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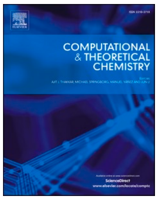

Theoretical estimations of dynamic first hyperpolarizability of D-π-A chromophores with fused (azinylmethylene)malononitrile macroacceptors

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ABSTRACT

DFT study of nonlinear-optical chromophores **Q′**, **Q_{Ph}**, **PP1** and **Q_{on}** with fused (azinylmethylene)malononitrile macro-acceptors (azine is quinoline, quinoxaline, pyridopyrazine and quinoxaline-2-one) is performed. Small effect of conformation on the first hyperpolarizability, β, values is demonstrated. The solvent effect on the molecular polarizabilities is considered by the example of dioxane and dichloromethane both for static and dynamic cases. The ratios of β(2ω) for the cases solvent/gas increase gradually in a series **Q′**, **Q_{Ph}**, **PP1** and **Q_{on}** correlating with azine moiety aromaticity decrease. The highest β(2ω), $2655 \cdot 10^{-30}$ esu, is obtained for **Q_{on}** in dichloromethane.

1. Introduction

One of the most popular directions in elaboration of novel materials with enhanced electro-optic (EO) response is the design of new organic chromophores which serve molecular sources of the effect [1]. The structure of the chromophores – D-π-A – results in the search for most effective components; however, most attention of the researchers was paid to donor and bridge moieties, while less studies were aimed at the choice of effective acceptors [2,3]. The most popular acceptors are those with heterocyclic groups: 2-dicyanomethylene-3-cyano-2,5-dihydrofuran, TCF, [4–7], 5-dicyanomethylene-2-oxo-4-cyano-1,2-dihydropyrrole, TCP, ones [8–11], and tricyanovinylene, TCV, containing cyano-groups [12,13] (Fig. S1). Recently we have synthesized chromophores based on novel macro-acceptors, composed of fused azine moieties (quinoline, quinoxaline, quinoxalinone, pyridopyrazine) and malononitrile one (Fig. 1), and examined some of their properties [14]. Here we continue this research by studying dynamic NLO characteristics of these chromophores at 1907 nm in gas and solvents (dioxane and dichloromethane). As chromophores are molecules with rather complex system of ordinary and conjugated bonds, special attention is paid to the effect of conformation on chromophore electric characteristics. Earlier by the example of chromophore with divinylthiophene bridge and TCF acceptor, FTC (Fig. S1), which serves a basis for many contemporary chromophores with recognized effectiveness as EO moieties, the strong conformational dependence of first hyperpolarizability was demonstrated [15]. On the other hand, for chromophores with divinyl quinoxaline bridge inessential effect of conformation on β was shown, maximal deviation from the average value being less than 10 % [16].

2. Computational details

The structure of the studied chromophores allows the existence of 4 rotational isomers (see Fig. 2 and S2); the corresponding isomers for each chromophore are designated according to the rules described in [16]: *t*(*c*) denotes trans(cis) mutual arrangement of the endocyclic sesquialteral CC bond of the aromatic heterocycle and nearest double bond in π-bridge vinylene moiety, and of the nearest double bonds in macro-acceptor fused ring and malononitrile moiety; the admitted rotations are shown in Fig. 2, S2. Conformational diversity was studied by molecular modeling in gas (and in dioxane for **Q_{Ph}**) in the energy window 5 kcal/mol using OPLS3e force field [17]; the ***tt***-conformer was used as the starting one. Conformational search was performed by Monte-Carlo method with Macromodel program software [18]; a set of unique conformations of the studied chromophores was obtained, the analysis of these data resulted in establishing the most stable conformers.

For various chromophore conformers the following electric characteristics [19] – dipole moment μ_i, average polarizability, α_{av},

$$\alpha_{av} = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right), \tag{1}$$

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and first hyperpolarizability β_{tot}

$$\beta_{tot} = \sqrt{\beta_x^2+\beta_y^2+\beta_z^2};\beta_i = \beta_{iii}+\frac{1}{3}\sum\nolimits_{i\neq k}(\beta_{ikk}+\beta_{kik}+\beta_{kki}), i = x, y, z \qquad (2)$$

were calculated at M06-2X/aug-cc-pVDZ level. The chromophores geometry was optimized at B3LYP/6-31G(d) level and their electric properties (μ, α_{av}, β_{tot}) were calculated at M06-2X/aug-cc-pVDZ level. The applicability of M06-2X for the assessment of (hyper)polarizability values was considered, in particular, in [20]. The chromophores geometry optimization in gas was performed with Jaguar program [18,21], geometry optimization in solvents (1,4-dioxane, $\varepsilon = 2.21$; dichloromethane, $\varepsilon = 8.93$) along with the electric characteristics (both static and dynamic) were performed with Gaussian16 [22]; for the solvent account PCM [23] was used. Dynamic first hyperpolarizabilities $\beta(-\omega;\omega,0)$, relevant for dc Pockels effect, and $\beta(-2\omega;\omega,\omega)$, relevant for the second harmonic generation (SHG) effect, were calculated at 0.65 eV ($\lambda = 1907$ nm) frequency by TD-DFT [24]; hereafter $\beta(-\omega;\omega,0)$ and $\beta(-2\omega;\omega,\omega)$ are denoted as $\beta(\omega)$ and $\beta(2\omega)$. This frequency is far from absorption maxima for these chromophores [14], thus providing first hyperpolarizability values without resonance enhancement.

