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Isophorone- and pyran-containing NLO-chromophores: a comparative study

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ABSTRACT

A series of merocyanines containing isophorone or pyran rings in the spacer have been synthesized. For a given pair of donor and acceptor groups, the isophorone derivatives show higher second-order optical nonlinearities, but lower thermal stabilities. The first NLO-chromophores endowed with a dihydropyran fragment in the spacer have also been prepared and studied.

Current achievements in the field of second-order nonlinear optical (NLO) materials are the result of the efforts carried out to establish structure/NLO–activity relationships, ultimately seeking to optimize the microscopic molecular nonlinearity (β) and the macroscopic (bulk) NLO response of such materials.[1–3] To this end, conjugated push–pull compounds, where an electron donor and an electron acceptor are linked through a conjugated spacer (D–π–A), have been extensively studied. While a great deal of research has been devoted in the last two decades to the development of new donors, acceptors and spacers, the effect of structural perturbations within these subunits (such as the modification of atoms or substituents) on the optical properties of D–π–A chromophores is much less known, there being only scant reports in the literature addressing this interesting question, from both the theoretical[4,5] and the experimental[6,7] points of view. Most of the hitherto carried out work along this line has focused on the replacement of acyclic polyenic spacers, suffering from limited thermal or photochemical stabilities, by carbo- or heterocyclic fragments. To this end, isophorone-derived moieties have been widely used as carbocyclic spacers since their introduction generally leads to increased thermal stabilities[8–10] of the corresponding chromophores (although exceptions are known).[11] A structurally related six-membered heterocyclic ring which has enjoyed widespread popularity is 4*H*-pyran-4-ylidene, since it has afforded not only one- and two-dimensional NLO-chromophores,[12–14] but also red dopants for organic light-emitting diodes (OLEDs).[15]

Comparisons between isophorone- and pyran-containing chromophores have usually focused on synthetic advantages or luminescence properties,[16–18] but their relative merits as spacers in second-order NLO-chromophores have not been previously discussed, except for one report where only two compounds (one of each family) were compared.[19] In this Letter, we disclose the effect that the presence of isophorone or 4*H*-pyran-4-ylidene rings has on the optical properties and thermal stabilities of D–π–A compounds endowed with aromatic or proaromatic donor groups and provide a rationale for the observed trends based on theoretical calculations. Moreover, we report the first merocyanines with a 2,3-dihydro-4*H*-pyran-4-ylidene moiety which, to the best of our knowledge, has not been exploited in the NLO field.

Five different isophorone derivatives (**12** and **13**) and their exactly comparable pyran counterparts (**14** and **15**) have been chosen for this study, as shown in Figure 1.

Compounds **13c**,[20] **14a**[21] and **14b**[14] are known and were prepared as previously described. The remaining compounds were synthesized as shown in Scheme 1. Thus, Knoevenagel reactions of isophorone derivative **1**[22,23] with aldehydes **2**, **3**[14,24] and iminium salt **4**[25] afforded compounds **12a**,[26] **12b** and **12c**, respectively. Similarly, compound **14c** was prepared by condensation of pyran derivative **7**[27] with aldehyde **8**.[28] Target thiobarbituric derivatives (**13a**[26] and **15a, c**) were analogously synthesized starting from acceptors **5**[29] and **6**,[14] respectively.

The experimentally determined linear and nonlinear optical properties of the studied compounds are collected in Table 1, inspection of which reveals several trends. Thus, in their UV–vis spectra pyran derivatives show blue-shifted absorptions relative

