Two Crystal Forms of 4'-Octyloxy-4-cyano-biphenyl† (8OCB)

KAYAKO HORI,[a]* MINAKO KUROSAKI,[a] HAIPING WU[a] AND KOICHI ITOH[b]

[a]*Department of Chemistry, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan, and* [b]*Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku-ku, Tokyo 169, Japan. E-mail: khori@fs.cc.ocha.ac.jp*

Abstract

Four crystalline phases were found for 4'-octyloxy-4-cyanobiphenyl, $C_{21}H_{25}NO$. These were square-plate, needle and long parallelepiped crystals, which are all metastable, and a phase found in a commercially available powder specimen which was the most stable. The structures of the needle and long parallelepiped crystals have been determined at room temperature and 243 K, respectively.

Comment

4'-Alkoxy-4-cyanobiphenyls (nOCB) are mesogens with typical mesophase sequences according to the alkoxy chain lengths, *i.e.* crystal–nematic–isotropic for $n = 5$–7, crystal–smectic A–nematic–isotropic for $n = 8$ and 9, and crystal–smectic A–isotropic for $n \geq 10$ (BDH catalogue data). In the course of the systematic X-ray analysis of longer homologs of the series, four crystalline phases for 4'-octyloxy-4-cyanobiphenyl (8OCB) were found. Crystallization from a solution in acetone containing a small amount of water or from a mixture of diethyl ether and methanol produced needle and parallelepiped crystals at 278 K and square-plate crystals at 253 K. All these crystals are metastable phases, especially the square-plate crystals, which are unstable even at 253 K. On the other hand, the needle crystals retain transparency at room temperature for several months. The most stable crystalline phase was found in a commercially available powder specimen. The structures of the needle (I) and long parallelepiped (II) crystals, determined at room temperature and 243 K, respectively, are presented here.

NC—⟨benzene⟩—⟨benzene⟩—OC_xH_{17}

8OCB
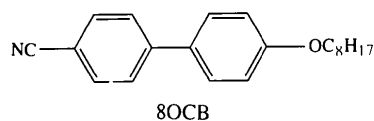
†Alternative nomenclature: 4'-octyloxy-4-biphenylcarbonitrile.

The molecular structures of crystals (I) and (II) are shown in Fig. 1 with their respective numbering schemes. Crystal form (I) contains two crystallographically independent molecules, *A* and *B*, the conformations of which are almost the same. The dihedral angles between the rings of the biphenyl moieties are 38.2 (3) for molecule *A* and 38.9 (3) for molecule *B* of (I) and 2.2 (1)° for (II). The alkoxy chains have fully extended conformations and are almost coplanar with their attached benzene rings (C8–C13) in all three molecules. The bond angles C4—C5—C6 and C9—C8—C13 are slightly smaller than 120°, as was also observed in related compounds (Zugenmaier & Heiske, 1993).
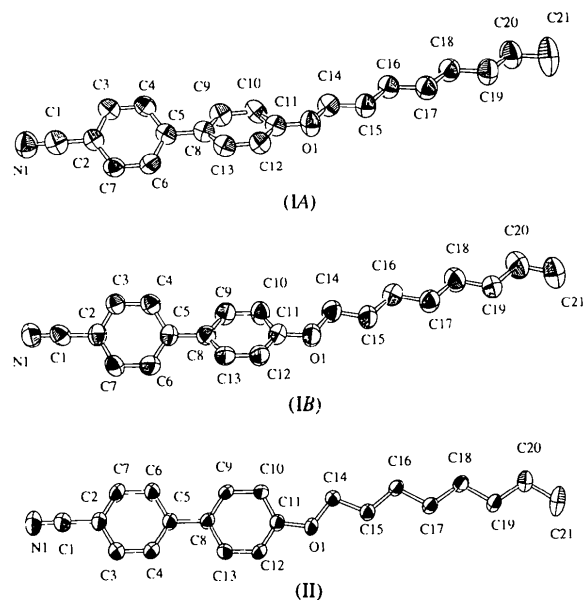

Fig. 1. The structures of molecules *A* and *B* of form (I) [(I*A*) and (I*B*), respectively] and form (II) shown with 50% probability ellipsoids. H atoms have been omitted for clarity.

