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Experimental and Theoretical Difference Densities for Urea. A Simple Refinement of Density Distributions of Bonding Electrons VII. Comparison of Observed and Calculated Electron Densities IX

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From a recently refined model of the electron density distribution in the urea molecule, dynamic and static density sections are calculated and presented as difference densities $\rho(\text{molecule}) - \rho(\text{isolated atoms})$. The sections obtained are compared to corresponding sections derived from a quantum-chemical calculation of 4-31G quality. In addition, a direct examination of this theoretical density distribution with the X-ray data is described.

Introduction

Mullen & Hellner (1978) measured X-ray data for urea at 123 K and determined the density distribution in the molecule by an empirical model (Hellner, 1977). In this paper the dynamic and static difference densities, obtained from Mullen & Hellner's refinement, are presented. Furthermore, a quantum-chemical calculation of the density distribution in the urea molecule, with a 4-31G basis set, has been carried out and dynamic and static difference densities for the theoretical model are presented. In addition, a test of this theoretical density distribution against the X-ray data by structure factor calculations and $F_o - F_c$ synthesis is reported. The procedure for thermal deconvolution and the treatment of series-termination effects have been described (Scheringer, 1977a; Scheringer, Mullen & Hellner, 1978).

Results

The experimental dynamic and static difference densities are presented in Fig. 1, the corresponding theoretical difference densities in Fig. 2.

The experimental densities are based on Mullen & Hellner's (1978) model. R for the 288 X-ray data is 1.60%, obtained with 63 density parameters and one scale factor. The $F_o - F_c$ synthesis based on the final model is nearly flat and shows positive and negative peaks up to $0.1 \text{ e } \text{Å}^{-3}$. The random error in the $\Delta\rho$ map, based on Rees's (1976) formula (10), is $\sigma(\Delta\rho) = 0.033 \text{ e } \text{Å}^{-3}$ where the term $\sigma(\rho_c)$ and the scale factor term $\sigma(k)/k$ have been neglected. The positional and thermal parameters of the C, N and O atoms were obtained by determining the parameters of the respective $1s^2$ orbital products (Kutoglu & Hellner, 1978). Similarly, the positional and isotropic thermal parameters of the H

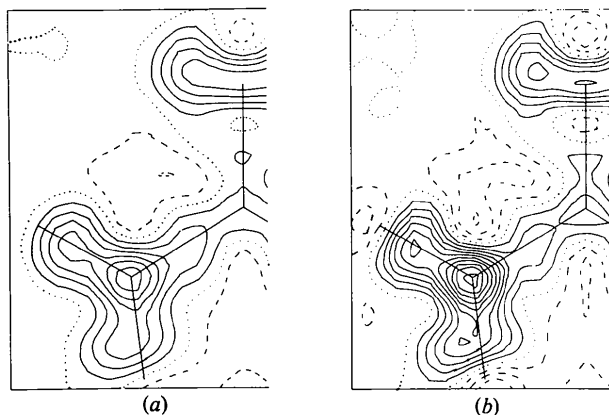


Fig. 1. Observed dynamic (a) and static (b) difference density in the plane of the molecule. Contour interval $0.1 \text{ e } \text{\AA}^{-3}$. Positive contours are shown as full lines; zero contours are dotted; negative contours are shown dashed.

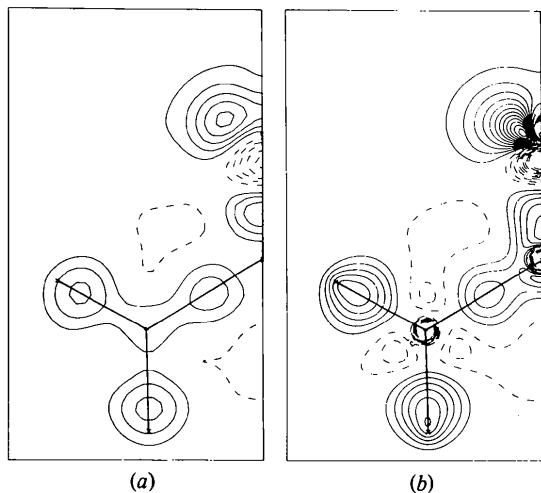


Fig. 2. Theoretical dynamic (a) and static (b) difference density in the plane of the molecule. Contours as in Fig. 1.

atoms were obtained from the X-ray data by determining the parameters of a charge ($<1 \text{ e}$) with the scattering factor of the H atom. The vibration tensors for the internuclear charge clouds were determined from the vibration tensors of the adjacent atoms by multiplication with a reduction factor of 0.80 (Scheringer, 1977b).

The theoretical densities are derived from AHF calculations using the 4-31G basis set (Ditchfield, Hehre & Pople, 1971) and the *POLYATOM* program system (Csizmadia, Harrison, Moscowitz & Sutcliffe, 1966). Thermal smearing was performed with the method of Hase, Reitz & Schweig (1976), the positional and thermal parameters of Mullen & Hellner (1978) being used.

