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New one- and two-dimensional 4*H*-pyranylidene NLO-phores

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ABSTRACT

Dipolar, V-shaped compounds derived from 4*H*-pyranylidene-linked acceptors have been synthesized, and their linear and nonlinear optical properties (displaying $\mu\beta$ values up to 3000×10^{-48} esu) have been compared to those of analogous one-dimensional derivatives. The pyranylidene ring behaves strictly as a spacer, and not as a donor group.

Second-order nonlinear optical (NLO) materials are at the forefront of research in the fields of optoelectronics and photonics which, for the last two decades, have undergone a rapid growth, in both academia and industry, with applications in telecommunication and optical information processing, to name just a few. To that end, donor–π–acceptor (D–π–A) compounds with one-dimensional charge transfer (1D-CT) character have been widely studied, leading to the establishment of useful structure/property relationships.[1] Alternatively, dipolar two-dimensional (2D) molecules with multiple donor/acceptor arrangements, such as 'X-shaped'[2] and 'V-shaped' (also called 'Λ-shaped')[3] NLO-phores, have attracted a great deal of attention since they show improved hyperpolarizabilities (β) when compared to their 1D counterparts and also offer the possibility of circumventing the nonlinearity-transparency trade-off.[4]

Polyenic spacers are very effective at promoting the intramolecular charge transfer (ICT) that is necessary for the second-order NLO response, but NLO-phores with such subunits often show decreased thermal or (photo)chemical stability,[5] a drawback that can be overcome by (partly) incorporating the π system into alicyclic, aromatic, or heterocyclic structures.[1b,d] Thus, it is not surprising that 2,6-dialkyl-4*H*-pyran-4-one derivatives had been studied to prepare both 1D and 2D (D–A–D) NLO-phores, since the incorporation of that fragment allows the introduction of (i) one C=C bond of the spacer into a ring, (ii) strong acceptor groups on position 4 of that ring and (iii) the linking of one or two donor groups through Knoevenagel reactions of the 2- (and 6-) alkyl groups.[6]

In this Letter, we report the synthesis and characterization of two new 2,6-dimethyl-4*H*-pyran-4-ylidene derivatives bearing strong acceptors, **1e** and **1f**, and their reactions with *p*-diethylaminobenzaldehyde. The electrochemical, linear, and nonlinear optical properties of the resulting push-pull V-shaped compounds (**6e–f**) are compared to those of similar derivatives (**6a–d**) prepared from previously known pyranylidene acceptors. Moreover, a comparison between the properties of some 1D and 2D compounds is made thanks to the use of closely related derivatives.

Compounds **1a** (commercially available),[7] **1b**,[8] **1c**,[6d,9] and **1d**[6d,9] were prepared as previously described. The hitherto unreported acceptors **1e** and **1f** were prepared by Ac_2O-mediated reaction of commercially available pyrone **2** with **3**[10] and **4**,[11] respectively (Scheme 1).

Target compounds **6a–f** were synthesized by the Knoevenagel reaction of *p*-diethylaminobenzaldehyde **5** (2 equiv) with acceptors **1a–f** (Scheme 2).

The design of linear chromophores comparable to V-shaped molecules **6** must take into account the reactivity of the methyl groups at positions 2 and 6 of the pyran ring, which may give rise to mixtures of mono- and disubstituted derivatives,[6b,6d,12] even when equimolar amounts of **1** and an aldehyde are used. Moreover, nonsymmetrical acceptors such as **1d–f** are expected to yield two different monosubstitution products, very difficult to separate. To avoid these problems we have chosen to prepare model compounds **8a–b**, bearing only one reactive position and a symmetric

