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Deformation Electron Density of α -Glycine at 120 K*

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Abstract

A study of the charge density in α -glycine, $C_2H_5NO_2$, has been carried out employing X-ray and neutron diffraction data measured at 120 K. The crystal is monoclinic, space group $P2_1/n$, with the following cell dimensions: $a = 5.084$ (1), $b = 11.820$ (2), $c = 5.458$ (1) Å and $\beta = 111.95$ (2)°. The X-ray data were collected in the $\sin \theta/\lambda$ range 0.00–1.20 Å⁻¹. The deformation densities were computed both by the $X-N$ method, using positional and thermal parameters from the neutron diffraction study, and by a multipole refinement method, where the asphericity in the electron charge distribution was accounted for in the refinement. Well defined peaks of deformation charge density are found in all covalent bonds. The positions of the peaks, however, vary slightly depending on the method used. The $X-N$ maps in the bonding regions are

in agreement with theoretical *ab initio* calculations, and with previous charge-density studies on α -glycine and α -glycylglycine.

Introduction

The direct analysis of electron densities in solids by means of diffraction techniques is presently widely employed. The effects of systematic experimental errors in the data and different approaches for extracting the information are, however, still much discussed. Here we report a study of the electron distribution in α -glycine at 120 K using both combined X-ray and neutron techniques ($X-N$) and a multipole refinement technique. Details of the neutron diffraction study (Kvick & Koetzle, 1980) will be presented in a later publication. A room-temperature electron density study of α -glycine has been reported (Almlöf, Kvick & Thomas, 1973), as have room-temperature and low-temperature (82 K) studies of α -glycylglycine (Griffin & Coppens, 1975; Kvick, Koetzle & Stevens, 1979). It is of interest here to compare the results with theoretical calcu-

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lations and the experimental determination at room temperature and also to compare the different techniques of obtaining the deformation electron densities.

Experimental

Crystal data

Crystals were obtained by cooling a hot concentrated aqueous solution. The crystal chosen for data collection was roughly bipyramidal (dimensions $0.21 \times 0.17 \times 0.14$ mm), bounded by the two forms $\{110\}$ and $\{011\}$ and truncated by the form $\{010\}$. It was mounted on a glass fiber and coated with a thin film of polyethylene to prevent sublimation.

The cell parameters were determined by least-squares fitting to the observed θ angles of 25 moderately intense reflexions in the region $19^\circ < \theta < 26^\circ$. Crystal data are given in Table 1.

Data collection

Intensity data were collected on the Enraf–Nonius CAD-4 diffractometer at the University of Uppsala with graphite-monochromatized Mo $K\alpha$ radiation. Cooling of the crystal during the experiment was

Table 1. *Crystal data at 120 K (first line: X-ray; second line: neutron)*

Estimated standard deviations in the least significant digits are given in parentheses throughout this paper.

Formula: $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$	$M_r = 75.07$
Space group: $P2_1/n$	
$a = 5.0835$ (10) Å	$V = 304.17$ Å ³
5.0830 (8)	304.15
$b = 11.820$ (2)	$\rho_x = 1.64$ Mg m ⁻³
11.816 (3)	
$c = 5.4579$ (9)	$Z = 4$
5.4590 (10)	
$\beta = 111.95$ (2)°	
111.93 (2)	

Linear absorption coefficient $\mu(\text{Mo } K\alpha) = 0.137$ mm⁻¹*

Data-collection parameters

Temperature: 120 ± 5 K
 Wavelength: $\lambda(\text{Mo } K\alpha) = 0.71069$ Å
 Detector aperture: height = 4 mm; width = 3 mm
 Take-off angle: 2.8°
 Scan mode: $\omega/2\theta$

Total number of reflexions: 4803
 Number of independent reflexions:
 1244 for $0 < \sin \theta/\lambda < 1.2$ Å⁻¹
 357 for $0.7 < \sin \theta/\lambda < 1.2$ Å⁻¹

* Calculated using mass-absorption coefficients given in *International Tables for X-ray Crystallography* (1974).

accomplished by means of a cold-nitrogen-gas stream obtained by a locally constructed low-temperature device. The temperature during the data collection was 120 K according to a previous calibration of the experimental set-up using a microthermocouple at the crystal position.

The repeat distance along the b axis is the most sensitive to temperature change in this compound and shrinks from 11.969 (2) Å at 298 K to 11.820 (2) Å at 120 K. This dimension was repeatedly monitored during the experiment to check the long-term temperature stability. The corresponding neutron experiment at 120 K (Kvick & Koetzle, 1980) gave a b axis of 11.816 (3) Å, in good agreement with the X-ray experiment.

