Synthesis and theoretical and experimental nonlinear optical studies of push–pull benzopyranic derivatives containing an oxo, thioxo or dicyanoethylene group as acceptor site†

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A series of new push–pull molecules, containing 4*H*-1-benzopyran-4-oxo-2-yl, 4*H*-1-benzopyran-4-thioxo-2-yl or 4*H*-1-benzopyran-4-(ylidene malononitrile)-2-yl as acceptor site and 4-dimethylaminophenyl or ferrocenyl as donor site, was synthesized and characterized. The X-ray structures of 2-(4′-dimethylaminophenyl)-4*H*-1-benzopyran-4-thione and 2-(4′-dimethylaminophenylethenyl)-4*H*-1-benzopyran-4-thione were established. Experimental dipole moments and first-order hyperpolarizability β data measured in solution by electric-field-induced second-harmonic generation (EFISHG) were compared to computed values obtained by the semiempirical PM3 method for optimized structures. The characteristics of the lowest energy singlet–singlet $\pi \rightarrow \pi^*$ transitions were determined through UV/VIS spectral measurements and semiempirical CNDO/S-CIS calculations. All of the experimental and computed results point out the NLO efficiency of the acceptor thioxo group, which was compared to the well-known aldehyde or dicyanomethylene substituents.

Synthèse et études théoriques et expérimentales en optique non-linéaire de composés benzopyraniques de type push–pull contenant des groupes accepteurs oxo, thioxo ou dicyanoéthylène. Une série de nouvelles molécules de type donneur–transmetteur–accepteur (D–T–A), comprenant un groupement 4*H*-1-benzopyrane-4-oxo-2-yle, 4*H*-1-benzopyrane-4-thioxo-2-yle ou 4*H*-1-benzopyrane-4-(ylidène malononitrile)-2-yle comme accepteur et un groupement 4-diméthylaminophényle ou ferrocènyle comme donneur, a été synthétisée puis caractérisée. Les structures cristallographiques des molécules 2-(4′-diméthylaminophényl)-4*H*-1-benzopyrane-4-thione et 2-(4′-diméthylaminophényléthènyl)-4*H*-1-benzopyrane-4-thione ont été établies. Des mesures en solution du moment dipolaire et de l'hyperpolarisabilité du premier ordre β (expérience EFISHG) ont éte comparées aux valeurs calculées par la méthode semi-empirique PM3 à partir de géométries optimisées. Les caractéristiques des transitions $\pi \rightarrow \pi^*$ singulet–singulet de plus basses énergies ont éte évaluées à l'aide des spectres UV/VIS et de calculs semi-empiriques CNDO/S-CIS. Tous les résultats expérimentaux et théoriques permettent de comparer l'efficacité du groupement accepteur thioxo à celle des substituants bien connus aldéhyde et dicyanométhylène.

Organic materials with first-order nonlinear optical (NLO) properties have been the subject of intense research owing to their larger nonlinearity as compared with inorganic compounds.[1] Particular emphasis has been put on intramolecular charge-transfer compounds having both electron-donating and electron-accepting groups at the ends of various conjugated systems (push–pull molecules). Most of the materials investigated so far contain amino or dialkylamino at the donor sites and nitro or cyano at the acceptor sites. However, some papers describe the research of less classical NLO chromophores[2–6] and the variety of organic chemicals is far from being fully explored. In this paper we wish to report on the interest of the thioxo group as a new acceptor site in NLO push–pull molecules. Sulfur-containing groups are known as donor sites in NLO molecules[7–9] or in organic metals[10] and can also be used inside the conjugated part of push–pull molecules.[11] Electron-withdrawing moieties containing a sulfur atom have been also investigated as NLO materials: sulfonyl substituents[5,8,9,12] and moieties containing a thiocarbonyl group.[13] The restricted number of these studies can be attributed to the difficulty in synthesizing and handling compounds like thioketones or thioaldehydes and to the poor acceptor effect of simple functional groups like thioamides.[14] These disadvantages are not met in the thiocarbonylated heterocyclic compounds investigated in this paper.

With the intent to compare with previous thione compounds, we have also synthesized molecules containing the dicyanomethylene group; this substituent shows interesting electron-withdrawing properties for NLO as previously evidenced in (dicyanomethylene)pyran derivatives.[15]

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† Electrostatic units [esu-cgs (esu)] used for nonlinear optical properties are generally used in this literature. Atomic units, SI units, esu and other equivalents for many physical properties are given below.[39]
μ (dipole moment): 1 au = 8.478×10^{-30} C m = 2.542×10^{-18} esu ($cm^{3/2}$ $erg^{1/2}$) = 2.542 D.
β (quadratic hyperpolarizability): 1 au = 3.206×10^{-53} C^3 m^3, J^{-2} = 8.639×10^{-33} esu ($cm^{9/2}$ $erg^{-1/2}$).
γ (cubic hyperpolarizability): 1 au = 6.235 C^4 m^4 J^{-3} = 5.037×10^{-40} esu (cm^6 erg^{-1}).
E (energy): 1 au = 4.3598×10^{-18} J = 4.3598×10^{-11} esu (erg) = 27.21 eV = 1.043×10^{-18} cal.

Results and Discussion

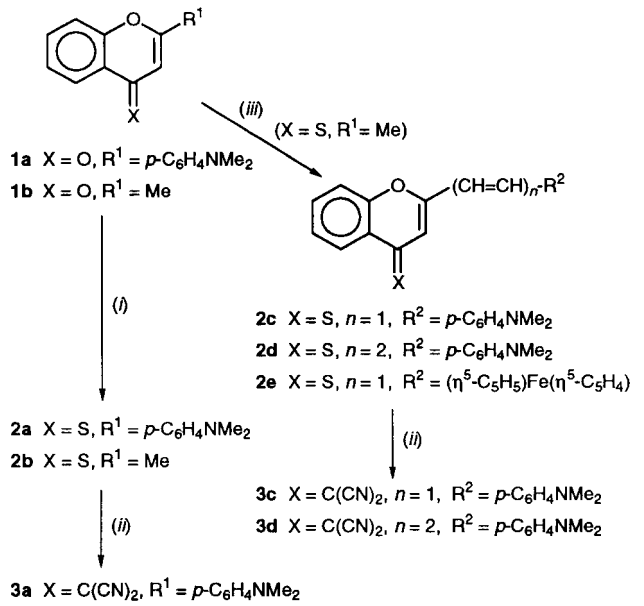
Preparation of benzopyranic derivatives

Benzopyranic compounds synthesized and studied in this work are presented in Scheme 1. The derivatives **1a** and **1b** were obtained following a Baker–Venkataraman transposition.[16] The carbonyl group was readily transformed into a thiocarbonyl one by reacting with P_4S_{10}.[17] The enhanced reactivity of the methyl group in 2-methylbenzopyranethione[18] (**2b**) has been used in the synthesis of the extended derivatives **2c**, **2d** and **2e** by condensation of commercially available aldehydes containing the corresponding donor groups (dimethylamino or ferrocenyl). The ease of this reaction demonstrates the electron-withdrawing effect of the thiocarbonyl group. The reaction of malononitrile with benzopyranethiones[19] allowed lengthening of the π-electron system and access to compounds **3a**, **3c** and **3d** containing the acceptor dicyanomethylene group.[20] All the compounds studied here were fully characterized using conventional spectroscopic techniques.