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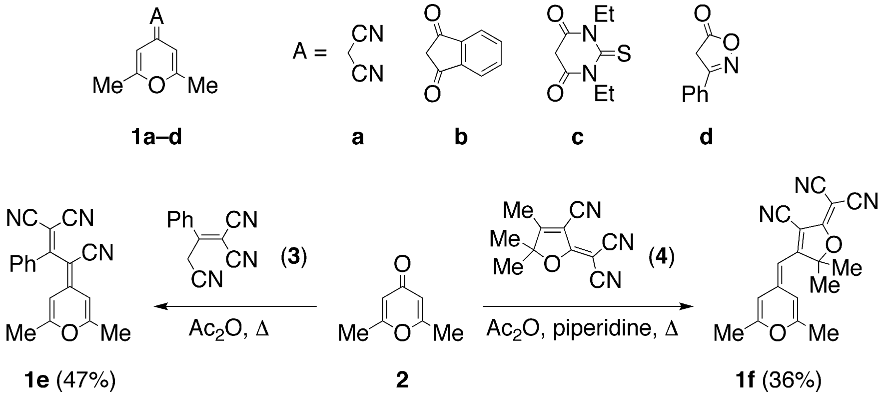
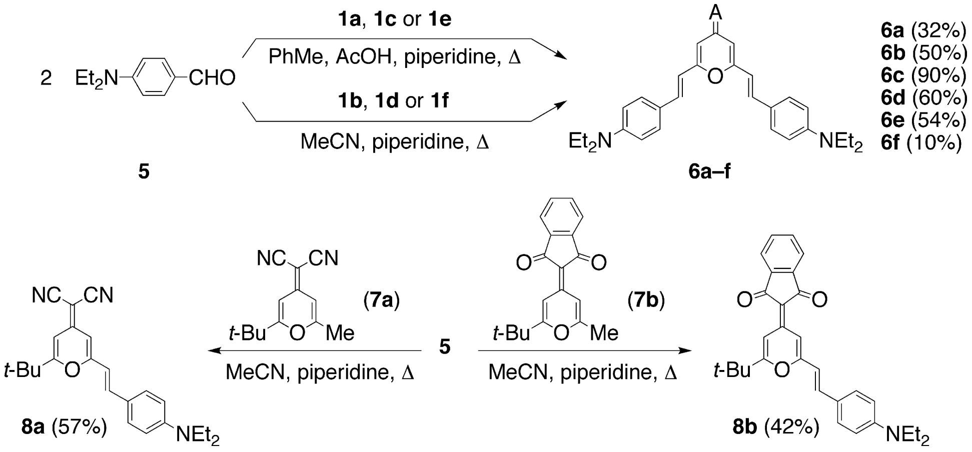


Scheme 1. Synthesis of pyranylidene acceptors.



Scheme 2. Synthesis of V-shaped and 1D compounds.

acceptor moiety, starting from the recently described 2-*tert*-butylpyran derivatives **7a–b**[13] (Scheme 2).

Single crystals of **1e** were obtained by slow evaporation from EtOH solution (Fig. 1).[14] It can be seen that the PhC–C(CN) bond adopts an *s-trans* conformation, like that found in a related derivative bearing a 1,3-dithiol-2-ylidene fragment,[15] and that the tricyanopropene moiety of **1e** is appreciably distorted from planarity, as evidenced by dihedral angles $C_8–C_{10}–C_{17}–C_{18}$ (17.1°) and $C_9–C_8–C_{10}–C_{17}$ (29.3°), and by the angle between the best-fit planes of the pyran and the phenyl rings (67.6°). Moreover, the bond distances in the pyran ring of **1e** are very similar to those of **1a**.[16]

To ascertain the effect that the presence of the donor groups has on the structure of the pyran ring, we have optimized the geometries of compounds **1a**, **6a,** and **8a**, with a common acceptor, at the B3P86/6-31G* level (Fig. 2).

Not unexpectedly, the length of the *a* bond increases on increasing the number of donor groups (**1a** < **8a** < **6a**), thus pointing to an enhanced contribution of the zwitterionic forms (**II** or **III**) (Fig. 3). In a similar way, the parameter $(b–c)$ (similar to the δr parameter, widely used for studying aromatic/quinoid contributions in push–pull benzenes and related derivatives)[17] decreases on passing from **1a** to either **6a** or **8a**, thus showing that the former derivative, devoid of strong donor groups, is more quinoid than the latter, which show decreased bond length alternation (BLA) along the pyran fragment. More important, in the unsymmetrical derivative **8a** the degree of bond length equalization is much larger on the donor-containing side than on the *t*-butyl-substituted side. This result suggests that the zwitterionic aromatic form **III** is not an important contributor (otherwise $(b–c) \approx (d–e)$) and, therefore, the pyran ring only acts as a spacer and not as a (proaromatic) auxiliary donor group.