The unit-cell packing diagrams for (I) and (II) are shown in Figs. 2 and 3, respectively. In (I), the CN groups of molecules *A* and *B* have a relatively close arrangement, with C···N distances of 3.555 (10) and 3.395 (10) Å. Considering the large dipole moment of the CN group, specific interaction is expected between these groups resulting in the formation of a dimer, which is further paired with the neighboring dimer [C···N 3.539 (9) Å] to form a tetramer. This packing mode is almost the same as that found in the needle crystal of 7OCB (Hori, Koma, Uchida & Ohashi, 1993).

In (II), the CN group is not close to another CN group, but is directed towards the biphenyl moiety of the adjacent molecule at $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + 1$, with N···C6 and N···C9 distances of 3.390 (4) and 3.694 (3) Å, respectively. These two molecules are almost coplanar, with N···H distances of 2.502 and 2.770 Å involving the H atoms attached to the C6 and C9 atoms, respectively. Comparing the former distance with the van der Waals
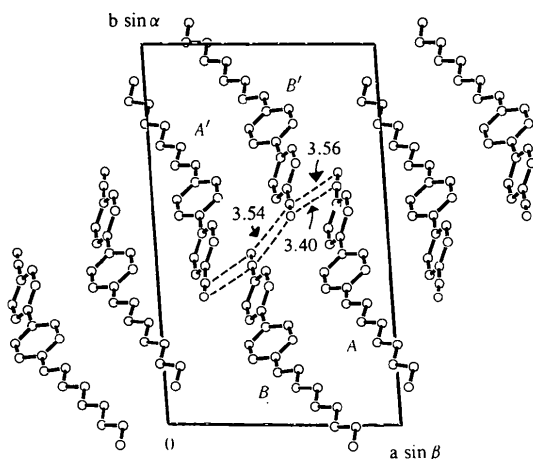
Fig. 2. The crystal structure of (I) viewed along the c axis. A' and B' are symmetry-related equivalents of molecules A and B, respectively. Interatomic distances are 3.40 Å between C1A and N1B'(1 − x, 1 − y, −1 − z), 3.56 Å between N1A and C1B'(1 − x, 1 − y, −1 − z) and 3.54 Å between N1A and N1B'(1 − x, 1 − y, −z).
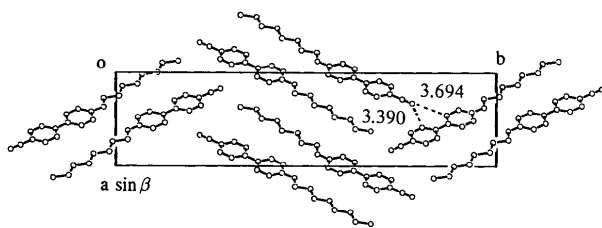
Fig. 3. The crystal structure of (II) viewed along the c axis. Distances are N$\cdots$C6($\frac{1}{2}$ + x, $\frac{3}{2}$ − y, 1 + z) 3.390 (4) and N$\cdots$C9($\frac{1}{2}$ + x, $\frac{3}{2}$ − y, 1 + z) 3.694 (3) Å.

radii of N (1.5 Å) and H (1.2 Å) atoms (Bondi, 1964), specific interaction is expected between the CN group and biphenyl moieties.

Different interactions are found in the two crystal forms of 8OCB, *i.e.* the CN$\cdots$CN interaction of the needle crystal and the CN$\cdots$biphenyl interaction of the long parallelepiped crystal.

Experimental

The sample of 4′-octyloxy-4-cyanobiphenyl was obtained from BDH. Single crystals of forms (I) and (II) were obtained from a solution in acetone containing a small amount of water at 278 K. The former was less frequently obtained.