Conformations and X-ray structures

As expected, the ethylenic compounds **2c**, **2e** and **3c** were obtained in their more stable *E* configuration, which was proved by characteristic spectroscopic data. An IR absorption observed near 965 cm^{-1} may be attributed to the out-of-plane vibrational deformation of the CH fragments of a *trans* CH=CH unit.[21] The ^1H NMR spectra of compounds **2c**, **2d**, **2e** and **3c** exhibit doublet(s) centered around 6.4 ppm with coupling constants about 15 Hz, in agreement with a *trans* conformation of the CC double bond(s). Other expected doublet(s) around 7.5 ppm are integrated with the aromatic proton signals.

Moreover, the X-ray structures of compounds **2a** (Fig. 1) and **2c** (Fig. 2) have been established. The molecules crystallize in a centrosymmetrical space group ($P2_1/c$) in agreement with the NLO inactivity of the solid materials (*vide infra*). X-Ray data for molecules **2a** and **2c** (Tables 1 and 2) show that the benzopyran ring is almost planar but evidence a small dihedral angle between the mean planes of the benzopyran ring and of the $C_6H_4NMe_2$ group, respectively 20.9(2)° and 21.5(2)°. In each case, this dihedral angle is not sufficient to prevent conjugation along the π-electron system. This is



Scheme 1 Reagents and conditions used in the preparation of the compounds studied: (*i*) P_4S_{10}–toluene reflux; (*ii*) $CH_2(CN)_2$ –HgO–EtOH reflux; (*iii*) R^2CHO–piperidine–EtOH, 35 °C

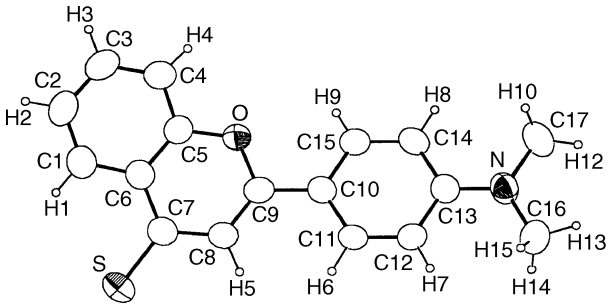


Fig. 1 Molecular structure of 2-(4′-dimethylaminophenyl)-4*H*-1-benzopyran-4-thione (**2a**)

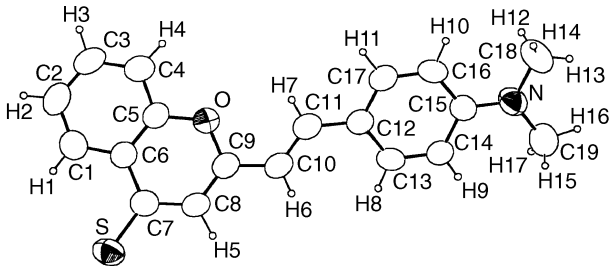


Fig. 2 Molecular structure of 2-(4′-dimethylaminophenylethenyl)-4*H*-1-benzopyran-4-thione (**2c**)

Table 1 Selected bond distances/Å and bond angles/° for **2a**

S—C7	1.672(2)	C5—C6	1.390(3)
O—C5	1.380(3)	C6—C7	1.463(3)
O—C9	1.367(3)	C7—C8	1.418(4)
N—C13	1.366(3)	C8—C9	1.362(3)
N—C16	1.455(3)	C9—C10	1.448(3)
N—C17	1.445(3)		
C5—O—C9	119.6(2)	C6—C7—C8	114.9(2)
C13—N—C16	120.7(2)	C7—C8—C9	123.1(2)
C13—N—C17	121.0(2)	O—C9—C8	120.7(2)
C16—N—C17	118.2(2)	O—C9—C10	112.1(2)
C8—C9—C10	127.2(2)	N—C13—C12	121.1(2)
N—C13—C14	122.2(2)	C1—C6—C7	123.9(2)
C5—C6—C7	119.3(2)	S—C7—C6	122.9(2)
S—C7—C8	122.2(2)	C9—C10—C11	120.4(2)
C9—C10—C15	122.6(2)	O—C5—C4	115.5(2)
O—C5—C6	121.8(2)		

Table 2 Selected bond distances/Å and bond angles/° for **2c**

S—C7	1.667(3)	C6—C7	1.461(3)
O—C5	1.384(3)	C7—C8	1.399(4)
O—C9	1.362(3)	C8—C9	1.359(4)
N—C15	1.364(4)	C9—C10	1.426(4)
N—C18	1.443(4)	C10—C11	1.333(4)
N—C19	1.445(4)	C11—C12	1.436(4)
C5—C6	1.391(4)		
C5—O—C9	119.0(2)	C7—C8—C9	124.0(2)
C15—N—C18	121.3(2)	O—C9—C8	120.6(3)
C15—N—C19	121.2(2)	O—C9—C10	113.0(2)
C18—N—C19	117.4(3)	C8—C9—C10	126.4(2)
C9—C10—C11	125.3(2)	C10—C11—C12	129.3(2)
O—C5—C4	115.1(2)	O—C5—C6	121.8(2)
N—C15—C14	121.4(2)	N—C15—C16	121.9(3)
C5—C6—C7	119.2(2)	S—C7—C6	123.0(2)
S—C7—C8	122.5(2)	C6—C7—C8	114.5(2)

emphasized in **2a** and **2c** by the intercyclic C—C bonds [1.448(3), 1.426(4) Å] and C_{sp^2}—N bonds [1.366(3), 1.364(4) Å], which are located between single and double bond length values. In another way, the plane defined by the C—N—C atoms of the NMe_2 group is almost planar with the phenyl ring. The X-ray structure of compound **2c** shows also an *E* configuration of the C_{10}—C_{11} bond (Fig. 2) and an *s-trans* conformation between the benzopyranic ethylenic bond (C_9—C_8) and the former one (C_{10}—C_{11}).

Ground-state properties

A theoretical study of ground and first excited states has been carried out on compounds **1**–**3**. Ground-state properties were determined with the semiempirical PM3 method[22,23] (except for molecule **2e** because Fe is not parametrized in this method). All the molecules were found to be planar with ethylenyl unit(s) in the *E* configuration (in agreement with ^{1}H NMR and IR spectroscopic data for **2c**, **2d**, **3c**, **3d** and X-ray data for **2c**) and butadienyl unit (molecules **2d** and **3d**) in the *s-trans* conformation; for molecules **2c**, **2d**, **3c** and **3d**, C_{10}—C_{11} and benzopyranic C_9—C_8 double bonds were also in the *s-trans* conformation as observed in the **2c** experimental structure (Fig. 2). We observed small differences between calculated (PM3) and experimental (X-ray) bond lengths and angles: the mean values of these differences are ±0.014 and ±0.018 Å in the bond lengths and ±1.1 and ±1.5° in the bond angles for **2a** and **2c**, respectively.

Agreement between experimental and calculated PM3 (planar geometries) dipole moment values is satisfactory (Table 3) within experimental error. For **2a** and **2c**, there is a clear discrepancy between the PM3 dipole moment values calculated for the X-ray geometries (**2a**: μ_g = 8.6 D; **2c**: μ_g = 9.5 D) and the corresponding experimental values (Table 3). These observations corroborate the relevance of the computed planar geometries, which seem to be more representative of molecules in solution than the X-ray ones. Therefore, these theoretical ground-state geometries were used for excited-state property calculations in the Franck–Condon approximation (see next paragraph). On the other hand, measured and calculated dipole moments show that the thioxo group induces greater dipole moments than the oxo one but a lower one than the dicyanoethylene group.