Electrochemical data of the newly prepared compounds (Table 1) suggest that the dicyanomethylene group is the weakest acceptor in this series, since E_{red} for **6a** is strongly cathodic, and that the best acceptor is that present in compound **6e**. UV–vis data also support the comparatively weak electron-withdrawing effect of the dicyanomethylene group, given that the wavelengths of the maxima of the lower energy bands of compounds **6** decrease in the following order in CH_2Cl_2: **6f** > **6c** > **6e** > **6d** > **6b** > **6a**. It is worth noting that this trend in λ_{max} values agrees very well with previous comparisons carried out on other V-shaped pyran derivatives featuring more limited sets of acceptor groups.[6b,6d] Although the high λ_{max} value of **6f** could be taken as an indication of the strength of the TCF acceptor, it must be taken into account that **6f** bears one more C=C bond in its conjugation path than other derivatives, such as **6e**.

Comparison of the UV–vis spectra of compounds **6a–b** and their 1D counterparts **8a–b** (Fig. 4) reveals that the former displays bathochromically shifted absorptions, in good agreement with previous experimental[6b,6d] and theoretical[18] studies on related 2,6-bis(thienylvinyl)pyran derivatives.

In fact, V-shaped systems display one broad absorption that, according to TDDFT calculations (Table 1), results from two closely spaced transitions, located near the transition of the corresponding 1D-derivative.[6a] This interpretation lends support to the observed red-shift and the increased extinction coefficients of compounds

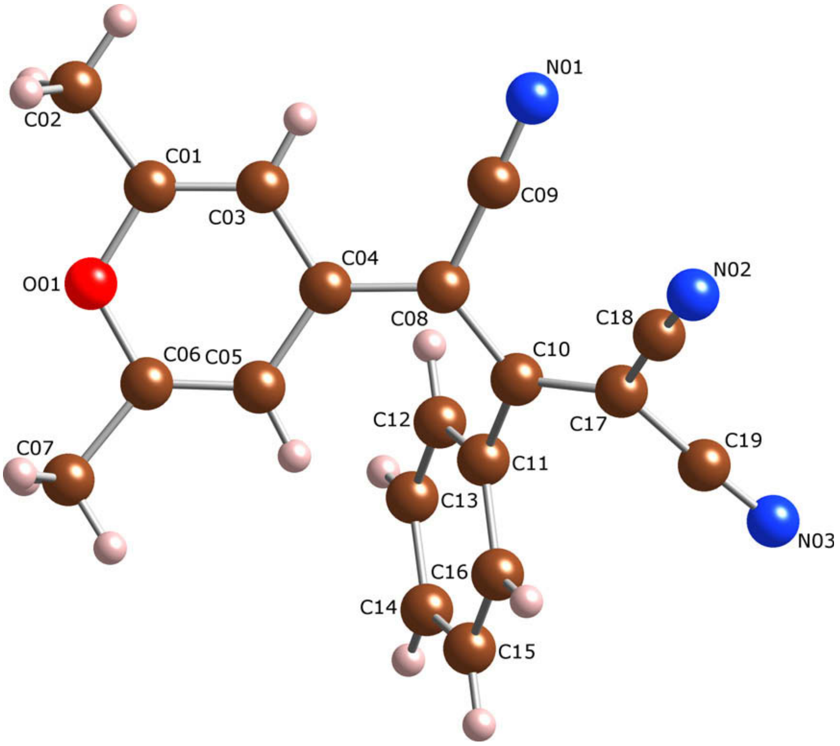
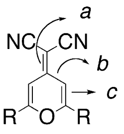
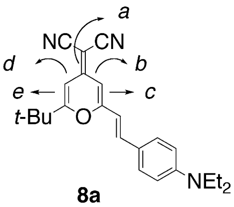


Figure 1. X-ray crystal structure of **1e**.



1a: R = Me
6a: R = p-Et_2N-C_6H_4-CH=CH

Compd	a	(b–c)	(d–e)
1a	1.390	0.082	—
6a	1.398	0.063	—
8a	1.395	0.059	0.082



8a

Figure 2. B3P86/6-31G* calculated bond lengths and bond length differences (Å) for **1a**, **6a**, and **8a**.

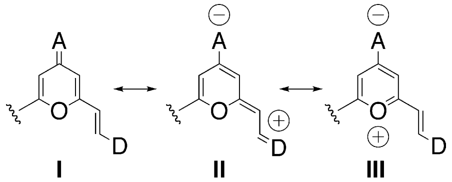


Figure 3. Limiting forms of compounds **6** and **8**.

