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Synthesis and Self-Assembled Helical Supramolecular Polymer of Ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4′-nitrophenyl)-6*H*-dibenzo[*c*]-pyran-6-one-8-carboxylate

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ABSTRACT: *A structurally novel compound was isolated as the main product of tandem Pechmann–dehydration between diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,3-dicarboxylate (**1**) and resorcinol in the presence of trifluoroacetic acid. The structure of the product was determined as a racemate of (7R,8R)- and (7S,8S)-ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4′-nitrophenyl)-6H-dibenzo[c]-pyran-6-one-8-carboxylate (**3a**) enantiomers by single crystal X-ray diffraction analysis. The X-ray crystal structure revealed that **3a** possesses an extended and more stable conjugated aromatic system as a consequence of the stereoselectivity of intramolecular dehydration behavior of Pechmann condensation product **2**. In the crystal superstructure, the (7R,8R)- and (7S,8S)-isomers of **3a** respectively self-assembled into left- and right-handed supramolecular helical chains with a channel size of 3.70 Å × 10.20 Å in virtue of intermolecular hydrogen bonding together with dramatic twisting between carboxylate group at C8 and tricyclic ring framework of **3a**, which are then arranged alternatively along the b-axis direction with a pitch length of 7.894 Å.* © 2013 Wiley Periodicals, Inc. Heteroatom Chem. 25:35–42, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21133

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INTRODUCTION

As an important moiety of coumarin derivatives, 3:4-fused six-member carbocyclic ring coumarins (3:4-carbocyclic fused ring system) are receiving growing interests due to their biological activities [1–23]. Typically, there are five kinds of 3:4-fused six-member carbocyclic ring coumarins (Fig. 1). Among them, derivatives of 7,8,9,10-tetrahydro-6*H*-benzo[*c*]chromen-6-ones (a) [1–11] and 6*H*-dibenzo[*c*]pyran-6-ones (e) [12–23] are well developed and documented, while other kinds of them, such as derivatives of 9,10-dihydro-6*H*-benzo[*c*]chromen-6-ones (b) [21, 22], 7,10-dihydro-6*H*-benzo[*c*]chromen-6-ones (c) [21,23], especially 7,8-dihydro-6*H*-benzo[*c*]chromen- 6-ones (d), are relatively seldom discussed in the literature, to the best of our knowledge.

As a part of our current research, we employed multisubstituted cyclic β-keto esters that underwent Pechmann reaction with phenols to construct 3:4-fused six-member carbocyclic ring coumarins (a). However, when diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,

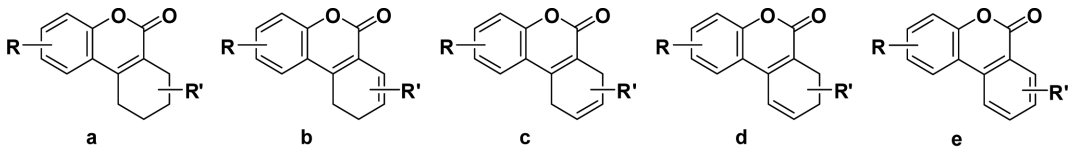
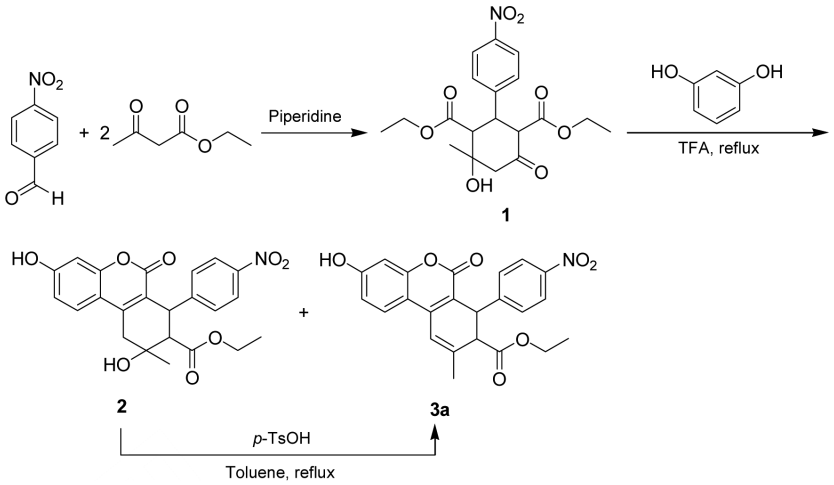


FIGURE 1 Structures of 3:4-fused six-member ring coumarins.