Transition properties

Transition properties (such as energy levels, transition dipoles, charge transfer or dipole moments) were determined within the CNDO/S-CIS scheme[24] with a specific parametrization for oxygen carbonyl[25] and sulfur thiocarbonyl atoms.[13b,13e] The 60 lowest energy single-excited configurations were used for the configuration interaction procedure.

All the studied compounds display an intense band in the visible region of their electronic absorption spectra (Table 3). The benzopyranethione **2a** is characterized by a 87 nm red-shifted band when compared to the corresponding benzopyranone **1a**. From the absorption data of **2** and **3** it may be concluded that the thiocarbonyl and dicyanoethylene groups induce analogous charge asymmetry in donor–acceptor compounds.

The CNDO/S-CIS method correctly reproduces the trend of the variations of λ_{max}, but the computed wavelength values are lower than the experimental ones. This discrepancy, which has been already observed,[7i] can be partially explained by the fact that the original CNDO/S parametrization does not take solvent effects into account, these effects may be important in donor–transmitter–acceptor (D–T–A) molecules.

In all cases, the theoretical calculations evidence a transition with a high oscillator strength for which the $\pi \rightarrow \pi^*$ character is unambiguously defined. For all molecules, this transition mainly involves the HOMO and LUMO. $\Delta\mu$ (the modulus of the difference between excited- and ground-state dipole moments) is always higher than 4 D and increases with the number of ethylenic units. As a result, the observed band may be considered as a charge-transfer one.

The intramolecular charge transfer that may contribute to this $\pi \rightarrow \pi^*$ transition has been analyzed in two different ways for all the compounds.

Firstly, the charge transfer has been calculated by arbitrarily 'splitting' the molecule into two fragments: the first fragment is the benzopyranic group and the other one the rest of the molecule as shown in Fig. 3 for molecule **2a**. The charge transfer is computed as:

$$\begin{aligned}\text{ICT[rest of the molecule} \rightarrow \text{benzopyranic group]} &= (Q^{e}_{benzopyran} - Q^{g}_{benzopyran}) - (Q^{e}_{rest} - Q^{g}_{rest}) \\ &= (-0.218 + 0.095) - (0.218 - 0.095) \\ &= -0.25\end{aligned}$$

where Q is the sum of net ($\sigma + \pi$) electron atomic charges for a fragment (g = ground state, e = excited state). If ICT[rest of the molecule → benzopyranic group] is less than zero, it means that there is a charge transfer upon excitation from the rest of the molecule (dimethylamino group for **2a**) towards the benzopyranic group. The results gathered in Table 3 show that the charge transfer is quite small compared to that in well-known D–T–A molecules such as *p*-dimethylaminonitrobenzene (ICT = 1.15).[13c]

Table 3 Experimental dipole moment, absorption wavelength and molar absorption coefficient values measured in chloroform along with calculated semiempirical values of dipole moments (PM3), transition energies, oscillator strengths, $\Delta\mu$ and internal charge transfer (CNDO/S-CIS)

	Experimental data in $CHCl_3$			Semiempirical calculated values				
				PM3	CNDO/S-CIS			
Compound[a]	μ_g/D	λ_{max}/nm	$10^3 \times \varepsilon$/ mol^{-1} l cm^{-1}	μ_g/D	λ_{max}/nm	Oscillator strength	$\Delta\mu$/D	ICT
[dma]bzp[=O], **1a**	6.1	367	26	5.4	300	0.95	7.1	−0.54
[dma]bzp[=S], **2a**	7.4	454	41	7.2	344	1.08	4.4	−0.25
[dma(CH=CH)]bzp[=S], **2c**	6.9	486	35	7.6	360	1.53	5.6	−0.30
[dma$(CH=CH)_2$]bzp[=S], **2d**	7.2	497	46	7.9	375	1.97	6.3	−0.30
[fc(CH=CH)]bzp[=S], **2e**	5.7	414	22	—	—	—	—	—
[dma]bzp[=$C(CN)_2$], **3a**	8.2	464	43	8.7	359	1.10	4.2	−0.26
[dma(CH=CH)]bzp[=$C(CN)_2$], **3c**	8.0	502	34	9.1	374	1.51	5.7	−0.34
[dma$(CH=CH)_2$]bzp[=$C(CN)_2$], **3d**	9.0	507	32	9.4	388	1.92	7.0	−0.36

[a] dma = 4-dimethylaminophenyl- and bzp = 4*H*-1-benzopyran-4-.

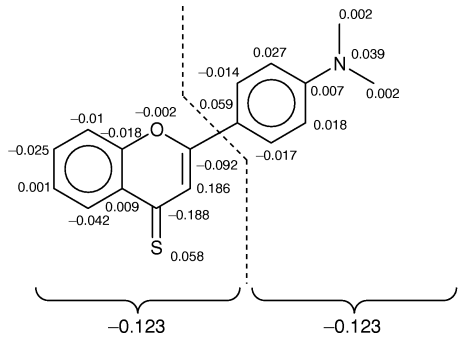


Fig. 3 Changes in the net ($\sigma + \pi$)-electron charges for the first lowest $\pi \rightarrow \pi^*$ transition energy (excited state–ground state) in each fragment (CNDO/S-CIS)

A second charge-transfer analysis has been realized in order to locate more precisely the charge-transfer sites and associated fluxes in these compounds. The percentages of ($\sigma + \pi$)-electron gain and loss for some fragments have been calculated from the changes in net ($\sigma + \pi$)-electron charges during excitation as shown in Fig. 3. For molecule **2a**, the $100 \times (-0.377/-0.408) = 92\%$ electron gain is located inside the benzopyranic group and 8% is in the rest of the molecule [-0.377: summation over the negative changes in the net ($\sigma + \pi$)-electron charges inside the benzopyranic group; -0.408: summation over the negative changes in the net ($\sigma + \pi$)-electron charges over the whole molecule]. A $100 \times (0.254/0.408) = 62\%$ electron loss is also located inside the benzopyranic group and 38% is in the rest of the molecule [same as previous calculations for positive changes in the net ($\sigma + \pi$)-electron charges]. These percentages clearly emphasize that the charge transfer during excitation is mainly located inside the benzopyranic group rather than between donor group (dimethylaminophenyl) and acceptor group (benzopyranic group) for molecule **2a**. The other results are gathered in Table 4. For all molecules, most of the electron gains (between 78 and 95%) are located inside the benzopyranic substituents. Electron losses are shared in a less systematical way: (*i*) if $n = 0$ (molecules **2a** and **3a**), 2/3 of electron losses are located inside the benzopyranic ring. So, the charge transfer is mainly located inside this ring during excitation. In contrast, for molecule **1a**, about 70% of electron losses affect the $PhNMe_2$ group, thus evidencing a more important charge transfer from this group towards the benzopyranic ring, which thereby can be considered as a withdrawing group in this case. Molecule **1a** is characterized by the greatest values of ICT and $\Delta\mu$ for the benzopyranic series. (*ii*) If the number of ethylenyl units increases ($n = 1, 2$), the charge transfer decreases inside the benzopyranic ring. Here the charge transfer is also partly located inside the $(CH)_n$ chain. This analysis shows that the studied benzopyranic substituents are not standard withdrawing groups, because they involve complex charge transfer upon excitation. Part of this transfer could be located inside the benzopyranic group.

