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

N—C1	1.510 (5)	C1—C12	1.518 (6)
N—C2	1.516 (7)	C2—C22	1.508 (5)
C1—C11	1.508 (7)	C2—C21	1.516 (5)
C1—N—C2	117.9 (3)	C22—C2—N	110.4 (5)
C11—C1—N	110.7 (3)	C22—C2—C21	112.7 (4)
C11—C1—C12	112.3 (4)	N—C2—C21	107.5 (5)
N—C1—C12	107.2 (3)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
N—H(3)···Br^i	0.82 (4)	2.51 (4)	3.325 (3)	173 (4)
N—H(4)···Br	0.81 (4)	2.55 (4)	3.350 (4)	171 (4)

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

The *SHELX* input files were prepared using the program *UTILITY* (Pickardt, 1994). All non-H-atoms were refined anisotropically and all H atoms were refined isotropically. The crystal was a racemic twin consisting of two individuals in the ratio 2:1, as established with a *TWIN/BASF* refinement (*SHELXL*93; Sheldrick, 1993).

Data collection: *Stadi*-4 *Software* (Stoe & Cie, 1995a). Cell refinement: *Stadi*-4 *Software*. Data reduction: *X-RED*, (Stoe & Cie, 1995b). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *PLUTON*92 (Spek, 1992), *PLATON* (Spek, 1990), *ZORTEP* (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: *SHELXL*93.

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A Substituted *cis,trans,cis,cis*-[4.5.5.5]Fenestrene

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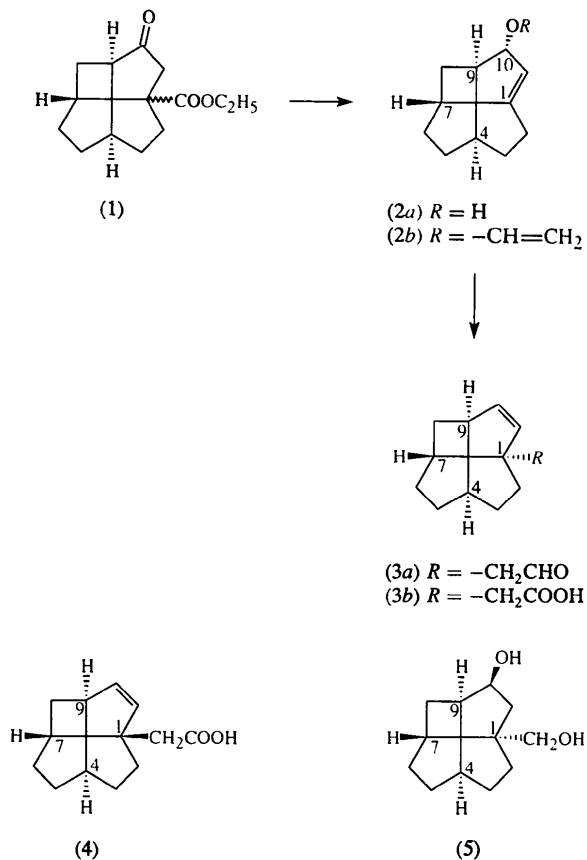
Abstract

The title compound, *rel*-(1S,4R,7R,9S)-tetracyclo-[5.4.1.0^{4,12}.0^{9,12}]dodec-10-enyl-1-acetic acid, $C_{14}H_{18}O_2$, has been prepared and its structure elucidated. The geometry of the central C(C)$_4$ substructure shows a considerable distortion from an ideal tetrahedral arrangement towards planarity, with two opposite bond angles of 119.2 (2) and 134.9 (2)°. The other bridgehead bond angle of the *trans*-bicyclo[3.3.0]octane subunit is also large, with a value of 128.0 (2)°.

Comment

Tetracyclic compounds, where four small rings share a common C atom, are of considerable interest for their propensity towards planarizing distortions at the central C atom, leading to two opposite bond angles markedly larger than 109.47° (Luef & Keese, 1992, 1993). In our systematic search for fenestranes with strong planarizing distortions, it was found that the simultaneous incorporation of *trans*-bicyclo[3.3.0]octane subunits and bridgehead substituents led to enlarged opposite bond angles at the central C atom. In order to verify this computational result and to compare the structure of (3b) with that of the structurally similar *cis,trans,cis,cis*-[4.5.5.5]fenestranediol, (5) (Hirschi, Luef, Gerber & Keese, 1992), the known compound (2a) was prepared from (1) by a new route, transformed *via* (2b) into (3a) by a previously published method (Grieco, Brandes, McCann & Clark, 1989) and oxidized with Jones reagent (acetone, 298 K) to compound (3b).