All reflexions with $\sin \theta/\lambda \leq 0.7$ Å⁻¹ were measured, but only reflexions estimated to have intensities larger than twice the background in the $0.7 \leq \sin \theta/\lambda \leq 1.2$ Å⁻¹ region were collected. Reliable intensity predictions were obtained using the coordinates and thermal parameters obtained from the neutron experiment. A total of 4803 reflexions (excluding monitors and systematic absences) were collected. Further details of the data collection are given in Table 1. In the neutron study all reflexions with $\sin \theta/\lambda \leq 0.61$ Å⁻¹ and $\pm h, \pm k, \pm l$ reflexions out to $\sin \theta/\lambda = 0.69$ Å⁻¹ were measured. Friedel-related reflexions were averaged producing a set of 1521 reflexions for use in the least-squares refinement. The agreement factor among the Friedel-related reflexions, defined as $R = \sum(F_o^2 - \bar{F}_o^2) / \sum \bar{F}_o^2$, was 0.013. The total number of reflexions measured was 2859.

Data reduction

Profile analysis according to Lehmann & Larsen (1974) was used for the computation of integrated intensities and the usual Lorentz–polarization correction was applied. Absorption corrections were calculated using the Gaussian integration method (Coppens, Leiserowitz & Rabinovich, 1965) with a $4 \times 4 \times 8$ point grid; the transmission factors were in the range 0.976–0.984. Equivalent reflexions were averaged producing a set of 1244 independent reflexions of which 373 were in the range $0.7 \leq \sin \theta/\lambda < 1.2$ Å⁻¹. The agreement factors among symmetry-related reflexions defined as $R = \sum(F_o^2 - \bar{F}_o^2) / \sum \bar{F}_o^2$ and $R_w = [\sum w(F_o^2 - \bar{F}_o^2)^2 / \sum w\bar{F}_o^4]^{1/2}$ were 0.015 and 0.022 respectively for the low-order data ($\sin \theta/\lambda < 0.7$ Å⁻¹); 0.025 and 0.031 for the high-order data and 0.016 and 0.024 for the full data set. The weights used were $w^{-1} = \sigma_c^2(F_o^2)$ where $\sigma_c^2(F_o^2)$ is based on counting statistics. \bar{F}_o^2 is the average of the symmetry-related reflexions in a form.

The quality of the data was also checked by analyzing the measured intensities of symmetry-related reflexions by the method of normal-probability analysis. This was made by plotting the observed

quantities $\delta R = (F_o^2 - \bar{F}_o^2)/\sigma_c(\bar{F}_o^2)$ against the values expected for a normal distribution (Abrahams & Keve, 1971; Lundgren & Liminga, 1979). The plot was perfectly linear with a slope of 1.38 and a y intercept of 0.01 (65 reflexions had $\delta R > 4.0$ and fell outside the plot). The slope indicated an underestimation of the standard deviation of F_o^2 ; these standard deviations were thus multiplied by 1.38 in all subsequent calculations.

Structure refinements

The programs used have been described by Lundgren (1979a). Full-matrix least-squares refinement was performed by minimization of the function $\sum w(F_o^2 - k^2 F_c^2)^2 \{w^{-1} = \sigma^2(F_o^2) \text{ where } \sigma^2(F_o^2) = [1.38\sigma_c(F_o^2)]^2 + (0.025 F_o^2)^2\}$. All unique reflexions but the strongest, 040, which might be severely affected by extinction, were included in the calculations. The scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974); for hydrogen, the spherical scattering factors of Stewart, Davidson & Simpson (1965) were used. Four different refinement procedures (denoted *A*, *B*, *C* and *D*) were performed. Initial parameters deduced from the neutron experiment were in all cases used as starting values. The results are summarized in Table 2.

Refinement *A* was a conventional X-ray refinement. Positional parameters for all atoms, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms were varied together with the scale factor. In the last cycles an isotropic extinction correction (type I, Lorentzian distribution) was introduced according to Becker & Coppens (1974, 1975) but refined to a non-significant value.

Refinement *B* was an X-ray high-order refinement using only the reflexions with $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$. Positional and anisotropic thermal parameters for the H atoms were fixed to their neutron values. Positional and anisotropic thermal parameters for the heavy atoms were varied together with the scale factor.