Nonlinear optical properties

To evaluate the non-linear optical properties of compounds **1**–**3** a comparative study based on both theoretical calculations and experimental measurements has been undertaken.

First, the macroscopic second-harmonic generation (SHG) efficiencies of compounds **1**–**3** have been investigated at 1.06 μm by means of the powder technique.[26] Only **1a** and **3a** showed positive responses, of smaller intensity than the standard urea response, however. The second-harmonic generation powder efficiencies of some 4*H*-1-benzothiopyran-4-one derivatives[27] have been published previously. The authors concluded that a more pronounced nonplanar structure leads to a noncentrosymmetric molecular packing and results in a compound exhibiting SHG efficiency.

NLO molecular measurements were further performed in chloroform by using an electric-field-induced second-harmonic-generation experiment (EFISHG).[28,13f] Table 5 gives the experimental values of the first-order hyperpolarizability $\beta_\mu(-2\omega; \omega, \omega)_{EFISHG}$ and the theoretical (PM3) values of the first-order hyperpolarizability: $\|\boldsymbol{\beta}(0)\|_{PM3}$, the vector part of the tensor β and $\beta_\mu(0)_{PM3}$, the projection of $\|\boldsymbol{\beta}(0)\|_{PM3}$ onto the ground-state dipole moment. PM3 β_{ijk} components of the hyperpolarizability tensors were calculated through the finite-field method,[29] based both on energy and dipole moment expansions using an electric field strength of 10^{-3} au.[30,31] Then $\beta_\mu(0)_{PM3}$ and $\|\boldsymbol{\beta}(0)_{PM3}\|$ were computed using the following equations:

$$\beta_\mu(0)_{PM3} = \sum_i \frac{\beta_i \mu_g^i}{\|\boldsymbol{\mu}_g\|} \quad \text{and} \quad \|\boldsymbol{\beta}(0)_{PM3}\| = \left(\sum_i \beta_i^2\right)^{\frac{1}{2}}$$

with $\beta_i = \sum_j \beta_{ijj}$ where i, j are the cartesian coordinates x, y, z.

Different conventions are frequently used to express the induced polarization as:

$$\mu_{induced} = \mu_0 + \alpha E + (1/2!)\beta E \cdot E + (1/3!)\gamma E \cdot E \cdot E + \cdots$$

(convention 'T' as in Taylor)

$$\mu_{induced} = \mu_0 + \alpha E + \beta E \cdot E + \gamma E \cdot E \cdot E + \cdots$$

(convention '**B**')

Then $\beta^T = 2\beta^B$. Additional numerical discrepancies may arise from improper treatment of the degeneracy factors in different types of nonlinear optical processes. Confusion frequently arises when comparing hyperpolarizabilities calculated with experimental values, because the conventions used are not explicitly stated. For a detailed discussion of this issue, see ref. 32.

We have tried to use a unique convention in this paper: namely the convention 'X' as defined by Willetts *et al.*[32] where all numerical factors appearing explicitly in eqn. (9) of

Table 4 Percentage of ($\sigma + \pi$)-electron gain and loss during the $\pi \rightarrow \pi^*$ transition (CNDO/S-CIS)

	% of electron gain inside:			% of electron loss inside:		
Compound	Benzopyranic ring	$(C{=}C)_n$ group ($n = 0, 1, 2$)	$PhNMe_2$ group	Benzopyranic ring	$(C{=}C)_n$ group ($n = 0, 1, 2$)	$PhNMe_2$ group
1a	87	—	13	32	—	68
2a	92	—	8	62	—	38
2c	85	13	2	43	18	39
2d	78	22	0	33	33	34
3a	95	—	5	68	—	32
3c	89	10	1	51	17	32
3d	84	16	0	38	33	29

Table 5 Experimental EFISHG and theoretical PM3 hyperpolarizability values according to the X convention and the angle between the dipole moment and hyperpolarizability vectors (PM3)[a]

Compound	$\beta_\mu(2\omega)_{EFISHG}$	$\beta_\mu(0)_{PM3/RHF/FF}$	$\|\boldsymbol{\beta}(0)\|_{PM3/RHF/FF}$	$\phi(\boldsymbol{\beta}_{PM3}, \boldsymbol{\mu}_g^{PM3})/^\circ$
1a	14	18	20	29
2a	27	32	38	32
2c	59	50	58	30
2d	102	68	77	28
2e	33	—	—	—
3a	36	31	38	35
3c	58	48	58	34
3d	50	66	77	32

[a] $\lambda_{laser} = 1907$ nm; β values given in units of 10^{-30} esu.

this reference are absorbed into the definition of the hyperpolarizability. Our EFISHG measurements[28,13f] use this convention.

The MOPAC 6.0 finite-field subroutine acknowledges conventions T and B and therefore provides the computed values for the static β_{ijk} components as β^T and β^B. For SHG frequency-dependent hyperpolarizabilities $\beta^X(2\omega) = \beta^B(2\omega)/2$, but this relationship is no longer valid in the static limit; it can be easily derived from the definitions of the X and B conventions that $\beta^X(0) = \beta^B(0)$.

Recently, a new value of the d_{11} quartz standard coefficient (0.3 pm V^{-1} at 1064 nm)[33,34] was reported (old value: 0.5 pm V^{-1} at 1064 nm).[35,36] We have assumed that the ratio between these two values (*e.g.*, 0.6 at 1064 nm) remains unchanged at 1340 and 1907 nm; consequently, we have chosen to adopt the new reference and the experimental values reported here (Tables 5, 6 and 7) have been thus scaled by 0.6. As mentioned by a referee, whether the 'new' value is more accurate that the 'old' one is still open to discussion; but readers should also be aware that from the start of the EFISHG technique, another d_{11} value (0.33 pm V^{-1}) was also used by different teams.[37]

Comparison of the experimental quadratic hyperpolarizabilities of molecules **1a**, **3a** and **3c** with those containing more usual withdrawing groups but having the same conjugated-system length (see Table 6) clearly show that the benzopyranic group reduces the increase of β with regards to a simple ethylenic unit. This result might originate from the ICT location within the benzopyranic ring, which limits the ICT along the conjugated system.

Then Table 5 shows satisfactory agreement between the trends of the experimental laser-frequency dependent and calculated PM3 $\beta_\mu(0)$ hyperpolarizabilities except for compound **3d**. Within the same convention, differences between calculated values and measured ones increase with the size of molecules. Many explanations can then be proposed: First, $\beta_\mu(2\omega)_{EFISHG}$ and $\beta_\mu(0)_{PM3}$ are both vectorial components of the first hyperpolarisability projected along the permanent dipole moment, but $\beta_\mu(2\omega)_{EFISHG}$ is laser-frequency dependent. Then, as these molecules have a large conjugated path and the solvent used for these measurements is polar [μ_g(chloroform) = 1.1 D], solvent effects on the β value probably increase with the size of the π-electron system in D–T–A molecules.[38a] Frequency dispersion effects always increase the value of β; solvent effects are more fickle and may increase or decrease the β value, depending on the molecular structure and solvent used.[38b]

From a different point of view, it may be necessary to use an extended basis set in *ab initio* calculations to reach quantitative results (these methods have not been used for molecules **1**–**3** in view of their large size).[39] Semiempirical methods have been parametrized using mainly small molecules (from 5 to 20 atoms) and valence atomic orbitals only were taken into account. It might be expected that the incidence of such limitations (namely, the valence basis set and the parameters) as to the computed properties will tend to increase with the molecule size.

