amplitude of the nitrogen atom in molecule *A* over that in molecule *B* undoubtedly reflects the weaker N···O interaction discussed earlier.

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The Conformation of Non-Aromatic Ring Compounds. XXVIII*. The Crystal Structure of α-Chloro-δ-valerolactam

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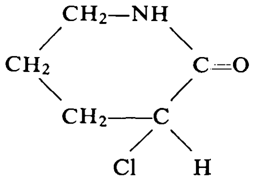
Crystals of α-chloro-δ-valerolactam are monoclinic with space group $P2_1/c$ and $Z=4$. The lattice constants at room temperature are $a=11{\cdot}73$, $b=6{\cdot}20$, $c=9{\cdot}51$ Å, $\beta=112{\cdot}0°$. The structure was solved from a minimum function M_4 which was directly computed and contoured at the machine output. Both *b*- and *c*-axis data were refined separately with a least-squares program and the results are compared. The molecule has a half-chair conformation with the chlorine atom in equatorial position. The peptide linkage NH–CO has the *cis* configuration. Unusual bond lengths are not observed.

Introduction

During the synthesis of α,ω-diaminohexanecarboxylic acid, *via* the amination of α-chloro-oenantholactam (Brenner & Rickenbacker, 1958) the corresponding compound α-chloro-δ-valerolactam



was used as a model substance for the study of the reactivity of the chloro-amino substitution (Henniger, 1966). The title compound contains the peptide linkage –NH–CO– in the *cis* configuration. In addition, it belongs to a class of non-aromatic cyclic compounds which are being extensively investigated in this laboratory [*trans*-2,5-, *cis*-2,3- and *trans*-2,3-dichloro-1,4-dioxane, Altona, Knobler & Romers (1963), Altona & Romers (1963*a*,*b*); *trans*-2,3-dichloro-, 2-phenyl- and *trans*-2,5-dibromo-1,4-dithiane, Kalff & Romers (1965, 1966*a*, 1966*b*); cyclohexane-1,4-dione, Mossel & Romers (1964)].

Experimental

α-Chloro-δ-valerolactam, C_5H_8NOCl, melting point 121–122°C, was crystallized from toluene. The monoclinic crystals are colourless, lath-shaped, frequently twinned and elongated along [010] with main face (100). The needle direction [010] appears to be bent about [001] in such a way as to give the main face (100) a slightly curved shape. The reflexions *h*00, and to a less degree reflexions *hk*0, but not 0*k*0, recorded on a zero layer non-integrated Weissenberg photograph, are extended on one side of the film and contracted on the other, in accordance with the focusing geometry of the reflecting plane (100).

Very small crystals cut perpendicular to the needle axis do not show this effect and, moreover, their reflexions at high θ values appear to be stronger than the corresponding ones of *b*-axis exposures. The diffraction photographs were taken with Cu *K*α radiation ($\lambda=1{\cdot}5418$ Å). The lattice constants at room temperature were determined from zero layer non-integrated Weissenberg photographs about [010] and [001]. These exposures were superposed with aluminum powder lines ($a=4{\cdot}0489$ Å at 20°C) for calibration purposes. The diffraction data

$a=11{\cdot}73\pm0{\cdot}02$ Å $\beta=112{\cdot}0°\pm0{\cdot}2°$ $Z=4$
$b=6{\cdot}20\pm0{\cdot}01$ Å $d_{\rm exp}=1{\cdot}38$ g.cm^{-3} $F(000)=280$
$c=9{\cdot}51\pm0{\cdot}01$ Å $d_x\ =1{\cdot}42$ g.cm^{-3} $\mu({\rm Cu}\,K\alpha)=43$ cm^{-1}

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* Part XXVII, Geise (1967).

indicate that four molecules have to be located in a unit cell with space group symmetry $P2_1/c$.

In order to measure the reflexion intensities two crystals were chosen: a needle with a cross-section $<0{\cdot}1$ mm and a specimen cut parallel to [001] with a cross-section $<0{\cdot}2$ mm. Integrated equi-inclination Weissenberg photographs (multiple film technique) were taken about [010] for the reciprocal layers $k=0,1\text{–}6$ and about [001] for the layers $l=0,1\text{–}8$. The diffraction intensities were measured with a microdensitometer in a manner described earlier (van Oijen & Romers, 1966).

They were reduced to structure factor moduli after multiplication with the usual Lorentz and polarization factors, no absorption correction being applied.

The b- and c-axis data were mutually scaled by means of a program devised by Rollett & Sparks (1960) and modified by Rutten (*vide* Geise, 1964). The results were not promising. The agreement factor

$$\Sigma\, 200(F_b-F_c)/\Sigma\,(F_b+F_c)$$

amounted to the rather high value of 15%. A close inspection revealed that the average isotropic temperature factor (see Table 2 for individual isotropic temperature factors) of the b-axis data (b-data) was about 45% higher than the corresponding factor of the c-axis data (c-data). A possible procedure for correlation of the data might have been the use of an artificial temperature factor $\exp(+B\sin^2\theta/\lambda^2)$ (Rietveld, Maslen & Clews, 1966). However the highly anisotropic vibrational parameter differences between the two crystals make this application infeasible in our case. In view of the different physical background of the chosen crystal specimens it was decided to determine the crystal structure with aid of the c-data and to use the sets separately for the refinement.

The minimum function

The position of the chlorine atom was found from a three-dimensional Patterson synthesis computed with aid of the c-data. The structure was revealed by calculation of a minimum function M_4 (Buerger, 1959) by successive superpositions of the Patterson function on the interactions of the chlorine atom.

Since this procedure can be considered to be a matter of routine for this class of simple molecule, one of us (E.W.M.R.) developed a computer program that can perform this kind of calculation as a part of general Fourier synthesis program (Rutten, 1967). The Patterson function is, one section at a time, stored in memory and its content at a position x,y,z is compared with the instantaneously computed value of the same function at the point $x+x_0,y+y_0,z+z_0$, where x_0,y_0,z_0 stands for a prescibed vector shift. The comparison of both functions is executed at each desired point in vector space and its result, the minimum of both functions, is stored in the memory instead of the original Patterson function. This process is repeated over the other desired $n-1$ vector shifts until the corresponding section of the M_{n+1} function is completed.

