PERKIN 2

Selenium- and tellurium-bridged overcrowded homomerous bistricyclic aromatic enes

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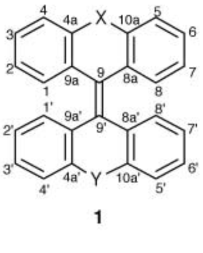
Received 2nd November 1999, Accepted 13th January 2000

The effects of selenium and tellurium bridges on the conformations of overcrowded homomerous bistricyclic aromatic enes were studied. The structures of the target molecules 9,9′-bi(9*H*-selenoxanthen-9-ylidene) (**7**) and 9,9′-bi(9*H*-telluroxanthen-9-ylidene) (**8**) were established by ^{1}H, ^{13}C, ^{77}Se, ^{125}Te NMR spectroscopy, and by X-ray analysis. The molecules adopted *anti*-folded conformations with 53.6 (**7**) and 53.1° (**8**) folding dihedrals between pairs of benzene rings of the tricyclic moieties, whereas the corresponding folding dihedral in 9-methylene-9*H*-selenoxanthene **20** was considerably lower, 32.4°. An X-ray analysis of 9,9′-bi(9*H*-selenoxanthene) (**9**) indicated an *anti*-folded conformation with a folding dihedral of 49.2° and short $Se_{10}\cdots H_{9'}$ and $Se_{10'}\cdots H_{9}$ distances. Compounds **7** and **8** exhibited low degrees of overcrowding in the fjord regions. Considerable overcrowding was evident in the short $Se_{10}\cdots C_{9}$ and $Te_{10}\cdots C_{9}$ contact distances in **7** and **8**. The high shielding of the protons in the fjord regions of **7** and **8** revealed *anti*-folded conformations in solution. The ^{13}C NMR chemical shifts of **7** and **8** were characterized by low-field absorptions of C_9 and $C_{9'}$. Semi-empirical PM3 calculations of the *anti*-folded, *syn*-folded, and twisted conformations indicated that *anti*-folded-**7** and *syn*-folded-**8** were the most stable conformations, respectively. The special stability of *syn*-folded-**8** was attributed to the short intramolecular $Te_{10}\cdots Te_{10'}$ distance (3.06 Å). Compounds **7** and **8** were synthesized by reductive “dimerizations” of 9*H*-selenoxanthene-9-thione (**13**) and 9*H*-telluroxanthene-9-thione (**17**) with copper in boiling toluene. Compound **7** was also synthesized by diazo–thione coupling between **13** and 9-diazo-9*H*-selenoxanthene (**14**), followed by elimination of sulfur from the intermediate thiirane **15**. 9,9′-Bi(9*H*-selenoxanthene) (**9**) and 9,9′-bi(9*H*-telluroxanthene) (**10**) were prepared by low valent titanium induced reductive “dimerizations” of 9*H*-selenoxanthen-9-one (**11**) and 9*H*-telluroxanthen-9-one (**12**), respectively, using $TiCl_4$/Zn/pyridine–THF.

Introduction

The bistricyclic aromatic enes (**1**) have fascinated chemists since the red hydrocarbon 9,9′-bi(9*H*-fluoren-9-ylidene) (**2**) was synthesized in 1875, the yellow 9,9′-bi(9*H*-xanthen-9-ylidene) (**3**) was synthesized in 1895, and thermochromism and piezochromism were revealed in 9,9′-bi(anthracen-9-ylidene)-10,10′-dione (**4**) in 1909.[1–3] The bistricyclic enes are representatives of the more general class of overcrowded polycyclic aromatic enes (PAEs).[3] They may be perceived as bridged tetraarylethenes and as tetrabenzofulvalenes. They can be classified into *homomerous* bistricyclic enes (**1**, X = Y) and *heteromerous* bistricyclic enes (**1**, X ≠ Y).[3,4]



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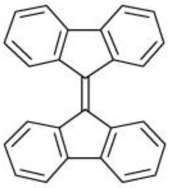

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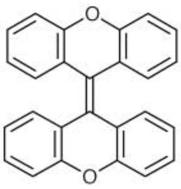

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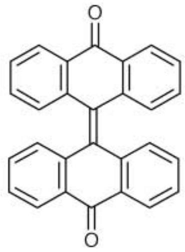

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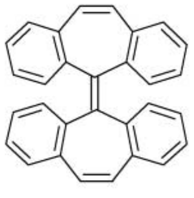

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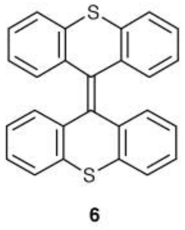

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The bistricyclic enes (**1**) are overcrowded. The intramolecular overcrowding in **1** requires out-of-plane deformations in order to accommodate the sterically demanding tricyclic moieties without prohibitively close contacts of non-bonded atoms in the fjord regions on both sides of the central double bond (C_9=$C_{9'}$). A hypothetical coplanar bistricyclic ene would maintain very short non-bonded carbon–carbon, carbon–hydrogen, and hydrogen–hydrogen distances in the fjord regions, at positions 1, 1′, 8, and 8′, leading to considerable overlaps of the van der Waals radii. Such repulsive interactions could be relieved by deviations from coplanarity and by various distortions of bond angles and bond lengths. Two principal modes of out-of-plane

DOI: 10.1039/a908715j

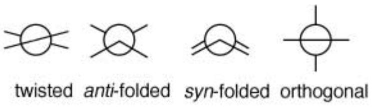


Fig. 1 Schematic projection along C_9=$C_{9'}$ of various conformations of bistricyclic enes (lines represent the peripheral benzene rings of the moieties).

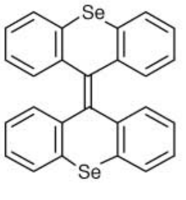
deformations were considered:[5] twisting around the double bond and out-of-plane bending (hence pyramidalization).[2] In **1** the bending is realized by folding of the tricyclic moieties at both ends of the central ene about the $C_9 \cdots X$ and $C_{9'} \cdots Y$ axes, resulting in boat conformations of the central rings. In addition, C_9 and $C_{9'}$ may be pyramidalized. Four pure conformations of **1** were considered: twisted (**t**), *anti*-folded (**af**), *syn*-folded (**sf**), and orthogonally twisted (**t**$_\perp$).[3] A schematic representation of these overall molecular shapes of bistricyclic enes is shown in Fig. 1. These modes strongly depend on the bridges X and Y and on the size of the rings. A variety of conformations has been revealed in the homomerous bistricyclic enes, including twisted 9,9′-bi(9*H*-fluoren-9-ylidene)[6,7] (**2**), *anti*-folded 9,9′-bi(9*H*-xanthen-9-ylidene)[8] (**3**), *anti*-folded bistricyclic enes with alkylidene bridges ((**1**, X = Y = $C(CH_3)_2$; X = Y = CH_2),[9] and *anti*-folded and *syn*-folded 5,5′-bi(5*H*-dibenzo[*a*,*d*]cyclohepten-5-ylidene) (**5**).[10] Metallo-based bistricyclic enes with $PdCl_2$ and $ZnCl_2$ bridges have been reported.[11]

In the series of chalcogeno-bridged homomerous bistricyclic enes (**1**, X = Y = O, S, Se or Te), only 9,9′-bi(9*H*-xanthen-9-ylidene) (**3**)[8,12] and 9,9′-bi(9*H*-thioxanthen-9-ylidene (**1**, X = Y = S) (**6**)[13,14] have previously been studied.[3] However, the 1963 crystal structure of **3** is of low quality and problematic,[8,15] whereas the crystal structure of **6** is not known. The present article describes the syntheses, molecular and crystal structures, NMR spectra and semi-empirical calculations of the selenium- and tellurium-bridged bistricyclic enes 9,9′-bi(9*H*-selenoxanthen-9-ylidene) (**7**) and 9,9′-bi(9*H*-telluroxanthen-9-ylidene) (**8**) and their dihydro derivatives, "bistricyclic ethanes" 9,9′-bi(9*H*-selenoxanthene) (**9**) and 9,9′-bi(9*H*-telluroxanthene) (**10**). The effect of the chalcogen bridges on the conformations of bistricyclic enes will also be discussed. The choice of selenium and tellurium as new bridges in bistricyclic enes with central six-membered rings was based on the following considerations: the Se–C and Te–C bonds[16] are markedly longer than the S–C and O–C bonds. In **7** and **8** the introduction of the selenium and tellurium bridges may increase the $C_{4a} \cdots C_{10a}$ and $C_{4a'} \cdots C_{10a'}$ distances. Such elongations are expected to result in larger folding dihedrals of the planes of the two benzene rings of each tricyclic moiety, as compared with **2**, **3**, **4**, and **6**. Under these circumstances, the degree of intramolecular overcrowding in the fjord regions of **7** and **8** is predicted to be smaller. Furthermore, the relative stabilities of the *syn*-folded conformations of **7** and **8**, as compared with the corresponding *anti*-folded conformations, are expected to increase (lower energies). The higher chalcogen homologs selenium and tellurium in **7** and **8**, due to their lower electronegativities, as compared with oxygen and sulfur,[17] may impose special electronic characteristics on these chalcogeno-bridged **1**.

Results and discussion

Syntheses

The starting materials in the syntheses of 9,9′-bi(9*H*-selenoxanthen-9-ylidene) (**7**), 9,9′-bi(9*H*-telluroxanthen-9-ylidene) (**8**), 9,9′-bi(9*H*-selenoxanthene) (**9**), and 9,9′-bi(9*H*-telluroxanthene) (**10**) were the tricyclic ketones 9*H*-selenoxanthen-9-one (**11**)[18,19] and 9*H*-telluroxanthen-9-one (**12**).[20,21] The chemistry of **11** and **12** has been reviewed.[20,22,23] However, little attention has been drawn to their "dimerization" reactions. The synthesis of **7** was accomplished by the following two methods, using 9*H*-selenoxanthene-9-thione (**13**)[24] as an intermediate (Scheme 1): (a) a diazo–thione coupling between **13** and 9-diazo-9*H*-selenoxanthene (**14**) in boiling benzene to give dispiro[selenoxanthene-9,2′-thiirane-3′,9″-selenoxanthene] (**15**) (61% yield) followed by an elimination of sulfur from **15** with triphenylphosphine in boiling benzene to give **7** in 67% yield; (b) a one step reductive "dimerization" of **13** with copper powder in boiling toluene to give **7** in 89% yield. The intermediate thioketone **13** was prepared from **11**, using Lawesson's reagent[25–27] in boiling benzene. The diazo intermediate **14** was prepared from **13** in two steps by conversion to the hydrazone **16**, followed by oxidation, using Ag_2O or HgO.



