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Syn and Anti Isomers of [2.2]Paracyclonaphthane

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Abstract

The structures of the *anti* (1) and *syn* (2) isomers of [2.2]paracyclonaphthane, $C_{24}H_{20}$, can be understood in terms of molecules composed of four segments, two naphthalene rings and two ethylene groups bridging the naphthalene rings. Distortions from ideal geometries are described and attributed primarily to intramolecular effects. Several observations have been made: the bridged portion of the naphthalene ring is deformed into a boat shape in both (1) and (2); much of the $\pi-\pi$ repulsion is taken up by bending angles α and β; the naphthalene rings are parallel to each other in (1), but are non-parallel in (2); one naphthalene ring in (2) is twisted relative to the other, indicating a mode of strain reduction which is unique to this molecule, and the C—C distances and valency angles in the ethylene bridges are larger than normal values.

Comment

The structural features of the paracyclophanes, a class of molecules which can accommodate strain through intramolecular distortions, have been summarized by Mak (1992) and Keehn (1983). In the area of new synthetic procedures, Loy & Assink (1992) recently reported the use of paracyclophanes in copolymerization reactions with C_{60}. This work, which involves the X-

ray structure determination of the *anti* (1) and *syn* (2) isomers of [2.2]paracyclonaphthane, extends the study of the effects of transannular $\pi-\pi$ interactions on molecular conformations to bridged naphthalenoid systems.
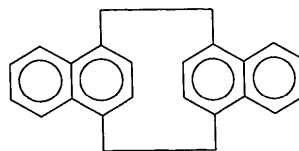
[2.2] Paracyclonaphthane

In the *anti* isomer, (1), the packing is determined by C···H and H···H interactions [2.87 (2) and 2.26 (3) Å, respectively]. The shortest C···C distance is 3.693 (3) Å. Since the intermolecular distances fall within the normal van der Waals range, distortions in the molecular geometry are attributed primarily to intramolecular interactions.

The asymmetric unit comprises two half molecules, designated A and B, each of which sits on a center of inversion. The averaging of bond distances in the molecule (Fig. 1) was carried out by superimposing the two halves, reasoning that one half was identical to the other. The average aromatic bond distance is 1.396 Å, which is equivalent to that found in benzene, 1.397 Å. The length of the bridging bond is 1.574 (3) Å in molecule A and 1.568 (4) Å in molecule B. This lengthening of the ethylene bridge is consistent with observations found in other [2.2]paracyclophanes (Mak, 1992).

A striking structural feature is the deformation of the bridged ring of the naphthalenoid system into a boat shape. C1A and C4A are 0.156 (2) and 0.158 (2) Å,
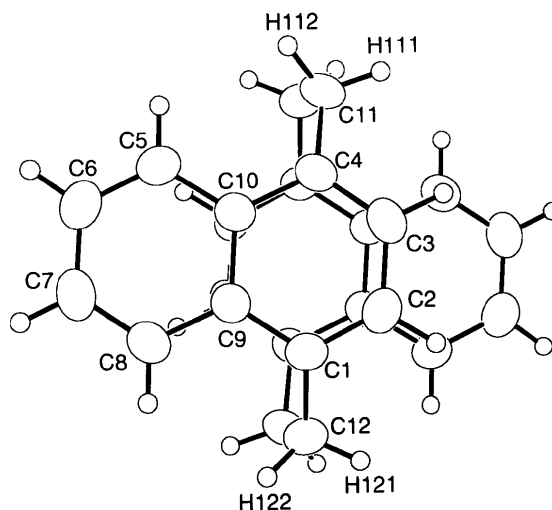

Fig. 1. *ORTEP*II (Johnson, 1976) view of (1) with displacement ellipsoids at the 50% probablility level. H atoms are numbered according to the attached C atom, except where indicated. A unit-cell diagram has been deposited with the supplementary material.

