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Synthesis and Conformation of *cis*-1,2-Disubstituted Cyclododecene

HAN, Xiang-Yu(韩翔宇) WANG, Ming-An(王明安)
LIANG, Xiao-Mei(梁晓梅) WANG, Dao-Quan*(王道全)

Department of Applied Chemistry, China Agricultural University, Beijing, 100094, China

Eight 1,2-disubstituted cyclododecenes were synthesized from α-alkoxycarbonyl-cyclododecanone and alkyl chloroformate. Their configuration and conformation determined by IR, NMR spectroscopy and X-ray diffraction analysis showed that the carbon-carbon double bond of all of the synthesized compounds has *cis*-configuration, and the ring skeleton of their preferred conformation is [1ene2333] in solid, and they may adopt two different [1ene2333] conformations，which exist in a dynamic equilibrium in solution.

Keywords disubstituted cyclododecene, *cis*-configuration, conformation

Introduction

As more and more studies focus on the large ring compounds in recent years, researchers have found that many derivatives of cyclododecane exhibit good bioactivities such as antifungal,[1a] plant growth regulation activity,[1b] and activity against murine *L*1210[1c] and *P*388 D_1[1d] lymphocytic leukemia cells. Furthermore, our group has found that a series of substituted cyclododecanone derivatives exhibit excellent weed controlling and fungicidal activities.[2] Recently, studies aimed at searching medicinal, pesticidal and plant growth regulating compounds that derived from corresponding parent large-ring compounds have increasingly aroused more and more researchers' intense interest. At the same time, twelve-membered ring compounds have been widely used in organic synthesis because these compounds as important intermediates were used to synthesize larger[3] or smaller[4] ring compounds. However, their chemical reactivities are significantly different from some normal ring compounds. It was reported that cyclic ketones of normal ring compounds form ketals very readily[5a] while the ketals of cyclododecanone system usually are not easily to prepare[5b] and only with very low yields. The characteristics of derivatives of twelve-membered ring system on bioactivities and chemical reactivities show intimate correlation with their stereochemistry, especially with their preferred conformations that are adopted in the reaction system. Vedejs[5c] also observed that there is local conformation effect in the reactivity of large ring compounds. Therefore, systematic studies on the conformation rules of twelve-membered ring compounds have important significance.

In 1979, Anet *et al*.[6] studied the conformation of *cis*-cyclododecene through dynamic NMR spectroscopy and iterative force-field calculation. These results suggested that *cis*-cyclododecene exists mainly as a mixture of two low-energy unsymmetrical conformations, labeled [1ene2333] and [1ene2342]. Furthermore, the calculated results with MMX molecular mechanics program were in good agreement with the conclusion of dynamic NMR and iterative force field methods.[7]

A few literatures[7b,8] describe the crystal structures of bicyclic compounds containing cyclododecene and showed that the double bond and the ring skeletons of the cyclododecene moiety of all compounds have *cis*-configuration and [1ene2333] conformation, respectively. However, no systematical studies on the conformation of the 1,2-disubstituted cyclododecene derivatives through experiments have been reported.

As a part of study on the conformation of 12-membered ring system, we are currently engaged in the synthesis and study of a series of 1,2-disubstituted cyclododecene derivatives to elaborate the stereochemistry of the ring skeleton of cyclododecene in order to improve the study of the structure-activity relationship of macrocylic compounds. In this paper we describe our results in this area with our systematical studies of the 1,2-disubstituted cyclododecene derivatives.

Results and discussion

A series of *cis*-1-alkoxycarbonyloxy-2-alkoxycarbonylcyclododecenes (**A_1—A_8**) were synthesized (as shown in Scheme 1) and their conformations were thoroughly discussed in this paper. The experimental results show that the reaction of α-alkoxycarbonyl-cyclododecanone and alkyl chloroformate had very high regioselectivity. The reaction occurred only at oxygen atom of the ambident ions, and yielded *O*-acylated

* E-mail: wangdq@cau.edu.cn
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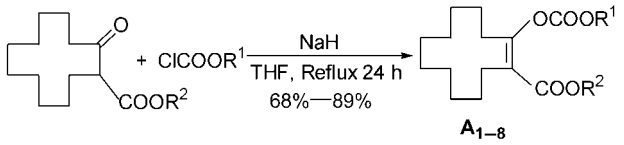
products without *C*-acylated product.

