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The Electron Density Distribution in Hexahydro-3,6-pyridazinedione

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The electron density deformation in hexahydro-3,6-pyridazinedione has been determined by $X-X_{HO}$ Fourier synthesis. These experimental results are compared with densities calculated by *ab initio* Hartree-Fock methods. In the theoretical densities the effect of thermal smearing has been approximately accounted for. The crystallographic results are based on a data set consisting of 1712 non-zero reflections collected at −165 °C. The heavy-atom parameters converged to their final values for a minimum sin θ/λ cutoff of 0.75 $Å^{-1}$, leaving 1026 reflections in the refinement. The final R_w is 0.046.

The present study was carried out as part of a series of deformation electron density investigations of compounds containing the N−N−C=O fragment. A series of structure investigations of such compounds has been carried out in which the experimental results have been complemented by theoretical calculations (for a review see Refs. 1 and 2). It has been found[1] that the readily delocalized π-system in the N−C=O fragment is one of the major factors in the ability of this fragment (the peptide linkage) to form hydrogen bonds, and that the conformation around the N−N bond is dominated by the degree of participation of the nitrogen lone-pairs in the conjugation.[2] Electron deformation density studies of these compounds may give a better understanding of these phenomena, and also of the biologically important peptide linkage.

In order to gain more information on the density distribution it was decided to complement the experimental results with theoretically computed deformation densities. Comparisons between experimental results and thermally smeared theoretical densities may also give information on systematic differences in the two methods,[3] and experimental densities may be utilized to test variations in basis sets used in the theoretical calculations.[3,4] Further, within a series of closely related molecules where the systematic differences between the experimental and theoretical results have been mapped, one may compare theoretical results in order to remove the effects of thermal vibrations inherent in the experimental results.

An earlier low-temperature structure determination of hexahydro-3,6-pyridazinedione[5] (HP) implied that this molecule was well-suited for deformation density studies within the series, which at the moment comprise 1,2-diformylhydrazine,[6] carbohydrazide,[7] and acetamide.[3] HP crystallizes in the centrosymmetric space group *Ibca* with only half a molecule in the asymmetric unit, the molecule having a crystallographically determined C_2 symmetry. The studies of 1,2-diformylhydrazine[6] and carbohydrazide[7] implied that it was possible by refinements using only high-angle data to obtain reasonable positional parameters for the hydrogen atoms [1,2-diformylhydrazine: C−H: 1.07(2) Å, N−H: 1.02(2) Å], and the redetermination of HP could be used to study such refinements further.

EXPERIMENTAL

Crystals of HP[5] were grown by slow evaporation of ethyl alcohol. A rhomb-shaped platy crystal of dimensions 0.44 × 0.36 × 0.10 mm was mounted on a computer-controlled Syntex $P\bar{1}$ four-circle diffractometer equipped with an incident-beam graphite monochromator and a modified Enraf-Nonius low-temperature device (liquid N_2). The temperature at crystal site was −165 °C. The angular coordinates of 13 Mo$K\alpha$ reflections (λ=0.71069 Å) with 2θ-values from 61 to 76° were used in a least-squares

calculation to determine the crystal orientation and cell dimensions. The cell dimensions are: $a=9.126(1)$ Å, $b=17.082(3)$ Å, $c=6.185(1)$ Å, $V=964.2(3)$ Å^3; space group: *Ibca*, $Z=8$.

Three-dimensional intensity data were recorded using the ω-2θ scanning mode with a scan speed of 2.0° (2θ) min^{-1} and a scintillation detector with pulse-height analyse. Each reflection was scanned from $[2\theta(\alpha_1)-0.7°]$ to $[2\theta(\alpha_2)+1.1°]$. Background counting time was equal to 0.35 × scan time at each end of the scan range. In order to study the electron density deformation all reflections within a quadrant with sin θ/λ values less than 0.65 Å^{-1} were recorded, whereas for reflections with sin θ/λ values between 0.65 Å^{-1} and 1.19 Å^{-1} only those were recorded which had integrated counts above 4 cps determined in a 2 s scan over the reflection, and for reflections with sin θ/λ values above 1.19 Å^{-1} only those with integrated counts above 2 cps. The intensities of three check reflections which were remeasured for every seventy reflections showed no systematic variations throughout the data collection.

