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A dipseudoacid, $C_{16}H_{18}O_6$

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Abstract

Pseudoacids, or cyclic oxocarboxylic acids commonly form non-planar, complementary and non-cooperative, dimeric hydrogen-bonds. A dehydration resistant arylpyran dipseudoacid, $C_{16}H_{18}O_6$, has been synthesized and characterized. Crystals of *trans*-4,4,8,8-tetramethyl-3,7-dihydroxy-1,2,3,4,5,6,7,8-octahydro-2,6-dioxaanthracen-1,5-dione occur in the monoclinic system and form linear hydrogen-bonded chains; it has an elevated melting point without decomposition at 574.6 K.

Keywords: Oxocarboxylic acids; Pseudoacids; Crystallography; Oxidation; Hydrogen-bonding

1. Introduction

Hydrogen-bonding is one of the more important intermolecular forces of attraction affecting the properties of polar organic substances. Systems such as purines and pyrimidines, carboxylic acids, oximes, and *syn*-amides engage in multiple, complimentary hydrogen-bonding and produce local ring structures and in combination support extended supramolecular structures [1,2]. Typically, these paired donor–acceptor systems are approximately co-planar. Cyclic oxocarboxylic acids form an exception. Intramolecular cyclization of aldehyde or ketone group with a carboxylic acid produces the lactol or pseudoacid function in which the (chiral) hydroxyl and carbonyl groups are not co-planar and lack an intervening π-system. It has been found previously that pseudoacids commonly, but not exclusively, form dimeric, complementary hydrogen-bonded intermolecular structures with a non-planar $R_2^2(12)$ ring [3,4]. These pair-wise hydrogen-bonds are weaker than in carboxylic acid dimers since the linkage is not cooperative. This is supported by the somewhat longer hydrogen-bonded O···O distances in pseudoacids (2.8 Å) compared to those in carboxylic acids (2.6 Å).

Lattice stabilization by introduction of a supramolecular hydrogen-bonded network can be illustrated by the contrast between benzoic acid (mp 395 K) and terephthalic acid (mp 673 K with sublimation). Benzoic acid forms local dimeric hydrogen-bonds, while terephthalic acid forms infinite linear chains [5,6]. At present, no example of a dipseudoacid with a structure permitting linear hydrogen-bonded chains has appeared. A simple system which may be elaborated to show two pseudoacid functions is the dehydration resistant arylpyran 3-hydroxy-4,4-dimethyl-3,4-dihydroisobenzopyran-1-one (**1**), mp 331 K, 337 K [7]. Thus, the target molecule is 4,4,8,8-tetramethyl-3,7-dihydroxy-1,2,3,4,5,6,7,8-octahydro-2,6-dioxaanthracen-1,5-dione (**2**) (Fig. 1).

In the usual scheme for forming oxocarboxylic acids that can cyclize, the interacting functional groups are introduced simultaneously by oxidative cleavage of a precursor α-hydroxyketone [8]. In the present work, we pursued a symmetric synthesis (Fig. 2) which begins with a double alkylation of benzene with mesityl oxide to produce diketone **3**. After oxidation to bis(2′-methyl-1′-carboxyprop-2-yl)benzene **4**, double cyclization produces a mixture of 3,3,7,7-tetramethyl-1,2,3,5,6,7-hexahydro-*s*- and *as*-indacen-1,5-diones (**5, 6**). Oxidation of **5** leads to the dipseudoacid system. The synthesis, structure, and spectral properties of the *trans*-dipseudoacid **2** are described.

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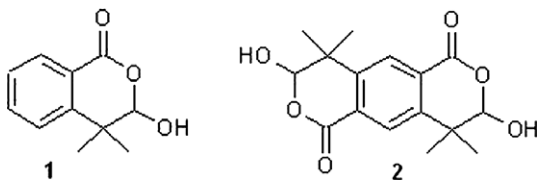

Fig. 1. Arylpyran pseudoacid, **1**, and dipseudoacid, **2**.

2. Experimental

Reagents and solvents in the best commercial purities were obtained from Aldrich Chemical Co. and used as received. Nuclear magnetic resonance spectra were obtained on a JEOL Eclipse 400 + (400 MHz) instrument; $(CH_3)_4Si$ reference. Melting points were determined on a Shimadzu DSC-5 differential scanning calorimeter (under dinitrogen, at a heating rate of 10 °C/min) and a melt-temp capillary apparatus.