Owing to the relatively small storage capacity of the $X1$ computer, it was possible to store in memory only one section of the Patterson function at a time. The value of the ultimate minimum function at the desired points is given in three decimal numbers and can be contoured on printed sheets exactly like the ordinary Fourier function.

The computation of the M_4 function required seven hours on the medium-sized $X1$ computer. Excluding the collection and measurement of diffraction data the solution of the structure and its refinement was performed within three weeks.

The refinement

The sets were used separately for the structure refinement with aid of a least-squares procedure minimizing $\Sigma\, w(|F_{\text{obs}}|-|F_{\text{calc}}|)^2$ in a block-diagonalized approximation to the matrix of normal equations (Geise, Romers & Rutten, 1966). The determination of n separate scaling factors for the respective reciprocal layers and one overall B factor with an $(n+1)\times(n+1)$ matrix is optional and was used during the refinement of both sets of data. The weighting factor w is defined by

$$w=(a+F_{\text{min}})/(a+|F_{\text{obs}}|+b|F_{\text{obs}}|^2)\;.$$

F_{min}, the observed minimum value of F_{obs} (per asymmetric unit) and the constants a and b were 3, 6 and 0·05 respectively, for c-data and 2, 4 and 0·04 respectively for the b-data.

The former set was refined during three cycles with one overall B ($R=35{\cdot}9\%$), four cycles with individual isotropic B's ($R=15{\cdot}9\%$) and four cycles with anisotropic vibrational parameters ($R=9{\cdot}5\%$). The latter set was treated in the same way and needed three cycles with one overall B ($R=19{\cdot}8\%$), three cycles with individual B's ($R=17{\cdot}4\%$) and four cycles with anisotropic vibrational parameters ($R=10{\cdot}1\%$). Contributions of hydrogen atoms (kept at fixed calculated positions with isotropic B's) were included in the anisotropic refinements. The anisotropic vibrational parameters U_{11}, U_{22}, *etc.* are defined by the temperature factor

$$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+\\+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]\;.$$

A complete list of structure factors (c-data) based upon the final cycle with $R=9{\cdot}5\%$ is given in Table 1.

The positional parameters together with their standard deviations obtained for both sets of data are to be found in Table 2. This table also includes the individual isotropic temperature factors. Finally the anisotropic vibrational parameters obtained for the two sets are listed in Table 3.

Discussion of parameters

In the following discussion subscripts b and c refer to b- and c-data. Inspection of Table 2 shows that B_b values are about 45% higher than B_c values. Standard deviations $\sigma_b(x)$ and $\sigma_b(y)$ are only slightly larger than $\sigma_c(x)$ and $\sigma_c(y)$, but standard deviations $\sigma_b(z)$ are about 24% higher than $\sigma_c(z)$.

The positional parameters do not differ significantly for the two sets, the largest differences being about twice the corresponding standard deviations. Judged by these minor differences it can be concluded that both sets yield the same geometrical structure.

Table 3 shows how the increase $B_b - B_c$ is distributed over the vibrational parameters U_{ij} $(i,j=1,2,3)$ in the refinement of b-data. In the bottom row of Table 3 are listed the ratios of mean values $\bar{U}_{ijb}$ and $\bar{U}_{ijc}$. It can be seen that the vibrational parameters U_{22} are not affected and U_{11}, U_{12}, U_{23} and U_{13} only moderately. On the other hand, the value of U_{33} is doubled for b-data. One would expect that U_{22} instead of U_{33}

Table 1. *Observed and calculated structure factors (per asymmetric unit) of α-chloro-δ-valerolactam*

