Structure Determination of Bicyclo[1.1.1]pentane Diesters

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We have synthesized and determined the crystal and molecular structures of three bicyclo[1.1.1]pentanes substituted by a spirodioxolane ring and carrying two carboxylate groups in endo,endo, exo,exo, and endo,exo orientations. The central nonbonding 1⋯3 contact of 1.903 Å is one of the shortest nonbonding C⋯C distances known. Short intramolecular contacts of the nucleophilic oxygen atoms of the carboxylate groups (O⋯C, 2.61 Å) generating deformations from the planar geometry of the carbonyl groups are also observed.

Introduction

With our goal the structure determination of small polycyclic compounds,[1] we determined the structures of the endo,endo, exo,exo, and endo,exo isomers of the bicyclo[1.1.1]pentane-4′,5′-dicarboxylates **1**, **2**, and **3** by X-ray analysis (Figure 1).

Synthesis of the bicyclo[1.1.1]pentane isomers was carried out as shown in Scheme I. Thus, the diol **4**[1b] was oxidized to the diacid **5** with ruthenium dioxide/sodium periodate. Treatment of the diacid **5** with diazomethane yielded the dimethyl ester **6**, which was transformed by using ethylene glycol and *p*-toluenesulfonic acid to the ketal diester **7**. The latter was opened by reductive cleavage of the carbon–carbon bond using sodium naphthalenide[2,3] to a mixture of *endo,endo-*, *exo,exo-*, and *endo,exo*-bicyclo[1.1.1]pentane diesters **1**, **2**, and **3**, which were separated into the pure isomers by chromatography on silica gel.

Bicyclo[1.1.1]pentanes exhibit extremely short nonbonding C1⋯C3 distances. For example, bicyclo[1.1.1]pentane, studied by electron diffraction,[4] shows a nonbonding C1⋯C3 distance of 1.874 Å, and a bicyclo[1.1.1]pentane derivative, examined by X-ray crystallography,[5] shows a C1⋯C3 distance of 1.89 Å. Large NMR coupling constants arise from this contact, and back lobe interactions have been discussed[5,7] in this connection. The nonbonding distances in the bicyclopentane series are not far from the bonding distance[8] calculated for the [1.1.1]propellane recently synthesized,[9] and excellent agreement with theoretical values calculated[6,8c] for bicyclo[1.1.1]pentane has also been reported.

Scheme I

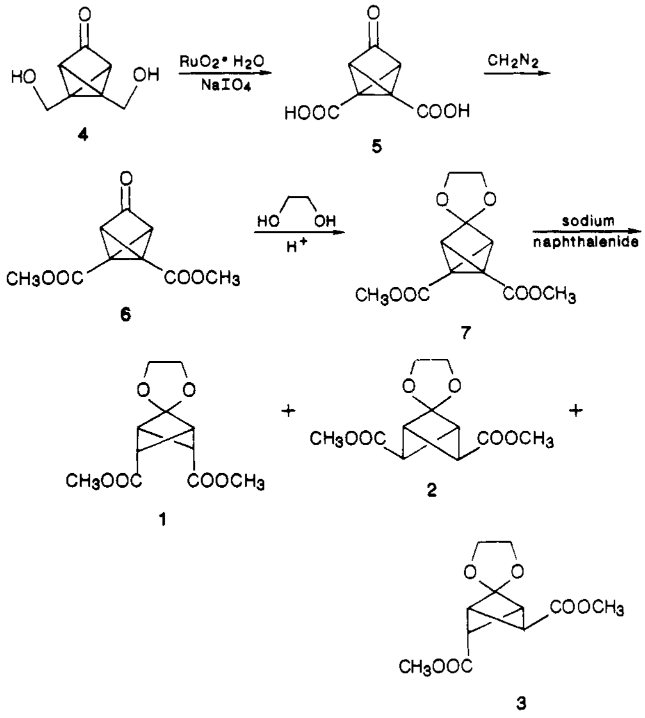

Table I. Bond Lengths (Å) of 1–3

	1a	1b	2	3a	3b
C1–C2	1.555 (3)	1.551 (3)	1.547 (3)	1.560 (4)	1.554 (5)
C1–C4	1.551 (3)	1.546 (3)	1.552 (3)	1.556 (4)	1.553 (5)
C1–C5	1.548 (3)	1.550 (3)	1.527 (2)	1.549 (5)	1.545 (6)
C2–C3	1.553 (3)	1.559 (3)	1.545 (3)	1.554 (6)	1.552 (6)
C2–C10	1.495 (3)	1.502 (3)	1.498 (3)	1.488 (4)	1.500 (4)
C3–C4	1.558 (3)	1.564 (3)	1.546 (3)	1.555 (4)	1.556 (5)
C3–C5	1.535 (3)	1.536 (3)	1.538 (3)	1.541 (5)	1.543 (5)
C4–C14	1.502 (3)	1.493 (3)	1.499 (3)	1.497 (6)	1.505 (4)
C5–O6	1.399 (3)	1.396 (3)	1.399 (2)	1.403 (3)	1.397 (3)
C5–O9	1.405 (3)	1.412 (3)	1.398 (2)	1.397 (6)	1.407 (4)
O6–C7	1.450 (3)	1.442 (3)	1.407 (3)	1.419 (7)	1.422 (5)
C7–C8	1.497 (4)	1.492 (4)	1.475 (4)	1.478 (5)	1.485 (5)
C8–O9	1.428 (3)	1.430 (4)	1.384 (3)	1.423 (5)	1.425 (5)
C10–O11	1.203 (3)	1.199 (3)	1.189 (3)	1.199 (4)	1.196 (5)
C10–O12	1.333 (3)	1.330 (3)	1.325 (3)	1.328 (5)	1.320 (6)
O12–C13	1.445 (4)	1.442 (3)	1.446 (4)	1.443 (5)	1.451 (5)
C14–O15	1.196 (3)	1.194 (3)	1.197 (3)	1.193 (4)	1.193 (6)
C14–O16	1.334 (3)	1.334 (3)	1.331 (2)	1.321 (5)	1.311 (6)
O16–C17	1.442 (4)	1.445 (4)	1.438 (3)	1.459 (8)	1.449 (7)