Crystal form (I)

Crystal data

$C_{21}H_{25}NO$
$M_r = 307.42$
Triclinic
$P\bar{1}$

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections

$a = 12.710\,(4)$ Å
$b = 20.410\,(6)$ Å
$c = 7.325\,(4)$ Å
$\alpha = 99.86\,(3)°$
$\beta = 99.44\,(3)°$
$\gamma = 92.55\,(2)°$
$V = 1841.7\,(13)$ Å^3
$Z = 4$
$D_x = 1.109$ Mg m^{-3}
D_m not measured

$\theta = 27.0–28.5°$
$\mu = 0.517$ mm^{-1}
$T = 293\,(2)$ K
Needle
$0.50 \times 0.05 \times 0.05$ mm
Colorless

Data collection

Rigaku AFC-7R diffractometer
$2\theta/\omega$ scans
Absorption correction:
　ψ scan (North, Phillips & Mathews, 1968)
　$T_{min} = 0.66$, $T_{max} = 1.00$
5776 measured reflections
5487 independent reflections
2181 observed reflections
　$[I > 2\sigma(I)]$

$R_{int} = 0.06$
$\theta_{max} = 60.16°$
$h = 0 \to 14$
$k = -22 \to 22$
$l = -8 \to 8$
3 standard reflections
　monitored every 150
　reflections
　intensity decay: 2.2%

Refinement

Refinement on F^2
$R(F) = 0.0845$
$wR(F^2) = 0.3781$
$S = 0.911$
5486 reflections
415 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.2318P)^2 + 0.6965P]$
　where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.052$
$\Delta\rho_{max} = 0.207$ e Å^{-3}
$\Delta\rho_{min} = -0.325$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
　from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1A	0.8031 (4)	0.3189 (3)	0.4249 (7)	0.0792 (15)
N1A	0.8115 (6)	0.6600 (4)	−0.5862 (10)	0.095 (2)
C1A	0.8016 (6)	0.6245 (4)	−0.4833 (11)	0.075 (2)
C2A	0.7961 (5)	0.5801 (4)	−0.3531 (10)	0.063 (2)
C3A	0.8395 (5)	0.6027 (4)	−0.1662 (10)	0.068 (2)
C4A	0.8412 (5)	0.5602 (4)	−0.0378 (10)	0.067 (2)
C5A	0.7995 (5)	0.4945 (4)	−0.0933 (9)	0.061 (2)
C6A	0.7528 (5)	0.4732 (3)	−0.2815 (10)	0.067 (2)
C7A	0.7525 (6)	0.5155 (4)	−0.4116 (10)	0.069 (2)
C8A	0.8031 (5)	0.4482 (3)	0.0405 (9)	0.061 (2)
C9A	0.8910 (5)	0.4496 (4)	0.1810 (10)	0.069 (2)
C10A	0.8951 (5)	0.4076 (4)	0.3124 (10)	0.070 (2)
C11A	0.8105 (5)	0.3622 (3)	0.3038 (9)	0.063 (2)
C12A	0.7208 (5)	0.3590 (4)	0.1633 (10)	0.069 (2)
C13A	0.7193 (5)	0.4011 (4)	0.0343 (10)	0.068 (2)
C14A	0.8903 (5)	0.3204 (4)	0.5780 (10)	0.072 (2)
C15A	0.8603 (6)	0.2713 (4)	0.6916 (10)	0.077 (2)
C16A	0.9465 (5)	0.2680 (4)	0.8608 (10)	0.071 (2)
C17A	0.9201 (6)	0.2167 (4)	0.9742 (10)	0.079 (2)
C18A	1.0057 (6)	0.2119 (4)	1.1379 (10)	0.079 (2)
C19A	0.9804 (7)	0.1601 (4)	1.2499 (11)	0.090 (3)
C20A	1.0653 (7)	0.1538 (4)	1.4126 (12)	0.100 (3)
C21A	1.0379 (9)	0.1021 (5)	1.5217 (15)	0.145 (5)