A traditional way to infer static βs from $\beta_\mu(2\omega)_{EFISHG}$ [for comparison with calcuated values of $\beta_\mu(0)_{PM3}$] consists in dividing $\beta_\mu(2\omega)_{EFISHG}$ by the dispersion factor $F(\omega, \omega_{eg})$, obtained from the so-called two-level model,[40,41] namely

$$\beta_{zzz}(2\omega) = \frac{3(\mu_{ge}^z)^2(\mu_e^z - \mu_g^z)}{2\hbar^2\omega_{ge}^2} F(\omega, \omega_{ge})$$

$$= \beta_{zzz}(0)F(\omega, \omega_{ge})$$

$$F(\omega, \omega_{ge}) = \frac{1}{\left(1 - 4\frac{\omega^2}{\omega_{ge}^2}\right)\left(1 - \frac{\omega^2}{\omega_{ge}^2}\right)}$$

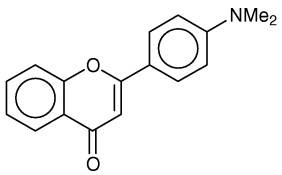
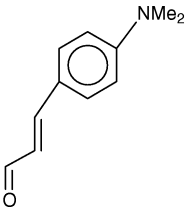
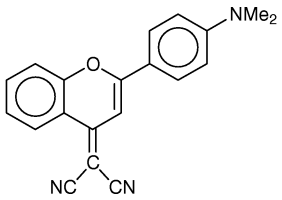
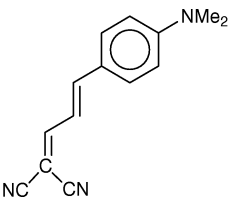
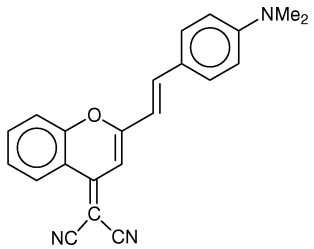
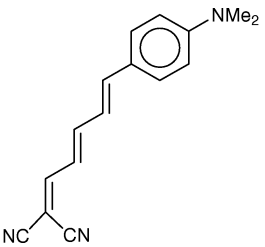
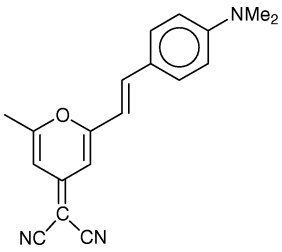
where $\beta_{zzz}(2\omega)$ is the component of $\beta_{ijk}(2\omega)$ calculated through the two-level model, ω is the laser frequency, ω_{ge} is the transition frequency, μ_{ge}^z is the transition dipole moment along the z axis, and $\mu_e^z - \mu_g^z$ is the difference between excited- and ground-state dipole moments along the z axis. When this dispersion term is used, all the approximations connected to this quantum two-level model-based equation are then implicitly assumed.‡ It means that the two-level equation is one-dimensional (consequently $\Delta\boldsymbol{\mu}_{ge}$, $\boldsymbol{\mu}_{ge}$ should be parallel) and only the ground and the first excited charge-transfer states can be taken into account in the calculation of the first hyperpolarizability.

The angles α between $\Delta\boldsymbol{\mu}_{ge}$ and $\boldsymbol{\mu}_{ge}$, obtained from CNDO/S-CIS calculations for the first $\pi \rightarrow \pi^*$-type transition with the highest oscillator strength, are: **1a**, 5°; **2a**, 45°; **2c**, 31°; **2d**, 23°; **3a**, 62°; **3c**, 41° and **3d**, 30°. These results show a decrease of α when the number of ethylenic units increases. At the same time, the $\boldsymbol{\mu}_{ge}$ and $\Delta\boldsymbol{\mu}_{ge}$ vectors tend to become parallel along the ethylenic unit chain axis. However, the *unidimensional* two-level model is clearly not adapted for molecules **1**–**3**. In the same way, the θ angles between $\Delta\boldsymbol{\mu}_{ge}$ and $\boldsymbol{\mu}_g$, derived from CNDO/S calculations, are: **1a**, 41°; **2a**, 53°; **2c**, 42°; **2d**, 36°; **3a**, 75°; **3c**, 58° and **3d**, 48°. These values also show a decrease of θ when the conjugated system length increases and evidence the inadequacy of the *unidimensionality* of the two-level model.

EFISHG measurements were also performed at 1.34 μm for compounds **2c** and **2d** (Table 7). Zero-frequency values [$\beta_\mu(0)_{EFISHG}^{2\ levels}$] are different from the zero-frequency values obtained from EFISHG measurements operating at 1.9 μm. This discrepancy is higher than the experimental uncertainty (±20%). One may first want to ascribe the lack of consistency of the $\beta_\mu(0)_{EFISHG}^{2\ levels}$ values to the electronic $\gamma^e(-2\omega;\ \omega,\ \omega,\ 0)$ cubic contribution, which might have been wrongly neglected in the experimental determination of $\beta_\mu(2\omega)_{EFISHG}$. This

‡ A CNDO/S-CIS/sum-over-states calculation of β, taking into account an increasing number of excited states, has been performed. This study has evidenced that the first $\pi \rightarrow \pi^*$ transition represents the most important contribution to the final β value for the compound series **2**–**3**.[13e]

Table 6 EFISHG $\beta_\mu(2\omega)$ at 1907 nm (X convention) and λ_{max} measured in chloroform

Compound		$\beta_\mu(2\omega)_{EFISHG}$ /10^{-30} esu	λ_{max}/nm
	**1a**	14	367
		27[a,b]	384[a]
	**3a**	36	464
		74[a,b]	486[a]
	**3c**	58	502
		147[a,b]	520[a]
		45[c,d]	468[c]

[a] Ref. 7(*g*). [b] The β values of ref. 7(*g*) have been multiplied by (3/2 × 0.6) to be consistent with the X convention. [c] Ref. 15(*b*). [d] The β value of ref. 15(*b*) has been scaled by one-half to be consistent with the X convention.

Table 7 Experimental EFISHG hyperpolarizability values of 2-(4′-dimethylaminophenylethylenyl)-4*H*-1-benzopyran-4-thione (**2c**) and 2-(4′-dimethylaminophenylbutadienyl)-4*H*-1-benzopyran-4-thione (**2d**) measured at 1.9 μm or 1.34 μm and their respective zero-frequency two-level values[a]

	1.34 μm		1.9 μm	
	$\beta_\mu(2\omega)_{EFISHG}$	$\beta_\mu(0)^{2\ levels}_{EFISHG}$	$\beta_\mu(2\omega)_{EFISHG}$	$\beta_\mu(0)^{2\ levels}_{EFISHG}$
2c	168	69	59	41
2d	287	118	102	69

[a] β values are given in units of 10^{-30} esu within the X convention.

assumption may be valid for small nonlinear chromophores but fails for larger molecules with extended π-electron systems whereby $\gamma^e(-2\omega;\ \omega,\ \omega,\ 0)$ increases with conjugation length faster than β. THG (third harmonic generation) measurements $[\gamma^{THG}_{1.9\ \mu m}(-3\omega;\ \omega,\ \omega,\ \omega)]$ were performed at 1.9 μm. We can approximate $\gamma^e_{1.34\ \mu m}(-2\omega;\ \omega,\ \omega,\ 0)$ by the experimental $\gamma^{THG}_{1.9\ \mu m}(-3\omega;\ \omega,\ \omega,\ \omega)$ value in view of the proximity of the 2ω and 3ω harmonic frequencies, both being far from resonance.[42] The third-order contribution is 21% (17%) of the $\beta_\mu(2\omega)_{EFISHG}$ value at 1.34 μm for **2c** (**2d**). These results reinforce the validity of our initial assumption in which the cubic contribution to the estimation of the first hyperpolarizability $\beta_\mu(2\omega)_{EFISHG}$ from experiments is neglected.

