

SYNTHESIS OF 2,2',2'',2'''-(1,2-ETHANEDIYLIDENE)TETRAFURAN AND
DIELS-ALDER REACTION WITH DIMETHYL ACETYLENE-
DICARBOXYLATE

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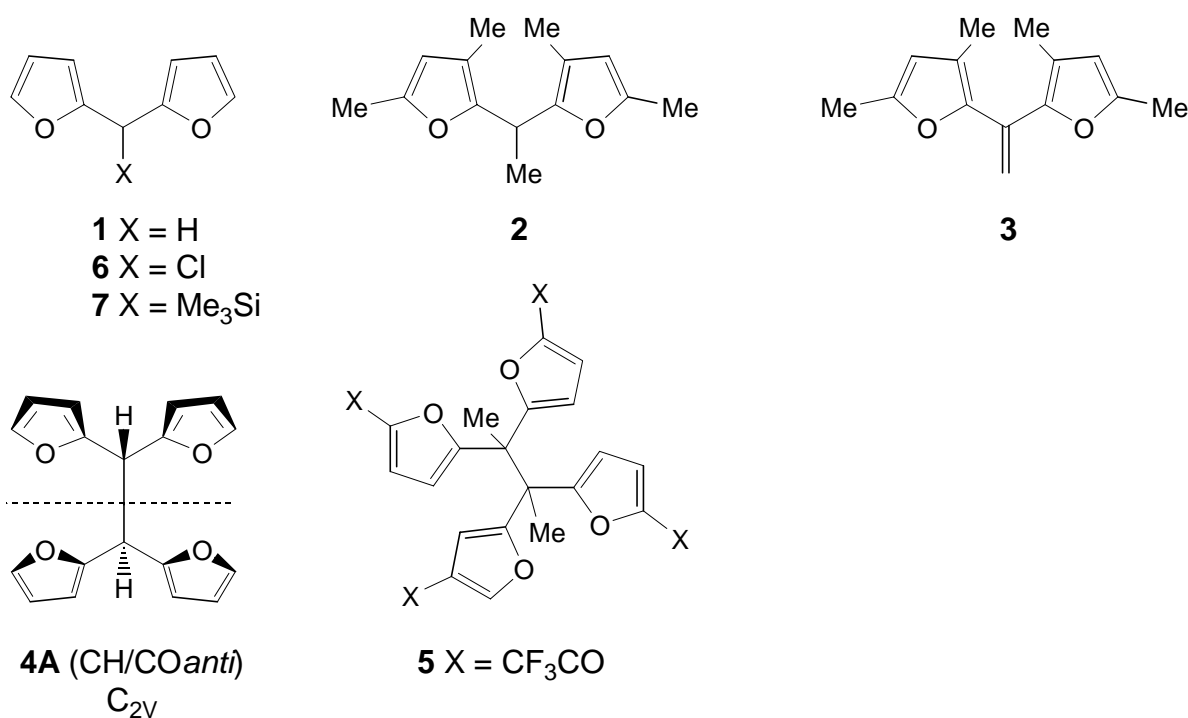
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Abstract - A one step procedure has been found that converts 2,2'-methylene-difuran (**1**) into 2,2',2'',2'''-(1,2-ethanediylidene)tetrafuran (**4**: 1,1,2,2-tetrakis(furan-2-yl)ethane). This compound adopts two similar C_{2v}-symmetrical conformations (**4A** and **4A'**) in the crystalline state in which the C-H bond of the 1,2-ethanediylidene moieties is *anti*-periplanar with the C(2)-O bond of the vicinal furan-2-yl groups. Tetrafuran (**4**) is little reactive toward dienophiles with normal electronic demand. With dimethyl acetylenedicarboxylate a single 1:1 adduct (**8**) (dimethyl (1*RS*,2*RS*,2*aRS*,5*SR*,5*aRS*,6*RS*,8*aRS*,8*bSR*)-1,2-di(furan-2-yl)-1,2-dihydro-5*H*,6*H*-2*a*,5:6,8*a*-diepoxyacenaphthylene-5*a*,8*b*-dicarboxylate) was isolated. Its structure was established by single crystal X-Ray radiocrystallography.

