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*Acta Cryst.* (1978). **B34**, 2162–2165

**Experimental and Theoretical Difference Densities for Cyanuric Acid.  
A Simple Refinement of Density Distributions of Bonding Electrons VI. Comparison of  
Observed and Calculated Electron Densities VIII**

BY C. SCHERINGER, A. KUTOGLU AND E. HELLNER

*Fachbereich Geowissenschaften, Universität Marburg, D-3550 Marburg, Federal Republic of Germany*

AND H. L. HASE, K.-W. SCHULTE AND A. SCHWEIG

*Fachbereich Physikalische Chemie, Universität Marburg, D-3550 Marburg, Federal Republic of Germany*

(Received 5 December 1977; accepted 13 January 1978)

From a recently refined model of the electron density distribution in cyanuric acid, dynamic and static density sections are calculated and are presented as difference densities  $\rho(\text{molecule}) - \rho(\text{isolated atoms})$ . The sections obtained are compared with the results of other workers, and with corresponding sections derived from a new 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

Since Verschoor & Keulen (1971) collected X-ray data of cyanuric acid at 100 K, this molecule has been the subject of several electron density studies. Coppens & Vos (1971) determined the positional and thermal parameters at 125 K by neutron analysis, and McIver, Coppens & Nowak (1971) presented an INDO calculation of the density distribution in the molecule. The dynamic difference density of the molecule obtained from a minimum basis set STO-3G calculation (R. F. Stewart, unpublished) was given by Jones, Pautler & Coppens (1972). Moreover, these authors determined the population parameters of

orbital products from Verschoor & Keulen's (1971) X-ray data, *i.e.* they refined a quantum-chemical model from the experimental data. Kutoglu & Hellner (1978) determined the density distribution in the molecule by means of an empirical model from Verschoor & Keulen's (1971) X-ray data. In this paper the dynamic and static difference densities obtained from Kutoglu & Hellner's (1978) refinement are given. Theoretical static and dynamic (Hase, Reitz & Schweig, 1976) difference densities obtained from a new quantum-chemical calculation with a 4-31G basis set are presented and compared with the corresponding experimental densities. An additional test of the theoretical density distribution against Verschoor & Keulen's (1971) X-

ray data by means of structure factor calculations and  $F_o - F_c$  synthesis is reported.

### Thermal deconvolution and series termination

The calculation of experimental static densities was discussed by Scheringer, Mullen & Hellner (1978). Thermal deconvolution does not present a problem if the temperature factors for all density units are known. In practice, it is performed by calculating a Fourier synthesis with structure factors obtained from the final density model with zero vibration tensors. Series termination poses a problem in that the density distribution of the final model can only be represented with the resolution given by the experimental data. Extrapolation to infinite resolution can be made for the heights of the observed peaks (Scheringer, 1977a), but otherwise a comparison with theoretical static densities is meaningless beyond the resolution limit.

### Results

Sections through the experimental static and dynamic difference densities in the molecular plane are shown in Fig. 1 and through the corresponding theoretical densities in Fig. 2. The experimental densities are based on Kutoglu & Hellner's (1978) model LQ2.  $R$  for 942 data is 0.0252, obtained with 140 density parameters and a scale factor. The  $F_o - F_c$  synthesis based on the final model is nearly flat with no positive or negative peak  $>0.1 \text{ e } \text{Å}^{-3}$ . The random error in the  $\Delta\rho$  map, based on Rees's (1976) formula (10), is  $0.045 \text{ e } \text{Å}^{-3}$  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), and are in excellent agreement with the parameters derived from the neutron data (Coppens & Vos, 1971). Similarly, the positional and isotropic thermal parameters of the H 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 average of the vibration tensors of the adjacent atoms by multiplication with a reduction factor of 0.78 (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 aforementioned positional and thermal parameters being used.

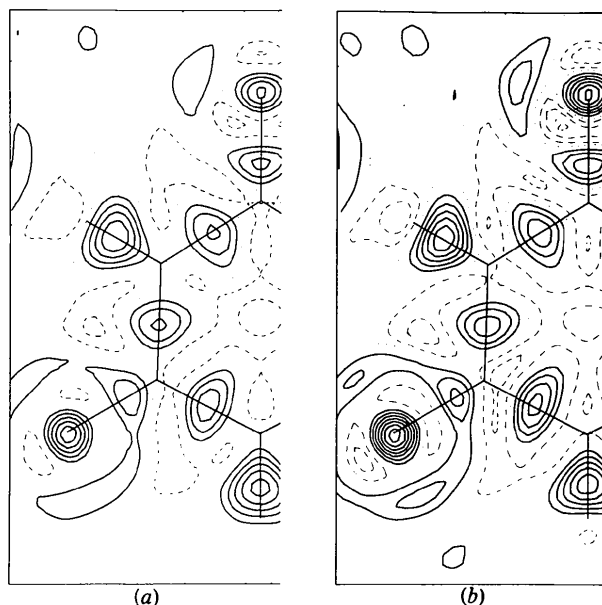


Fig. 1. Observed (a) dynamic and (b) static difference density in the plane of the molecule. Contour interval  $0.1 \text{ e } \text{Å}^{-3}$ . Positive contours: full; zero: dotted; negative: dashed.