Scheme 1 Synthesis of *cis*-1-alkoxycarbonyloxy-2-alkoxycarbonylcyclododecene



A_{1-8}

	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
R^1	Me	Et	Me	Et	Me	Ph	Et	Ph
R^2	Et	Me	Me	Et	Ph	Me	Ph	Et

IR and NMR data of compounds **A**$_1$—**A**$_8$ exhibit that each compound has similar characteristic data (Table 1).

Table 1 Selected IR and NMR data of Compounds **A**$_1$—**A**$_8$

	$IR_{(C=C)}$	^{1}H NMR	^3J (Hz)	^{13}C NMR
A$_1$	1640	2.43 (t，2H)	7.2	152.6
		2.37 (t，2H)	7.1	121.8
A$_2$	1642	2.43 (t，2H)	7.2	153.2
		2.37 (t，2H)	7.1	122.1
A$_3$	1652	2.43 (t，2H)	7.2	153.2
		2.37 (t，2H)	7.1	121.8
A$_4$	1640	2.43 (t，2H)	7.2	152.5
		2.37 (t，2H)	7.1	122.2
A$_5$	1640	2.51 (t，2H)	7.2	153.1
		2.50 (t，2H)	7.1	126.2
A$_6$	1660	2.49 (t，2H)	7.2	151.2
		2.39 (t，2H)	7.1	120.9
A$_7$	1638	2.51 (t，4H)	7.1	150.6
				121.5
A$_8$	1640	2.43 (t，2H)	7.2	151.3
		2.37 (t，2H)	7.1	120.9

All compounds exhibit typical carbon-carbon double bond absorptions at 1660—1638 cm^{-1} in their IR spectra. Two groups of typical triplet signals at δ 2.5—2.3 with similar coupling constants of 7.1—7.2 Hz were observed in the ^{1}H NMR spectra of compounds **A**$_1$—**A**$_8$, which corresponded to methylene of propenylene. A group of typical carbon signals of carbon-carbon double bonds were observed at δ 151—153 and δ 120—126 in the ^{13}C NMR spectra, while the carbonyl signals of these compounds were not observed. Compounds **A**$_5$ and **A**$_6$ were suitable for X-ray crystal structure analysis to determine the double bond configuration of cyclododecene moiety. The results indicate that these 1,2-disubstituted cyclododecenes have *cis*-configurations, and the four atoms attached to carbon-carbon double bonds are nearly coplanar in the crystals (Figure 1, Tables 2 and 3). These results confirmed that all of the compounds **A** are derivatives of cyclododecene, which have *cis*-configuration.

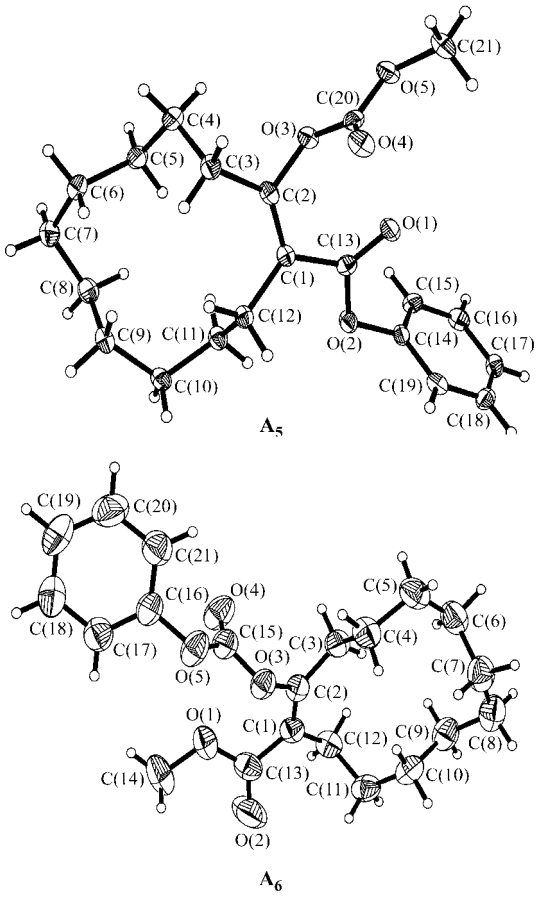


Figure 1 X-ray crystal structures of compounds **A**$_5$ and **A**$_6$.

