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# *N*-Carboxy-L-Alanine Anhydride

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**Abstract.** $C_4NO_3H_5$, $M=115{\cdot}09$; orthorhombic, $P2_12_12_1$; $a=7{\cdot}749$ (2), $b=10{\cdot}699$ (3), $c=6{\cdot}063$ (2) Å; $Z=4$, $D_m=1{\cdot}52$ (by flotation), $D_x=1{\cdot}52$ g cm$^{-3}$. The compound was synthesized from L-alanine and trichloromethyl chloroformate, and crystallized from isopropyl ether at $-5$°C. The final $R$ value was 0·047 for 681 reflexions. The molecules are linked by weak hydrogen bonds formed between N(1)–H(1) and O(3′) in the **b** direction.

**Introduction.** The *N*-carboxy anhydrides (NCA) of amino acids are the most useful monomers for the synthesis of polypeptides. These compounds are generally unstable to moisture and heating. A study has been made on a series of crystal structures of these compounds to explain their polymerizability in the crystalline state. A crystal with the approximate dimensions 0·2×0·4×0·6 mm was mounted on a Rigaku rotating-anode automated four-circle diffractometer, and the intensity data with $2\theta<55°$ were collected by the usual $\omega$–$2\theta$ scans [8° (in $2\theta$) min$^{-1}$] with Zr-filtered Mo $K\alpha$ radiation. 693 independent reflexions were obtained, 681 of which were regarded as observed. Accurate cell parameters were determined by least-squares refinements with 26 high-angle reflexions. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). The non-hydrogen atoms were located on an $E$ map computed with 116 phased reflexions ($E\geq 1{\cdot}2$). When the $R(\sum||F_o|-|F_c||/\sum|F_o|)$ value dropped to 0·13 by block-diagonal least-squares refinement, a difference Fourier map revealed all the H atoms. The weights were 0·5 for unobserved reflexions

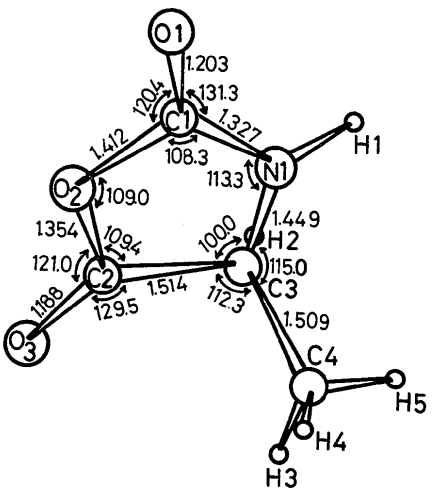


Fig. 1. A perspective view of L-alanine-NCA seen along **a**, with the numbering of the atoms, the bond lengths (Å) and the bond angles (°). The estimated standard deviations are 0·004–0·005 Å, and 0·03–0·04°. The bond lengths involving H atoms are N(1)–H(1) 0·936 (38) and C(3)–H(2) 0·944 (39) Å. The bond angles involving H atoms are C(1)–N(1)–H(1) 121·8 (23), C(3)–N(1)–H(1) 123·9 (23), C(4)–C(3)–H(2) 116·4 (24), N(1)–C(3)–H(2) 114·9 (14) and C(2)–C(3)–H(2) 112·0 (14)°.

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Table 1. *Final atomic coordinates and thermal parameters for* L-*alanine-NCA with their estimated standard deviations*

Anisotropic thermal parameters ($\times 10^5$) are expressed in the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. The isotropic thermal parameters of the H atoms are $B$ (Å$^2$).

| | $x$ | $y$ | $z$ | $B_{11}$ (or $B$) | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 0·6449 (5) | 0·3067 (4) | 0·6152 (6) | 1333 (58) | 828 (33) | 2068 (96) | 11 (84) | −133 (144) | −389 (114) |
| C(2) | 0·4785 (4) | 0·2359 (3) | 0·8929 (6) | 1311 (56) | 577 (27) | 2058 (92) | −81 (70) | −382 (141) | −178 (90) |
| C(3) | 0·4436 (4) | 0·3746 (3) | 0·8717 (6) | 1270 (55) | 597 (27) | 1869 (89) | 55 (71) | 116 (139) | −55 (87) |
| C(4) | 0·4801 (5) | 0·4444 (3) | 1·0823 (6) | 1975 (78) | 658 (31) | 2197 (105) | −204 (89) | 264 (173) | −389 (102) |
| N(1) | 0·5574 (4) | 0·4046 (3) | 0·6898 (5) | 1856 (60) | 561 (23) | 2124 (82) | 200 (69) | 409 (137) | 205 (80) |
| O(1) | 0·7466 (4) | 0·2967 (3) | 0·4664 (5) | 2018 (59) | 1279 (33) | 2868 (90) | 151 (84) | 1479 (137) | −595 (113) |
| O(2) | 0·5996 (3) | 0·2016 (2) | 0·7436 (4) | 1465 (43) | 597 (20) | 2651 (75) | 190 (56) | −65 (110) | −220 (76) |
| O(3) | 0·4187 (4) | 0·1621 (2) | 1·0176 (5) | 2430 (63) | 682 (23) | 2849 (83) | −358 (69) | 698 (143) | 424 (81) |
| H(1) | 0·5548 (47) | 0·4814 (32) | 0·6123 (62) | 1·3 (9) | | | | | |
| H(2) | 0·3320 (47) | 0·3841 (34) | 0·8119 (64) | 1·7 (9) | | | | | |
| H(3) | 0·4017 (53) | 0·4165 (36) | 0·1973 (71) | 2·7 (10) | | | | | |
| H(4) | 0·5913 (58) | 0·4384 (39) | 0·1532 (76) | 3·9 (11) | | | | | |
| H(5) | 0·4464 (54) | 0·5307 (36) | 0·5801 (72) | 2·9 (10) | | | | | |