SCHEME 1 Construction of 3:4-fused six-member ring coumarins.

3-dicarboxylate (**1**) and resorcinol were chosen as representative model reactants and subjected to reflux conditions in trifluoroacetic acid (TFA) (Scheme 1), we obtained a small amount of desired coumarin-fused 3-hydroxy-2-cyclohexene derivative **2** (Pechmann condensation product), together with a large amount of its intramolecular dehydrated product. Because there are three different types of alpha-hydrogen atoms relative to hydroxyl group in **2** that can be eliminated with the hydroxyl group, and the exact structure of product **3** was hard to elucidate by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) determination due to its unusual coupling effect between the adjacent protons. So, we felt that it would be desirable to extensively investigate the intramolecular dehydration behavior of **2** and determine the exact structure of the intramolecular dehydrated product of **3**. In this context, we further examined and presented the structure of a representative example, namely ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4′-nitrophenyl)-6*H*-dibenzo[*c*]pyran-6-one-8-carboxylate **3a**, by single crystal X-ray diffraction studies.

EXPERIMENTAL

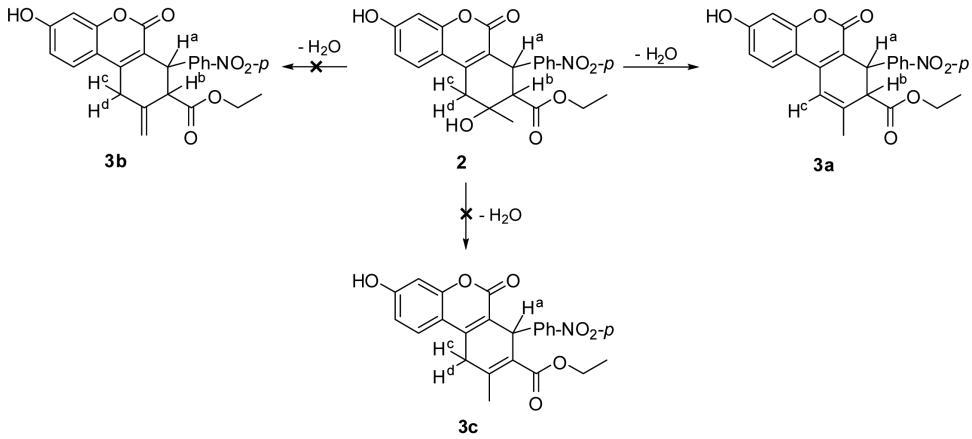
Materials and Methods

All reagents were obtained from commercial suppliers and used without further purification. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX-300 (300 MHz) NMR spectrometer (Bruker, Karlsruhe, Germany). Mass spectrometry electrospray ionization (MS-ESI) spectra were obtained on a Finnigan-Mat LCQ mass spectrometer (Thermo Finnigan, San Jose, CA). Elemental analyses were carried out on an Elementar Vario MICRO CUBE (German). Melting points were determined on an electrically heated RK-Z melting point apparatus (Analytical Instrument Factory in Tianjin, People's Republic of China) and were uncorrected.

Crystals were obtained by slow evaporation from mixture of EtOAc:hexane = 1:1 solution of the pure compound **3a**. A yellow single crystal of suitable size was selected for X-ray diffraction analysis. Measurements were made on an Enraf–Nonius CAD4 diffractometer equipped with graphite crystal monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) at 293(2) K.

Synthesis of Intermediates and the Target Compounds

Diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,3-dicarboxylate (**1**) was synthesized according to the method reported by Pandiarajan et al. [24] except that piperidine was used instead of methylamine. A mixture of ethyl acetoacetate (2.66 g, 20.4 mmol), 4-nitrobenzaldehyde (1.51 g, 10 mmol), and piperidine (0.4 mL) in



SCHEME 2 Possible dehydrated structures of compound **2**.

ethanol (20 mL) was stirred at room temperature for about 12 h. The precipitate formed was filtered and purified by recrystallization from ethanol. Pure compound 1 was white solid, melting point (mp): 187–189°C (literature [24]: 188°C).

