The Deformation Electron Density Distribution in s-Diformohydrazide (s-Diformylhydrazine) at 85 K

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Abstract

The valence-electron deformation density in diformohydrazide, $C_2H_4N_2O_2$, has been determined by $X-X_{HO}$ Fourier calculations. 2683 reflections [$(\sin \theta/\lambda)_{max} = 1.39$ Å^{-1}] with $I > \sigma(I)$ were used in the refinements (Hope & Ottersen, 1978). The structure model consists of the O, N and C parameters refined on data with $\sin \theta/\lambda > 0.85$ Å^{-1} (1842 F_o's) and the H parameters refined on data with $\sin \theta/\lambda > 0.75$ Å^{-1} (2090 F_o's). The 841 reflections with $\sin \theta/\lambda \leq 0.85$ Å^{-1} were used in the calculations of deformation densities. The density in the N—N bond is remarkably low, maximum density 0.21 e Å^{-3}. This feature is in agreement with results from theoretical calculations. The peak density in the C=O bond is 0.4 e Å^{-3}, and in the O lone pairs it is 0.2 e Å^{-3}. The lone-pair–core–lone-pair angle is 137°.

Introduction

In our study of s-diformohydrazide (Hope & Ottersen, 1978) we found that acceptable (nuclear) H atom parameters can be obtained by refinement on extensive high-order X-ray data. This brings within reach a solution to the problem of deducing an accurate, complete structural model from X-ray data alone. Geometric and thermal parameters as well as reliable deformation densities can thereby be obtained by straightforward least-squares and Fourier methods from a single set of experimental data. This reduces some sources of error which may arise from the use of combined data sets.

The diformohydrazide molecule is planar with a crystallographically imposed center of symmetry. The space group is $P2_1/c$ with two molecules in the unit cell. The redetermination of this structure presented an excellent opportunity to study the deformation densities in the —NH—C=O moiety, which can be considered a simple example of the biologically important peptide

linkage. Diformohydrazide and some related molecules have recently been studied by theoretical methods (Ottersen & Jensen, 1975), and the conjugated —NH—C=O moiety has been widely used as a model for theoretical investigations of hydrogen bonding (Ottersen, 1976, and references cited therein). The NH···O bond found in the crystal structure of diformohydrazide is typical of those hydrogen bonds found for compounds containing the peptide linkage (*e.g.* Ottersen, 1975). A systematic study of the deformation densities in this linkage by experimental ($X-X_{HO}$) and theoretical (*ab initio* calculations) methods is now being carried out (see also Ottersen & Almlöf, 1978).

Data and calculation of $X-X_{HO}$ maps

A detailed description of the collection and treatment of data and the refinements of the structure model is given in the earlier paper (Hope & Ottersen, 1978). 2693 selected Mo $K\alpha$ reflections ($2\theta_{max} = 163°$) were measured with the crystal at 85 K on a Picker automatic four-circle diffractometer. In order to study the deformation electron density all reflections with $\sin \theta/\lambda < 0.65$ Å^{-1} were collected, whereas for higher-order reflections only those which had predicted $I/\sigma(I) > 15$ were measured. The intensities were corrected for Lorentz, polarization and scan-truncation errors (Denne, 1977). A correction for absorption was found unnecessary in view of the small absorption coefficient ($\mu = 0.157$ mm^{-1}) and the crystal shape (crystal dimensions are approximately: $0.40 \times 0.40 \times 0.25$ mm), and a comparison between observed and calculated structure factors did not indicate any effect from secondary extinction.

The 2683 reflections which had $I \geq \sigma(I)$ were used. Of these the subset consisting of 841 reflections with $\sin \theta/\lambda \leq 0.85$ Å^{-1} were used in the calculation of deformation densities computed with the Fourier coefficients $\Delta F = F_o - F_{c,HO}$.

Table 1. *Fractional atomic coordinates and temperature factors* ($\mathring{A}^2$) *used in the calculation of F_c's*

The anisotropic temperature factor is given by: $\exp\{-\frac{1}{4}[B_{11}(a^*h)^2 + \ldots + 2B_{23}b^*c^*kl]\}$.