respectively, below the plane of C2*A*, C3*A*, C9*A*, and C10*A*. The dihedral angles, α, between the latter plane and those of atoms C2*A*, C1*A*, C9*A* and C3*A*, C4*A*, C10*A* are 12.6 (7) and 12.5 (7)°, respectively. C1*B* and C4*B* exhibit similar displacements from the plane of C2*B*, C3*B*, C9*B*, C10*B* of 0.164 (2) and 0.161 (2) Å, respectively. The dihedral angles between the plane C2*B*, C3*B*, C9*B*, C10*B* and planes C2*B*, C1*B*, C9*B* and C3*B*, C4*B*, C10*B* are 13.1 (6) and 12.8 (6)°, respectively. The average value of α is 12.8°. The exocyclic bonds, C1*A*—C12*A* and C4*A*—C11*A*, are bent below the planes at each end by β angles of 11.5 and 11.0°, respectively. The corresponding β angles in molecule *B* are 11.8 and 10.0°. Table 5 summarizes average values for selected geometrical parameters. In the paracyclophanes, the decrease of the internal angle, λ, at the substituted atoms C1 and C4 below 120° is characteristic of substitution at these atoms. The decrease is also associated, at least in part, with the boat conformation of the bridged ring. The puckered geometry can be viewed in terms of a folding angle about the line connecting atoms C1 and C4. This folding angle, defined as the dihedral angle between the two planes C1, C2, C3, C4 and C1, C9, C10, C4, is 15.0 (3)°. The corresponding angle in molecule *B* is 15.6 (3)°. The internal valency angles, γ, associated with the bridging C atoms are some 3–5° larger than the normal value of 109°. The torsion angles associated with the ethylene bridge, C1—C12—C11'—C4', are 15.8 (3)° in molecule *A* and 17.4 (3)° in *B*.

The intramolecular distances between overlapping atoms that lie on the lines essentially normal to the ring planes are 2.756 (3), 3.064 (3) and 3.061 (3) Å for the C1*A*···C4*A'*, C2*A*···C10*A'* and C3*A*···C9*A'* distances, respectively. The primed symbols designate symmetry-generated atoms. Similar distances [2.756 (3), 3.061 (3) and 3.084 (3) Å] are observed for molecule *B*. These short distances together with the deformation of the bridged rings are indicative of inherent strain in the structure of (1).

The *syn* isomer, (2), has a shortest C···C distance of 3.528 (4) Å; the shortest C···H and H···H distances are 2.66 (3) and 2.50 (3) Å, respectively. As discussed for (1), intramolecular interactions are considered to be the primary source of molecular distortions.

The asymmetric unit comprises one complete molecule (Fig. 2). The average aromatic distance is 1.392 Å, which is in agreement with a typical aromatic bond length. The elongation of the ethylene bridge distances is indicative of strain in the molecule. The bridging-bond distances for C11—C12 and C23—C24 are 1.563 (5) and 1.575 (5) Å, respectively. The bridged aromatic ring is distorted into a boat shape (Fig. 3). The folding dihedral angle between planes C1, C2, C3, C4 and C1, C9, C10, C4 is 16.4 (4)°, and 16.6 (4)° between planes C13, C14, C15, C16 and C13, C21, C22, C16. Atoms C1 and C4 are 0.178 and 0.165 Å, respectively,

below the plane of atoms C2, C3, C9, C10. Similarly, C13 and C16 deviate from the plane of C14, C15, C21, C22 by 0.183 and 0.160 Å, respectively. The angles, α, between the plane of atoms C2, C3, C9, C10 and those of atoms C2, C1, C9 and C3, C4, C10 are 14.3 (6) and 13.2 (7)°, respectively. For the other naphthalenoid ring, the dihedral angles between the plane C14, C15, C21, C22 and planes C13, C14, C21 and C15, C16, C22 are 14.5 (6) and 12.8 (6)°, respectively. The exocyclic bonds C1—C11, C4—C24, C12—C13 and C16—C23 are bent additionally out of the planes at each end by β angles of 9.8, 9.9, 10.0 and 10.1°, respectively. Average values of these geometrical parameters are shown in Table 5.

