

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian, calculated
 $T_{\min} = 0.900$, $T_{\max} = 0.963$
 1350 measured reflections
 654 independent reflections
 248 reflections with $I > \sigma(I)$

$R_{\text{int}} = 0.036$
 $\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = 0 \rightarrow 8$
 3 standard reflections
 frequency: 240 min
 intensity decay: 3%

Refinement

Refinement on F
 $R = 0.049$
 $wR = 0.040$
 $S = 1.169$
 248 reflections
 30 parameters
 H atoms: see below
 Weights: calculated from measured e.s.d.'s

$(\Delta/\sigma)_{\max} = 0.0002$
 $\Delta\rho_{\max} = 0.322 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.428 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1189). Services for accessing these data are described at the back of the journal.

References

- Ansell, G. B., Forkey, D. M. & Moore, D. W. (1970). *J. Chem. Soc. Chem. Commun.* pp. 56–57.
 Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
 Hall, S. R., Flack, H. D. & Stewart, J. M. (1995). Editors. *Xtal3.4 Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Acta Cryst. (1997). **C53**, 1154–1156

N-Carboxy-DL-phenylalanine Anhydride

HITOSHI KANAZAWA,^a HIDEHIRO UEKUSA^b AND YUJI OHASHI^b

^aDepartment of Education, Fukushima University, Matsukawa-machi, Fukushima, 960-12, Japan, and
^bDepartment of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan. E-mail: uekusa@chem.titech.ac.jp

(Received 24 September 1996; accepted 12 March 1997)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	1	0.21604 (14)	1/4	0.0509 (9)
C1	1	0.3662 (5)	1/4	0.038 (3)
C2	1.0785 (6)	0.5578 (3)	1/4	0.050 (2)
C3	1.2903 (5)	0.3993 (4)	1/4	0.060 (3)
N1	1.1263 (4)	0.4391 (3)	1/4	0.0404 (16)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

S—C1	1.681 (5)	C2—N1	1.390 (5)
C1—N1	1.346 (4)	C3—N1	1.458 (5)
C2—C2 ⁱ	1.329 (7)		
N1 ⁱ —C1—N1	105.3 (4)	C1—N1—C2	110.4 (4)
N1—C1—S	127.4 (2)	C1—N1—C3	124.8 (3)
C2 ⁱ —C2—N1	106.9 (4)	C2—N1—C3	124.7 (4)
S—C1—N1—C2	180.0	H2—C2—N1—C3	0.0
S—C1—N1—C3	0.0	N1—C2—C2 ⁱ —N1 ⁱ	0.0
H2—C2—N1—C1	180.0	H2—C2—C2 ⁱ —N1 ⁱ	180.0

Symmetry code: (i) $2 - x, y, \frac{1}{2} - z$.

All non-H atoms were located from electron density maps and were refined anisotropically by full-matrix least squares. H atoms were located from difference Fourier synthesis and were not refined positionally, while the displacement parameters were refined isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.4* (Hall, Flack & Stewart, 1995). Program(s) used to solve structure: *Xtal3.4*. Program(s) used to refine structure: *Xtal3.4*. Molecular graphics: *ORTEPII* (Johnson, 1976) in *Xtal3.4*. Software used to prepare material for publication: *Xtal3.4*.

DWT acknowledges support from Air Force contract F33615-94-D-5801/TMC-94-5801-0026-1, and PAF acknowledges support from Air Force contract F33615-95-C-5423. The authors thank Al Fratini and Doug Dудis for helpful discussions.

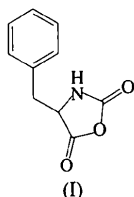
Abstract

The N1—H1 imino group of the five-membered ring of the title compound, C₁₀H₉NO₃, forms intermolecular hydrogen bonds between O1 along the *a* axis and between O3 along the *b* axis. Thus, a two-dimensional hydrogen-bonding network forms a layer perpendicular to the *c* axis. The layer, which consists of one of two independent molecules, stacks alternately along the *c* axis and produces a sandwich structure.

Comment

The relationship between the crystal structures of *N*-carboxy anhydrides (NCAs) of L-amino acids and their polymerizability in the solid state has been studied by Kanazawa (1992a) and Kanazawa & Kawai (1980). The crystal structures of glycine NCA (Kanazawa, Matsura, Tanaka, Kakudo, Komoto & Kawai, 1976a), L-alanine NCA (Kanazawa, Matsura, Tanaka, Kakudo, Komoto & Kawai, 1976b), γ -benzyl-L-glutamate NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978a), L-leucine NCA (Kanazawa, Ohashi, Sasada & Kawai, 1978b), L-valine NCA (Kanazawa, Ohashi & Sasada, 1984) and DL-valine NCA (Takenaka, Ohashi & Kanazawa, 1994) have been determined so far.

The crystal of the title compound, (I), contains two independent molecules, *A* and *B*. However, as the molecular structures are almost identical, only the dimensions of molecule *A* are listed in Table 1. The geometrical structure of the five-membered ring of this molecule is similar to that of the other six NCAs so far determined.