The estimated standard deviations of the net intensities, I, were calculated as:

$$\sigma(I)=[(B_1+B_2)\times\left(\frac{\text{scan time}}{2\times\text{background time}}\right)^2+I_s+(0.010\times I)^2]^{\frac{1}{2}}$$

where B_1 and B_2 are the two background counts and I_s is the integrated intensity. The factor 0.010 reproduces the observed variance in the check reflections. Of the 2224 symmetry-independent reflections measured ($2\theta_{max}=134°$), the 1712 which had net intensities larger than twice their e.s.d.'s were used in the refinement procedure.

The intensities were corrected for the truncation error. Using the notation of Denne,[8] the formula utilized is:

$$I_{corr}=I/[A_1C_1+A_2C_2+\tfrac{1}{2}(\lambda_a-\lambda_b)\{A_1[I_1(\lambda_a)+I_1(\lambda_b)]+A_2[I_2(\lambda_a)+I_2(\lambda_b)]\}]$$

The line widths and relative intensity data were obtained from Compton and Allison.[9]

Lorentz and polarization corrections were applied to the corrected net intensities. The polarization factor includes the polarization by the monochromator crystal assuming this to be half perfect. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 and is described in Ref. 10.

REFINEMENT

The quantity $\Sigma w(F_{obs}-K|F_{calc}|)^2$ was minimized in full-matrix least-squares refinements with $w=1/\sigma^2(F_{obs})$. The atomic scattering factors used were those calculated by Doyle and Turner[11] for carbon, nitrogen and oxygen, and the contracted spherical scattering factors calculated by Stewart *et al.*[12] for hydrogen.

The sin θ/λ cutoff value was varied systematically, refinements were performed with minimum cutoff values of 0, 0.40, 0.50, 0.65, 0.75, and 0.85 Å^{-1}. A summary of the results from these refinements is given in Table 1. The standard deviations in hydrogen atomic parameters increased rapidly for cutoffs above 0.40 Å^{-1} (see Table 1). These parameters were, therefore, not refined for cutoffs above 0.65 Å^{-1}.

The C–H and N–N bond lengths obtained in the refinements are listed in Table 1. The variations in these lengths with increasing sin θ/λ minimum cutoff follow the pattern found in the refinements of diformylhydrazine[6] and carbohydrazide.[7] The bond

Table 1. Summary of results from the refinements. $R=\Sigma|kF_{obs}-|F_{calc}||/\Sigma kF_{obs}$, where k is the scale factor, R_t is R-factor taken over all observed reflections, $R_w=[\Sigma w(kF_{obs}-|F_{calc}|)^2/\Sigma wkF_{obs}{}^2]^{\frac{1}{2}}$, $G=[\Sigma w(kF_{obs}-|F_{calc}|)^2/(n-m)]^{\frac{1}{2}}$, where n is the number of observations and m is the number of parameters. The numbering of the atoms may be found in Fig. 1.

$(\sin\theta/\lambda)_{min}$ (Å^{-1})	n	m	R(%)	R_w(%)	R_t(%)	G	k	Bond lengths N–H	C2–H2	C2–H3
0	1712	49	4.76	4.42	4.76	2.22	0.318(1)	0.926(12)	0.969(9)	0.967(11)
0.40	1586	49	4.51	3.99	4.63	1.58	0.328(1)	0.888(17)	0.891(16)	0.949(16)
0.50	1473	49	4.64	4.15	4.67	1.42	0.329(1)	0.817(32)	0.856(30)	0.939(26)
0.65	1229	49	4.83	4.53	4.86	1.28	0.330(1)	1.021(69)	0.984(71)	0.988(75)
0.75	1026	37	5.20	4.60	4.86	1.12	0.330(2)			
0.85	808	37	5.76	5.32	5.06	1.13	0.332(3)			

Table 2. Fractional atomic coordinates and temperature factors with estimated standard deviations. The heavy atom parameters are from the refinement with $(\sin\theta/\lambda)_{min}$ cutoff of 0.75 Å^{-1} and the hydrogen parameters from the refinement with $(\sin\theta/\lambda)_{min}$ cutoff of 0.65 Å^{-1}. The anisotropic temperature factor is given by: $\exp\{-2\pi^2[U_{11}(a^*h)^2\cdots+2U_{23}(b^*c^*kl)]\}$.