Since the lengths of the bridging bonds are equivalent to those seen in (1), the increased π-orbital overlap of (2) is not relieved by a bond-stretching mechanism. The unfavored face-to-face contact of naphthalene rings is alleviated by two alternate mechanisms. First, the rings are rotated relative to each other about an axis perpendicular to and passing through the center
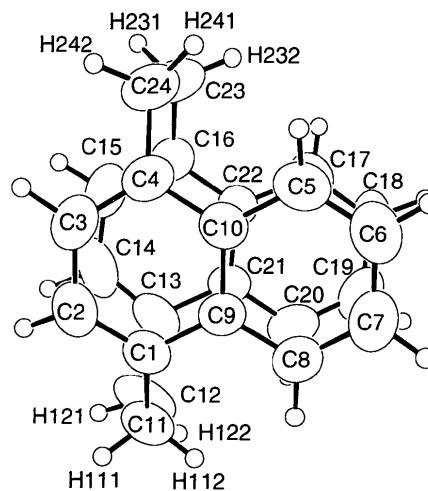

Fig. 2. *ORTEP*II (Johnson, 1976) view of (2) with displacement ellipsoids at the 50% probability level. H atoms are numbered according to the attached C atom, except where indicated. A unit-cell diagram has been deposited with the supplementary material.
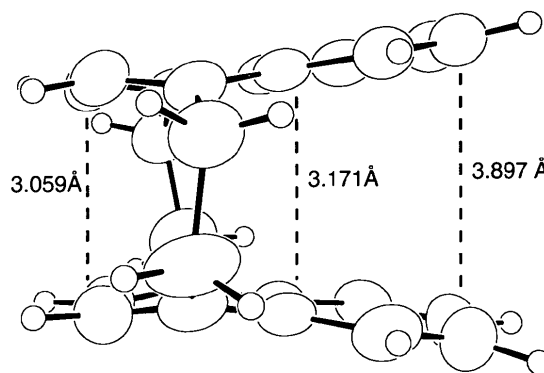

Fig. 3. Side view of (2) showing average inter-ring separations.

of the bridged ring. The extent of rotation can be approximated by the torsion angles C1—C11—C12—C13 [11.1 (4)°] and C16—C23—C24—C4 [12.5 (4)°]. The twisting of rings is not observed in (1) and establishes another mode of strain reduction in (2). Second, the non-parallel disposition of naphthalene rings causes the inter-ring separation to increase with distance from the bridged C atoms (Fig. 3). The non-bonded distances between overlapping atoms on opposite rings range from 3.053 (5) Å (C3···C15) and 3.066 (4) Å (C2···C14), nearest to the bridge, to 3.936 (5) Å (C7···C19) and 3.857 (4) Å (C6···C18) on the outer rings. As expected, the C9···C21 [3.186 (3) Å] and C10···C22 [3.156 (3) Å] distances exhibit intermediate values. Table 5 shows a comparison of selected non-bonded distances for (1), (2) and [2.2]paracyclophane.

An examination of Table 5 reveals that the average geometric parameters found in the present work compare favorably with those reported for [2.2]-paracyclophane (Hope, Bernstein & Trueblood, 1972). The exception is the higher α value in (2). Thus, the greater deformation of the bridged ring in (2) is taken as the primary strain-relieving mechanism and an indication of additional strain associated with overlapping napthalene rings.

Experimental

Isomer (1)

Crystal data

$C_{24}H_{20}$
$M_r = 308.43$
Monoclinic
$P2_1/c$
$a = 14.589 (3)$ Å
$b = 13.384 (3)$ Å
$c = 8.158 (3)$ Å
$\beta = 91.65 (3)°$
$V = 1592 (1)$ Å^3
$Z = 4$
$D_x = 1.29$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–18°$
$\mu = 0.067$ mm^{-1}
$T = 294$ K
Parallelepiped
$0.60 \times 0.30 \times 0.10$ mm
Transparent
Crystal source: Professor Harry Wasserman of Yale University

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical
$T_{min} = 0.9793$, $T_{max} = 0.9916$
4924 measured reflections
4623 independent reflections

2009 observed reflections
$[I > 3.0\sigma(I)]$
$R_{int} = 0.041$
$\theta_{max} = 29.97°$
$h = -20 \rightarrow 20$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 11$
3 standard reflections frequency: 120 min intensity decay: -1.80%

Refinement

Refinement on F
$R = 0.047$

$\Delta\rho_{max} = 0.180$ e Å^{-3}
$\Delta\rho_{min} = -0.085$ e Å^{-3}

$wR = 0.058$
$S = 1.347$
2009 reflections
298 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.008$

Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.30×10^{-6}
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) *for* (1)

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

	x	y	z	U_{eq}
C1A	−0.0068 (2)	0.0014 (2)	0.2423 (3)	0.0389 (6)
C2A	0.0839 (2)	0.0166 (2)	0.2159 (3)	0.0429 (7)
C3A	0.1126 (1)	0.0835 (2)	0.0948 (3)	0.0436 (7)
C4A	0.0514 (1)	0.1359 (2)	−0.0010 (3)	0.0381 (6)
C5A	−0.1077 (2)	0.2037 (2)	−0.0227 (3)	0.0455 (7)
C6A	−0.1970 (2)	0.2030 (2)	0.0231 (3)	0.0538 (8)
C7A	−0.2254 (2)	0.1359 (2)	0.1420 (3)	0.0544 (8)
C8A	−0.1645 (2)	0.0714 (2)	0.2132 (3)	0.0467 (7)
C9A	−0.0707 (1)	0.0714 (2)	0.1731 (3)	0.0370 (6)
C10A	−0.0419 (1)	0.1395 (2)	0.0507 (3)	0.0366 (6)
C11A	0.0761 (2)	0.1690 (2)	−0.1704 (3)	0.0492 (8)
C12A	−0.0372 (2)	−0.0977 (2)	0.3091 (3)	0.0492 (7)
C1B	0.4907 (2)	0.5119 (2)	0.2421 (3)	0.0423 (7)
C2B	0.5009 (2)	0.6084 (2)	0.1940 (3)	0.0469 (7)
C3B	0.4523 (2)	0.6464 (2)	0.0564 (3)	0.0463 (7)
C4B	0.3939 (1)	0.5879 (2)	−0.0363 (3)	0.0403 (6)
C5B	0.2958 (2)	0.4365 (2)	−0.0376 (3)	0.0511 (8)
C6B	0.2715 (2)	0.3473 (2)	0.0267 (4)	0.0627 (9)
C7B	0.3176 (2)	0.3108 (2)	0.1655 (4)	0.0661 (9)
C8B	0.3876 (2)	0.3639 (2)	0.2378 (3)	0.0547 (8)
C9B	0.4144 (1)	0.4578 (2)	0.1752 (2)	0.0373 (6)
C10B	0.3662 (1)	0.4955 (2)	0.0343 (3)	0.0370 (6)
C11B	0.3759 (2)	0.6112 (2)	−0.2153 (3)	0.0577 (8)
C12B	0.5696 (2)	0.4591 (2)	0.3316 (3)	0.0588 (9)

Table 2. *Selected geometric parameters* (Å, °) *for* (1)

C1A—C2A	1.363 (3)	C1B—C2B	1.359 (3)
C1A—C9A	1.427 (3)	C1B—C9B	1.424 (3)
C1A—C12A	1.505 (3)	C1B—C12B	1.519 (3)
C2A—C3A	1.407 (3)	C2B—C3B	1.406 (3)
C3A—C4A	1.364 (3)	C3B—C4B	1.369 (3)
C4A—C10A	1.437 (3)	C4B—C10B	1.427 (3)
C4A—C11A	1.505 (3)	C4B—C11B	1.509 (3)
C5A—C6A	1.365 (4)	C5B—C6B	1.355 (4)
C5A—C10A	1.409 (3)	C5B—C10B	1.410 (3)
C6A—C7A	1.394 (4)	C6B—C7B	1.389 (4)
C7A—C8A	1.358 (3)	C7B—C8B	1.364 (4)
C8A—C9A	1.415 (3)	C8B—C9B	1.416 (3)
C9A—C10A	1.425 (3)	C9B—C10B	1.422 (3)
C11A—C12A^i	1.574 (3)	C11B—C12B^{ii}	1.568 (4)
C2A—C1A—C9A	117.8 (2)	C2B—C1B—C9B	117.6 (2)
C2A—C1A—C12A	119.1 (2)	C2B—C1B—C12B	119.6 (2)
C9A—C1A—C12A	121.7 (2)	C9B—C1B—C12B	121.4 (2)
C1A—C2A—C3A	121.1 (2)	C1B—C2B—C3B	121.2 (2)
C2A—C3A—C4A	121.7 (2)	C2B—C3B—C4B	121.7 (2)
C3A—C4A—C10A	117.4 (2)	C3B—C4B—C10B	116.9 (2)
C3A—C4A—C11A	120.4 (2)	C3B—C4B—C11B	120.3 (2)
C10A—C4A—C11A	120.9 (2)	C10B—C4B—C11B	121.7 (2)
C6A—C5A—C10A	121.5 (2)	C6B—C5B—C10B	121.9 (2)
C5A—C6A—C7A	120.0 (2)	C5B—C6B—C7B	119.9 (2)
C6A—C7A—C8A	120.2 (2)	C6B—C7B—C8B	120.6 (2)
C7A—C8A—C9A	121.8 (2)	C7B—C8B—C9B	121.1 (2)
C1A—C9A—C8A	122.2 (2)	C1B—C9B—C8B	122.2 (2)
C1A—C9A—C10A	119.7 (2)	C1B—C9B—C10B	119.5 (2)
C8A—C9A—C10A	117.9 (2)	C8B—C9B—C10B	118.2 (2)
C4A—C10A—C5A	122.3 (2)	C4B—C10B—C5B	121.9 (2)
C4A—C10A—C9A	119.0 (2)	C4B—C10B—C9B	119.7 (2)