Orbital composition analysis, estimating contributions of definite molecular fragments (donors, bridges, acceptors) to frontier orbitals, was performed with MULTWFN program [25]. To perform orbital composition analysis, Hirshfeld method is used [26].

3. Results and discussion

3.1. Conformational search

In [14] we have considered the conformational variety of the studied chromophores and determined the set of unique conformations for each chromophore. The structure of the studied chromophores allows the existence of 4 rotational isomers (Fig. 2, S2); it was shown that all chromophores except **Q′** are realized with *tc*- and *cc*-conformations with the probability estimated by the Boltzmann weight factor, P_i, as 0.77, 0.23; 0.72, 0.28; 0.59, 0.41 for $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **PP1**, respectively (Table S1). In the absence of Ph substituent in hetarene fragment of **Q′** and $\mathbf{Q_{on}}$ the structure of macro-acceptor is close to planar (conformers *tc* and *cc*, Table S2); for other two conformers of $\mathbf{Q_{on}}$ which are not realized (within 5 kcal/mol energy window), the angle between hetarene and dicyanovinylene, DCV, moieties is above 20°; for **Q′** all four conformers can be realized, *tt* conformer being the most probable; however, *tc* one is only 0.4 kcal/mol higher in energy. The presence of Ph substituent results in the noticeable deviation from the planarity of macro-acceptor (up to 14° for *tc*-$\mathbf{Q_{Ph}}$ and up to 17° for *tc*-**PP1**); when the angle between the hetarene and DCV moieties planes is large, about 45° (the case of $\mathbf{Q_{Ph}}$ and **PP1**), the conformers are not realized within the energy window 5 kcal/mol (Table S1, S2); the Cartesian coordinates optimized for the most stable conformers are given in Tables S3-S7.

Thus, in macro-acceptor *cis*-arrangement of double bonds is favorable (*tc* and *cc* conformers); the values of BLA [27] for these conformers being reduced: 0.087 and 0.088 Å against 0.111 and 0.108 Å in *ct* and *tt* conformers, respectively.

The effect of the solvent results in a small change in the geometry of the chromophores (Tables S2, S8). By the example of $\mathbf{Q_{Ph}}$ we have examined whether the obtained stable conformers are realized in the solvent as well. The conformational search performed in dioxane revealed that the *tc*-conformer stays the most stable, *cc* one is only 0.5 kcal/mol less stable, the relative stability of other conformers being somewhat smaller than in gas (Table S9); P_i values estimated for all conformers of $\mathbf{Q_{Ph}}$ in dioxane differ inessentially from those calculated for the gas case.

3.2. Composition of frontier orbitals

To reveal the role of macro-acceptor components in the charge transfer, conditioning the formation of the NLO response, we have analyzed the composition of HOMO/LUMO orbitals (Table 1, Fig. 3). As it was expected, HOMO is determined mostly by donor and the bridge, while LUMO – by the macro-acceptor moiety. The contributions to HOMO from donor and the bridge fragments of $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **Q′** differ insignificantly; as for macro-acceptor, heterocyclic moiety also gives quite close contributions (14.7, 15.4 and 15.1 for $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **Q′** respectively), while the contribution from the DCV moiety for $\mathbf{Q_{on}}$ is somewhat more pronounced.

The contributions to LUMO from macro-acceptor are rather close for these three chromophores as well, however, its composition differs depending on the hetarene (Het) moiety nature: the hetarene

