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Substituted 2,4,4,6-tetraphenyl-4*H*-selenopyrans: preparation, photocolouration and 4*H*-selenopyran ring geometry; an X-ray and DFT calculation study †

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1,5-Diaryl-3,3-diphenylpentane-1,5-diones **3a**–**d** react with Al_2Se_3–HCl–AcOH reagent to give the 2,6-diaryl-4,4-diphenyl-4*H*-selenopyrans **4a**–**d** in satisfactory yields while the same procedure starting from 1,5-diketone **5** affords small amounts of spiroheterocycle **6**. 2,4,4,6-Tetraphenyl-4*H*-selenopyran **4a** can be brominated or nitrated at positions 3 and 5 to give substituted derivatives **7**–**9**. Dibromo derivatives **4c** and **7** were converted with copper(I) cyanide to dicyano derivatives **4e** and **10**,**11**, respectively. Similarly to 4*H*-pyrans **1** and 4*H*-thiopyrans **2**, the 1-selena analogues **4a**–**d** and **8** exhibit solid state photocolouration which was investigated in terms of dispersive first-order reaction kinetics. The influence of selenium heteroatom on the geometry of the heterocyclic ring of molecules **4a**,**c** and **6** is discussed on the basis of X-ray structure determinations, quantum DFT and semiempirical PM3 calculations.

Introduction

The application of photochromism in data storage technologies[1] has considerably enhanced the importance of this phenomenon. Increasingly, research activity has been focused on the development of new compounds with photochromic properties.[1a] Therefore we have investigated the possible consequences connected with the introduction of selenium into favourable 4*H*-pyranoid photosensitive systems. So far, the number of compounds in this category which show photochromic reactivity in the crystalline phase is still quite restricted[2,3] due to the loss of reactivity in rigid crystalline lattices.

2,4,4,6-Tetraaryl-4*H*-(hetero)pyrans like **1** and **2** represent an interesting group of substances exhibiting solid state photocolouration when illuminated with UV light or sunlight.[4–6] An exhaustive number of both experimental[4,5] and/or theoretical[6] reports has led to the postulation of photolysis and photocolouration mechanisms. In particular quantum chemical calculations have specified hypervalent photoisomers as possible compounds responsible for the photocolouration processes.[6] This area of such nonclassical bonding configurations coincides with various important current topics.[7] Therefore it should be pointed out that although the optical behaviour of structures like **1** appear to be conserved either if the sulfur,[4,6a] oxygen[4a,5a–c,6b] or nitrogen heteroatoms[5,6c] are present, nothing is known about other possible heteroatom effects. Little is known[8,9] about the reactivity and properties of the analogous substituted 2,4,4,6-tetraaryl-4*H*-selenopyrans **4**. In fact, only the parent 2,4,4,6-tetraphenyl-4*H*-selenopyran **4a** has been prepared by the reaction of 2,4,6-triphenylselenopyrylium salt with phenylmagnesium bromide and its reaction with bromine has been attempted.[9a] In comparison to photochemical transformations of other 2,4,4,6-tetraphenyl-4*H*-(hetero)pyran systems[4–6] we have recently found that photolysis of 2,4,4,6-tetraphenyl-*4H*-selenopyran proceeds in quite a different manner.[10] In addition, photochemical changes of related π-selenide systems have received very little attention.[11] In this paper the preparation and photocolouration in the crystalline state of a series of substituted 2,4,4,6-tetraphenyl-4*H*-selenopyrans are presented.

Results and discussion

Preparation of 4*H*-selenopyrans 4a–d and 6

2,4,6-Trisubstituted 4*H*-selenopyrans have generally been prepared[8,9b] by the introduction of the gaseous H_2Se–HCl mixture into AcOH solutions of the corresponding pentane-1,5-diones. This procedure applied to 1,3,3,5-tetraphenylpentane-1,5-dione **3a** yielded 77% of the expected 4*H*-selenopyran **4a** (Experimental section, method A). To avoid the external generation of H_2Se a novel approach was developed based on *in situ* reaction of Al_2Se_3 with HCl–AcOH. In this way 4*H*-selenopyrans **4a**–**d** and **6** were prepared from appropriate 1,5-diones **3a**–**d** and **5**, respectively (Scheme 1). We have observed that the ability of the 1,5-diones **3a**–**d**, **5** to undergo heterocyclisation strongly depends on the substitution pattern. For instance, the cyclisation **3d** ⟶ **4d** (Ar = 4-Bu^{t}C$_6$H$_5$) was completed in 2.25 h, the transformation **3b** ⟶ **4b** (Ar = 4-FC$_6$H$_4$) needed more than

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† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C, MS, X-ray and DFT data. See http://www.rsc.org/suppdata/p2/b2/b204976g/

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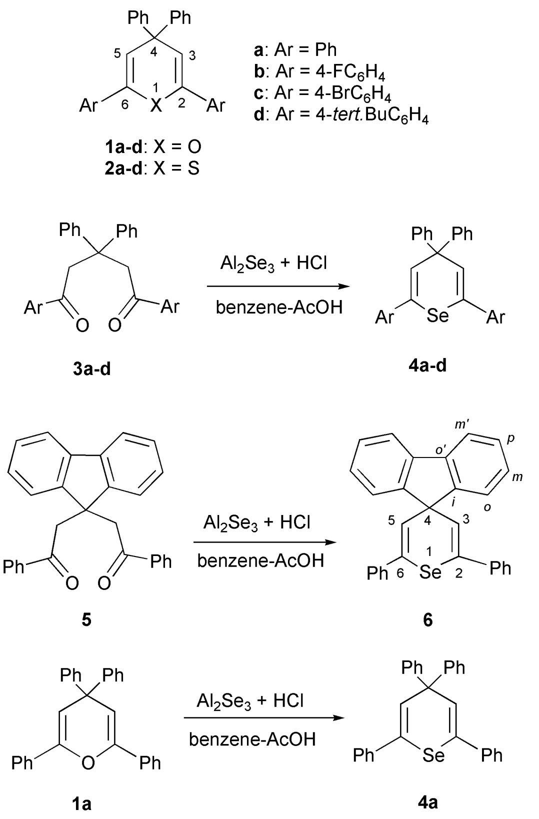
Table 1 Preparation of 4*H*-selenopyrans **4a**–**d** and **6**

4*H*-Selenopyran	Reaction time/h	Preparative yield (%)
4a	6	72
4b	8.25	65
4c	6	45[a]
4d	2.25	57
6	54	6[b]

[a] Accompanied with 20% of 4*H*-pyran **4c**. [b] Resulting mixture after work up contained 80% of starting diketone **5** and 14% of **1**-like spiro[fluorene-9,4′-pyran].