Table 2 Double bond lengths and partial torsion angles for compounds **A**$_5$ and **A**$_6$

	Double bond lengths/nm		Torsion angles/(°)	
A$_5$	C(1)—C(2)	0.1338	C(13)-C(1)-C(2)-O(3)	8.7
			C(12)-C(1)-C(2)-O(3)	−173.4
			C(13)-C(1)-C(2)-C(3)	−173.2
			C(12)-C(1)-C(2)-C(3)	4.6
A$_6$	C(1)—C(2)	0.1334	C(13)-C(1)-C(2)-O(3)	11.8
			C(12)-C(1)-C(2)-O(3)	−167.1
			C(13)-C(1)-C(2)-C(3)	−173.2
			C(12)-C(1)-C(2)-C(3)	7.8

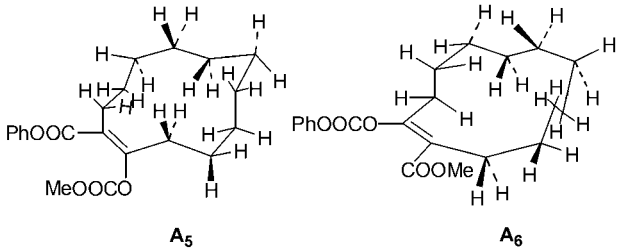
The X-ray crystal structures of compounds **A**$_5$ and **A**$_6$ also show that their ring skeletons adopt [1ene2333] conformations. The project formulas are shown in Figure 2. It can be seen that the two protons of 3-CH_2 and 12-CH_2 of compounds **A**$_5$ and **A**$_6$ occupy side-*exo* and side-*endo*-positions respectively, therefore they appear to have different chemical shifts in the ^{1}H NMR spectra. However, the ^{1}H NMR data indicated that two protons

of 3-CH_2 and 12-CH_2 appeared as chemical shift equivalent protons and coupled with their adjacent protons to split as triplet signals.