	x	y	z	Ueq
O1B.	0.4848 (4)	0.1376 (2)	0.8975 (7)	0.083 (2)
N1B	0.4133 (6)	0.4485 (3)	-0.1964 (9)	0.090 (2)
C1B	0.4137 (5)	0.4176 (4)	-0.0809 (10)	0.069 (2)
C2B	0.4203 (5)	0.3776 (3)	0.0634 (9)	0.060 (2)
C3B	0.4686 (5)	0.4043 (3)	0.2465 (9)	0.065 (2)
C4B	0.4766 (5)	0.3652 (3)	0.3809 (9)	0.064 (2)
C5B	0.4369 (5)	0.2988 (3)	0.3415 (10)	0.062 (2)
C6B	0.3851 (6)	0.2740 (4)	0.1575 (10)	0.071 (2)
C7B	0.3754 (6)	0.3124 (4)	0.0199 (10)	0.073 (2)
C8B	0.4504 (5)	0.2562 (3)	0.4853 (9)	0.060 (2)
C9B	0.5454 (5)	0.2617 (3)	0.6160 (10)	0.070 (2)
C10B	0.5602 (6)	0.2228 (4)	0.7541 (10)	0.073 (2)
C11B	0.4802 (6)	0.1775 (3)	0.7661 (10)	0.067 (2)
C12B	0.3859 (6)	0.1712 (4)	0.6385 (10)	0.078 (2)
C13B	0.3724 (6)	0.2092 (3)	0.5029 (10)	0.070 (2)
C14B	0.5768 (6)	0.1461 (3)	1.0441 (10)	0.075 (2)
C15B	0.5585 (6)	0.0987 (4)	1.1732 (10)	0.076 (2)
C16B	0.6507 (6)	0.0995 (4)	1.3306 (10)	0.078 (2)
C17B	0.6332 (6)	0.0504 (4)	1.4581 (10)	0.076 (2)
C18B	0.7263 (7)	0.0495 (4)	1.6138 (11)	0.091 (3)
C19B	0.7090 (7)	-0.0002 (4)	1.7396 (10)	0.086 (2)
C20B	0.7991 (8)	-0.0008 (5)	1.8975 (13)	0.119 (3)
C21B	0.7809 (10)	-0.0515 (5)	2.0191 (14)	0.146 (4)

Table 2. Selected geometric parameters (Å, °) for (I)

O1A—C11A	1.365 (8)	O1B—C11B	1.358 (8)
O1A—C14A	1.437 (7)	O1B—C14B	1.435 (8)
N1A—C1A	1.149 (8)	N1B—C1B	1.138 (8)
C1A—C2A	1.431 (10)	C1B—C2B	1.437 (10)
C5A—C8A	1.471 (9)	C5B—C8B	1.470 (9)
C11A—O1A—C14A	118.2 (5)	C11B—O1B—C14B	118.5 (6)
N1A—C1A—C2A	176.6 (8)	N1B—C1B—C2B	176.7 (8)
C4A—C5A—C6A	117.9 (6)	C4B—C5B—C6B	116.8 (6)
C9A—C8A—C13A	116.4 (6)	C9B—C8B—C13B	115.6 (6)

Crystal form (II)

Crystal data

$C_{21}H_{25}NO$
$M_r = 307.42$
Monoclinic
$P2_1/a$
$a = 8.551 (3)$ Å
$b = 36.140 (10)$ Å
$c = 5.857 (2)$ Å
$\beta = 95.09 (3)°$
$V = 1802.9 (10)$ Å^3
$Z = 4$
$D_x = 1.133$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 15 reflections
$\theta = 8.5–12.0°$
$\mu = 0.069$ mm^{-1}
$T = 243 (2)$ K
Long parallelepiped with an apex angle of 40°
0.40 × 0.30 × 0.20 mm
Colorless