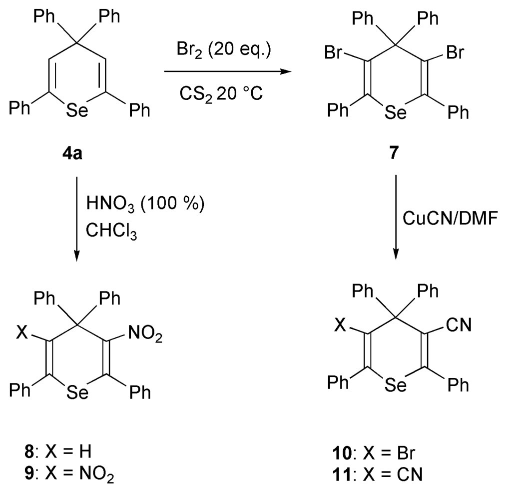
Scheme 1

8 hours. The same procedure with 1,5-dione **5** afforded less than 6% of spirocyclic 4*H*-selenopyran **6** even after two days. The preparations are summarized in Scheme 1 and Table 1. It can also be noted, that the independent conversion of 2,4,4,6-tetraphenyl-4*H*-pyran **1a** gave under the same conditions, the selena analogue **4a** in 55% yield (Scheme 1). Therefore, we assume that the formation of 4*H*-selenopyrans **4a**–**d** and **6** is a result of an acid catalyzed multistep process where the protonated forms of the dione **3**, 4*H*-pyran **1** and 4*H*-selenopyran **4** are the most thermodynamically stable species. It is also consistent with the related investigations on analogous recyclization of 2,4,6-triphenyl-4*H*-pyran.[9c]

Bromination, nitration and cyanodebromination of 4*H*-selenopyrans

Whereas 4*H*-pyran **1a** and its 1-thia analogue **2a** were found to be easily brominated or nitrated at the 3- and 5-positions[12] no similar conversions have been reported with 4*H*-selenopyrans.[8] Nevertheless, the reaction of bromine with 2,4,4,6-tetraphenyl-4*H*-selenopyran **4a** with bromine under mild conditions was reported[9a] to afford probably an 1,1-dibromo adduct. Repeating this work, we have observed that the substrate **4a** reacts with excess bromine to give a four component mixture where the predominating 3,5-dibromo-2,4,4,6-tetraphenyl-4*H*-selenopyran **7** was separated in moderate yield as light-sensitive crystals. On the other hand, we have shown that the nitration of **4a** proceeds with comparable selectivity as other pyranoids[12a] to give both 3-nitro-2,4,4,6-tetraphenyl-4*H*-selenopyran **8** and 3,5-dinitro-2,4,4,6-tetraphenyl-4*H*-selenopyran **9**.

By analogy with 4*H*-thiopyrans,[12b] we have also attempted to introduce two cyano groups onto the 2,6-phenyl groups as well as onto 4*H*-selenopyran ring by cyanodebromination[13] of the corresponding dibromo derivatives **4c** and **7**. In the case of the substrate **4c** we have isolated the expected bis-4-cyanophenyl derivative **4e** (Ar = 4-cyanophenyl) in yield 20%, while the same transformation with 3,5-dibromo derivative **7** gave a mixture of 3-bromo-5-cyano derivative **10** and 3,5-dicyano derivative **11** in total yield 72%. All the reactions are summarized in Scheme 2.



Scheme 2

Photocolouration of 4*H*-selenopyrans

Analogous with 4*H*-pyran **1a** and 4*H*-thiopyran **2a**,[4,5] the 4*H*-selenopyrans **4a**–**d**, **8** exhibit solid state reversible photocolouration after exposure to sunlight and UV light. The basic characteristics λ_{max} (solution) and λ_{max} (solid state) are summarized in Table 2. The optical absorptions of the molecules in crystalline colourless form are located in the UV region (see Fig. 1). Under the irradiation by UV light new bands appear. For coloured material of 4*H*-selenopyrans **4a**–**d** two absorption maxima appeared consistent with green or yellow–green colouration. The example of the spectrum for material **4b** is given in Fig. 1. Generally, the photochromic effect is very weak for this group of compounds. The photochromic activity was

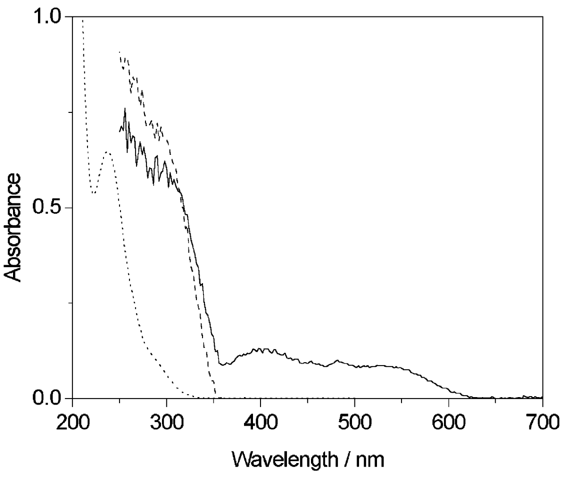


Fig. 1 Absorption spectra of compound **4b** (in arbitrary units). (· · ·) absorbance of acetonitrile solution, (- - -) diffusion reflection K/S of polycrystalline powder mixed with MgO in the dark, (——) diffusion reflection K/S of polycrystalline powder mixed with MgO after 15 s illumination by a high pressure 200 W mercury discharge lamp.

