H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.01$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O10	0.18481 (9)	−0.04613 (5)	0.9297 (2)	4.02 (3)
O11	0.11514 (7)	0.02299 (5)	0.7871 (1)	3.04 (2)
O15	0.0918 (1)	−0.13784 (6)	1.0106 (2)	1.35 (3)
O16	−0.0589 (1)	−0.14516 (5)	0.9295 (2)	4.39 (3)
N3a	−0.0162 (1)	0.17968 (6)	0.4842 (2)	3.50 (3)
C1	0.1473 (1)	0.13100 (8)	0.6446 (3)	3.63 (4)
C2	0.1591 (2)	0.16806 (8)	0.4864 (3)	4.00 (4)
C3	0.0765 (2)	0.20831 (8)	0.4694 (3)	4.19 (4)
C4	−0.0965 (2)	0.21220 (8)	0.4136 (3)	4.40 (5)
C5	−0.1914 (2)	0.19139 (9)	0.4799 (3)	4.71 (5)
C6a	−0.1167 (1)	0.09841 (7)	0.5440 (2)	3.01 (3)
C6	−0.1989 (1)	0.12762 (9)	0.4556 (3)	3.78 (4)
C7a	−0.0498 (1)	0.01832 (6)	0.7001 (2)	2.77 (3)
C7	−0.1265 (1)	0.04585 (7)	0.6166 (2)	3.10 (3)
C8	−0.0554 (1)	−0.03539 (7)	0.7769 (2)	2.96 (3)
C9	0.0215 (1)	−0.05973 (6)	0.8569 (2)	2.93 (3)
C10	0.1105 (1)	−0.02935 (7)	0.8623 (2)	2.99 (3)
C11a	0.0384 (1)	0.04772 (6)	0.7054 (2)	2.66 (3)
C11b	0.0527 (1)	0.10053 (7)	0.6354 (2)	2.81 (3)
C11c	−0.0264 (1)	0.12731 (7)	0.5532 (2)	2.84 (3)
C14	0.0135 (1)	−0.11722 (7)	0.9343 (2)	3.36 (3)

Table 2. *Geometric parameters (Å, °)*

O11—C10	1.362 (2)	O10—C10	1.230 (2)
C9—C10	1.436 (2)	C8—C9	1.368 (2)
C9—C14	1.481 (2)	C7a—C8	1.397 (2)
C7a—C7	1.411 (2)	C7a—C11a	1.414 (2)
C6a—C7	1.363 (2)	C6a—C6	1.505 (2)
C6a—C11c	1.435 (2)	N3a—C11c	1.348 (2)
C11b—C11c	1.425 (2)	C11a—C11b	1.368 (2)
C1—C11b	1.505 (2)	O11—C11a	1.377 (2)
C1—C2	1.519 (3)	C2—C3	1.497 (3)
N3a—C3	1.465 (2)	N3a—C4	1.466 (2)
C4—C5	1.505 (3)	C5—C6	1.511 (3)
O15—C14	1.337 (2)	O15—H15	0.92 (3)
O16—C14	1.207 (2)		
C10—O11—C11a	122.8 (1)	O10—C10—O11	115.7 (1)
O10—C10—C9	126.0 (1)	O11—C10—C9	118.4 (1)
C8—C9—C10	119.2 (1)	C8—C9—C14	120.4 (1)
C10—C9—C14	120.3 (1)	C7a—C8—C9	121.9 (1)
C7—C7a—C8	124.7 (1)	C7—C7a—C11a	117.0 (1)
C8—C7a—C11a	118.4 (1)	C6—C6a—C7	121.7 (2)
C6—C6a—C11c	118.7 (2)	C7—C6a—C11c	119.6 (1)
N3a—C11c—C6a	120.2 (1)	N3a—C11c—C11b	119.9 (1)
C6a—C11c—C11b	119.9 (1)	C1—C11b—C11a	122.6 (1)
C1—C11b—C11c	119.7 (1)	C11a—C11b—C11c	117.7 (1)
O11—C11a—C7a	119.2 (1)	O11—C11a—C11b	116.9 (1)
C7a—C11a—C11b	123.8 (1)	C2—C1—C11b	109.2 (2)
C1—C2—C3	110.4 (2)	N3a—C3—C2	112.8 (1)
C3—N3a—C4	114.3 (2)	C3—N3a—C11c	122.8 (1)
C4—N3a—C11c	122.9 (2)	N3a—C4—C5	112.2 (2)
C4—C5—C6	109.8 (2)	C5—C6—C6a	109.9 (2)
C6a—C7—C7a	122.0 (1)	O15—C14—O16	120.3 (2)
O15—C14—C9	116.7 (2)	O16—C14—C9	123.0 (2)
O15—C14—C9—C10	1.4 (2)	C5—C4—N3a—C11c	19.9 (3)
N3a—C4—C5—C6	−51.5 (2)	C2—C3—N3a—C11c	17.8 (3)
C3—C2—C1—C11b	55.8 (2)	N3a—C3—C2—C1	−49.8 (2)
C3—N3a—C11c—C11b	8.1 (2)	C2—C1—C11b—C11a	148.9 (2)
C5—C6—C6a—C7	146.9 (2)	C4—N3a—C11c—C6a	6.6 (2)
C4—C5—C6—C6a	57.0 (2)		