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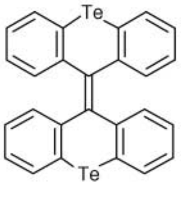

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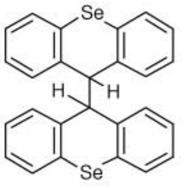

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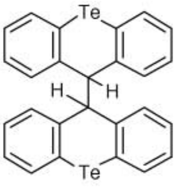

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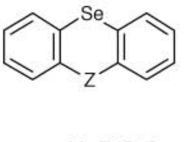
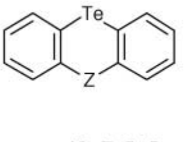
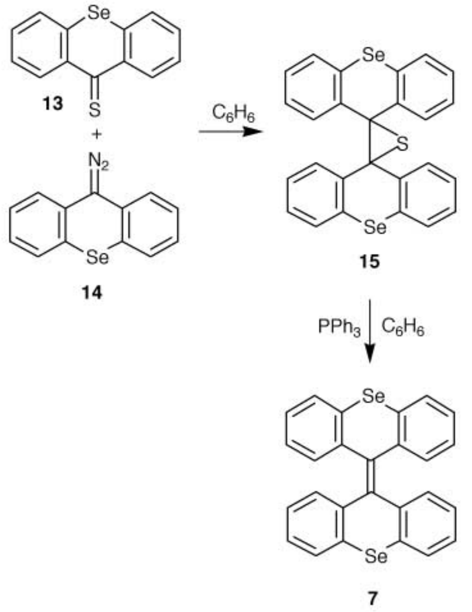




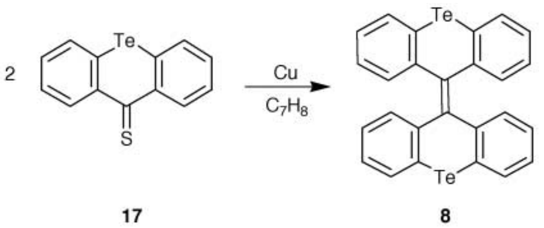
11, Z: C=O
13, Z: C=S
16, Z: C=NNH$_2$
14, Z: C=N$_2$
19, Z: CH$_2$
20, Z: C=CH$_2$

12, Z: C=O
17, Z: C=S
18, Z: C=N$_2$
21, Z: C=CH$_2$
22, Z: CH$_2$

The attempted synthesis of 9,9′-bi(9*H*-telluroxanthen-9-ylidene) (**8**) in analogy to **7**, by adopting the above methods used in the synthesis of **7**, was confronted with certain difficulties which were absent in the selenium series. Treatment of the starting material, ketone **12**, with Lawesson's reagent gave 9*H*-telluroxanthene-9-thione (**17**). However, the thioketone **17** turned out to be quite sensitive, as compared with **13**. Its purification by chromatography on silica gel had to be performed quickly, in order to minimize the decomposition (to **12**). The preparation of 9-diazo-9*H*-telluroxanthene (**18**) was also problematic, due to its instability. 9,9′-Bi(9*H*-telluroxanthen-9-ylidene) (**8**) was eventually synthesized by a one step reductive "dimerization" of **17**, using copper powder in boiling toluene, in 40% yield (Scheme 2). Attempted syntheses of **7** and **8** by low-valent titanium induced reductive "dimerizations" of **11** and **12**, respectively, using the Mukayama–Lenoir recipe[28–30] of the McMurry reaction[30,31] ($TiCl_4$/Zn/pyridine/THF), were unsuccessful. The reactions products were the dihydro derivatives, 9,9′-bi(9*H*-selenoxanthene) (**9**) and 9,9′-bi(9*H*-telluroxanthene) (**10**), in 30% and 41% yield, respectively. The reductive "dimerization" of **11** gave also 9*H*-selenoxanthene (**19**) (in small yield). The ^{77}Se and ^{125}Te NMR spectra of the crude reactions products indicated that the overcrowded enes **7** and **8** were absent from the mixtures of products. The dihydro derivative **9** has previously been prepared by sunlight irradi-



Scheme 1



Scheme 2

ation of selenoxanthene (**19**)[32] and as a by-product of the reactions of selenoxanthenylium perchlorate with methylmagnesium iodide and of **19** with butyllithium.[33] The dihydro derivative **10** has previously been prepared by a reductive "dimerization" of **12** using zinc in HOAc/HCl.[34] 9,9′-Bi(9*H*-thioxanthen-9-ylidene) (**6**) was prepared analogously to **7** and **8** from 9*H*-thioxanthene-9-thione and copper powder in boiling toluene in 71% yield. This method[35,36] is superior to the original synthesis of **6** by a reductive "dimerization" of 9*H*-thioxanthen-9-one with zinc in HOAc/HCl, which may give a mixture of **6** and 9,9′-bi(9*H*-thioxanthene).[37] The tricyclic enes, 9-methylene-9*H*-selenoxanthene (**20**) and 9-methylene-9*H*-telluroxanthene (**21**) which lack overcrowded regions were synthesized for comparison with **7** and **8**, by Grignard reactions of **11** and **12** with methylmagnesium iodide.

Molecular and crystal structures

The crystal structures of bistricyclic enes have recently been reviewed.[3] Among the chalcogeno-bridged members of this series, only the old crystal structures of 9,9′-bi(9*H*-xanthen-9-ylidene) (**3**)[8,15] and that of 9-(2-methyl-9*H*-thioxanthen-9-ylidene)-9*H*-xanthene (**1**, X = O, Y = S)[38] have been reported. Compound **7** crystallized in the space group $Pca2_1$. The molecules in the unit cell are not centrosymmetric. Fig. 2 gives an ORTEP diagram of **7** as determined by X-ray analysis. Compound **8** crystallized in space group $P\bar{1}$. There are two independent half molecules of **8** in the asymmetric unit, each residing on an independent crystallographic center of symmetry (on the middle of each $C_9{=}C_{9'}$ bond). Fig. 3 gives the ORTEP diagram of one molecule of **8**. Compound **20** crystallized in the space group $Cmc2_1$. The two benzene rings are reflected by each other *via* a mirror plane passing through the Se_{10}, C_9, and $C_{9'}$ atoms. Fig. 4 gives an ORTEP diagram of **20**. Table 1 gives the conformations and selected geometrical parameters of **7**–**10** and **20**, **21** derived from the crystal structures and from PM3 calculations (*vide infra*).

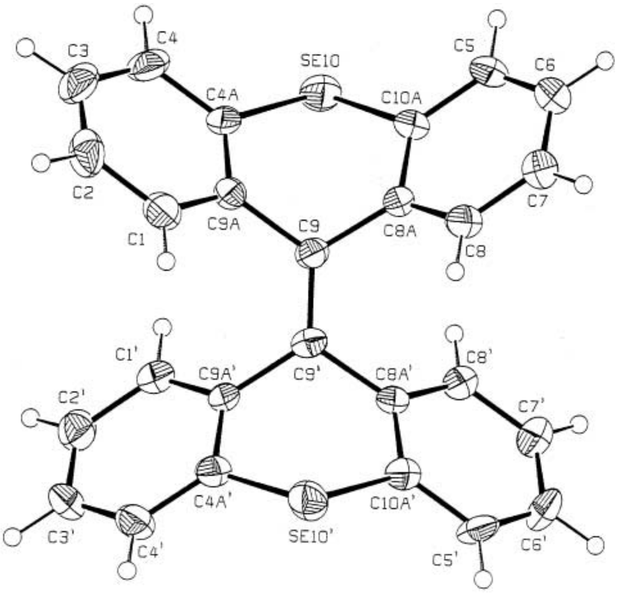


Fig. 2 An ORTEP diagram of the crystal structure of compound **7**.

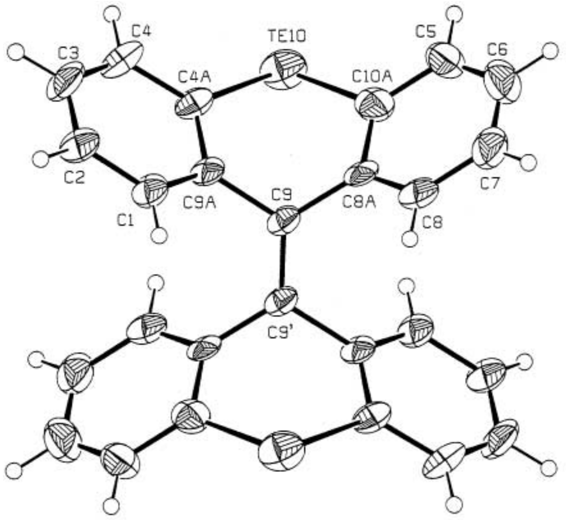


Fig. 3 An ORTEP digram of the crystal structure of compound **8**.

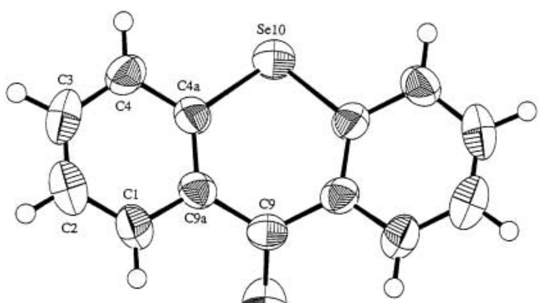


Fig. 4 An ORTEP diagram of the crystal structure of compound **20**.