A more serious issue is the inadequacy of the two-level dispersion term $F(\omega, \omega_{ge})$, which has been applied to infer a static β from experiments in the case of molecules **2c** and **2d**. Consequently, direct comparison between $\beta_\mu(0)^{2\ levels}_{EFISHG}$ (calculated from a quantum two-level one-dimensional term) and $\beta_\mu(0)_{PM3}$ values may not be valid. Moreover, there is an angular deviation φ between the dipole moment $\boldsymbol{\mu}^{PM3}_g$ and the vector component $\boldsymbol{\beta}(0)_{PM3}$ of the first-order hyperpolarizability close to 30° (Table 7) for all molecules. The modulus of the vector component of the experimental tensor β should be increased by 15% as compared to the experimental β_μ value from EFISHG, assuming a one-dimensional mode along μ.

The theoretical $\|\boldsymbol{\beta}(0)_{PM3}\|$ values for series **2** and **3** being identical, it may be concluded that the thiocarbonyl and dicyanoethylene groups induce analogous second-order nonlinear properties. $\beta_\mu(2\omega)_{EFISHG}$ values show the same trend, within experimental error, except for compound **3d**, which has a value clearly lower than the corresponding value for **2d** and even lower than for **3c**. This specificity of compound **3d** remains unaccounted for at this stage.

Conclusion

The aim of this work was to study benzopyranic push–pull molecules for first-order nonlinear optics. To this purpose eight molecules have been synthesized and characterized and two X-ray structure determinations have been performed. UV/VIS spectra, ground-state dipole moments and first-order hyperpolarizability values have been determined for the full series of molecules. These experimental data have been completed with theoretical semiempirical calculations that have, in particular, permitted the angle between dipole moment and β vectors, internal charge transfer, Δμ and the transition dipole moments upon the first energy-allowed charge-transfer transition to be determined.

4*H*-1-benzopyran-4-thioxo-2-yl and 4*H*-1-benzopyran-4-(ylidene malononitrile)-2-yl substituents are characterized by larger hyperpolarizabilities than 4*H*-1-benzopyran-4-oxo-2-yl at the expense of molecular transparency. Such electron-withdrawing substituents induce a complex internal charge transfer as a result of excitation. This unusual ICT seems to limit β enhancement in relation to π-electron system

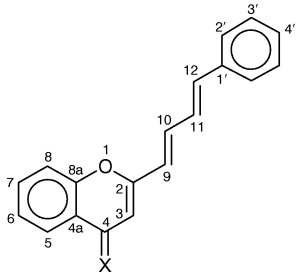
lengthening with regards to usual acceptor substituents (such as dicyanomethylene). A one-dimensional two-level model does not seem to be adapted for molecules **1**–**3** and the use of the two-level dispersion factor to extract the β zero frequency then clearly becomes inadequate. PM3 finite-field calculations are able to reproduce satisfactorily the evolution of experimental hyperpolarizability values within experimental errors.

Experimental

^1H and ^{13}C NMR data were collected in $CDCl_3$ with a Jeol FX 90Q spectrometer operating at 89.55 and 22.50 MHz, respectively. Chemical shifts δ are reported with the usual abbreviations relative to TMS as an internal standard. Coupling constants are in Hz. The atom numbering used for NMR data is given in Scheme 2. IR spectra were determined on a Shimadzu IR 435 spectrometer (ν_{max} in cm^{-1}). Mass spectra were recorded on a Finnigan Mat-Incos 500 EX spectrometer using chemical ionization with methane or ammonia. Thin-layer chromatography was performed on Merck 60H plates precoated with silica F_{254}. Chromatographic separations were carried out on glass plates coated with silica gel (Merck 60 G; 1 mm thickness). Melting points were determined on a Kofler heating bench. Elemental analyses were performed by the Service Central d'Analyses du CNRS (Vernaison, France). Compounds **1b**[16,43] and **2b**[17,18a,44] were prepared according to literature procedures.

Syntheses

2-(4′-Dimethylaminophenyl)-4*H*-1-benzopyran-4-one, 1a. 4-$Me_2NC_6H_4COCl$ was prepared from the corresponding carboxylic acid and cyanuric chloride[45] and then was used in the acylation of commercial 2-hydroxyacetophenone in pyridine, leading to 2-(4′-dimethylaminobenzoyloxy)acetophenone **4**. Recrystallization from ethanol gave yellow crystals, mp 122 °C. Yield: 61%. ^1H NMR: δ 8.07 and 6.71 (2d, 4H, C_6H_4, $^3J = 9.1$); 7.96–7.19 (m, 4H, ArH); 3.09 [s, 6H, $N(CH_3)_2$]; 2.54 (s, 3H, $COCH_3$). IR: ν 1720 and 1680. Compound **4** was submitted to a Baker–Venkataraman transposition[16] in DMF, leading to the expected diketone 2-$HOC_6H_4COCH_2COC_6H_4N(CH_3)_2$(p) **5**. Recrystallization from toluene gave orange crystals, mp 180 °C. Yield: 72%. ^1H NMR: δ 16.01 (s, 1H, enol form); 12.30 (s, 1H, ArOH); 7.86 and 6.70 (2d, 4H, C_6H_4, $^3J = 9.4$); 7.72–6.79 (m, 4H, ArH); 6.71 (s, 1H, enol form); 3.08 [s, 6H, $N(CH_3)_2$]. IR: ν 3360 and 1680. A solution of **5** (8 g) and concd. H_2SO_4 (2.3 ml) in CH_3CO_2H (60 ml) was refluxed for 5 h. After cooling the reaction mixture was poured on ice (300 g). After ice had melted the precipate was filtered and washed with water. The product was recrystallized from toluene to afford yellow crystals of **1a**, mp 162 °C. Yield: 78%. ^1H NMR: δ 8.24–8.16 (dd, 1H, ArH, $^3J = 8$, $^4J = 2$); 7.80–6.73 (2d, 4H, C_6H_4, $^3J = 9.1$); 7.63–7.19 (m, 3H, ArH); 6.69 (s, 1H, H_3); 3.05 [s, 6H, $N(CH_3)_2$]. ^{13}C NMR: δ 177.5 (C_4=O); 163.7 (C_2); 155.6 (C_{8a}); 151.8 ($C_{4'}$), 132.6 (C_7); 127.0 ($C_{2'}$), 124.9 (C_5); 124.2 (C_6); 123.6 (C_{4a}); 117.4 (C_8 and $C_{1'}$); 111.0 ($C_{3'}$); 103.5 (C_3); 39.4 [$N(CH_3)_2$]. Off-resonance: 132.6 (d, C_7, $^1J = 46$); 127.0 (d, $C_{2'}$, $^1J = 42$); 124.2 (d, C_6, $^1J = 46$); 117.4 (d, C_8, $^1J = 46$); 111.0 (d, $C_{3'}$, $^1J = 39$); 103.5 (d, C_3, $^1J = 40$); 39.4 [q, $N(CH_3)_2$, $^1J = 21$]. IR: ν 1630. MS: *m/z* 266 (100) $[M + H]^+$; 267 (16). *M* calcd. 265.110. Anal. calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.22; H, 5.73; N, 5.16.