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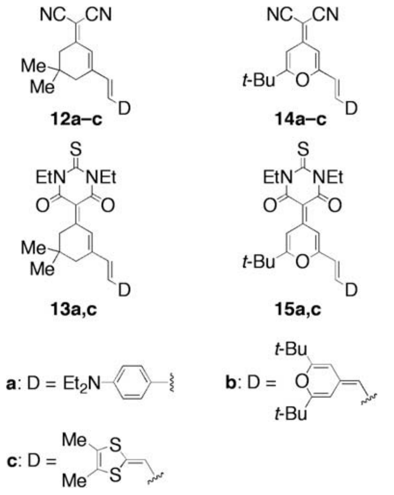
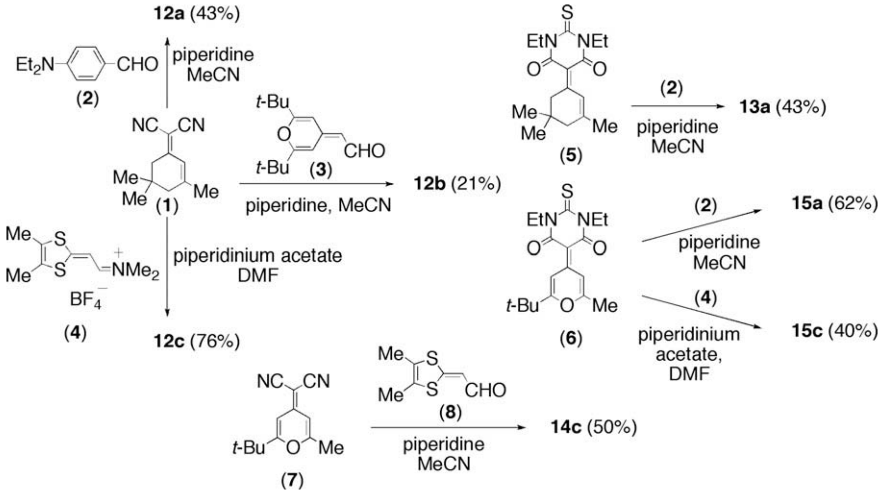


Figure 1. Isophorone and pyran derivatives studied.

to those of their isophorone analogues, both in dichloromethane and in DMSO. The second-order nonlinear optical properties (measured by the electric field-induced second harmonic generation (EFISH) technique) parallel this trend, since a comparison of the corresponding μβ or $\mu\beta_0$ values (extrapolated at zero frequency using the two-level model) reveals the higher nonlinearities of compounds **12** and **13**, when compared to those of **14** and **15**, respectively.

In order to understand the linear and nonlinear optical properties of both series of compounds, Coupled-perturbed Hartree–Fock (CPHF) and TDDFT calculations have been carried out (Table 1). In particular, TDDFT provides the parameters involved in the two-level model since, in this approach $\beta_0 \propto \Delta\mu_{ge} f/E^3$, where $\Delta\mu_{ge}$ is the difference between the excited- and ground-state dipole moments (μ_e and μ_g, respectively), f is the oscillator strength and E is the excitation energy. It can be seen that TDDFT calculations correctly predict the observed hypsochromic shift on passing from isophorone to pyran derivatives. Moreover, this increase in E, together with the calculated decrease in f and in $\Delta\mu_{ge}$, is responsible for



Scheme 1. Synthesis of isophorone- and pyran-based chromophores.

Table 1
Experimental and calculated[a] optical properties and thermal stabilities of **12–15**

Compound	λ_{max} (log ε)[d]	λ_{max}[e]	μβ[f]	$\mu\beta_0$[g]	CPHF[b]		TDDFT[c]			T_d[j]
					μβ	$\mu\beta_0$	E[h]	f	$\Delta\mu_{ge}$[i]	
12a	519 (4.49)	538	1150	750	1477	1192	2.67	1.35	19.8	288
12b	561 (4.68)	579	1430	850	2007	1434	2.64	1.86	8.85	257
12c	560 (4.56)	569	1590	950	1242	940	2.59	1.31	16.2	258
13a	594 (4.69)	620[k]	2500	1410	1789	1387	2.46	1.56	17.6	236
13c	638 (4.50)	661	2315	1135	1655	1190	2.39	1.61	14.2	181
14a	478 (4.57)	498	889	623	843	702	2.88	1.27	14.6	341
14b	519 (4.72), 558 (sh)	526	1070	698[l]	612	416	2.78	1.57	2.13	293
14c	518 (4.47)	530	570	370	462	340	2.77	1.18	10.7	269
15a	537 (4.70)	553	1220	765	747	597	2.69	1.35	12.9	308
15c	575 (4.62)	585	1080	623	364	225	2.57	1.33	11.5	257

[a] On B3P86/6-31G* geometries.
[b] CPHF/6-31G* level. μβ and $\mu\beta_0$ values in 10^{-48} esu.
[c] B3P86/6-31G* level.
[d] In nm, measured in CH_2Cl_2.
[e] In nm, measured in DMSO.
[f] In 10^{-48} esu, measured in CH_2Cl_2 at 1907 nm. Experimental accuracy: ±10%.
[g] In 10^{-48} esu, determined using the two-level model.
[h] In eV.
[i] In Debyes.
[j] In °C, determined by thermogravimetric analysis.
[k] Decomposes.
[l] Approximate value (two low-lying transitions).