INTRODUCTION

We have shown that long-chain 1,3-polyols (polyketides) can be obtained *via* the double [4+3]-cycloaddition of 1,1,3-trichloro-2-oxyallyl cation to 2,2'-methylene-difuran (**1**).^{1,2} Our group has reported also that long-chain polypropionates can be prepared through Diels-Alder additions of 2,2'-ethylidenebis[3,5-dimethylfuran] (**2**).^{3,4} Earlier we had shown that the cycloadditions of 1,1-bis(3,5-dimethylfur-2-yl)ethene (**3**) have chemoselectivities depending strongly on the nature of the dienophiles.⁵ During our exploration of the reactivity of the bisfuryl derivative (**1**) we discovered a possibility to

convert it into the yet unknown 2,2',2'',2'''-(1,2-ethanediylidene)tetrafuran (**4**). To our knowledge only derivative (**5**) had been reported as the first member of this tetrafuryl family. It was obtained by one-electron oxidation of 1,1-bis[(5-trifluoroacetyl)fur-2-yl]ethane by cupric salts.⁶ We report the synthesis of **4** and on its Diels-Alder reactivity toward dimethyl acetylenedicarboxylate. X-Ray diffraction studies on **4** demonstrate that this compound adopts a C_{2V} -symmetrical conformation in the crystalline state with the C_2 -axis cutting the middle of the σ (C-C) bond of the ethanediylidene moiety and with the furyl groups eclipsing the C-H bond of the ethanediylidene moiety.



RESULTS AND DISCUSSION

Treatment of **1** with 1.1 equivalent of butyllithium in anhydrous THF at -78°C gave the corresponding product of hydrogen/metal exchange. Attempts to quench it with electrophilic chlorinating agents (NCS, Cl_2) all failed to give the expected chloro derivative (**6**), but generated intractable tars. Quenching with hexachloroethane led to the exclusive formation of **4** and polymeric material. Compound (**4**) was isolated in 51% yield. Its structure was given by its spectral data, elemental analysis and by X-Ray diffraction studies (see below). Quenching the lithiated **1** with trimethylsilyl chloride gave silane (**7**) in 74% yield. The molecular structure of **4** in the crystalline state is represented in Figure 1 (see Table 1). It shows two similar C_{2V} -symmetrical conformers (**4A**) and (**4A'**). As expected for steric reasons (Pitzer strain), the 1,1,2,2-tetrasubstituted ethane system adopts staggered *anti*-conformations that minimize repulsions between the four furyl moieties. This was also reported for 1,1,2,2-tetraphenylethane.⁸ The orientation

adopted by the furan rings makes them to eclipse the C-H bonds of the ethanediylidene moiety, as expected for isopropyl and other alkyl substituents of alkenes and arenes.⁹ It is interesting to note that the C_{2V} -conformer (**4B**), the C_2 -conformer (**4C**), and the centro-symmetric conformer (**4D**) are not present in the crystalline state. The selection of conformers (**4A** and **4A'**) in the crystalline state might also be the result of lattice effect. Conformational analysis of **4** in the gas phase will have to be carried out before concluding on the origin of the preference for conformations (**4A**, **4A'**) in the crystalline state.

