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Tetrahedron Letters 49 (2008) 1870–1876
Tetrahedron Letters

Protection of the carbonyl groups in 1,2-indanedione: propellane versus acetal formation

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Received 11 November 2007; revised 16 December 2007; accepted 3 January 2008
Available online 8 January 2008

Abstract

The product resulting from the reaction between 1,2-indanedione and ethylene glycol under acidic catalysis is 2,5,7,10-tetraoxapropellane and not 1,2-dispirane as previously reported. Similar reactions also occur with 2-mercaptoethanol and 1,2-ethanedithiol, which form analogous propellanes and not corresponding thioacetals. This explains the difficulty of removing the protective groups under acidic conditions. These findings were corroborated by quantum chemical calculations. Under similar conditions, the longer-chain diol, 1,3-propyleneglycol and its thiol-analogue, 1,3-propanedithiol, form only mono-acetals, even when a 3-fold excess of the diol is applied. The nucleophilic attack, however, takes place at different positions: while propanedithiol forms the acetal at C-1, propylene glycol forms the acetal at C-2.

Keywords: 1,2-Indanedione; Acetals; Propellanes; Protective groups

1. Introduction

Of the two isomeric diketones that are derived from indane, 1,3-indanedione has drawn most attention. Over the last decade, however, there has also been a growing interest in the chemistry of the other isomer, 1,2-indanedione (**1**). It has become a major component of patented hair-dyes,[1] a starting material in the synthesis of Crixivan, a leading HIV protease inhibitor,[2] and a fluorogenic amino acid and fingerprint reagent.[3]

In the search for more sensitive reagents for amino acids and latent fingerprints, novel methods for preparing derivatives of **1**, bearing substituents on the aromatic ring have been devised[3a,g,4] and the reactivity of the 1,2-dicarbonyl system has also been studied.[3f,5] A systematic study of the enantioselective hydrogenation of **1** was published recently.[6] Substituted indanediones have been prepared by introducing the substituents at the first stage and forming the diketone moiety in the final stage.[3] Any attempt to functionalize directly the aromatic ring of **1** would require protection of the carbonyl groups, which are quite sensitive to nucleophilic attack.[3a] In a recent article, Butenschön et al. reported a simple route to the interesting planar chiral tricarbonyl(indane-1,2-dione)chromium complex, which involved acetal protection of the keto groups of 1,2-indanedione.[7] They treated **1** with ethylene glycol in the presence of *p*-toluenesulfonic acid (PTSA) and obtained what they thought to be diacetal **2a** in good yield, along with some of mono-acetal **3**. Their attempts to remove the protective groups with 6 N hydrochloric or sulfuric acid were unsuccessful and oxidative deacetalization with trityl tetrafluoroborate was required for this purpose. We have recently conducted a series of experiments in an attempt to substitute the aromatic ring of **1**, which already contains the two keto groups. Our protection experiments show that the assumed diacetals or their sulfur analogues **2a**–**c** are not obtained under the reaction conditions described by the previous authors.[7] The actual products are their isomeric acetals, which possess a propellane, **4a**–**c** rather than

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0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.01.012

a dispiro structure. This also explains the difficulty of removing the protective groups under conditions that should hydrolyze common cyclic acetals.

The product which was obtained by us in the same reaction, with two different acidic catalysts, PTSA and $BF_3{\cdot}OEt_2$, showed identical properties to **2a** (see Section 2), but had the propellane structure **4a** rather than the dispirane structure **2a**.

A few years ago, we reported the formation of 2,7-dioxa-5,10-dithiapropellane **4b**, upon an attempt to obtain dispirane **2b**, by reacting **1** with excess mercaptoethanol under acidic conditions.[5c] The expected bis-oxathiolane **2b**, an isomer of **4b**, was not observed in the reaction mixture. Also derivatives of **1** bearing methoxy groups, at positions 5 and 5,6 of the aromatic ring, showed the same regioselectivity. Only propellanes and no dispiro acetals were obtained by this reaction. The propellanes always had the two oxygen atoms attached to C-2, while the sulfur atoms were attached to C-1.[5c] The propellanes and mono-acetals in the present work, as well as in the previous study,[5c] were obtained in moderate yields only, between 40% and 69%. Besides containing propellane, the reaction mixture contained up to 25% of unreacted **1**, along with a much more polar byproduct (TLC, GC), probably a polymer resulting from a competitive self aldol-condensation of **1**. In some of the reactions small amounts (<5%) of the mono-acetals, were also noticed (determined by GC/MS).