6a–b, which are ca. 1.8 times larger than those of **8a–b**. Compounds **6** and **8** show positive solvatochromism, in agreement with previous reports on related derivatives, such as the well-known laser dye DCM (4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran).[19] This is a consequence of the large increase in the dipole moment upon excitation[20] ($\Delta\mu_{01}$), calculated as 13.38 D and 15.09 D for **8a** and **8b**, respectively (TD-B3P86/6-31G* level).

Given the prominent role played by DCM derivatives in the search for new red organic light-emitting devices (OLEDs),[21] we have studied the fluorescent properties of some of the herein reported compounds. Photoluminescence data for **8a–b** are summarized in Table 2, where DCM and its 2D-analog **6a** have been included for the sake of comparison.

All of them show large Stokes shifts (ca. 100 nm) and inspection of Table 2 reveals that **6a** shows a longer emission wavelength than **8a**, in agreement with previous comparisons on related 1D/2D compounds.[22] Concerning the 1D-derivatives, λ_{em} decreases in the following order: **8b** > **8a** > DCM, thus revealing that replacement of the dicyanomethylene group by the indanedione moiety[13] and introduction of a stronger donor (diethylamino instead of dimethylamino) both cause a red-shift of the fluorescence emission. The fluorescence quantum yields (Φ_f) of **8a,b** relative to Rhodamine 101 (Φ_f = 1.0 ± 0.02 in EtOH)[23] are slightly higher than that of DCM and much higher than Φ_f of **6a**. The lower fluorescence efficiency of V-shaped derivatives when compared to that of their 1D-analogs has previously been noted.[22]

The second-order NLO properties of **6** and **8** were measured by the electric field-induced second harmonic generation (EFISH) technique. Comparison of $\mu\beta_0$ values (Table 1) reveals that the most efficient nonlinear derivative is **6e**, followed by **6d** and **6f**. Therefore, the herein reported acceptor **1e** is a promising building block in the search for new pyranylidene-based NLO-phores. The remaining V-shaped derivatives have somewhat lower $\mu\beta_0$ values, and a reliable comparison between **6a–c** is hampered by the close similarity of such values and the experimental accuracy in the measurement of $\mu\beta$ (ca. ±10%). In fact, acceptor **1a** has been reported to give either higher[6b] or lower[6d] hyperpolarizabilities than

Table 1
Electrochemical, linear, and nonlinear optical properties

Compound	E_{ox}[a]	E_{red}[a]	λ_{max} (lg ε)[b]	λ_{max}[c]	λ_{max}[d]	$\mu\beta$[e]	$\mu\beta_0$[f]
6a	0.85	−1.38	492 (4.84)	498, 557 (sh)	450, 480	1440	989
6b	0.88, 1.34	−1.31	526 (4.98)	535	466, 494	1570	1007
6c	0.86, 1.07	−1.06[g]	530 (4.85), 598 (sh)	541, 618 (sh)	475, 519	1500	945
6d	0.88, 1.08	−1.19	533 (4.85)	540	472, 496	2299	1454
6e	0.83	−0.97	589 (4.78)	598	513, 528	3000	1700
6f	0.80, 0.96	−1.23	649 (4.82)	654	538, 571	2202	1045
8a	0.80[g]	−1.49	478 (4.57)	498	425	889	623
8b	0.81, 1.16	−1.35	520 (4.74)	533	442	900	586

[a] E in V versus Ag/AgCl, glassy carbon working electrode, TBAPF$_6$ 0.1 M in CH$_2$Cl$_2$, 0.1 V/s. All compounds display irreversible waves, except where noted.
[b] In nm, measured in CH$_2$Cl$_2$.
[c] In nm, measured in DMSO.
[d] In nm, calculated by TD-B3P86/6-31G* in the gas phase.
[e] In 10^{-48} esu, measured in CH$_2$Cl$_2$ at 1907 nm.
[f] In 10^{-48} esu, determined using the two-level model.
[g] Reversible wave ($E_{1/2}$).