Compounds **1** and **3** crystallize with two independent molecules in the asymmetric unit. Taken together with **2**, the bicyclo[1.1.1]pentane group was determined five

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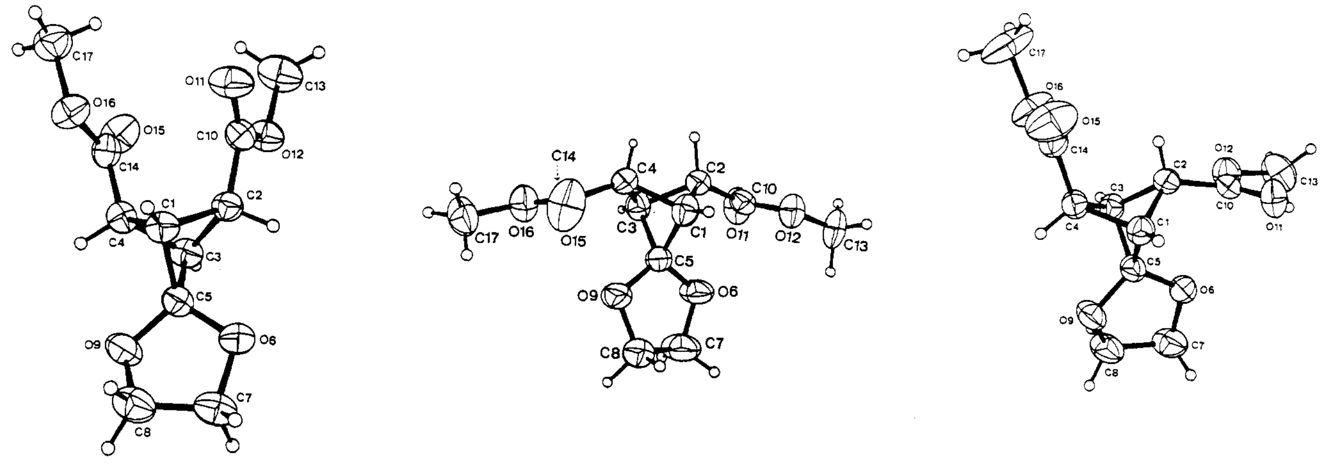

1 2 3

Figure 1. Molecular structures of bicyclo[1.1.1]pentane diesters 1, 2, and 3.