*Ethyl 3,9-dihydroxy-9-methyl-7-(4′-nitrophenyl)-6-oxo-7,8,10-trihydro-6H-benzo[c]-chromene-8-carboxylate (**2**) and ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4′-nitro-phenyl)-6H-dibenzo[c]pyran-6-one-8-carboxylate (**3a**)*. A mixture consisting of 4.2 mmol (0.46 g) of resorcinol, 4.0 mmol (0.79 g) of diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,3-dicarboxylate (**1**), and 15 mL of TFA was refluxed for 12 h. After completion of the reaction, TFA in the reaction mixture was evaporated in vacuum with a rotary evaporator. The residue was diluted with ethyl acetate (30 mL), and then washed with saturated $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate twice (2 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, EtOAc–hexane = 1:2 as eluent) to afford pure **2** and **3a**.

*Ethyl 3,9-dihydroxy-9-methyl-7-(4′-nitrophenyl)-6-oxo-7,8,10-trihydro-6H-benzo[c]-chromene-8-carboxylate (**2**)*. Yield: 21%, white solid; mp 252–254°C. ^{1}H NMR (300 MHz, dimethyl sulfoxide (DMSO)-d_6) δ (ppm): 10.47 (s, 1H), 8.08 (d, J = 8.7 Hz, 2H), 7.64 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 8.7 Hz, 2H), 6.82 (dd, J = 8.4, 2.4 Hz, 1H), 6.67 (d, J = 2.4 Hz, 1H), 4.84 (s, 1H), 4.39 (d, J = 10.8 Hz, 1H), 4.05–3.90 (m, 2H), 3.15 (d, J = 18.6 Hz, 1H), 2.98 (d, J = 18.6 Hz, 1H), 2.82 (d, J = 10.8 Hz, 1H), 1.34 (s, 3H), 1.03 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 171.5, 161.0, 159.7, 154.3, 152.7, 148.4, 146.4, 129.8, 126.5, 123.7, 118.8, 113.5, 112.2, 102.4, 68.1, 60.5, 57.9, 43.0, 40.5, 28.2, 14.5. MS-ESI m/z $[M+H]^+$ Calcd. for $C_{23}H_{22}NO_8$: 440.13; found: 440.25. Anal. Calcd for $C_{23}H_{21}NO_8$: C, 62.87; H, 4.82. Found: C, 62.93; H, 4.91.

*Ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4′-nitrophenyl)-6H-dibenzo[c]pyran-6-one-8-carboxylate (**3a**)*. Yield: 61%, yellow solid; mp 184–187°C. ^{1}H NMR (300 MHz, DMSO-d_6) δ (ppm): 10.61 (s, 1H), 8.12 (d, J = 8.7 Hz, 2H), 7.91 (d, J = 8.7 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 7.09 (s, 1H), 6.85 (dd, J = 9.0, 2.4 Hz, 1H), 6.76 (d, J = 2.7 Hz, 1H), 4.76 (s, 1H), 4.14–4.02 (m, 2H), 3.58 (s, 1H), 2.05 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 170.4, 161.6, 160.9, 155.3, 149.0, 147.1, 144.1, 142.9, 129.1, 126.4, 124.2, 118.5, 113.7, 112.3, 109.5, 103.0, 61.6, 51.2, 39.0, 24.6, 14.4. MS-ESI m/z $[M+H]^+$ Calcd. for $C_{23}H_{20}NO_7$: 422.12; found: 422.10. Anal. Calcd for $C_{23}H_{19}NO_7$: C, 65.55; H, 4.54. Found: C, 65.65; H, 4.59.

X-Ray Crystallography

A single crystal of compound **3a** suitable for X-ray diffraction analysis was obtained by slow evaporation from EtOAc–hexane (1:1) solutions. A yellow crystal having dimensions of 0.30 × 0.20 × 0.10 mm^3 was mounted on the top of the glass fibers. The data were collected at 293(2) K on an Enraf–Nonius CAD4 diffractometer (Delft, the Netherlands) using graphite monochromatic Mo K_α radiation (λ = 0.71073 Å). The intensity data were corrected for L*p* factors and empirical. The structure was solved by direct methods with the SHELXTL-97 program [25]. The final refinement was made by full-matrix least-squares techniques with anisotropic thermal parameters for the nonhydrogen atoms on F^2. All the H