Without reference compounds, it would not be easy to assess the correct structure just from the spectroscopic data, which should be quite similar for isomers, **2a** and **4a**. The structure of these compounds was unequivocally resolved by X-ray spectroscopy (Fig. 1a and b).

When the longer-chain diol, 1,3-propylene glycol, or its thiol-analogue, 1,3-propanedithiol were reacted with **1** under similar conditions, only the mono-acetals were obtained, even when a 3-fold excess of the diols was used. The two reagents attacked at different positions: propylene glycol produced 1,3-dioxane **5**, in which acetalization occurred at C-2, whereas the reaction with propanedithiol produced only 1,3-dithiane **6**, in which **1** had been attached at C-1. These structures were also elucidated by X-ray crystallography (Fig. 2a and b).

A plausible mechanism for the formation of propellanes **4** is depicted in Scheme 1. Propellane formation by reaction of glycols with α-diketones, is not limited to 1,2-indanedione **1**. Plater et al. reported that the treatment of acenaphthenequinone **7** with ethylene glycol and a catalytic amount of PTSA gave a single product that was not diacetal **8**, but its isomer, **9a**.[8] In an earlier work, Levine et al. reported that both the isomers could be obtained under similar conditions.[9] As a matter of fact, quite a few open-chained or cyclic 1,2-diones have failed to produce diacetals. This behavior has been explained by steric or electronic limitations.[10] In this work, we found that reaction of **7**, with excess 2-mercaptoethanol, forms only propellane **9b**. Its reaction with 1,3-propanedithiol, at 3-fold excess under the same conditions, produces only mono 1,3-dithiane **10**. These structures have also been confirmed by X-ray crystallography (Figs. 3 and 4, respectively).

Our experimental findings were corroborated by quantum chemical calculations. They show that all the three propellanes **4** to be more stable than their dispiro isomers **2** by 8.8–22.2 kJ/mol (Table 1). Molecular mechanics force field calculations (MMFF94) using SPARTAN code (Spartan SGI, version 5.1.3 OpenGL) were used to determine the most stable structures of the molecules under study. In further calculations, we used the Becke three-parameter hybrid method[11] with the Lee–Yang–Parr correlation functional approximation[12] and the Dunning correlation consistent polarized valence double ζ basis set[13] (B3LYP/cc-pVDZ).

It is noteworthy that when protection of **1** was carried out with ethylene glycol at a 1:1 ratio, two isomeric mono-acetals were formed, (compounds **3** and **11**), along with a small amount of the propellane (**4a**) and unreacted starting material. Ethanedithiol, however, produced only one dithiolane, at position 1 (compound **12**, Fig. 5b). Acetal **3** was separated and crystallized, and its structure determined by XRD (Fig. 5a). Its positional isomer, **11**, did not crystallize and its structure was deduced by GC/MS (retention time very close to that of **3**, and $m/z = 190$). Propellane **4a** was identified by comparison with an authentic sample.

2. Experimental

Crystallographic data (excluding structure factors) for the structures in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 232194–232197, CCDC 646070–646072, and CCDC 651936. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or deposit@ccdc.cam.ac.uk).

2.1. 2,5,7,10-Tetraoxa[4.4.3]propellane (**4a**)

$BF_3{\cdot}OEt_2$ (2.85 g, 20 mmol) was added dropwise, over 2 h to a refluxing solution of **1** (1.46 g, 10 mmol) and ethylene glycol (1.86 g, 30 mmol) in dry THF (18 ml). The solution was allowed to cool to room temperature. Aq $NaHCO_3$ (0.1 N, 10 ml) and CH_2Cl_2 (10 ml) were added and the mixture was shaken. The organic layer was washed with brine (5 ml), dried ($MgSO_4$), filtered, and the solvent was evaporated. A thick oil was obtained, which solidified upon the addition of MeOH to yield the product 1.05 g (45%) as colorless plates, mp 119 °C (from MeOH), TLC (silica): R_f 0.66 (EtOAc/cyclohexane 1:1); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.4 (m, 4H, arom); 4.1 (m, 4H, CH_2–O); 3.75 (m, 2H, CH_2–O); 3.65 (m, 2H, CH_2–O), 3.14 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 139.6, 138.3, 129.9, 127.3, 125.7, 122.9, 100.3, 97.9, 61.6, 61.1, 37.0; IR (chloroform):