The overall conformations of the bistricyclic enes are characterized by the pure twist of the central ethene group $\omega = 1/2(C_{9a}–C_9–C_{9'}–C_{9a'} + C_{8a}–C_9–C_{9'}–C_{8a'})$, and by the folding dihedrals of the tricyclic moieties.[1,3] The folding dihedral (or propeller twist) is defined as the dihedral angle of the least-squares planes of the carbon atoms C_1, C_2, C_3, C_4, C_{4a}, C_{9a} and C_5, C_6, C_7, C_8, C_{8a}, C_{10a} of the two benzene rings of a tricyclic moiety.[1,3] The pyramidalization angles $\chi_9 = (C_{9a}–C_9–C_{9'}–C_{8a}$

Table 1 Conformations and selected geometrical parameters of compounds **7**–**10** and **20**–**21** derived from crystal structures and PM3 calculations

Compound	X = Y	Method	Conformation[a]	Folding angle/°		Pure twist/°	$C_1\cdots C_{1'}$/Å	$C_1\cdots H_{1'}$/Å	$H_1\cdots H_{1'}$/Å	$X\cdots Y$/Å	$X_{10}\cdots C_9$/Å	C_9–$C_{9'}$/Å	C_{9a}–C_9–C_{8a}/°	χ_9/°	C–X/Å	C–X–C/°	$C_{4a}\cdots C_{10a}$/Å
7	Se	X-Ray	**af**	52.5	54.7	1.6	3.26	3.24	3.49	7.15	3.08	1.338	112.8	0.5	1.911	94.3	2.80
7	Se	PM3	**af**	51.6	51.6	0.0	3.30	3.37	3.75	7.00	3.02	1.351	114.0	2.2	1.885	96.5	2.81
7	Se	PM3	**sf**	54.8	54.8	0.0	3.03	2.57	1.78	4.85	3.01	1.351	112.5	7.4	1.886	95.9	2.80
7	Se	PM3	**t**	8.6	8.6	56.1	3.02	2.80	2.99	7.98	3.29	1.406	122.6	0.0	1.886	99.9	2.86
8	Te	X-Ray[b]	**af**	53.1	53.1	0.0	3.25	3.28	3.56	7.42	3.23	1.351	115.3	1.7	2.116	89.3	2.97
8	Te	PM3	**af**	57.8	57.8	0.0	3.62	3.80	4.25	6.09	3.06	1.346	114.9	1.5	2.136	90.9	3.05
8	Te	PM3	**sf**	59.6	59.6	0.0	3.43	3.20	2.65	3.06	2.96	1.346	114.6	12.2	2.142	91.3	3.06
8	Te	PM3	**t**	18.6	18.6	54.8	3.04	2.95	3.22	8.41	3.50	1.408	125.0	0.0	2.105	92.4	3.04
9	Se	X-Ray	**af**	49.2	49.2		3.60	3.70	4.04	6.62	3.15	1.501	112.2		1.904	95.2	2.81
10	Te	X-Ray[34]	**af**	39.5	41.2		3.52	3.77	4.25	6.85	3.33	1.574	115.3		2.101	91.5	3.01
20	Se[c]	X-Ray	**f**	32.4		0.0			2.35[e]		3.16	1.37	117.4	9.0	1.896	96.3	2.83
20	Se[c]	PM3	**f**	22.3		0.0			1.91[e]		3.22	1.343	121.3	1.1	1.874	99.5	2.86
20	Se[c]	PM3	**p**	0.0		0.0			1.74[e]		3.29	1.346	122.8	0.0	1.868	100.2	2.87
21	Te[d]	PM3	**f**	47.3		0.0			2.73[e]		3.16	1.336	118.4	0.3	2.128	91.9	3.06
21	Te[d]	PM3	**p**	0.0		0.0			1.71[e]		3.51	1.347	125.8	0.0	2.104	92.3	3.03

[a] Conformation: **af**, *anti*-folded; **sf**, *syn*-folded; **t**, twisted; **p**, planar; **f**, folded. [b] Average of the two independent molecules. [c] Tricyclic, X = Se. [d] Tricyclic, X = Te. [e] $H_1\cdots H_{9'}$.

mod360°) − 180° and $\chi_{9'} = (C_{9a'}–C_{9'}–C_9–C_{8a'}$ mod360°) − 180° should also be considered.[3] The molecular and crystal structures of **7** and **8** indicate that both molecules adopt *anti*-folded conformations (**af-7** and **af-8**, respectively). In the case of **7**, the folding dihedrals are 52.5 and 54.7° for the two selenoxanthene moieties, respectively. In the case of **8** the folding dihedrals of the two crystallographically non-equivalent centrosymmetric molecules are 53.0 and 53.3°, respectively. These folding dihedrals are almost identical to the respective dihedrals in 10,10,10′,10′-tetramethyl-9,9′,10,10′-tetrahydro-9,9′-bi(anthracen-9-ylidene) (**1**, X = Y = $C(CH_3)_2$), 53.0.[9] For comparison, the degrees of folding in 9,9′-bi(9*H*-xanthen-9-ylidene) (**3**)[8] and in the above-mentioned heteromerous sulfur/oxygen-bridged[38] **1** are 40.1° (α-modification) and 51.1/36.2°, respectively. The molecular structures of **7** and **8** closely resemble each other. They differ mainly in the geometrical parameters pertaining directly to the chalcogen bridges. Thus, C–Se, C–Se–C and $C_{4a}\cdots C_{10a}$ in **7** are 1.911 Å, 94.3° and 2.80 Å, while C–Te, C–Te–C and $C_{4a}\cdots C_{10a}$ in **8** are 2.116 Å, 89.3° and 2.97 Å. For comparison, in bis(*p*-tolyl) selenide, Se–C is 1.93 Å and C–Se–C is 106.2°;[39] in bis(biphenyl-2-yl) telluride Te–C is 2.105 and 2.125 Å and C–Te–C is 96.2°;[40] in bis(*p*-methoxyphenyl) telluride, C–Te is 2.110 and 2.112 Å and C–Te–C is 99.5°.[41] Thus, the C–Se–C and C–Te–C angles in **7** and **8** are considerably smaller. The degree of overcrowding in the fjord regions of **7** and **8**, as reflected in the intramolecular distances $C_1\cdots C_{1'}$ and $C_1\cdots H_{1'}$, is relatively low and quite similar: 3.26 and 3.24 Å in **7** and 3.25 and 3.28 Å in **8**, respectively. For comparison, the van der Waals radii of carbon and hydrogen are 1.71 and 1.15 Å,[42] resulting in a van der Waals $C\cdots C$ contact distance of 3.42 Å. Thus, the above $C_1\cdots C_{1'}$ distances in **7** and **8** reflect only about 5% penetration. The pyramidalization angles χ_9 and $\chi_{9'}$[3] and the pure twist ω, are negligible. The close similarity in the degree of folding between the selenium-bridged **7** and the tellurium-bridged **8** was, at first sight, unexpected. In order to rationalize this similarity, a comparison with the folding dihedrals of the tricyclic enes **20** and **21** may be helpful.[43] The folding dihedral of the selenium bridged **20**, derived from the crystal structure is 32.4°, considerably lower than that of **7** (52.5/54.7°). Furthermore, the PM3 calculated folding dihedral of **20** (22.3°) is markedly lower than that of the tellurium bridged **21**, 47.3°. The selenium-bridged **7** solves the problem of overcrowding in the fjord regions by adopting an *anti*-folded conformation, reaching a degree of folding of 53–55°. The tellurium-bridged **8** with its longer C–X bonds and smaller C–Te–C angles has the potential of reaching a higher degree of folding as compared with **7** (*cf.* **21** *vs.* **20**). However, it does not have to take advantage of this option in order to reach a non-planar conformation with a permissible degree of overcrowding in the fjord regions. The degree of folding of **7** and **8** is constrained also by the proximity of the bridging atoms Se and Te to C_9. In **7** and **8** the $Se_{10}\cdots C_9$ and $Te_{10}\cdots C_9$ distances, 3.08 (**7**) and 3.23 Å (**8**), are considerably shorter than the $Se\cdots C$ and $Te\cdots C$ van der Waals contact distances, 3.61 and 3.79 Å, respectively.[42,44] These short distances indicate an additional effect of intramolecular overcrowding in folded bistricyclic enes. Furthermore, a higher degree of folding may result in even shorter $Se_{10}\cdots C_9$ and $Te_{10}\cdots C_9$ distances and enhanced overcrowding.

The crystal structures of the bi(9*H*-chalcogenoxanthene)s **9** and **10** deserve a few comments. The crystal structure of **10** has been reported.[34] Fig. 5 gives the ORTEP diagram resulting from the structure determination of **9**. Compounds **9** and **10** crystallize in the space groups $P2_1/c$ and $P2_1/b$, respectively. Both adopt *anti*-folded conformations, with folding dihedrals of 49.2 and 41.2/39.5°, respectively. For comparison, the degree of folding in the crystal structure of 9*H*-telluroxanthene (**22**) is 50.4°.[34] The torsion angles C_{8a}–C_9–$C_{9'}$–$C_{8a'}$ and C_{9a}–C_9–$C_{9'}$–$C_{9a'}$ are 49.5 and −49.5° in **9** and 51.8 and −48.8° in **10**. Compounds **9** and **10** differ also in the C_9–$C_{9'}$ bond length: 1.501 (**9**) *versus* 1.574 Å (**10**). The $Se_{10}\cdots H_{9'}$ and $Te_{10}\cdots H_{9'}$ distances 2.84 and

Table 2 ^{1}H NMR Chemical shifts (δ) of compounds **2**, **3**, **5**–**10**, **20**–**21**[a]

Compound	X = Y	Conformation	H_1	H_2	H_3	H_4	H_9	H_{10}
7	Se	**af**	6.787	6.904	7.072	7.656		
8	Te	**af**	6.796	6.879	6.963	7.801		
9	Se	**af**	6.455	6.804	7.034	7.537	4.828	
10	Te	**af**	6.590	6.777	6.926	7.655	5.275	
2[46]	—	**t**	8.38	7.20	7.32	7.69		
3	O	**af**	7.146	6.877	7.226	7.270		
6	S	**af**	6.815	6.911	7.129	7.537		
20	Se	**f**	7.595	7.285	7.220	7.506	5.549[b]	
21	Te	**f**	7.550	7.283	7.152	7.679	5.481[b]	
5a	CH=CH	**af**	6.603	6.908	7.080	7.297		7.109
5b	CH=CH	**sf**	7.549	7.173	7.016	7.058		6.707

[a] In $CDCl_3$ (relative to $CHCl_3$, δ 7.26). [b] $\delta(C{=}CH_2)$.

