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Synthesis and optical properties of new 2-oxo-4-vinyl-2*H*-chromene-3-carbonitrile dyes

Konstantin S. Levchenko,*[a] Konstantin A. Chudov,[a] Evgeni V. Zinoviev,[a]
Konstantin A. Lyssenko,[b,c] Artem N. Fakhrutdinov,[d] Dmitri U. Demin,[a]
Nikolay O. Poroshin,[a] Anna A. Zhukova,[e] Pavel S. Shmelin[a] and Evgeni P. Grebennikov[a]

[a] *Central Research Institute of Technology 'Tekhnomash,' 121108 Moscow, Russian Federation.*
E-mail: k.s.levchenko@gmail.com
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *G. V. Plekhanov Russian University of Economics, 117997 Moscow, Russian Federation*
[d] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[e] *I. M. Sechenov First Moscow State Medical University, 119991 Moscow, Russian Federation*

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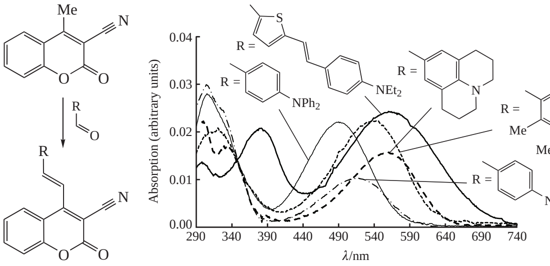
New derivatives of 2-oxo-4-vinyl-2*H*-chromene-3-carbonitrile have been synthesized by the Knoevenagel reaction of 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile with aromatic and heteroaromatic aldehydes. The first hyperpolarizability β for the obtained compounds was calculated using M05-2X functional and 6-31+G(d) basis set; their optical properties and solvatochromism in solvents of various polarity were examined. The crystal structure for one representative of the synthesized compounds was determined by XRD.



In the last decades the development of organic nonlinear optical (NLO) materials has attracted much attention due to their potential application in information processing, fiber communication, optical switching and information storage.[1–7] The increasing amount of transmitted data requires the use of high-speed electro-optical modulators operating at a frequency above 100 GHz, which can be achieved with the NLO materials only. Compared to the well-known inorganic NLO crystals, such as lithium niobate, KH_2PO_4 or TeO_2, the organic NLO materials are characterized with less response time, wider bandwidth, higher electro-optic coefficient and better processability.[1,8]

The organic NLO materials are based on donor–acceptor chromophores D–π–A, where the donor and acceptor moieties are connected through conjugated bonds. Diethylaniline and julolidine derivatives are commonly used as the donor parts. Olefinic polyene-type structures and heteroaromatic compounds with low aromatization energy, utilized as the π-bridges between the donor and the acceptor parts, provide an effective charge transfer. The most commonly used acceptors are malononitrile derivatives, such as 5,5-disubstituted 3-cyano-2-dicyanomethylidene-5*H*-furan-4-yl,[9,10] 3-cyano-2-dicyanomethylidene-5-oxo-1*H*-pyrrol-4-yl[11,12] and 1,3-bis(dicyanomethylene)-1*H*-inden-2-yl[13] derivatives, *etc*. There are as well several examples of using benzopyran-type moieties, namely 4-dicyanomethylidene-4*H*-chromen-2-yl, as an acceptor in push–pull chromophores.[14]

Previously we demonstrated the use of 3-cyano-2-oxo-2*H*-chromen-4-yl part as an acceptor as well as its application as a cheap raw material for the synthesis of donor–acceptor chromophores.[15,16]

2-Oxo-2*H*-chromenes are well-known as donor parts of fluorescent dyes,[17,18] light-stable dyes as fluorescent components of solid state lasers[19,20] as well as dye sensitizers for solar cells having high photovoltage.[21,22] However, there are only few investigations of dyes with a 3-cyano-2-oxo-2*H*-chromen-4-yl moiety as an acceptor part.