Table 2 Solution and solid state absorption maxima

Starting 4*H*-selenopyran	Ar	X (pos. 3)	$\lambda_{max}{}^{a}$/nm	log ε^{b}	$\lambda_{max}{}^{c}$/nm	Colour^{d}
4a	Phenyl	H	238, (287)	3.73	395, 483	Green
4b	4-F-Phenyl	H	237, (283)	3.38	402, 535	Unstable
4c	4-Br-Phenyl	H	250, (300)	3.53	402, 483	Yellow–green
4d	4-Bu^t-Phenyl	H	246, (300)	3.61	385, 544	Green
8	Phenyl	NO_2	(280), 378	2.46	560^{e}	Green

[a] Solution in acetonitrile, parentheses denote shoulders. [b] ε in dm^3 mol^{-1} cm^{-1}. [c] Reversible maxima of coloured species measured on polycrystalline powder in MgO after 60 s illumination by a high pressure 200 W mercury discharge lamp. [d] Polycrystalline sample kept for three days under the sunlight. [e] Illuminated through band filter 300–400 nm.

improved by a factor of 100–1000 by the introduction of a NO_2 group into the position 3. The resulting photochromic spectrum changed; only one band was observed in the visible region as shown in Fig. 2. The colour change for nitroselenopyran **8** was from yellow to green.

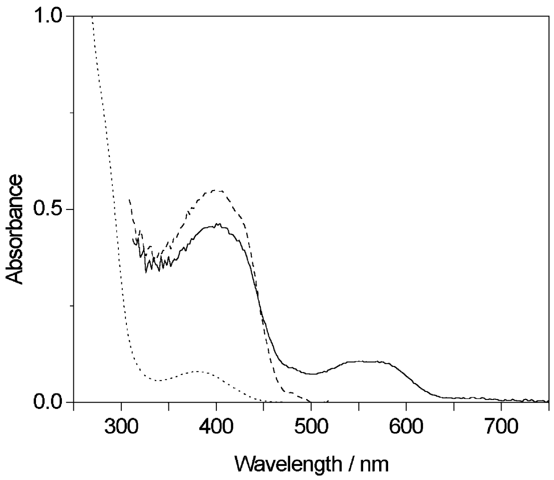


Fig. 2 Absorption spectra of compound **8** (in arbitrary units). (· · ·) absorbance of acetonitrile solution, (- - -) diffusion reflection K/S of polycrystalline powder mixed with MgO in the dark, (——) diffusion reflection of K/S of polycrystalline powder mixed with MgO after 15 s illumination by a high pressure 200 W mercury discharge lamp with the band filter 300–400 nm.

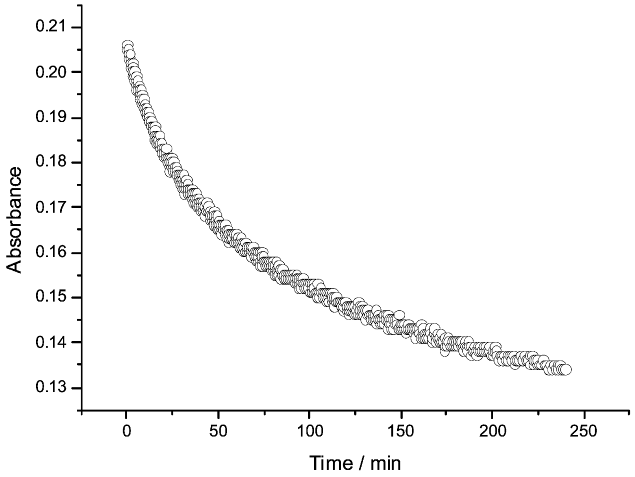


Fig. 3 Thermal decay curve of the normalized concentration of coloured species of polycrystalline sample **8** mixed with MgO at room temperature.

The thermal course of bleaching of the solid polycrystalline materials mixed with magnesium oxide can generally be described at the first approximation by two exponential functions

$$A(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \qquad (1)$$

with the time constants being τ_1 = 4.7 min and τ_2 = 41 min typically for compound **8**. In eqn. (1) $A(t)$ is the absorbance, t is the time, and A_1 and A_2 are constants. Because the measurements were performed using diffusion reflection, the Munk–Kubelka function[13a] was used to recalculate the experimental data to the absorbance. The typical decay curve for compound **8** is given in Fig. 3. However, the detail analysis of the decay curves shows that, at least, the faster decay of the normalized concentration $[M(t)/M(0)]$ of the coloured species is better described by dispersive kinetics. Basically, this shape could represent the superposition of several exponentials, but the use of the statistical distribution of thermodynamic reaction parameters seems to be a more sensible approach because of the linear $\log[[M(t)]/[M(0)]]$ *vs.* t^a relation, where a was determined as $a = 0.43$ at room temperature for compound **8**. The optical properties of disordered polycrystalline materials must be regarded as resulting from a set of individual processes of different rates, weighted by the distribution of parameters. If the kinetics are of the first-order at each site, the superposition of time-independent rates will cause the overall rate of the process to be time dependent. Then, the corresponding decay law for these dispersive processes differs from the pure exponential form and follows $\exp(-t^a)$, where a is the dispersion parameter which measures the strength of dispersion. Hence, the photochromic bleaching process could be described by a stretched exponential[13b,c]

$$[M(t)] = [M(0)]\exp[-(\nu t)^a] \qquad (2)$$

where $0 < a < 1$ is the deviation from the pure exponential behaviour and ν is a decay rate constant. In irregular systems, such as our polycrystalline material, the activation energy and entropy of the photochromic back reaction depend on the local geometry around the reacting species, and, consequently, they are quantities with statistical variation. The thermally-induced back reaction is associated with the rate constant $\nu(E)$ according to the eqn. (3)

$$\nu(E) = \nu_0\exp[-(E_m - E)/kT] \qquad (3)$$

where ν_0 is the frequency factor. Since the energy difference between the ground state E and the maximum of the energy barrier (E_m) depends on a set of conformational parameters, each varying statistically, the most probable distribution function for ($E_m - E$) was assumed by Richert and Bässler[13d] to be the Gaussian one characterized by its width σ. Therefore, the time dependence of the concentration of coloured species of **8** should be the convolution of first-order decay functions reflecting the unimolecular nature of the process and the distribution function for the reaction rates expressed by eqn. (4).[13d]

$$[M(t)] = \\ [[M(0)]/(2\pi\sigma^2)]\int\exp[-(E_0 - E)^2/2\sigma^2]\exp[-\nu(E)t]\mathrm{d}E \qquad (4)$$