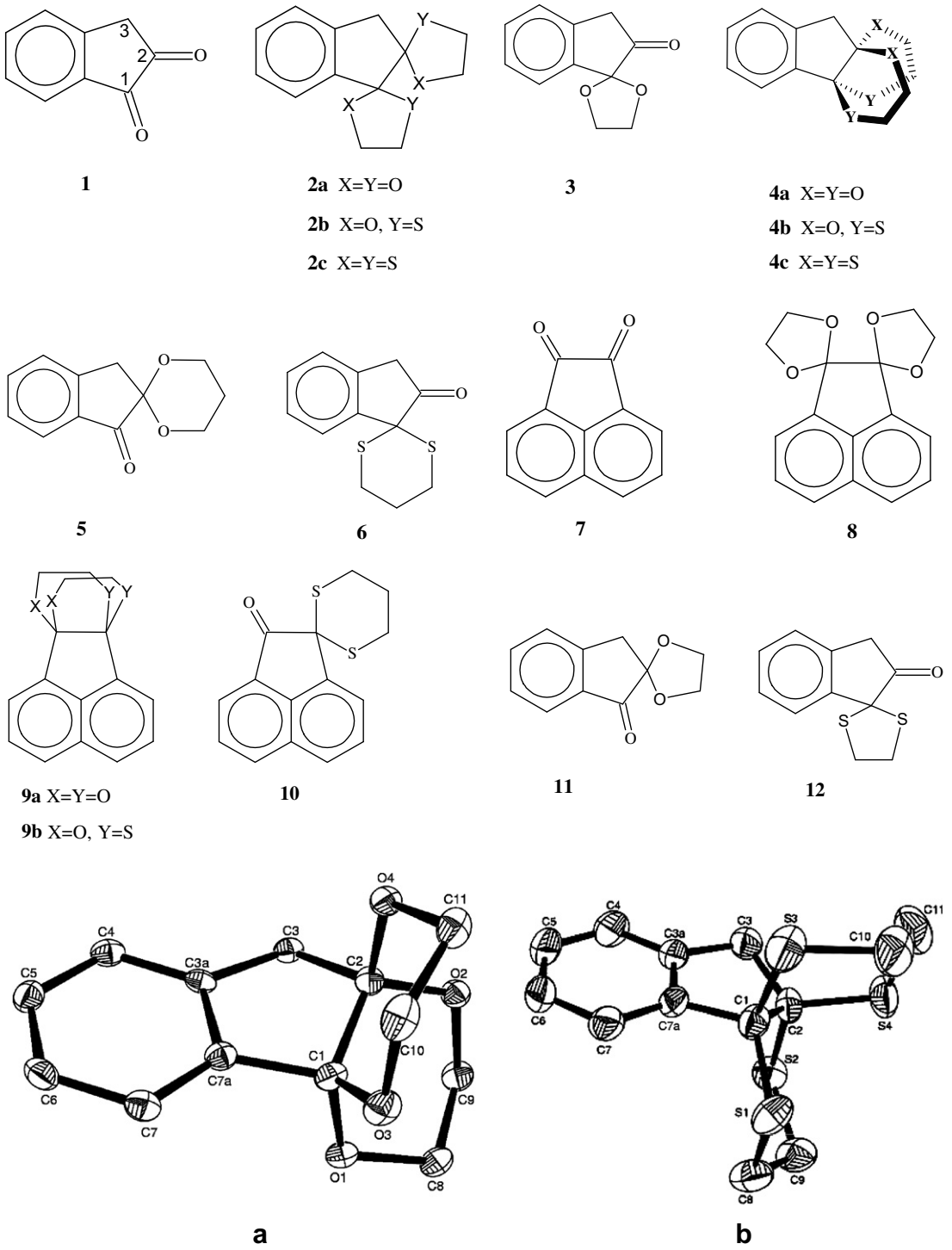


Fig. 1. ORTEP drawings for propellanes **4a** (a) and **4c** (b): ellipsoids enclose 50% probability.

2960, 2932, 2874, 1613, 1478, 1452, 1298, 1253, 1221, 1142, 1095, 1053, 1030, 972, 904, 852, 765, 727, 685 cm^{-1}. Calcd for $C_{13}H_{14}O_4$ (234.25): C, 66.66; H, 6.02. Found: C, 66.62; H, 6.16. Crystallographic data CCDC 232195 (Fig. 1a): $C_{13}H_{14}O_4$, monoclinic, space group $P2(1)/c$ with $a = 20.910(3)$, $b = 6.9417(8)$, $c = 16.271(2)$ Å, $\beta = 112.527(2)°$, $V = 2181.5(4)$ $Å^3$, and $Z = 8$.