In procedures *C* and *D* attempts were made to account for the asphericity in the electron density due to bonding. The method developed by Hirshfeld (1971, 1977) and Harel & Hirshfeld (1975) was employed to modify the atomic scattering factors. Each atomic scattering factor was calculated as $f = f_s + \sum c_i \varphi_i$, where f_s is the spherical free-atom scattering factor and φ_i are the Fourier transforms of the deformation functions. The coefficients c_i are refined in the least-squares process. The deformation functions on each atomic center were of the form:

$$g_n(r, \theta_k) = N_n r^n \exp(-\gamma r^2) \cos^n \theta_k$$

where r is the distance from the atomic center; θ_k is the angle between radius vector r and a specified polar axis k ; $n = 0, 1, 2$ and 3 for all heavy atoms and $n = 0, 1, 2$ for the H atoms; N_n is a normalizing factor and γ a parameter governing the radial dependence. Refinement attempts using a radial dependence $\exp(-\alpha r)$ failed to converge. In order to reduce the number of refined parameters, reasonable geometrical constraints were applied to the deformation model. The heavy atoms were constrained to local m symmetry and the H atoms to cylindrical symmetry about their bonding direction; furthermore, the two methylene H atoms were constrained to have identical deformation coefficients, as were the three H atoms of the $-\text{NH}_3^+$ group. The positional and thermal parameters of the H atoms were kept fixed at their neutron values whereas the

Table 2. Summary of refinements

$$\Delta = (F_o^2 - k^2 F_c^2), \sigma = \{[1.38\sigma_c(F_o^2)]^2 + (0.025 F_o^2)^2\}^{1/2}.$$

Refinement	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
	(conventional refinement)	(high-order refinement)	(deformation refinement)	(deformation refinement)
k^{-1} (multiplying F_o)	0.1493 (4)	0.1454 (5)	0.1448 (6)	0.146508 (37)
g (isotropic extinction type I)	non-significant	—	$0.59 (8) \times 10^4$	$0.48 (7) \times 10^4$
N (number of reflexions)	1243	373	1243	1243
M (number of refined parameters)	67	46	120	120
$R(F^2) = \sum \Delta / \sum F_o^2$	0.046	0.022	0.021	0.019
$R_w(F^2) = (\sum w\Delta^2 / \sum wF_o^4)^{1/2}$	0.079	0.028	0.037	0.035
$R(F) = \sum F_o - kF_c / \sum F_o$	0.030	0.013	0.016	0.015
$S(F^2) = [\sum w\Delta^2 / (N - M)]^{1/2}$	2.53	0.96	1.20	1.14
Number of reflexions with $ \Delta/\sigma > 3.0$	183	255 (all in low order)	18	17
Maximum $ \Delta/\sigma $	26.4	27.1	10.2	10.5
δR plot				
slope	0.52	1.12	0.97	0.97
y intercept	-0.13	-0.04	-0.09	-0.09
number of reflexions out of the range $-4 < \delta R < 4$	96	0	8	5

Table 3. *Coordinates* ($\times 10^5$) of heavy atoms

First line = conventional refinement (*A*); second line = high-order refinement (*B*); third line = deformation refinement (*C*); fourth line = deformation refinement (*D*); fifth line = neutron refinement. $\Delta/\sigma = (P1 - P2)/[\sigma(P1)^2 + \sigma(P2)^2]^{1/2}$, where *P1* is the parameter concerned, *P2* is the parameter from deformation refinement *D*, $\sigma(P1)$ and $\sigma(P2)$ are the standard deviations.

	<i>x</i>	Δ/σ	<i>y</i>	Δ/σ	<i>z</i>	Δ/σ
N	29653 (13)	-0.8	8876 (5)	0.8	-25921 (12)	0.4
	29666 (10)	0.1	8875 (4)	0.6	-25930 (10)	-0.3
	29664 (15)	-0.1	8873 (4)	0.4	-25941 (16)	-0.8
	29666 (9)		8871 (3)		-25926 (9)	
	29614 (4)	-5.0	8869 (2)	-0.8	-25940 (4)	-1.3
O(1)	30295 (11)	-1.0	9388 (5)	0.7	23632 (10)	0.7
	30299 (9)	-0.8	9392 (4)	1.5	23624 (10)	0.1
	30337 (17)	1.4	9385 (3)	0.1	23614 (18)	-0.5
	30310 (10)		9384 (2)		23623 (9)	
	30217 (7)	-7.7	9384 (3)	-0.2	23624 (7)	0.1
O(2)	-15367 (11)	0.7	14217 (5)	-0.2	10653 (11)	1.6
	-15376 (9)	0.1	14209 (5)	-1.6	10650 (11)	-1.8
	-15393 (16)	-0.8	14220 (3)	0.5	10676 (18)	0.0
	-15378 (10)		14218 (3)		10677 (10)	
	-15392 (7)	-1.2	14218 (3)	-0.2	10644 (7)	-2.7
C(1)	7057 (14)	0.2	12504 (6)	-1.1	6603 (13)	1.7
	7069 (9)	1.1	12507 (4)	-0.8	6539 (12)	-2.1
	7074 (15)	1.1	12507 (3)	-0.7	6615 (17)	2.0
	7054 (10)		12511 (3)		6573 (11)	
	7026 (6)	-2.4	12504 (2)	-1.7	6576 (6)	0.2
C(2)	5958 (14)	-1.1	14564 (6)	1.1	-21368 (14)	-1.0
	5989 (9)	0.9	14549 (4)	-1.3	-21358 (12)	-0.5
	5983 (13)	0.4	14554 (4)	-0.5	-21343 (18)	0.4
	5977 (9)		14556 (3)		-21351 (11)	
	5933 (6)	-4.1	14566 (2)	2.4	-21392 (5)	-3.4

positional and anisotropic thermal parameters of the heavy atoms were varied along with the 73 coefficients c_p , the scale factor and the isotropic extinction coefficient.