Atom	x	y	z	$U_{11}(B)$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	.04205(5)	.60423(5)	.04555(17)	.0071(1)	.0115(2)	.0173(3)	.0002(1)	−.0010(2)	−.0015(2)
N	−.17349(7)	.54101(3)	−.00006(19)	.0076(1)	.0078(1)	.0161(2)	.0000(1)	.0006(2)	−.0010(2)
C1	−.09423(7)	.60561(5)	.04037(18)	.0074(1)	.0086(2)	.0124(3)	.0006(1)	.0000(2)	−.0004(2)
C2	−.18343(8)	.67877(4)	.07550(18)	.0091(2)	.0086(2)	.0196(3)	.0005(2)	−.0017(2)	−.0028(2)
H1	−.110(6)	.492(4)	−.014(12)	1.91(79)					
H2	−.125(7)	.727(4)	.061(10)	1.76(63)					
H3	−.211(9)	.677(4)	.230(12)	2.22(84)					

lengths decrease with increasing $(\sin\theta/\lambda)_{min}$ with the shortest lengths obtained for the 0.50 Å^{-1} cutoff. At the 0.65 Å^{-1} cutoff the hydrogens shift away from the heavy atoms and the N−H bond increases to the reasonable value of 1.02(7) Å. The two C−H bonds obtained are still too short (0.99 Å). The results obtained in the refinements of diformylhydrazine[6] and carbohydrazide[7] implied that hydrogens bonded to carbon atoms should converge to their "true" (nuclear) positions for the 0.65 Å^{-1} cutoff, whereas hydrogens bonded to nitrogen atoms converge to their nuclear positions for the 0.75 Å^{-1} cutoff. At present we have no decent theoretical explanation of this most remarkable behavior of the X−H bond length as a function of the $\sin\theta/\lambda$ cutoff. However, the e.s.d.'s of the hydrogen positional parameters in the present study are large and one may only observe that the hydrogen positional shifts follow the pattern obtained in the highly accurate studies of diformylhydrazine and carbohydrazide. The overdetermination ratio in the refinement with $(\sin\theta/\lambda)_{min}$ of 0.65 Å^{-1} in the present case is 25.1, and in the studies of diformylhydrazine and carbohydrazide 63.4 and 36.0, respectively.

The heavy atom parameters converged to their final values for the 0.75 Å^{-1} cutoff, in agreement with the results found for diformylhydrazine,[6] carbohydrazide[7] and acetamide.[3] All parameters changed less than twice their e.s.d.'s when the cutoff was increased to 0.85 Å^{-1}. The correlation coefficients between the scale factor and the B_{ii}'s in this refinement were in the order of −0.3 to −0.5, and the correlation between the O and Cl x-parameters is −0.40, and between the y-parameters −0.45. The absolute values of other coefficients are less than 0.3.

Final atomic parameters are listed in Table 2. A list of observed and calculated structure factors is available from the authors upon request. (May also be obtained from: Department of Chemistry, University of Oslo, Oslo 3, Norway.) Standard deviations in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell dimensions.

The r.m.s. difference between the observed U_{ij}'s (refinement using only data above 0.75 Å^{-1}) and those calculated from the "rigid body" model[13] is 0.0002 Å^2, which implies that the molecule may be regarded as a rigid body. The atomic positions were accordingly corrected for the librational motion. The eigenvalues of **T** are 0.10, 0.09 and 0.09 Å^2, and the librational amplitudes are 4.07, 1.79 and 1.36°. The major librational axis is very nearly parallel with a line through O and O′.