2.2. 2,5,7,10-Tetrathia[4.4.3]propellane (**4c**)

$BF_3{\cdot}OEt_2$ (1.2 g, 8.5 mmol) was added dropwise over 2 h to a refluxing solution of **1** (600 mg, 4.1 mmol) and ethanedithiol (1.2 g, 13 mmol) in dry THF (10 ml). The solution was allowed to cool to room temperature. Aq $NaHCO_3$ (0.1 N, 10 ml) and CH_2Cl_2 (10 ml) were added and the

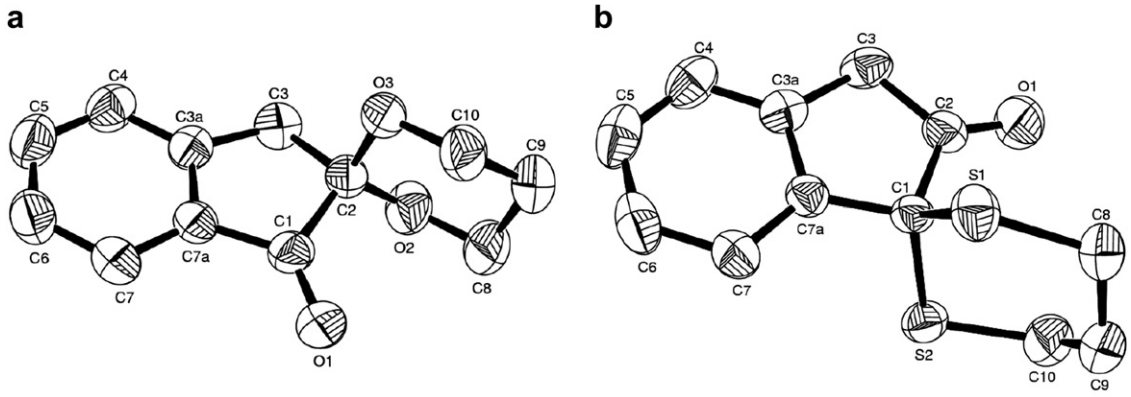
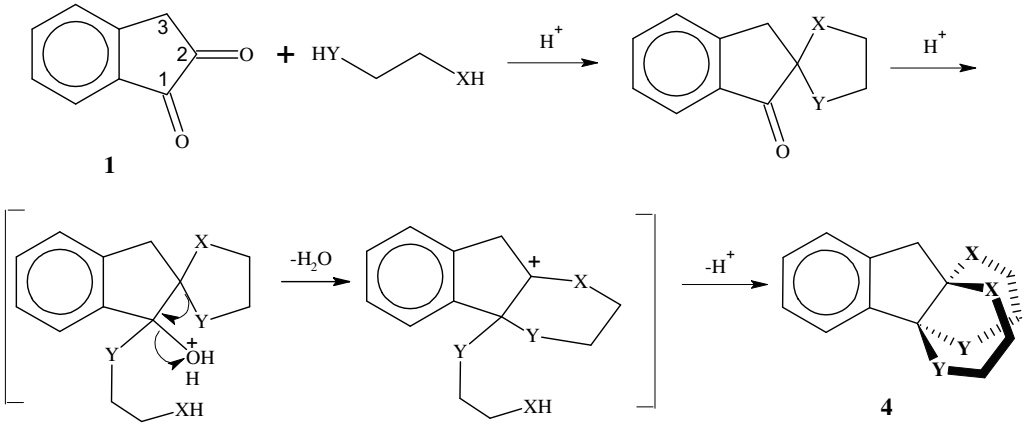


Fig. 2. ORTEP drawings for compounds **5** (a) and **6** (b): ellipsoids enclose 50% probability.



Scheme 1. Suggested mechanism for propellane formation by the reaction of 1,2-indanedione and ethylene glycol, or its thiol-analogues. With ethanedithiol the order is reversed and the initial ketalization takes place at C1 (**a**. X = Y = O; **b**. X = O, Y = S; **c**. X = Y = S).

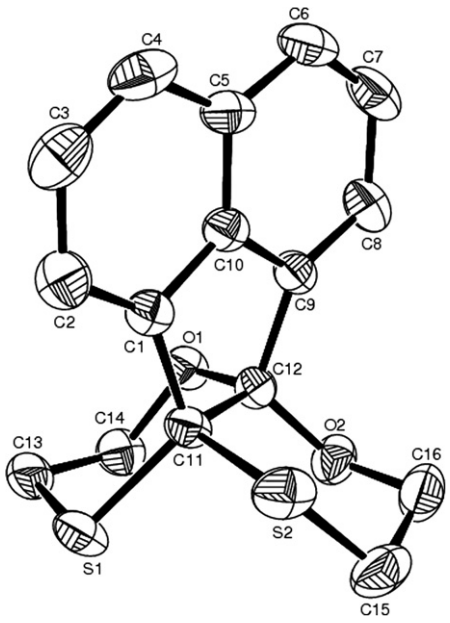


Fig. 3. ORTEP drawing for compound **9b**: ellipsoids enclose 50% probability.