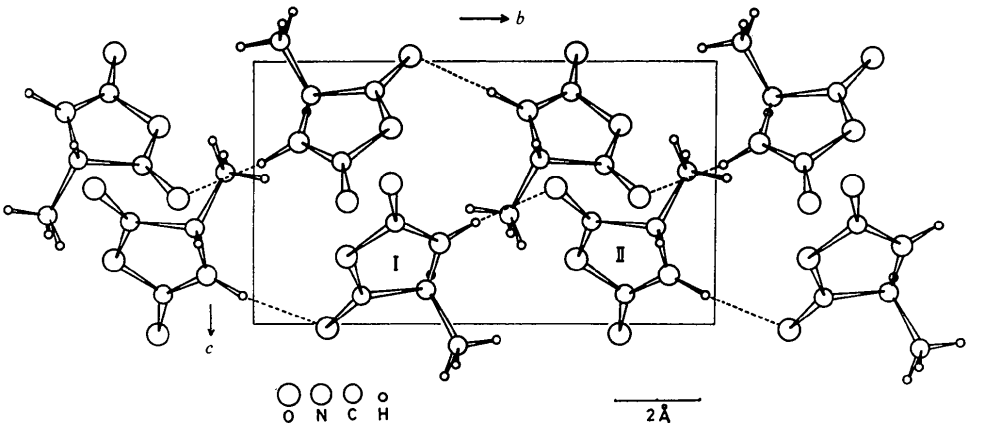


Fig. 2. Projection of the crystal structure of L-alanine-NCA along **a**. General coordinates: (I) $(x,y,z)$; (II) $(1-x,\frac{1}{2}+y,\frac{3}{2}-z)$. Hydrogen bonds are shown by broken lines.

and 1·0 for others. The final $R$ value was 0·047 for all reflexions. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Atomic coordinates and thermal parameters are given in Table 1.* A perspective view of the molecule along **a** is shown in Fig. 1, together with the bond lengths and angles.

**Discussion.** A significant difference in bond length between C(1)–O(2) and C(2)–O(2) is observed, unlike in glycine-NCA (Kanazawa, Matsuura, Tanaka, Kakudo, Komoto & Kawai, 1976) where the corresponding lengths are 1·394 (2) and 1·381 (2) Å. An explanation of this will be given when the analyses of related compounds have been completed. Other bond lengths seem to be normal.

The equation of the best plane through C(1), C(2), C(3) and N(1) in the five-membered ring is shown in Table 2, the maximum deviations of the atoms from the plane being 0·002 Å. Both the exocyclic atoms O(1) and O(3) are displaced on the side opposite O(2). The crystal structure projected along **a** is shown in Fig. 2. As shown by the broken lines, the hydrogen bond is formed between N(1)–H(1) and O(3′); N(1)–O(3′) is 3·034 (5) Å and N(1)–H(1)–O(3′) is 170 (3)°. Therefore, this hydrogen bond is not considered to be strong. The molecular packing is quite different from that of glycine-NCA, in spite of the similarity of the chemical structure. In the glycine-NCA crystal, a pair of molecules form a dimer structure about a centre of symmetry, with two N(1)–H(1)···O(1′) hydrogen bonds. We have observed that the reactivity of L-alanine-NCA is higher than that of glycine-NCA. The hydrogen-bond linkage in L-alanine-NCA may be favourable for the propagation of polymerization.

Table 2. *The equation of the least-squares plane through the atoms in* L-*alanine-NCA, and the deviations of atoms from this plane*

Equation: $-0{\cdot}7364X-0{\cdot}1927Y-0{\cdot}6486Z+6{\cdot}7296=0$
$(X=ax,\ Y=by,\ Z=cz)$

| Atom | Deviation (Å) | Atom | Deviation (Å) |
|---|---|---|---|
| C(1) | −0·002 | *O(1) | 0·023 |
| C(2) | 0·001 | *O(2) | −0·031 |
| C(3) | −0·002 | *O(3) | 0·005 |
| N(1) | 0·002 | *H(1) | 0·164 |
| *C(4) | −1·185 | *H(2) | 0·851 |

* Atoms not included in the least-squares calculation.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31922 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

## References

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