*2.1. 1,4-Bis-(4′-oxo-2′-methylpent-2′-yl)benzene (**3**)*

Benzene (8.550 g, 109.6 mmol) was combined with 50 mL of petroleum ether and 33.758 g (253.2 mmol) $AlCl_3$. The mixture was stirred vigorously while 22.462 g mesityl oxide (229.2 mmol) dissolved in 40 mL petroleum ether was added dropwise over 30 min. During the addition, the mixture began to boil, and the reaction was controlled by occasional cooling. After the addition, the mixture was stirred for 1 h; stirring halts due to formation of a solid product mass below a light-colored organic layer. The contents of the reaction flask were transferred into a 2 L beaker half filled with ice and 150 mL of 12 M HCl; the mixture was stirred until all of the solids were hydrolyzed. The organic phase was decanted, and the solvent was removed, leaving an amber-colored oil, which crystallized on standing. Yield 27.9 g, 93%. Analysis: ^{1}H NMR (δ_H, $CDCl_3$, 20 °C): δ 7.30, 4H, s, aryl-H; 2.70, 6H, s, CH_3CO; 1.77, 4H, s, CH_2; 1.40, 12H, s, CH_3's; $^{13}C\{^1H\}$ δ_C, $CDCl_3$, 20 °C): 208.3, C=O; 145.8, C_{ar}—CMe_2; 125.5, $C_{ar}H$; 57.1, CH_2; 37.1, C quaternary); 32.0 CH_3 terminal; 29.0 CH_3's.

*2.2. 1,4-Bis(1′-carboxy-2′-methylprop-2′-yl)benzene (**4**)*

In a 1 L flask fitted with a reflux condenser, 8.3 g (30.3 mmol) diketone **3** was combined with 250 mL of 6% commercial bleach. The two-phase mixture was stirred vigorously and heated to 70 °C for 18 h. After cooling, the clear aqueous phase was separated from the yellow oily residue by decantation through several layers of filter paper. A sample of the aqueous phase showed absence of hypochlorite on testing with potassium iodide. The aqueous mixture was cooled to 2 °C, and 22 mL of 12 M HCl was added; after vigorous agitation, a white precipitate separated. The product was isolated by suction filtration, washed with water, dried, and then recrystallized from a minimum of 95% ethanol producing **4** as a colorless solid; yield: 4.83 g, 60%. Analysis: ^{1}H NMR (δ_H, $CDCl_3$, 20 °C): 7.27, 4H, s, aryl-H's; 6.27, 2H, broad s, hydroxyl-H; 2.64, 4H, s, CH_2's; 1.43, 12H, s, CH_3's; $^{13}C\{^1H\}$ (δ_C, $CDCl_3$, 20 °C): 177.5, CO_2; 145.2, C_{ar}—CMe_2; 125.4, C_{ar}—H; 48.1, CH_2's; 36.8, C(quaternary); 29.3 CH_3's.

*2.3. Cyclic diketones: 3,3,7,7-tetramethyl-1,2,3,5,6,7-hexahydro-s-indacen-1,5-dione, "anti" isomer (**5**) and 3,3,7,7-tetramethyl-1,2,3,5,6,7-hexahydro-as-indacen-1,5-dione, "syn" isomer (**6**)*

About 30 mL of polyphosphoric acid (PPA) was placed in a 100 mL beaker, and heated on a hot plate to 90 °C. While stirring with a glass rod, 4.60 g (16.5 mmol) of **4** was added, and the mixture was continuously stirred while maintaining 91–99 °C. After 20 min, 25 mL of PPA was added, and heating and stirring continued for a total reaction time of 1 h. The deep brown mixture was allowed to cool to ambient temperature, and 100 g ice was added and the mixture was stirred to discharge the dark color. After extraction twice with 20 mL portions of ether, the combined yellow organic phases were washed with saturated $NaHCO_3$, then with water. The monocyclized keto-acid byproduct was isolated by acidifying the bicarbonate wash solution; yield 2.205 g, 51%. After drying the ether solution with anhydrous Na_2SO_4, ether was evaporated leaving crude **5** and **6** as an orange-colored solid; yield