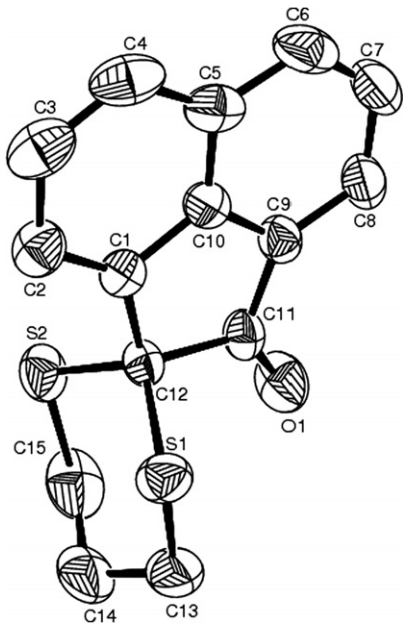


Fig. 4. ORTEP drawing for compound **10**: ellipsoids enclose 50% probability.

mixture was shaken. The organic layer was washed with brine, dried ($MgSO_4$) and the solvent evaporated to yield 790 mg (65%) of **4c** as colorless plates, mp 186–190 °C (from MeOH), TLC (silica): R_f 0.82 (EtOAc/cyclohexane 1:1), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62 (m, 1H, arom); 7.34 (m, 3H, arom); 3.53 (s, 2H, CH_2); 2.7–3.1 (m, 8H,

CH_2–S); ^{13}C NMR ($CDCl_3$): δ 143.3, 140.2, 128.7, 127.5, 125.5, 123.7, 58.9, 56.8, 44.3, 41.5, 40.5; IR (chloroform): 3040, 2907, 1689, 1540, 1462, 1411, 1280, 1174, 1018, 910, 852, 747, 682 cm^{-1}. Calcd for $C_{13}H_{14}S_4$ (298.51): C, 52.31; H, 4.73; S, 42.97. Found: C, 52.30; H, 4.87; S, 42.44. Crystallographic data CCDC 232194 (Fig. 1b): $C_{13}H_{14}S_4$, monoclinic, space group $P2(1)/n$ with $a = 7.720(2)$, $b = 13.166(4)$, $c = 13.780(4)$ Å, $\beta = 104.551(5)°$, $V = 1355.7(7)$ $Å^3$, and $Z = 4$.

2.3. Spiro[1,3-dithiolane-2,1′-inden]-2′(3′H)-one (12)

$BF_3{\cdot}OEt_2$ (500 mg, 3.4 mmol) was added dropwise over 2 h to a refluxing solution of **1** (500 mg, 3.4 mmol) and ethanedithiol (320 mg, 12 mmol) in THF (12 ml). Reflux was continued for 40 h, until the starting **1** had disappeared. The solution was allowed to cool to room temperature. Aq $NaHCO_3$ (0.1 N, 10 ml) and CH_2Cl_2 (10 ml) were added and the mixture was shaken. The organic layer was washed with brine (5 ml), dried ($MgSO_4$), filtered, and the solvent was evaporated to yield 450 mg (60%) of **12** as colorless plates, mp 118 °C (from THF), TLC (silica): R_f 0.75 (EtOAc/cyclohexane, 1:1), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68 (m, 1H, arom); 7.33 (m, 2H, arom); 7.29 (m, 1H, arom); 3.73 (s, 2H, CH_2); 3.72 (t, $J = 2.2$ Hz, 1H, CH_2–S), 3.69 (t, $J = 2.2$ Hz, 1H, CH_2–S), 3.62 (t, $J = 2.2$ Hz, 1H, CH_2–S), 3.60 (t, $J = 2.2$ Hz, 1H, CH_2–S); ^{13}C NMR ($CDCl_3$): δ 210.1, 137.9, 136.3, 129.6, 128.3, 126.2, 124.7, 69.1, 40.3, 39.8; Calcd for $C_{11}H_{10}OS_2$ (222.33): C, 59.42; H, 4.53; S, 28.85. Found: C, 59.50; H, 4.64; S, 28.78. Crystallographic data CCDC 646071 (Fig. 5b): $C_{11}H_{10}OS_2$, orthorhombic, space group $P2(1)2(1)2(1)$ with $a = 6.8857(14)$, $b = 9.1851(19)$, $c = 16.333(3)$ Å, $\beta = 90°$, $V = 1033.0(4)$ $Å^3$, and $Z = 4$.