Most non-H atoms were located by direct methods using the program *SAPI*91 (Fun, 1991). Some H atoms were found from difference Fourier maps. The positions of the remaining H atoms were calculated geometrically. All non-H atoms were refined anisotropically and all H atoms isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SAPI*91. Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Cyclic Hexa-Pseudopeptide Constructed from *N*,*N*′-Ethylene-Bridged (*S*)-Phenylalanyl-(*S*)-Phenylalanine and Glycine

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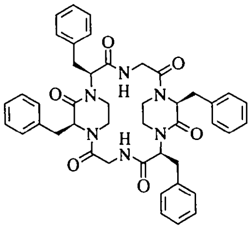
Abstract

(6*S*,9*S*,15*S*,18*S*)-6,9,15,18-Tetrabenzyl-1,4,7,10,13,16-hexaazatricyclo[14.2.2.2^{7,10}]docosane-2,5,8,11,14,17-hexaone crystallizes with two water molecules ($C_{44}H_{46}N_6O_6$.-$2H_2O$). The two piperazin-2-one rings are perpendicular to the 18-membered ring, thus producing a molecular cavity. A water molecule is located in this cavity and interacts with the macrocyclic ring.

Comment

Inclusion phenomena and structural studies of macrocycles are very interesting topics in current chemistry (Behr, 1994; Atwood, 1990). Cyclic peptides are considered to be important species for protein models, but their cyclic skeletons are highly flexible compared to those of other macrocyclic compounds such as cyclodextrin and calixarene. Usually, macrocyclic peptides containing only naturally occurring amino acids do not display effective inclusion of small molecules into their central cavities because the intramolecular hydrogen bonds (NH···O═C) formed in the central rings make the macrocyclic ring relatively planar, which prevents small molecules from entering into the cavities. It has been shown by us that modification of the macrocyclic skeleton using *N*,*N*′-ethylene bridges can provide fixed and deep cavities without the formation of intramolecular hydrogen bonds (Kojima, Yamashita & Miyake, 1995). This paper describes the crystal structure of a new 18-membered cyclic pseudopeptide, cyclo-(Gly–eFF)$_2$ [where Gly is glycine and eFF is (2*S*,3′S)-2-(3′-benzyl-2′-oxopiperazin-1′-yl)-3-phenylpropanoic acid] (Yamashita *et al.*, 1990).