Table II. Bond Angles (deg) of 1–3

	1a	**1b**	**2**	**3a**	**3b**
C1–C2–C3	75.5 (2)	75.5 (2)	75.7 (1)	75.5 (2)	75.6 (3)
C1–C4–C3	75.5 (2)	75.4 (2)	75.5 (1)	75.6 (2)	75.5 (2)
C1–C5–C3	76.2 (2)	76.1 (2)	76.5 (1)	76.2 (2)	76.1 (2)
C1–C5–O6	119.3 (2)	119.3 (2)	117.1 (2)	117.2 (3)	117.6 (3)
C1–C5–O9	116.8 (2)	117.1 (2)	118.2 (2)	119.0 (2)	119.0 (3)
C1–C2–C10	120.5 (2)	120.4 (2)	122.5 (2)	123.2 (3)	123.1 (3)
C1–C4–C14	121.5 (2)	120.2 (2)	120.7 (2)	119.6 (3)	119.6 (3)
C2–C3–C1	52.3 (1)	52.1 (1)	52.2 (1)	52.4 (2)	52.3 (2)
C2–C1–C4	88.0 (2)	88.5 (2)	85.5 (1)	86.5 (2)	86.6 (3)
C2–C3–C4	87.8 (2)	87.6 (2)	85.8 (2)	86.7 (3)	86.6 (3)
C2–C1–C5	85.5 (2)	85.5 (2)	86.6 (1)	86.4 (2)	86.6 (3)
C2–C3–C5	86.0 (2)	85.7 (2)	86.2 (1)	86.9 (3)	86.8 (3)
C2–C10–O11	126.2 (2)	125.9 (2)	125.0 (2)	124.3 (3)	123.7 (4)
C2–C10–O12	110.4 (2)	110.6 (2)	111.1 (2)	111.8 (3)	111.6 (3)
C3–C1–C2	52.2 (1)	52.5 (1)	52.1 (1)	52.1 (2)	52.2 (2)
C3–C1–C4	52.4 (1)	52.7 (1)	52.1 (1)	52.2 (1)	52.3 (2)
C3–C1–C5	51.6 (1)	51.6 (1)	52.0 (1)	51.7 (2)	51.9 (2)
C3–C5–O6	117.3 (2)	117.3 (2)	118.9 (2)	118.5 (3)	118.7 (3)
C3–C5–O9	118.5 (2)	118.4 (2)	116.7 (2)	116.7 (3)	116.5 (3)
C3–C2–C10	120.8 (2)	120.1 (2)	121.9 (2)	120.5 (3)	120.5 (3)
C3–C4–C14	121.3 (2)	121.6 (2)	122.6 (2)	118.5 (3)	118.8 (3)
C4–C3–C1	52.1 (1)	51.9 (1)	52.4 (1)	52.2 (2)	52.2 (2)
C4–C1–C5	85.0 (2)	85.3 (2)	86.4 (1)	85.2 (2)	85.6 (3)
C4–C3–C5	85.2 (2)	85.2 (2)	86.2 (1)	85.5 (2)	85.5 (3)
C4–C14–O15	125.3 (2)	125.4 (2)	124.7 (2)	124.7 (4)	124.2 (4)
C4–C14–O16	110.6 (2)	111.6 (2)	111.1 (2)	111.3 (3)	111.5 (3)
C5–C3–C1	52.2 (1)	52.3 (1)	51.5 (1)	52.1 (2)	52.0 (2)
C5–O6–C7	105.1 (2)	104.8 (2)	107.7 (2)	108.6 (3)	109.0 (2)
C5–O9–C8	109.0 (2)	108.2 (2)	109.1 (2)	105.6 (3)	105.6 (3)
O6–C7–C8	102.8 (2)	102.3 (2)	103.7 (2)	104.1 (3)	103.9 (3)
O6–C5–O9	106.8 (2)	106.7 (2)	107.3 (2)	107.1 (3)	107.0 (2)
C7–C8–O9	104.2 (2)	104.2 (2)	105.6 (3)	103.3 (3)	103.4 (3)
C10–O12–C13	116.5 (2)	116.7 (2)	115.7 (2)	116.8 (3)	116.1 (4)
O11–C10–O12	123.5 (2)	123.4 (2)	123.6 (2)	123.8 (3)	124.5 (3)
C14–O16–C17	115.6 (2)	115.3 (2)	116.2 (2)	116.6 (3)	117.1 (4)
O15–C14–O16	124.0 (2)	123.0 (2)	124.1 (2)	123.9 (4)	124.3 (3)

times. The four-membered rings within this group are folded by 57–67° (deviation from planarity) in contrast to the folding angles of only 20–35° in normal, unbridged cyclobutane derivatives.[10] Any consequences for the bond lengths of this group which might have emerged from the large folding angles were not detected. The average C–C bond length of the bicyclo[1.1.1]pentane group in **1**–**3** is 1.549 (8) [30] Å (Table I; the number in parentheses after an averaged value is the scatter, and the second figure, in brackets, gives the number of bond lengths averaged) compared to 1.55 (2) [46] Å for the bond length of the four-membered rings of the cyclobutanecarboxylates.[11]

Table III. Short Intramolecular Contacts (Å) in 1–3

	1a	**1b**	**2**	**3a**	**3b**
C1···C3	1.903 (3)	1.902 (3)	1.898 (3)	1.907 (3)	1.903 (6)
C1···O6	2.544 (3)	2.543 (3)	2.498 (1)	2.521 (4)	2.518 (4)
C1···O9	2.517 (3)	2.528 (3)	2.511 (2)	2.540 (4)	2.544 (5)
C3···O6	2.505 (3)	2.504 (3)	2.531 (3)	2.531 (4)	2.530 (4)
C3···O9	2.527 (3)	2.532 (3)	2.501 (3)	2.503 (5)	2.509 (4)
C2···C4	2.157 (3)	2.161 (3)	2.104 (3)	2.135 (5)	2.131 (4)
C2···C5	2.106 (3)	2.104 (3)	2.108 (3)	2.129 (6)	2.125 (4)
C4···C5	2.093 (3)	2.097 (3)	2.108 (3)	2.102 (5)	2.104 (4)
O6···O9	2.250 (2)	2.252 (2)	2.252 (2)	2.253 (3)	2.255 (3)
C5···C7	2.261 (4)	2.248 (4)	2.266 (3)	2.291 (6)	2.296 (5)
C5···C8	2.306 (4)	2.302 (4)	2.267 (4)	2.246 (7)	2.256 (5)
O6···C10			2.616 (3)	2.617 (6)	2.623 (4)
O9···C14			2.569 (2)		
C2···O6	2.655 (3)	2.648 (3)	2.667 (3)	2.682 (6)	2.684 (4)
C4···O9	2.619 (3)	2.631 (3)	2.647 (3)	2.635 (6)	2.639 (4)

The bond distances of the carboxylate groups in **1**–**3** compare well with the corresponding values in cyclobutanecarboxylates.