DESCRIPTION OF THE STRUCTURE

Bond lengths and bond angles are listed in Fig. 1 where also the numbering of the atoms is given. The torsional angles Cl−N−N′−Cl′ and Cl−C2−C2′−Cl′ are 25.6(3) and 56.3(2)°, respectively, and N−Cl−C2−C2′ is −37.0(2)°. Deviations from least-squares planes may be found in the legends to Figs. 2 and 3. Apart from H2 and H3 the other atoms in the asymmetric unit are coplanar.

The molecular parameters are essentially the same as those found in the earlier low-temperature, high-angle data structure determination.[5] The maximum deviation occurs in the values of the N−N bond length which earlier was found to be 1.402(1) Å and in the present structure model is 1.398(1) Å. These small deviations do not alter the conclusions made in the earlier publication.[5]

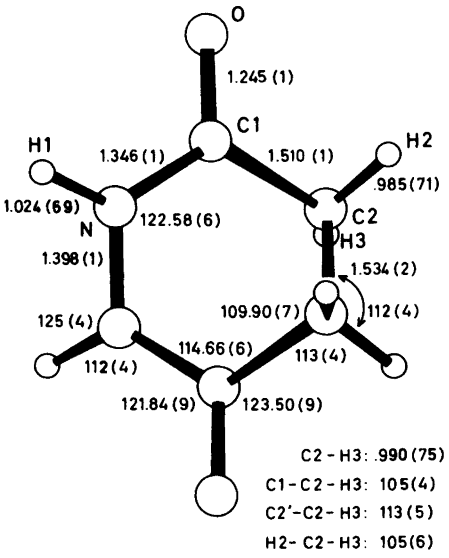

Fig. 1. Bond lengths (Å) (corrected for thermal vibration effects) and bond angles (°) with estimated standard deviations.

CALCULATION OF ELECTRON DENSITY DEFORMATIONS

a. *Experimental densities.* The electron difference densities were obtained using the 904 observed reflections with sin θ/λ-values ≤ 0.85 Å^{-1} in the Fourier summation. The F_{calc}'s are calculated utilizing the heavy atom parameters found in the refinement with a $(\sin\theta/\lambda)_{min}$ cutoff of 0.75 Å^{-1} and the hydrogen parameters obtained in the refinement with a $(\sin\theta/\lambda)_{min}$ cutoff of 0.65 Å^{-1}. The scale factor for the F_{obs}'s [0.322(1)] was obtained by refinement using this structure model and subset of data, in accordance with other studies of similar structures.[3,6,7] Difference density maps through various sections of the molecule are plotted in Figs. 2, 3 and 4. A difference density map calculated using the same structure model and subset of data but with the scale factor obtained in the refinement with $(\sin\theta/\lambda)_{min}$ cutoff of 0.75 Å^{-1} (0.330), showed positive densities in the atomic positions, whereas there were only minor differences in bond and lone-pair densities between this map and the one presented here.

b. *Theoretical densities.* The theoretical deformation densities were obtained from *ab initio* calculations within the Hartree-Fock approximation. The MOLECULE[14] program system was used, employing a basis set of contracted Gaussians. For each of C, N and O, a 7*s*3*p* basis set[15] was contracted to 4*s*2*p*, whereas for H a 4*s* basis[16] was contracted to 2*s*. Thus, the entire basis for the molecular calculation comprised 92 basis functions.

From the wavefunction obtained, the total electron density was computed. The deformation density was then found by subtracting calculated densities for the isolated atoms in their ground states. The atomic densities were calculated using exactly the same contracted basis sets as in the