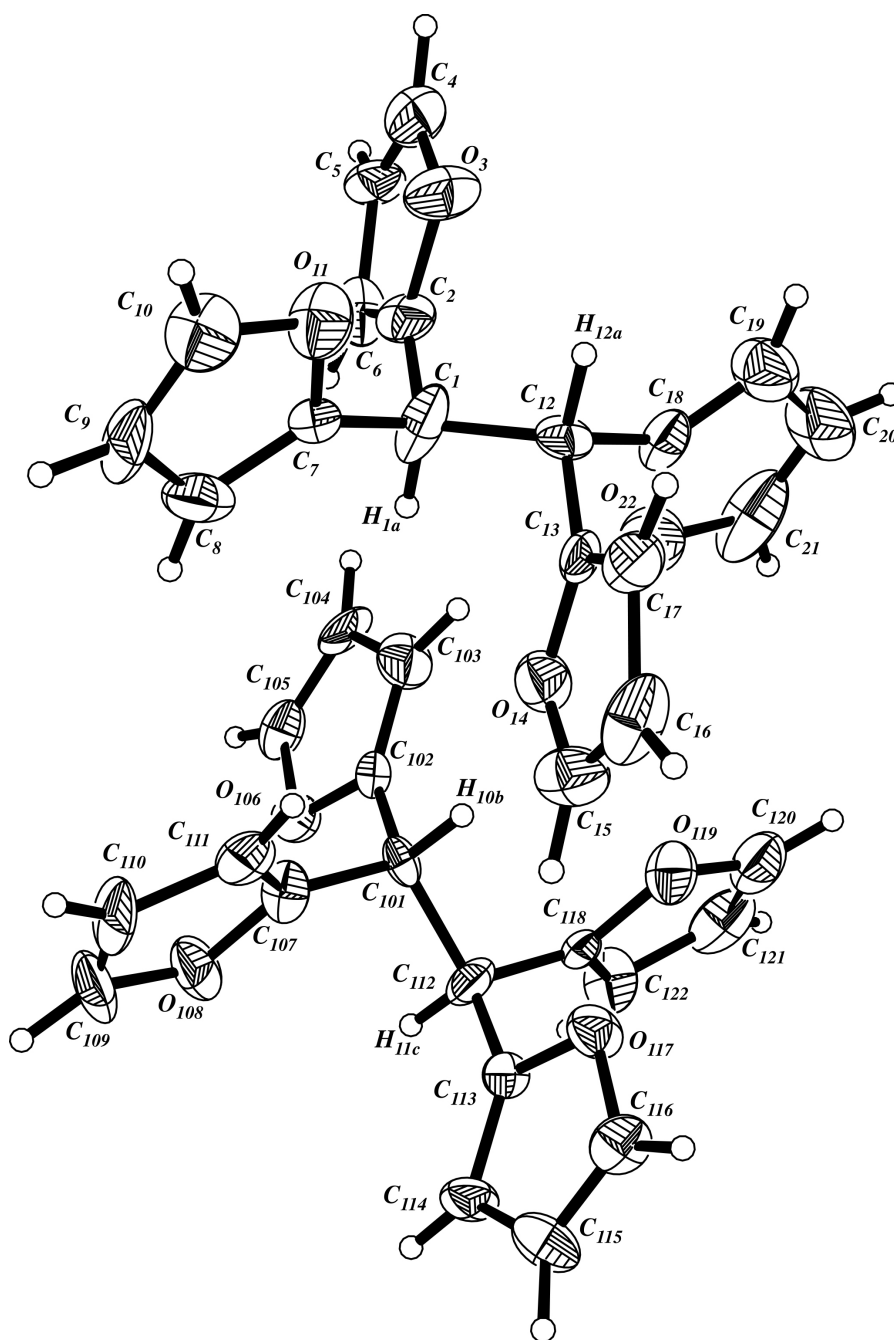


Figure 1. ORTEP representation⁷ of the two C_{2V} -conformers (**4A** and **4A'**) found in the crystalline state. For reasons of commodity, the atom numbering does not follow the IUPAC rules.

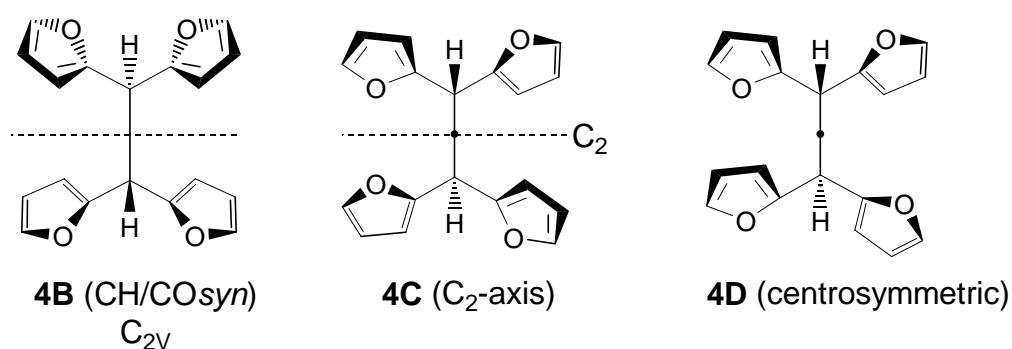


Table 1. Selected bond lengths, interatomic separations and torsion angles for **4A** and **4A'**.

Bond distances (Å)					
C1-C2	1.499(12)	C1-C12	1.5118(6)	C1-C7	1.446(10)
C7-C8	1.775(12)	C8-C9	1.456(14)	C9-C10	1.32(2)
C10-O11	1.410(13)	C7-O11	1.327(10)	C1-C12	1.518(6)
C101-C112	1.547(6)	C110-C111	1.432(13)	C103-C104	1.435(11)
C114-C115	1.463(11)				
Interatomic distances (Å)					
O3-O11	3.108(0.011)	O3-O22	4.260(0.012)	O3-O14	5.214(0.006)
O11-O14	4.176(0.011)	O11-O22	5.300(0.007)	O14-O22	3.170(0.013)
O106-O108	2.978(0.010)	O106-O119	4.322(0.008)	O106-O117	5.298(0.004)
O108-O117	4.319(0.008)	O108-O119	5.221(0.005)	O117-O119	3.019(0.011)
Selected torsion angles in degrees					
C2-C1-C12-C18	45.04	(0.98)	C102-C101-C112-C118	-50.22	(0.68)
C2-C1-C12-C13	175.21	(0.98)	C102-C101-C112-C113	-179.69	(0.99)
C2-C1-C12-H12A	-69.65	(0.73)	C102-C101-C112-H11C	64.71	(0.54)
H1A-C1-C12-C18	-66.01	(0.64)	C107-C101-C112-C118	-178.27	(0.85)
H1A-C1-C12-C13	64.16	(0.57)	C107-C101-C112-C113	52.26	(0.66)
H1A-C1-C12-H12A	179.30	(0.01)	C107-C101-C112-H11C	-63.35	(0.47)
C7-C1-C12-C18	-177.36	(1.09)	H10B-C101-C112-C118	65.44	(0.55)
C7-C1-C12-C13	-47.20	(0.99)	H10B-C101-C112-C113	-64.03	(0.60)
C7-C1-C12-H12A	67.94	(0.78)	H10B-C101-C112-H11C	-179.63	(0.00)