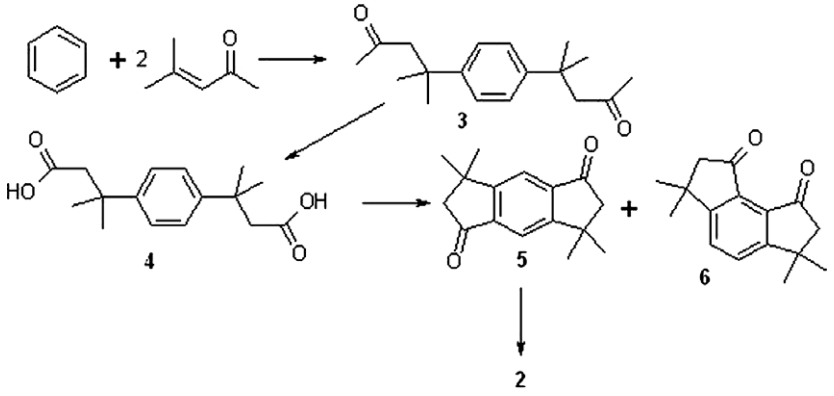

Fig. 2. Symmetric synthesis of a dipseudoacid.

0.767 g, 19%. NMR analysis (see below) showed 78:22 ratio of *anti* to *syn* diketone isomers. They were separated by column chromatography on silica gel (100 mesh; diameter 1.5 cm, length 6 cm) eluting first with $CHCl_3$ to remove the less polar anti isomer **5**; then switching to $CHCl_3$:ethyl acetate (3:1) to elute the minor *syn* isomer **6**. Analysis for **5**: ^1H NMR (δ_H, $CDCl_3$, 20 °C): 7.73, 2H, s, aryl-H; 2.63, 4H, s, CH_2; 1.41, 12H, s, CH_3's; $^{13}C\{^1H\}$ (δ_C, $CDCl_3$, 20 °C): 202.7, C=O; 164.8, 132.4, C_{ar}—C(Me_2); 129.7, $C_{ar}H$; 53.5, CH_2; 38.64, C quaternary; 30.0, CH_3. The crystal structure of **5** was determined (see below). For **6**: (δ_H, $CDCl_3$, 20 °C): 7.79, 2H, s, aryl-H; 2.66, 4H, s, CH_2; 1.43, 12H, s, CH_3's; $^{13}C\{^1H\}$ (δ_C, $CDCl_3$, 20 °C): 205.8, C=O; 162.8, 140.6, C_{ar}—CMe_2; 118.6, C_{ar}—H; 53.7, CH_2; 38.59, C(quaternary); 30.2, CH_3's.

2.4. Nitric acid oxidation of the "anti" diketone (5)

In a small glass vial, 0.050 g (0.21 mmol) of the "*anti*"-diketone **5** was dissolved in 1.0 mL concentrated sulfuric acid and cooled to 0 °C. A cooled mixture of 1 mL concentrated (70%) nitric acid and 1 mL concentrated sulfuric acid was added, and the resulting mixture was thoroughly mixed at 0 °C. After 45 min at 0 °C, the sample was allowed to warm to room temperature, and the mixture was transferred at once into 50 mL water. The aqueous solution formed was extracted twice with 10 mL portions of CH_2Cl_2. On evaporation of the solvent, an oily pale-yellow solid was obtained. Thin layer chromatography (silica gel, chloroform:ethyl acetate 10:1) showed essentially three components with R_f 0.0 (**2**), 0.2 (**7a**), and 0.8 (**7b**). The most polar component was nearly insoluble in $CHCl_3$, which solvent was used to transfer the mixture of the two less polar components for separation by column chromatography on silica gel (100 mesh; 1.2 cm diameter, 6 cm length). The column was eluted with $CHCl_3$ at first, then combined with increasing proportions of ethyl acetate. A small amount of the most polar component (**2**) finally elutes with $CHCl_3$:ethyl acetate (1:1). Analyses: **7a**, ^1H NMR (δ, $CDCl_3$, 20 °C, each resonance minutely doubled except hydroxyl H): 8.15, 1H, s, aryl-H; 8.10, 1H, s, aryl-H; 6.42, 1H, s, H—$CONO_2$; 5.55, 1H, s, H—CO_2; 4.2, 1H, s (br), OH; 1.502, 1.489, 6H, s, CH_3; 1.420, 1.404, 6H, s, CH_3; $^{13}C\{^1H\}$ (δ, $CDCl_3$, 20 °C, *cis* and *trans* isomers): 163.05, 160.84/160.79, CO_2; 145.72/145.68, 143.31, C_{ar}—CMe_2; 128.98, 127.74, C_{ar}—CO; 127.27/127.22, 126.41, $C_{ar}H$; 102.96, 102.09/102.00, O—C—O; 38.567/38.539, 37.007/36.965, C quaternary; 28.778/28.653, 27.330/27.056, 22.046/22.011, 21.919/21.891, CH_3. This component crystallizes as the *cis* isomer, and the crystal structure of *cis*-**7a** was determined (see below). For **7b**, ^1H NMR (δ, $CDCl_3$, 20 °C, *cis* and *trans* isomers) 8.114/8.111, 2H, s, aryl-H; 6.438/6.435, 2H, s, methine-H; 1.587/1.580, 6H, s, methyl-H; 1.539/1.527, 6H, s, methyl; $^{13}C\{^1H\}$ (δ, $CDCl_3$, 20 °C, *cis* and *trans* isomers): 160.49/160.44, CO_2; 144.08, C_{ar}—CMe_2; 127.86/127.82, C_{ar}—CO;127.01, $C_{ar}H$; 102.87/102.85, O—C—O; 37.10/37.06, C(quaternary); 28.80/28.71, 21.87, CH_3.