Table 3 Bond angles (°) of compounds $\mathbf{A_5}$ and $\mathbf{A_6}$

$\mathbf{A_5}$		$\mathbf{A_6}$	
C(13)-O(2)-C(14)	116.50(11)	C(13)-O(1)-C(14)	117.68(14)
C(20)-O(3)-C(2)	115.41(11)	C(15)-O(3)-C(2)	117.47(11)
C(20)-O(5)-C(21)	113.98(11)	C(15)-O(5)-C(16)	116.71(12)
C(2)-C(1)-C(13)	119.24(13)	C(2)-C(1)-C(13)	122.19(14)
C(2)-C(1)-C(12)	122.41(13)	C(2)-C(1)-C(12)	124.45(14)
C(13)-C(1)-C(12)	118.32(13)	C(13)-C(1)-C(12)	113.35(13)
C(1)-C(2)-O(3)	118.89(13)	C(1)-C(2)-O(3)	118.32(13)
C(1)-C(2)-C(3)	131.13(14)	C(1)-C(2)-C(3)	128.92(14)
O(3)-C(2)-C(3)	109.96(13)	O(3)-C(2)-C(3)	112.59(12)
C(2)-C(3)-C(4)	114.04(12)	C(2)-C(3)-C(4)	114.84(13)
C(5)-C(4)-C(3)	112.29(12)	C(5)-C(4)-C(3)	112.95(14)
C(6)-C(5)-C(4)	113.16(13)	C(4)-C(5)-C(6)	114.74(14)
C(5)-C(6)-C(7)	114.47(13)	C(7)-C(6)-C(5)	114.58(15)
C(8)-C(7)-C(6)	114.46(12)	C(8)-C(7)-C(6)	116.01(14)
C(7)-C(8)-C(9)	115.07(13)	C(7)-C(8)-C(9)	115.36(13)
C(8)-C(9)-C(10)	113.38(12)	C(10)-C(9)-C(8)	114.77(14)
C(9)-C(10)-C(11)	114.20(12)	C(9)-C(10)-C(11)	113.84(14)
C(10)-C(11)-C(12)	113.01(12)	C(10)-C(11)-C(12)	115.05(13)
C(1)-C(12)-C(11)	115.27(12)	C(1)-C(12)-C(11)	114.13(13)
O(1)-C(13)-O(2)	121.77(13)	O(2)-C(13)-O(1)	121.78(16)
O(1)-C(13)-C(1)	127.08(14)	O(2)-C(13)-C(1)	123.48(17)
O(2)-C(13)-C(1)	111.12(12)	O(1)-C(13)-C(1)	114.60(15)
C(19)-C(14)-C(15)	122.12(14)	O(4)-C(15)-O(3)	127.43(15)
C(19)-C(14)-O(2)	118.32(13)	O(4)-C(15)-O(5)	127.43(14)
C(15)-C(14)-O(2)	119.46(13)	O(3)-C(15)-O(5)	105.14(13)
C(14)-C(15)-C(16)	118.72(14)	C(21)-C(16)-C(17)	122.05(15)
C(17)-C(16)-C(15)	120.38(15)	C(21)-C(16)-O(5)	120.50(15)
C(16)-C(17)-C(18)	119.61(14)	C(17)-C(16)-O(5)	117.28(15)
C(17)-C(18)-C(19)	120.99(14)	C(16)-C(17)-C(18)	118.72(17)
C(14)-C(19)-C(18)	118.16(14)	C(19)-C(18)-C(17)	120.39(18)
O(4)-C(20)-O(5)	127.27(14)	C(18)-C(19)-C(20)	119.98(17)
O(4)-C(20)-O(3)	126.41(14)	C(19)-C(20)-C(21)	120.45(18)
O(5)-C(20)-O(3)	106.31(12)	C(16)C(21)-C(20)	118.40(17)

These results suggested that compounds **A** may adopt two different [1ene2333] conformations as shown in Figure 3, which exist in a dynamic equilibrium in solution. The ^{1}H NMR spectra in solution are the averaged results of these two non-equivalent [1ene2333] conformations. It happens that the ring skeletons of compounds $\mathbf{A_5}$ and $\mathbf{A_6}$ adopt one of the two conformations in their crystal.



$\mathbf{A_5}$ $\mathbf{A_6}$

Figure 2 Project formulas of $\mathbf{A_5}$ and $\mathbf{A_6}$.

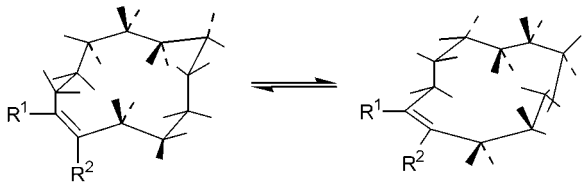


Figure 3 Dynamic equilibrium of two different [1ene2333] conformations in solution.

Conclusion

In summary, the 1,2-disubstituted cyclododecene derivatives have been prepared and structurally characterized. From the results, it is suggested that compounds **A** may adopt two non-equivalent [1ene2333] conformations, which exist in a dynamic equilibrium in solution. The ^{1}H NMR spectra are the averaged results of these two non-equivalent [1ene2333] conformations. It happens that the ring skeletons of compounds $\mathbf{A_5}$ and $\mathbf{A_6}$ adopt one of the two conformations in their crystal.