In procedure *C* the values of the radial γ exponents were taken from Hirshfeld (1971): $\gamma(N) = 6.0$, $\gamma(O) = 6.5$, $\gamma(C) = 5.5$, $\gamma(H) = 4.0 \text{ \AA}^{-2}$. In accordance with previous experience (Lundgren, 1979*b*) no attempt was made to refine the γ exponents along with other parameters. However, two cycles of refinement with only the γ exponents as variables led to the values $\gamma(N) = 6.16$ (2), $\gamma(O(1)) = 6.6$ (1), $\gamma(O(2)) = 5.9$ (1), $\gamma[C(1)] = 5.41$ (2), $\gamma[C(2)] = 5.48$ (2), $\gamma[H(1)] = \gamma[H(2)] = \gamma[H(3)] = 4.4$ (1), $\gamma[H(4)] = \gamma[H(5)] = 3.9$ (1) \AA^{-2} . These values were kept constant in the subsequent refinements.

In procedure *D* the γ exponents for all atoms were given the value 3.5 \AA^{-2} as suggested by Lundgren (1979*b*). No significant shift was observed in an attempt to refine the γ exponents alone starting from the value 3.5 \AA^{-2} . As can be seen in Table 2, this procedure gave the best fit between observed and calculated structure factors and will therefore be referred to in the following discussions.*

* Lists of structure factors and deformation coefficients from refinement *D* have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35554 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Anisotropic thermal parameters* ($\text{\AA}^2 \times 10^5$) of heavy atoms

The form of the temperature factor is $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$. For refinement notation see Table 3.

	U_{11}	Δ/σ	U_{22}	Δ/σ	U_{33}	Δ/σ	U_{12}	Δ/σ	U_{13}	Δ/σ	U_{23}	Δ/σ
N	1071 (21)	-3.4	1491 (24)	-1.1	808 (23)	-1.0	199 (20)	-1.2	460 (17)	-1.7	83 (20)	-0.6
	1174 (12)	1.2	1526 (14)	0.2	831 (15)	-0.2	222 (11)	-0.2	498 (10)	0.4	95 (13)	0.0
	1168 (14)	0.8	1528 (16)	0.3	844 (19)	0.4	221 (14)	-0.2	491 (12)	-0.1	98 (12)	0.1
	1154 (12)		1522 (13)		835 (14)		225 (11)		492 (9)		96 (10)	
	948 (11)	-12.7	1277 (11)	-14.4	795 (14)	-2.1	218 (7)	-0.5	412 (8)	-6.8	85 (7)	-1.0
O(1)	1200 (20)	0.1	1792 (23)	-1.3	858 (21)	-0.8	256 (18)	-2.0	425 (16)	0.1	182 (18)	-0.9
	1208 (12)	0.6	1847 (16)	0.9	882 (13)	0.2	311 (12)	1.0	425 (9)	0.1	217 (12)	1.0
	1215 (16)	0.9	1842 (18)	0.6	871 (17)	-0.4	291 (11)	-0.4	448 (14)	1.4	204 (11)	0.2
	1198 (12)		1828 (13)		879 (13)		297 (9)		424 (10)		201 (9)	
	1022 (14)	-9.5	1565 (14)	-13.6	812 (16)	-3.3	256 (11)	-2.9	392 (11)	-2.2	178 (11)	-1.7
O(2)	1050 (20)	-1.7	2104 (27)	0.4	1277 (23)	-1.4	5 (19)	-1.1	722 (17)	0.3	-191 (19)	-0.6
	1092 (12)	0.2	2135 (18)	1.8	1324 (20)	0.4	17 (12)	-0.7	724 (10)	0.6	-171 (13)	0.5
	1098 (15)	0.5	2073 (20)	-0.8	1274 (19)	-1.7	26 (11)	-0.2	697 (13)	-1.2	-171 (11)	0.5
	1089 (12)		2093 (16)		1314 (14)		28 (10)		716 (10)		-179 (9)	
	909 (14)	-9.7	1796 (15)	-13.8	1133 (16)	-8.5	37 (11)	0.6	603 (12)	-7.4	-145 (12)	2.2
C(1)	1056 (25)	2.8	874 (22)	-5.6	904 (25)	1.4	-117 (19)	-4.1	493 (19)	0.8	-82 (20)	-2.7
	995 (13)	1.0	1025 (13)	0.5	891 (17)	1.2	-42 (10)	-0.8	487 (10)	0.8	-41 (12)	-1.2
	962 (18)	-0.5	1073 (16)	2.9	866 (21)	0.2	-11 (11)	1.4	473 (14)	-0.1	-5 (11)	1.1
	975 (15)		1016 (13)		862 (16)		-31 (9)		475 (11)		-22 (10)	
	804 (12)	-8.9	822 (11)	-11.5	768 (13)	-4.4	-15 (9)	1.3	404 (9)	-4.8	-36 (9)	-1.1
C(2)	997 (23)	-2.3	1268 (26)	0.2	855 (24)	-0.7	181 (21)	0.7	445 (19)	-0.3	136 (22)	0.1
	1080 (14)	1.2	1256 (15)	-0.3	899 (18)	0.9	155 (11)	-0.5	466 (11)	1.0	139 (14)	0.2
	1075 (15)	0.9	1268 (17)	0.2	899 (20)	0.8	152 (14)	-0.7	451 (12)	0.0	141 (13)	0.4
	1057 (13)		1262 (14)		877 (16)		163 (11)		451 (10)		134 (11)	
	869 (12)	-10.4	1028 (12)	-2.4	817 (14)	-2.8	135 (9)	-2.0	375 (10)	-5.3	144 (9)	0.7