	(sin θ/λ)$_{min}$ (Å⁻¹)	x	y	z	B_{11} (B)	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	0·85	0·38048 (4)	0·14611 (2)	0·26208 (1)	0·864 (3)	0·722 (2)	0·547 (2)	−0·027 (2)	−0·084 (2)	−0·057 (2)
N	0·85	−0·06488 (4)	0·10465 (2)	0·00325 (1)	0·672 (3)	0·566 (2)	0·475 (2)	0·057 (2)	−0·002 (2)	−0·031 (2)
C	0·85	0·10702 (5)	0·21815 (2)	0·13872 (1)	0·697 (3)	0·561 (2)	0·552 (2)	−0·004 (2)	0·058 (2)	−0·065 (2)
HC	0·75	−0·0128 (54)	0·3780 (29)	0·1360 (21)	1·27 (16)					
HN	0·75	−0·2906 (59)	0·1710 (31)	−0·0953 (23)	1·35 (16)					

The structure model used in the calculation of $F_{c,HO}$ consists of the O, N and C parameters obtained from data with sin θ/λ > 0·85 Å⁻¹ (1842 F_0's) and the H parameters from data with sin θ/λ > 0·75 Å⁻¹ (2090 F_0's). These parameters are listed in Table 1. Atomic form factors used were those calculated by Doyle & Turner (1968) for O, N and C and the contracted spherical form factor of Stewart, Davidson & Simpson (1965) for H. The scale factor for the F_0's was found by least-squares refinement using the above-described structure model and subset of data ($R = 0·031$, $R_w = 0·044$). The value obtained, 0·0364 (1), is in good agreement with that found in the refinement using all data, 0·0365, and the one found in the refinement using data with sin θ/λ > 0·85 Å⁻¹, 0·0360. For comparison, corresponding calculations were also performed on data without correction for scan-truncation error.

Discussion

Deformation densities through various sections in the molecule are shown in Figs. 1 and 2. Data corrected for scan-truncation errors lead to better peak definitions, less noise and increased densities than do uncorrected data. The maximum positive densities in bond and lone-pair regions generally increased by about 10–20%, probably as a result of the decrease of about 0·04 Å² in the B_{ii} values.

The remarkably low density at the center of the N—N bond, maximum density 0·21 e Å⁻³, may seem suspect at first sight. Since the bond is disposed around an inversion center one might consider this result to be an artifact, due to the usual accumulation of experimental errors at symmetry elements (Cruickshank, 1949). However, this feature is also found in the theoretical deformation density map (Almlöf, 1979) and in experimental and theoretical deformation density maps of similar moieties in other molecules [hexahydro-3,6-pyridazinedione, exp. and theor. (Ottersen & Almlöf, 1978); carbonohydrazide, exp. (Ottersen & Hope, 1979); carbonohydrazide, theor. (Ottersen, Almlöf & Hope, 1979)].

Theoretical calculations (Ottersen & Jensen, 1975) imply that the N lone pair is highly utilized in the conjugation over the N—C=O moiety; this effect would be enhanced by the formation of an N—H···O hydrogen bond such as is found in the present structure (Ottersen, 1976). The shape of the C—N bonding peak, the relatively high experimental deformation density in
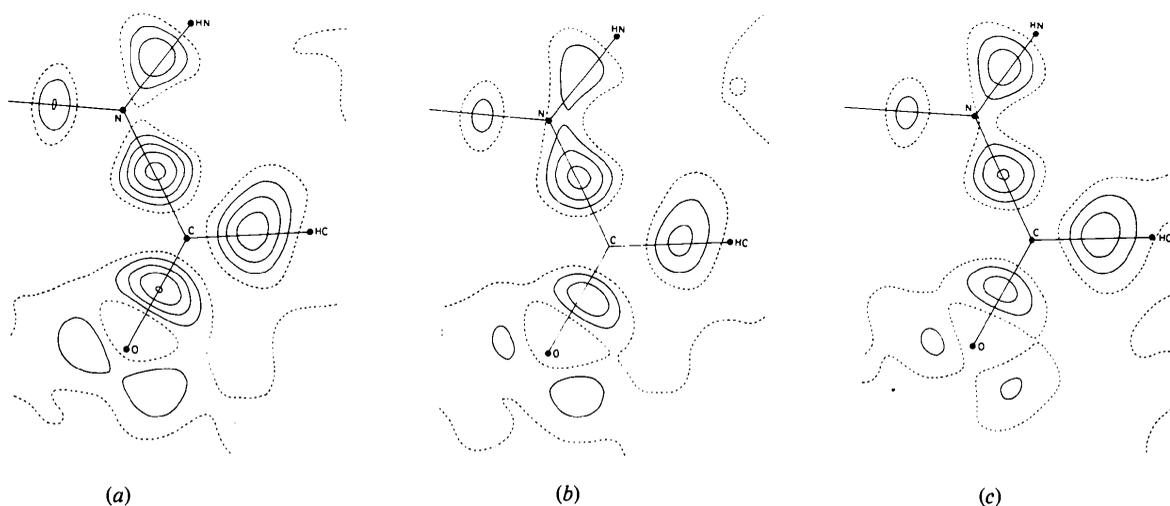