(1)

(2a) R = H
(2b) R = -CH=CH₂

(3a) R = -CH₂CHO
(3b) R = -CH₂COOH

(4)

(5)

The structure of (3b) (Fig. 1) shows unique deformations of the central $C(C)_4$ substructure and the trans-bicyclo[3.3.0]octane subunit. Whereas in (4), the epimer of (3b), the bond angles of the central C atom, C4—C12—C9 and C1—C12—C7, are 124.9 (2) and 122.4 (2)°, respectively, the corresponding values in (3b) are 134.9 (2) and 119.2 (2)°. Furthermore, the bond angle C2—C1—C11 in (3b) [128.0 (2)°] is considerably larger than that observed in (4) (113.0°; Grieco et al., 1989). Other salient structural features are the bridgehead bond angles C3—C4—C5 and C8—C9—

C10, which are approximately 5° larger in compound (4) (117.3 and 114.8°, respectively) than in (3b) [112.3 (2) and 110.0 (2)°]. It is apparent that inversion of the bridgehead geometry at C1 has led to planarizing distortions at the central C atom. This is further supported by the structure of (5), where the planarizing distortions were slightly decreased due to the formal replacement of the double bond by a secondary hydroxy group. The enlargement of the bond angle C2—C1—C11 to 124.3° is also observed.

Compared with the average bond angles of 126 (4) and 127 (6)° determined from 19 trans-bicyclo[3.3.0]-octane subunits retrieved from the Cambridge Structural Database (Allen & Kennard, 1993), the C4—C12—C9 bridgehead angle of 134.9 (2)° in (3b) is significantly larger (Hirschi et al., 1992).

Experimental

Compound (1) was reduced to the corresponding diol with LiAlH₄ in diethyl ether and reoxidized to the ketoacid with Jones reagent. Decarboxylation to the α,β-unsaturated ketone was performed with Cu(OAc)₂ and Pb(OAc)₄ in pyridine and benzene at 353 K. Subsequent reduction with 9-borabicyclo-[3.3.1]nonane (9-BBN) in tetrahydrofuran gave a 1.5:1 mixture of (2a) and its 10-epimer in 45% overall yield (Guidetti-Grept, 1994). Compound (2a) was transformed via (2b) into (3a) by the previously published method of Grieco, Brandes, McCann & Clark (1989) and oxidized with Jones reagent (acetone, 298 K) to compound (3b). Crystals of m.p. 399–401 K were obtained from 'BuOMe/octane solution.

Crystal data

$C_{14}H_{18}O_2$	Mo $K\alpha$ radiation
$M_r = 218.28$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 16
$P\bar{1}$	reflections
$a = 5.618 (4)$ Å	$\theta = 5.7–20.1°$
$b = 7.995 (4)$ Å	$\mu = 0.082$ mm^{-1}
$c = 13.428 (6)$ Å	$T = 293 (2)$ K
$\alpha = 77.85 (4)°$	Flat elongated prism
$\beta = 85.55 (6)°$	$0.35 \times 0.33 \times 0.20$ mm
$\gamma = 80.46 (4)°$	Colourless
$V = 580.9 (6)$ Å^3	
$Z = 2$	
$D_x = 1.248$ Mg m^{-3}	
D_m not measured	

Data collection

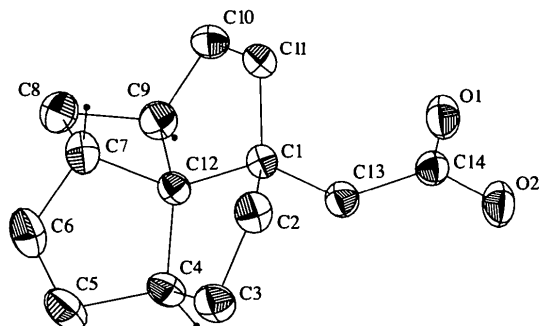|	
Siemens P4/RA diffractometer	2222 observed reflections
	$[I > 2\sigma(I)]$
ω scans	$\theta_{max} = 24.99°$
Absorption correction:	$h = -1 \rightarrow 7$
empirical via ψ scan	$k = -11 \rightarrow 11$
(XSCANS; Siemens, 1994)	$l = -18 \rightarrow 18$
$T_{min} = 0.939$, $T_{max} =$	3 standard reflections
1.000	monitored every 100
3129 measured reflections	reflections
3129 independent reflections	intensity decay: 12%

Fig. 1. The molecular structure of the title compound showing the atomic labelling. Displacement ellipsoids are shown at 30% probability. Only the three bridgehead H atoms are represented, with arbitrary radii.