The photochemical activity of 4*H*-selenopyrans in the crystalline state is evident. However, in order to explain the mechanism of photocolouration, it should be pointed out that

Table 3 Calculated and X-ray geometrical parameters of 4*H*-selenopyran ring

	4a				**4c**			**6**			
			X-Ray							X-Ray	
Parameters	PM3	B3LYP/ 6-31G*	A[a]	B[a]	PM3	B3LYP/ 6-31G*	X-Ray	PM3	B3LYP/ 6-31G*	A[a]	B[a]
Bond lengths /Å											
Se–C2	1.884	1.917	1.889	1.901	1.883	1.915	1.913	1.885	1.920	1.898	1.878
C2–C3	1.330	1.340	1.339	1.315	1.327	1.339	1.329	1.327	1.341	1.315	1.313
C3–C4	1.508	1.525	1.521	1.523	1.508	1.522	1.532	1.498	1.525	1.517	1.521
C4–C5	1.509	1.522	1.514	1.525	1.508	1.525	1.522	1.498	1.525	1.519	1.503
C5–C6	1.327	1.339	1.328	1.335	1.327	1.340	1.323	1.327	1.341	1.316	1.316
C6–Se	1.888	1.916	1.900	1.901	1.883	1.917	1.910	1.885	1.920	1.898	1.878
Bond angles (°)											
Se–C2–C3	122.2	122.1	123.3	124.1	124.1	122.8	119.3	123.9	120.9	123.0	121.8
C2–C3–C4	127.2	129.4	129.9	130.2	127.4	128.7	125.9	126.7	126.7	129.7	131.1
C3–C4–C5	116.3	113.3	113.9	112.8	117.7	113.3	109.4	119.3	111.9	113.9	114.4
C4–C5–C6	125.7	128.7	129.4	130.7	127.4	129.4	125.0	126.7	126.7	130.1	129.0
C5–C6–Se	123.6	122.7	124.1	122.9	124.1	122.1	120.6	123.9	120.9	122.5	123.9
C6–Se–C2	98.8	98.0	98.4	98.2	99.3	97.9	97.0	99.6	97.0	98.8	99.8
Torsion angles[b] (°)											
Se–C2–C3–C4	−0.8	−5.6	−5.0	4.9	0.1	−5.4	7.2	−0.6	2.7	1.1	2.2
C2–C3–C4–C5	22.5	23.5	11.4	−11.8	0.0	23.5	−45.0	0.6	−35.5	−12.3	−1.6
C3–C4–C5–C6	−23.4	−19.3	−8.0	9.0	−0.2	−19.2	44.5	0.0	35.5	10.9	2.1
C4–C5–C6–Se	2.6	−1.9	−0.9	0.0	0.1	−2.4	−6.7	−0.5	−2.7	1.4	−3.1
C5–C6–Se–C2	15.4	16.6	6.3	−6.1	0.0	17.1	−26.7	0.4	−25.0	−10.5	2.9
C6–Se–C2–C3	−16.2	−13.2	−3.6	4.0	−0.1	−13.6	26.2	0.1	25.0	9.3	−2.3
Conformation	Boat	Boat	Boat	Planar	Planar	Boat	Boat	Planar	Boat	Boat	Planar

[a] Two different molecules are present in elemental unit. [b] Absolute value.

colouration is a complicated process in which multiple photochemical pathways probably take place. The most probable structures responsible for colouration are either isoelectronic hypervalent structure(s) similar to those described in our related studies on photocolouration of analogous 4*H*-thiopyrans[6a] or intermediate(s) occurring during photochemical rearrangement(s) stabilized by effects of the surrounding crystalline lattice.

4*H*-Selenopyran ring geometry;[14] an X-ray and DFT calculation study of 4*H*-selenopyrans 4a, 4c and 6

Because the photocolouration occurs in the crystalline state crucial information is associated with the geometrical parameters of molecules in the crystalline matrix. Hence, the X-ray diffraction and quantum semiempirical PM3 and DFT at B3LYP/6-31G* level optimizations were used to prove the correct structures of **4** as well as to acquire a deeper insight into hitherto not investigated molecular configurations of the 4*H*-selenopyran ring.[14]

The structural parameters describing the 4*H*-selenopyran ring of derivatives **4a**, **4c** and **6** are given in Table 3 together with the same data obtained by DFT and the PM3 molecular geometry optimizations, there is good agreement between theoretical and experimental values. In comparison with published X-ray data[4d] for 4*H*-pyran **1a** and 4*H*-thiopyran **2a** it can be summarized that all the bond lengths, except for the heteroatom–carbon bonds, are almost conserved (the largest deviation being within 0.03 Å). The consistency is also apparent for both the bond angles, only the angle C2–Se–C6 is partially contracted within 3°, as well as the torsion angles. The heterocyclic ring tends to be planar or form a slight boat-like conformation. The most intriguing discovery is the effect of the remote bromine atoms of 4*H*-selenopyran **4c** these cause considerable distortion of the heterocyclic ring from planarity. For instance the torsion angle C(2)–C(3)–C(4)–C(5) of 4*H*-selenopyran **4a** is −11.8° while the same value for 4*H*-selenopyran **4c** is −45° (*cf.* Table 3). Similarly, the torsion angle C(6)–Se(1)–C(2)–C(3) differs by 22°. This fact was not predicted by calculation methods and is probably related to the molecular packing.

