

A Simple Refinement of Density Distributions of Bonding Electrons. V. Bond Electron Density Distribution in Urea, CO(NH₂)₂, at 123 K

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A model for urea is described in which valence electrons are included separately in the refinement. A significantly better R is obtained for this model (0.016) compared with the usual spherical-atom refinement (0.029). Core parameters agree well with those from a high-order X-ray refinement. N–H lengths which are excessively short (~ 0.8 Å) with parameters from a spherical-atom refinement have normal values in our valence model (~ 1.0 Å). Bond and atom populations are given, and a dynamic valence density based on the refined model is presented.

Introduction

A model in which valence density distributions are refined has been described in previous papers in this series (Hellner, 1977; Mullen & Hellner, 1977).

The method was applied to urea to compare the results with the related thiourea, which is also being investigated in this laboratory. In particular, the C=O and C=S bonds and the lone-pair distributions on O and S are of interest.

Urea has the advantage that it is a small molecule with high symmetry, thus reducing the number of parameters to be refined. In addition, crystals of good quality can be obtained.

Experimental

Single crystals of urea grown in this laboratory were used for data collection. A crystal $0.35 \times 0.45 \times 0.60$ mm and of good optical quality was mounted on a Philips four-circle diffractometer (PW 1100) equipped with a Heraeus–Leyboldt liquid-nitrogen cryostat. The temperature at the crystal was measured by a copper–constantan thermocouple. This was centered at the crystal position in a dummy run to fix the parameters of the low-temperature system. During the actual measurement the thermocouple is not in place. This method overcomes such problems as differences in temperature at crystal and thermocouple position. The temperature at the crystal during data collection was 123 ± 2 K.

Urea crystallizes in the tetragonal space group $P\bar{4}2_1m$. Eight symmetry-equivalent reflections (half the sphere) were measured out to $\sin \theta/\lambda = 0.90$ Å⁻¹ with Mo $K\alpha$ (graphite-monochromated) radiation ($\lambda =$

0.7107 Å). The agreement between equivalent reflections was 3.4%. On averaging symmetry-equivalent reflections, 288 independent reflections were obtained. Of these, five had $F \leq 2\sigma$ and were designated as unobserved. Cell dimensions at 123 K were measured as $a = b = 5.576$ (3), $c = 4.686$ (3) Å.

Refinement of the structure including valence electrons

The data were corrected for Lorentz and polarization effects. Absorption is negligible ($\mu = 1.2$ cm⁻¹). An isotropic extinction correction was calculated with the Zachariasen (1967) model modified by Coppens & Hamilton (1970) and incorporated in the program written by Finger (1972). The largest extinction factor was 0.74 for the 110 reflection. The correction factors were applied to F_o instead of F_c , and the corrected data were used in the refinement. For the starting model core parameters were taken from high-order X-ray diffraction results. For H, the room-temperature parameters of Pryor & Sanger (1970) were used as starting values. Bond charges were placed at the mid-points of bonds. The lone pairs on O and N were placed at the respective core positions. For the cores, form factors were taken from *International Tables for X-ray Crystallography* (1974). Bond charges were given Gaussian form factors (like temperature factors) and weighted to 4 e for a double bond (*i.e.* C=O) and 2 e for a single bond. The H cores were given occupancies of 0.5 e and the N–H bonds 1.5 e.

In the first stages of the refinement the population parameters and β_{ij} of the bond charges were allowed to vary. In later stages the positional parameters of the bond charges were refined. Finally, all parameters,

including positional and thermal parameters of the cores, were refined. The occupancy parameters for the cores were kept fixed throughout to the two 1s electrons which are regarded as non-valence electrons.

Refinement by the method outlined above led to an R of 0.016 ($R_w = 0.015$) compared with 0.029 ($R_w = 0.033$) for the usual spherical-atom refinement with the same data set. This is a significant improvement (Hamilton, 1965) at the 0.005 level.*

Discussion of results

The bond-charge distributions (β_{ij}) are represented as 50% ellipsoids (Fig. 1; drawn by ORTEP, Johnson, 1965). Core and charge parameters (x, y, z, β_{ij}) are given in Table 1 and populations of bond charges and lone pairs in Table 2. Mulliken populations appear in Table 3.