Scheme 2 Atom numbering of benzopyran, substituted in the 2-position, used in NMR spectra

2-(4′-Dimethylaminophenyl)-4*H*-1-benzopyran-4-thione, 2a. A mixture of **1a** (5 mmol) and P_4S_{10} (0.8 g) in toluene (90 ml) was refluxed for 4 h. The hot mixture was filtered and the solid washed with hot toluene. After evaporation of the toluene the product was chromatographed on silica with chloroform as eluent ($R_f = 0.5$). Recrystallization from ethanol gave red-purple crystals, mp 181 °C. Yield: 37%. ^1H NMR: δ 8.64 (d, 1H, ArH, $^3J = 8$); 7.87–6.72 (2d, 4H, C_6H_4, $^3J = 9.1$); 7.75 (s, 1H, H_3); 7.70–7.28 (m, 3H, ArH); 3.07 [s, 6H, $N(CH_3)_2$]. ^{13}C NMR: δ 199.3 (C_4=S); 155.8 (C_2); 152.7 (C^*_{8a}); 151.5 ($C^*_{4'}$); 133.3 (C_7); 129.4 (C_{4a}); 128.8 (C_5); 128.3 ($C_{2'}$); 125.6 (C_6); 118.0 (C_3 and C_8); 116.7 ($C_{1'}$); 111.7 ($C_{3'}$); 40.0 [$N(CH_3)_2$]. IR: ν 1160 (C=S). MS: *m/z* 282 (100) $[M + H]^+$; 284 (5). *M* calcd. 281.087. Anal. calcd. for $C_{17}H_{15}NOS$: C 72.57; H 5.37; N 4.98; S 11.40. Found: C 72.94; H 5.39; N 4.91; S 11.12.

[2-(4′-Dimethylaminophenyl)-4*H*-1-benzopyran-4-ylidene]-malononitrile, 3a. A mixture of **2a** (2.5 mmol), malononitrile (2.5 mmol) and HgO (2.5 mmol) in ethanol (15 ml) was refluxed for 6 h. The hot mixture was filtered and the solid washed with hot ethanol. After ethanol evaporation the product was chromatographed on silica with chloroform as eluent ($R_f = 0.35$). Recrystallization from ethanol gave red crystals, mp 242 °C. Yield: 96%. ^1H NMR: δ 8.90 (d, 1H, ArH_5, $^3J = 8$); 7.82–6.71 (2d, 4H, C_6H_4, $^3J = 9.1$); 7.73–7.29 (m, 3H, ArH); 7.12 (s, 1H, H_3); 3.10 [s, 6H, $N(CH_3)_2$]. ^{13}C NMR: δ 158.9 (C_4); 153.1 (C_2); 152.9 (C_{8a}); 152.5 ($C_{4'}$); 134.0 (C_7); 128.3 and 128.2 ($C_{2'}$); 125.7 (C_5 and C_6); 118.7 and 118.6 (C_8); 118.3, 116.8, 116.6 and 111.7 ($C_{3'}$); 100.0 (C_3); 40.1 [$N(CH_3)_2$]. IR: ν 2210. MS: *m/z* 300 (13); 314 (100) $[M + H]^+$; 331 (18) $[M + NH_4]^+$. *M* calcd. 313.122. Anal. calcd: C 76.66; H 4.82; N 13.41. Found: C 76.15; H 4.89; N 13.49.

2-(4′-Dimethylaminophenylethenyl)-4*H*-1-benzopyran-4-thione, 2c. A mixture of **2b** (1 g, 5.67 mmol), 4-(dimethylamino)-benzaldehyde (5.67 mmol) and piperidine (0.56 ml) was dissolved in a minimal volume of ethanol. The solution was heated at 30–35 °C for 24 h. After cooling to room temperature, the mixture was filtered and the precipitate was chromatographed on silica with chloroform as eluent ($R = 0.40$). Recrystallization from ethanol gave dark grey crystals, mp 189 °C (lit.[18a] 176 °C). Yield: 93%. ^1H NMR: δ 8.58 (d, 1H, ArH, $^3J = 8$); 7.75–7.27 (m, 5H, ArH, 1H, CH=); 7.23 (s, 1H, H_3); 6.69 (d, 2H, C_6H_4, $^3J = 8.9$); 6.49 (d, 1H, CH=, $^3J_{trans} = 15.9$); 3.04 [s, 6H, $N(CH_3)_2$]. ^{13}C NMR: δ 200.1 (C_4=S); 154.8 (C_2); 151.7 (C^*_{8a}); 151.3 ($C^*_{4'}$); 139.5 (C_{10}); 133.5 (C_7); 129.7 ($C_{2'}$); 128.6 (C_5); 125.5 (C_6); 123.1 (C_{4a}); 122.6 (C_3); 117.9 (C_8); 113.6 (C_9); 111.9 ($C_{3'}$); 40.1 [$N(CH_3)_2$]. Off-resonance: 139.5 (d, C_{10}, $^1J = 41$); 133.5 (d, C_7, $^1J = 46$); 129.7 (d, $C_{2'}$, $^1J = 43$); 128.6 (d, C_5, $^1J = 48$); 125.5 (d, C_6, $^1J = 44$); 122.6 (d, C_3, $^1J = 44$); 117.9 (d, C_8, $^1J = 46$); 113.6 (d, C_9, $^1J = 36$); 111.9 (d, $C_{3'}$, $^1J = 40$); 40.1 [q, $N(CH_3)_2$, $^1J = 23$]. IR: ν 1340; 1140; 965. MS: *m/z* 308 (100) $[M]^+$. *M* calcd: 307.103. Anal. calcd. for $C_{19}H_{17}NOS$: C 74.24; H 5.57; N 4.56; S 10.43. Found: C 73.90; H 5.23; N 4.20; S 10.51.

2-(4′-Dimethylaminophenylbutadienyl)-4*H*-1-benzopyran-4-thione, 2d. The condensation of **2b** and 4-(dimethylamino)cinnamaldehyde was performed following the same procedure as that described for **2c**. Purification by chromatography on silica ($R_f = 0.37$ in chloroform) and then recrystallization from chloroform–petroleum ether gave dark grey crystals, mp 177 °C. Yield: 48%. ^1H NMR: δ 8.55 (d, 1H, ArH_5, $^3J = 8$); 7.67–

Table 8 Crystal structure and refinement data for compounds **2a** and **2c**

Compound	$C_{17}H_{15}SON$	$C_{19}H_{17}SON$
M	281.38	307.42
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.785(4)	12.194(2)
b/Å	10.233(11)	9.949(2)
c/Å	13.185(3)	14.117(3)
β/°	103.22(2)	112.27(2)
U/Å^3	1416(2)	1585(3)
Z	4	4
$d_{calcd.}$/g cm^{-3}	1.319	1.288
Crystal dimensions/mm	0.7 × 0.4 × 0.2	0.4 × 0.3 × 0.1
T/K	293	293
μ(MoKα)/cm^{-1}	2.124	1.955
h, k, l limits	0, 12/0, 12/−15, 15	0, 14/0, 11/−16, +15
No reflections:		
unique	2570	2642
$I \geqslant 3\sigma(I)$	1636	1409
R_{int}	0.030	0.039
No variables	241	268
R^a, $R_w{}^b$	0.040, 0.045	0.037, 0.040
G.O.F^c	1.642	1.407
Δ/σ	0.57	0.01
Δρ/e Å^{-3}	0.300	0.449

^{a} $R = \Sigma[|F_o| - |F_c|]/S|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ $w = 4F_o^2/[\sigma^2(I) - (0.04|F_o|^2)^2]$. ^{c} Goodness-of-fit (G.O.F) $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs.} - N_{var.})]^{\frac{1}{2}}$.