cyclo-(Gly–eFF)$_2$

The two piperazin-2-one rings are approximately perpendicular to the 18-membered ring, forming a deep cavity in the center of this macrocyclic pseudopeptide (Fig. 1). A water molecule [O(57)] located in this cavity is hydrogen bonded to atoms N(49) and O(37) of the central ring as an acceptor and donor, respectively. This hydrogen-bonding bridge *via* a water molecule [N(49)—H···O(57)—H···O(37)] resembles the N(49)—H···O(37) intramolecular hydrogen bond and divides the 18-membered ring into 13- and 15-membered rings. There is none of the intramolecular hydrogen bonds, such as β turns, that have generally been observed in cyclic peptides constructed from naturally occurring amino acids (Brown & Yang, 1979). Such water-bridging conformations (water complexes of cyclic peptides) have been observed in cyclo-(Phe–Pro–D-Ala)$_2$ (Kartha, Bhandary, Kopple, Go & Zhu, 1984) and valinomycin crystallized from dioxane (Langs, Blessing & Duax, 1992). Fig. 2 is a crystal-packing diagram showing that the crystal structure is stabilized by extensive hydrogen-bond networks. Both water molecules are hydrogen bonded to at least one peptide carbonyl O atom. All carbonyl O atoms, except for O(10) and O(38) in the peptide, are hydrogen bonded to either water molecules or an amide group. Intermolecular hydrogen bonding between atom O(19) and H—O(58), and between atom O(47) and H—N(21) plays an important role in fixing the configurations of the amide bonds [C(18)—N(3) and C(46)—N(31) are *cis* and *trans*, respectively].

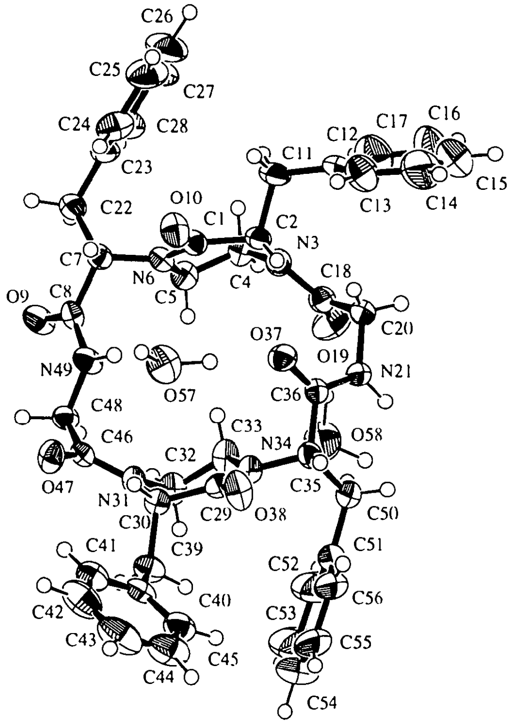


Fig. 1. *ORTEP*II drawing (Johnson, 1976) of cyclo-(Gly–eFF)$_2$.2H$_2$O, with ellipsoids plotted at the 50% probability level.

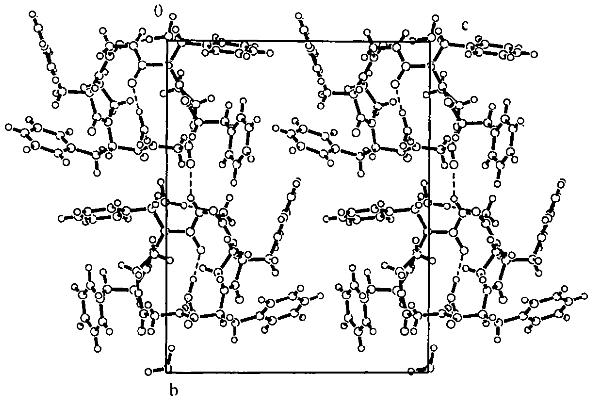


Fig. 2. The crystal packing of cyclo-(Gly–eFF)$_2$.2H$_2$O viewed down the *a* axis.