The tetrafuryl derivative (**4**) is much less reactive than simpler furan derivatives¹⁰ in Diels-Alder reactions. With maleic anhydride,¹¹ **4** refused to equilibrate with any adduct, even after 5 days at 50°C. In 5 molar LiClO₄ ether, **4** reacted with maleic anhydride at 25°C giving intractable tars. With dimethyl

acetylenedicarboxylate and without Lewis acid promoter, a complex mixture of product was formed slowly at 20-40°C. As no major product could be formed selectively under these conditions, we treated **4** with dimethyl acetylenedicarboxylate in the presence of LiClO₄ in ether¹² at 20°C. After 20 h and *ca.* 40% conversion of **4**, a major product (**8**) was formed and could be purified by flash chromatography on silica gel and isolated in 34% yield.¹³ It consisted of a 1:1 adduct of **4** and dimethyl acetylenedicarboxylate, the structure of which was deduced from its spectral data and by single crystal X-Ray radiocrystallography (Figure 2, Table 2). Attempts to generate a 1:2 adduct of **4** and dimethyl acetylenedicarboxylate applying high pressure (1200 and 1950 MPa, LiClO₄/Et₂O) led to complex mixtures of products of high molecular mass from which no single compound could be isolated.

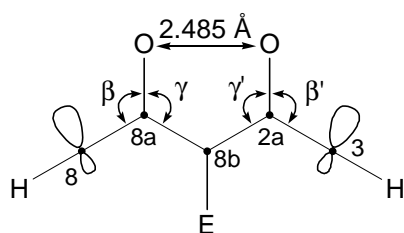
Table 2 Selected bond lengths, torsion angles and angles between averaged planes of **8**

bond lengths in Å

C(1)-C(2) ^{a)}	C11-C12 ^{b)}	1.594(2)	C(5a)-C(8a) ^{a)}	C1-C6 ^{b)}	1.548(2)
C(1)-C(8a)	C10-C12	1.539(2)	C(8a)-C(8b)	C6-C10	1.577(2)
C(2)-C(2a)	C5-C11	1.529(2)	C(2a)-C(8b)	C5-C6	1.571(2)
C(1)-C(2')	C12-C21	1.483(2)	C(5a)-C(6)	C1-C7	1.575(2)
C(2)-C(2'')	C11-C17	1.490(2)	C(5)-C(5a)	C1-C2	1.600(2)
C(8a)-C(8)	C9-C10	1.520(2)	C(6)-C(7)	C7-C8	1.528(3)
C(2a)-C(3)	C4-C5	1.514(2)	C(4)-C(5)	C2-C3	1.529(2)
C(3)-C(4)	C3-C4	1.327(3)	C(7)-C(8)	C8-C9	1.330(3)

Torsion angles in degrees

C(8a)-C(1)-C(2')-O(1') ^{a)}	C10,C12,C21,O8 ^{b)}	-121.25(17)	}	C(1)-H/furanyl eclipsed
C(2)-C(1)-C(2')-O(1')	C11,C12,C21,O8	116.90(16)		
C(2a)-C(2)-C(2'')-O(1'')	C12,C11,C17,O7	177.26(15)	}	C(2)-H/furanyl bisecting
C(1)-C(2)-C(2'')-O(1'')	C5,C11,C17,O7	55.3(2)		
C(8a)-C(1)-C(2)-C(2a)	C10,C12,C11,C5	-8.38(17)	}	Twisted cyclopentane
C(2)-C(1)-C(8a)-C(8b)	C11,C12,C10,C6	-16.98(17)		



a) IUPAC atom numbering, see structure (**8**).