Data collection

Rigaku AFC-5R diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3254 measured reflections
3254 independent reflections
2377 observed reflections [$I > 2\sigma(I)$]

$\theta_{max} = 25.73°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 43$
$l = 0 \rightarrow 6$
3 standard reflections monitored every 100 reflections
intensity decay: 2.55%

Refinement

Refinement on F^2
$R(F) = 0.0674$
$wR(F^2) = 0.2524$

$(\Delta/\sigma)_{max} = 0.097$
$\Delta\rho_{max} = 0.223$ e Å^{-3}
$\Delta\rho_{min} = -0.326$ e Å^{-3}

$S = 0.682$
3254 reflections
208 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.3078P)^2 + 0.1395P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	Ueq
O1	0.8733 (2)	0.53040 (4)	0.2491 (2)	0.0496 (5)
N1	1.3273 (4)	0.77735 (8)	1.1960 (6)	0.1111 (12)
C1	1.2847 (4)	0.75201 (9)	1.0921 (5)	0.0787 (9)
C2	1.2285 (3)	0.72037 (7)	0.9604 (4)	0.0594 (7)
C3	1.2548 (4)	0.68557 (8)	1.0454 (5)	0.0710 (8)
C4	1.1974 (3)	0.65512 (8)	0.9237 (5)	0.0655 (8)
C5	1.1112 (2)	0.65849 (6)	0.7129 (4)	0.0430 (5)
C6	1.0886 (4)	0.69395 (8)	0.6291 (5)	0.0847 (10)
C7	1.1456 (5)	0.72452 (8)	0.7503 (6)	0.0952 (12)
C8	1.0481 (2)	0.62565 (6)	0.5833 (3)	0.0408 (5)
C9	0.9576 (2)	0.62873 (6)	0.3740 (4)	0.0455 (6)
C10	0.8973 (2)	0.59791 (6)	0.2559 (4)	0.0450 (6)
C11	0.9256 (2)	0.56290 (6)	0.3465 (4)	0.0401 (5)
C12	1.0155 (2)	0.55918 (6)	0.5526 (4)	0.0450 (5)
C13	1.0755 (2)	0.58996 (6)	0.6685 (4)	0.0453 (6)
C14	0.7792 (2)	0.53015 (6)	0.0342 (4)	0.0428 (5)
C15	0.7538 (2)	0.48975 (6)	-0.0201 (4)	0.0426 (5)
C16	0.6507 (2)	0.48119 (6)	-0.2393 (3)	0.0423 (5)
C17	0.6246 (2)	0.43973 (6)	-0.2641 (4)	0.0423 (5)
C18	0.5209 (2)	0.42797 (6)	-0.4763 (4)	0.0444 (5)
C19	0.4966 (3)	0.38641 (6)	-0.4925 (4)	0.0471 (6)
C20	0.3948 (3)	0.37411 (7)	-0.7021 (4)	0.0604 (7)
C21	0.3713 (4)	0.33251 (9)	-0.7140 (7)	0.0915 (11)

Table 4. Selected geometric parameters (Å, °) for (II)

O1—C11	1.363 (2)	C1—C2	1.438 (4)
O1—C14	1.433 (3)	C5—C8	1.484 (3)
N1—C1	1.141 (4)		
C11—O1—C14	120.7 (2)	C9—C8—C13	116.8 (2)
N1—C1—C2	179.0 (4)	O1—C11—C12	114.8 (2)
C6—C5—C4	116.4 (2)	O1—C11—C10	126.0 (2)

The relatively high R values are caused by the fact that crystals of form (II) had rather broad peak profiles even at low temperature, as was the case for crystals of form (I) at room temperature. The broadness is attributable to the crystal growth rates, which were rapid enough to produce metastable crystals and not the most stable crystals. H-atom positions were calculated geometrically [C—H = 0.96 for primary, 0.97 for secondary and 0.93 Å for aromatic H atoms of (I), and 0.97 for primary, 0.98 for secondary and 0.94 Å for aromatic H atoms of (II)] and included in the structure-factor calculations, but were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a) for (I); Rigaku AFC/SOF software system for (II). Cell refinement: *MSC/AFC Diffractometer Control Software* for (I); Rigaku AFC/ SOF software system for (II). For both compounds, data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KH1089). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1754–1756