The conformations of the two piperazin-2-one rings are similar to each other, both having nearly chair forms. The torsion angles C(1)—C(2)—C(11)—C(12) and C(29)—C(30)—C(39)—C(40) are 165.2 (4) and 85.9 (4)°, respectively, indicating that the α–β conformation of the side chain on atom C(2) is the $U_{\rm I}$ form (Kojima *et al.*, 1991), while the side chain on atom C(30) has the $U_{\rm II}$ form. It seems that this is controlled by the steric hindrance between the phenyl group and amide O atom. That is to say, *cis*-peptide bonding on the N-terminal end of eFF induces a $U_{\rm I}$ form, while the *trans*-peptide bonding induces the $U_{\rm II}$ form. This result is similar to that obtained from MM2 calculations for Boc–Gly–eFF-OH (Kojima *et al.*, 1991).

Experimental

The title cyclic pseudopeptide was prepared by conventional liquid-phase methods, from eFF-OMe and Boc–Gly-OH, and cyclization of an active ester of linear hexa-pseudopeptide, HCl.(Gly–eFF)$_2$-OSu (where OSu is *N*-hydroxysuccinimide), under highly dilute conditions. Recrystallization was from CH_3OH [40% cyclic yield from Boc–(Gly–eFF)$_2$-OH]; m.p. 534–543 K; analysis found C 70.0, H 6.2, N 11.1%, M^+ 754; $C_{44}H_{46}N_6O_6$ requires C 70.0, H 6.1, N 11.1%, M^+ 754; $[\alpha]_D = +17° \ dm^{-1} \ g^{-1} \ cm^3$ (in $CHCl_3$).

Crystal data

$C_{44}H_{46}N_6O_6.2H_2O$
$M_r = 790.91$
Monoclinic
$P2_1$
$a = 7.055 (3)$ Å
$b = 19.118 (5)$ Å
$c = 15.568 (5)$ Å
$\beta = 98.32 (4)°$
$V = 2077 (1)$ Å^3
$Z = 2$
$D_x = 1.264$ Mg m^{-3}
$D_m = 1.26$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 14.8$–$15.0°$
$\mu = 0.088$ mm^{-1}
$T = 293$ K
Prismatic
0.85 × 0.53 × 0.15 mm
Colorless

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\rm min} = 0.892$, $T_{\rm max} = 1.000$
4273 measured reflections
3797 independent reflections

3205 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.032$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 22$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 150 reflections
intensity decay: 0.43%