b) Atom numbering used in Figure 2

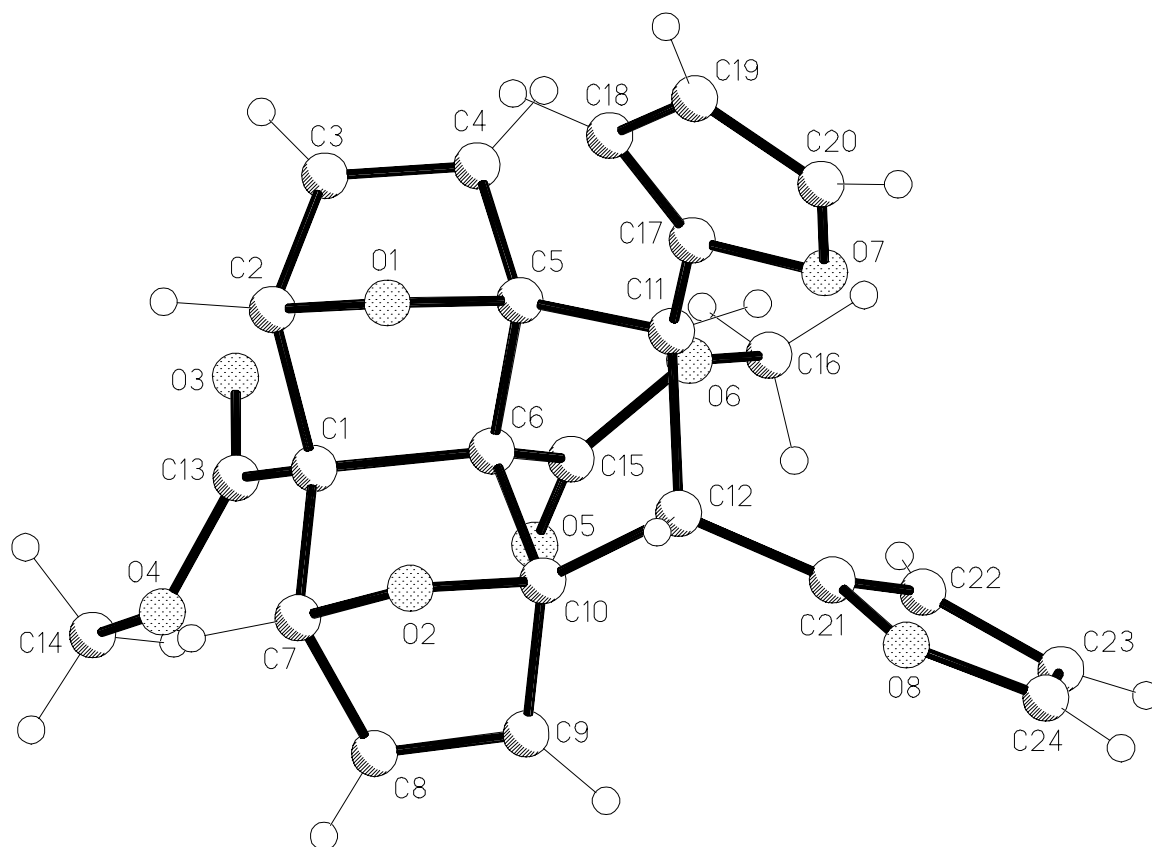
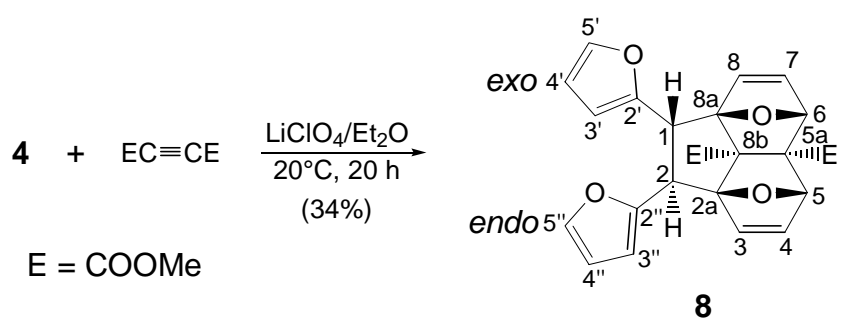
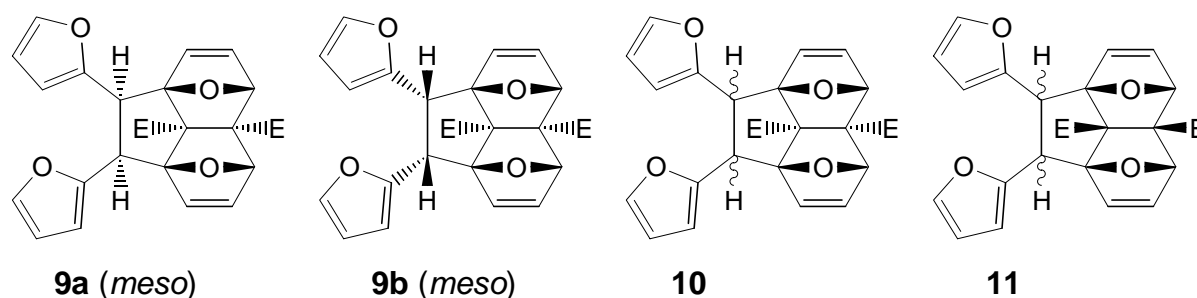


Figure 2. ORTEP representation⁷ of adduct (**8**). For reasons of commodity the atom numbering does not follow the IUPAC rules.