Experimental

General procedure

A three-necked round bottom flask equipped with a reflux condenser and a nitrogen inlet tube was charged with NaH (0.45 g, 9.2 mmol) and in dried THF (or toluene, benzene) (20 mL). A solution consisting of α-ethoxycarbonyl cyclododecanone (1.6 g, 6.1 mmol) in THF (or toluene, benzene) (10 mL) was added dropwise and then methyl chloroformate (30.5 mmol) was added dropwise. The mixture was then heated at refluxing state for 24 h, allowed to cool, and to this mixture cautiously added acetic acid (5 mL) and water (10 mL). The organic layer was separated and the aqueous layer was extracted with ether (10 mL×3). The combined organic layer was washed with saturated $NaHCO_3$ solution, water and brine, dried with Na_2SO_4, filtered and concentrated under vacuum. The crude product was chromatographed on silica gel eluting with ethyl acetate∶petroleum ether (1∶15, *V*∶*V*) to give 1.6 g (84%, yield) colorless liquid of $\mathbf{A_1}$.

Methoxycarbonyloxy-2-ethoxycarbonylcyclododecene (A_1) ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.25 (q, ^3J=7.1 Hz, 2H), 3.71 (s, 3H), 2.43 (t, ^3J=7.2 Hz, 2H), 2.37 (t, ^3J=7.1 Hz, 2H), 1.69—1.55 (m, 4H), 1.39—1.32 (m, 12H), 1.27 (t, ^3J=7.1 Hz, 3H); ^{13}C NMR δ: 166.7, 154.9, 152.6, 121.8, 64.5, 51.6, 28.3, 26.4, 26.0, 24.8, 24.7, 24.5, 24.3, 23.7, 22.5, 22.3, 14.2; IR (neat) v: 2937, 2860, 1760, 1725, 1640 (C=C), 1470, 1441, 1266, 1175, 1060, 1030, 860, 760 cm^{-1}. Anal. calcd for $C_{17}H_{28}O_5$: C 65.38, H 8.97; found C 65.25, H 9.14.

Ethoxycarbonyloxy-2-methoxycarbonylcyclododecene (A_2) Colorless liquid (68%, yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.19 (q, ^3J=7.1 Hz, 2H), 3.84 (s, 3H), 2.43 (t, ^3J=7.2 Hz, 2H), 2.37 (t, ^3J=7.1 Hz, 2H), 1.68—1.59 (m, 4H), 1.39—1.32 (m, 12H), 1.27 (t, ^3J=7.1 Hz, 3H); ^{13}C NMR δ: 166.2, 154.5, 153.2, 122.1, 60.4, 55.0, 28.1, 26.3, 26.0, 24.8, 24.7, 24.4, 24.2, 23.7, 22.4, 22.2, 13.9; IR (neat) v: 2937, 2860, 1765, 1721, 1642 (C=C), 1470, 1448, 1260, 1173, 1060, 1034, 936, 770 cm^{-1}. Anal. calcd for $C_{17}H_{28}O_5$: C 65.38, H 8.97; found C 65.48, H 9.19.

1-Methoxycarbonyloxy-2-methoxycarbonyl-1,2-cyclododecene (A_3) Colorless crystal (74%, yield), m.p. 69—70 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.85 (s, 3H), 3.72 (s, 3H), 2.43 (t, ^3J=7.2 Hz, 2H), 2.36 (t, ^3J=7.1 Hz, 2H), 1.65—1.57 (m, 4H), 1.39—1.32 (m, 12H); ^{13}C NMR δ: 166.7, 155.1, 153.2, 121.8, 55.2, 51.6, 28.2, 26.4, 26.1, 24.8, 24.7, 24.5, 24.3, 23.8, 22.5, 22.3; IR (KBr) v: 2905, 2850, 1750, 1720, 1652 (C=C), 1462, 1440, 1328, 1295, 1270, 1170, 1090, 1055, 1035, 980, 940, 770, 725 cm^{-1}. Anal. calcd for $C_{16}H_{26}O_5$: C 64.42, H 8.72; found C 64.54, H 8.92.