Refinement

Refinement on *F*
$R = 0.047$
$wR = 0.059$
$S = 1.630$
3205 reflections
520 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.03F^2]$
$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.274$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.280$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
O(9)	1.0951 (4)	−0.1461	0.0843 (2)	0.0523 (9)
O(10)	0.6206 (4)	−0.2221 (2)	0.2797 (2)	0.0529 (9)
O(19)	0.8793 (5)	−0.4871 (2)	0.1773 (3)	0.073 (1)
O(37)	0.3849 (4)	−0.3703 (2)	0.1315 (2)	0.0499 (9)
O(38)	0.0631 (4)	−0.3177 (2)	−0.0693 (2)	0.0568 (10)
O(47)	0.4794 (4)	−0.1259 (2)	−0.0920 (2)	0.0485 (9)
O(57)	0.4291 (4)	−0.2279 (2)	0.0839 (2)	0.066 (1)
O(58)	0.8483 (6)	−0.5128 (3)	−0.0049 (3)	0.087 (1)
N(3)	0.8244 (5)	−0.3917 (2)	0.2537 (2)	0.0421 (10)
N(6)	0.8853 (4)	−0.2507 (2)	0.2202 (2)	0.0342 (8)
N(21)	0.4646 (5)	−0.4830 (2)	0.1260 (2)	0.0411 (10)
N(31)	0.5104 (4)	−0.2418 (2)	−0.1043 (2)	0.0344 (8)
N(34)	0.3589 (4)	−0.3650 (2)	−0.0475 (2)	0.0337 (8)
N(49)	0.7909 (4)	−0.1799 (2)	0.0511 (2)	0.0425 (10)
C(1)	0.7331 (5)	−0.2660 (2)	0.2618 (3)	0.039 (1)
C(2)	0.7039 (6)	−0.3413 (2)	0.2893 (3)	0.038 (1)
C(4)	1.0213 (6)	−0.3667 (3)	0.2528 (3)	0.047 (1)
C(5)	1.0194 (6)	−0.3032 (3)	0.1969 (3)	0.043 (1)
C(7)	0.9272 (5)	−0.1772 (2)	0.2042 (3)	0.038 (1)
C(8)	0.9463 (5)	−0.1663 (2)	0.1073 (3)	0.035 (1)
C(11)	0.7291 (7)	−0.3438 (3)	0.3905 (3)	0.056 (1)
C(12)	0.6544 (7)	−0.4106 (3)	0.4236 (3)	0.050 (1)
C(13)	0.4638 (8)	−0.4180 (3)	0.4295 (4)	0.070 (2)
C(14)	0.392 (1)	−0.4811 (5)	0.4564 (5)	0.099 (3)
C(15)	0.504 (2)	−0.5341 (5)	0.4793 (5)	0.103 (3)
C(16)	0.691 (1)	−0.5298 (5)	0.4749 (6)	0.121 (3)
C(17)	0.7683 (9)	−0.4676 (4)	0.4467 (5)	0.088 (2)
C(18)	0.7691 (6)	−0.4524 (3)	0.2135 (3)	0.045 (1)
C(20)	0.5681 (6)	−0.4811 (2)	0.2149 (3)	0.044 (1)
C(22)	1.1044 (6)	−0.1507 (3)	0.2634 (3)	0.045 (1)
C(23)	1.1104 (6)	−0.1726 (3)	0.3574 (3)	0.044 (1)
C(24)	0.9621 (7)	−0.1567 (3)	0.4038 (3)	0.062 (2)
C(25)	0.9693 (9)	−0.1804 (4)	0.4896 (4)	0.079 (2)
C(26)	1.124 (1)	−0.2174 (5)	0.5273 (4)	0.091 (2)
C(27)	1.2694 (9)	−0.2328 (4)	0.4825 (3)	0.082 (2)
C(28)	1.2627 (7)	−0.2100 (3)	0.3971 (3)	0.062 (2)
C(29)	0.2336 (5)	−0.3137 (2)	−0.0754 (3)	0.036 (1)
C(30)	0.3009 (5)	−0.2507 (2)	−0.1212 (3)	0.0344 (10)
C(32)	0.6144 (6)	−0.3072 (3)	−0.1107 (3)	0.047 (1)
C(33)	0.5671 (5)	−0.3573 (2)	−0.0451 (3)	0.046 (1)
C(35)	0.2932 (5)	−0.4269 (2)	−0.0055 (3)	0.037 (1)
C(36)	0.3850 (5)	−0.4249 (2)	0.0911 (3)	0.035 (1)
C(39)	0.2286 (6)	−0.2538 (3)	−0.2199 (3)	0.045 (1)
C(40)	0.0308 (5)	−0.2240 (3)	−0.2465 (2)	0.042 (1)
C(41)	−0.0028 (6)	−0.1539 (3)	−0.2376 (3)	0.054 (1)
C(42)	−0.1808 (8)	−0.1246 (4)	−0.2671 (4)	0.075 (2)
C(43)	−0.3263 (8)	−0.1655 (5)	−0.3049 (4)	0.082 (2)
C(44)	−0.2968 (7)	−0.2360 (4)	−0.3137 (3)	0.074 (2)
C(45)	−0.1193 (6)	−0.2654 (3)	−0.2836 (3)	0.058 (2)
C(46)	0.5805 (5)	−0.1780 (2)	−0.0841 (2)	0.034 (1)
C(48)	0.7894 (5)	−0.1721 (2)	−0.0427 (2)	0.037 (1)
C(50)	0.3257 (7)	−0.4942 (3)	−0.0543 (3)	0.048 (1)
C(51)	0.2679 (8)	−0.4862 (3)	−0.1513 (3)	0.060 (2)
C(52)	0.403 (1)	−0.4942 (5)	−0.2063 (4)	0.107 (3)
C(53)	0.352 (2)	−0.4837 (7)	−0.2952 (6)	0.161 (5)
C(54)	0.167 (3)	−0.4696 (6)	−0.3285 (6)	0.158 (5)
C(55)	0.033 (2)	−0.4619 (4)	−0.2761 (6)	0.118 (3)
C(56)	0.080 (1)	−0.4707 (3)	−0.1856 (4)	0.079 (2)