No isomeric forms (**9-11**) of adduct (**8**) could be seen in the ¹H-NMR spectrum of the crude reaction mixture of **4** with dimethyl acetylenedicarboxylate (LiClO₄, 20°C). As for most furan derivatives, their Diels-Alder additions are reversible, thus **8** might correspond to the most stable Diels-Alder product between **4** and dimethyl acetylenedicarboxylate. The high-molecular weight material that forms under forcing conditions arises probably from Michael additions of the furan moieties of **4** and **8**.¹⁰

The X-Ray data for **8** shows that the “endo”-O(1’),C(2’’,3’’,4’’,5’’)–furan-2-yl adopts a staggered conformation with its ring *syn*-periplanar with the adjacent C(2)–H bond (C(12) in Figure 2) whereas the “exo”-O(1’),C(2’,3’,4’,5’)–furan-2-yl moiety (at C(11) in Figure 2) adopts a nearly bisected conformation with the adjacent C(1)–H bond. This is probably due to the fact that the oxygen atom or the C(5’)-H bond

of this furan-2-yl moiety would get too close to the adjacent 7-oxa ethereal bridge if a “normal” staggered conformation (as for **4** and the other furan-2-yl ring of **8**) should prevail. Distance between H-C(18) and O(1) (Figure 2) is evaluated to 2.655 Å, which is already relatively short. Most interesting is the observation of long allylic C-C bonds $\sigma(\text{C}(2\text{a}),\text{C}(8\text{b}))$, $\sigma(\text{C}(8),\text{C}(8\text{b}))$, $\sigma(\text{C}(5),\text{C}(5\text{a}))$ and $\sigma(\text{C}(5\text{a}),\text{C}(6))$ of 1.571(2), 1.577(2), 1.600(2) and 1.575(2) Å, respectively, to be compared with the “normal” $\sigma(\text{C}(5\text{a}),\text{C}(8\text{b}))$ bond of 1.548 Å. This phenomenon had been noticed by neutron diffraction



measurements of *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride¹⁴ and that has been interpreted by us as the manifestation that bicyclo[2.2.1]hept-2-ene and 7-oxabicyclo[2.2.1]hept-2-ene systems admit in their ground state some properties of their products of retro-Diels-Alder cycloreversion (hyperconjugation model¹⁵). Interesting also is the C(1), C(2), C(2a), C(8b), C(8a) cyclopentane ring of **8** that adopts a twist conformation (Table 2) with carbon centres C(8b) and C(2a) lying above and below, respectively of the plane of C(8a),C(1),C(2). In 7-oxabicyclo[2.2.1]hept-2-ene systems angle β between average plane containing the bridgehead centre and the alkene moiety with the ethereal moiety (plane C(1)-O(7)-C(4)) is significantly larger than angle γ between the same ethereal moiety and average plane C(1)-C(6)-C(5)-C(4).¹⁶ In the case of **8**, this is not the case as a result of the repulsion between the two *syn* 7-oxa bridges separated by short distance of 2.485 Å (Table 2).

CONCLUSION

An efficient synthesis of 2,2',2'',2'''-(1,2-ethanediylidene)tetrafulan (**4**) has been developed starting from furfuryl alcohol and furan¹ (2 steps). This new tetrafulan adopts a C_{2v} -symmetrical conformation in the crystalline state. It is not a reactive diene in Diels-Alder additions. Nevertheless a 1:1 adduct of **4** with dimethyl acetylenedicarboxylate has been isolated. It involves a “pincer” tandem Diels-Alder addition in which two vicinal furan rings add in a *syn* fashion of the acetylenic dienophile.