2.5. 4,4,8,8-Tetramethyl-3,7-dihydroxy-1,2,3,4,5,6,7,8-octahydro-2,6-dioxaanthracen-1,5-dione, the dipseudoacid, (2)

This substance was found in the chloroform insoluble component of the products of the nitric acid oxidation (see above), and formed the most polar chromatographic fraction. It is also derived from the R_f 0.2 material, which was dissolved in 2 mL ethanol and 1 mL water, and treated with a few drops of 0.5 N NaOH solution and allowed to react for 5 min. The mixture was acidified with 0.5 N HCl and became slightly cloudy. The alcohol was evaporated under an air stream, and the noticeably cloudy aqueous layer was extracted with dichloromethane. On evaporation dipseudoacid **2** was recovered as colorless crystals; it was recrystallized from chloroform, acetone or methanol. Melting point: 574.6 K (DSC peak; broad), 569–576 K (capillary, without decomposition). Analysis: ^1H NMR ($CDCl_3$, recrystallized from MeOH, 20 °C, most resonances minutely doubled except hydroxyl H's, δ_H): 8.06, 2H, s, aryl-H; 5.58, 2H, s, methine-H; 6.0, 2H, s (br), OH; 1.46, 6H, s, CH_3; 1.39, 6H, s, CH_3; $^{13}C\{^1H\}$ (δ_C, $CDCl_3$, 20 °C, *cis* and *trans* isomers): 162.8, CO_2; 145.2, C_{ar}—CMe_2; 128.8, C_{ar}—CO; 126.2, $C_{ar}H$; 101.9, O—C—O; 38.4, C quaternary; 26.3, 21.4, CH_3. The crystal structure of **2** was determined (see below). In $CDCl_3$, most ^{13}C and ^1H resonances are doubled from contributions for each of the diastereomers. In acetone-d_6, each resonance is broadened into single features, indicating interconversion between diastereomers is faster in this polar solvent. In $CDCl_3$ (70%): d_4-methanol (30%) at 295 K, methyl protons are a broad singlets, and two very broad carbon methyl resonances are seen suggesting an even faster rate of interconversion.

2.6. Crystallographic analysis

Crystal structures were obtained for compounds **3**, **4**, **5**, **7a**, and **2**. Data were obtained on an Oxford Diffraction Gemini S system with a charge coupled device operating under the CrysalisPro system [9] using Mo or CuKα radiation. Structures were solved with SHELXS-86 and refined with SHELXL-97 [10]. Referenced CCDC numbers contains the supplementary crystallographic data for these structures. For open diketone **3**, CCDC 647883, crystals were obtained from the oil, monoclinic, space group $P2_1/n$, $a = 11.5966(15)$ Å, $b = 6.6798(7)$ Å, $c = 11.7635(13)$ Å, $\beta = 116.476(15)°$, $V = 815.7(2)$ Å^3, with four molecules in the cell, 293 K, 2550 data, $R_1 = 0.071$, $wR_2 = 0.200$ [$I > 2\sigma(I)$], $S = 1.01$. For open diacid **4**, CCDC 647881, crystals from 95% ethanol, monoclinic, space group $P2_1/n$, $a = 18.4117(18)$ Å, $b = 9.0649(10)$ Å, $c = 18.4506(19)$Å, $\beta = 99.666(11)°$, $V = 3035.7(5)$ Å^3, with eight molecules in the cell, 293 K, 4968 data, $R_1 = 0.081$, $wR_2 = 0.229$ [$I > 2\sigma(I)$], $S = 1.08$. For open diacid **4** at 102 K, CCDC