Redetermination of L-Leucine at 120 K

Carl Henrik Görbitz* and Bjørn Dalhus

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway. E-mail: c.h.gorbitz@kjemi.uio.no

Abstract

This redetermination of L-leucine, C$_6$H$_{13}$NO$_2$, forms part III in a series of crystal structure determinations of hydrophobic amino acids. The L-leucine crystals were grown from a dilute acetic acid solution. E.s.d.'s for bond lengths between heavy atoms are in the range 0.001–0.002 Å.

Comment

As part of a program aimed at providing high precision X-ray structures of hydrophobic amino acids for multivariate analysis of hydrogen-bond parameters, we have presented previously results for L-valine (L-Val) and L-methionine (L-Met) (Dalhus & Görbitz, 1996), and L-isoleucine (L-Ile) (Görbitz & Dalhus, 1996). The crystal structure of L-leucine (L-Leu) was first determined by Harding & Howieson (1976) with an R factor of 0.13 and standard deviations for bond lengths between heavy atoms in the range 0.03–0.05 Å. A redetermi-

nation was carried out by Coll, Solans, Font-Alba & Subirana (1986) with a significantly lower R factor of 0.058. This redetermination, however, was based on a rather limited number of observed reflections (686) and bond-length standard deviations were high by current standards, ranging from 0.01 to 0.02 Å. More important for our purpose is the fact that some of the hydrogen bonds in the structure were distributional outliers in our preliminary statistical investigations of hydrogen-bond geometries, suggesting that the published H-atom positions, obtained from refinements with fixed N—H distances of 1.080 Å, are not very accurate. The current low-temperature study yields a further improvement in the R factor, with a value of 0.044, and is based on 3546 reflections [3195 observed for $I > 2\sigma(I)$]. E.s.d.'s for the bond lengths are in the range 0.001–0.002 Å. The unit-cell volume is 734.0(3) Å^3, a 1.9% reduction from the room temperature value of 748(1) Å^3.
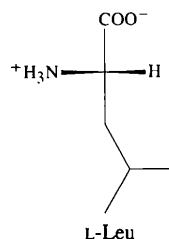
The asymmetric unit of L-Leu, with two crystallographically independent molecules L-Leu(A) and L-Leu(B), is shown in Fig. 1. There are no unusual bond distances or angles and only small differences between the two molecules. The common hydrophobic amino acids crystallize in monoclinic space groups with two molecules in the asymmetric unit. L-Leu is unique within this group in that both molecules have essentially the same side-chain conformation, with N1—C2—C3—C4 (χ^1) *trans* and C2—C3—C4—C5/C2—C3—C4—C6 ($\chi^{2,1}, \chi^{2,2}$) *gauche$^+$/trans*. In the most closely related structure, that of L-Met (Dalhus & Görbitz, 1996), both molecules have *trans* orientations for χ^1, while χ^2 is *trans* for L-Met(A) and *gauche$^+$* for L-Met(B).
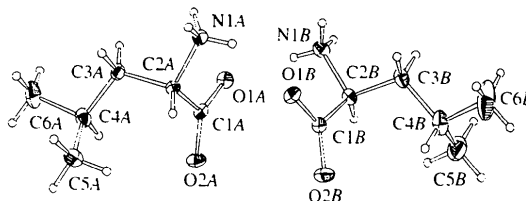

Fig. 1. The asymmetric unit of L-Leu with atomic numbering (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary size.

The crystal packing, with characteristic hydrophilic and hydrophobic layers, is depicted in Fig. 2. The structure and hydrogen-bond pattern are very similar to those