The bond angles, with an average value of 86.2 (8)° [30] (Table II) on the bridgehead carbon atoms C1 and C3, are larger than the corresponding angles on the spiro carbon atom C5 and the atoms C2 and C4, which are substituted by the carboxylate groups. Therefore, the four-membered rings in **1**–**3** are compressed along C1···C3. This 1···3 contact has a distance of 1.903 (3) [5] Å (Table I), which is also among the shortest known nonbonding C···C distances. The 1···3 contacts between atoms C2, C4, and C5 have distances of 2.10–2.16 Å (Table III).

The endo and exo carboxylate groups have parallel orientations relative to the four-membered ring. The π-orbitals of the carbonyl groups are perpendicular (±8°) to the Walsh orbitals[8a] of the bicyclo[1.1.1]pentane. Therefore, a substituent effect cannot be detected. Chemically equivalent bonds of the carbonyl groups in **1**–**3** have equal lengths irrespective of the endo or exo orientation of the carboxylate substituents, and they are comparable to the bond lengths of cyclobutanecarboxylate derivatives.[11]

The substituents around the bicyclo[1.1.1]pentane nucleus of **1**–**3** have close contacts, which give rise to two different nucleophilic orientations. The oxygen atoms of

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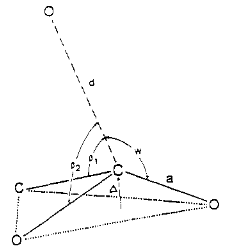
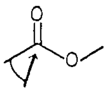
Table IV. Distortions of the Carbonyl Groups Attacked by Nucleophilic Oxygen Atoms[a]





molecule	N	E	d	Δ	a	W
1a	O11	C14	3.037 (3)	0.023 (3)	1.203 (3)	98.4 (2)
1a	O15	C10	3.069 (3)	0.013 (3)	1.196 (3)	96.6 (2)
1b	O11	C14	3.075 (3)	0.013 (3)	1.199 (3)	98.7 (2)
1b	O15	C10	3.037 (3)	0.018 (3)	1.194 (3)	100.6 (2)
2	O6	C10	2.616 (3)	0.038 (3)	1.189 (3)	104.2 (2)
2	O9	C14	2.569 (2)	0.032 (3)	1.197 (3)	101.8 (1)
3a	O6	C10	2.617 (6)	0.034 (4)	1.199 (4)	99.7 (3)
3b	O6	C10	2.623 (4)	0.035 (5)	1.195 (5)	99.9 (3)

molecule	O6···C10–C2, β_1	O6···C10–O12, β_2	O9···C14–C4, β_1	O9···C14–O16, β_2
2	75.4 (1)	93.6 (1)	76.2 (1)	94.6 (1)
3a	76.1 (2)	97.6 (3)		
3b	75.8 (2)	97.5 (2)		

[a] N = nucleophile (oxygen atom); E = electrophile (carbonyl C atom); d = distance N···E (Å); Δ = deviation of the carbonyl C atom from the C,O,O plane (Å); a = C=O distance (Å); W = O···C=O angle.

the dioxolane rings approach the carbonyl groups of the exo oriented carboxylate substituents of **2** and **3**, and both carbonyl groups of the endo-oriented carboxylates in **1** have mutual nucleophilic approaches. X-ray structure investigations[12] have established that tetrahedron-like distortions of carboxyl groups are observed if a nucleophile is within a short distance of the central carbon atom of this group. Our results are in agreement with these findings.[12] The oxygen atoms O6 and O9 of the dioxolane rings have very short contacts, on the order of 2.61 Å (Table IV), to the C10 (**2**, **3**) and C14 (**2**) carbon atoms of the exo carbonyl groups. The van der Waals distance is 3.1 Å. The electrophilic carbon atoms are shifted by 0.035 Å (Table IV) out of the plane of the carbonyl group in the direction of the nucleophilic oxygen atoms. In accord with the angle of attack, the O···C=O angle is 101° (Table IV). The corresponding distances of the carbonyl oxygen atoms to the neighboring carbonyl carbon atoms in compound **1** are somewhat longer than the O···C distances in **2** and **3**. Therefore the deviations from planarity of the carbonyl groups in **1** are smaller (Table IV). The distortions generated by an oxygen atom acting as a nucleophile are smaller than those due to a nitrogen atom because of the weaker nucleophilic character of oxygen.[12] In a more detailed analysis of the preferred nucleophilic approach geometry of an oxygen atom to a carboxylate group according to the "approach vector analysis method"[13] the O···C–C angle should be smaller than the O···C–O angle. The corresponding angles in **2** and **3** are β_1 = 76° and β_2 = 96° (Table IV).

The dioxolane rings of **1–3** have envelope or half-chair forms. Because of disorder effects the C7–C8 bonds are short (Table I). Thus, the bonds C5–O6 and C5–O9 (Table I) are shorter by 0.02 Å than in other dioxolane derivatives.[11] Conjugation effects with the Walsh orbitals of the bicyclo[1.1.1]pentane system are probably responsible for this effect.