647882, monoclinic, space group Cc, $a = 21.8163(2)$ Å, $b = 8.9653(1)$ Å, $c = 23.2716(2)$ Å, $\beta = 104.718(1)°$, $V = 4402.33(7)$ Å^3, with 12 molecules in the cell, 6914 data, $R_1 = 0.036$, $wR_2 = 0.096$ [$I > 2\sigma(I)$], $S = 0.96$. For cyclic diketone **5**, CCDC 647884, crystals from benzene, monoclinic, space group $P2_1/n$, $a = 5.7765(2)$ Å, $b = 15.9490(5)$ Å, $c = 7.5342(3)$ Å, $\beta = 110.015(5)°$, $V = 652.20(7)$ Å^3, with four molecules in the cell, 293 K, 1910 data, $R_1 = 0.046$, $wR_2 = 0.133$ [$I > 2\sigma(I)$], $S = 1.073$. For the *cis*-heminitryloxy pseudoacyl anhydride **7a**, CCDC 647885, crystals from chloroform, orthorhombic, space group $Pbca$, $a = 11.6085(11)$ Å, $b = 3.6901(12)$ Å, $c = 20.8707(19)$ Å, $V = 3316.8(5)$ Å^3, with eight molecules in the cell, 294 K, 3344 data and $R_1 = 0.126$, $wR_2 = 0.227$ [$I > 2\sigma(I)$], $S = 0.96$. For the *trans*-dipseudoacid **2**, CCDC 647886, crystals from chloroform, monoclinic, space group $C2/c$, $a = 14.2880(3)$ Å, $b = 11.2230(2)$ Å, $c = 10.1703(2)$ Å, $\beta = 101.898(2)°$, $V = 1595.81(5)$ Å^3, with four molecules in the cell, 293 K, 1364 data, $R_1 = 0.038$, $wR_2 = 0.116$ [$I > 2\sigma(I)$], $S = 1.05$. CCDC data can be obtained free of charge from www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

3. Results and discussion

In the system and synthetic strategy pursued, symmetry and simplicity are repeatedly encountered. Dialkylation of benzene proceeds in good yield to the diketone **3** which shows four singlets for its 26 hydrogens in the PMR spectrum. In the crystal, molecules reside on inversion centers of the monoclinic lattice (Fig. 3) and therefore show C_i symmetry. The conformation adopted places one of the side-chain methyl groups nearly in the ring plane. Diacid **4** is obtained by haloform oxidation of **3**, and its PMR spectrum also shows four singlets. In the solid state at 100 K, three diacid molecules comprise the asymmetric unit, and each shows approximate C_i symmetry, though not required by their general locations in the monoclinic lattice (Fig. 4). Molecular conformations differ in the orientation of the side-chain groups. In two of the three, the conformations show methyl groups nearly in the approximate aryl ring plane. On warming to room temperature (293 K), crystals of **4** show a transformation to a different monoclinic cell without fracture. In this modification, two molecules comprise the asymmetric unit, each with approximate C_i symmetry, and with conformational variety as before. Diacid molecules in each modification form infinite hydrogen-bonded chains supported by the typical dimer carboxylic acid motif.