7.36 (m, 5H, ArH, 1H, CH=); 7.16 (s, 1H, H_3); 6.80 (d, 1H, CH=, $^3J_{trans} = 14.8$); 6.70 (d, 1H, CH=, $^3J_{trans} = 15.1$); 6.16 (d, 2H, C_6H_4, $^3J = 9.1$); 6.16 (d, 1H, CH=, $^3J_{trans} = 15.1$); 3.01 [s, 6H, $N(CH_3)_2$]. IR: ν 1150; 960. MS: *m/z* 308 (10); 334 (100) $[M + H]^+$; 336 (11). *M* calcd: 333.119.

2-(Ferrocenylethenyl)-4*H*-1-benzopyran-4-thione, 2e. The condensation of **2b** and ferrocenecarboxaldehyde was performed following the same procedure as that described for **2c**. Purification by chromatography on silica ($R_f = 0.49$ in chloroform) and then recrystallization from chloroform–petroleum ether gave dark brown crystals, mp 174 °C. Yield: 62%. ^{1}H NMR: δ 8.57 (d, 1H, ArH_5, $^3J = 8$); 7.68–7.27 (m, 3H, ArH, 1H, CH=); 7.19 (s, 1H, H_3); 6.32 (d, 1H, CH=, $^3J_{trans} = 15.7$); 4.58 (d, 2H, η^5-C_5H_4, $^3J = 1.8$); 4.51 (d, 2H, η^5-C_5H_4, $^3J = 1.8$); 4.20 (s, 5H, η^5-C_5H_5). ^{13}C NMR: δ 200.9 (C_4=S); 153.5 (C_2); 151.3 (C_{8a}); 140.2 (C_{10}); 133.6 (C_7); 129.8 (C_{4a}); 128.6 (C_5); 125.7 (C_6); 122.2 (C_3); 118.0 (C_8); 116.3 (C_9); 80.1 ($C_{1'}$); 71.3 ($C_{2'}$); 69.8 (η^5-C_5H_5); 68.4 ($C_{3'}$). Off-resonance: 140.2 (d, C_{10}, $^1J = 42$); 133.6 (d, C_7, $^1J = 48$); 128.6 (d, C_5, $^1J = 49$); 125.7 (d, C_6, $^1J = 44$); 122.2 (d, C_3, $^1J = 45$); 118.0 (d, C_8, $^1J = 46$); 116.3 (d, C_9, $^1J = 37$); 71.3 (d, $C_{2'}$, $^1J = 35$); 69.8 (d, η^5-C_5H_5, $^1J = 34$); 68.3 (d, $C_{3'}$, $^1J = 34$). IR: ν 1620; 1155; 965. MS: *m/z* 371 (7) $[M - H]^+$; 373 (100) $[M + H]^+$; 374 (21); 375 (13). *M* calcd: 372.027. Anal. calcd. for $C_{21}H_{16}OSFe$: C 67.76; H 4.33; S 8.61; Fe 15.00. Found: C 67.94; H 4.42; S 8.18; Fe 15.34.

[2-(4′-Dimethylaminophenylethenyl)-4*H*-1-benzopyran-4-ylidene]malononitrile, 3c. The conversion of **2c** into **3c** was carried out following the same procedure as that described for **3a**. Purification by chromatography on silica ($R_f = 0.35$ in chloroform) and then recrystallization from ethanol gave dark purple crystals, mp 212 °C. Yield: 59%. ^{1}H NMR: δ 8.87 (d, 1H, ArH, $^3J = 8$); 7.80–7.20 (m, 5H, ArH, 1H, CH=); 6.65 (d, 2H, C_6H_4, $^3J = 8.9$); 6.70 (s, 1H, H_3); 6.51 (d, 1H, CH=, $^3J_{trans} = 15.7$); 3.05 [s, 6H, $N(CH_3)_2$]. ^{13}C NMR: δ 159.0 (C_2); 152.1 ($C_{4'}$); 139.9 (C_{10}); 134.2 (C_7); 130.0 ($C_{2'}$); 125.9 (C_5); 125.6 (C_6); 122.6 (C_{4a}); 119.0 ($C_{1'}$); 118.1 (C_8); 112.1 ($C_{3'}$); 105.3 (C_3); 40.2 [$N(CH_3)_2$]. IR: ν 2195; 960. MS: *m/z* 340 (100) $[M + H]^+$; 341 (16); 342 (5). *M* calcd. 339.137.

[2-(4′-Dimethylaminophenylbutadienyl)-4*H*-1-benzopyran-4-ylidene]malononitrile, 3d. The conversion of **2d** into **3d** was carried out following the same procedure as that described for **3a**. Purification by chromatography on silica ($R_f = 0.30$ in chloroform) and then recrystallization from ethanol gave dark purple crystals, mp 231 °C. Yield: 32%. IR: ν 2205; 960. MS: *m/z* 366 (100) $[M + H]^+$; 367 (16); 368 (5). *M* calcd: 365.153.

Optical studies

Electronic absorption spectroscopic data were collected with a Varian DMS 200 UV/VIS spectrophotometer using a 1 cm quartz cell and spectroscopic grade chloroform solvent. Dipole moments were measured in $CHCl_3$ following the Guggenheim mthod.[46,13f] Cubic and quadratic hyperpolarizabilities were determined in chloroform solutions respectively by third-harmonic generation[47,7f] and electric-field-induced second-harmonic generation[28,13f] experiments at 1.9 μm using a H_2 Raman cell pumped by a Q-switched Nd^{3+} : YAG laser at 1.06 μm. Complementary EFISHG measurements were performed at 1.34 μm using a Q-switched, mode-locked Nd^{3+} : YAG laser.

X-Ray crystal structure analysis

Crystals of $C_{17}H_{15}SON$ (**2a**) and $C_{19}H_{17}SON$ (**2c**) were mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-crystal-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The intensities were collected by $\theta-2\theta$ scans up to $2\theta = 50°$. Three standard reflections were measured every hour and reveal no fluctuations in intensities. Lorentz polarization corrections were applied. The cell dimensions have been refined by least-squares methods from setting angles of 25 centered reflections. The crystal data are summarized in Table 8.

The structures were solved by direct methods and successive Fourier difference synthesis and were refined by weighted anisotropic full-matrix least-squares methods. Refinements were carried on positional and anisotropic (β_{ij}) thermal parameters for all non-hydrogen atoms, the H atoms were refined isotropically. Scattering factors and corrections for anomalous dispersion were taken from ref. 48. The molecular and crystal structure illustrations were drawn with ORTEP.[49] All the calculations were performed on a Micro Vax 3100 computer using the MOLEN programs.[50]

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