Table V. Crystallographic Data of 1–3

	1	2	3
formula		$C_{11}H_{14}O_6$	
molecular weight		242.2	
size of the crystal, mm	0.6 × 0.3 × 0.3	0.4 × 0.35 × 0.5	0.5 × 0.3 × 0.3
solvent		ether/n-pentane	
space group	$P2_1/n$	$Pbca$	Cc
Z	8	8	8
density (calcd), g/cm^3	1.42	1.39	1.37
θ range, deg	1.5–26	1.5–28	1.5–28
radiation	Mo Kα	Mo Kα	Mo Kα
diffractometer	Siemens AED	Siemens AED	Nonius CAD4
cell dimensions			
a, Å	12.802 (1)	18.602 (3)	12.831 (1)
b, Å	7.574 (1)	8.720 (2)	11.364 (1)
c, Å	23.513 (3)	14.185 (2)	17.306 (2)
β, deg	94.395 (11)	90.0	111.745 (7)
unique reflctns	4991	2787	2748
unobsd reflctns	2206	1089	750
R factor	0.055	0.050	0.031

Experimental Section

The X-ray data (Table V) were collected on automatic diffractometers with Mo Kα radiation (graphite monochromator, ω–2θ scan). The LP correction has been applied; the absorption effects correction has been neglected. The structures have been solved by direct methods (MULTAN[14]). The structural parameters (C and O anisotropic, H isotropic) have been refined in a full-matrix technique. Further details are listed in Table V. The atomic coordinates are given in Table VI.

Syntheses. 3-Oxotricyclo[2.1.0.0^{2,5}]pentane-1,5-dicarboxylic Acid (5). Sodium periodate (7.610 g, 35.57 mmol) and ruthenium dioxide (0.782 mmol) were added to an ice-cold solution of 943 mg (6.73 mmol) of 1,5-bis(hydroxymethyl)tricyclo[2.1.0.0^{2,5}]pentan-3-one[15] in 64 mL of 1:1 acetone–water. The resulting suspension was stirred vigorously for 3.5 h while the temperature was maintained between 0 and 20 °C. A thin-layer

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Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^3$ Å^2) of 1–3

	atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{equ}
1	C1A	−1858 (2)	5367 (3)	1304 (1)	37 (1)
	C2A	−2169 (2)	6794 (3)	1735 (1)	40 (1)
	C3A	−2975 (2)	7026 (3)	1213 (1)	40 (1)
	C4A	−2054 (2)	6763 (3)	825 (1)	37 (1)
	C5A	−3048 (2)	5004 (3)	1207 (1)	40 (1)
	O6A	−3569 (1)	4204 (2)	1641 (1)	51 (1)
	C7A	−3725 (2)	2387 (4)	1461 (1)	54 (2)
	C8A	−3907 (2)	2548 (4)	827 (1)	52 (2)
	O9A	−3397 (1)	4159 (2)	696 (1)	51 (1)
	C10A	−1425 (2)	8246 (4)	1917 (1)	41 (1)
	O11A	−1611 (1)	9803 (3)	1899 (1)	63 (1)
	O12A	−509 (1)	7578 (2)	2123 (1)	47 (1)
	C13A	294 (2)	8835 (4)	2310 (1)	55 (2)
	C14A	−1279 (2)	8212 (3)	741 (1)	39 (1)
	O15A	−347 (1)	8061 (2)	797 (1)	55 (1)
	O16A	−1774 (1)	9687 (2)	564 (1)	48 (1)
	C17A	−1107 (3)	11173 (5)	466 (2)	67 (2)
	C1B	1876 (2)	6881 (3)	3711 (1)	36 (1)
	C2B	2250 (2)	5511 (3)	3280 (1)	38 (1)
	C3B	2982 (2)	5214 (3)	3832 (1)	40 (1)
	C4B	1995 (2)	5444 (3)	4178 (1)	38 (1)
	C5B	3057 (2)	7236 (3)	3862 (1)	39 (1)
	O6B	3642 (1)	8075 (2)	3464 (1)	49 (1)
	C7B	3754 (2)	9869 (4)	3664 (1)	53 (2)
	C8B	3884 (2)	9635 (4)	4295 (1)	52 (2)
	O9B	3339 (1)	8030 (2)	4395 (1)	53 (1)
	C10B	1530 (2)	4064 (3)	3055 (1)	40 (1)
	O11B	1739 (1)	2522 (2)	3045 (1)	60 (1)
	O12B	622 (1)	4728 (2)	2841 (1)	50 (1)
	C13B	−168 (2)	3479 (4)	2635 (1)	52 (2)
	C14B	1192 (2)	4021 (3)	4200 (1)	39 (1)
	O15B	271 (1)	4206 (2)	4097 (1)	63 (1)
	O16B	1624 (1)	2487 (2)	4370 (1)	51 (1)
	C17B	911 (3)	1008 (4)	4372 (2)	60 (2)
2	C1	8632 (1)	2689 (2)	−264 (0)	44 (1)
	C2	9415 (1)	3090 (2)	−536 (2)	48 (1)
	C3	9354 (1)	1351 (2)	−730 (2)	47 (1)
	C4	8961 (1)	1265 (2)	229 (1)	47 (1)
	C5	8613 (1)	1713 (2)	−1158 (1)	45 (1)
	O6	8580 (1)	2491 (2)	−2020 (1)	64 (1)
	C7	8241 (2)	1517 (3)	−2674 (2)	64 (2)
	C8	7797 (2)	502 (5)	−2081 (2)	79 (2)
	O9	8121 (1)	504 (2)	−1203 (1)	67 (1)
2	C10	9593 (1)	4211 (2)	−1301 (2)	50 (1)
	O11	10080 (1)	4086 (2)	−1839 (1)	82 (1)
	O12	9177 (1)	5441 (2)	−1252 (1)	59 (1)
	C13	9331 (2)	6637 (4)	−1929 (2)	77 (2)
	C14	8497 (1)	−69 (2)	504 (1)	44 (1)
	O15	7937 (1)	35 (2)	913 (1)	64 (1)
	O16	8815 (1)	−1394 (2)	295 (1)	54 (1)
	C17	8426 (2)	−2761 (3)	542 (2)	63 (2)
3	C1A	8641 (3)	565 (2)	1274 (2)	33 (1)
	C2A	9079 (3)	1233 (2)	2121 (2)	34 (1)
	C3A	10143 (3)	658 (2)	2058 (2)	35 (1)
	C4A	9418 (3)	−466 (3)	1740 (2)	36 (1)
	C5A	9690 (3)	1047 (2)	1140 (2)	34 (1)
	O6A	9700 (3)	2251 (2)	960 (2)	44 (1)
	C7A	9952 (4)	2377 (3)	232 (3)	59 (2)
	C8A	9843 (4)	1171 (3)	−110 (3)	56 (2)
	O9A	10099 (3)	445 (2)	607 (2)	47 (1)
	C10A	9004 (3)	2534 (2)	2191 (2)	36 (1)
	O11A	9745 (3)	3141 (2)	2639 (2)	49 (1)
	O12A	7985 (3)	2933 (2)	1747 (2)	48 (1)
	C13A	7785 (5)	4172 (4)	1815 (3)	66 (2)
	C14A	9115 (3)	−1187 (2)	2350 (2)	41 (1)
	O15A	9767 (3)	−1529 (2)	3001 (2)	74 (2)
	O16A	8041 (3)	−1471 (2)	2051 (2)	64 (1)
	C17A	7648 (6)	−2208 (5)	2578 (4)	93 (3)
	C1B	3070 (3)	1933 (2)	132 (2)	34 (1)
	C2B	2663 (3)	1269 (2)	−713 (2)	34 (1)
	C3B	3789 (3)	1840 (2)	−651 (2)	34 (1)
	C4B	3381 (3)	2964 (2)	−332 (2)	34 (1)
	C5B	4250 (3)	1448 (2)	268 (2)	33 (1)
	O6B	4443 (3)	250 (2)	448 (2)	45 (1)
	C7B	5422 (4)	118 (3)	1176 (3)	57 (2)
	C8B	5660 (4)	1330 (3)	1520 (3)	56 (2)
	O9B	5196 (3)	2057 (2)	803 (2)	48 (1)
	C10B	2514 (3)	−42 (2)	−783 (2)	35 (1)
	O11B	2807 (3)	−640 (2)	−1234 (2)	49 (1)
	O12B	1942 (3)	−432 (2)	−339 (2)	48 (1)
	C13B	1679 (5)	−1680 (4)	−411 (4)	67 (3)
	C14B	2466 (3)	3695 (2)	−940 (2)	40 (1)
	O15B	2470 (3)	4025 (2)	−1594 (2)	74 (2)
	O16B	1694 (3)	3971 (2)	−645 (2)	64 (1)
	C17B	781 (6)	4710 (6)	−1159 (4)	93 (3)