The data were only to a small extent affected by extinction. In procedure *D* the extinction correction factor multiplying F_o had a maximum value of 1.06 and only six reflexions had extinction corrections larger than 1.02. Strong correlation often occurs in deformation refinements. In the present case the largest correlations (0.8) occurred between coefficients of cubic deformation functions ($n = 3$) belonging to the same atom. The scale factor was correlated with the coefficients of the spherical functions ($n = 0$) and the positional parameters were correlated with the coefficients of the dipolar deformation functions ($n = 1$). No strong correlation is observed between the thermal parameters and the coefficients of the even functions ($n = 0, 2$).

Results and discussion

Comparison of different refinements

The positional and thermal parameters for non-hydrogen atoms from the different refinement procedures (see Table 2) are compared in Tables 3 and 4. The following conclusions may be drawn from the results.

(a) Procedure *D* gives markedly smaller standard deviations in refined parameters than those obtained from procedure *C*.

(b) The positional parameters from conventional, high-order and deformation refinements agree very well; the maximum discrepancy being -2.1σ , where σ is based on the combined standard deviation. The 'asphericity' shifts (distance between atomic positions obtained from conventional refinement and deformation refinements) are therefore small (≤ 0.002 Å).

(c) Some significant differences between positional parameters obtained from the neutron and X-ray refinements can be observed. The largest is a shift of 0.005 Å towards the lone-pair region for the oxygen atom O(1). The discrepancies are mainly found in the x coordinates of the atoms.

(d) Thermal parameters from the X-ray deformation and high-order refinements agree very well. As a result of the aspheric electron density distribution the agreement is, as expected, less good when compared to the thermal parameters from the conventional refinement.

(e) The U_{11} and U_{22} X-ray thermal parameters are systematically about 20% larger than the neutron parameters. The discrepancy is smaller but significant also for the U_{33} parameters. There are no obvious structural reasons for a different behavior of the U_{33} parameters. The discrepancy between neutron and X-ray thermal parameters could conceivably be attributed to a difference in temperature between the neutron and X-ray experiments. However, if the

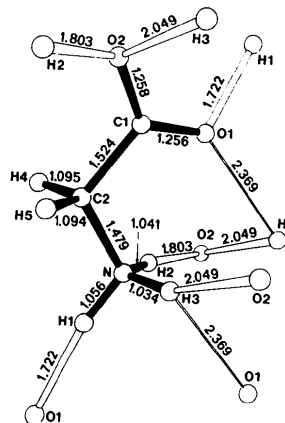


Fig. 1. Bond distances (Å) and hydrogen-bonding scheme in α -glycine. The bond distances are calculated with the heavy-atom coordinates from the X-ray deformation refinement (*D*) and H atom coordinates from the neutron study (Kvick & Koetzle, 1980). The standard deviations are 0.001 Å or less in all bond distances.

variation of the U parameters with temperature is considered to be linear in the range 120–298 K, a comparison with room-temperature U parameters (Jönsson & Kvick, 1972) leads to the conclusion that a 20% discrepancy corresponds to a temperature difference of about 35 K between the X-ray and neutron experiments. The observed cell dimensions for the two experiments show that a temperature difference of this size is highly unlikely. Similar systematic discrepancies in combined X-ray and neutron studies at low temperatures have already been observed and reviewed by Bats, Coppens & Koetzle (1977), who suggested that differences between the X-ray and neutron TDS contributions could be responsible for such discrepancies.