Table 3 ^{13}C NMR Chemical shifts (δ) of **6**–**12** and related compounds[a]

Compound	C_1	C_2	C_3	C_4	C_{4a}	C_{8a}	C_9	CH_2
7	130.47	126.18	126.68	129.47	132.42	137.44	137.44	
8	130.67	127.02	126.57	134.98	118.01	141.27	143.69	
9	130.77	126.04	126.52	128.91	129.11	137.12	49.86	
10	131.49	126.59	126.78	134.88	114.29	139.85	52.25	
2[46]	127.1	127.3	129.6	120.3	141.7	138.7	141.0	
3	128.31	122.40	128.12	117.08	155.48	124.92	121.44	
6	129.85	125.73	126.72	127.10	135.65	135.99	133.59	
11	131.39	126.77	132.16	128.28	135.05	130.95	182.01	
12	132.97	131.87	127.70	133.78	119.96	134.54	186.46	
20	126.94	127.19	127.67	128.37	128.19	137.02	146.03	116.23
21	127.76	127.98	127.66	134.12	113.56	141.65	152.03	118.31

[a] In $CDCl_3$ (relative to $CDCl_3$, δ 77.01).

Table 4 ^{77}Se and ^{125}Te NMR Chemical shifts of **7**–**10** and related compounds

Se Compound	δ^{77}Se[a]	$\Delta\delta$[b]	Te Compound	δ^{125}Te[c]	$\Delta\delta$[d]	δTe/δSe
11	334.7	0.0	**12**	473.4	0.0	1.40
7	366.3	31.6	**8**	547.1	73.7	1.49
9	326.0	−8.7	**10**	481.0	7.6	1.47
19	353.2	18.5	**22**	515.8	42.4	1.46
20	336.1	1.4	**21**	514.6	41.2	1.53

[a] In $CDCl_3$ (relative to Me_2Se in $CDCl_3$).[58] [b] Relative to selenoxanthone.[58] [c] In $CDCl_3$ (relative to Me_2Te in C_6D_6).[58] [d] Relative to telluroxanthone.

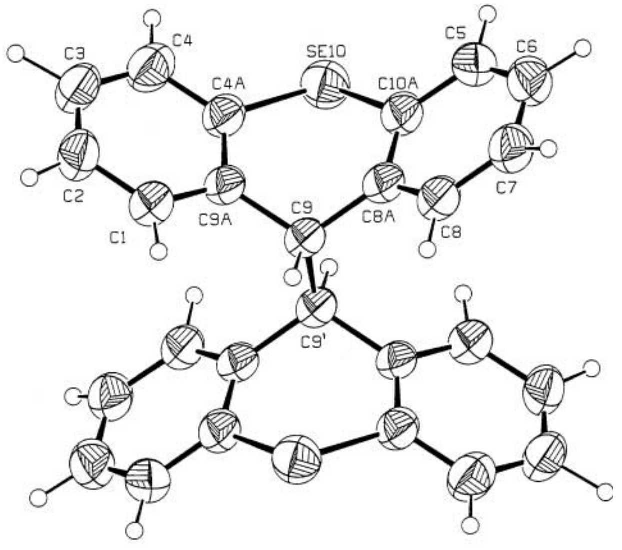


Fig. 5 An ORTEP diagram of the crystal structure of compound **9**.

3.01 Å are shorter than the van der Waals contact distances, 3.05 and 3.23 Å, respectively,[44] pointing to an intramolecular overcrowding effect in these "bistricyclic ethanes". It is interesting that the overcrowding due to a short $Se_{10} \cdots C_9$ distance is evident also in **9**, 3.15 Å. The fjord regions of **9** and **10** are not overcrowded.

NMR spectroscopy

Table 2 gives the ^{1}H NMR chemical shifts of compounds **6**–**10** and related homomerous bistricyclic enes and tricyclic enes, and Table 3 the ^{13}C NMR chemical shifts of **6**–**12**. Table 4 gives the ^{77}Se and ^{125}Te NMR chemical shifts of **7**–**10** and related Se- and Te-bridged tricyclics. Complete assignments were made through 2-dimensional correlation spectroscopy [COSY, heteronuclear single quantum coherence (HSQC), heteronuclear multiplet bond coherence (HMBC)]. It is possible to distinguish qualitatively among the twisted conformation, the *anti*-folded conformation and the *syn*-folded conformation of homomerous bistricyclic enes (**1**, X = Y) in solution, using ^{1}H NMR spectroscopy. For a twisted conformation the protons at the fjord regions (H_1, H_8, $H_{1'}$, $H_{8'}$) appear in the ^{1}H NMR spectrum at low aromatic field (*e.g.*, δ 8.38 for **2**),[45,46] while for an *anti*-folded conformation these protons appear at a relatively high aromatic field (*e.g.*, δ 7.146 for **3**). For a *syn*-folded conformation the above protons appear at a relatively normal aromatic field. Thus, for *anti*-folded **5a** and *syn*-folded **5b** the fjord region protons appear at δ 6.603 and 7.549, respectively

(Table 2).[47–49] In the cases of **7** and **8** the fjord region protons appear at δ 6.787 and 6.796, respectively (Table 2), indicating that these 9,9′-bi(9*H*-chalcogenoxanthen-9-ylidene)s adopt *anti*-folded conformations not only in the solid state but also in solution. The shielding of the fjord region protons is attributed to their exposure to the diamagnetic ring current of the opposing aromatic rings.[50] In the *anti*-folded conformations these protons lie somewhat above (or below) the planes of the opposing aromatic rings (Figs. 2, 3; see also Fig. 6, *vide infra*). The alternative explanation of attributing the shielding of the fjord region protons to the chalcogen (Se and Te)-induced effect is ruled out by the ^{1}H NMR spectra of the tricyclic enes **20** and **21**. The chemical shifts of H_1 and H_8 of these selenium- and tellurium-bridged dibenzofulvenes appear at δ 7.595 and 7.550, and are thus (slightly) deshielded. The neighboring protons H_2, H_7, $H_{2'}$, and $H_{7'}$ are also influenced by this shielding effect although its magnitude is usually smaller. An exception is 9,9′-bi(9*H*-xanthen-9-ylidene) (**3**) which is considerably (>10°) less *anti*-folded than **7** and **8**.[3,8] In the case of **3** the upfield shift is more pronounced in H_2 and H_7 than in H_1 and H_8 (δ 6.877 *versus* 7.146, respectively). By contrast, in *syn*-folded **8** the fjord protons would not lie above (or below) the opposing aromatic rings but are expected to adopt a bucking orientation (H_1 *versus* $H_{1'}$ and H_8 *versus* $H_{8'}$). The shielding of the fjord protons in **7** and **8** is very similar, thus confirming the close resemblance in their degrees of folding. The shielding of H_1, H_8, $H_{1'}$, and $H_{8'}$ in the dihydro derivatives **9** and **10** (δ 6.455 and 6.590, respectively) is even more pronounced than in **7** and **8**. The upfield shift in **9** relative to **10** is consistent with the higher degree of folding in **9** (49.2°) as compared with **10** (39.5/41.2°). The protons *ortho* to the chalcogen atoms (H_4, H_5, $H_{4'}$, and $H_{5'}$) in the 9,9′-bi(9*H*-chalcogenoxanthen-9-ylidene)s are somewhat shifted down field. This effect is gradually enhanced in the series O, S, Se and Te, reaching δ 7.801 for **8**. It is somewhat smaller for the dihydro derivatives **9** and **10**. The difference in the chemical shifts of the protons bonded to the sp^3 carbon atoms (H_9 and $H_{9'}$) (δ(**10**) − δ(**9**) = 0.447) may be due to a through space effect of the opposing chalcogen atom (*e.g.*, $Te_{10}\cdots H_{9'}$ in **10** *versus* $Se_{10}\cdots H_{9'}$ in **9**).

The ^{13}C NMR chemical shifts of compounds **7** and **8** (Table 3) are characterized by low field absorptions of C_9 and $C_{9'}$ (δ(**7**) 137.44 and δ(**8**) 143.69), as compared with **3** (δ 121.44) and **6** (δ 133.59). This effect may be due to through space interactions of the selenium and the tellurium atoms with the sp^2 carbon atoms C_9 and $C_{9'}$ (*e.g.*, $Se_{10}\cdots C_9$, and $Te_{10}\cdots C_9$, *vide supra*). Noteworthy also is the chemical shift of C_{4a} in **8** (δ 118.01) as compared with **3** (δ 155.48) and **7** (δ 132.42). This effect, which appears also in **10**, in Te-bridged tricyclics (*e.g.*, **12**, **22**) and in diphenyl telluride,[51] is probably governed by the direct bonding of the chalcogen atom to C_{4a}. In the chalcogen series, tellurium causes the lowest chemical shift of C_{4a}.[51] Indeed, a comparison between the ^{13}C NMR chemical shifts of **7** and **8** indicates that C_{4a} is the most affected carbon atom (δ(**8**) − δ(**7**) = −14.41, while an opposite effect is observed in C_9 and C_4 (δ(**8**) − δ(**7**) = 6.25 and 5.51, respectively). A similar trend is seen in **9** and **10** [δ(**10**) − δ(**9**) = −14.82 (C_{4a}), 2.39 (C_9) and 5.97 (C_4)]. However, the effect is significantly smaller in sp^3 hybridized C_9.