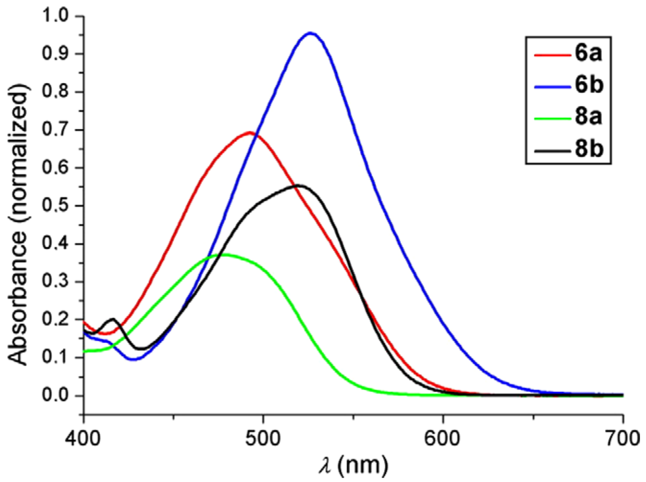


Figure 4. Normalized UV–vis spectra of **6a–b** and **8a–b** (10^{-5} M in CH$_2$Cl$_2$).

Table 2
Fluorescence data

Compound	λ_{em}[a]	Φ_f[b]
6a	609	0.15
8a	576	0.48
8b	604	0.43
DCM[c]	572	0.42

[a] In nm, measured in CH$_2$Cl$_2$.
[b] In CH$_2$Cl$_2$, relative to Rhodamine 101.
[c] λ_{max}^{abs} (CH$_2$Cl$_2$) = 468 nm.

acceptor **1c** in closely related derivatives. There is also a close similarity between the hyperpolarizabilities of the linear derivatives **8a** and **8b** which are, in turn, lower than those of the corresponding two-dimensional compounds **6a–b**.

To gain a better understanding of the NLO behavior of 2D compounds and their 1D analogs we have calculated the $\mu\beta_0$ values of **6a** and **8a** using the CPHF approach on the B3P86/6-31G* optimized geometries. The resulting values, 875×10^{-48} esu for **6a** and 623×10^{-48} esu for **8a**, are in excellent agreement with experimental results (Table 1) and confirm the enhanced hyperpolarizability of the 2D chromophore compared to its 1D analog. Theoretical studies[3] have shown that this kind of chromophores displays a large and positive off diagonal component of the hyperpolarizability (β_{zyy}) and a small diagonal component (β_{zzz}) that can be either positive or negative. Our CPHF results for **6a** ($\beta_{zyy} = 60 \times 10^{-30}$ esu, $\beta_{zzz} = -12 \times 10^{-30}$ esu) are in good agreement with these studies, although the sign of β_{zzz} differs from that calculated by the TDHF/AM1 method.[3]

In fact, TD-DFT calculations on **6a** indicate that its first and second excited states are close in energy (2.58 and 2.75 eV above the ground state) and polarized orthogonally to each other, in good agreement with experimental results on its dibutylamino analog.[6a] The first excited state arises from the promotion of one electron from the HOMO − 1 to the LUMO. The large dipole moment change (+12.0 D) associated to this transition and its B_2 symmetry account for a large and positive contribution of this excited state to β_{zyy}. The second excited state is generated from the ground state by a one electron HOMO→LUMO transition involving a dipole moment change of +5.3 D. This state displays A$_1$ symmetry and therefore is expected to give rise to a small positive contribution to β_{zzz}. The origin of the overall negative value of β_{zzz} must be found in higher excited states of A_1 symmetry with a decreased dipole moment compared to that of the ground state, for example, the transition to the fourth excited state (A_1 symmetry) involving the promotion of one electron from the HOMO − 1 to the LUMO + 1 gives rise to a dipole moment change of −1.3 D.

Finally, it is noteworthy that, for the same number of conjugated carbon atoms, the diethylanilino derivatives **8a** and **8b**, while being more transparent, show similar or higher $\mu\beta_0$ values than their 2-pyrrolidinothiophene analogs.[6b]

In conclusion, the synthesis of two new tricyano-containing 4*H*-pyran-4-ylidene derivatives has allowed to study the effect of six different acceptor groups on the linear and nonlinear optical properties of dipolar V-shaped compounds, the one with a tricyanopropene fragment showing the highest second-order NLO response. The selected 1D analogs that have been prepared for the sake of comparison display slightly higher fluorescence efficiencies than DCM and show blue-shifted absorptions and decreased $\mu\beta$ values relative to their 2D counterparts. The pyranylidene ring does not behave as an auxiliary donor group but as a polyenic spacer.

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Supplementary data

Supplementary data (experimental section and characterization data of new compounds, NLO and fluorescence measurements, UV–vis spectra and theoretical calculations) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.197.

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