Crystal structure determination

To date only limited reports on selenopyran crystal have been published.[8] Therefore we have devoted considerable attention to X-ray structure determination of compounds **4a**, **4c**, and **6**.

Crystal structure determination data are summarized in Table 4. Compound **4a** crystallizes in noncentrosymmetric spacegroup $Pna2_1$ (No. 33). Similarly to the crystal structure of 4*H*-thiopyran **2a**[4d] there are two independent molecules in the asymmetric unit. Fig. 4 shows an ORTEP diagram[15a] of one

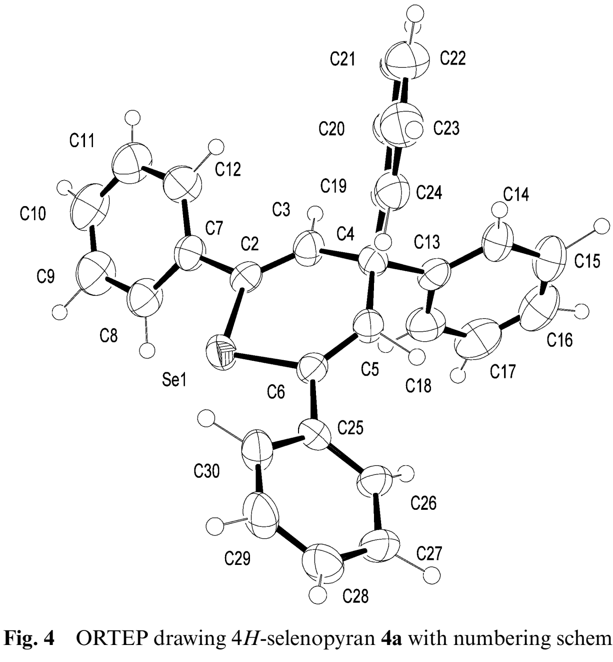


Fig. 4 ORTEP drawing 4*H*-selenopyran **4a** with numbering scheme.

Table 4 Crystal structure determination of 4*H*-selenopyrans **4a**,**c** and **6**

	4a	**4c**	**6**
Asymmetric unit	2 × $C_{29}H_{22}Se$ (898.91)	$C_{29}H_{20}SeBr_2$ (607.25)	2 × $C_{29}H_{20}Se$ (894.88)
Space group	$Pna2_1$	$P2_1/n$	$P2_1/c$
a/Å	18.117(3)	12.047(1)	10.862(3)
b/Å	7.088(1)	12.814(2)	14.597(3)
c/Å	34.009(7)	16.307(1)	27.479(3)
β/°	–	105.510(6)	90.83(3)
V/Å^3	4367.0	2425.7	4356.4
Z	8	4	8
ρ_{calc}/g cm^{-1}	1.37	1.66	1.36
$\mu(K_\alpha)$/cm^{-1}	24.0	60.6	24.1
λ/Å	1.54184	1.54184	1.54184
$2\theta_{max}$/°	78	60	55
No. of unique reflections	8281	3608	5475
No. of reflections with $\sigma > 1.96$	7769	3357	4485
R	0.0621	0.0943	0.0828
R_w	0.0529	0.0698	0.0790

molecule of **4a** as determined by X-ray analysis. Compound **4c** crystallizes in monoclinic centrosymmetric spacegroup $P2_1/n$ (No. 14). In comparison with **4a** and **6**, there is a single molecule of **4c** (ORTEP drawing given in Fig. 5) present in the asymmetric unit. Compound **6** crystallizes in monoclinic centrosymmetric spacegroup $P2_1/c$ (No. 14). As mentioned before, there are two independent molecules in the asymmetric unit. One selected molecule of **6** is shown in ORTEP form in Fig. 6.

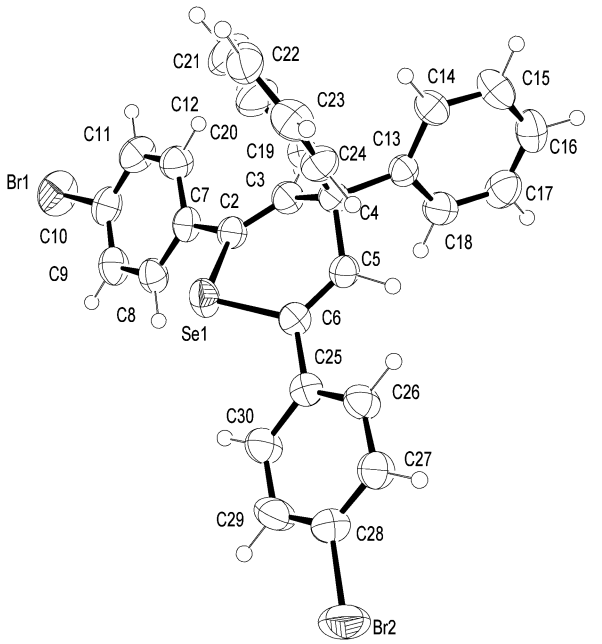


Fig. 5 ORTEP drawing 4*H*-selenopyran **4c** with numbering scheme.

The properties of the neighbouring crystalline matrix should be considered as a potential factor in the conformational and photocolouration behaviour. Thus, the planar conformation of 4*H*-selenopyran **4a** is slightly distorted towards the boat conformation for both independent molecules present in the elemental cell. The effect of the force field of the surrounding molecules is amplified by the addition of the bromine atoms for the case of 4*H*-selenopyran **4c**, because bromine atoms actively participate in Van der Waals interactions. There are two different conformations of 4*H*-selenopyran **6** in the unit cell. One ring adopts a boat conformation, the second one is planar. This is probably due to the packing of the molecules.