C5A—C10A—C9A	118.5 (2)	C5B—C10B—C9B	118.3 (2)
C4A—C11A—C12A^i	113.0 (2)	C4B—C11B—C12B^ii	112.6 (2)
C1A—C12A—C11A^i	112.2 (2)	C1B—C12B—C11B^ii	112.3 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, 1 - y, -z$.

Isomer (2)

Crystal data

$C_{24}H_{20}$
$M_r = 308.43$
Monoclinic
$P2_1/n$
$a = 8.371$ (3) Å
$b = 11.807$ (4) Å
$c = 16.704$ (8) Å
$\beta = 103.49$ (3)°
$V = 1605$ (2) Å^3
$Z = 4$
$D_x = 1.28$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11–19°$
$\mu = 0.067$ mm^{-1}
$T = 294$ K
Rectangular block
$0.50 \times 0.50 \times 0.40$ mm
Transparent
Crystal source: Professor Harry Wasserman of Yale University

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical
$T_{min} = 0.9775$, $T_{max} = 0.9932$
4981 measured reflections
4672 independent reflections

1555 observed reflections
$[I > 3.0\sigma(I)]$
$R_{int} = 0.029$
$\theta_{max} = 29.96°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 23$
3 standard reflections frequency: 120 min intensity decay: 0.22%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.056$
$S = 1.431$
1555 reflections
298 parameters
H atoms refined isotropically
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.017$

$\Delta\rho_{max} = 0.117$ e Å^{-3}
$\Delta\rho_{min} = -0.076$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.53×10^{-6}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
C1	0.4133 (3)	0.0413 (2)	0.6354 (2)	0.0545 (9)
C2	0.4612 (3)	-0.0003 (2)	0.7133 (2)	0.066 (1)
C3	0.5879 (4)	0.0510 (3)	0.7724 (2)	0.069 (1)
C4	0.6706 (3)	0.1427 (2)	0.7531 (2)	0.0598 (9)
C5	0.7562 (3)	0.2455 (2)	0.6398 (2)	0.063 (1)
C6	0.7366 (3)	0.2698 (2)	0.5589 (2)	0.072 (1)
C7	0.6112 (4)	0.2192 (3)	0.5007 (2)	0.071 (1)
C8	0.5058 (3)	0.1460 (2)	0.5250 (2)	0.0589 (9)
C9	0.5230 (3)	0.1171 (2)	0.6080 (1)	0.0484 (8)
C10	0.6533 (3)	0.1681 (2)	0.6674 (2)	0.0513 (8)
C11	0.2387 (3)	0.0252 (2)	0.5870 (2)	0.070 (1)
C12	0.1138 (4)	0.1047 (3)	0.6159 (2)	0.087 (1)
C13	0.1944 (3)	0.1963 (2)	0.6744 (2)	0.062 (1)