chromatogram in 9:1 ethyl acetate–methanol showed an elongated spot centered at R_f 0.09. No starting material was detected at R_f 0.36. The reaction mixture was filtered by suction, and the filter cake was washed with 100 mL of acetone. A white precipitate formed in the filtrate so it was refiltered through Celite and washed with another 100-mL portion of acetone. The solvent was removed on the rotary evaporator, yielding 1.276 g of a tan solid, which was extracted with five 100-mL portions of warm acetone. The combined extracts were filtered through 2 g of silica gel CC-7 and eluted with acetone. Solvent removal gave 1.014 g (90%) of a white solid, which, upon melting, began to discolor at ~120 °C and decomposed with gas evolution at ~170 °C.

The NMR spectrum (acetone-d_6) showed a broad two-proton carboxylic acid singlet at δ 10.87 and a sharp two-proton bridgehead methine singlet at δ 3.20. The IR spectrum (KBr) showed a very broad carboxylic acid band between 3600 and 2500 cm^{-1}. The EI mass spectrum (70 eV) showed *m*/*z* (relative intensity) 168 (1, M$^+$), 167 (1, M$^+$ − H), 140 (33, M$^+$ − CO), 112 (43), 96 (45, M$^+$ − COCO$_2$), 84 (30), 79 (15), 77 (10), 68 (65), 67 (13), 66 (13), 53 (50), 52 (15), 51 (100), 50 (75), and 49 (23). Exact mass calcd for $C_7H_4O_5$ 168.0059, found 168.0060.

1,5-Dicarbomethoxytricyclo[2.1.0.0^{2,5}]pentan-3-one (6). A solution of 1.002 g (5.960 mmol) of the diacid **5** in 40 mL of acetone was placed in a 250-mL, round-bottomed flask equipped with a stirring bar. After cooling to 0 °C, 50 mL of ice-cold ethereal ~0.3 M diazomethane was added slowly with stirring. The yellow reaction mixture was stirred at 0 °C for 30 min, and then 20 drops of acetic acid was added to decompose the excess diazomethane. The ether was removed, yielding 1.173 g of a tan solid, which was dissolved in 25 mL of dichloromethane and filtered through 2 g of CC-7 silica gel eluting further with 60 mL of dichloromethane. Removal of the solvent yielded 1.089 g of white crystals, mp 128–130 °C. Recrystallization from dichloromethane/hexanes gave 1.058 g (90%) of white crystals, mp 129–130 °C. For analysis a sample was recrystallized from dichloromethane/hexanes, mp 130–131 °C.