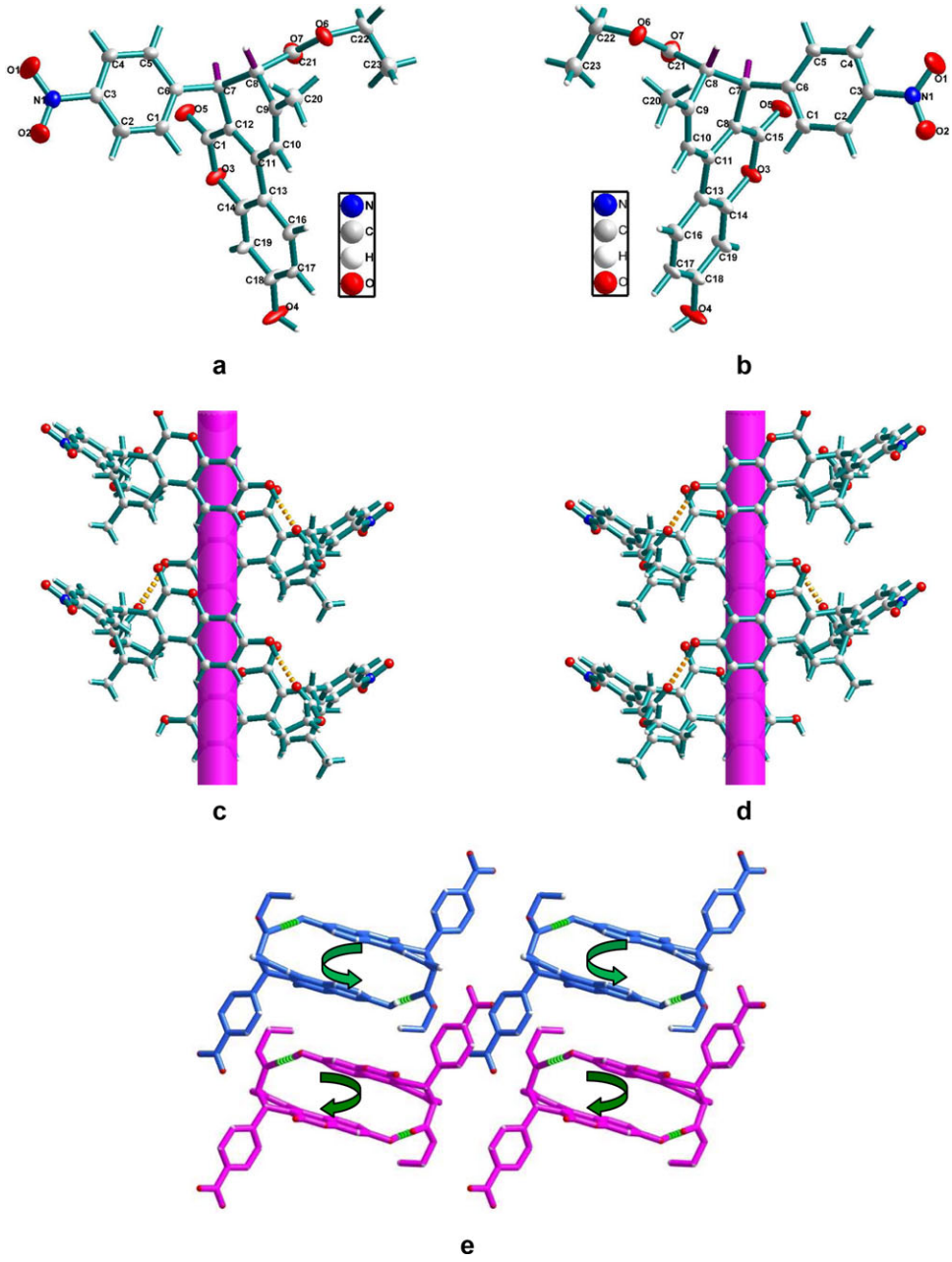


FIGURE 2 (a) and (b) ORTEP view of the crystal structure of (7R,8R)- and (7S,8S)-isomers of **3a**; (c) and (d) the illustration of left-handed helix (M helix) and right-handed helix (P helix) by H-bonding interaction in **3a**; (e) view of 1D helical chains in **3a** along the b-axis direction (hydrogen atoms are omitted for clarity).

atoms were added according to the theoretical models. Multiscan absorption correction was applied by use of the SADABS program [26].