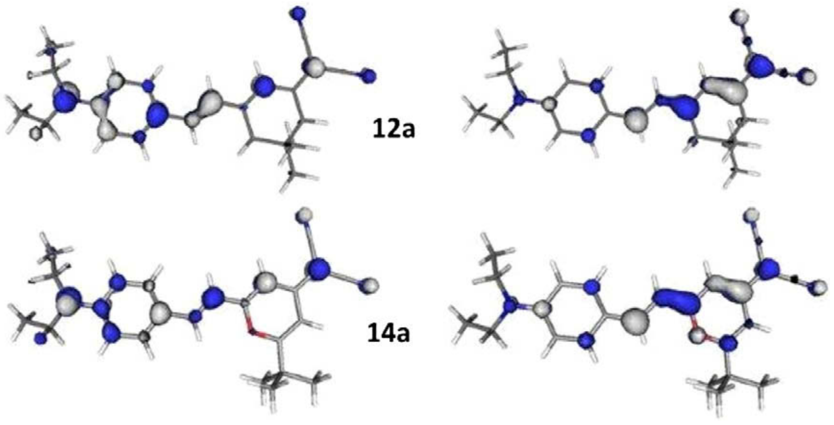


Figure 2. HOMO (left) and LUMO (right) of **12a** and **14a**.

the observed decrease in $\mu\beta_0$ values on passing from **12** and **13** to **14** and **15**.

As TDDFT calculations show that most of the hyperpolarizability (β) is accounted for by the low-lying HOMO→LUMO transition, it is useful to examine such orbitals to rationalize the observed trend in β on modifying the nature of the spacer. Thus, the frontier orbitals of compounds **12a** and **14a** are shown in Figure 2 and serve to exemplify the general behaviour of the herein reported compounds.

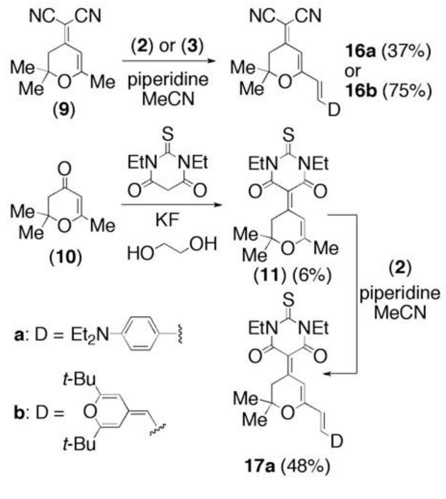
It can be seen that the HOMO of **14a** is topologically nearly identical to that of **12a** and that it shows a very small coefficient at the attachment point of the oxygen atom to the D–π–A system. This precludes π-donation from the heteroatom to the conjugated pathway so that the oxygen atom essentially acts as an inductive electron-withdrawing group. Both factors lie at the origin of the small decrease in the HOMO energy on going from isophorones to pyrans (**12a**: −5.89 eV; **14a**: −5.96 eV). On the other hand, the replacement of the carbocyclic by the heterocyclic ring has a much more noticeable effect on the corresponding LUMOs, since the LUMO of **14a** is destabilized by antibonding interactions between the **12a**-like LUMO and the oxygen (and C5 atom) of the pyran ring. This leads to a marked increase in the LUMO energies (**12a**: −3.20 eV; **14a**: −2.94 eV). Taken together, the frontier orbital energy trends are in excellent agreement with the excitation energies, which are calculated to increase on passing from isophorones to pyrans. Moreover, the high LUMO coefficients of the pyran moiety in **14a** are responsible for the lower $\Delta\mu_{ge}$ value for this compound since on excitation most of the charge-transfer goes into the pyran ring and not into the acceptor.[12,14] This feature gives rise to effective electron-transfer distances (calculated as $R = \Delta\mu_{ge}/e$, where e is the unit electronic charge),[30] which decrease as follows: **12a**: 4.1 Å; **14a**: 3.0 Å.