NMR and mass spectral properties

Assigned ^1H and ^{13}C NMR spectra are given in Tables S1–S4 (Supplementary material).† Protons H-3, H-5 in compounds **4a**–**4e** resonate as easily distinguishable singlets. Their chemical shifts reflect the effect of substitution. With compound **6**, the ring current effect is operating. Chemical shifts of the phenyl group protons attached to C-4 remain constant throughout the series. *ortho, meta*-, and *para*-Protons were assigned on the basis of their characteristic multiplet pattern. With *para*-substituted phenyl groups in **4b**–**4e**, NOE between H-3 and the *ortho*-protons of C-2 attached to the phenyl was used to differentiate them from their *meta*-counterparts. Carbons were assigned by HETCOR or HMQC. Quaternary carbons were assigned using HMBC. Different carbon coupling partners of *ortho*-protons in compounds **7**–**11** were used to distinguish 4-Ph from 2-Ph (sp^3-type C-4 *vs.* sp^2-type C-2). All NMR data support the reported structures.

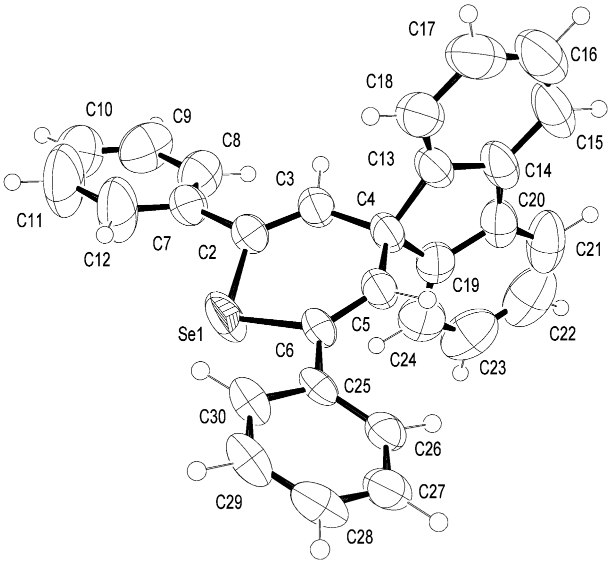


Fig. 6 ORTEP drawing 4*H*-selenopyran **6** with numbering scheme.

The elemental compositions of prepared selenopyrans including the presence of selenium were analysed by mass spectrometry with electron ionisation. All compounds give intense EI spectra with significant fragmentation. The molecular ion peak is dominant for the majority of the studied selenopyrans. Dibromoderivative **7** and nitroderivatives **8**, **9** represent the only exceptions with major peaks corresponding to $[M - Br]^+$ and $[M - NO_2]^+$ ions, respectively. To explain the fragmentation behaviour of **4a** the elemental composition of the most relevant fragments were measured. Nearly the same fragmentation was observed for the analogue **4b**. The initial aromatization of 4*H*-selenopyrans by the loss of neutral particles leading to stable selenopyrilium ion is the most characteristic process.[12]

Conclusion

Heterocyclization of substituted 1,3,3,5-tetraphenylpentane-1,5-diones[5a–c] into corresponding 4*H*-selenopyran depends on *in situ* generation of air and light-sensitive hydrogen selenide by using the Al_2Se_3–HCl–AcOH mixture. The reactivity of parent 2,4,4,6-tetraphenyl-4*H*-selenopyran towards electrophilic agents (bromine and nitric acid) is consistent with other 2,4,4,6-tetraaryl-4*H*-(hetero)pyranoids.[12] Some 2,4,4,6-tetraphenyl-4*H*-selenopyran derivatives were observed to exhibit photocolouration in the crystalline state. The introduction of the selenium atom into 2,4,4,6-tetraaryl-4*H*-(hetero)pyran system is accompanied by only minor changes of heterocyclic ring geometry, as it follows from comparative DFT quantum calculations and a X-ray geometry study of three 4*H*-selenopyran derivatives. The 4*H*-selenopyran ring tends to preserve planar or slightly boated conformation.

Experimental

Temperature data are uncorrected. Melting points were determined using a Boetius apparatus. Starting diketones **3a**–**d** or **5** were prepared by sodium amide catalyzed condensation of appropriately substituted acetophenone with benzophenone or 9-fluorenone respectively.[5a,d] Aluminium selenide was prepared by direct seleno-aluminium fusion.[16]

Spectra and kinetics of photochromism of polycrystalline materials (powder mixed with MgO) were determined from measurements of diffuse reflection in air by means of a recording Perkin-Elmer-Hitachi 340 spectrophotometer. The Munk–Kubelka function $F(R_\infty) = (1 - R_\infty)^2/2R_\infty = K/S$ (ref. 13*a*), was used to plot solid state experimental data. Here, R_∞ is the diffuse reflectance of the sample, *K* is the absorption coefficient, and *S* is the scattering coefficient.

IR spectra (ν, cm^{-1}; $CHCl_3$) were taken on a FTIR spectrometer NICOLET 740. For NMR and positive-ion mass spectra see supplementary material.†

X-Ray measurements were taken with the Enraf–Nonius CAD4 diffractometer, λ(CuKα) = 1.54184 Å.

General procedure for the preparation of 4*H*-selenopyrans 4a–d and 6

2,4,4,6-Tetraphenyl-4*H*-selenopyran (4a). *Method A.* A solution of 1,3,3,5-tetraphenylpentane-1,5-dione (**3a**) (0.5 g, 1.24 mmol) in glacial acetic acid (30 ml) was added under an argon atmosphere to a solution of hydrogen chloride (17 g) in the same solvent. This mixture was stirred under argon and saturated with hydrogen selenide generated by the reaction of Al_2Se_3 with diluted hydrochloric acid[16] for 5 hours and then allowed to stand for 12 hours. The solvent was then evaporated in well ventilated hood and the residue was subjected to column chromatography on silica gel (35 g) in benzene. Crystallization of the crude product from EtOH–benzene produced **4a** (0.43 g, 77%, colourless needles, mp 138–140 °C; ref. 9*a* mp 138–139 °C). Anal. Calcd. for $C_{29}H_{22}Se$: C, 77.50; H, 4.93. Found: C, 77.30; H, 5.02%. IR ($CHCl_3$, cm^{-1}): 1598, 1596.