CCDC-951554 contain the supplementary crystallographic data for this paper (excluding the structure factors), which can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data request/cif; or a copy of the cif file of compound **3a** can be obtained free of charge by e-mail inquiry to deposition: deposit@ccdc.cam.ac.uk) and is also available as supporting information.

RESULTS AND DISCUSSION

To initiate our study, diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclo-hexane-1,3-dicarboxylate (**1**) was prepared in excellent yield by condensing 4-nitrobenzaldehyde with ethyl acetoacetate under the catalysis of piperidine. As shown in

Scheme 1, condensation of diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,3-di-carboxylate (**1**) with resorcinol gave 3-hydroxy-2-cyclohexene derivative **2** in 21% isolated yield (Pechmann condensation product), together with an unexpected product **3** in 61% yield, which probably was formed by dehydration of compound **2**. Molecular ion peak in MS-ESI of the unexpected product also supported this supposition. When compound **2** was subjected to reaction conditions normally used for dehydration, for example, p-Toluenesulfonic acid in toluene, the same product **3** can be obtained in 92% yield (Scheme 1). So it can be safely concluded that the Pechmann condensation was accompanied by a tandem Pechmann–dehydration reaction. Theoretically, three different alpha-hydrogen atoms related to hydroxyl group in **2** can be eliminated with the hydroxyl group (Scheme 2). The exact structure of the product of the tandem Pechmann–dehydration reaction needs to be further elucidated.

The postulated structures **3b** and **3c** (Scheme 2) were excluded by the analysis of ^{1}H and ^{13}C NMR spectroscopy of the Pechmann–dehydration product, and **3a** was left as the only possible structure. Quite unexpectedly, the adjacent protons H^{a} and H^{b} in ^{1}H NMR spectrum (in DMSO-d_6) of structure **3a** are both represented as singlets and no coupling effect is seen between them, while the same protons H^{a} and H^{b} in the ^{1}H NMR spectrum of **2** (in DMSO-d_6) are split into two doublets with a coupling constant of $^{3}J_{\mathrm{Ha-Hb}} = 10.8$ Hz, an observation of an AX-type spin system.

To reveal the stereochemical information and especially the special orientation of the two adjacent protons H^{a} and H^{b}, pure **3a** was left to stand for 1 week, at which time a single crystal was obtained and its structure solved by X-ray crystallography (Fig. 2). The relevant crystallographic data are presented in Table 1, the selected bond lengths, bond angles, and torsion angles are given in Tables 2, 3, and 4, respectively. The H-bonding data are listed in Table 5. X-ray analysis reveals that the structure of **3a** crystallized in the monoclinic crystal system, space group of $P2_1/c$.

In the crystal structures of (7*R*,8*R*)- and (7*S*,8*S*)-**3a** (Figs. 2a and 2b), a 1,3-cyclohexadiene-fused coumarin ring system represents the central core of the molecule, with two side chains attached at C7 and C8 atoms, respectively. The 1,3-cyclohexadiene ring (C7-C8-C9-C10-C11-C12) which annulated at the 3,4-positions of the coumarin scaffold adopts a flattened half-chair conformation [27, 28] with atoms C8 and C9 deviating by 0.693 and 0.280 Å, respectively, from the mean plane defined by other atoms C7/C12/C11/C10. The value of the total puckering amplitude, Q_T, is 0.693 Å. The C9-C8-C7-C12 torsion angle was determined as –44.13°. It is worthy to note that the bond C9═C10 is somewhat out of the plane of the coumarin ring, making the torsion angle of C9-C10-C11-C12 being –13.00°. Careful inspection shows that the distance between the two hydrogen atoms respectively attached to C10 and C16 is 2.182 Å, which is shorter than the sum of the van der Waals radii of two hydrogen atoms (2.4 Å) [29], indicating a steric interaction between them. Hence, this kind of arrangement can ease the steric hindrance caused by the two hydrogen atoms. Overall, the tricyclic framework of the 1,3-cyclohexadiene-fused coumarin ring system displays a nearly coplanar configuration.