Intermolecular hydrogen-bond distances and angles are listed in Table 2. Although the six NCA crystals listed above show ribbon-type or dimer-type hydrogen bonding, only this crystal has a two-dimensional hydrogen-bond network that forms layers in molecules *A* and *B* perpendicular to the *c* axis. The layers are stacked alternately along the *c* axis to form a sandwich structure.

In Fig. 2, benzyl groups are packed in a layer with the five-membered NCA rings in another layer; the two

layers are aligned alternately. This sandwich structure is very important for the solid-state polymerization of amino acid NCAs (Kanazawa, 1992*b*).

Experimental

The title compound was obtained by the reaction of DL-phenylalanine and trichloromethyl chloroformate in tetrahydrofuran, as for the other NCAs. The reaction product was recrystallized from a mixture of ethyl acetate and hexane.

Crystal data

C₁₀H₉NO₃
M_r = 191.18
 Orthorhombic
*Pna*2₁
a = 9.606 (2) Å
b = 6.378 (2) Å
c = 30.077 (5) Å
V = 1842.7 (7) Å³
Z = 8
D_x = 1.378 Mg m⁻³
D_m not measured

Cu Kα radiation
 λ = 1.54184 Å
 Cell parameters from 25 reflections
 θ = 25.79–27.48°
 μ = 0.864 mm⁻¹
T = 296 (2) K
 Plate
 0.30 × 0.10 × 0.10 mm
 Colorless

Data collection

Rigaku AFC-5R diffractometer
 ω–2θ scan
 Absorption correction:
 empirical via ψ scans
 (North, Phillips & Mathews, 1968)
T_{min} = 0.881, *T_{max}* = 0.917
 1503 measured reflections
 1503 independent reflections

1304 reflections with
I > 2σ(*I*)
 θ_{max} = 62.48°
h = 0 → 10
k = 0 → 7
l = –34 → 0
 3 standard reflections
 every 100 reflections
 intensity decay: 1.928%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.034
wR (*F*²) = 0.090
S = 1.089
 1443 reflections
 253 parameters
 H atoms not refined
w = 1/[σ²(*F_o*²) + (0.0479*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.135 e Å⁻³
 Δρ_{min} = –0.154 e Å⁻³

Extinction correction:
SHELXL93 (Sheldrick, 1993)
 Extinction coefficient:
 0.0019 (2)
 Scattering factors from
International Tables for Crystallography (Vol. C)
 Absolute configuration:
 Flack (1983)
 Flack parameter = 0.3 (4)

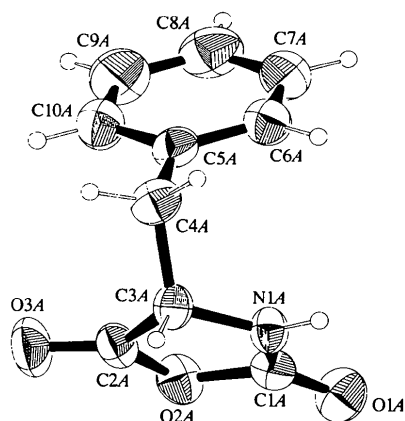


Fig. 1. Structure of L-phenylalanine NCA (ORTEP; Johnson, 1976) with the numbering scheme for the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level; H atoms are drawn as small circles of arbitrary radii. (The structures of molecules *A* and *B* are very similar; thus, only the structure of molecule *A* is shown.)

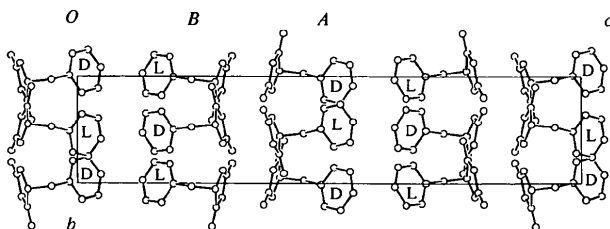


Fig. 2. Projection of the crystal structure of DL-phenylalanine NCA along the *a* axis. The labels D and L represent the D- and L-enantiomers, respectively. Molecules *A* and *B* are indicated by the labels *A* and *B*.

Table 1. Selected geometric parameters (Å, °)

O1A—C1A	1.204 (4)	N1A—C3A	1.446 (4)
O2A—C2A	1.369 (4)	C2A—C3A	1.499 (5)
O2A—C1A	1.394 (4)	C3A—C4A	1.541 (5)
O3A—C2A	1.195 (4)	C4A—C5A	1.511 (5)
N1A—C1A	1.325 (4)		
C2A—O2A—C1A	109.0 (2)	O2A—C2A—C3A	109.1 (3)
C1A—N1A—C3A	113.4 (3)	N1A—C3A—C2A	100.0 (3)
O1A—C1A—N1A	130.9 (3)	N1A—C3A—C4A	114.0 (3)
O1A—C1A—O2A	120.9 (3)	C2A—C3A—C4A	111.4 (3)
N1A—C1A—O2A	108.3 (3)	C5A—C4A—C3A	113.5 (3)
O3A—C2A—O2A	121.5 (3)	C6A—C5A—C4A	121.2 (3)
O3A—C2A—C3A	129.4 (3)	C10A—C5A—C4A	120.4 (3)