h	k	l	F_c	F_o
+2	+0	+0	-24.0	-19.9
+4			-41.6	-33.8
+5			+1.1	+2.8
+6			-6.1	-6.5
+7			-3.2	-3.5
+8			+17.3	+18.7
+9			+7.1	+7.8
+11			-2.6	-3.4
+12			-3.2	-3.7
+13			-2.3	-2.2
+1	+1		-10.9	-11.7
+2			-22.6	-23.5
+3			-19.0	-18.2
+4			-6.8	-6.5
+5			+10.6	+10.3
+6			+7.7	+7.7
+7			+10.2	+11.1
+8			+8.5	+9.5
+10			-6.5	-7.2
+11			-7.6	-9.1
+12			-2.7	-3.7
+13			+1.5	+1.2
+0	+2		-35.5	-38.0
+1			-6.2	-6.5
+2			+3.4	+4.2
+4			+16.2	+15.9
+5			+7.0	+6.9
+6			+7.8	+7.2
+8			-12.9	-13.6
+9			-5.3	-6.3
+12			+4.3	+5.5
+13			+2.5	+2.2
+1	+3		+7.0	+7.5
+2			+11.1	+11.5
+3			+21.4	+22.7
+4			-3.7	-3.9
+5			-6.8	-7.0
+6			-7.2	-7.2
+7			-9.4	-9.4
+8			+4.6	+4.8
+11			+5.3	+5.7
+0	+4		+4.1	+3.9
+1			+4.1	+4.4
+2			+2.2	+2.7
+4			-6.5	-6.2
+5			-6.8	-6.3
+6			-2.7	-2.5
+8			+5.3	+5.5
+9			+2.1	+1.8
+11			+2.6	+3.1
+3	+5		-4.7	-4.9
+0	+6		-6.6	-7.2
+4			+3.8	+4.0
-15	+1	+1	-2.1	-2.5
-12			-2.2	-2.7
-8			+2.2	+2.8
-7			+3.9	+3.9
-6			-3.8	-3.4
-5			-7.8	-7.0
-3			-8.4	-8.3
-2			+26.2	+28.3
-1			+9.7	+10.6
+0			-22.4	-24.5
+1			+6.6	+6.5
+2			-8.3	-8.7
+3			+5.5	+4.9
+4			+3.2	+2.9
+5			-10.0	-6.8
+6			+2.5	+2.3
-11	+2		+5.3	+5.7
-10			-2.6	-3.3
-8			+8.3	+9.0
-7			-6.2	-6.1
-6			-4.8	-3.8
-5			-5.5	-5.5
-4			-8.8	-9.1
-3			+16.7	+17.5
-2			+7.3	+8.1
-1			+2.3	+2.2
+0			+6.7	+7.4
+1			+1.8	+2.2
+2			-15.6	-15.8
+3			-10.3	-10.2
+4			+1.1	+1.4
+6			+10.7	+9.9
+7			+5.9	+5.5
+8			-6.0	-5.6
-15	+3		+2.3	+2.1
-10			-1.0	-1.7
-9			-5.1	-4.1
-8			-2.5	-3.3
-7			-3.7	-3.8
-5			+4.5	+4.8
-4			+8.7	+9.0
-3			+8.7	+8.7
-2			-9.3	-9.4
-1			-5.3	-5.2
+0			-2.9	-2.9
+1			-5.2	-5.1
+2			+1.7	+2.1
+3			-3.9	-3.8
+4			+8.2	+8.5
+5			+9.8	+9.4
+6			-3.6	-3.7
+7			-2.5	-2.2
+8			-3.6	-2.8
+9			-2.4	-2.3
-11	+4		-1.7	-1.8
-10			-5.1	-5.3
-6			+9.7	+9.5
-4			-3.8	-3.8
-3			-2.7	-2.5
-2			-8.3	-8.4
+1			+6.3	+6.9
+2			+7.6	+7.4
+4			+2.8	+2.0
+5			-4.3	-4.3
+8			-4.6	-4.0
+9			+2.5	+2.7
+10			+2.4	+1.8
-9	+5		+2.6	+2.9
-8			+2.2	+2.0
-4			-6.5	-6.3
-3			-3.4	-3.7
+0			+11.2	+11.7
+4			-7.9	-8.6
+8			+2.9	[illegible]
+9			+2.8	+2.5
-7	+6		-2.6	-2.7
-6			-4.2	-3.9
-2			+5.2	+4.3
+0			+2.5	+2.6
+1			-3.4	-3.4
+2			-6.6	-6.6
+6			+1.7	+2.3
-3	+7		+2.1	+1.7
-1			-1.5	-1.1
+0			-1.6	-2.2
-14	+0	+2	-3.6	-4.0
-13			-3.2	-3.5
-12			-3.0	-3.1
-10			+4.8	+5.2
-9			+10.6	+12.0
-8			+7.0	+7.7
-7			-2.5	-2.7
-6			+1.9	+2.4
-5			-2.4	-21.8
-4			-18.6	-17.7
-3			+13.1	+13.4
-2			-28.5	-26.1
+0			+37.5	+36.1
+1			+18.1	+13.9
+2			+23.5	+21.0
+3			-30.3	-27.1
+4			-25.2	-24.4
+5			-3.5	-3.1
+6			-4.3	-3.3
+7			+5.3	+5.9
+8			+6.3	+6.7
+9			+11.9	+11.5
+10			+3.2	+3.6
+11			-5.2	-4.8
-13	+1		+1.1	+2.5
-12			+2.5	+3.4
-11			+2.6	[illegible]
-10			+12.6	+14.8
-8			-11.8	-12.6
-7			-7.5	-7.4
-6			-22.4	-21.2
-5			+7.8	+7.9
-4			+13.9	+12.7
-3			-7.2	-8.1
-2			+51.8	+57.0
-1			+13.5	+15.6
+0			-21.9	-25.2
+1			-15.0	-12.8
+2			-31.5	-29.2
+4			+5.7	+5.2
+6			+12.6	+12.0
+7			+6.8	+6.9
+10			-5.3	-5.5
+11			-4.7	[illegible]
+12			-2.0	-2.2
-13	+2		+4.7	+4.6
-12			+3.1	+3.6
-11			-2.4	-3.0
-9			-7.9	-8.4
-8			-6.9	-7.2
-7			-2.7	-2.5
-6			+3.1	+3.0
-5			+20.6	+21.4
-4			+16.5	+17.7
-3			+2.7	+2.7
-2			-12.7	-13.9
-1			-14.7	-17.0
+0			-11.6	-12.9
+1			-18.7	-19.9
+3			+16.6	+16.5
+4			+9.6	+9.0
+5			+7.7	+7.1
+7			-4.2	-4.3
+8			-5.5	-5.2
+9			-6.2	-6.4
+10			-2.9	-3.6
+11			+2.1	+2.5
-12	+3		-3.8	-4.0
-11			-3.7	-4.0
-8			+4.1	+3.8
-7			+5.6	+5.9
-6			+2.6	+2.6
-5			+3.8	+4.0
-4			-2.5	-2.2
-3			-5.2	-5.8
-2			-14.1	-15.9
-1			-6.2	-7.1
+0			+8.5	+9.1
+1			-4.5	-5.2
+2			+14.8	+14.7
+3			+8.4	+8.2
+5			+4.6	+4.5
+6			-16.8	-14.9
+7			-7.5	-7.2
+8			+4.5	+4.2
+10			+5.6	+5.7
+11			+2.5	+2.0
-9	+4		+3.1	+2.9
-5			-9.4	-9.4
-4			-7.3	-7.4
-2			+9.2	+10.5
-1			+6.4	+6.9
+1			+5.3	+5.5
+2			-2.2	-2.2
+3			-3.1	-3.0
+4			-5.5	-5.4
+5			-5.5	-4.5
-3	+5		+2.4	+2.5
-2			+6.1	+5.9
+0			-5.3	-5.5
+11	-4	-2	+2.7	+3.5
+4	-5		+3.7	+4.0
-8	+1	+3	+2.9	+2.8
-7			+4.2	+4.2
-4			-15.2	-16.0
-3			-11.1	-12.1
-2			+17.8	+21.9
+0			+11.4	+12.3
+1			+3.2	+2.6
+2			-13.5	-13.3
+3			+4.3	+3.8
+5			-3.5	-2.9
+6			+2.7	+2.4
-12	+2		+3.3	+2.6
-11			+4.5	+4.5
-10			-2.6	-2.4
-7			-3.2	-2.9
-6			+5.3	+5.1
-5			-12.7	-14.2
-4			+3.6	+2.7
-3			+9.2	+9.8
-1			+3.1	+3.1
+0			-7.4	-8.5
+1			+8.0	+9.1
+3			-8.1	-7.0
+6			+10.1	+9.2
+7			+4.2	+3.7
-5	+3		+3.7	+3.8
-4			+9.4	+10.2
-3			+1.8	+1.7
-2			-2.8	-2.8
-1			-3.8	-3.2
+0			-11.5	-13.0
+2			+3.0	+2.6
+4			+5.5	+4.8
+8			-5.2	-5.0
-11	+4		-2.5	-3.9
-6			+8.0	+7.7
-5			+3.7	+3.9
-3			-5.1	-4.8
-2			-9.3	-9.4
-1			-4.8	-4.9
+0			+5.1	+4.7
+1			+3.5	+3.8
+2			+4.0	+3.4
+3			+7.6	+7.5
+4			-3.7	-3.5
+5			-5.3	-4.5
+7			-3.4	-2.8
+9			+1.8	+2.5
-2	+5		-3.9	-3.6
+0			+8.3	+8.2
+2			+2.4	+2.7
+3			-3.7	-4.1
+10	+2		-3.8	-3.4
-14	+0	+4	-4.1	-4.3
-12			-5.8	-6.6
-10			+9.0	+9.6
-9			+8.1	+8.6
-8			+11.1	+13.1
-7			-5.2	-5.1
-6			-16.8	-17.8
-5			-9.9	-10.1
-4			-8.5	-7.0