C14	0.2317 (4)	0.1794 (3)	0.7576 (2)	0.079 (2)
C15	0.3621 (4)	0.2371 (3)	0.8091 (2)	0.074 (2)
C16	0.4580 (3)	0.3101 (2)	0.7798 (2)	0.0586 (9)
C17	0.4682 (3)	0.4424 (2)	0.6652 (2)	0.0592 (9)
C18	0.4047 (4)	0.4820 (3)	0.5882 (2)	0.075 (1)
C19	0.2710 (4)	0.4296 (3)	0.5379 (2)	0.080 (1)
C20	0.2045 (3)	0.3373 (2)	0.5645 (2)	0.068 (1)
C21	0.2625 (3)	0.2946 (2)	0.6447 (1)	0.0486 (8)
C22	0.3974 (3)	0.3499 (2)	0.6978 (1)	0.0464 (8)
C23	0.6339 (4)	0.3289 (3)	0.8267 (2)	0.085 (1)
C24	0.7494 (4)	0.2260 (3)	0.8193 (2)	0.077 (1)

Table 4. Selected geometric parameters (Å, °) for (2)

C1—C2	1.361 (4)	C12—C13	1.507 (4)
C1—C9	1.432 (4)	C13—C14	1.366 (4)
C1—C11	1.508 (4)	C13—C21	1.431 (4)
C2—C3	1.406 (4)	C14—C15	1.399 (4)
C3—C4	1.364 (4)	C15—C16	1.345 (4)
C4—C10	1.436 (4)	C16—C22	1.425 (3)
C4—C24	1.512 (4)	C16—C23	1.514 (4)
C5—C6	1.354 (4)	C17—C18	1.355 (4)
C5—C10	1.406 (4)	C17—C22	1.411 (4)
C6—C7	1.388 (4)	C18—C19	1.380 (4)
C7—C8	1.363 (4)	C19—C20	1.345 (4)
C8—C9	1.401 (4)	C20—C21	1.409 (4)
C9—C10	1.426 (3)	C21—C22	1.421 (3)
C11—C12	1.563 (5)	C23—C24	1.575 (5)
C2—C1—C9	117.6 (2)	C12—C13—C21	120.8 (3)
C2—C1—C11	120.0 (3)	C14—C13—C21	117.1 (2)
C9—C1—C11	121.4 (2)	C13—C14—C15	121.0 (3)
C1—C2—C3	121.5 (3)	C14—C15—C16	122.3 (3)
C2—C3—C4	121.1 (3)	C15—C16—C22	116.8 (2)
C3—C4—C10	117.6 (2)	C15—C16—C23	119.8 (2)
C3—C4—C24	120.2 (3)	C22—C16—C23	122.3 (3)
C10—C4—C24	121.2 (2)	C18—C17—C22	121.7 (2)
C6—C5—C10	121.6 (2)	C17—C18—C19	120.4 (3)
C5—C6—C7	120.2 (3)	C18—C19—C20	120.1 (3)
C6—C7—C8	120.1 (3)	C18—C19—H19	118 (1)
C7—C8—C9	121.6 (2)	C20—C19—H19	121 (1)
C1—C9—C8	122.9 (2)	C19—C20—C21	121.8 (2)
C1—C9—C10	119.0 (2)	C13—C21—C20	122.9 (2)
C8—C9—C10	118.1 (2)	C13—C21—C22	118.7 (2)
C4—C10—C5	122.4 (2)	C20—C21—C22	118.4 (2)
C4—C10—C9	119.3 (2)	C16—C22—C17	122.6 (2)
C5—C10—C9	118.3 (2)	C16—C22—C21	120.1 (2)
C1—C11—C12	113.2 (2)	C17—C22—C21	117.4 (2)
C11—C12—C13	113.6 (2)	C16—C23—C24	112.8 (2)
C12—C13—C14	121.1 (3)	C4—C24—C23	112.8 (2)

Table 5. Selected average intramolecular distances and angles (Å, °)
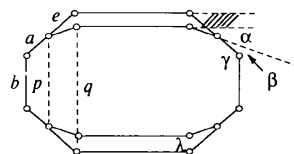
	(1)	(2)	[2.2]Paracyclophane*
a	1.510(2)	1.510(2)	1.514
b	1.571(3)	1.569(4)	1.569
e	1.396(1)	1.395(1)	1.394
p	2.756(3)	2.769(3)	2.78
q	3.068(2)	3.115(2)	3.09
α	12.8(4)	13.7(3)	12.6
β	11.1	10.0	11.2
γ	112.3(2)	113.1(1)	113.7
λ	117.4(1)	117.3(1)	117.3

* Hope, Bernstein & Trueblood (1972).