2.4. Spiro[1,3-dioxane-2,1′-indene]-2′(3′H)-one (3) and spiro[1,3-dioxalane-2,1′-inden]-2′(3′H)-one (11)

A solution of **1** (3.66 g, 25 mmol) and ethylene glycol (1.55 g, 25 mmol) in dry toluene (250 ml) was stirred in a round bottomed flask equipped with a Dean–Stark distillation system. PTSA (20 mg) was added in one portion. The temperature was raised to 120 °C and the solution kept at this temperature, under stirring, for 48 h. The solution was allowed to cool to room temperature. After washing with aq $NaHCO_3$ (0.1 N, 25 ml) the solution was dried ($MgSO_4$) and filtered, and the volume reduced by evaporation to 30 ml. MeOH (5 ml) was added and colorless crystals precipitated. X-ray crystallography proved the structure as **3**. Yield 900 mg of colorless crystals (19%), mp 87 °C (from MeOH), TLC (silica): R_f 0.28 (CH_2Cl_2/*n*-hexane, 1:1), ^1H NMR and IR were in good agreement with the data reported by Butenschön et al.:[7] ^1H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, $J = 7.3$ Hz, 1H, arom);

Table 1
Total energies E_{total} (in a.u.), zero point energies and relative energies ΔE[a] of propellane versus spiro structures in indanedione diacetals and their sulfur analogs

Propellane structure	E_{total}	ZPE	Spiro structure	E_{total}	ZPE	ΔE[a]
4a	−804.720986	664.8	**2a**	−804.711024	660.4	22.2
4b	−1450.693771	646.0	**2b**	−1450.687145	664.5	15.9
4c	−2096.665960	626.9	**2c**	−2096.662347	626.0	8.8

[a] ZPE and relative energies in kJ/mol.

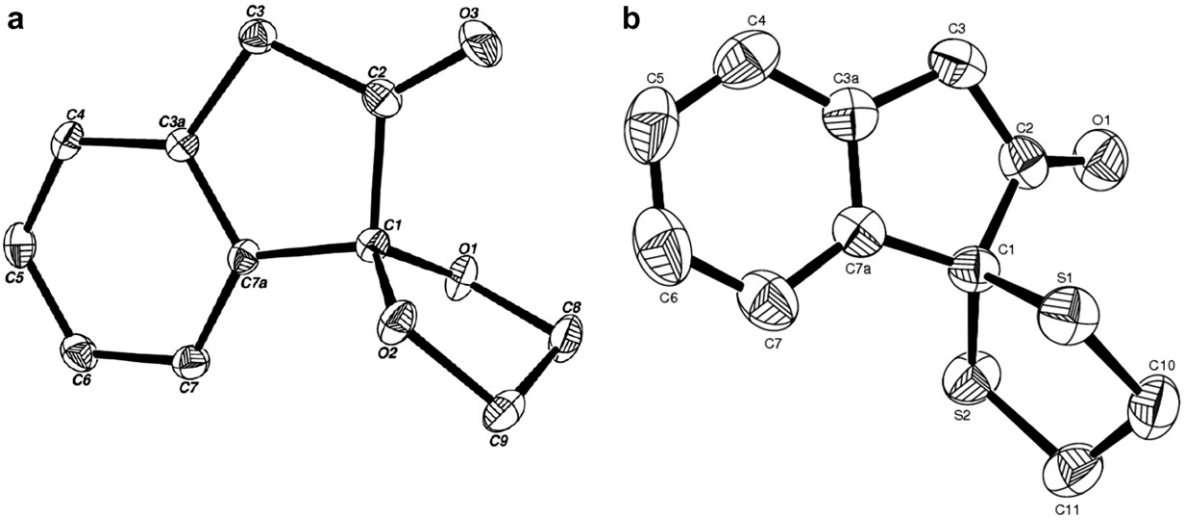


Fig. 5. ORTEP drawings for compounds **3** (a) and **12** (b): ellipsoids enclose 50% probability.

