Republic of Germany.