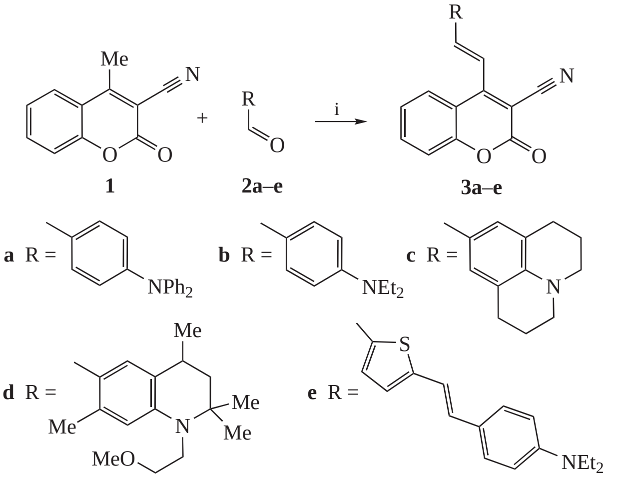
Here, the synthesis and the optical properties of new chromophores containing the 3-cyano-2-oxo-2H-chromen-4-yl acceptor are described. The synthesis was carried out starting from 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile **1** obtained according to the known method[23,24] by heating ethyl cyanoacetate, ammonium acetate and *o*-hydroxyacetophenone at 220 °C for 15 min (Scheme 1). The introduction of the donor fragments into 4-position of compound **1** was realized by the Knoevenagel reaction with corresponding aldehydes.[†] Aldehydes **2a–c** are commercially available or can be easily obtained.[25] Aldehydes **2d** and **2e** were synthesized by known procedures.[25,26] The reactions were carried out in acetonitrile or ethanol medium in the presence of L-proline or piperidine as a catalyst with similar results. Acetic anhydride was also tested as a solvent and a dehydrating agent. We have found that acetonitrile is the most suitable solvent due to negligible amount of by-products, although the total yields are comparable when using ethanol or acetic anhydride.

[†] *General procedure for the synthesis of compounds* **3a–e**. To a solution of 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile **1** (185 mg, 1 mmol) and aldehyde **2a–e** (1 mmol) in acetonitrile (5 ml) one drop of piperidine was added. The reaction mixture was stirred under reflux for appropriate time (see Scheme 1). The precipitate formed was filtered off, washed with ethanol and dried in air. If no solid precipitate formed, the solvent was distilled off *in vacuo*. The residue was purified by crystallization or by column chromatography.

Table 1 The absorption data for the synthesized products **3a–e** in various solvents.

Compound	λ_{max}/nm						$\Delta\lambda_{max}$/nm[a]	ε[b]/dm^3 mol^{-1} cm^{-1}	β (a.u.)[c]
	1,4-dioxane	PhCl	CH_2Cl_2	Me_2CO	MeCN	EtOH			
$E_T(30)$[d]	36	36.8	40.7	42.2	45.6	51.9	–	–	–
3a	466	488	490	468	470	489	24	15660	19303.3
3b	486	508	518	501	506	523	37	9261	15598.9
3c	518	549	560	548	545	568	50	5792	15097.7
3d	506	534	540	524	527	548	42	15140	8434.2
3e	529	560	560	535	574	559	45	15698	54453.0

[a] $\Delta\lambda_{max}$ is the maximum difference between absorption maxima in different solvents. [b] ε is the molar extinction calculated for 1,4-dioxane solution. [c] β is the first hyperpolarizability. [d] $E_T(30)$ is the empirical parameter of solvent polarity (kcal mol^{-1}).[27]



3	Reaction time/h	Yield (%)
a	23	47
b	24	50
c	24	38
d	48	39
e	21	30

Scheme 1 *Reagents and conditions*: i, MeCN, piperidine, reflux.

All products were characterized by ^{1}H and ^{13}C NMR as well as HRMS methods. Optical properties of compounds **3a–e** are summarized in Figure 1 and Table 1.

With the solvents varying from slightly polar 1,4-dioxane to moderately polar dichloromethane, a shift of 24–42 nm of the absorption maxima to longer wavelength has been observed for all the chromophores **3a–e**.

In a series from weakly or moderately polar solvents to highly polar ones, a negative solvatochromism was observed. With increasing polarity in a group of highly polar solvents, namely acetone, acetonitrile and ethanol, a linear relationship occurs for compounds **3a**, **3b** and **3d**. Interestingly, the absorption maximum in acetonitrile for compound **3e** is in a longer wavelength range, compared with the absorption maximum in ethanol, which is accounted for by the formation of specific solvate forms.

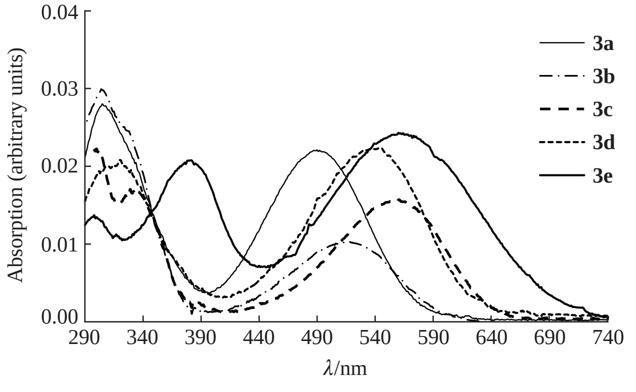


Figure 1 The absorption spectra of the synthesized products **3a–e**, C = = 0.003 mg ml^{-1}.