ACKNOWLEDGMENTS

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EXPERIMENTAL

General, see ref. 17

2,2',2'',2'''-(1,2-Ethanediylydene)tetrafulan (**4**). 2,2'-Methylenedifuran (**1**) (3 g, 20 mmol) was dissolved in anhydrous THF (100 mL). The mixture was cooled under N₂ to -78°C and BuLi (1.57 M in hexane, 14 mL, 22 mmol) was added dropwise. After 1 h the lithiated derivative was reacted with a solution of hexachloroethane (5.21 g, 22 mmol) in THF (10 mL). During the overnight reaction, the temperature was allowed to reach slowly 20°C. The solution was then treated with 5% aqueous NaHSO₄ (50 mL) and successively washed with H₂O (50 mL) and brine (50 mL). The aqueous phases were extracted with ether (10 mL, twice). The organic phases were collected and dried (MgSO₄). After solvent evaporation, the dark red residue was purified by flash chromatography on silica gel (light petroleum ether/Et₂O 9:1) to collect an orange oil which solidifies. The latter can be crystallised from heptane (50 mL) furnishing pure **4** (1.5 g, 51%), colorless crystals, mp 117-118°C (heptane). UV (MeCN): λ_{max} = 230 nm (ε = 8300 M⁻¹cm⁻¹). IR (KBr) ν: 3150, 3120, 1600, 1515, 1380, 1250, 1210, 1145, 1065, 1015, 955, 885, 770, 740, 720, 595, 540 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ_H 7.29 (*d*, ³*J* = 1.0, H-C(5,5')), 6.22 (*dd*, ³*J* = 3.2, ³*J* = 1.8, H-C(4,4')), 6.03 (*d*, ³*J* = 3.1, H-C(3,3')), 4.92 (*s*, H-C(6)). ¹³C-NMR (100.6 MHz, CDCl₃): δ_C 152.6 (*s*, C(2,2')), 141.5 (*d*, ¹*J*(C,H) = 202, C(5,5')), 110.2 (*d*, ¹*J*(C,H) = 175, C(4,4')), 107.0 (*d*, ¹*J*(C,H) = 175, C(3,3')), 42.8 (*d*, ¹*J*(C,H) = 132, C(6)). MS-CI (NH₃): 148 (19, [M-35]⁺), 147 (100, [M/2]⁺), 118 (4), 91 (45), 89 (12). Anal. Calcd for C₁₈H₁₄O₄: C 73.46, H 4.79. Found: C 73.53, H 4.88. Crystal for X-Ray diffraction, see Table 3.

Table 3. Crystal data and structure refinement for **4A**, **4A'**

Empirical formula	C ₁₈ H ₁₄ O ₄	
Formula weight	294.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.007(2) Å	α = 77.88(3)°
	b = 9.022(2) Å	β = 73.51(3)°
	c = 11.319(2) Å	γ = 78.48(3)°
Volume	758.0(3) Å ³	
Z	2	
Density (calculated)	1.289 Mg/m ³	

Table 3 (continued)

Absorption coefficient	0.091 mm ⁻¹
F(000)	308
Crystal size	n/a
Theta range for data collection	3.66 to 24.99°
Index ranges	-10<=h<=11, -12<=k<=11, -14<=l<=76
Reflections collected	3632
Independent reflections	3106 [R(int) = 0.0269]
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3103 / 30 / 397
Goodness-of-fit on F ²	1.661
Final R indices [I>2sigma(I)]	R1 = 0.0774, wR2 = 0.2082
R indices (all data)	R1 = 0.0956, wR2 = 0.2206
Weight	[$\sigma^2(F_o,^2) + (0.1 * P)^2$] ⁻¹
Absolute structure parameter	1(3) \emptyset meaningless
Largest diff. peak and hole	0.314 and -0.232 e.Å ⁻³

2,2'-(Trimethylsilylmethylene)difuran (**7**). 2,2'-Methylenedifuran (**1**) (3 g, 20 mmol) was dissolved in anhydrous THF (100 mL). After cooling to -78°C, BuLi (1.57 M in hexanes, 14 mL, 22 mmol) was added dropwise. After stirring at -78°C for 1 h, Me₃SiCl (4.35 g, 40 mmol) was added and the mixture stirred at -78°C for 30 min. A saturated solution of NH₄Cl in MeOH (10 mL) was added and the cooling bath removed. The mixture was stirred and allowed to warm up to 20°C. The organic phase was dried (MgSO₄) and the solvent evaporated under vacuum. Bulb-to-bulb distillation of the residue gave **7** (3.75 g, 74%), yellowish oil, bp 63°C/4 mbar. In the condensed state, **7** was polymerized slowly already at -25°C. ¹H-NMR (400 MHz, CDCl₃): δ_{H} 7.32 (*dd*, ³*J* = 1.9, ⁴*J* = 0.8, H-C(5,5')), 6.31 (*dd*, ³*J* = 3.0, 1.9, H-C(4,4')), 6.02 (*br d*, *J* = 3.0, H-C(3,3')), 3.75 (*s*, HC(methylene)), 0.07 (*s*, Me₃Si). ¹³C-NMR (100.6 MHz, CDCl₃): δ_{C} 140.5 (*d*, ¹*J*(C,H) = 192, C(5,5')), 154.2 (*s*, C(2,2')), 110.3 (*d*, ¹*J*(C,H) = 170, C(4,4')), 104.8 (*d*, ¹*J*(C,H) = 173, C(3,3')), 32.0 (*d*, ¹*J*(C,H) = 121, CH-Si), 2.3 (*q*, ¹*J*(C,H) = 119, Me₃Si).