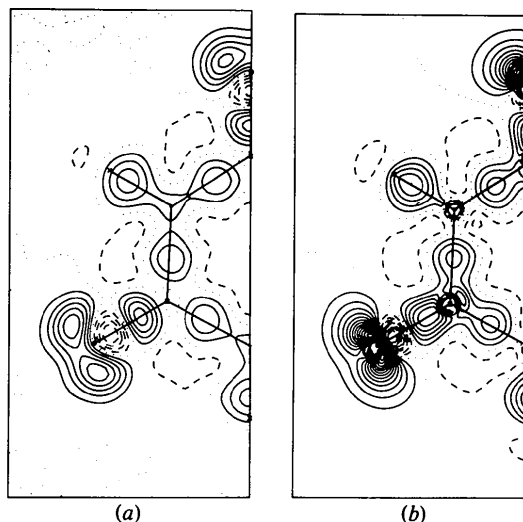


Fig. 2. Theoretical (a) dynamic and (b) static difference density in the plane of the molecule. Contours as in Fig. 1.

A direct comparison of our experimental dynamic density (Fig. 1a) can be made with Jones, Pautler & Coppens's (1972, Fig. 2) population asphericity maps, since, in principle, these maps are calculated in the same manner, but for another model. The best map is given in their Fig. 2(b), and the resemblance of this to our Fig. 1(a) is quite close. There is also fair agreement between the present experimental dynamic map and Coppens & Vos's (1971, Fig. 4)  $X - N$  map and the corresponding theoretical map (Fig. 2a).

Table 1. Peak heights in difference densities of cyanuric acid

Experimental cut-off at  $(\sin \theta)/\lambda = 0.8 \text{ \AA}^{-1}$ .  $\infty$  means extrapolation to infinite resolution. l.p. stands for lone pair. AM = asphericity map of Jones, Pautler & Coppens (1972, Fig. 2b).  $X-N = X-N$  map of Coppens & Vos (1971, Fig. 4).

Peak heights in the difference densities ( $e \text{ \AA}^{-3}$ )

Method	Dynamic				Static			
	C=O	C-N	N-H	l.p.	C=O	C-N	N-H	l.p.
exp (0.8)	0.2, 0.3	0.3, 0.3, 0.3	0.5, 0.4	0.5, 0.4	0.3, 0.4	0.4, 0.4, 0.4	0.6, 0.6	0.8, 0.6
exp ( $\infty$ )					0.5, 0.5	0.6, 0.5, 0.5	0.8, 0.8	1.4, 1.3
Theoretical	0.4	0.2	0.3	0.5	0.6	0.4	0.5	1.4
AM	0.4, 0.2	0.5, 0.5, 0.4	0.5, 0.5	0.3, 0.2				
$X-N$	0.5, 0.3	0.5, 0.4, 0.5	0.5, 0.4	0.5, 0.3				

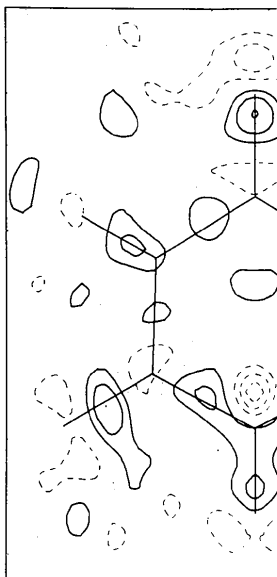


Fig. 3.  $F_o - F_c$  synthesis of the theoretical 4-31G density model. Contours as in Fig. 1.

A direct comparison between the experimental (Fig. 1b) and theoretical (Fig. 2b) static densities cannot be made since the experimental results suffer from series termination. 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 ( $\infty$ )] along with all other types of peak heights of the present and other investigations are listed in Table 1. There is good 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 calculating the theoretical dynamic

density were used.  $R$  obtained with 942 X-ray data is 0.0301, which is slightly worse than  $R$  for the empirical models. Judging from the  $F_o - F_c$  synthesis based on the theoretical model (Fig. 3) this might indicate that the 4-31G densities are too low by  $0.1/0.3 e \text{ \AA}^{-3}$  in the C-N/N-H bonding regions. For the C=O bonds, the  $F_o - F_c$  synthesis (Fig. 3) shows peaks which are located more closely to the O atoms. This might indicate that the minima of the theoretical densities close to the O atoms (Fig. 2) are too deep. Finally, the minimum in the ring close to N(1) and the maximum that is extended towards H(1) (Fig. 3) seem to indicate that the density of the isolated molecule is not fully appropriate for describing the actual density distribution in the crystal. This conclusion is in accordance with the fact that the hydrogen bond on the twofold axis is shorter than the other and gives rise to a higher stretching frequency (Verschoor & Keulen, 1971). The transfer of the charge from N(1) towards H(1) in the molecules in the crystal may further explain why the  $R$  of 0.0301 for the theoretical model (where  $3m$  symmetry is assumed) is a little higher than that for the experimental model, 0.0252.