4-Nitrophenyl attached at C7 and carboxylate group attached at C8 are on the opposite side of the tricyclic framework of the compound **3a**. The benzene ring of 4-nitrophenyl group is almost perpendicular to the 1,3-cyclohexadiene ring (dihedral angle of 88.797°), this can be attributed to the flattened half-chair conformation of 1,3-cyclohexadiene ring and the steric interaction of aryl group with carboxylate group on coumarin ring. A dramatic twisting is also observed between carboxylate group

TABLE 1 Crystal Data and Structure Refinement for Compound **3a**

Empirical Formula	$C_{23}H_{19}NO_7$
Formula weight	421.39
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	16.069(3)
b (Å)	7.8940(16)
c (Å)	15.980(3)
α (°)	90.00
β (°)	90.15(3)
γ (°)	90.00
Volume (Å^3)	2027.0(7)
Z	4
Density (calcd.) (g/cm^3)	1.381
Absolute coefficient (mm^{-1})	0.103
F(000)	880
Crystal size (mm)	0.3 × 0.2 × 0.1
Temperature (K)	293(2)
Radiation (Å)	Mo K_α 0.71073
θ Min, max (°)	1.3, 25.4
Data set	limiting indices $-19 < h < 19$; $-9 < k < 0$; $-19 < l < 0$
Total Unique Data	3876, 3725
R (int)	0.032
N_{ref}, N_{par}	3725, 280
R, wR_2, *S*	0.0589, 0.1760, 1.01
CCDC number	951554

TABLE 2 Selected Bond Lengths for Compound **3a**

Bond Lengths	*(Å)*	*Bond Lengths*	*(Å)*
C7-C8	1.533(3)	C11-C13	1.445(4)
C7-C12	1.507(4)	C11-C12	1.354(3)
C8-C21	1.505(4)	C7-H7A	0.9800
C8-C9	1.519(3)	C8-H8A	0.9800
C9-C20	1.498(4)	C10-H10A	0.9300
C9-C10	1.335(4)	C12-C15	1.445(4)
C10-C11	1.460(4)	C6-C7	1.519(4)
C10-C11	1.460(4)		

attached at C8 and the 1,3-cyclohexadiene ring with the dihedral angle between them being 86.263°. Further inspection shows that the hydroxyl group at C18 and carboxylate group at C8 of adjacent molecules of **3a** are linked by strong H bonding. In addition, several intralayer C—H—O interactions are also observed for the title compound, despite their weakness. However, no obvious π–π interaction is found in the crystal structure.

Interestingly, the cooperation of the dramatic twisting between the carboxylate group attached at C8 and the 1,3-cyclohexadiene ring as well as the continuous H bonding induces the formation of attractive left- and right-handed 1D helical supramolecular polymer chains as shown in Figs. 2c and 2d. The (7*S*,8*S*)-isomer of **3a** induced a left-handed helical channel, while a right-handed helical channel was obtained from its enantiomer, the (7*R*,8*R*)-isomer of **3a**. Both the channel sizes of the left- and right-handed helical channels were determined as ~3.70 × 10.20 Å, and they arranged alternatively along the *b* axis with the pitch of 7.894 Å (Fig. 2e). As the left- and right-handed helical chains coexist in the crystal structure, the whole crystal is racemic and does not exhibit optical activity. It is noteworthy that molecular structures with helical polymer chain morphology, as shown in **3a**, have practical implication in multidisciplinary areas on account of their structure similarities with DNA [30–35].

TABLE 5 Geometry for Hydrogen Bonds in the Crystal Structure of **3a**

D—H . . . A	*D—H*	*H—A*	*D—A*	*D—H—A*
O4—H4B . . . O7	0.8200	1.8800	2.700(4)	174.00
C10—H10A . . . O5	0.9300	2.4300	3.327(3)	162.00
C20—H20C . . . O6	0.9600	2.5500	3.120(4)	118.00
C22—H22A . . . O1	0.9700	2.4900	3.354(5)	149.00

A much more detailed analysis of X-ray crystallography of **3a** shown that the H7-C7-C8-H8 torsion angle is 78.862°, and therefore explained the reason of the unusual coupling effect between C—H^a and C—H^b (H7 and H8 in Fig. 2) mentioned above. It is well known that the maximum coupling constant ^3J will occur when the dihedral angle is 0° or 180° and the minimum coupling constant (often ≈0 Hz) occurs when the dihedral angle is near 90° (actually occurring around 85°), according to the Karplus relationship [36–38]. Therefore, this phenomenon could be explained by the Karplus relationship so that the H^a–H^b coupling constant ^3J is about 0 Hz. The X-ray crystallography and ^{1}H NMR spectrum of **3a** are also indicative of the intramolecular dehydration taking place only between the hydroxyl group and the H^c/H^d