The proton NMR spectrum (60 MHz, CDCl$_3$) showed a six-proton methyl ester singlet at δ 3.85 and a two-proton bridgehead methine singlet at δ 3.10. The ^{13}C NMR spectrum (75.46 MHz, CDCl$_3$) showed a ketone carbonyl singlet at 177.13 ppm, an ester carbonyl quartet (^3J = 3.9 Hz) at 163.62 ppm, a methyl quartet (^1J = 148.32 Hz) at 53.42 pm, a bridgehead methine doublet of doublets (^1J = 195.9 Hz and ^4J = 14.8 Hz)) at 49.24 ppm, and a quaternary bridge carbon singlet at 19.01 ppm. The IR spectrum (CHCl$_3$) showed a ketone carbonyl band at 1803 cm^{-1} and ester carbonyl bands at 1747 and 1730 cm^{-1}. The mass spectrum (70 eV) showed *m*/*z* (relative intensity) 196 (0.15, M$^+$), 181 (3.8, M$^+$ − CH$_3$), 168 (31, M$^+$ − CO), 165 (19, M$^+$ − OCH$_3$), 153 (5.8), 140 (100), 137 (27, M$^+$ − COOCH$_3$), 125 (15), 112 (25), 110 (9.6), 109 (23), 97 (13), 82 (12), 81 (7.7), 77 (17), 75 (7.7), 69 (35), 67 (9.6), 66 (15), 59 (63), 53 (52), and 50 (48). Exact mass calcd for $C_9H_8O_5$ 196.0372, found 196.0375.

Anal. Calcd for $C_9H_8O_5$: C, 55.10; H, 412. Found: C, 55.33; H, 4.23.

1,5-Dicarbomethoxyspiro[bicyclo[2.1.0.0^{2,5}]pentane-3,2′-[1,3]dioxolane] (7). The keto diester **6** (2.097 g, 0.011 mol), 201 mg (1.06 mmol) of *p*-toluenesulfonic acid monohydrate, and 2.053 g (0.033 mol) of ethylene glycol were combined in 100 mL of benzene in a 250-mL round-bottom flask. The flask was equipped with a stirring bar, a Soxhlet extractor containing 4-Å molecular sieves, and a reflux condenser protected from the atmosphere. The mixture was refluxed at 99–105 °C for 7 h. A thin-layer chromatogram in 1:1 ethyl acetate–hexanes showed the desired product at R_f 0.40; no starting ketone was detected at R_f 0.56. The reaction was cooled to room temperature, and 400 μL (305 mg, 2.36 mmol) of Hünig's base (ethyldiisopropylamine) was added. The entire mixture was poured onto a 20-g column of CC-7 silica gel and the column was eluted with 200 mL each of 9:1 benzene–ethyl acetate, 7:3 benzene–ethyl acetate, and ethyl acetate. Aliquots of 50 mL were collected and the separation was monitored by thin-layer chromatography in 1:1 ethyl acetate–hexanes. Fractions 3 and 4 were combined, and the solvent was removed, yielding 1.475 g of ketal diester **7** as white crystals, mp 83–86 °C (ether–pentane).

The NMR spectrum of **7** (60 MHz, $CDCl_3$) showed a four-proton ethylene ketal singlet at δ 3.90, a six-proton methyl ester singlet at δ 3.78, and a two-proton bridgehead methine singlet at δ 3.13. The IR spectrum (CCl_4) showed ester carbonyl bands at 1740 and 1722 cm^{-1}. The mass spectrum (15 eV) showed m/z (relative intensity) 240 (1.4, M^+), 225 (74, $M^+ - CH_3$), 197 (55), 181 (21), 1679 (100), 156 (26), 153 (29), 137 (12), and 125 (14). Exact mass calcd for $C_{11}H_{12}O_6$ 240.0634, found 240.0629.

Anal. Calcd for $C_{11}H_{12}O_6$: C, 54.99; H, 5.05. Found: C, 55.24; H, 5.08.