1-Ethoxycarbonyloxy-2-ethoxycarbonylcyclododecene (A_4) Colorless liquid (79%, yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.25 (q, ^3J=7.1 Hz, 2H), 4.18 (q, ^3J=10.9 Hz, 2H), 2.43 (t, ^3J=7.2 Hz, 2H), 2.37 (t, ^3J=7.1 Hz, 2H), 1.73—1.56 (m, 4H), 1.39— 1.35 (m, 12H), 1.33 (t, ^3J=7.1 Hz, 3H), 1.27 (t, ^3J=7.1 Hz, 3H); ^{13}C NMR δ: 166.3, 154.3, 152.5, 122.2, 64.4, 60.4, 28.2, 26.4, 26.1, 24.8, 24.7, 24.5, 24.3, 23.8, 22.5, 22.3, 14.1, 14.0; IR (neat) v: 2930, 2860, 1760, 1720, 1640 (C=C), 1465, 1445, 1390, 1365, 1250, 1180, 1100, 1030, 860, 770 cm^{-1}. Anal. calcd for $C_{18}H_{30}O_5$: C 66.25, H 9.20; found C 66.48, H 9.31.

1-Methoxycarbonyloxy-2-phenoxycarbonylcyclododecene (A_5) Colorless crystal (81%, yield), m.p. 72—73 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.40—7.07 (m, 5H), 3.79 (s, 3H), 2.51 (t, ^3J=7.1 Hz, 2H), 2.50 (t, ^3J=7.1 Hz, 2H), 1.75—1.73 (m, 4H), 1.42 (br.s, 12H); ^{13}C NMR δ: 164.7, 156.4, 153.1, 150.6, 129.4, 125.8, 121.62,121.61, 55.3, 28.5, 26.5, 26.3, 24.9, 24.8, 24.5, 24.3, 23.8, 22.5, 22.4; IR (KBr) v: 2939, 2860, 1752, 1735, 1640 (C=C), 1585, 1453, 1286, 1198, 1163, 1092, 969, 750, 696 cm^{-1}. Anal. calcd for $C_{21}H_{28}O_5$: C 70.00, H 7.77; found C 70.03, H 7.83.

1-Phenoxycarbonyloxy-2-methoxycarbonylcyclododecene (A_6) Needle crystalline (69%, yield), m.p. 99—100 ℃; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.42—7.36 (m, 2H), 7.27—7.22 (m, 3H), 3.77 (s, 3H), 2.50 (t, ^3J=7.2 Hz, 2H), 2.40 (t, ^3J=7.1 Hz, 2H), 1.73—1.57 (m, 5H), 1.40—1.33 (m, 12H); ^{13}C NMR δ: 166.5, 155.2, 151.2, 151.1, 129.4, 126.0, 122.0, 120.9, 51.8, 28.4, 26.4, 26.1, 24.9, 24.8, 24.4, 24.3, 23.8, 22.5, 22.3; IR (KBr) v: 2935, 2863, 1770, 1712, 1660 (C=C), 1594, 1490, 1471, 1363, 1338, 1316, 1282, 1260, 1219, 1158, 1082, 1020, 967, 768 cm^{-1}. Anal. calcd for $C_{21}H_{28}O_5$: C 70.00, H 7.77; found C 70.29, H 7.91.

1-Ethoxycarbonyloxy-2-phenoxycarbonylcyclododecene (A_7) Colorless liquid (79%, yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.39—7.08 (m, 5H), 4.20 (q, ^3J=7.1 Hz, 2H), 2.51 (t, ^3J=7.2 Hz, 2H), 2.51 (t, ^3J=7.2 Hz, 2H), 1.73 (s, 4H), 1.52—1.42 (m, 12H), 1.26 (t, ^3J=7.1 Hz, 3H); ^{13}C NMR δ: 164.7, 156.1, 152.5, 150.6, 129.3, 125.7, 121.6, 121.5, 66.8, 64.6, 44.3, 28.5, 26.5, 26.3, 24.9, 24.8, 24.5, 24.3, 23.8, 22.5, 22.3, 14.0; IR (neat) v: 2920, 2860, 1745, 1730, 1638, 1590, 1490, 1465, 1390, 1365, 1250, 1190, 1150, 1090, 1050, 1030, 920, 890, 740, 685 cm^{-1}. Anal. calcd for $C_{22}H_{30}O_5$: C 70.59, H 8.02; found C 70.77, H 8.18.