The core parameters obtained from our model are, in general, in good agreement with those from a high-angle X-ray analysis using the same data with $\sin \theta / \lambda > 0.60 \text{ \AA}^{-1}$. All parameters agree within 3σ except for β_{11} of O where the agreement is within 5σ

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33252 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

(Table 1). In the high-order X-ray refinement the scale factor and H atom parameters were kept fixed at the values they have for the full-data refinement, since these parameters have a limited dependence on high-order data (*cf.* Bats & Coppens, 1977).

Mulliken populations are about 3–8% below the ideal value, except for H (Table 3).

Bond lengths from the spherical-atom refinement and our model are compared in Table 4. The rather short N–H(2) bond [0.84 (6) Å] in the spherical-atom model is not found in the molecular model [N–H(2) =

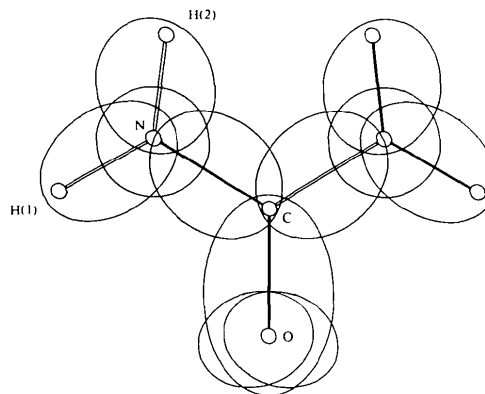


Fig. 1. Urea molecule at 123 K showing the nature of the density distributions in the plane of the molecule as 50% probability ellipsoids.

Table 1. Comparison of core positional parameters and thermal parameters ($\times 10^4$) for urea at 123 K

		(a) Spherical atom, X-ray; (b) molecular model, X-ray; (c) high-angle, $\sin \theta / \lambda > 0.60 \text{ \AA}^{-1}$.								
		x	y	z	β_{11} (or B)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C	<i>a</i>			0.3277 (4)	85 (5)	85 (5)	62 (5)	3 (4)		
	<i>b</i>	0	$\frac{1}{2}$	0.3284 (2)	82 (2)	82 (2)	50 (2)	3 (2)	0	0
	<i>c</i>			0.3283 (2)	85 (2)	85 (2)	56 (2)	1 (2)		
O	<i>a</i>			0.5971 (3)	118 (5)	118 (5)	44 (4)	15 (4)		
	<i>b</i>	0	$\frac{1}{2}$	0.5966 (2)	105 (2)	105 (2)	47 (2)	11 (2)	0	0
	<i>c</i>			0.5969 (1)	115 (2)	115 (2)	47 (1)	10 (2)		
N	<i>a</i>	0.1449 (4)	0.6449 (4)	0.1792 (2)	168 (5)	168 (5)	70 (3)	-93 (4)	1 (4)	1 (4)
	<i>b</i>	0.1448 (2)	0.6448 (2)	0.1787 (1)	161 (3)	161 (3)	74 (2)	-88 (2)	1 (2)	1 (2)
	<i>c</i>	0.1451 (2)	0.6451 (2)	0.1783 (1)	164 (2)	164 (2)	75 (1)	-91 (1)	1 (2)	1 (2)
H(1)	<i>a</i>	0.244 (7)	0.744 (7)	0.268 (4)	0.74 (52)					
	<i>b</i>	0.262 (9)	0.762 (9)	0.291 (6)	3.72 (92)					
H(2)	<i>a</i>	0.138 (7)	0.638 (7)	0.000 (7)	2.25 (62)					
	<i>b</i>	0.129 (9)	0.629 (9)	-0.042 (8)	2.84 (87)					

Positional parameters and $\beta_{ij} (\times 10^3)$ for charges in urea at 123 K

Charge	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C=O	0	0.5	0.511 (4)	120 (12)	120 (12)	376 (18)	-8 (7)	0	0
C-N	0.066 (4)	0.566 (4)	0.256 (4)	144 (16)	144 (16)	154 (12)	-28 (9)	-22 (13)	-22 (13)
N-H(1)	0.200 (7)	0.700 (7)	0.228 (8)	109 (15)	109 (15)	137 (16)	12 (7)	28 (18)	28 (18)
H-N(2)	0.142 (10)	0.642 (10)	0.068 (3)	97 (7)	97 (7)	173 (13)	-6 (7)	-6 (19)	-6 (19)
O (l.p.)*	-0.016 (24)	0.484 (24)	0.604 (1)	86 (19)	86 (19)	86 (1)	1 (10)	-8 (15)	-8 (15)
N (l.p.)†	0.127 (6)	0.664 (6)	0.187 (6)	108 (10)	129 (10)	115 (7)	-36 (6)	-20 (10)	-20 (10)

* Lone-pair on O.