(a)   (b)   (c)

Fig. 1. Deformation electron density (a) in the least-squares plane defined by N, C and O, (b) and (c) 0·25 Å on each side of this plane. Contours are given at intervals of 0·1 e Å⁻³. The zero-line is broken.
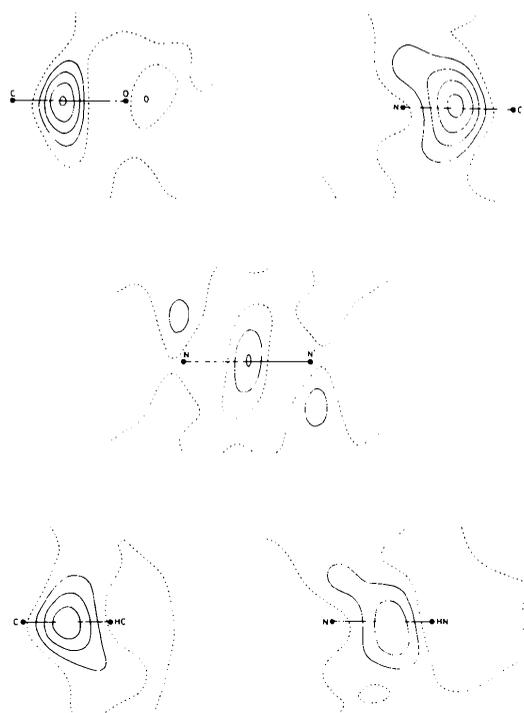
Fig. 2. Deformation electron density in the bonds normal to the molecular plane. Contours are given at intervals of 0·1 c Å⁻³. The zero-line is broken.

the bond, the low density in the N—N bond, and the absence of lone-pair density indicate that the N lone pair is fully utilized in the conjugation.

The O lone-pair densities are comparable to those found for other compounds containing the C=O group [*e.g.* glycine (Almlöf, Kvick & Thomas, 1973); oxalic acid dihydrate (Coppens, Sabine, Delaplane & Ibers, 1969)]. The maximum densities are 0·18 e Å⁻³ and 0·20 e Å⁻³, whereas theoretical results including thermal damping give a maximum density of 0·30 e Å⁻³. According to *ab initio* calculations using a double zeta basis (Ottersen, 1976) the large conjugation over the N—C=O moiety leads to a density build-up on the O atom, which is enhanced by the formation of

N—H···O bonds. In view of this, the relatively low density in the O lone-pair regions is surprising. However, a systematic theoretical study (Almlöf, 1978) has shown that most of the lone-pair densities are subtracted by the spherical-atom model, and further that an increase in the basic set leads to a decrease in the lone-pair and an increase in the bond regions. The lone-pair–core–lone-pair angle is 137°. The peak density in the C=O bond is 0·40 e Å⁻³.

No deformation density is found in the hydrogen bond. Similar results have been reported for glycine (Almlöf, Kvick & Thomas, 1973) and formamide (Stevens & Coppens, 1976). Theoretical results also give overlap populations of about 0·1 in the O···H bonds.

References

ALMLÖF, J. (1979). To be published.
ALMLÖF, J., KVICK, Å. & THOMAS, J. O. (1973). *J. Chem. Phys.* **59**, 3901–3906.
COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2460.
CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
DENNE, W. A. (1977). *Acta Cryst.* **A33**, 438–440.
DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
HOPE, H. & OTTERSEN, T. (1978). *Acta Cryst.* **B34**, 3623–3626.
OTTERSEN, T. (1975). *Acta Chem. Scand. Ser. A*, **29**, 939–944.
OTTERSEN, T. (1976). *Adv. Mol. Relaxation Processes*, **9**, 105–129.
OTTERSEN, T. & ALMLÖF, J. (1978). *Acta Chem. Scand. Ser. A*, **32**, 219–224.
OTTERSEN, T., ALMLÖF, J. & HOPE, H. (1979). To be published.
OTTERSEN, T. & HOPE, H. (1979). *Acta Cryst.* **B35**, 373–378.
OTTERSEN, T. & JENSEN, H. H. (1975). *J. Mol. Struct.* **26**, 355–363.
STEVENS, E. D. & COPPENS, P. (1976). *Abstr. Am. Crystallogr. Assoc. Summer Meeting*, p. 54.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.