-1			+15.3	+9.9
+0			+11.5	+8.4
+1			+7.8	+6.0
+2			-2.9	-2.2
+3			-5.6	-4.9
+4			-12.5	-12.8
+5			-8.9	-9.3
+8			+4.8	+5.3
+9			+6.7	+6.5
-13	+1		+3.6	+4.6
-11			+4.5	+5.0
-10			+5.9	+6.5
-9			-4.2	-5.0
-7			-14.2	-15.0
-6			-19.4	-20.1
-5			+11.4	+11.5
-4			+3.7	+5.9
-3			+15.1	+18.1
-2			+14.3	+17.2
-1			+3.7	+4.0
+0			+7.1	+7.9
+1			-19.4	-19.5
+2			-21.7	-21.9
+3			-6.1	-5.2
+4			+5.5	+4.7
+5			+12.4	+13.2
+6			+5.0	+5.1
+7			+5.3	+4.5
+9			-4.7	-3.9
-10	+2		-5.2	-5.3
-9			-4.9	-4.5
-8			-6.2	-6.0
-6			+8.5	+8.5
-4			+18.5	+22.7
-3			+11.6	+14.4
-2			-18.8	-22.9
-1			-3.7	-3.7
+0			-17.1	-20.2
+1			-7.9	-8.9
+2			+12.0	+12.0
+4			+13.3	+12.3
+5			+10.0	+9.1
+6			-6.4	-5.5
+7			-2.9	-2.5
+8			-5.3	-4.7
+9			-3.8	-3.1
-12	+3		-5.0	-5.6
-11			-4.1	-4.2
-8			+6.2	+6.0
-7			+6.2	+5.9
-6			+3.6	+3.4
-4			-11.0	-12.0
-3			-9.5	-10.7
-2			-3.5	-5.0
+0			+2.8	+3.3
+1			+6.1	+5.6
+2			+6.7	+6.7
+4			+5.0	+2.5
+6			-7.5	-6.8
+8			-3.1	-3.5
+10			+4.6	+3.6
-10	+4		+3.9	+3.1
-4			-9.5	-9.3
-3			-5.8	-6.0
-2			+11.7	+13.0
-1			+3.0	+2.6
+0			+6.7	+6.7
+2			-6.7	-6.0
+4			-5.9	-4.7
+5			-5.6	-4.5
+8			+5.	+2.6
-2	+5		+4.5	+3.6
+2			-2.9	-2.9
+11	+1		-3.9	-3.3
-13	+1	+5	-2.6	-2.1
-8			-2.4	-2.0
-6			+3.4	+3.4
-5			+4.2	+4.1
-4			-8.8	-7.9
-3			-3.6	-3.8
-2			+2.5	+2.8
-1			-3.4	-3.6
+0			+9.9	+10.6
+2			-3.4	-3.8
+3			+3.5	+3.0
+4			-5.9	-6.3
+5			-3.5	-3.3
+8			+2.7	+3.0
+9			+1.1	+1.5
+11			-2.0	-0.7
-13	+2		-1.5	-1.9
-12			+3.0	+2.9
-11			+1.6	+2.0
-10			+3.4	+3.2
-9			+1.8	+2.0
-8			-7.1	-6.2
-6			-4.1	-3.9
-5			-6.5	-6.4
-4			+7.3	+7.4
-2			+10.2	+11.6
+0			-9.0	-9.7
+2			-1.3	-1.7
+3			+5.2	+5.1
+4			-3.6	-3.1
+5			-3.2	-3.1
+6			+3.4	+5.8
+8			+2.1	+2.5
-13	+3		+2.6	+2.2
-12			+2.0	+1.9
-10			-2.7	-2.3
-9			-2.7	-2.6
-7			-2.5	-2.5
-5			+4.0	+4.3
-4			+6.3	+6.6
-3			+4.5	+4.7
-2			-4.8	-5.2
-1			-4.5	-5.2
+0			-3.1	-3.7
+1			-4.1	-4.5
+2			+2.3	+2.1
+3			+2.4	+2.5
+4			+2.8	+2.5
+5			+3.3	+3.3
+7			-1.8	-1.6
+8			-1.8	-1.9
-10	+4		-3.5	-3.4
-7			+2.7	+2.8
-6			+3.3	+3.7
-5			-2.6	-2.1
-2			-9.5	-10.5
-1			-3.0	-3.0
+0			+1.8	+2.0
+2			+6.5	+6.4
+3			+2.9	+3.1
+4			-1.7	-1.8
+6			-4.1	-4.2
+7			-3.2	-3.6
+8			+1.8	+1.6
-10	+5		+1.0	+2.0
-9			+2.6	+2.9
-6			-2.6	-2.3
-2			+2.2	+2.4
-1			+4.0	+4.1
+1			+4.6	+4.8
+3			-5.5	-5.3
+5			-1.5	-1.1
-7	+6		-2.6	-2.1
-6			-3.1	-2.3
-2			+3.5	+2.7
+2			-3.5	-2.8
-12	+0	+6	-3.7	-3.2
-11			+4.1	+4.8
-9			+5.2	+5.3
-8			+14.6	+15.7
-7			-2.2	-1.7
-6			-11.1	-9.3
-5			-16.1	-15.3
-4			-4.8	-2.9
-2			+4.7	+3.7
-1			+12.7	+11.2
+0			+7.8	+6.8
+1			+5.6	+6.5
+2			-5.6	-5.4
+3			-14.2	-15.3
+4			-3.3	-4.0
+7			+4.5	+4.7
+8			+2.5	+1.4
-13	+1		+1.8	+1.9
-12			+3.3	+3.2
-11			+4.5	+4.4
-9			-2.7	-3.1
-8			-5.8	-5.4
-7			-6.9	-6.1
-6			-3.9	-3.7
-5			-2.2	-1.9
-4			+9.6	+9.5
-3			+10.1	+10.8
-2			+4.8	+5.9
-1			+4.8	+5.2
+0			-8.7	-8.9
+1			-1.7	-2.5
+2			-8.0	-8.5
+3			-13.6	-14.5
+4			+8.0	+7.7
+5			+6.0	+7.1
+6			+4.9	+5.9
+7			+5.3	+6.0
+8			-4.2	-4.4
-13	+2		+2.3	+2.2
-11			-3.3	-3.3
-10			-2.8	-2.6
-9			-3.5	-3.4
-8			-5.8	-5.1
-7			+5.1	+4.8
-6			+6.1	+5.8
-5			+4.6	+4.4
-4			+7.5	+8.5
-3			-5.5	-5.4
-1			-4.1	-4.8
+0			-14.4	-16.7
+2			+5.3	+5.4
+3			+4.1	+3.8
+4			+7.1	+7.7
+7			-3.2	-2.9
+8			-5.0	-4.6
-12	+3		-3.9	-3.6
-10			-3.0	-3.1
-8			+9.3	+8.9
-6			+4.9	+3.9
-5			+6.4	+6.4
-4			-11.7	-12.3
-3			-6.1	-6.7
-2			-7.4	-7.7
+0			+12.3	+12.8
+1			+4.0	+4.6
+3			+1.8	+2.8
+5			-3.6	-3.5
-11	+4		+2.0	+1.8
-10			+3.8	+2.9
-7			-3.4	-3.1
-6			-3.2	-2.8
-4			-4.4	-4.6
+0			+8.3	+8.4
+1			-3.0	-3.2
+2			-3.2	-2.6
+4			-3.5	-2.9
+0	+5		-3.2	-3.5
-10	+1	+7	+4.2	+4.6
-7			-2.9	-3.1
-5			+2.2	+2.1
-4			-3.7	-3.6
-3			+2.3	+2.4
-2			-2.2	-2.3
+0			+5.5	+6.0
+1			-5.2	-4.9
+3			+3.7	+3.6
+4			-2.6	-3.0
+6			-2.3	-2.5
-10	+2		+3.8	+3.8
-7			+2.7	+1.9
-6			-6.3	-6.1
-5			-3.1	-2.8
-4			+2.1	+1.7
-2			+7.3	+7.9
-1			+3.3	+3.6
+0			-4.1	-4.3
+1			-6.2	-6.4
+5			+2.9	+3.3
-12	+3		+2.6	+2.3
-10			-3.3	-2.6
-8			-2.8	-2.6
-4			+5.9	+6.7
-3			+3.5	+3.8
-2			-2.9	-3.3
-1			-2.7	-2.9
+0			-5.8	-5.6
+2			+2.7	+2.3
+4			+2.9	+2.6
-11	+4		-3.1	-2.8
-7			+5.2	+4.8
-3			-3.6	-3.7
+2			+2.6	+2.2
-11	+0	+8	+3.8	+3.5
-7			+4.3	+4.2
-6			-6.2	-5.3
-5			-7.5	-4.8
-3			-4.3	-2.2
-2			+13.5	+11.8
-1			+2.3	+3.1
+1			+13.0	+15.0
+2			-6.9	-8.4
+3			-7.8	-9.7
+4			-4.1	-5.1
+5			-5.5	-6.1
+6			+6.8	+7.2
-8	+1		-5.9	-6.0
-7			-6.9	-6.5
-6			-2.9	-2.6
-5			+4.2	+4.1
-4			+6.5	+7.0
-3			+3.9	+4.5
-2			+4.9	+5.1
+0			-5.1	-6.6
+1			-3.1	-3.3
+2			-5.0	-5.4
+6			+5.7	+5.2
-10	+2		-5.4	-4.5
-6			+5.1	+6.4
-5			+6.5	+7.9
-4			+2.5	+2.9
-3			-1.6	-1.1
-2			-6.7	-7.9
-1			-4.3	-5.2
+3			+4.7	+4.2
-9	+3		+3.9	+3.4
-8			+4.5	+3.9
-6			+4.6	+4.9
-5			-3.0	-3.4
-2			-9.6	-11.1
-1			-1.6	-1.3
+0			+6.2	+5.7
+1			+5.1	+4.1
+2			+3.1	+1.3
-10	+4		+4.3	+4.1
-6			-2.9	-2.8
+6	-5	-2	-4.0	-3.7.
+8	-3	-3	-4.8	-3.7
+5	-5	-5	-6.5	-6.8