Table 2. *Selected geometric parameters (Å, °)*

O(9)—C(8)	1.220 (4)	N(34)—C(35)	1.458 (5)
O(10)—C(1)	1.215 (5)	N(49)—C(8)	1.326 (5)
O(19)—C(18)	1.219 (5)	N(49)—C(48)	1.466 (5)
O(37)—C(36)	1.217 (5)	C(1)—C(2)	1.524 (6)

O(38)—C(29)	1.222 (4)	C(2)—C(11)	1.560 (6)
O(47)—C(46)	1.221 (4)	C(4)—C(5)	1.492 (6)
N(3)—C(2)	1.448 (5)	C(7)—C(8)	1.547 (5)
N(3)—C(4)	1.472 (5)	C(7)—C(22)	1.528 (6)
N(3)—C(18)	1.349 (6)	C(11)—C(12)	1.500 (7)
N(6)—C(1)	1.364 (5)	C(18)—C(20)	1.523 (6)
N(6)—C(5)	1.461 (5)	C(22)—C(23)	1.517 (6)
N(6)—C(7)	1.465 (5)	C(29)—C(30)	1.511 (6)
N(21)—C(20)	1.468 (5)	C(30)—C(39)	1.547 (6)
N(21)—C(36)	1.326 (5)	C(32)—C(33)	1.473 (6)
N(31)—C(30)	1.473 (4)	C(35)—C(36)	1.549 (5)
N(31)—C(32)	1.460 (5)	C(35)—C(50)	1.529 (6)
N(31)—C(46)	1.337 (5)	C(39)—C(40)	1.508 (6)
N(34)—C(29)	1.350 (5)	C(46)—C(48)	1.525 (5)
N(34)—C(33)	1.471 (4)	C(50)—C(51)	1.514 (6)

C(2)—N(3)—C(4)	113.2 (3)	C(8)—C(7)—C(22)	111.3 (3)
C(2)—N(3)—C(18)	127.2 (3)	O(9)—C(8)—N(49)	122.2 (4)
C(4)—N(3)—C(18)	119.0 (4)	O(9)—C(8)—C(7)	122.0 (3)
C(1)—N(6)—C(5)	123.7 (3)	N(49)—C(8)—C(7)	115.9 (3)
C(1)—N(6)—C(7)	118.5 (3)	O(19)—C(18)—N(3)	121.4 (4)
C(5)—N(6)—C(7)	117.6 (3)	O(19)—C(18)—C(20)	117.9 (4)
C(20)—N(21)—C(36)	119.2 (3)	N(3)—C(18)—C(20)	120.7 (4)
C(30)—N(31)—C(32)	112.9 (3)	N(21)—C(20)—C(18)	109.4 (3)
C(30)—N(31)—C(46)	118.4 (3)	O(38)—C(29)—N(34)	122.4 (4)
C(32)—N(31)—C(46)	128.7 (3)	O(38)—C(29)—C(30)	117.8 (3)
C(29)—N(34)—C(33)	122.7 (3)	N(34)—C(29)—C(30)	119.7 (3)
C(29)—N(34)—C(35)	119.8 (3)	N(31)—C(30)—C(29)	112.6 (3)
C(33)—N(34)—C(35)	116.8 (3)	N(31)—C(30)—C(39)	111.1 (3)
C(8)—N(49)—C(48)	121.5 (3)	C(29)—C(30)—C(39)	110.9 (3)
O(10)—C(1)—N(6)	123.2 (4)	N(31)—C(32)—C(33)	110.0 (3)
O(10)—C(1)—C(2)	118.0 (3)	N(34)—C(33)—C(32)	111.9 (3)
N(6)—C(1)—C(2)	118.9 (3)	N(34)—C(35)—C(36)	107.5 (3)
N(3)—C(2)—C(1)	114.3 (3)	N(34)—C(35)—C(50)	112.3 (3)
N(3)—C(2)—C(11)	112.2 (4)	C(36)—C(35)—C(50)	115.6 (3)
C(1)—C(2)—C(11)	108.2 (3)	O(37)—C(36)—C(35)	119.4 (3)
N(3)—C(4)—C(5)	110.0 (3)	N(21)—C(36)—C(35)	118.0 (3)
N(6)—C(5)—C(4)	111.4 (3)	O(47)—C(46)—C(48)	119.8 (3)
N(6)—C(7)—C(8)	110.1 (3)	N(31)—C(46)—C(48)	118.0 (3)
N(6)—C(7)—C(22)	112.5 (3)	N(49)—C(48)—C(46)	106.3 (3)