The ^{77}Se and ^{125}Te NMR chemical shifts of compounds **7**–**10** (Table 4) were very helpful, due to their sensitivity, in monitoring the progress of the syntheses leading to these selenium- and tellurium-bridged bistricyclic enes and ethanes. Gronowitz *et al.* have shown that in the series of 4,4′-disubstituted diphenyl selenides the ^{77}Se NMR chemical shifts vary in a regular way with the character of the substituent, electron donating and withdrawing groups causing large upfield and downfield shifts, respectively,[52] An analogous trend has been revealed in the diaryl telluride series.[53] We have previously shown that in a series of selenium- and tellurium-bridged tricyclics, these chemical shifts were significantly shielded relative to diphenyl selenide and diphenyl telluride and were dependent on the conformation.[43] Within the selenium-bridged series (**7**, **9**, **11**, **19**, **20**) and within the tellurium-bridged series (**8**, **10**, **12**, **21**, **22**) the downfield shifts of $\Delta\delta^{77}$Se and $\Delta\delta^{125}$Te of **7** and **8** are higher: 31.6 and 73.7, relative to the respective ketones. For the dihydro derivatives **9** and **10** the corresponding shifts are relatively small (−8.7 and 7.6, respectively). The above downfield shifts of **7** and **8** may be due to the proximity of the selenium and tellurium bridges to the overcrowded $C_9{=}C_{9'}$ in the *anti*-folded conformations. The differences in the ^{77}Se and in the ^{125}Te chemical shifts between **7** and **20** and between **8** and **21** are 30.2 and 32.5 ppm respectively. These differences are tentatively ascribed to an effect of the ring currents of the opposing aromatic rings, which is present in the tetrabenzofulvalenes **7** and **8** and is absent in the dibenzofulvenes **20** and **21**. They may also be due to the interactions of the selenium and tellurium atoms with the non-polar $C_9{=}C_{9'}$ bond in **7** and **8**, respectively, as compared with the corresponding interactions with the somewhat polar exocyclic $C{=}CH_2$ bonds in **20** and **21**. In **7** and **8**, due to their symmetries, the charge populations on C_9 and $C_{9'}$ are identical so that the $C_9{=}C_{9'}$ bonds are non-polar, while in **20** and **21** the exocyclic $C{=}CH_2$ bonds are somewhat polar, as reflected in the ^{13}C NMR chemical shifts [$\delta(C_9)$ 146.03 (**20**) and 152.03 (**21**); $\delta(CH_2)$ 116.23 (**20**) and 118.31 (**21**)]. A previous correlation between ^{77}Se and ^{125}Te NMR chemical shifts in related heterocyclics gave a linear relationship with a slope of δTe/δSe = 1.3.[54] Most of the pairs of tricyclics studied previously gave δTe/δSe of 1.40–1.46.[43] The pair of dibenzofulvenes **20** and **21** gave a δTe/δSe of 1.53, pointing, perhaps, to a different degree of folding.[43] In the case of the pair **7** and **8**, δTe/δSe = 1.49, while in the case of the pair **9** and **10**, δTe/δSe = 1.47.

Semi-empirical calculations

Recently, a systematic theoretical survey of overcrowded homomerous and heteromerous bistricyclic enes (**1**) has been carried out, using the semi-empirical method PM3.[3] The present article reports the results of PM3 calculations[55,56] of the selenium- and tellurium-bridged bistricyclic enes **7** and **8** and the corresponding dibenzofulvenes, **20** and **21**. The following conformations have been considered: *anti*-folded (**af**), *syn*-folded (**sf**), twisted (**t**), for **7** and **8**, folded (**f**), and planar (**p**) for **20** and **21**. The various conformations have been fully optimized and were found to be *bona fide* minima (positive vibrational frequencies) with the exception of **t-7**, **t-8**, **p-20** and **p-21** which are transition states (one imaginary frequency). Table 5 gives the semi-empirical (PM3) enthalpies of formation (ΔH°_f) of the conformations of **7**, **8**, **20** and **21**, the conformational energies ($\Delta\Delta H^\circ_f$) of **7** and **8** relative to the respective *anti*-folded conformations, and the strain energies (SE) of **7** and **8** (derived from isodesmic reactions) [eqns. (1) and (2)].

$$\mathrm{SE}\ (\mathbf{7}) = \Delta H^\circ_f(\text{conformation-}\mathbf{7}) - 2\Delta H^\circ_f(\mathbf{20}) + \Delta H^\circ_f(\text{ethene}) \quad (1)$$

$$\mathrm{SE}\ (\mathbf{8}) = \Delta H^\circ_f(\text{conformation-}\mathbf{8}) - 2\Delta H^\circ_f(\mathbf{21}) + \Delta H^\circ_f(\text{ethene}) \quad (2)$$

Among the conformations of compound **7** the most stable is **af-7**. Its enthalpy of formation is 3.3 kcal mol^{-1} lower than that of **sf-7**. An unexpected result of the present calculations is the striking stability of **sf-8**. It is the global minimum in the conformational space of **8**. Its calculated enthalpy of formation is 9.7 kcal mol^{-1} lower than that of **af-8**. Furthermore, **8** is the only case among the homomerous **1** where the *syn*-folded conformation is predicted to be more stable than the respective *anti*-folded conformation and where the strain energy is negative (−6.1 kcal mol^{-1}). 3-D structures of the PM3-optimized **af-8** and **sf-8** are given in Fig. 6. Selected geometrical

Table 5 Enthalpies of formation, conformational energies and strain energies of **7**, **8**, **20** and **21**

Compound	X = Y	Compounds conformation[a]	Symmetry	$\Delta H^{\circ}_{\mathrm{f}}$[b]	$\Delta\Delta H^{\circ}_{\mathrm{f}}$[b]	SE[b,c]
7	Se	**af**	C_{2h}	108.814	0.0	5.1
7	Se	**sf**	C_{2v}	112.118	3.3	8.4
7	Se	**t**	D_2	135.061	26.2	31.3
8	Te	**af**	C_{2h}	158.113	0.0	3.7
8	Te	**sf**	C_{2v}	148.404	−9.7	−6.1
8	Te	**t**	D_2	195.648	37.5	41.2
20	Se	**f**	C_s	60.177	0.0	
20	Se	**p**	C_{2v}	61.056	0.9	
21	Te	**f**	C_s	85.546	0.0	
21	Te	**p**	C_{2v}	91.610	6.1	

[a] Conformation: **af**: *anti*-folded; **sf**: *syn*-folded; **t**: twisted; **f**: folded; **p**: planar. [b] In kcal mol^{-1}. [c] The PM3 heat of formation of ethene: 16.630 kcal mol^{-1}.

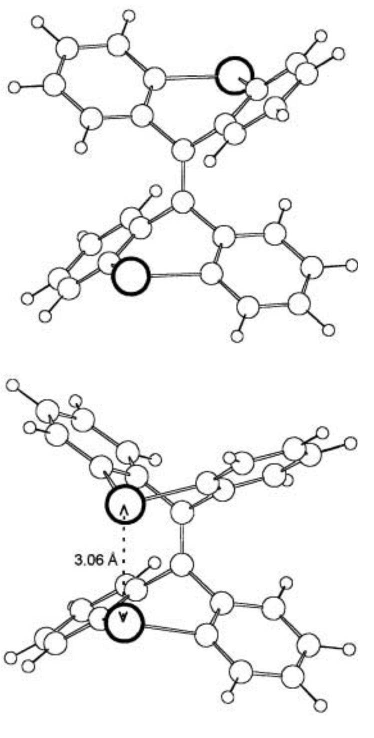


Fig. 6 *anti*-Folded **8** and *syn*-folded **8** obtained by PM3 calculations.

parameters of the calculated conformations of **7** and **8** are given in Table 1. In **sf-8** the calculated C–Te bonds are elongated (2.142 Å), folding and pyramidalization angles are high (59.6 and 12.2°, respectively). There is no indication of overcrowding in the fjord regions ($C_1 \cdots C_{1'}$ 3.43 Å). The special stability of **sf-8** may be attributed to the short intramolecular Te···Te distance, 3.06 Å. This short distance could be compared with the Te–Te bond length of 2.71 Å in Ph–Te–Te–Ph[57] and the Te···Te van der Waals contact distance of 4.16 Å.[44] It may be indicative of an attractive interaction between the two tellurium atoms. A Te–Te bond order of 0.08 was indicated by the population analysis. By contrast, in **sf-7**, the calculated intramolecular Se···Se distance is 4.85 Å, far longer than the Se···Se van der Waals contact distance of 3.80 Å[44] (bond order 0.000). The fjord regions of **sf-7** are overcrowded ($C_{1'} \cdots H_{1'}$ 2.57 and $H_1 \cdots H_{1'}$ 1.78 Å). The PM3 calculations indicate the presence of an overcrowding effect due to the short $Se_{10} \cdots C_9$ and $Te_{10} \cdots C_9$ contact distances in **af-7**, **sf-7**, **af-8**, and **sf-8**. In spite of the special stability of **sf-8** predicted by PM3, the present experimental study indicates that **af-8** was the only bistricyclic ene product in the synthesis of **8** (*vide supra*). This "inconsistency" may be due to kinetically controlled reactions which favor **af-8** over **sf-8** and/or to limitations of the PM3 method. An attempted thermal *anti*⟶*syn* isomerization of **af-8** in boiling tetralin (under argon) was unsuccessful.

In conclusion, the syntheses and conformations of the selenium- and tellurium-bridged overcrowded homomerous bistricyclic enes **7** and **8** open up the possibility of entering the series of selenium- and tellurium-bridged *heteromerous* bistricyclic enes, including the Se/Te blended **1** (X = Se, Y = Te). It remains to be seen whether the PM3 predicted special stability of the *syn*-folded conformation of **8** can be extended and verified by high level *ab initio* calculations and by experiment.

Experimental

Melting points are uncorrected. All NMR spectra were recorded with a Bruker DRX 400 spectrometer: ^{1}H at 400.1 MHz using $CDCl_3$ as solvent and as internal standard ($\delta(CHCl_3)$ 7.26); ^{13}C at 100.6 MHz using $CDCl_3$ as solvent and as internal standard ($\delta(CDCl_3)$ 77.01); ^{77}Se at 76.3 MHz using $CDCl_3$ as a solvent and 9*H*-selenoxanthen-9-one (**11**) as external standard, δ 334.7 (relative to Me_2Se in $CDCl_3$);[58] ^{125}Te at 126.2 MHz using $CDCl_3$ as solvent and 9*H*-telluroxanthen-9-one (**12**) as external standard, δ 473.6.[58] UV-Vis spectra were measured using a UVIKON 860 spectrometer, IR spectra with a Perkin- Elmer System 2000 FT-IR spectrometer.