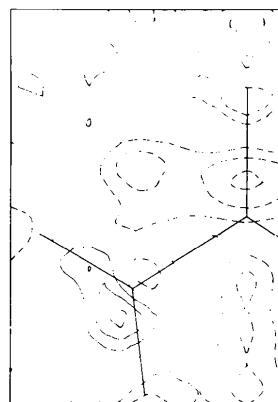


Fig. 3. $F_o - F_c$ synthesis of the theoretical 4-31G density model. Contours as in Fig. 1.

When comparing the experimental and theoretical densities one has to observe that the molecules in the crystal are linked by hydrogen bonds, whereas the theoretical densities are calculated for the isolated molecules. Our results may indicate that this difference becomes significant for the comparison. In the experimental maps (Fig. 1) there are maxima at the centres of the N atoms, and there is only a small peak of $0.11 \text{ e } \text{\AA}^{-3}$ in the C=O bond. Here the bond charge appears to be shifted towards the lone-pair region of the O atom. The results are in accord with the fact that the C=O bond is relatively long (1.26 \AA). This type of charge transfer seems to be consistent with the formation of hydrogen bonds where the non-hydrogen atoms accumulate and the H atom loses charge. The charge transfer towards the N atom was also observed in α -glycine where hydrogen-bonding is also present (Almlöf, Kvick & Thomas, 1973, Figs. 3 and 4). The reduction of density in the C=O bond (to $0.14 \text{ e } \text{\AA}^{-3}$) and the lengthening of the bond (1.26 \AA) due to strong and multiple hydrogen-bond formation was also found in the study of an oxalate ion (Thomas, 1977, Fig. 2a). (In contrast, the other two C=O bonds, where only one weaker hydrogen bond is involved, are shorter at 1.226 and 1.214 \AA .) Further examples of highly reduced bond densities, where even negative bond peaks were observed in the deformation maps, are the structures of *p*-nitropyridine *N*-oxide (Wang, Blessing, Ross & Coppens, 1976) and uronium nitrate (Harkema, 1971). In the theoretical dynamic density (Fig. 2a), however, there are no maxima at the N centres although the density does not vanish there and the C=O bond peak is higher ($0.40 \text{ e } \text{\AA}^{-3}$). On the other hand, both the N-H bond peaks ($0.32 \text{ e } \text{\AA}^{-3}$) are a little lower than the corresponding experimental peaks (0.37 and $0.46 \text{ e } \text{\AA}^{-3}$).

A direct comparison between the experimental (Fig. 1b) and theoretical (Fig. 2b) static densities cannot be

Table 1. *Peak heights in difference densities of urea*Experimental cut-off ($\sin \theta_{\max}/\lambda = 0.9 \text{ \AA}^{-1}$). ∞ means extrapolation to infinite resolution. LP stands for lone pair.

Method	Peak heights in the difference densities ($e \text{ \AA}^{-3}$)							
	C=O	Dynamic			LP	Static		
		C-N	N-H			C-N	N-H	LP
exp(0.9)	0.11	0.25	0.46, 0.37	0.46	0.12	0.29	0.65, 0.52	0.57
exp(∞)					0.19	0.43	0.99, 0.78	0.88
Theoretical	0.40	0.24	0.32	0.52	0.51	0.34	0.55	1.20

made since the experimental results suffer from series termination, ($\sin \theta_{\max}/\lambda = 0.9 \text{ \AA}^{-1}$). A correction for the peak heights, however, can be made by fitting the peaks in Fig. 1 as closely as possible to a Gaussian distribution with one charge parameter and two variance parameters $V_{11} = V_{22}$, V_{33} (Scheringer, 1977a). The resulting peak heights extrapolated to infinite resolution, $\exp(\infty)$, and all other types of peak heights of the present investigation are listed in Table 1. There is fair agreement between the various experimental and theoretical values.

Further comparison between the theoretical density and the X-ray data can be made by calculating the structure factors for the theoretical density model. For this purpose, the same positional and thermal parameters as for the calculation of the theoretical dynamic density were used. R obtained with 283 observed X-ray data is 0.0255 which is significantly higher than that for the experimental model (0.0160). The $F_o - F_c$ synthesis with the 4-31G model (Fig. 3) shows maxima in the N-H bonds which might indicate that the 4-31G model produces bond peaks which are a little too low (only s and p orbitals are used in this model). The minimum of $0.3 e \text{ \AA}^{-3}$ in the C=O bond close to the C atom (Fig. 3) corresponds to the fact that the theoretical bond peak is higher, as already discussed.

A final word of caution appears to be appropriate. The differences between theoretical and experimental results are certainly due not only to intermolecular interactions (hydrogen bonding), but also to systematic errors in the experimental and theoretical procedures. Given the present state of the art such errors might easily amount to $0.1\text{--}0.3 e \text{ \AA}^{-3}$ (Meyer & Schweig, 1978).

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