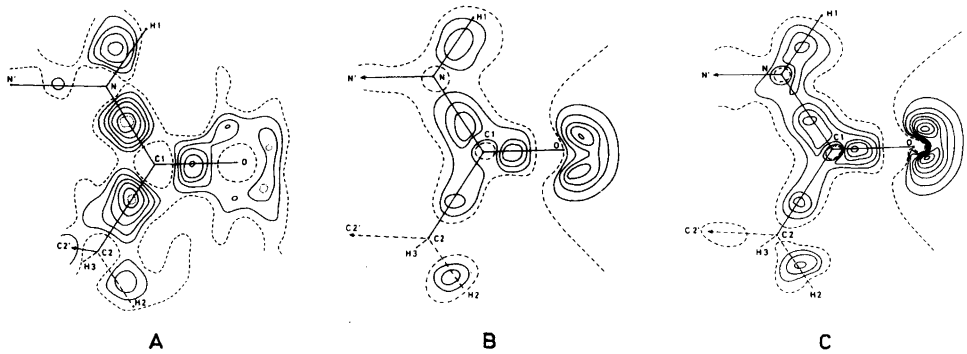

Fig. 2. Deformation electron densities in the least-squares plane through O, N, C1 and C2. Distances of the atoms from this plane are: O: 0.001 Å; N: 0.001 Å; C1: −0.004 Å; C2: 0.001 Å, N′: −0.046 Å, C2′: 0.986 Å, H1: −0.061 Å, H2: 0.266 Å, H3: −0.948 Å. The contours are given at intervals of 0.1 e Å^{-3} for the experimental map, 0.2 e Å^{-3} for the theoretical ones. The zero-line is broken, whereas the dotted lines indicate differences of 0.05 e Å^{-1}. A, Experimental results; B, thermally smeared theoretical results; C, theoretical results.

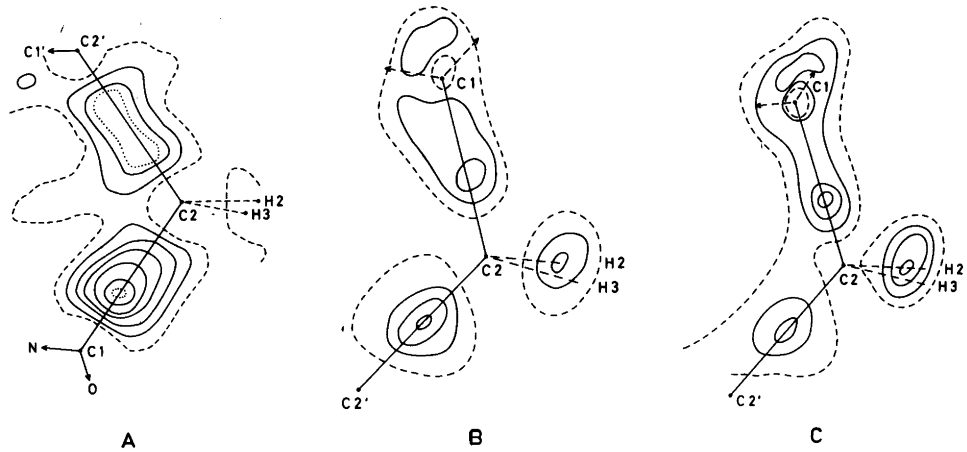

Fig. 3. Deformation electron densities in the plane defined by C1, C2 and C2′. Distances of other atoms from this plane are: N: −0.734 Å; C1′: −1.179 Å; H2: 0.735 Å; H3: −0.819 Å. Contour levels are as in Fig. 2. A, Experimental results; B, thermally smeared theoretical results; C, theoretical results.