N(3)—C(2)—C(1)—N(6)	−10.7 (5)
N(3)—C(4)—C(5)—N(6)	51.1 (5)
N(3)—C(18)—C(20)—N(21)	116.4 (4)
N(6)—C(7)—C(8)—N(49)	62.1 (4)
N(21)—C(36)—C(35)—N(34)	−133.4 (3)
N(31)—C(30)—C(29)—N(34)	−19.4 (5)
N(31)—C(32)—C(33)—N(34)	50.9 (5)
N(31)—C(46)—C(48)—N(49)	−87.2 (4)
C(1)—N(6)—C(5)—C(4)	−23.2 (5)
C(1)—N(6)—C(7)—C(8)	−128.5 (3)
C(1)—C(2)—N(3)—C(4)	40.4 (5)
C(1)—C(2)—N(3)—C(18)	−130.8 (4)
C(1)—C(2)—C(11)—C(12)	165.2 (4)
C(2)—N(3)—C(4)—C(5)	−61.7 (5)
C(2)—C(1)—N(6)—C(5)	2.6 (5)
C(8)—N(49)—C(48)—C(46)	−169.0 (4)
C(8)—C(7)—C(22)—C(23)	−168.9 (3)
C(18)—C(20)—N(21)—C(36)	−80.9 (5)
C(29)—N(34)—C(33)—C(32)	−27.4 (5)
C(29)—N(34)—C(35)—C(36)	−111.8 (4)
C(29)—C(30)—N(31)—C(32)	44.7 (4)
C(29)—C(30)—N(31)—C(46)	−134.0 (4)
C(29)—C(30)—C(39)—C(40)	85.9 (4)
C(30)—N(31)—C(32)—C(33)	−61.9 (4)
C(30)—C(29)—N(34)—C(33)	11.5 (6)
C(36)—C(35)—C(50)—C(51)	−168.2 (4)

Program used for data collection and cell refinement: *MSC/AFC Data Collection and Refinement Software* (Rigaku Corporation, 1988). Programs used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF* (Beurskens *et al.*, 1992). Program used for all calculations, including data reduction: *TEXSAN* (Molecular Structure Corporation, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1202). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydrogen-Bonding Pattern of a β-Keto Acid: (±)-10-Oxo-3,4-benzobicyclo[4.3.1]dec-3-ene-1-carboxylic Acid

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Abstract

In the title compound, $C_{15}H_{16}O_3$, enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxy groups, with the ketone not involved in the hydrogen bonding. The plane of the carboxy group [O(2)—C(11)—O(3)] makes a

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