Table 2. *Hydrogen-bonding geometry* (Å, °)

D—H...A	H...A	D...A	D—H...A
N1A—H1A...O1A ⁱ	2.319 (3)	2.898 (4)	124.88 (9)
N1A—H1A...O3A ⁱⁱ	2.471 (4)	3.110 (4)	131.59 (9)
N1B—H1B...O1B ⁱⁱⁱ	2.340 (4)	2.918 (4)	124.8 (1)
N1B—H1B...O3B ^{iv}	2.444 (4)	3.099 (4)	133.45 (9)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{z}{2} - y, z$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} + x, -\frac{1}{2} - y, z$; (iv) $x, y - 1, z$.

Extinction conditions indicated that the space group was *Pna*2₁ (No. 33) or *Pnam* (No. 62). Successful structure solution by direct methods and successive refinement confirmed the space group to be *Pna*2₁. Although two independent enantiomers (molecules *A* and *B*) are related by a local inversion center at $x = 0.86$, $y = 0.50$, $z = 0.33$, this crystal structure can not be described by the centrosymmetric space group (*Pnam*). The absolute structure was not determined [$\chi = 0.3$ (4); Flack, 1983]. H atoms were located at geometrically calculated positions and were included in the refinement using the riding model. Polar axis restraints were applied according to the method of Flack & Schwarzenbach (1988). Data collection was performed for the independent region of the reciprocal space. Because some reflections were in a blind region of the equipment, their equivalent reflections, *i.e.* $h\ k\ -l$, were measured instead.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TEXSAN* and *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1051). Services for accessing these data are described at the back of the journal.

References

- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* **A44**, 499–506.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kanazawa, H. (1992a). *Polymer*, **33**, 2557–2566.
 Kanazawa, H. (1992b). *Gendai Kagaku (Mod. Chem.)*, **259**, 28–34.
 Kanazawa, H. & Kawai, T. (1980). *J. Polym. Sci. Polym. Chem. Ed.* **18**, 629–642.
 Kanazawa, H., Matsuura, Y., Tanaka, N., Kakudo, M., Komoto, T. & Kawai, T. (1976a). *Bull. Chem. Soc. Jpn.*, **49**, 954–956.
 Kanazawa, H., Matsuura, Y., Tanaka, N., Kakudo, M., Komoto, T. & Kawai, T. (1976b). *Acta Cryst.* **B32**, 3314–3315.
 Kanazawa, H., Ohashi, Y. & Sasada, Y. (1984). *Acta Cryst.* **C40**, 1094–1096.
 Kanazawa, H., Ohashi, Y., Sasada, Y. & Kawai, T. (1978a). *Bull. Chem. Soc. Jpn.*, **51**, 2200–2204.
 Kanazawa, H., Ohashi, Y., Sasada, Y. & Kawai, T. (1978b). *Bull. Chem. Soc. Jpn.*, **51**, 2205–2208.
 Molecular Structure Corporation (1992a). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (1992b). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Takenaka, Y., Ohashi, Y. & Kanazawa, H. (1994). *Acta Cryst.* **C50**, 1950–1952.

Acta Cryst. (1997). **C53**, 1156–1158

4-(1-Phenylpiperidin-4-ylidene)cyclohexanone

HUUB KOOIJMAN,^a ANTHONY L. SPEK,^a FRANS J. HOOGESTEGER^b AND LEONARDUS W. JENNESKENS^b

^a*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and*
^b*Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: huub@chem.ruu.nl*

(Received 22 October 1996; accepted 10 March 1997)

Abstract

The title compound, C₁₇H₂₁NO, crystallizes with two independent molecules in the asymmetric unit. The conformation of the molecules is essentially the same. All saturated rings adopt a chair conformation, which is a prerequisite for efficient charge transfer.

Comment

End-functionalized oligo(cyclohexylidenes), which consist of chair-type cyclohexane rings connected via double bonds (Hoogesteger *et al.*, 1995), are versatile molecular building blocks for the preparation of supramolecular assemblies, such as non-covalent polymer-like systems (Hoogesteger, Jenneskens, Kooijman, Veldman & Spek, 1996), Langmuir–Blodgett mono- and multilayers (Hoogesteger *et al.*, 1997), and the ripening and growth of microcrystals deposited on silicon by spin-coating (ten Grotenhuis, van der Eerden, Hoogesteger & Jenneskens, 1996). Since oligo(cyclohexylidenes) are semi-rigid aliphatic bridges, possessing a σ – π – σ topology, it was envisaged that end-functionalization with an electron-donor and an electron-acceptor moiety would give opto-electric compounds, *i.e.* materials which give long-range charge separation by electron transfer from the donor to the acceptor upon photoexcitation (Paddon-Row, 1994, and references therein).