1-Phenoxycarbonyloxy-2-ethoxycarbonylcyclododecene (A_8) Colorless liquid (89%, yield); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.41—7.36 (m, 2H), 7.27—7.24 (m, 3H), 4.23 (q, ^3J=7.1 Hz, 2H), 2.50 (t, ^3J=7.2 Hz, 2H), 2.40 (t, ^3J=7.1 Hz, 2H), 1.74—1.72 (m, 2H), 1.64—1.59 (m, 2H), 1.39 (br.s, 12H), 1.30 (t, ^3J=7.1 Hz, 3H); ^{13}C NMR δ: 166.1, 154.7, 151.3, 129.4, 125.9, 122.5, 120.9, 66.8, 60.6, 44.5, 28.3, 26.4, 26.1, 24.8, 24.7, 24.4, 24.3, 23.8, 22.5, 22.3, 14.2; IR (neat) v: 2920, 2850, 1770, 1710, 1640, 1590, 1490, 1485, 1365, 1260, 1160, 1030, 970, 760, 720, 685 cm^{-1}. Anal. calcd for $C_{22}H_{30}O_5$: C 70.59, H 8.02; found C 70.80, H 8.02.

X-ray crystallography

The crystal data, data collection and refinement parameters are listed in Table 4. All measurements were made with a Siemens CCD area detector using graphite monochromatized Mo Kα (λ=0.071073 nm) radiation at 293 K. Full spheres of data were collected to a 2θ limit of 27.48°. Space groups were determined from systematic absence and checked for higher symmetry. The structures were solved by direct methods using SHELX,[9] and refined on F^2 using all data by full-matrix least-squares procedures with SHELXL-97.[10] All non-hydrogen atoms were refined with anisotropic displacement parameters. An empirical absorption correction based on X scans was made on all data. Hydrogen atoms were located from the difference map and were constrained to geometrical estimates. Final refinement was carried out with isotropic displacement parameters applied to hydrogen atoms. A weighting scheme of type $[\sigma^2(F_0^2+(aP)^2+bP)^{-1}$, where a=0.0211 and b=0 (0.0474 and 0), was used where P=[max(F_0^2, 0)+2F_0^2]/3.

Table 3 Crystal data and structure refinement for compounds $\mathbf{A_5}$ and $\mathbf{A_6}$

	$\mathbf{A_5}$	$\mathbf{A_6}$
Formula	$C_{21}H_{28}O_5$	$C_{21}H_{28}O_5$
Formula weight	360.43	360.43
Wavelength/nm	0.071073	0.071073
Crystal system	Monoclinic	Monoclinic
Space group	C_2/C	$P_2(1)/C$
Unit cell dimensions/(nm, deg)	a=2.84693(14), b=0.60089(2), β=103.698(2) c=2.28626(10)	a=2.21951(12), b=0.59343(4), β=104.13(2) c=1.54004(14)
Volume/nm^3	3.7998(3)	1.9671(2)
Z	8	4
ρ_{calcd}/(Mg•m^{-3})	1.260	1.217
Absorption coefficient/mm^{-1}	0.089	0.086
F (000)	1552	776
Crystal size/mm^3	0.36×0.35×0.28	0.64×0.50×0.24
θ range for data collection/(°)	2.06—27.48	2.66—27.48
Limiting indices	$-35\leqslant h\leqslant 36$, $-7\leqslant k\leqslant 7$, $-29\leqslant l\leqslant 29$	$-28\leqslant h\leqslant 28$, $-7\leqslant k\leqslant 7$, $-19\leqslant l\leqslant 20$
Reflections collected/unique	7565/4235 [R(int)=0.0386]	7990/4478 [R(int)=0.0315]
Completeness to θ=27.48	97.4%	99.2%
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.9753 and 0.9690	0.9796 and 0.9473
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4235/0/235	4478/0/235
Goodness-of-fit on F^2	0.693	0.773
Final R indices [$I>2\sigma(I)$]	R_1=0.0327, wR_2=0.0566	R_1=0.0393, wR_2=0.0828
R indices (all data)	R_1=0.0825, wR_2=0.0618	R_1=0.0946, wR_2=0.0926
Largest diff. peak and hole/(e•nm^{-3})	158 and −292	187 and −167

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(E0308229 SONG, J. P.)