Bond distances calculated from the parameters obtained from the deformation refinement *D* are illustrated in Fig. 1. The reduction of the low-frequency librations of the molecule with temperature results in lengthenings of the observed intramolecular bond distances of between 0.002 and 0.009 Å [with the exception of the C(1)–C(2) bond] relative to the room-temperature results. The H...O hydrogen-bond distances, however, are all shortened by between 0.006 and 0.072 Å. H(2)...O(2) [1.803 (1) Å] and H(3)...O(2) [2.049 (1) Å] are shortened by 0.024 and 0.072 Å respectively. The stronger H(1)...O(1) bond [1.722 (1) Å] is only shortened by 0.006 Å. A detailed discussion of the reasons for these results will be given in the paper dealing with the neutron diffraction study (Kvick & Koetzle, 1980). The phenomenon has, however, already been discussed in the case of the neutron diffraction studies of γ -glycine at 83 K and 298 K (Kvick, Canning, Koetzle & Williams, 1980).

*X-N versus multipole deformation techniques**X-N difference density maps*

These were calculated in the usual way using the values of $F_o - F_c$ as coefficients in a Fourier synthesis. The F_c values were calculated using the atomic parameters from the neutron study and the X-ray spherical free-atom scattering factors. The scale factor was determined by a cycle of refinement with all other parameters fixed; it refined to 0.1572 (3), to be compared with the considerably lower values for the X-ray refinements (Table 2).

Dynamic multipole deformation maps

These were obtained from an F_c synthesis calculated from the deformation functions only. An $F_o - F'_c$ synthesis (Hirshfeld, 1971) was also computed where F'_c are the structure factors calculated with atomic parameters deduced from deformation refinements and the spherical free-atom scattering factors. Both procedures resulted in virtually identical maps.

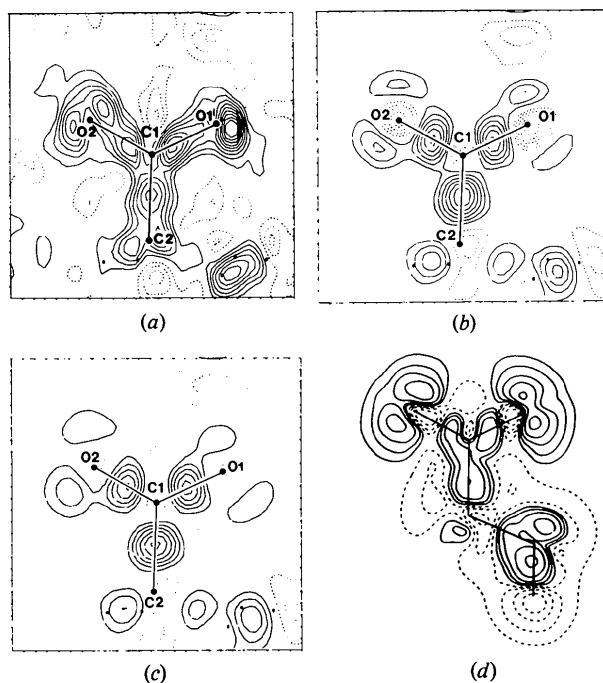


Fig. 2. (a) $X-N$ difference map through the plane defined by atoms C(1), O(1) and O(2). (b) Multipole deformation map (refinement procedure C). (c) Multipole deformation map (refinement procedure D). Contour levels in (a), (b) and (c) are $0.08 \text{ e } \text{Å}^{-3}$. (d) Theoretical difference map for a molecule in a crystal field. Contours are at ± 0.04 , ± 0.10 , ± 0.20 , ± 0.40 and $\pm 0.80 \text{ e } \text{Å}^{-3}$. The zero level is dashed in (d) but not included in (a), (b) and (c). Standard errors in the experimental maps are estimated to be approximately $0.05 \text{ e } \text{Å}^{-3}$.

Static multipole deformation maps

Static multipole deformation maps were calculated in the same way as the dynamic ones but with the thermal parameters reset to zero. This procedure sharpened the features of the maps and the peak heights increased to C(1)–C(2) 0.56 , C–O 0.48 , C(2)–N 0.32 , C–H 0.42 , and N–H $0.36 \text{ e } \text{Å}^{-3}$. The nonbonding areas around the O atoms showed peaks with heights between 0.08 and $0.24 \text{ e } \text{Å}^{-3}$.

Fig. 2(a), (b), and (c) compares the $X-N$ difference density map and the multipole maps obtained by procedures C and D in the plane of the carboxyl group where the observed differences between the two procedures are most pronounced. The lone-pair regions of the O atoms look different; particularly the high single peak at the back of the O(1) atom in the $X-N$ map does not have any equivalent in the deformation maps. In addition, the C(1)–O(1) and C(1)–O(2) bond peaks are fairly off-centered and displaced towards the C(1) atom in the $X-N$ map, whereas they are almost centered in the deformation maps.