7.45 (m, 2H, arom); 7.35 (d, $J = 7.3$ Hz, 1H, arom); 4.46 (m, 2H, CH–O); 4.33 (m, 2H, CH–O); 3.56 (s, 2H, CH_2); IR (chloroform) 2487, 2408, 2388, 2369, 2340, 1977, 1950, 1852, 1674, 1655, 1559, 1337, 1200, 1130, 970, 743, 729, 690, 650 cm^{-1}. Crystallographic data CCDC 651936 (Fig. 5a): $C_{11}H_{10}O_3$, monoclinic, space group $P2(1)/n$ with $a = 9.683(1)$, $b = 6.9722(8)$, $c = 13.408$ (2) Å, $\beta = 105.949(2)°$, $V = 870.28(17)$ $Å^3$, and $Z = 4$. A compound assumed to be the other isomer, **11**, was detected in the mother liquor and identified by GC/MS, along with some **4a** and unconverted **1** as a thick yellow oil that did not crystallize, TLC (silica): R_f 0.38 (CH_2Cl_2/*n*-hexane 1:1) MS (70 eV): *m*/*z* (%) = 190(100) (M^+), 162(60) (M−CO).

2.5. *Spiro[1,3-dioxane-2,2′-indene]-1′(3′H)-one* (**5**)

$BF_3{\cdot}OEt_2$ (1.9 g, 14 mmol) was added dropwise over 1 h to a stirred solution of **1** (1.0 g, 6.8 mmol) and 1,3-propylene glycol (1.6 g, 20 mmol) in toluene (40 ml) in a two-neck flask fitted with a Dean–Stark distillation system. The temperature was raised to 120 °C for another hour. The solution was allowed to cool to room temperature, and washed with $NaHCO_3$ (0.1 N, 10 ml) and brine (5 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness to afford 1.19 g (85%) of **5** as colorless plates, mp 50 °C (from Et_2O), TLC (silica): R_f 0.64 (EtOAc/cyclohexane 1:1), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.74 (m, 1H, arom); 7.59 (m, 1H, arom); 7.37 (m, 2H, arom); 4.74 (dt, $J = 14.0$, 4.7 Hz, 2H, CH_2–O); 3.92 (m, 2H, CH_2–O); 3.27 (s, 2H, CH_2), 2.17 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ 200.0, 149.2, 135.8, 134.2, 127.8, 126.3, 124.8, 98.7, 61.7, 41.7, 25.3; IR (chloroform) 3846, 3742, 3615, 2959, 2353, 1712, 1605, 1466, 1301, 1222, 1148, 1097, 1039, 907, 769 cm^{-1}. Calcd for $C_{12}H_{12}O_3$ (204.22): C, 70.57; H, 5.92. Found: C, 70.51; H, 6.00. Crystallographic data CCDC 232197 (Fig. 2a): $C_{12}H_{12}O_3$, monoclinic, space group $P2(1)/n$ with $a = 9.514(2)$, $b = 9.530(2)$, $c = 11.236$ (3) Å, $\beta = 93.011(4)°$, $V = 1017.4(4)$ $Å^3$, and $Z = 4$.

2.6. *Spiro[1,3-dithiane-2,1′-indene]-2′(3′H)-one* (**6**)

$BF_3{\cdot}OEt_2$ (4.9 g, 30 mmol) was added dropwise over 2 h to a refluxing solution of **1** (2.5 g, 17 mmol) and 1,3-propanedithiol (5.7 g, 50 mmol) in dry THF (40 ml). The solution was allowed to cool to room temperature, and was washed with aq $NaHCO_3$ (0.1 N, 15 ml) and brine (5 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness to yield 2.2 g (56%) of **6** as colorless plates, mp 123–126 °C (from MeOH), TLC (silica): R_f 0.82 (EtOAc/cyclohaxane 1:1), ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52 (m, 1H, arom); 7.33 (m, 3H, arom); 3.78 (s, 2H, CH_2); 3.70 (dt, 2H, S–CH_2), 2.62 (m, 2H, S–CH_2), 2.27 (m, 1H, S–CH_2–CH_2), 2.05 (m, 1H, S–CH_2–CH_2); ^{13}C NMR ($CDCl_3$): δ 207.4, 140.5, 135.5, 129.6, 128.1, 125.7, 124.7, 52.1, 40.4, 27.4, 24.2; IR (chloroform) 3728, 2919, 2352, 1733, 1533, 1466, 1416, 1194, 1132, 1068, 893, 748, 665 cm^{-1}. Calcd for $C_{12}H_{12}OS_2$ (236.35): C, 60.98; H, 5.12; S, 27.13. Found: C, 60.84; H, 5.30; S, 26.91. Crystallographic data CCDC 232196 (Fig. 2b): $C_{12}H_{12}OS_2$, monoclinic, space group $P2(1)/c$ with $a = 7.539(2)$, $b = 7.165(2)$, $c = 21.186(5)$ Å, $\beta = 99.386(4)°$, $V = 1129.0(4)$ $Å^3$, and $Z = 4$.