The structure of compound **3e** was confirmed by XRD (Figure 2).[‡] It crystallizes as solvate with chloroform in the centrosymmetric space group $P2_1/n$. The molecule **3e** is almost planar with maximum deviation from planarity due to rotation around the C(3)–C(11) bond, with torsion angle C(2)–C(3)–C(11)–C(12) being 18.7°. In the crystal, the cyano group of compound **3e** participates in the shortened N···Cl interactions with the chloroform molecule: N–Cl distance is 2.99–3.07 Å and N–Cl–C angle is 159–167°, which can be considered as the halogen bond. In addition, the molecules participate in a strong stacking interaction between the 2-oxo-2*H*-chromene-3-carbonitrile rings, with the shortest C···C contact being 3.37 Å.

Considering the pronounced solvatochromism of compounds **3a–e**, it is reasonable to suppose that these molecules can be characterized by high values of first hyperpolarizability β for the thermal ellipsoids at p = 50%. For all the molecules we performed the geometry optimization without symmetry restriction using the density functional theory with PBE0 approximation and def-2-TZVP basis set. The calculations of β were carried out

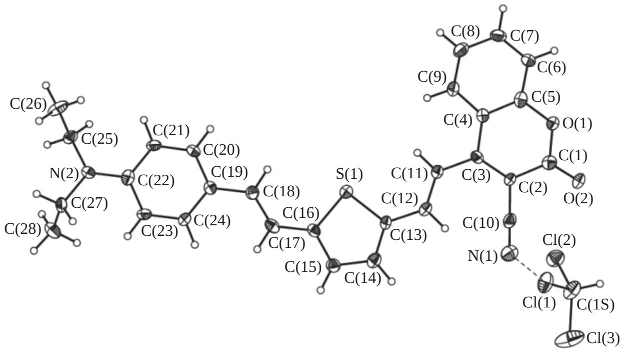


Figure 2 Molecular structure of compound **3e**.

[‡] *Crystal data for* **3e**. $C_{29}H_{25}Cl_3N_2O_2S$, monoclinic, space group $P2_1/n$, at 120(2) K: a = 9.511(3), b = 7.209(2) and c = 39.548(12) Å, β = = 90.018(6)°, V = 2711.8(15) Å^3, Z = 4, Z' = 1, d_{calc} = 1.401 g cm^{-3}. Intensities of 30208 reflections were measured using Bruker APEX-II CCD [λ(MoKα) = 0.71072 Å], $2\theta < 55°$ and 6252 independent reflections were used in the further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. The refinement converged to wR_2 = 0.1755 and GOF = 0.877 for all independent reflections [R_1 = 0.0691 was calculated against F for 2507 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL-2014/6.

CCDC 1874236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

using M05-2X/6-31+G(d) approximation that had been shown to be the appropriate method.[28–31]

The β values were calculated by the numerical second derivative of electric dipole moment with respect to the applied field, as implemented into the Gaussian 09 program. For all molecules **3a**–**e**, the nature of the emission band was estimated by means of TD-DFT calculation with application of the conductor-like polarization continuum model CPCM[32] of acetonitrile solvent. The TD-DFT calculations have revealed that the lowest energy transitions S1→S0 are mainly HOMO to LUMO, which corresponds to the transition from the donor part, designated as R in Scheme 1, to the acceptor one, namely the 2-oxo-2*H*-chromene-3-carbonitrile ring. The β values are significantly higher than those for the family of stilbene derivatives or their thiophene analogues.[33–35] Compound **3e** has the highest β value equal to 54453.0 a.u., which is only slightly lower that for 2-dicyanomethylidene-3-cyano-4-{2*E*-[2-(2*E*-{4-[di(2-acetoxyethyl)-amino]phenyl}vinyl)-3,4-dibutylthien-5-yl]vinyl}-5,5-dimethyl-2,5-dihydrofuran (FTC).[36,37] Thus, we can propose that the synthesized compounds can be promising for the design of NLO materials.

In summary, a series of new 2-oxo-4-vinyl-2*H*-chromene-3-carbonitrile derivatives were synthesized by the Knoevenagel reaction of 4-methyl-2-oxo-2*H*-chromene-3-carbonitrile with aromatic and heteroaromatic aldehydes. The first hyperpolarizability β of the obtained compounds was calculated using M05-2X functional and 6-31+G(d) basis set. Optical properties and solvatochromism in solvents of various polarity, namely 1,4-dioxane, chlorobenzene, dichloromethane, acetonitrile and ethanol, were explored. The new class of dyes may be useful for NLO devices and other applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.020.

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