4,5-Dicarbomethoxyspiro[bicyclo[1.1.1]pentane-2,2′-[1,3]-dioxolanes] 1, 2, and 3. A three-neck, round-bottom flask equipped with a Hershberg stirrer, a gas inlet tube, and a 125-mL addition funnel was flame-dried under vacuum and pressurized with dry argon. Naphthalene (6.599 g, 0.05148 mol) was added to the reaction flask against a stream of argon followed by 300 mL of dry, oxygen-free tetrahydrofuran (freshly distilled from the sodium–benzophenone ketyl). Sodium (0.786 g, 0.0342 mol) was added to the solution, and the mixture was stirred vigorously at 21 °C. After a few minutes the green color of sodium naphthalenide appeared. Stirring was continued for 7 h, until all the sodium had reacted, yielding a deep olive green solution. A solution of 2.501 g (0.01 mol) of ketal diester **6** in 50 mL of tetrahydrofuran was added dropwise over a period of 1 h with vigorous stirring to the sodium naphthalenide solution at −78 °C. The olive green reaction mixture was stirred at −78 °C for an hour, and then 5.0 mL of nitrogen-purged acetic acid was added dropwise. Stirring was continued at −78 °C for 30 min resulting in a clear yellow solution. After warming to room temperature, the reaction mixture was filtered through Celite. The solvent was removed on a rotary evaporator, yielding 9.240 g of yellow solid. This was dissolved in 15 mL of hot benzene and placed on a 300-g silica gel column, 4 cm in diameter and 75 cm long. The column was eluted with 2 L each of 9:1, 4:1, 7:3, and 3:2 hexanes–ethyl acetate. Aliquots of 100 mL were collected, and the course of the separation was monitored by thin-layer chromatography in 1:1 ethyl acetate–hexanes. Fractions 6–8 were combined, and the solvent was removed, yielding 5.4 g of naphthalene, R_f 0.53 in hexanes. Fractions 38–41 yielded 269 mg of white crystalline endo,endo ketal diester **1**, mp 79–80 °C, R_f 0.62. Recrystallization from ether–pentane gave 243 mg (10%) of white crystals, mp 81.5–83.0 °C. For analysis a sample was recrystallized from ether–hexanes, mp 82–83 °C.

The NMR spectrum of **1** (60 MHz, $CDCl_3$) showed a four-proton ethylene ketal singlet at δ 3.98, a six-proton methyl ester singlet at δ 3.66, a two-proton methine singlet at δ 3.45, and a two-proton bridgehead methine singlet at δ 3.34. The IR spectrum ($CHCl_3$) showed an ester carbonyl band at 1724 cm^{-1}. The mass spectrum (70 eV) showed m/z (relative intensity) 242 (0.16, M^+), 211 (13, $M^+ - OCH_3$), 210 (9, $M^+ - CH_3OH$), 183 (100, $M^+ - CO_2CH_3$), 167 (19), 139 (13), 123 (13), 111 (63), 79 (16), 68 (13), and 59 (22). Exact mass calcd for $M^+ - CH_3OH$, $C_{10}H_{10}O_5$ 210.0528, found 210.0533.

Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.53; H, 5.84. Found: C, 54.79; H, 5.94.

Fraction 42 gave 33 mg of a 2:1 mixture of the endo,endo and endo,exo isomers as a colorless oil. Fractions 43–50 yielded 526 mg of white, crystalline endo,exo ketal diester **3**, mp 111–113 °C, R_f 0.56. Recrystallization from ether gave 468 mg (19%) of white prisms, mp 115–117 °C. For analysis a sample was recrystallized from diethyl ether–hexanes, mp 115–117 °C.

The NMR spectrum of **3** (60 MHz, $CDCl_3$) showed a broad four-proton ethylene ketal singlet at δ 3.92, a six-proton methyl ester singlet at δ 3.68, a two-proton bridgehead methine singlet at δ 3.34, a one-proton exo methine singlet at δ 3.19, and a one-proton endo methine singlet at δ 3.05. The IR spectrum ($CHCl_3$) showed an ester carbonyl band at 1725 cm^{-1}. The mass spectrum (15 eV) showed m/z (relative intensity) 242 (0.15, M^+), 210 (14, $M^+ - CH_3OH$), 183 (100, $M^+ - CO_2CH_3$), and 111 (15). Exact mass calcd for $M^+ - CH_3OH$, $C_{10}H_{10}O_5$ 210.0528, found 210.0529.

Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.53; H, 5.84. Found: C, 54.57; H, 5.84.

Fractions 60–70 yielded 318 mg of yellow crystalline exo,exo ketal diester **2**, mp 144–145 °C, R_f 0.40. Recrystallization from ether gave 274 mg (11%) of white prisms, mp 146–147 °C. For analysis a sample was recrystallized from diethyl ether–hexanes, mp 146–148 °C.

The NMR spectrum of **2** (60 MHz, $CDCl_3$) showed a four-proton ethylene ketal singlet at δ 3.88, a six-proton methyl ester singlet at δ 3.69, a two-proton bridgehead methine singlet at δ 3.35, and a two-proton endo methine singlet at δ 2.25. The IR spectrum ($CHCl_3$) showed an ester carbonyl band at 1728 cm^{-1}. The mass spectrum (70 eV) showed m/z (relative intensity): 242 (0.32, M^+), 211 (3, $M^+ - OCH_3$), 210 ($M^+ - CH_3OH$), 183 (100, $M^+ - CO_2CH_3$), 167 (15), 122 (11), 111 (63), 79 (14), 68 (15), and 59 (26). Exact mass calcd for $M^+ - CH_3OH$, $C_{10}H_{10}O_5$ 210.0528, found 210.0527.

Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.53; H, 5.84. Found: C, 54.81; H, 5.95.

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Supplementary Material Available: Tables 7a–c, coordinates (×10^3) of the hydrogen atoms of **1**–**3** with the isotropic thermal parameters (×10^2 Å^2) and Tables 8a–c, anisotropic thermal parameters (×10^2 Å^2) for the C and O atoms of **1**–**3** (5 pages). Ordering information is given on any current masthead page. Tables with the structure amplitudes of **1**–**3** may be obtained from H.I. (69 pages).