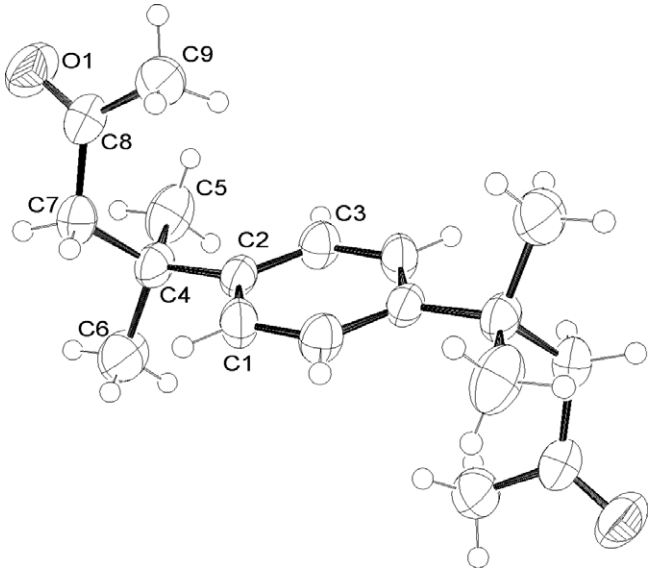

Fig. 3. Ellipsoid plot of diketone **3**.

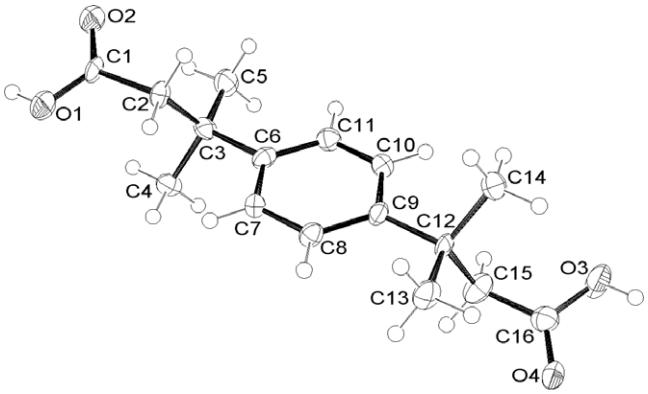

Fig. 4. Ellipsoid plot of one of three inequivalent molecules of diacid **4** at 100 K.

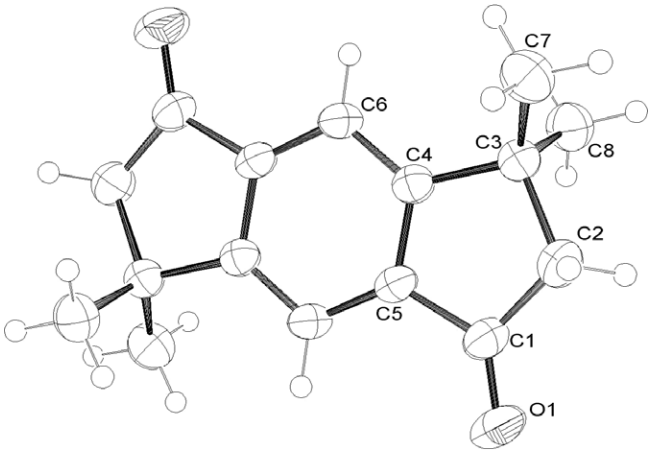

Fig. 5. Ellipsoid plot of "*anti*"-diketone **5**.

Double cyclization of diacid **4** with polyphosphoric acid produces a mixture of cyclic diketones **5** and **6** in relatively poor yields. PMR spectra of the separated cyclic diketones each show three singlets for their 18 hydrogens. Molecules of the major isomer, **5**, show C_i symmetry, occupying inversion centers on the monoclinic lattice (Fig. 5). Oxidation of **5** to form the diacetoxy diketone derivatives (**8**) proceeds in good yield, but subsequent saponification leads to