The $X-N$ and multipole maps may also be compared with the *ab initio* MO–LCAO SCF calculations using a Gaussian basis set of ‘double- ξ ’ type performed by Almlöf, Kvik & Thomas (1973) and given in Fig. 2(d). When comparing the maps it should be remembered that the theoretical map is not subject to thermal smearing, which will reduce the electron levels if applied. It can be seen that the agreement between the theoretical map and the $X-N$ map is good, especially if one allows for a small overestimation of the scale factor in the $X-N$ procedure, which mainly raises the electron levels close to the nuclei. The multipole models used appear to be slightly less detailed upon comparison with the theoretical map. It may well be that the multipole refinement procedure, as it is employed here, is sensitive to the inclusion of more complete high-order data or a more general set of deformation functions used in order to resolve the finer details of the deformation densities.

A comparison of the multipole maps obtained by procedures C and D shows some differences and illustrates the difficulty of quantitative discussions. The

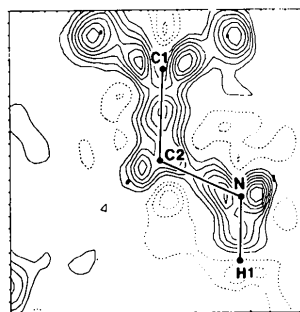


Fig. 3. $X-N$ difference map in the plane defined by atoms N, C(1) and C(2). Contours are at $0.08 \text{ e } \text{Å}^{-3}$ intervals.

peaks are lower in procedure *D* and the minima at the nuclei are shallower. The latter feature is connected with the difference in the scale factors, while the former must be connected with the lower values of the γ exponents of the deformation functions used in procedure *D*. The choice of the γ exponents therefore appears to be important in any quantitative study. As already pointed out, the best fit between observed and calculated structure factors and the lowest standard deviations of the parameters have been obtained by procedure *D*; therefore, the deformation maps obtained by procedure *D* are used in the remaining discussion.

Deformation electron density maps

The *X-N* deformation maps are in excellent agreement with the theoretical map. The excellent fit does not only pertain to the carboxylate group, but also to the amino end of the molecule (Fig. 3). As noted above, the appropriate scale factor in *X-N* maps is difficult to ascertain. The immediate vicinities of the nuclei are therefore often troubled by large errors, partly because of this fact and partly because of a lack of extremely high-resolution data. The densities between the nuclei are, however, often quite reliable as evidenced by the comparison with the theoretical maps. Furthermore, the 120 K glycine maps are also in good agreement with the 298 K maps (Almlöf *et al.*, 1973), the most striking difference being the more detailed features of the 120 K maps with higher density in the peaks as a result of smaller thermal smearing and the use of

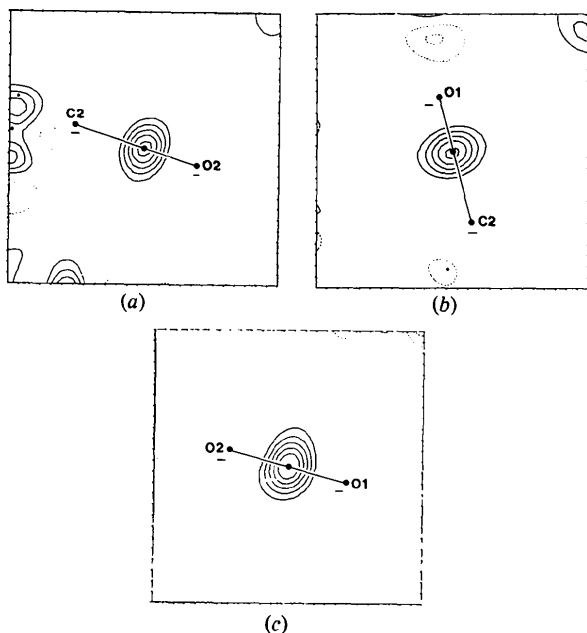


Fig. 4. Multipole deformation maps in the plane through the midpoint of (a) the C(1)-O(1) bond, (b) the C(1)-O(2) bond and (c) the C(1)-C(2) bond. The planes are perpendicular to the bonds. Contours are at $0.08 \text{ e } \text{Å}^{-3}$ intervals.