Refinement

Refinement on F^2
$R(F) = 0.0419$
$wR(F^2) = 0.1181$
$S = 1.029$
3103 reflections
218 parameters
H atoms freely refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.2214P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.149$ e Å^{-3}
$\Delta\rho_{min} = -0.165$ 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)*

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

	x	y	z	U_{eq}
O1	0.5489 (3)	0.6584 (2)	0.40420 (11)	0.0626 (5)
O2	0.1972 (3)	0.6311 (2)	0.48825 (12)	0.0687 (5)
C1	0.3640 (3)	0.9838 (2)	0.27865 (13)	0.0404 (5)
C2	0.5198 (4)	1.0752 (3)	0.3318 (2)	0.0545 (6)
C3	0.3332 (5)	1.2246 (3)	0.3615 (2)	0.0614 (6)
C4	0.1182 (4)	1.2628 (2)	0.2886 (2)	0.0515 (5)
C5	0.0933 (6)	1.4462 (3)	0.2231 (2)	0.0729 (8)
C6	0.3092 (6)	1.4409 (3)	0.1478 (2)	0.0755 (8)
C7	0.3375 (5)	1.2613 (3)	0.1242 (2)	0.0577 (6)
C8	0.1534 (5)	1.2307 (3)	0.0518 (2)	0.0685 (7)
C9	0.0960 (4)	1.0732 (3)	0.13260 (15)	0.0532 (6)
C10	0.2846 (5)	0.9173 (3)	0.1249 (2)	0.0607 (6)
C11	0.4427 (4)	0.8777 (3)	0.1976 (2)	0.0535 (6)
C12	0.2110 (3)	1.1405 (2)	0.21572 (13)	0.0415 (5)
C13	0.2047 (4)	0.8798 (3)	0.3597 (2)	0.0478 (5)
C14	0.3374 (4)	0.7121 (3)	0.41852 (14)	0.0454 (5)

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

O1—C14	1.209 (2)	C5—C6	1.519 (4)
O2—C14	1.310 (2)	C6—C7	1.516 (3)
C1—C11	1.513 (3)	C7—C8	1.554 (3)
C1—C12	1.527 (3)	C7—C12	1.594 (3)
C1—C2	1.529 (3)	C8—C9	1.540 (3)
C1—C13	1.546 (3)	C9—C10	1.512 (3)
C2—C3	1.550 (3)	C9—C12	1.560 (3)
C3—C4	1.564 (3)	C10—C11	1.323 (3)
C4—C12	1.529 (3)	C13—C14	1.514 (3)
C4—C5	1.533 (3)		
C11—C1—C12	100.02 (15)	C1—C12—C4	106.21 (15)
C11—C1—C2	128.0 (2)	C1—C12—C9	106.72 (15)
C12—C1—C2	100.1 (2)	C4—C12—C9	134.9 (2)
C11—C1—C13	107.4 (2)	C1—C12—C7	119.2 (2)
C12—C1—C13	110.8 (2)	C4—C12—C7	103.0 (2)
C2—C1—C13	109.2 (2)	C9—C12—C7	86.78 (15)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PEANUT* (Hummel, Hauser & Bürgi, 1990). Software used to prepare material for publication: *SHELXL*93.

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3a,7a-Dibromo-2-butyl-4,7-methano-1,3,3a,4,7,7a-hexahydro-2*H*-isoindole-1,3-dione from the Reaction of 3,4-Dibromo-1-butylmaleimide with Cyclopentadiene

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Abstract

It is shown that reaction of 1-butylpyrrole successively with *N*-bromosuccinimide then nitric acid gives 3,4-dibromo-1-butylmaleimide since the latter then undergoes Diels–Alder cycloaddition with cyclopentadiene to give the title compound, $C_{13}H_{15}Br_2NO_2$.

Comment

Interest in the cycloaddition reactions of oxidopyrazini-ums (Yates, Peters, Beddoes, Scopes, & Joule, 1995) drew our attention to the recent report (Brockmann