Dimethyl (1*RS*,2*RS*,2*aSR*,5*SR*,5*aRS*,6*RS*,8*aRS*,8*bSR*)-1,2-di-2-(furan-2-yl)-1,2-dihydro-5*H*,6*H*-2*a*,5:6,8*a*-diepoxyacenaphthylene-5*a*,8*b*-dicarboxylate (**8**). A mixture of anhydrous LiClO₄ (535 mg, 5 mmol), ether (1 mL) and **4** (60 mg, 0.2 mmol) was stirred at 20°C until complete dissolution. Dimethyl acetylenedicarboxylate (104 mg, 0.7 mmol) was added and the mixture stirred at 20°C for 20 h. Water (1

mL) was added and the mixture extracted with EtOAc (2 mL, 3 times). After drying (MgSO₄) and solvent evaporation the residue was purified by flash chromatography on silica gel (light petroleum ether/Et₂O 3:7) giving pure **8** (30 mg, 34%), colorless crystals, mp 126-127°C (light petroleum ether/Et₂O). UV (MeCN): $\lambda_{\max} = 222$ nm ($\epsilon = 2200$ M⁻¹cm⁻¹). IR (KBr) ν : 3435, 3145, 3110, 1730, 1725, 1505, 1435, 1285, 1265, 1115, 1080, 1015, 980, 965, 910, 770, 745, 730, 715, 680, 600, 555 cm⁻¹. ¹H-NMR (400 MHz, CDCl₃): δ_{H} 7.38 (*m*, 2H, H-C(5',5'')), 6.86 (*d*, ³*J* = 5.5, H-C(8) or H-C(3)), 6.69 (*dd*, ³*J* = 5.5, 1.6, H-C(7) or H-C(4)), 6.68 (*dd*, ³*J* = 5.5, 1.7, H-C(4) or H-C(7)), 6.39-6.24 (*m*, 4H, H-C(3',3'',4',4'')), 5.28 (*d*, ³*J* = 1.6, H-C(6) or H-C(5)), 5.21 (*d*, ³*J* = 1.5, H-C(5) or H-C(6)), 4.75 (*d*, ³*J* = 7.4, H-C(2) or H-C(1)), 4.20 (*d*, ³*J* = 7.4, H-C(1) or H-C(2)), 3.63, 3.58 (*2s*, 6H, 2 MeO). ¹³C-NMR (100.6 MHz, CDCl₃): δ_{C} 170.3, 169.8 (*2s*, 2 COO), 152.6, 151.3 (*2s*, C(2',2'')), 142.2, 142.0 (*2d*, ¹*J*(C,H) = 203, C(5'5'')), 139.9, 139.7 (*2d*, ¹*J*(C,H) = 180, C(4), C(7)), 137.9, 137.7 (*2d*, ¹*J*(C,H) = 179, C(3), C(8)), 110.5, 110.2 (*2d*, ¹*J*(C,H) = 176, C(4',4'')), 107.4, 106.9 (*2d*, ¹*J*(C,H) = 172, C(3',3'')), 98.5, 96.3 (*2s*, C(2a), C(8a)), 84.7, 83.7 (*2d*, ¹*J*(C,H) = 167, C(5), C(6)), 81.8 (*s*, C(5a)), 70.3 (*s*, C(8b)), 52.2, 52.0 (*2q*, ¹*J*(C,H) = 147, 2 MeO), 47.9, 46.9 (*2d*, ¹*J*(C,H) = 132, C(1), C(2)). MS-EI (MeCN/H₂O/AcOH) *m/z*: 437 (75, *M*⁺), 392 (30), 289 (100), 273 (60). Crystal for X-Ray diffraction, see Table 4.

Table 4. Crystal data and structure refinement for adduct (**8**)

Empirical formula	C ₂₄ H ₂₀ O ₈	
Formula weight	436.40	
Temperature	143(2) K	
Wavelength	0.71070 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.362(2) Å	$\alpha = 90^\circ$
	b = 12.051(2) Å	$\beta = 105.77(3)^\circ$
	c = 14.949(3) Å	$\gamma = 90^\circ$
Volume	1969.9(7) Å ³	
Z	4	
Density (calculated)	1.471 Mg/m ³	
Absorption coefficient	0.111 mm ⁻¹	
F(000)	912	
Crystal size	0.16 x 0.14 x 0.11 mm ³	
Theta range for data collection	1.86 to 24.41°.	

Table 4 (continued)

Index ranges	-12<=h<=13, -13<=k<=14, -15<=l<=16
Reflections collected	8611
Independent reflections	2791 [R(int) = 0.0425]
Completeness to theta = 24.41°	86.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2791 / 0 / 290
Goodness-of-fit on F ²	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0457, wR2 = 0.1228
R indices (all data)	R1 = 0.0535, wR2 = 0.1286
Extinction coefficient	0.056(4)
Largest diff. peak and hole	0.251 and -0.242 e.Å ⁻³

CCDC-184219 (**4A**, **4A'**) and CCDC-181825 (**8**) contain the supplementary crystallographic data for this report. These data can be obtained free of charge via 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 336 033; or deposit@ccdc.cam.ac.uk).

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