Therefore, TDDFT calculations explain why isophorone derivatives show larger $\mu\beta$ values than their pyran analogues, a behaviour which had been noted only once in the literature and for which no explanation was offered.[19] On the other hand, thermal stability is important for the incorporation of the chromophores into electrooptic devices and inspection of Table 1 reveals that compounds **14** and **15** are more thermally stable than their isophorone counterparts. Since the pairs of compounds studied bear the same donor and acceptor groups, it is clear that the pyran ring is more stable than the isophorone-related moiety.

Based on theoretical calculations (see below) we also reasoned that in order to achieve second-order NLO responses higher than those of **14** and **15**, a 2,3-dihydro-4*H*-pyran fragment could advantageously replace the pyran ring. To the best of our knowledge that fragment resulting from the formal replacement of a CH_2 group of the isophorone ring by an oxygen atom has not been exploited in the NLO field. To this end, we decided to prepare three dihydropyran derivatives, directly comparable to some of the studied isophorone and pyran compounds. As shown in Scheme 2, they were prepared from acceptor **9**[31] and the previously unreported compound **11**, in turn synthesized from **10**.[32]

The experimentally determined and calculated properties of **16a, b** and **17a** are gathered in Table 2 and comparison with Table 1 shows that these dihydropyrans show red-shifted λ_{max} values and generally higher $\mu\beta$ values than their pyran analogues (for **16b** and **14b** they are identical within the experimental error). These trends are in reasonably good agreement with CPHF calculations, which predicted an increase in $\mu\beta$ on passing from pyrans to dihydropyrans and with TDDFT results, predicting a decrease in the excitation energy and an increase of the oscillator strength when the pyran fragment is replaced by dihydropyran. Unfortunately, this improvement in nonlinearity relative to that of pyrans has an associated drawback, namely the limited thermal stability of compounds **16** and **17**, much lower than that shown by compounds **14** and **15** (and even by **12** and **13**).

Finally, it is noteworthy that our experimental results (isophorone compounds showing larger $\mu\beta$ values than their pyran or dihydropyran analogues) are in good agreement with a recent theoretical work[5] suggesting the detrimental effect on the second-order NLO properties of D–π–A systems caused by placing electron-donating substituents in 'even' positions of the conjugated chain



Scheme 2. Synthesis of dihydropyran-based chromophores.

Table 2
Experimental and calculated[a] optical properties and thermal stabilities of **16** and **17**

Compound	λ_{max} (log ε)[d]	λ_{max}[e]	$\mu\beta$[f]	$\mu\beta_0$[g]	CPHF[b]		TDDFT[c]			T_d[j]
					$\mu\beta$	$\mu\beta_0$	E[h]	f	$\Delta\mu_{ge}$[i]	
16a	516 (4.65)	529	1040	682	1175	965	2.79	1.50	16.0	170
16b	565 (4.75), 605 (sh)	616	1000	592[k]	974	688	2.72	1.93	3.21	117
17a	599 (4.81)	570, 614 (sh)	1850	1009	1269	1010	2.58	1.73	10.9	162

[a] On B3P86/6-31G* geometries.
[b] CPHF/6-31G* level. $\mu\beta$ and $\mu\beta_0$ values in 10^{-48} esu.
[c] B3P86/6-31G* level.
[d] In nm, measured in CH_2Cl_2.
[e] In nm, measured in DMSO.
[f] In 10^{-48} esu, measured in CH_2Cl_2 at 1907 nm. Experimental accuracy: ±10%.
[g] In 10^{-48} esu, determined using the two-level model.
[h] In eV.
[i] In Debyes.
[j] In °C, determined by thermogravimetric analysis.
[k] Approximate value (two low-lying transitions).

(in our structures, atom C3 of the isophorone ring occupies an 'even' position bearing a CH_2 substituent, which is formally replaced by an alkoxy group on passing to pyrans or dihydropyrans).

In summary, a comparative study of the optical properties of D–π–A chromophores bearing isophorone or pyran fragments in the spacer reveals that for a given pair of D/A moieties, λ_{max} and $\mu\beta$ values decrease in the order isophorone > pyran, this trend being supported by theoretical calculations. On the other hand, pyran derivatives are considerably more thermally stable than their isophorone counterparts. The NLO properties of merocyanines featuring a dihydropyran moiety in the spacer have also been studied for the first time and are compared to those of the two other series.

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Supplementary data

Supplementary data (general experimental methods, synthesis and characterization of new compounds, NMR and UV–vis spectra, NLO measurements and computational procedures) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.05.033.

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