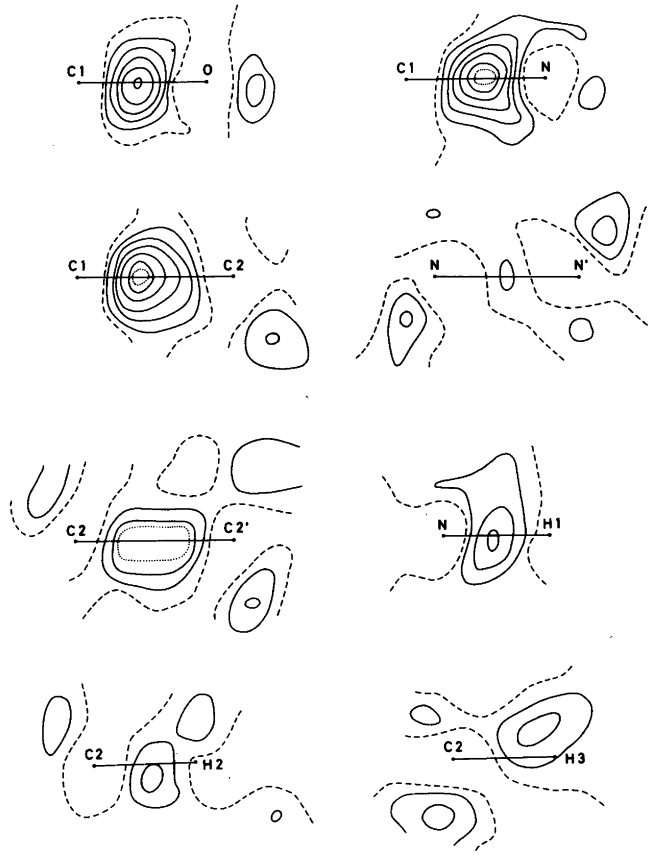

Fig. 4. Experimental deformation electron densities in the bonds normal to the plane through O, N, C1, C2, except for C2−C2′ which is given normal to the plane of C1, C2, C2′. Contour levels are as in Fig. 2.

molecule. This ensures a close cancellation of possible errors due to deficiencies in the basis sets used.

A direct comparison between experimental and theoretical deformation densities is somewhat complicated by the fact that the former have been smeared out as a result of thermal vibration. It is not trivial to apply the same thermal smearing to the theoretical densities, since these are not uniquely decomposable into fragments that can be associated to individual atoms. Therefore, the thermal effects have been only roughly accounted for in the theoretical maps by applying an isotropic, overall smearing factor according to the formula:

$$\rho(r)=(\frac{\alpha}{\pi})^{3/2}\int\rho_0(r')\exp[-\alpha(r'-r)^2]\,dv'$$

Here, ρ_0 and ρ are the computed densities before and after the smearing is applied. A value of 40 was used for the parameter α, corresponding to a conventional B factor of about 1.0.

DISCUSSION

When comparing the experimental deformation density maps with those obtained from the quantum-mechanical calculations, one should first note that the agreement is encouragingly good. It would seem reasonable to interpret the minor discrepancies that still occur as largely due to imperfections in the theoretical maps, resulting from the limited basis set and the approximate theory used in the calculations. Typical such features in the theoretical maps are exaggerated densities in the lone-pair regions on oxygen, and also too low bond densities. The latter are frequently displaced from the centre of the bond as compared to the experimental results. In systematic studies on similar systems[4] such effects have been suggested to originate from the truncations of the basis set used. It can thus be anticipated that a more flexible basis also would have yielded an even better agreement in this work.

The abnormally low density at the centre of the N – N bond obtained in the experimental map may look improbable at first sight. Since the bond is centred on a two-fold axis one could suspect this result to be an artifact, due to the usual accumulation of experimental errors at symmetry elements in the structure. However, this feature is also found in the theoretical maps, where no such accumulation is likely to occur. Furthermore, recent investigations on other, similar systems have also shown very low N – N bond densities.[3,6,7]

Besides the somewhat abnormal N – N bond, the deformation densities – both the experimental and the theoretical ones – show only effects that one would expect on simple, valence-theoretical grounds, *i.e.* accumulation of charge in covalent bonds and in the lone-pair regions. The theoretically obtained integrated density in these regions corresponds to 0.15 – 0.25 electrons in the C – C and C – N covalent bonds, 0.40 – 0.60 in C – H and N – H, and about 0.30 electrons in each of the oxygen lone-pairs. The excess of charge in these parts of the molecule necessitates a flow of charge from other regions in order for the number of electrons to remain constant. The most dominant charge-deficient regions occur close to the nuclei of the heavy atoms. This deficiency of charge can be rationalized in terms of a valence state being the best approximate representation of the atom in the molecule. In the ground state, exactly *two* 2*s* electrons contribute to the density at the nucleus of the atom. In the valence state, on the contrary, a distribution of the valence electrons into sp^n hybrides will always result in *less than* two 2*s* electrons. Although this picture is extremely over-simplified, the number of 2*s* electrons on each atom is always less than two, according to a Mulliken population analysis.

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