† Lone-pair on N.

1.04 (8) Å]. Extremely short bond lengths arise partly from thermal effects and partly from the inadequacy of the spherical-atom model to describe the correct electron density distribution in the molecule. This latter effect was also described for diborane (Mullen & Hellner, 1977), where a similar improvement in bond lengths involving H was obtained.

Table 2. Population parameters for cores and charges in urea at 123 K

Atom/charge	Population (e)	Atom/charge	Population (e)
O	2.00	C-N	1.89 (2)
C	2.00	N-H(1)	1.35 (2)
N	2.00	N-H(2)	1.30 (2)
H(1)	0.40 (2)	O (l.p.)*	2.08 (2)
H(2)	0.37 (2)	N (l.p.)†	2.36 (3)
C=O	3.27 (5)		

* Lone pair on O. The value given represents half the total lone-pair population on O.

† Lone pair on N.

Table 3. Mulliken population in urea at 123 K

	Population (e)		Population (e)
O	7.80 (7)	H(1)	1.08 (3)
C	5.53 (5)	H(2)	1.02 (3)
N	6.63 (6)		

Table 4. Bond lengths in two models of urea at 123 K

(a) Spherical atom, X-ray; (b) molecular model, X-ray.

C=O	a	1.262 (2) Å	N-H(1)	a	0.89 (6) Å
	b	1.257 (1)		b	1.06 (8)
C-N	a	1.338 (4)	N-H(2)	a	0.84 (6)
	b	1.340 (2)		b	1.04 (8)

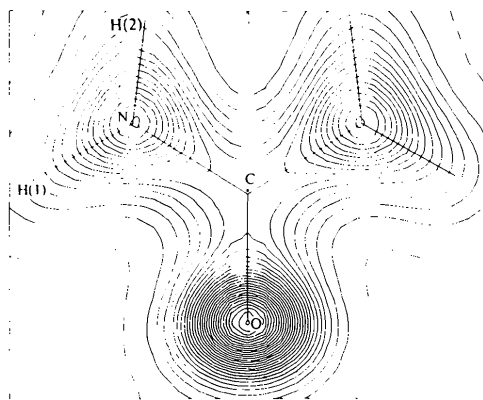


Fig. 2. Valence density map for urea at 123 K in the molecular plane. $1s^2$ cores of C, O, and N are subtracted but not H. Contours are at $0.25 e \text{ \AA}^{-3}$; zero and positive contours are solid lines and negative contours are dashed.

Table 5. Valence density distribution in urea at 123 K

Atom/bond		Atom/bond	
O	$7.06 e \text{ \AA}^{-3}$	C-O*	$2.00 e \text{ \AA}^{-3}$
C	1.50	C-N	1.79
N	3.80	N-H(1)	2.05
H(1)	0.65	N-H(2)	2.20
H(2)	0.60		

* Approximately at mid-points of bonds.

A dynamic density map for urea appears in Fig. 2. This is calculated according to

$$\rho_{\text{valence}} = \rho_{\text{molecule}} - \rho_{1s^2 \text{ cores}}$$

H atoms are considered to have no core structure and are not subtracted from the molecular density. The map is dominated by the high peaks on O ($7.0 e \text{ \AA}^{-3}$) and N ($3.75 e \text{ \AA}^{-3}$). The density on C is lower at $1.5 e \text{ \AA}^{-3}$.

Electron densities for bonds in Table 5 are quoted for approximately the mid-points of the bonds since valence peaks generally occur at atom positions. An error map based on the coefficients ($F_o - F_c$) for the molecular model had density lying within the range $\pm 0.1 e \text{ \AA}^{-3}$. This is about 3σ , the standard deviation for the electron density in the model being $0.033 e \text{ \AA}^{-3}$.