would be affected most by bending of the crystal about [001]. It was hoped that this unexpected result could be understood in terms of the packing of the molecules. Afterwards we realized that a separate scaling of the different reciprocal layers by the least-squares method is an ambiguous procedure, because there is a coupling between the interlayer scaling factors k_l and the corresponding U_{ll} (Lingafelter & Donohue, 1966). It is striking that the ratio $\bar{U}_{ijb}/\bar{U}_{ijc}$ averaged over $i,j=1,2,3$ has the value 1·40, about the same as the average value of B_b/B_c. The ratios $\bar{U}_{22b}/\bar{U}_{22c}$ and $\bar{U}_{33b}/\bar{U}_{33c}$ deviate most from this value and we suspect that the values U_{22b} and k_c are too low and the values U_{33c} and k_b too high.

The difference Fourier functions $\varrho_c(xyz)$ and $\varrho_b(xyz)$, calculated during the final isotropic stages of refinement, show distinct clover leaves in about the same directions for the chlorine atom and the oxygen atom, but only vague indications for the thermal motions of the other atoms. It is evident that the anisotropic refinement has partly eliminated or compensated a source of systematic error (caused by the vibrational motions, errors in scaling factors and absorption) and that the interpretation of thermal motion at most has only qualitative meaning for the chlorine and oxygen atom. Moreover it must be pointed out that the different background or different degrees of disorder present in both crystals make the structure determination irreproducible with respect to the thermal parameters. Nevertheless it is possible to find the positional parameters with reasonable accuracy and to derive from them the geometrical structure which is of interest for the chemist.