2.7. *2,5-Dithio-7,10-dioxa[4.4.3]propellane of acenaphthoquinone* (**9b**)

$BF_3{\cdot}OEt_2$ (630 mg, 4.4 mmol) was added dropwise over 3 h to a refluxing solution of **7** (800 mg, 4.4 mmol) and 2-mercaptoethanol (1.2 g, 13 mmol) in dry THF (15 ml). The solution was allowed to cool to room temperature, and was washed with aq $NaHCO_3$ (0.1 N, 8 ml), and brine (5 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness to afford 530 mg (40%) of **9b** as colorless plates, mp 213.5 °C (from MeOH), TLC (silica): R_f 0.66 (EtOAc/cyclohexane 1:1), ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83 (d, $J = 7.7$ Hz, 1H, arom); 7.74 (d, $J = 8.3$ Hz, 1H, arom); 7.59 (m, 4H, arom); 4.54 (m, 2H, CH–O); 4.02 (m, 2H, CH–O); 2.84 (m, 2H, CH–S); 2.56 (m, 2H, CH–S); ^{13}C NMR ($CDCl_3$): δ 142.3, 138.3, 131.2, 128.2, 128.1, 126.5, 125.2, 120.1, 119.6, 105.1, 63.9, 51.2, 26.0, 20.1; IR (chloroform) 2949, 2912, 2865, 1488, 1359, 1294, 1256, 1219, 1184, 1137, 1094, 1074, 1038, 968, 944, 806, 774 cm^{-1}. Calcd for $C_{16}H_{14}O_2S_2$ (302.41): C, 63.55; H, 4.67. Found: C, 63.35; H, 4.99. Crystallographic data CCDC 646070 (Fig. 3): $C_{16}H_{14}O_2S_2$, orthorhombic, space group *Pbca* with $a = 11.6663(17)$, $b = 13.898(2)$, $c = 16.719(2)$ Å, $\beta = 90°$, $V = 2710.7(7)$ $Å^3$, and $Z = 8$.

2.8. *6,10-Dithiaspiro-acenaphthenequinone* (**10**)

$BF_3{\cdot}OEt_2$ (1.14 g, 8 mmol) was added dropwise over 3 h to a refluxing solution of **7** (600 mg, 3.3 mmol) and 1,3-propanedithiol (1.27 g, 11.7 mmol) in dry THF. The solution was allowed to cool to room temperature, and washed with aq $NaHCO_3$ (0.1 N, 15 ml) and brine (10 ml). The organic layer was dried ($MgSO_4$) and evaporated to dryness to yield 790 mg (89%) of **10** as colorless plates, mp 163–170 °C (from MeOH), TLC (silica): R_f 0.80 (EtOAc/cyclohexane 1:1), ^1H NMR ($CDCl_3$, 300 MHz): δ 8.11 (d, $J = 8.2$ Hz, 1H, arom); 7.99 (d, $J = 6.8$ Hz, 1H, arom); 7.85 (d, $J = 8.2$ Hz, 1H, arom); 7.69 (m, 3H, arom); 4.05 (t, $J = 15.3$ Hz, 2H, CH–S); 2.68 (m, 2H, CH–S); 2.39 (m, 1H, CH); 2.15 (m, 1H, CH); ^{13}C NMR ($CDCl_3$): δ 198.1, 139.2, 138.3, 131.8, 130.5, 130.1, 128.7, 125.9, 123.7, 122.6, 50.6, 26.7, 24.5; IR (Chloroform) 3744, 3041, 2930, 2356, 1696, 1605, 1424, 1354, 1223, 1125, 1006, 907, 833, 769 cm^{-1}. Calcd for $C_{15}H_{12}OS_2$ (272.39): C, 66.14; H, 4.44; S, 23.54. Found: C, 66.10; H, 4.64; S, 23.71. Crystallographic data CCDC 646072 (Fig. 4): $C_{15}H_{12}OS_2$, monoclinic, space group $P2(1)/c$ with $a = 6.9999(15)$, $b = 9.455(2)$, $c = 19.025(4)$ Å, $\beta = 95.184$ (4)°, $V = 1254.0(5)$ $Å^3$, and $Z = 4$.

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