Summary

The valence density map shows high peaks, as expected, at O and N where lone pairs occur close to the core positions. The density on O ($7.0 e \text{ \AA}^{-3}$) where two lone pairs occur is about twice as large as that on N ($3.75 e \text{ \AA}^{-3}$) with one lone pair.

The molecular model gives a significantly better R (0.016) compared with the spherical-atom model (0.029), and core parameters in agreement with high-order X-ray data. Moreover, better lengths for the N-H bonds are obtained. The excessive shortening of these bonds in the spherical-atom refinement was also found by Caron & Donohue (1969) for room-temperature data [$N-H(1) = 0.68 (7) \text{ \AA}$]. From room-temperature neutron data N-H lengths of $0.998 (5)$ and $1.003 (4) \text{ \AA}$ were obtained (Pryor & Sanger, 1970). These latter values correspond more closely to the lengths found in our molecular model. Lone-pair populations of 2.36 and $4.16 e$ on N and O respectively are somewhat higher than the ideal values of 2 and 4 respectively. The C=O bond with 3.27 e has rather less than the ideal occupancy of 4. It is intended in future papers in this series to publish deformation densities for urea and to compare these with quantum-mechanically derived models. Additionally, form factors for the bond charges in urea will be compared with those of Fritchie (1966).

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Antiviral Nucleic Acid Derivatives. II.* Crystal Structure of 5-Vinyl-2'-deoxyuridine

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$C_{11}H_{14}N_2O_5$ is orthorhombic, space group $P2_12_12_1$, with $a = 4.861$ (5), $b = 16.70$ (1), $c = 14.01$ (1) Å, $Z = 4$. The structure was refined by least squares calculations to $R = 5.9\%$ for 748 observed counter amplitudes. The pyrimidine ring is planar with the vinyl group inclined at 12° to it and the glycosidic torsion angle is 39° (*anti* conformation). The sugar ring has the C(3')-*exo* conformation, and the arrangement about C(4')–C(5') is such that O(5') is oriented *gauche-trans* with respect to O(1') and C(3').

Introduction

The 5-substituted uracils and the corresponding nucleosides have recently attracted attention because of their antiviral activity. 5-Vinyl-2'-deoxyuridine first appeared in the literature in 1975, having been prepared by two different routes (Sharma & Bobek, 1975; Barwölf & Langen, 1975*a*). Since then studies have been made of its antiviral characteristics (Cheng, Domin, Sharma & Bobek, 1976; de Clercq, 1977) and also its mode of action (Barwölf & Langen, 1975*b*).

Interest in the title compound in this laboratory has stemmed not only from its potential antiviral activity, but also from its ability to replace thymidine in the DNA of some organisms (Jones & Walker, 1975).

Experimental

Suitable crystals were obtained from methanol–water. Cell dimensions and intensities were measured on a Stoe two-circle computer-controlled diffractometer with

graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The ω -scan technique was employed with a scan speed of $0.6^\circ \text{ min}^{-1}$ and 30 s background counts at the beginning and end of each scan. For layers $0kl$ and $1kl$, $\Delta\omega$ was 1.4° and for the higher layers it was calculated from $(A + B \sin \mu / \tan \theta')^\circ$, where μ is the equi-inclination angle, $2\theta'$ is the azimuth angle, and A and B were assigned the values of 1.0 and 0.5. 1644 reflexions were scanned, of which 748 [$I > 2.5\sigma(I)$] were used in the analysis.

Crystal data

$C_{11}H_{14}N_2O_5$, $M_r = 254.2$, orthorhombic, $a = 4.861$ (5), $b = 16.70$ (1), $c = 14.01$ (1) Å, $U = 1137$ Å³, $Z = 4$, $D_c = 1.485 \text{ g cm}^{-3}$, $F(000) = 536$. Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd. Space group $P2_12_12_1$. Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å; $\mu(\text{Mo } K\alpha) = 0.75 \text{ cm}^{-1}$.

Structure determination

The structure was solved by direct methods with *SHELX* (Sheldrick, 1975), the E map revealing the

* Part I: Hamor, O'Leary & Walker [*Acta Cryst.* (1977), **B33**, 1218–1223].