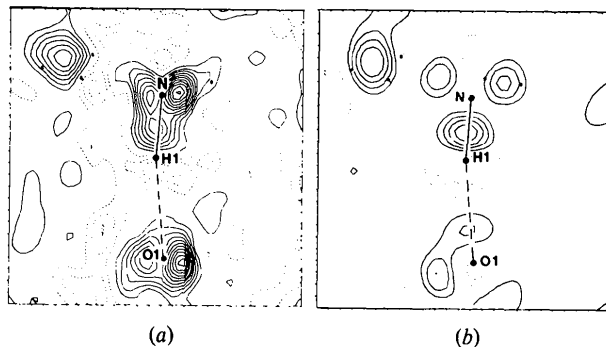


Fig. 5. (a) *X-N* and (b) multipole deformation maps in the plane defined by atoms involved in the N-H(1)...O(1) hydrogen bond. Contours are at $0.06 \text{ e } \text{Å}^{-3}$ intervals.

higher-resolution data. It is also of interest to note that the C-C and C-O bond regions in α -glycine and in the corresponding parts in α -glycylglycine (Kvick, Koetzle & Stevens, 1979) are virtually identical, indicating very little disturbance of the glycine molecule as it enters into the dipeptide. The main differences occur in the areas outside the O atoms.

In the *X-N* maps the deformation density peaks are located markedly closer to the C atom in the C-O bonds and also closer to the N atom in the C-N bonds, in agreement with the 82 K study of α -glycylglycine and with the theoretical map. These features do not appear in the multipole deformation maps, where all peaks are centered on the covalent bonds half way between the C, N, and O atoms.

Fig. 4 illustrates the density in a plane perpendicular to the C-C and C-O bonds as found by plotting the multipole deformation functions. The C-O and C-C bond distances suggest partial π -bonding character in these bonds. This assumption is nicely corroborated by the elongation of the peaks perpendicular to the plane of the molecule.

Fig. 5 illustrates the electron densities in the shortest hydrogen bond N-H(1)...O(1) where the H(1)...O(1) distance at 120 K is $1.722 (1) \text{ Å}$. Both the *X-N* and multipole methods qualitatively give the same picture of the hydrogen bond. In accordance with the electrostatic model of hydrogen bonding, no charge build-up is found in the bond. The positive side of the H atom points towards the O atom. In the multipole procedure the H points towards a small peak in the lone-pair region.

The *X-N* maps and the other multipole maps of the hydrogen bonds, however, show very little sign of lone-pair directionality. The smooth electrostatic potential around the O atoms (see Almlöf *et al.*, 1973) gives considerable geometrical freedom in forming the hydrogen bonds.

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Struktur von *trans*-3,6-Dimethoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid

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Abstract

$C_2H_{10}N_4O_2P_2S_2$ is triclinic, $P\bar{1}$, with $a = 6.396$ (2), $b = 7.987$ (2), $c = 9.652$ (3) Å, $\alpha = 89.23$ (10), $\beta = 86.24$ (10), $\gamma = 87.92$ (10)°, $V = 491.7$ (9) Å³, $Z = 2$, $D_c = 1.676$ Mg m⁻³. The structure was solved by direct methods and refined to $R = 0.068$ ($R_w = 0.048$). The two symmetry-independent centrosymmetric molecules show a flattened chair conformation for the saturated six-membered rings [mean torsional angle of ring bonds 44.2 (1.9)°]. The S atoms are in equatorial, the methoxy groups in axial positions. Mean bond distances: N–N 1.435 (7), P–N 1.663 (8), P–S 1.897 (3), P–O 1.551 (7) and O–C 1.484 (11) Å.

Einleitung

Bei Strukturuntersuchungen an dem Isomerenpaar *trans*- und *cis*-3,6-Diphenoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid (*trans*- und *cis*-Dithio-

dihydrazidodimetaphosphorsäurediphenylester) (1a) und (2a) hatten wir gefunden, dass das *trans*-Isomere die erwartete Sesselkonformation des gesättigten Phosphor-Stickstoff-Ringsystems besitzt, während das *cis*-Isomere im Kristall in der ungewöhnlichen Twistkonformation vorliegt (Engelhardt & Hartl, 1975a,b, 1976). Inzwischen haben wir auch die entsprechenden Dimethoxy- und Diethoxy-Verbindungen (1b), (2b), (1c) und (2c) und einige N-methylierte Derivate von (1a) und (2a) dargestellt und in fast allen Fällen in die reinen Isomere aufgetrennt (Engelhardt & Jürgens, 1977; Engelhardt & Merrem, 1977; Engelhardt, Merrem & Bauer, 1979; Merrem, Ehehalt & Engelhardt, 1979; Jürgens, 1979). Kernresonanzspektroskopische Untersuchungen machen sehr wahrscheinlich, dass in Lösung in vielen Fällen jeweils das *cis*-Isomere (2) die Twistkonformation bevorzugt, das *trans*-Isomere (1) dagegen die Sesselkonformation. Diese Ergebnisse sollten sich durch Röntgenstrukturuntersuchungen an einem weiteren Isomerenpaar bestätigen und absichern lassen. Da es erst vor ganz kurzer Zeit gelang, auch