Elemental microanalyses were determined by Chemisar Laboratories Inc., N. Guelph, Ontario, Canada. Single crystals of compounds **7**–**9** were obtained by slow sublimation in a high vacuum sealed tube at 240–250 °C in a Büchi GKR 50 oven; those of **20** were obtained in a similar manner at 90 °C.

X-Ray crystallographic analysis

The crystal data of compounds **7**–**9** and **20** are given in Table 6. The lattice parameters were obtained by a least-squares fit of 24 centered reflections. Intensity data were collected using the ω–2θ technique (at rt). The intensities of three standard reflections were monitored during data collection, and no decay was observed. Intensities were corrected for Lorentz-polarization effects. The positions of all non-hydrogen atoms were obtained using the results of the SHELXS 86 direct method analysis.[59] After several cycles of refinements the positions of the hydrogen atoms were either found, for **9** or calculated for **7**, **8**, and **20**, and added to the refinement process. All non-hydrogen atoms were refined anisotropically, while the positions of hydrogen atoms were either kept fixed, using a riding model for compounds **7**, **8**, and **20** or refined isotropically for **9**. The refinement proceeded to convergence by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma_F^{-2}$.

CCDC reference number 188/221.

See http://www.rsc.org/suppdata/p2/a9/a908715j/ for crystallographic files in .cif format.

Table 6 Crystallographic data of compounds **7**, **8**, **9** and **20** determined at rt

	7	8	9	20
Asymmetric unit	$C_{26}H_{16}Se_2$ (486.33)	2 × 1/2 $C_{26}H_{16}Te_2$ (583.61)	1/2 $C_{26}H_{18}Se_2$ (244.17)	1/2 $C_{14}H_{10}Se$ (122.59)
Space group	$Pca2_1$	$P\bar{1}$	$P2_1/c$	$Cmc2_1$
Crystal system	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
a/Å	18.215(3)	8.967(1)	8.767(5)	11.535(5)
b/Å	5.947(1)	15.968(3)	6.241(3)	14.111(4)
c/Å	18.071(3)	7.526(1)	18.042(8)	6.929(1)
α/°		97.20(1)		
β/°		102.59(1)	95.71(4)	90.0
γ/°		84.91(1)		
V/Å^3	1957.5(7)	1041.3(5)	982.3(8)	1127.9(4)
Z	4	2	4	8
$\rho_{calc.}$/g cm^{-3}	1.65	1.86	1.65	1.52
$\mu(K_\alpha)$/cm^{-1}	37.46	28.16	48.73	41.69
λ/Å	0.71069	0.71069	1.54178	1.54178
$2\theta_{max}$/°	55	50	140	140
No. unique reflections	2624	3660	2055	732
No. reflections with $I > 3\sigma_I$	1885	3050	1614	590
R	0.035	0.031	0.051	0.045
R_w	0.043	0.051	0.074	0.054

Preparations

9*H*-Selenoxanthen-9-one (11).[18] ^{1}H NMR (CDCl$_3$): δ 7.467 (td, ^3J = 8.0, 7.0, ^4J = 1.4, 2H, H_2, H_7), 7.536 (td, ^3J = 7.9, 7.1, ^4J = 1.7, 2H, H_3, H_6), 7.634 (ddd, ^3J = 7.9, ^4J = 1.4, ^5J = 0.5, 2H, H_4, H_5), 8.648 (ddd, ^3J = 8.0, ^4J = 1.7, ^5J = 0.5 Hz, 2H, H_1, H_8). ^{13}C NMR (CDCl$_3$): δ 126.77 (C_2, C_7), 128.28 (C_4, C_5), 130.95 (C_{8a}, C_{9a}), 131.39 (C_1, C_8), 132.16 (C_3, C_6), 135.05 (C_{4a}, C_{10a}), 182.01 (C_9), (*cf.* lit.[58]). ^{77}Se NMR (CDCl$_3$): δ 334.7.[58] Mp 192–194 °C (lit. 192,[18] 189.5–190.5,[19] 182–185 °C[60]).

9*H*-Telluroxanthen-9-one (12).[21] ^{1}H NMR (CDCl$_3$): δ 7.419 (m, 4H, H_2, H_7, H_3, H_6), 7.720 (m, 2H, H_4, H_5), 8.639 (m, 2H, H_1, H_8). ^{13}C NMR (CDCl$_3$): δ 119.96 (C_{4a}, C_{10a}), 127.70 (C_3, C_6,), 131.87 (C_2, C_7), 132.97 (C_1, C_8), 133.78 (C_4, C_5), 134.54 (C_{8a}, C_{9a}), 186.46 (C_9), (*cf.* lit.[58]). ^{125}Te NMR (CDCl$_3$): δ 473.4[58] (lit.[53,61] 468). Mp 116 °C (lit. 115,[21] 116 °C[62]).

9*H*-Selenoxanthene-9-thione (13). To a stirred solution of ketone **11** (0.150 g, 5.790 mmol) in anhydrous benzene (50 mL) protected by a CaCl$_2$ tube, Lawesson's reagent (1.170 g, 2.850 mmol) was added and the reaction mixture was refluxed for 9 h. The solution changed from yellow to dark green. After cooling to rt, silica gel (5 g) was added and the solvent evaporated under reduced pressure. Column chromatography of the crude product was performed on dry silica gel using the eluent petrol ether (60–80 °C)–Et$_2$O (98 : 2). The color of compound **13** on the column was brown; it was eluted first as a green solution. After evaporating the solvent black shining crystals were obtained (1.456 g, 91% yield); mp 126–128 °C. ^{1}H NMR (CDCl$_3$): δ 7.381 (td, ^3J = 8.3, 7.0, ^4J = 1.4, 2H, H_2, H_7), 7.496 (td, ^3J = 7.9, 7.0, ^4J = 1.5, 2H, H_3, H_6), 7.625 (ddd, ^3J = 7.9, ^4J = 1.4, ^5J = 0.5, 2H, H_4, H_5), 8.800 (ddd, ^3J = 8.3, ^4J = 1.5, ^5J = 0.5 Hz, 2H, H_1, H_8). ^{13}C NMR (CDCl$_3$): δ 127.07 (C–H), 127.81 (C–H), 129.66 (C), 131.18 (C–H), 133.53 (C–H), 140.40 (C), 218.10 (C=S). ^{77}Se NMR (CDCl$_3$): δ 363.1. UV-Vis (cyclohexane): $c = 3.63 \times 10^{-3}$ M, λ_{max}/nm (ε/M^{-1} cm^{-1}): 625 (110); $c = 3.63 \times 10^{-5}$ M λ_{max} (ε): 461 (9180), 311(9818), 307 (9482).

9*H*-Selenoxanthen-9-one hydrazone (16). To a stirred solution of thione **13** (0.400 g, 1.450 mmol) in benzene (20 mL) and ethanol (40 mL), hydrazine hydrate (0.1 mL) was added. The green solution changed within minutes to light yellow. The reaction mixture was refluxed for 1.5–2 h. The solvent was evaporated under reduced pressure, and the crude product treated several times with ethanol and the solvent evaporated. A colorless powder of compound **16** was obtained (0.384 g, 97% yield), mp 102–104 °C. ^{1}H NMR (CDCl$_3$): δ 5.850 (bs, 2H, NH$_2$), 7.212–7.381 (m, 4H), 7.489 (d, 1H), 7.691 (d, 1H), 7.758 (d, 1H), 7.952 (d, 1H). ^{13}C NMR (CDCl$_3$): δ 126.23 (C–H), 127.10 (C–H), 127.26 (C–H), 127.75 (C–H), 127.98 (C–H), 128.20 (C), 128.38 (C–H), 128.79 (C), 128.86 (C–H), 130.70 (C–H), 132.35 (C), 136.87 (C), 144.06 (C). ^{77}Se NMR (CDCl$_3$): δ 352.9.

9-Diazo-9*H*-selenoxanthene (14). (a) Dried hydrazone **16** (0.130 g, 0.476 mmol), mercuric oxide (0.534 g, 2.46 mmol) and anhydrous sodium sulfate (0.129 g, 0.57 mmol) were ground together for a few minutes then transferred to a dry flask equipped with a magnetic stirrer protected by a CaCl$_2$ tube and containing dry Et$_2$O (30 mL). After 1 h, a freshly prepared, concentrated solution of KOH in ethanol was added (0.3 mL). The solution changed gradually from yellow to purple. The reaction was stirred at rt for 48 h, its progress being monitored by TLC on silica gel (petrol ether–Et$_2$O 8 : 2, R_f = 0.74). The solution was filtered and the residue washed with Et$_2$O. The combined organic fractions were evaporated under reduced pressure, to give compound **14** as green crystals 0.077 g, yield 59%; mp 90–92 °C.

(b) A stirred solution of hydrazone **16** (0.150 g, 0.549 mmol) in anhydrous Et$_2$O (30 mL) protected by a CaCl$_2$ tube was cooled to −10 °C, whereupon MgSO$_4$ (0.300 g), Ag$_2$O (0.190 g, 0.823 mmol) and a saturated solution of KOH in methanol (1 mL) were added. The reaction mixture was stirred for 30 min at *ca.* 0 °C and then raised to rt and stirred for 2 h. It changed gradually from yellow to purple. The reaction was monitored with TLC. Work-up as in procedure (a) gave green crystals of compound **14** (0.125 g), yield 84%; mp 90–92 °C. ^{1}H NMR (CDCl$_3$): δ 6.870 (ddd, ^3J = 7.9, ^4J = 1.3, ^5J = 0.4, 2H), 6.994 (td, ^3J = 7.7, 7.4, ^4J = 1.4 Hz, 2H), 7.161–7.227 (m, 4H). ^{13}C NMR (CDCl$_3$): δ 122.02 (C–H), 124.76 (C), 125.25 (C), 125.94 (C–H), 127.37 (C–H), 128.46 (C–H). ^{77}Se NMR (CDCl$_3$): δ 318.6. IR, KBr: $\tilde{\nu}_{max}$/cm^{-1} 2036.