Table 2. *Final atomic parameters (fractions of cell edges), their standard deviations* (Å) *and isotropic B's* (Å^2, *for cycle no.* 7 *c-axis data and cycle no.* 6 *b-axis data*)

The top line of each double row refers to *c*-axis data, the bottom line to *b*-axis data.

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B
Cl	0·1161	0·2809	0·5142	0·0026	0·0033	0·0028	3·87
	0·1159	0·2802	0·5139	0·0029	0·0036	0·0034	5·71
O	0·3782	0·2168	0·6951	0·0068	0·0080	0·0064	3·92
	0·3783	0·2137	0·6937	0·0069	0·0080	0·0080	5·19
N	0·3997	−0·0997	0·5807	0·0076	0·0087	0·0075	3·25
	0·4001	−0·0999	0·5807	0·0080	0·0092	0·0090	4·52
C(1)	0·2193	0·1221	0·4532	0·0090	0·0105	0·0087	2·63
	0·2186	0·1194	0·4500	0·0098	0·0112	0·0110	4·15
C(2)	0·3381	0·0839	0·5885	0·0088	0·0102	0·0084	2·27
	0·3385	0·0808	0·5879	0·0096	0·0106	0·0105	4·10
C(3)	0·3594	−0·2811	0·4690	0·0108	0·0114	0·0099	4·03
	0·3588	−0·2802	0·4695	0·0118	0·0116	0·0127	5·62
C(4)	0·2494	−0·2167	0·3284	0·0114	0·0114	0·0098	4·27
	0·2481	−0·2170	0·3298	0·0122	0·0118	0·0121	5·44
C(5)	0·1563	−0·0865	0·3735	0·0100	0·0114	0·0091	3·85
	0·1555	−0·0865	0·3721	0·0113	0·0121	0·0115	5·10

Table 3. *Final vibrational parameters* (Å^2)

The top line of each double row refers to *c*-axis data, the bottom line to *b*-axis data.

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl	0·044	0·073	0·052	0·023	−0·029	0·017
	0·056	0·081	0·083	0·027	−0·031	0·018
O	0·049	0·065	0·037	−0·010	−0·026	−0·003
	0·058	0·059	0·073	−0·016	−0·036	−0·005
N	0·039	0·053	0·034	0·005	0·010	0·021
	0·048	0·065	0·059	0·015	0·004	0·015
C(1)	0·037	0·050	0·027	0·010	−0·011	0·010
	0·047	0·054	0·062	0·023	−0·010	0·026
C(2)	0·038	0·054	0·024	−0·006	0·003	0·024
	0·046	0·050	0·056	−0·012	0·003	0·028
C(3)	0·067	0·052	0·039	0·013	−0·004	0·042
	0·078	0·043	0·082	0·009	−0·012	0·050
C(4)	0·068	0·060	0·031	−0·007	−0·019	0·031
	0·084	0·054	0·062	−0·008	−0·032	0·025
C(5)	0·050	0·060	0·029	−0·013	−0·016	0·012
	0·064	0·063	0·062	−0·006	−0·028	0·018
U_b/U_c	1·23	1·00	1·97	1·33	1·32	1·16

Molecular geometry and packing

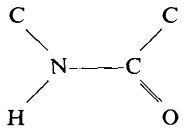
Interatomic bond distances (uncorrected for vibrational effects), valency angles, torsional (dihedral) angles (Fig. 1) and least-squares planes were calculated for the two sets. They result in essentially the same geometry with the exception, perhaps, of the interatomic bond distances listed in Table 4. Although the individual differences for the same bonds are statistically insignificant, it is remarkable that all ring bonds are systematically shorter for the *b*-data. Further discussion will be confined to a description of the geometry resulting from the somewhat more accurate *c*-data.

Table 4. *Interatomic bond distances for c- and b-axis data and standard deviations* (Å)

	c	*b*	*σ*	*Δ*/*σ*
C(1)–Cl	1·815	1·818	0·010	0·3
C(2)–O	1·254	1·223	0·012	2·7
C(1)–C(2)	1·520	1·514	0·013	0·5
C(2)–N	1·365	1·355	0·013	0·8
C(3)–N	1·495	1·463	0·013	2·5
C(3)–C(4)	1·524	1·493	0·016	1·9
C(4)–C(5)	1·543	1·514	0·015	1·9
C(1)–C(5)	1·540	1·515	0·014	1·8

The mean standard deviation of the bond angles is 0·8°. The standard deviations of bond distances are stated in Table 4. The bond distances [Fig. 1(*a*)] and bond angles [Fig. 1(*b*)] show the regular pattern to be expected for this class of ring compound. The interatomic distances C(1)–C(2), C(1)–C(5), C(4)–C(5) and C(3)–C(4) (average value 1·532 Å) have values to be expected for sp_3–sp_3 bonds (1·526 Å; Lide, 1962). The ring valency angles of C(1), C(3), C(4) and C(5) (mean value 111°) are quite regular for secondary carbon atoms in cyclic compounds. The valency angle N–C(2)–C(1) (114·8°) with C(2) part of a carbonyl bond, is about the same as the corresponding angles found in cyclohexane-1,4-dione (mean value 116·2°; Mossel & Romers, 1964).