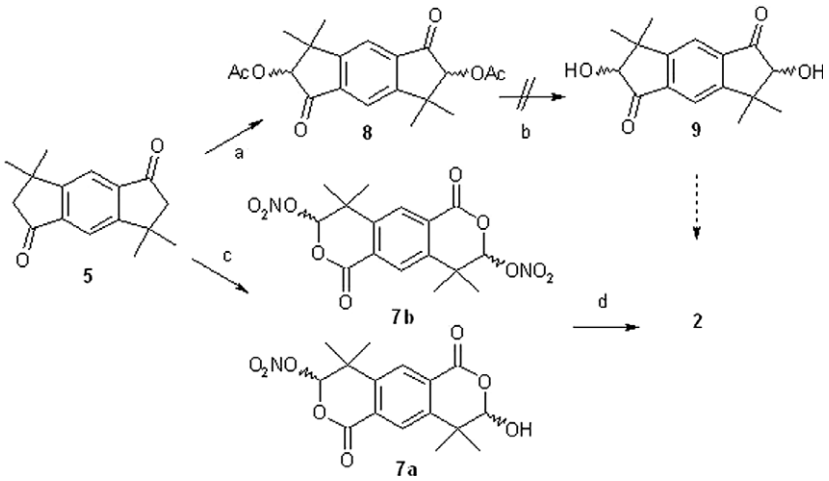

Fig. 6. Revised final oxidative steps; (a) $Pb(OAc)_4$, AcOH, Ac_2O; (b) MeOH, H_2O, K_2CO_3, N_2, 25 °C; (c) HNO_3, H_2SO_4, 0 °C, then H_2O; (d) $NaOH_{(aq)}$, then H_3O^+.

unidentified polar products, without evidence for the formation of di(α-hydroxy)diketones (**9**). The precursor for periodate oxidative cleavage was therefore not accessible by this route. Oxidation and oxidative cleavage of **5** was accomplished with nitric acid (Fig. 6) following the discovery of this reaction by Cooper et al. [7]. Diketone **5** seemed less likely to undergo ring nitration due to steric constraints, so treatment with concentrated nitric and sulfuric acid at 273 K and hydrolysis with water produced good yields of a mixture of the diastereomeric heminitryloxy pseudoanhydrides **7a**, dinitryloxy pseudoanhydrides **7b**, and dipseudoacids **2**. Nitryloxy derivatives were identified by the characteristic magnetic resonance features of their pseudoacyl H at about δ_H 6.5 ppm and pseudoacyl C at about δ_C 103 ppm; in comparison, pseudoacyl H occurs at about δ_H 5.5 ppm. For each of these reaction products, the magnetic resonance spectra show solution mixtures of diastereomers. Comparable carbon resonances varying in the range <0.01–0.09 ppm. Aryl carbon assignments are well fit by use of typical substitutent shieldings [11] and supported by DEPT experiments. Compound **7a** forms the *cis* isomer on crystallization, and confirmed the nitryloxy substitution (Fig. 7). Hydrolysis of the nitryloxy pseudoanhydrides with dilute aqueous base, then acidification produces dipseudoacids **2**, which crystallize as the *trans* diastereomer.

In the solid state, molecules of the dipseudoacid, **2** (*trans*-4,4,8,8-tetramethyl-3,7-dihydroxy-1,2,3,4,5,6,7,8-octahydro-2,6-dioxaanthracen-1,5-dione) show C_i symmetry, lay on inversion centers of the monoclinic space group $C2/c$, a half-molecule comprising the asymmetric unit (Fig. 8). Hydroxy groups are disposed axially, as is typical for this function and possibly indicating an operative anomeric effect. Molecules are hydrogen-bonded to neighbors on each side forming infinite chains, with the links occurring by complementary pairing (Fig. 9). Crystals of **2** melt without decomposition or apparent sublimation at 574.6 K, over 230 K above that for either of the two modifications of **1** [5]. Clearly the formation of infinite chains has lent considerable stability to the lattice of the dipseudoacid. Still, it is not as robust as terephthalic acid (mp 673 K), which also forms infinite hydrogen-bonded chains [4]. Carboxylic acids form complementary and cooperative dimeric hydrogen-bonds, in which π systems may be thought to overlap throughout the process of proton exchange between equivalent carboxyl groups. In pseudoacids, cooperativity is lost since proton exchange would

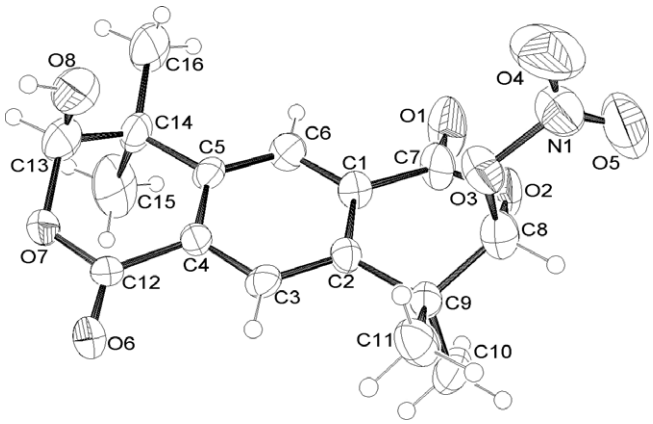

Fig. 7. Ellipsoid plot of *cis*-heminitryloxy pseudoanhydride **7a**.