This work was supported by the Deutsche Forschungsgemeinschaft, SFB Kristallstruktur und Chemische Bindung, Projekt H and the Fonds der Chemischen Industrie. The quantum-chemical calculations were carried out on the TR 440 computer of the Rechenzentrum der Universität Marburg and the IBM 370-168 computer of the Rechenzentrum der TH Darmstadt.

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*Acta Cryst.* (1978). B34, 2165–2168

## 4,5,10,11,12,13-Hexahydro-10,13a-methanocycloocta[*c*]pyrrolo[3,2,1-*ij*]quinoline-7,9,14-trione and Dimethyl 4,5,10,11,12,12a-Hexahydroindolo[1,7-*cd*]benzazepine-7,8-dicarboxylate

BY PATRICK J. ABBOTT, R. MORRIN ACHESON AND GARRY PROCTER

*Department of Biochemistry, South Parks Road, Oxford OX1 3QU, England*

AND DAVID J. WATKIN

*Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England*

(Received 10 December 1977; accepted 14 January 1978)

The trione  $C_{18}H_{15}NO_3$  is monoclinic,  $P2_1/n$ , with  $a = 7.340$  (1),  $b = 11.647$  (1),  $c = 16.100$  (3) Å,  $\gamma = 80.96$  (1)°,  $Z = 4$ ,  $D_m = 1.43$ ,  $D_c = 1.432$  g cm<sup>-3</sup>,  $\mu = 1.056$  cm<sup>-1</sup> (Mo  $K\alpha$  radiation). The diester  $C_{20}H_{21}NO_4$  is triclinic,  $P1$ , with  $a = 9.605$  (2),  $b = 9.693$  (2),  $c = 9.871$  (3) Å,  $\alpha = 100.49$  (2),  $\beta = 108.47$  (2),  $\gamma = 99.34$  (2)°,  $Z = 2$ ,  $D_m = 1.39$ ,  $D_c = 1.393$  g cm<sup>-3</sup>,  $\mu = 0.99$  cm<sup>-1</sup> (Mo  $K\alpha$  radiation). The identification of these compounds by X-ray analysis has led to an understanding of the reaction between 1,2,6,7,8,9-hexahydropyrrolo[3,2,1-*jk*]carbazole and dimethyl acetylenedicarboxylate in acetic acid.

### Introduction

The synthesis and isolation of these compounds was carried out by Dr R. M. Letcher (Acheson, Letcher & Procter, 1978).

Precession photographs gave the space groups. The crystals were transferred to an Enraf–Nonius CAD-4 four-circle diffractometer, and cell dimensions determined by a least-squares fit to the setting angles of 25 reflections measured on both sides of the incident beam. The data were collected by an  $\omega/2\theta$  scan, and standards checked every hour. Details of the data and  $R$  factors appear in Table 1. Lorentz and polarization corrections were applied. The structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971), and refined by full-matrix least squares to  $R = R(1)$  with isotropic temperature factors. Further refinement with anisotropic thermal motion to  $R = R(2)$ , followed by a difference synthesis, led to the location of all the H atoms [except for H(163) in the trione (IV) which was placed by calculation]. The structures were refined to

Table 1. *Experimental data and R values*

	Compound (IV)*†	Compound (V)†
Crystal dimensions (mm)	0.3 × 0.3 × 0.4	0.4 × 0.5 × 0.8
Crystallization solvent	Ethyl acetate	CH <sub>2</sub> Cl <sub>2</sub> /petrol
Radiation	Mo $K\alpha$	Mo $K\alpha$
Maximum $2\theta$ (°)	44	60
Total unique data	1561	3756
Data with $I \geq 3\sigma(I)$	1416	2974‡
$R(1)$	0.189	0.153
$R(2)$	0.088	0.048
Final $R$	0.035	0.046

Weighting scheme:  $w = [a_0 t_0(x) + a_1 t_1(x) + \dots + a_n t_n(x)]^{-1}$ , where  $a_i$  are coefficients of a Chebyshev series in  $t_i(x)$ ,  $(x) = F_o/F_{(max)}$ .  
 Final parameters: (IV):  $a_0 = 47.77$ ,  $a_1 = 78.12$ ,  $a_2 = 42.82$ ,  $a_3 = 15.26$ ,  $a_4 = 3.14$ ,  $a_5 = 0.16$ ; (V):  $a_0 = 71.10$ ,  $a_1 = 97.10$ ,  $a_2 = 27.53$ .

\* C–H distances constrained to be  $1.00 \pm 0.01$  Å.

† An extinction correction was applied during the later refinements.

‡ In the final refinements, three reflections were omitted because they suffered excessive extinction.