The peptide linkage



has the unusual *cis* configuration. One would expect this group to be planar and calculation of least-squares planes (Schomaker, Waser, Marsh & Bergman, 1959) through the atoms C(1), C(2), C(3) and N (plane 1) and through the same atoms and O (plane 2):

$$0{\cdot}7321\,X + 0{\cdot}4498\,Y - 0{\cdot}5116\,Z + 1{\cdot}0178 = 0 \qquad (1)$$

$$0{\cdot}7392\,X + 0{\cdot}4614\,Y - 0{\cdot}4906\,Z + 0{\cdot}9157 = 0 \qquad (2)$$

leaves little doubt concerning the planarity of the planes defined with respect to an orthogonal coordinate system *xyz* with directions $\bar{a}$, $\bar{b}$ and $\bar{c}^*$. Table 5 shows, however, that N and C(1) are consistently above and O and C(3) below these planes. The same deviations are found from planes calculated with *b*-axis parameters. Consulting Fig. 1(*b*), we observe, moreover, that the torsional angle C(3)–N–C(2)–C(1) is 9° (standard deviation 2°), implying that C(3) is 0·09 Å below and C(1) 0·11 Å above a plane bisecting the dihedral angle C(3)–N–C(2)–C(1). In view of the total deviation of 0·2 Å with respect to this plane we conclude that the peptide linkage in α-chloro-δ-valerolactam is indeed, not completely planar.

Table 5. *Atomic distances* (Å) *from least-squares planes* (1) *and* (2)

	Plane (1)	Plane (2)		Plane (1)	Plane (2)
Cl	−0·86	−0·85	C(2)	−0·03	−0·01
O	−0·08	−0·02	C(3)	−0·02	−0·04
N	0·04	0·05	C(4)	0·22	0·17
C(1)	0·02	0·01	C(5)	−0·54	−0·57

An orthogonal projection of the molecule on a plane perpendicular to plane (1) is shown in Fig. 2.

It is easy to see that α-chloro-δ-valerolactam has a half-chair conformation with the chlorine atom in a

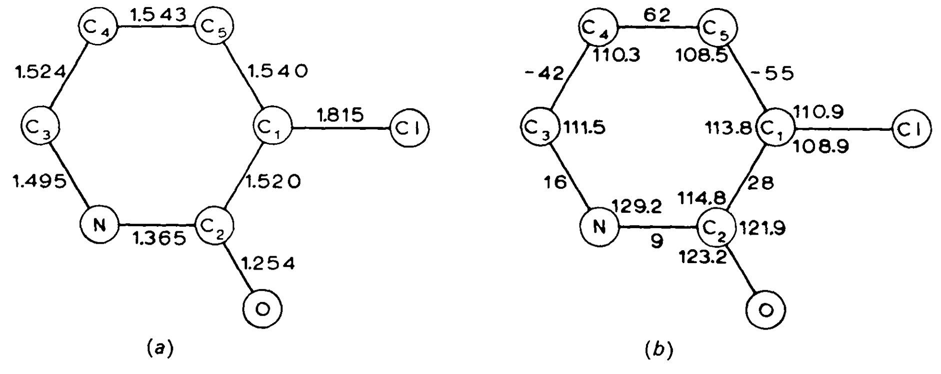


Fig. 1. (*a*) Bond lengths and (*b*) valency and torsional angles of α-chloro-δ-valerolactam.

(pseudo-) equatorial position. Its shape is, however, distorted, since C(5) and C(4) (see also Table 5) have unequal distances to plane (1). One arrives at the same conclusion by comparison of observed torsional angles [Fig. 1(*b*)] with predicted values for an ideal cyclohexane half-chair (Bucourt & Hainaut, 1965).

The packing (Fig. 3) is dominated by intermolecular hydrogen bridges N–H---O arranged in helices around screw axes at $\frac{1}{2},y,\frac{1}{4}$ and $\frac{1}{2},y,\frac{3}{4}$. Instead of a dimer arrangement around centres of symmetry as found in most solid carboxylic acids we encounter a polymer arrangement resembling similar long chair polymers of solid formic and acetic acid (Holtzberg, Post & Fankuchen, 1953; Jones & Templeton, 1958). With exception of the hydrogen bonds with a length of 2·91 Å no short intermolecular distances occur, the shortest distance being 3·48 Å between two nitrogen atoms belonging to molecules at x,y,z and $1-x,\bar{y},1-z$.

The shortest distance between chlorine atoms is rather large: 3·79 Å. As usual they are clustered around centres of symmetry at $0,\frac{1}{2},0$ and at $0,0,\frac{1}{2}$. At distances smaller than 4·2 Å each molecule x,y,z is surrounded by 14 neighbours at $x,1+y,z$; $1-x,\frac{1}{2}+y,1\frac{1}{2}-z$; $1-x,-y,1-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$; $x,-\frac{1}{2}-y,\frac{1}{2}+z$; $x,\frac{1}{2}-y,-\frac{1}{2}+z$; $x,-\frac{1}{2}-y,-\frac{1}{2}+z$; $x,-1+y,z$; $1-x,-\frac{1}{2}+y,1\frac{1}{2}-z$; $1-x,-1-y,1-z$; $-x,1-y,1-z$; $-x,-y,1-z$; $-x,\frac{1}{2}+y,\frac{1}{2}-z$ and $-x,-\frac{1}{2}+y,\frac{1}{2}-z$.

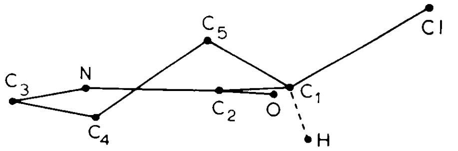


Fig. 2. Orthogonal projection of the molecule viewed on a plane perpendicular to the plane of atoms C(1), C(2), N and C(3) and perpendicular to the bond C(2)–N.