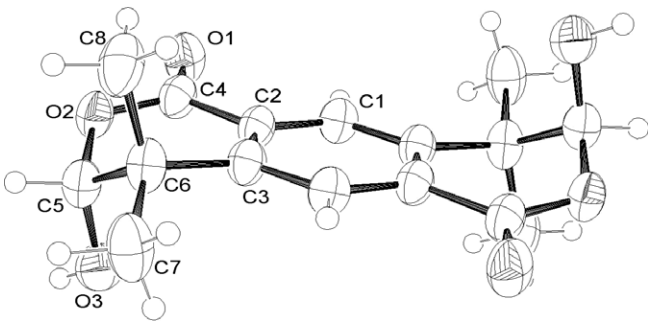

Fig. 8. Ellipsoid plot of the *trans*-dipseudoacid **2**.

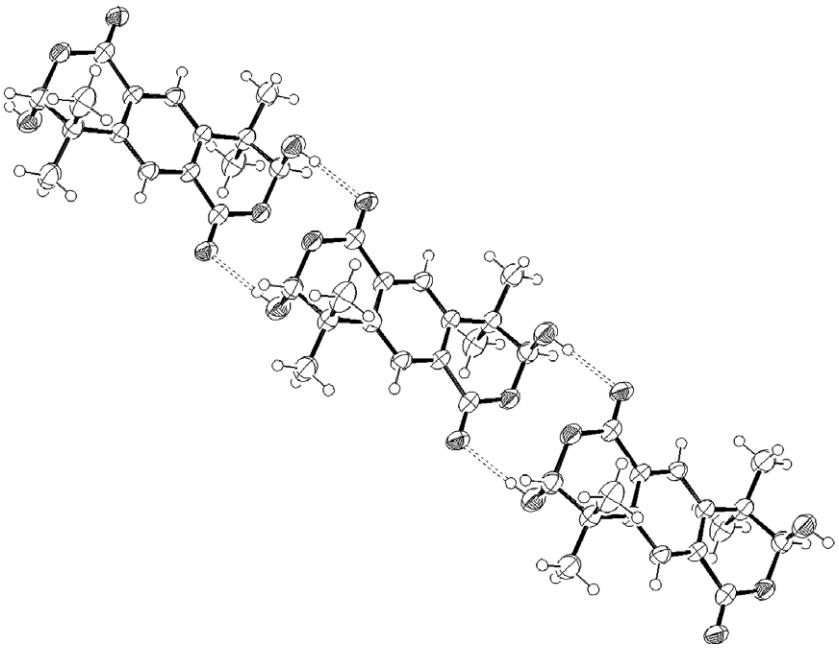

Fig. 9. Plot showing hydrogen-bonded chains formed by *trans*-dipseudoacid **2**.

Table 1
Relevant metrics of complementary hydrogen-bonded pseudoacids[a]

Compound	Angle O—H···O (°)	Distance O···O (Å)	Reference
1	172.2	2.759	[7]
	159.4	2.833	
1	169.1	2.809	[7]
2	168.9	2.767	This work
7a	169.8	2.789	This work

[a] OH bond lengths normalized to 0.96 Å; angle esd's $\leqslant 1.5^{o}$, distance esd's $\leqslant 0.005$ Å.

involve inequivalent molecular forms (cyclic and open forms) and rehybridization at the lactol carbon. Without coplanarity of the interacting groups, effective π overlap between the two forms does not occur. In solution, equilibration between the two diastereomeric of **2** occurs, with the rate of interconversion apparently depending on solvent polarity. An intermediate open form has not been detected. Both **7a** and **2** show complementary hydrogen-bonding between pseudoacid groups. The hydrogen-bond features (Table 1) are similar to those observed in the modifications of pseudoacid **1**.

4. Conclusions

A arylpyran dipseudoacid has been synthesized by oxidation of the precursor *anti*-diketone with nitric and sulfuric acids. The dipseudoacid shows chain hydrogen-bonding with complementary but non-cooperative dimeric links, and a remarkably high melting point.

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