Method B, in situ generation of H_2Se. To the flask equipped with balloon filled with nitrogen the well pulverized aluminium selenide (20 g, 68.7 mmol) was suspended in benzene (25 ml). A part (25 ml) of a solution of hydrogen chloride in glacial acetic acid (15 g of HCl in 100 ml of CH_3COOH) was added under stirring and cooling with ice followed by solution of diketone **3a** (0.5 g, 1.24 mmol) in benzene (25 ml). The remaining HCl-solution in acetic acid (75 ml) was then added and the reaction mixture was stirred and maintained at overpressure by manipulation of the balloon in order to increase the concentration of dissolved hydrogen selenide. The reaction was monitored by TLC (eluent: benzene). After the starting diketone **3a** had disappeared (6 h) the insoluble parts were filtered off on Celite, the filtrate was diluted with water (500 ml) and extracted with benzene (50 ml). The organic extract was washed with water, 5% aqueous solution of NaOH (2 × 300 ml) and water and then dried over magnesium sulfate and evaporated. Column chromatography on silica (25 g, eluent petroleum ether–chloroform 1 : 1) and crystallization from EtOH–benzene afforded **4a** (0.40 g,72%) identical with the compound obtained by method A.

2,6-Bis(4-fluorophenyl)-4,4-diphenyl-4*H*-selenopyran (4b). Reaction of diketone **3b** (0.5 g, 1.14 mmol) with Al_2Se_3 (20 g) for 8.25 h, according to method B, work-up, column chromatography and crystallization from acetonitrile afforded selenopyran **4b** (0.36 g, 65%, colourless crystals, mp 113–115 °C). Anal. Calcd. for $C_{29}H_{20}F_2Se$: C, 71.75; H, 4.15. Found: C, 71.63; H, 4.09. IR ($CHCl_3$, cm^{-1}): 1600, 1506.

2,6-Bis(4-bromophenyl)-4,4-diphenyl-4*H*-selenopyran (4c). Reaction of diketone **3c** (0.5 g, 0.89 mmol) with Al_2Se_3 (20 g) according to method B for 6 h, work-up, and column chromatography led to a crude mixture of selenopyran **4c** accompanied with 20% (HPLC) of pyran **1c** which was then dissolved in ethanol and allowed to crystallize. The first well developed needles consisted of practically pure selenopyran **4c**. Recrystallization from EtOH–benzene afforded selenopyran **4c** (0,24 g, 45%, colourless robust needles, mp 167–169 °C). Anal. Calcd. for $C_{29}H_{20}Br_2Se$: C, 57.36; H, 3.32. Found: C, 57.16; H, 3.49%. IR ($CHCl_3$, cm^{-1}): 1599, 1585.

2,6-Bis(4-*tert*-butylphenyl)-4,4-diphenyl-4*H*-selenopyran (4d). Reaction of diketone **3d** (0.5 g, 0.97 mmol) with Al_2Se_3 (20 g) according to method B for 2.25 h, work-up, column chromatography and crystallization from acetone afforded selenopyran **4d** (0.31 g, 57%, fine colourless needles, mp 144–146 °C). Anal. Calcd. for $C_{37}H_{38}$ Se: C, 79.12; H, 6.82. Found: C, 79.14; H, 6.82%. IR ($CHCl_3$, cm^{-1}): 1599, 1506.

2′,6′-Diphenylspiro[fluorene-9,4′-selenopyran] (6). Reaction of diketone **5** (0.5 g, 1,24 mmol) with Al_2Se_3 (20 g) according to method B for 54 h, work-up and column chromatography (eluent: petroleum ether–chloroform 5 : 1) led to a crude mixture of selenopyran **6** accompanied by **1**-like pyran. The purification step was achieved by preparative thin-layer chromatography in multiple elution mode (eluent: petroleum ether–chloroform 15 : 1) until two non-polar bands separated. The first least polar band was extracted from silica with chloroform, evaporated and crystallized twice from ethanol–benzene and then from ethanol–acetone. Selenopyran **6** (0.034 g, 6%) was obtained as colourless crystals, mp 173–175 °C. Anal. Calcd. for $C_{29}H_{20}Se$: C, 77.85; H, 4.51. Found: C, 77.66; H, 4.53. IR ($CHCl_3$, cm^{-1}): 1599, 1578.

Recyclization of 4*H*-pyran 1a into 4*H*-selenopyran 4a. According to Method B. Reaction of pyran **1a** (0.10 g, 0.26 mmol) with Al_2Se_3 (4 g, 13.74 mmol) for 4 h afforded 0.064 g (55%) of compound identified as selenopyran **4a**. Mp 139–141 °C.

3,5-Dibromo-2,4,4,6-tetraphenyl-4*H*-selenopyran (7). Bromine (3.56 g, 22.3 mmol) was added under stirring to a solution of selenopyran **4a** (0.5 g, 1.11 mmol) in carbon disulfide (10 ml), the reaction was allowed to continue for 20 hours at laboratory temperature. Then the reaction mixture was decomposed with a saturated aqueous solution of sodium sulfite, treated with dichloromethane and the combined organic extracts were dried over magnesium sulfate. After evaporation of the solvent *in vacuo* the mixture was subjected to column chromatography on silica gel with gradient elution (100 g silica, eluent: petroleum ether–chloroform 5 : 1 ⟶ 1 : 1). Subsequent crystallization from heptane–benzene yielded dibromoderivative **7** (0.22 g, 32%) as colourless, light sensitive robust needles, mp 189–191 °C. Anal. Calcd. for $C_{29}H_{20}Br_2Se$: C, 57.36; H, 3.32. Found: C, 57.42; H, 3.57%. IR ($CHCl_3$, cm^{-1}): 1598, 1578.