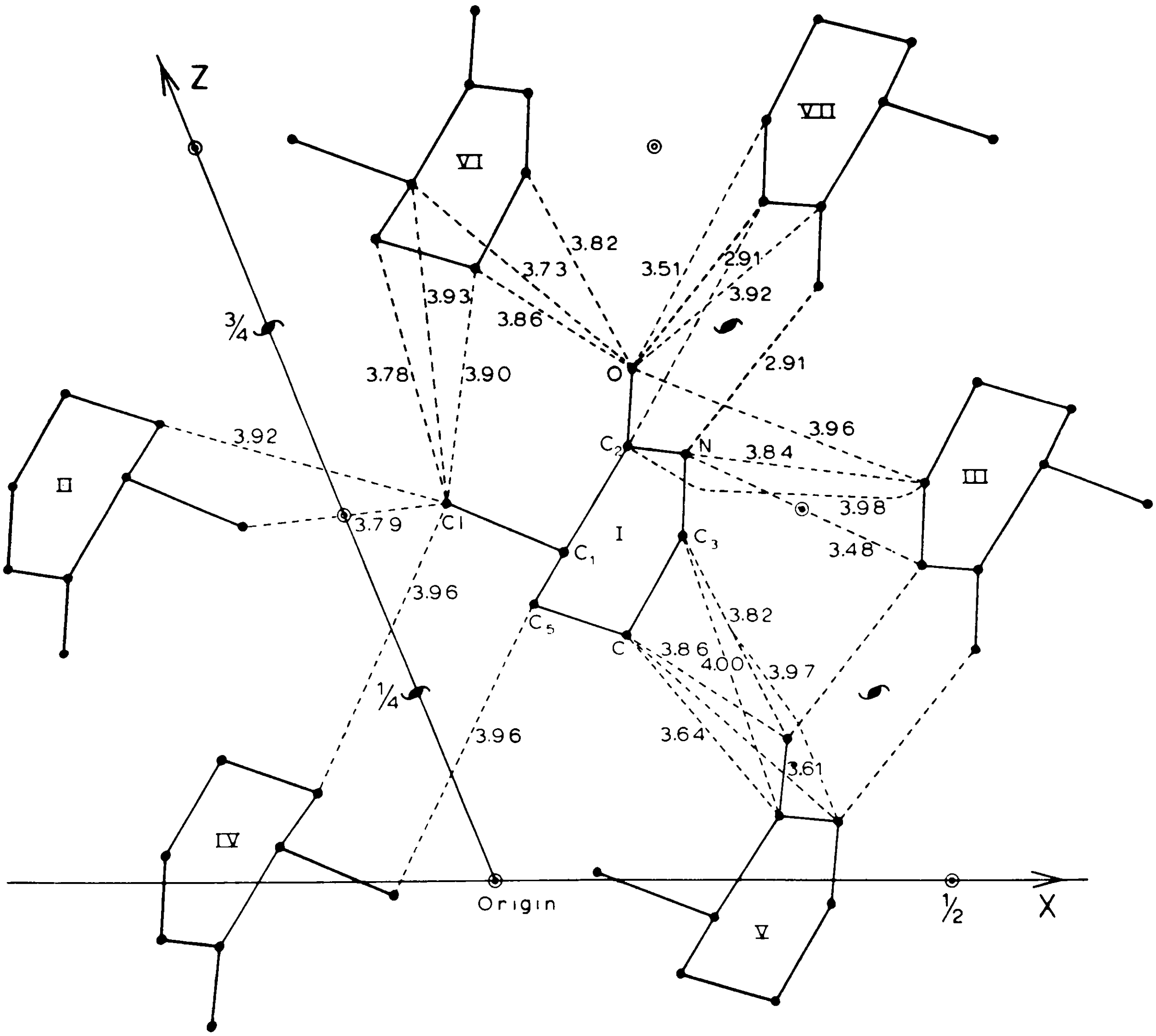


Fig. 3. Packing of the molecules viewed along [010]. Intermolecular contacts less than 4 Å are indicated by dashed lines.

Although the molecules are close-packed according to the requirements of Kitaigorodsky (1961) the packing appears to be quite loose and may offer opportunities for stacking faults and disordering phenomena. One observed stacking fault is the bending of the crystal face (100) about the direction [001]. Apparently helices of hydrogen-bonded molecules can be slightly bent.

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Molecular Complexes Exhibiting Polarization Bonding. IX. The Crystal and Molecular Structure of the Tetracyanoethylene – Naphthalene Complex

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The 1:1 complex formed between tetracyanoethylene and naphthalene crystallizes as red-brown prisms, space group $C2/m$, with two molecules of complex in the unit cell of dimensions $a=7{\cdot}26\pm0{\cdot}01$, $b=12{\cdot}69\pm0{\cdot}01$, $c=7{\cdot}21\pm0{\cdot}01$ Å, $\beta=94{\cdot}4\pm0{\cdot}2°$. The structure was solved by Patterson methods and refined to $R=0{\cdot}137$ by least-squares methods using 512 independent reflexions measured on a linear diffractometer. The component molecules are stacked alternately in infinite columns which are parallel to the c axis. The normals to the mean molecular planes are inclined at approximately 28·5° to the stacking axis. This positions the C=C group of a tetracyanoethylene molecule adjacent to each ring of the naphthalene molecule, so that the relative molecular orientations are those necessary for a Diels–Alder reaction. The mean perpendicular separation of the molecules is 3·30 Å.

Introduction

The 1:1 molecular complex formed between tetracyanoethylene (TCNE) and naphthalene was first described by Merrifield & Phillips (1958). They postulated a sandwich type structure in which the components lie in planes parallel to each other. The structure of the complex was investigated to determine the separations and the relative orientations of the component molecules in view of the strong acceptor properties of TCNE.

Experimental

Red-brown crystals of the complex were deposited slowly after warm equimolar proportions of concentrated solutions of the components in ethyl acetate were mixed and allowed to cool. Micro-analysis indi-

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