Dispiro[selenoxanthene-9,2′-thiirane-3′,9″-selenoxanthene] (15). To a stirred solution of diazo derivative **14** (0.101 g, 0.372 mmol) in anhydrous benzene (20 mL) and protected by a CaCl$_2$ tube, thione **13** (0.070 g, 0.254 mmol) was added. Evolution of N$_2$ was observed and the dark color slowly disappeared, while the reaction mixture was refluxed for 2 h. The termination of the reaction was judged by NMR. The solution was evaporated under reduced pressure. The crude product was triturated with boiling ethanol. The precipitate was filtered off using a sintered glass frit to give 0.080 g of compound **15** as a light yellow powder, in 61% yield; mp 220–222 °C (decomp). ^{1}H NMR (CDCl$_3$): δ 6.912 (td, ^3J = 7.4, ^4J = 1.5, 2H), 6.976 (td, ^3J = 7.4, ^4J = 1.5, 2H), 7.259 (ddd, ^3J = 7.5, ^4J = 1.5, ^5J = 0.3, 2H), 7.735 (ddd, ^3J = 7.9, ^4J = 1.5, ^5J = 0.4 Hz, 2H). ^{13}C NMR (CDCl$_3$):

δ 69.90 (C–S), 125.56 (C–H), 126.81 (C–H), 128.37 (C–H), 131.80 (C–H), 132.22 (C), 132.51 (C). ^{77}Se NMR ($CDCl_3$): δ 364.6.

9,9′-Bi(9*H*-selenoxanthen-9-ylidene) (7). (a) To a stirred solution of thiirane **15** (0.070 g, 0.135 mmol) in anhydrous benzene (20 mL), protected by a $CaCl_2$ tube, PPh_3 (0.038 g, 0.148 mmol) was added. After refluxing for 30 h, the mixture was cooled to rt, and the solvent removed under reduced pressure. Trituration of the crude product in boiling ethanol gave a precipitate which was filtered off using a sintered glass frit. Thus, compound **7** was obtained as a colorless powder (0.044 g), yield 67%; mp 338–340 °C.

(b) To freshly distilled toluene (100 mL), copper powder (1.00 g) was added, and the toluene (20 mL) was distilled off. Thione **13** (0.400 g, 1.454 mmol) was added to the reaction flask (protected by a $CaCl_2$ tube) and the reaction stirred and refluxed with stirring for 3 h under an argon atmosphere. The black reaction mixture was filtered off while hot, giving a red solution. The solvent was removed *in vacuo* to give crude compound **7** as a pink powder (0.321 g) yield 89%. Repeated recrystallizations from toluene gave colorless crystals of **7**, suitable for analysis; mp 338–340 °C. ^{1}H NMR ($CDCl_3$): δ 6.787 (ddd, $^3J = 7.7$, $^4J = 1.3$, 4H, H_1, H_8, $H_{1'}$, $H_{8'}$), 6.904 (td, $^3J = 7.7$, 7.5, $^4J = 1.4$, 4H, H_2, H_7, $H_{2'}$, $H_{7'}$), 7.072 (td, $^3J = 7.7$, 7.5, $^4J = 1.4$, 4H, H_3, H_6, $H_{3'}$, $H_{6'}$), 7.656 (ddd, $^3J = 7.7$, $^4J = 1.0$ Hz, 4H, H_4, H_5, $H_{4'}$, $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ 126.18 (C_2, C_7, $C_{2'}$, $C_{7'}$), 126.68 (C_3, C_6, $C_{3'}$, $C_{6'}$), 129.47 (C_4, C_5, $C_{4'}$, $C_{5'}$), 130.47 (C_1, C_8, $C_{1'}$, $C_{8'}$), 132.42 (C_{4a}, C_{10a}, $C_{4a'}$, $C_{10a'}$), 137.44 (C_{8a}, C_{9a}, $C_{8a'}$, $C_{9a'}$, C_9, $C_{9'}$). ^{77}Se NMR ($CDCl_3$): δ 366.3. UV-Vis (cyclohexane): $c = 2.47 \times 10^{-4}$ M, λ_{max}/nm (ε/M^{-1} cm^{-1}): 340 (7936). Calc. for $C_{26}H_{16}Se_2$: C, 64.21; H, 3.31; Se, 32.47. Found: C, 64.52; H, 3.23; Se, 32.70%. MS: *m*/*z* (%, molecular ion) 491.95839 (2, $^{12}C_{26}H_{16}{}^{82}Se_2$, and/or $^{12}C_{25}{}^{13}CH_{15}{}^{82}Se_2$), 490.96365 (8, $^{12}C_{25}{}^{13}CH_{16}{}^{80}Se^{82}Se$), 489.95997 (34, $^{12}C_{26}H_{16}{}^{80}Se^{82}Se$, and/or $^{12}C_{25}{}^{13}CH_{15}{}^{80}Se^{82}Se$), 488.96288 (22, $^{12}C_{25}{}^{13}CH_{16}{}^{80}Se_2$, and/or $^{12}C_{25}{}^{13}CH_{16}{}^{78}Se^{82}Se$), 487.95974 (100, $^{12}C_{26}H_{16}{}^{80}Se_2$, and/or $^{12}C_{25}{}^{13}CH_{15}{}^{80}Se_2$, and/or $^{12}C_{26}H_{16}{}^{78}Se^{82}Se$, and/or $^{12}C_{25}{}^{13}CH_{15}{}^{78}Se^{82}Se$), 485.96143 (97, $^{12}C_{26}H_{16}{}^{78}Se^{80}Se$, and/or $^{12}C_{25}{}^{13}CH_{15}{}^{78}Se^{80}Se$), 484.96486 (42, $^{12}C_{25}{}^{13}CH_{16}{}^{78}Se_2$), 483.96233 (56%, $^{12}C_{26}H_{16}{}^{78}Se_2$).

9*H*-Telluroxanthene-9-thione (17). Thione **17** was obtained analogously to thione **13** with some modifications. Ketone **12** (0.307 g, 1.00 mmol) and Lawesson's reagent (0.202 g, 0.500 mmol) in dried benzene (35 mL) were refluxed for 10 h. The chromatographic purification of **17** should be carried out very quickly, using a nitrogen pressure on the column, and a quick evaporation of solvents from the desired green fractions. Crude **17** dissolved in benzene was introduced on top of the chromatography column. The fraction on the column containing **17** was purple–red. After evaporation a red–purple film was obtained. It was not possible to store the thione for a long period; it must be used immediately upon removal of the solvent. ^{1}H NMR ($CDCl_3$): δ 7.320 (m, 4H, H_2, H_7, H_3, H_6), 7.660 (ddd, 2H, H_4, H_5), 8.420 (ddd, 2H, H_1, H_8). ^{13}C NMR ($CDCl_3$): δ 113.69 (C), 127.73 (C–H), 130.59 (C–H), 132.78 (C–H), 133.16 (C–H), 146.53 (C), 230.48 (C=S). ^{125}Te NMR ($CDCl_3$): δ 529.9.

9,9′-Bi(9*H*-telluroxanthen-9-ylidene) (8). Freshly distilled toluene (40 mL) was partially distilled on copper powder (1.00 g), and the mixture treated with a solution of thione **17** in toluene [freshly prepared from ketone **12** (0.200 g, 0.649 mmol), Lawesson's reagent (0.134 g, 0.330 mmol), in dried benzene (30 mL)]. The reaction was refluxed under an argon atmosphere for 12 h, its progress being monitored by NMR. The dark mixture was filtered while hot and the filtrate evaporated under reduced pressure. The resulting red residue was triturated in hot ethanol, and filtered off. A red powder was obtained, 0.077 g, 40% yield (based on the ketone **12**); mp 355–357 °C. A sample for analysis was purified by column chromatography on dry silica gel using petrol ether–Et_2O (98 : 2) as eluent. ^{1}H NMR ($CDCl_3$): δ 6.796 (ddd, $^3J = 7.7$, $^4J = 1.5$, $^5J = 0.5$, 4H, H_1, H_8, $H_{1'}$, $H_{8'}$), 6.879 (td, $^3J = 7.7$, 7.3, $^4J = 1.3$, 4H, H_2, H_7, $H_{2'}$, $H_{7'}$), 6.963 (td, $^3J = 7.3$, $^4J = 1.5$, 4H, H_3, H_6, $H_{3'}$, $H_{6'}$), 7.801 (ddd, $^3J = 7.5$, $^4J = 1.3$, $^5J = 0.5$ Hz, 4H, H_4, H_5, $H_{4'}$, $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ 118.01 (C_{4a}, C_{10a}, $C_{4a'}$, $C_{10a'}$), 126.57 (C_3, C_6, $C_{3'}$, $C_{6'}$), 127.02 (C_2, C_7, $C_{2'}$, $C_{7'}$), 130.67 (C_1, C_8, $C_{1'}$, $C_{8'}$), 134.98 (C_4, C_5, $C_{4'}$, $C_{5'}$), 141.27 (C_{8a}, C_{9a}, $C_{8a'}$, $C_{9a'}$), 143.69 (C_9, $C_{9'}$). ^{125}Te NMR ($CDCl_3$): δ 547.1. UV (cyclohexane): $c = 6.6 \times 10^{-3}$ M, λ_{max}/nm (ε/M^{-1} cm^{-1}): 342 (9755.3), shoulder 412 (539). Calc. for $C_{26}H_{16}Te_2$: C, 53.51; H, 2.76; Te, 43.72. Found: C, 53.71; H, 2.90; Te, 43.29%. MS: *m*/*z* (%, molecular ion) 587.93164 (14, $^{12}C_{26}H_{16}{}^{130}Te_2$ and/or $^{12}C_{25}{}^{13}CH_{15}{}^{130}Te_2$), 586.93625 (7, $^{12}C_{25}{}^{13}CH_{15}{}^{128}Te^{130}Te$ and/or $^{12}C_{26}H_{15}{}^{130}Te_2$), 585.93502 (25, $^{12}C_{26}H_{16}{}^{128}Te^{130}Te$), 584.93645 (7, $^{12}C_{25}{}^{13}CH_{16}{}^{126}Te^{130}Te$ and/or $^{12}C_{25}{}^{13}CH_{16}{}^{128}Te_2$ and/or $^{12}C_{26}H_{15}{}^{128}Te^{130}Te$), 583.93740 (26, $^{12}C_{26}H_{16}{}^{128}Te_2$, and/or $^{12}C_{26}H_{16}{}^{126}Te^{130}Te$), 582.94047 (10, $^{12}C_{25}{}^{13}CH_{16}{}^{126}Te^{128}Te$ and/or $^{12}C_{26}H_{16}{}^{125}Te^{130}Te$), 581.77021 (22, $^{12}C_{26}H_{16}{}^{126}Te^{128}Te$), 580.05842 (13, $^{12}C_{26}H_{16}{}^{126}Te_2$).