3- Nitro- and 3,5-dinitro-2,4,4,6-tetraphenyl-4*H*-selenopyran (8,9). *Method A.* Fuming 100% HNO_3 (1.38 ml, 33.38 mmol) was added at 0 °C to a stirred solution of selenopyran **4a** (1.00 g, 2.23 mmol) in chloroform (15 ml) and the stirring was continued for 0.5 h at the same temperature. Combined organic layers obtained after washing with water to pH 7 and an additional extraction of the aqueous phase with dichloromethane were dried over magnesium sulfate and evaporated. Column chromatography on silica gel (150 g, eluent: petroleum ether–dichloromethane 1 : 1 and then dichloromethane-ethyl acetate 1 : 1). *Band 1:* crystallization of crude product from heptane–benzene afforded mononitroderivative **8** (0.42 g, 38%, yellow, light sensitive crystals, mp 175–177 °C). Anal. Calcd. for $C_{29}H_{21}NO_2Se$: C, 70.45; H, 4.28; N, 2.83. Found: C, 70.78; H, 4.54; N, 2.80%. IR ($CHCl_3$, cm^{-1}): 1598, 1527 (NO_2), 1350 (NO_2). *Band 2*: crystallization of crude product from heptane–benzene afforded dinitroderivative **9** (0.081 g, 7%) as yellow, light sensitive crystals, mp 283–284 °C. Anal. Calcd. for $C_{29}H_{20}N_2O_4Se$: C, 64.57; H, 3.74; N, 5.19. Found: C, 64.73; H, 4.09; N, 5.38%. IR ($CHCl_3$, cm^{-1}): 1596, 1535 (NO_2), 1343 (NO_2).

Method B. The reaction of compound **4a** performed in the same manner for 1 h yielded mononitroderivative **8** (0.34 g, 31%) and dinitroderivative **9** (0.16 g, 13%), both identical with the previously described compounds.

2,6-Bis(4-cyanophenyl)-4,4-diphenyl-4*H*-selenopyran (4e). Dried dimethyl formamide (20 ml) was added under argon and stirring to bromo derivative **4c** (0.80 g, 1.32 mmol) and copper(I) cyanide (4 g, 22.3 mmol) and the mixture was then stirred and heated at 175–185 °C for 9 hours. After cooling the reaction mixtures were poured into a saturated solution of ammonium chloride in aqueous ammonia. The resulting precipitates were filtered off, washed with water, and the filtrate was extracted with dichloromethane. Combined organic layers were dried over magnesium sulfate, evaporated and subjected to the column chromatography on silica with gradient elution (100 g, petroleum ether–dichloromethane 1 : 1 ⟶ 0 : 1). Crystallization from ethanol–benzene afforded dicyanoderivative **4e** (0.13 g, 20%) as colourless needles, mp 195–196 °C. Anal. Calcd. for $C_{31}H_{20}N_2Se$: C, 74.55; H, 4.04; N, 5.61. Found: C, 72.62; H, 4.34; N, 5.61%. IR ($CHCl_3$, cm^{-1}): 2232 (CN), 1605, 1501.

3-Bromo-5-cyano- and 3,5-dicyano-2,4,4,6-tetraphenyl-4*H*-selenopyran (10,11). The above described procedure applied to **7** (0.15 g, 0.25 mmol) and CuCN (0.22 g, 1.24 mmol) in DMF (10 ml) for 6.5 hours resulted in a mixture which was separated by column chromatography on silica gel (50 g, petroleum ether–dichloromethane 1 : 1). *Band 1:* crystallization from ethanol yielded derivative **10** (0.021 g, 15%) as colourless needles. Mp 186–188 °C. Anal. Calcd. for $C_{30}H_{20}BrNSe$: C, 65.12; H, 3.64; N, 2.53. Found: C, 64.28; H, 3.44; N, 2.46%. IR ($CHCl_3$, cm^{-1}): 2210 (CN), 1599, 1568. *Band 2:* crystallized from ethanol–acetone. Derivative **11** (0.071 g, 57%) was obtained as yellowish plates, mp 191–193 °C. Anal. Calcd. for $C_{31}H_{20}N_2Se$: C, 74.55; H, 4.04; N, 5.61. Found: C, 73.74; H, 3.93; N, 5.54%. IR ($CHCl_3$, cm^{-1}): 2213 (CN), 1574.

X-Ray crystallographic analyses of 4*H*-selenopyrans ‡

The crystal structure determination data of compounds **4a**, **4c** and **6** are given in Table 4. The lattice parameters were obtained by least-squares fit of 20 reflections from the 2θ-range of 38–40°. Data collection was performed using ω-2θ scan. Three standard reflections were monitored during data collection, resulting with decay lower than 3%. Decay correction and ψ-scan [15b] empirical absorption procedure were applied. The structure was solved using SIR92 direct methods.[15c] The hydrogen atoms were located from $\Delta\rho$-map for **4a** or set and kept fixed in the ideal geometry using the riding models for **4c** and **6**. For **4a**, the positional and U_{iso} thermal parameters of hydrogen atoms were refined. The least-squares refinements were performed in CRYSTALS [15d] computing system by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, wherein w represents Chebychev's polynomial weighting scheme.[15e]

Computational details

All the systems calculated were of C_1 symmetry (totally asymmetric) without any symmetry restrictions. Almost planar starting conformations (angle Se–C2–C3–C4 = 5°) were used in order to find the conformation of heterocyclic ring.

The DFT calculations were carried out according to the original proposal [17a] exploiting the standard program.[17b] The starting conformations were preliminary estimated by a PM3 calculation.[17c] Although the use of a more suitable basis set with extended polarization d-functions (*e.g.* LANL2DZ) would be desirable for selenium containing compounds [17d] the performance of smaller ones (B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311+G(d,p)) has been assessed to provide also satisfactory results.[17e–i] Considering dimensions of the systems studied, the exact geometry and energy was calculated at a B3LYP/6-31G(d) level. All the structures represented local energy minima according to the vibrational analysis. The coordinates of optimized structures are provided in supplementary data.

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