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Software*; data reduction: *Molen PROCESS* (Fair, 1990); program(s) used to solve

structures: direct methods in *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN BTABLE PTABLE CIF*.

We thank the Research Corporation for financial support.

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Triterpenoide. VII.† Über die Struktur von neuen 2-oxa- und 1,2-seco-Derivaten des Olenanolsäuremethylesters

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Abstract

The X-ray crystal structure analysis of 3β-hydroxy-28-methoxy-11,28-dioxo-2-oxaolean-12-ene-3,1-carbolactone, (2), and dimethyl 1,3,11-trioxo-1,2-secoolean-12-

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† 6. Mitteilung: Zaprutko (1994a).

ene-2,28-dioate, (3), confirms the structure of (2) and (3) previously derived by spectroscopic methods. The hydroxyl group at C(3) in (2) and the side chain at C(5) in (3) are in equatorial positions. In (3), the C(1)=O(4) carbonyl group is antiperiplanar with respect to the C(25) methyl group, the C(3)=O(1) carbonyl group synperiplanar relative to the C(5)—C(6) bond and anticlinal to the C(2)=O(3) carbonyl group. In both compounds, C(28), O(6), O(7) and C(31) in the C(17) ester group are coplanar; the torsion angles C(18)—C(17)—C(28)—O(6) are quite different. The position of the ester group in (2) is stabilized by an intermolecular hydrogen bond. In both compounds, ring *C* has a slightly distorted sofa conformation; all other rings have deformed chair conformations. Rings *D* and *E* are *cis*-fused.

Kommentar

Die Einwirkung von Chromtrioxyd auf Oleanolsäure-methylester (1) in Eisessig unter Zusatz von Schwefelsäure führt neben anderen Oleanolsäurederivaten zur Verbindung (2). Bei Behandlung mit Diazomethan erfolgt eine Umwandlung von (2) zu (3) (Zaprutko, 1994b).

(1)   (2)

(3)
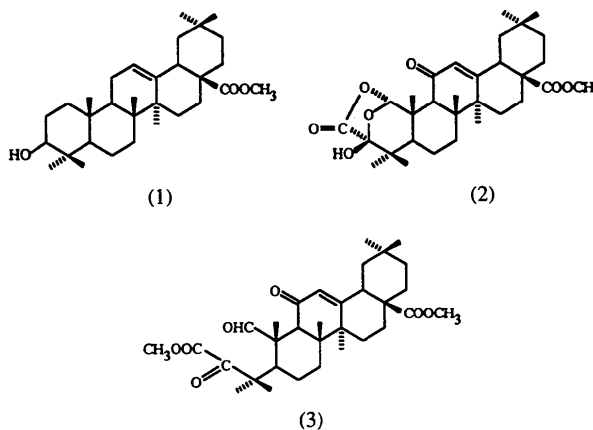
Aufgrund spektroskopischer Untersuchungen (IR, MS, ^{1}H-, ^{13}C-, ^{2}D-NMR) hat Zaprutko (1994b) für diese Verbindungen die im Schema aufgeführten Strukturen vorgeschlagen. In dieser Mitteilung werden die Strukturen von (2) and (3) durch Röntgenstruktur-analysen bestätigt.

Die Laktonbrücke in (2) mit der mit dem C(3) Atom benachbarten Carbonylgruppe verbindet C(1) und C(3). Die an das zuletzt genannte C Atom gebundene Hydroxylgruppe nimmt die äquatoriale, die Carbonylgruppe des Laktonringes die axiale Lage ein.

Der Ring *A* von (2), in dem das O(2) Atom eine Methylengruppe ersetzt, liegt in einer verzerrten Sesselform vor.

Die C(1)=O(4) Carbonylgruppe in (3) nimmt eine antiperiplanare Stellung zur C(25) Methylgruppe