Reductive coupling of compound 11 in $TiCl_4$/Zn/pyridine–THF. The reaction was carried out under an argon atmosphere in a 100 mL three necked round flask equipped with a reflux condenser protected from moisture, septum, and magnetic stirrer. Freshly distilled dry THF (distilled over sodium diphenylketyl, 10 mL) was added to the flask and cooled to −15 to −18 °C. After 5–10 min, a dropwise slow injection of $TiCl_4$ (0.25 mL, 2.25 mmol) using a plastic syringe with stirring gave a yellow complex, which was treated after 20 min with Zn dust (0.252 g, 3.86 mmol). The temperature was gradually raised to room temperature, and kept for 45 min. The mixture was refluxed for 3.5 h, giving a gray suspension. The mixture was cooled to 0 °C, pyridine (0.15 mL) added, followed by a dropwise addition over 20 min of a solution of compound **11** (0.393 g, 1.52 mmol) in dry THF (10 mL) with a plastic syringe. The resulting mixture was refluxed for 9 h. After cooling to rt, water (20 mL) with several drops of HCl and CH_2Cl_2 (30 mL) were added and stirred for 0.5 h. The mixture was transferred to a dropping funnel, the organic layer separated, and the aqueous layer extracted with CH_2Cl_2. The organic layers were dried ($MgSO_4$) and the solvent was removed *in vacuo*. The crude products were dissolved again in CH_2Cl_2, silica gel added, the solvent evaporated and the powder chromatographed on a silica gel column using a petrol ether–CH_2Cl_2 gradient (2 to 20%, CH_2Cl_2). The following compounds were isolated.

9*H*-Selenoxanthene (**19**). 0.012 g, mp 144 °C (lit.[32,63] 145 °C). ^{1}H NMR ($CDCl_3$): δ 3.844 (s, $H_{9\alpha}$, $H_{9\beta,}$ 2H), 7.154 (td, $^3J = 7.4$, $^4J = 1.4$, 2H), 7.234 (td, $^3J = 7.3$, $^4J = 1.1$, 2H), 7.366 (ddd, $^3J = 7.3$, 2H), 7.592 (ddd, $^3J = 7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 42.93 (C_9), 126.59 (C–H), 127.02 (C–H), 128.26 (C–H), 129.44 (C–H), 131.32 (C), 137.63 (C). ^{77}Se NMR ($CDCl_3$): δ 353.2.

Compound **9**. 0.059 g, yield 15%; mp 338–340 °C (lit.[32] >300 °C). ^{1}H NMR ($CDCl_3$): δ 4.828 (s, H_9, $H_{9'}$, 2H), 6.455 (ddd, $^3J = 7.6$, 4H, H_1, H_8, $H_{1'}$, $H_{8'}$), 6.804 (td, $^3J = 7.5$, 4H, H_2, H_7, $H_{2'}$, $H_{7'}$), 7.034 (ddd, $^3J = 7.7$, 4H, H_3, H_6, $H_{3'}$, $H_{6'}$), 7.537 (ddd, $^3J = 7.7$ Hz, 4H, H_4, H_5, $H_{4'}$, $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ 49.86 (C_9 C_9), 126.04 (C_2, C_7, $C_{2'}$, $C_{7'}$), 126.52 (C_3, C_6, $C_{3'}$, $C_{6'}$), 128.91 (C_4, C_5, $C_{4'}$, $C_{5'}$), 129.11 (C_{4a}, C_{10a}, $C_{4a'}$, $C_{10a'}$), 130.77 (C_1, C_8, $C_{1'}$, $C_{8'}$), 137.12 (C_{8a}, C_{9a}, $C_{8a'}$, $C_{9a'}$). ^{77}Se NMR ($CDCl_3$): δ 326.0.

Ketone **11**. 0.1023 g. The ^{1}H, ^{13}C, ^{77}Se NMR spectra were identical to those of an authentic sample, mp 192 °C.

An additional crop of compound **9** (0.052 g) was obtained by further extraction of the aqueous layer with CH_2Cl_2. The total yield was 30% (0.111 g).

Reductive coupling of compound 12 in $TiCl_4$/Zn/pyridine–THF. The reaction was carried out analogously to the reductive coupling of compound **11** starting with **12** (0.500 g, 1.62 mmol), $TiCl_4$ (0.26 mL, 2.43 mmol), Zn dust (0.27 g, 4.11 mmol), pyridine (0.20 mL). Trituration of the crude material in hot ethanol gave **10**, 0.195 g yield 41%, mp 262 °C from CH_2Cl_2 (lit.[34] >300 °C). Evaporation of the solvent of the filtrate gave the starting ketone **12** (0.322 g), mp 115 °C. Compound **10**: ^{1}H NMR ($CDCl_3$): δ 5.275 (s, 2H, H_9, $H_{9'}$), 6.590 (ddd, $^{3}J = 7.6$, $^{4}J = 1.4$, 4H, H_1, H_8, $H_{1'}$, $H_{8'}$), 6.777 (td, $^{3}J = 7.6$, $^{4}J = 1.3$, 4H, H_2, H_7, $H_{2'}$, $H_{7'}$), 6.926 (td, $^{3}J = 7.4$, $^{4}J = 1.5$, 4H, H_3, H_6, $H_{3'}$, $H_{6'}$), 7.655 (ddd, $^{3}J = 7.5$, $^{4}J = 1.2$ Hz, 4H, H_4, H_5, $H_{4'}$, $H_{5'}$). ^{13}C NMR ($CDCl_3$): δ 52.25 (C_9, $C_{9'}$), 114.29 (C_{4a}, C_{10a}, $C_{4a'}$, $C_{10a'}$), 126.59 (C_2, C_7, $C_{2'}$, $C_{7'}$), 126.78 (C_3, C_6, $C_{3'}$, $C_{6'}$), 131.49 (C_1, C_8, $C_{1'}$, $C_{8'}$), 134.88 (C_4, C_5, $C_{4'}$, $C_{5'}$), 139.85 (C_{8a}, C_{9a}, $C_{8a'}$, $C_{9a'}$). ^{125}Te NMR ($CDCl_3$): δ 481.0.

Ketone **12**: the ^{1}H, ^{13}C, ^{125}Te NMR spectra were identical to those of an authentic sample.

9-Methylene-9*H*-selenoxanthene (20). The reaction was carried out in a 250 mL three-necked round-bottomed flask equipped with a reflux condenser (protected from moisture), a magnetic stirrer and a septum. 9*H*-Selenoxanthen-9-one (**11**) (0.500 g, 1.93 mmol) and dry benzene (60 mL) were added to the flask. The solution was heated to 80°C and treated by dropwise injection of a solution of MeMgI in anhydrous Et_2O (30 mL, 20 mmol). The reaction mixture was refluxed with stirring for 24 h. The reddish reaction mixture was decomposed with an aqueous solution of NH_4Cl. The organic layer was separated and the aqueous layers were extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and the solvents removed *in vacuo*. The resulting yellow oil (0.581 g) was chromatographed on a dry silica gel column, using petrol ether–Et_2O (96:4) as eluent. The first fraction contained the desired product **20** (0.276 g). It was obtained as colorless needles, mp 72–75 °C, yield 55%. ^{1}H NMR ($CDCl_3$): δ 5.549 (s, CH_2, 2H), 7.220 (dt, $^{3}J = 7.5$, $^{4}J = 1.6$, 2H, H_3, H_6), 7.285 (dt, $^{3}J = 7.6, 7.2$, $^{4}J = 1.4$ Hz, 2H, H_2, H_7), 7.506 (ddd, $^{3}J = 7.6$, $^{4}J = 1.5$, $^{5}J = 0.5$, 2H, H_4, H_5), 7.595 (ddd, $^{3}J = 7.7$, $^{4}J = 1.6$, $^{5}J = 0.5$ Hz, 2H, H_1, H_8). ^{13}C NMR ($CDCl_3$): δ 116.23 (CH_2), 126.94 (C_1, C_8), 127.19 (C_2, C_7), 127.67 (C_3, C_6), 128.19 (C_{4a}, C_{10a}), 128.37 (C_4, C_5), 137.02 (C_{8a}, C_{9a}), 146.03 (C_9). ^{77}Se NMR ($CDCl_3$): δ 336.1.

9-Methylene-9*H*-telluroxanthene (21). The reaction was carried out analogously to the preparation of compound **20**, starting with **12** (0.300 g, 0.974 mmol), MeMgI (1.1 mmol), Et_2O (35 mL) and benzene (75 mL). The reaction period was 15 h. Column chromatography of the crude product (0.268 g) gave **21** (first fraction, 0.060 g) as a yellow oil. The yield was 20%. ^{1}H NMR ($CDCl_3$): δ 5.481 (s, CH_2, 2H), 7.152 (dt, $^{3}J = 7.5$, $^{4}J = 1.5$ Hz, 2H, H_3, H_6), 7.283 (dt, $^{3}J = 7.5$, $^{4}J = 1.3$, 2H, H_2, H_7), 7.550 (ddd, $^{3}J = 7.7$, $^{4}J = 1.4$, 2H, H_1, H_8), 7.679 (ddd, $^{3}J = 7.6$, $^{4}J = 1.3$ Hz, 2H, H_4, H_5). ^{13}C NMR ($CDCl_3$): δ 113.56 (C_{4a}, C_{10a}), 118.31 (CH_2), 127.66 (C_3, C_6), 127.76 (C_1, C_8), 127.98 (C_2, C_7), 134.12 (C_4, C_5), 141.65 (C_{8a}, C_{9a}), 152.03 (C_9). ^{125}Te NMR ($CDCl_3$): δ 514.6.

Acknowledgements

We deeply thank Professor V. I. Minkin and Professor I. D. Sadekov (Rostov University, Rostov-on-Don, Russia) for valuable discussions.

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Paper a908715j