TABLE 3 Selected Bond Angles for Compound **3a**

Bond Angles	*(°)*	*Bond Angles*	*(°)*	*Bond Angles*	*(°)*
C10-C11-C12	119.0(2)	C7-C8-C21	110.3(2)	C8-C7-H7A	107.00
C7-C12-C15	116.3(2)	C8-C9-C20	118.8(2)	C12-C7-H7A	107.00
C11-C12-C15	121.8(2)	C10-C9-C20	122.4(2)	C7-C8-H8A	109.00
C7-C12-C11	121.8(2)	C8-C9-C10	118.7(2)	C9-C8-H8A	109.00
C8-C7-C12	110.5(2)	C9-C10-C11	122.4(2)	C21-C8-H8A	109.00
C6-C7-C12	111.2(2)	C10-C11-C13	121.3(2)	C9-C10-H10A	119.00
C7-C8-C9	112.4(2)	C12-C11-C13	119.7(2)	C11-C10-H10A	119.00
C9-C8-C21	107.6(2)	C6-C7-H7A	107.00		

TABLE 4 Selected Torsion Angles for Compound **3a**

Torsion Angles	*(°)*	*Torsion Angles*	*(°)*	*Torsion Angles*	*(°)*
C6-C7-C8-C9	81.3(3)	C12-C7-C8-C21	76.0(3)	C9-C10-C11-C12	–13.0(4)
C12-C7-C8-C9	-44.1(3)	C7-C8-C9-C10	33.6(3)	C13-C11-C12-C7	175.4(2)
C8-C7-C12-C11	30.1(3)	C7 -C8-C9-C20	–148.7(2)	C10-C11-C12-C7	–1.7(4)
C6-C7-C12-C15	79.3(3)	C21-C8-C9-C20	89.7(3)	C13-C11-C12-C15	–0.1(4)
C6-C7 -C8-C21	–158.6(2)	C8-C9-C10-C11	–4.4(4)	C10-C11-C12-C15	–177.1(3)
C8-C7-C12-C15	–154.2(2)	C20-C9-C10-C11	178.0(3)		
C6-C7-C12-C11	–96.4(3)	C9-C10-C11-C13	170.0(3)		

to form **3a**, but not between the hydroxyl group and the H^b to form **3c**, or methyl to form **3b** (Scheme 2). This is probably because the former can form an extended and more stable conjugated aromatic system (**3a**) when compared with **3b** and **3c**.

CONCLUSIONS

In an attempt to construct 3:4-fused six-member carbocyclic ring coumarin, an unknown Pechmann–dehydration product was isolated as the main product when condensation of diethyl 4-hydroxy-4-methyl-2-(4′-nitrophenyl)-6-oxocyclohexane-1,3-dicarboxylate (**1**) with resorcinol in the presence of TFA. The exact structure of the Pechmann–dehydration product was determined as a racemate of enantiomers (7*R*,8*R*)- and (7*S*,8*S*)-ethyl 7,8-dihydro-3-hydroxy-9-methyl-7-(4-nitro-phenyl)-6H-dibenzo-[*c*]pyran-6-one-8-carboxylate (**3a**) by single crystal X-ray diffraction studies together with MS-ESI, ^{1}H, and ^{13}C NMR spectroscopy. The X-ray crystal structure also revealed that **3a** possesses an extended and more stable conjugated aromatic system as a consequence of the selectivity of intramolecular dehydration behavior of Pechmann condensation product **2**. An attractive feature of the crystal structure of compound **3a** is that the (7*S*,8*S*)- and (7*R*,8*R*)-isomers respectively form left- and right-handed helical polymer chains via supramolecular self-assembly with the channel size of 3.70 × 10.20 Å, which are arranged alternatively along the *b*-axis direction with pitch length of 7.894 Å. Further inspection shows that the continuous H bonding, together with the dramatic twisting between carboxylate group attached at C8 and the 1,3-cyclohexadiene ring favor the formation of the helical supramolecular chains.

SUPPORTING INFORMATION

Supporting information related to the crystallographic data of compound **3a** is available from Chaoyue Chen njuchaoyuechen@163.com on request.

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