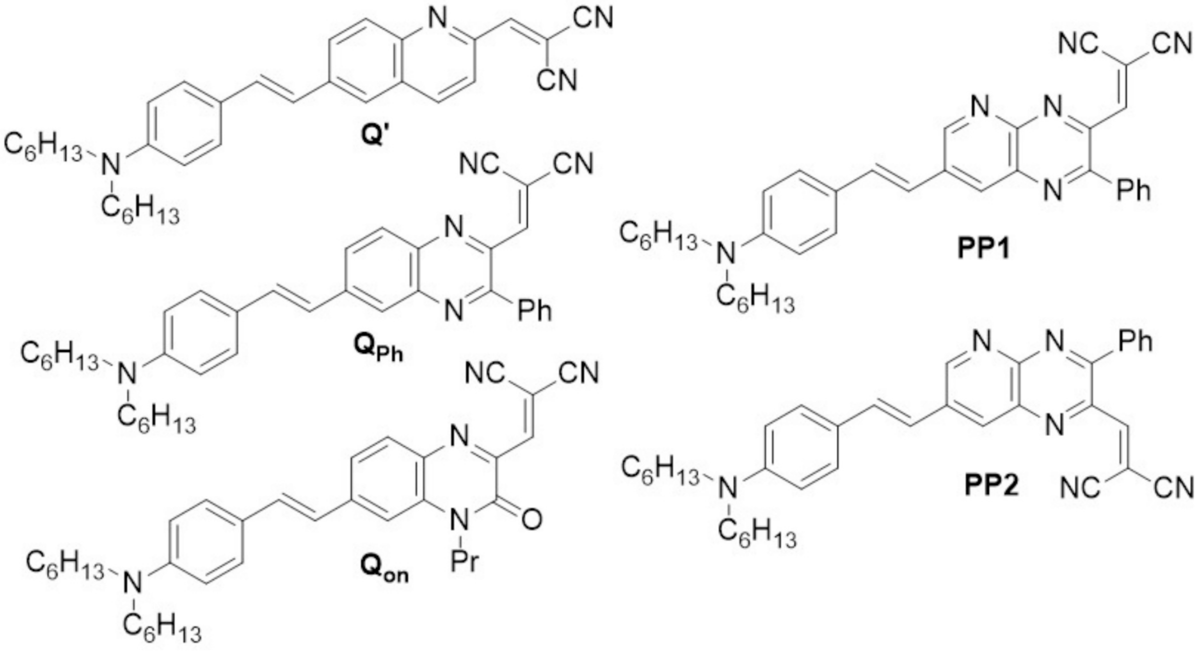

Fig. 1. Chromophores with dihexylaniline donor, vinylene π-bridge and various fused (azinylmethylene)malononitrile macro-acceptors.

contribution increases in a series **Q′** < $\mathbf{Q_{Ph}}$ < $\mathbf{Q_{on}}$, the largest is that from quinoxalinone moiety (50.4). The tendency in DCV contribution change is reverse: it grows in a series $\mathbf{Q_{on}}$ < $\mathbf{Q_{Ph}}$ < **Q′**, becoming for **Q′** greater than that from quinoline moiety.

For chromophores with pyridopyrazine moiety the picture is somewhat different. The contribution from donor and bridge, defining HOMO, is notably higher both for **PP1** and **PP2** than in the case of $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **Q′**, the contribution from the acceptor being smaller for **PP1** than for $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **Q′**; the specific feature of **PP2**, where vinylene bridge is attached at the site 6 of the hetarene moiety, is negligible contribution from DCV to HOMO. LUMO for **PP2** is characterized by extremely low contribution from donor and bridge, the contribution from macro-acceptor being very high - close to 99 %. Contribution to LUMO from pyridopyrazine moiety in **PP1** is quite large (50.0), slightly lower than that from quinoxalinone fragment in $\mathbf{Q_{on}}$. Thus the analysis of HOMO/LUMO composition demonstrates effective charge transfer permitting one to expect high NLO characteristics for **Q′**, $\mathbf{Q_{Ph}}$, **PP1** and $\mathbf{Q_{on}}$.

To further clarify the effect of the macro-acceptor components, we considered two model chromophores **M-Het** and **M-DCV** (Fig. S3) with either quinoxaline or DCV moieties as the acceptor (Table S10). In the absence of the DCV fragment, the contribution to HOMO from the quinoxaline fragment changes a little (14.7 and 16.7), while in the absence of the hetarene fragment the contribution to HOMO from DCV becomes very large (20.8). In the case of LUMO, DCV provides contributions comparable in magnitude with that in macro-acceptor (43.3 for $\mathbf{Q_{Ph}}$ and 47.5 for **M-DCV**), regardless of the presence of the hetarene fragment; in **M-Het** the contribution from the quinoxaline fragment is predominant, comparable in magnitude to that from macro-acceptor as a whole (87.2 in **M-Het** versus 90.1 in $\mathbf{Q_{Ph}}$), while in $\mathbf{Q_{Ph}}$ the quinoxaline fragment contribution to LUMO decreases almost twofold, to 46.8. It is interesting to note that for **M-DCV** the contribution to LUMO from the donor and the bridge is very large (52.7), in contrast to the case of all other considered chromophores with macro-acceptor (e.g. 9.9 in the case of $\mathbf{Q_{Ph}}$). The dipole moment of the **M-Het** is significantly smaller than that of the $\mathbf{Q_{Ph}}$, while the dipole moment of the **M-DCV** differs little from that of $\mathbf{Q_{Ph}}$ (Table S11). At the same time, the first hyperpolarizability values of these model chromophores are very close (Table S11) and, in both cases, much smaller (almost 4 times) than that of the $\mathbf{Q_{Ph}}$ chromophore. Thus, when the hetarene and malononitrile moieties are parts of the macro-acceptor, a certain synergistic effect appears, leading to a significant increase in the first hyperpolarizability of the chromophore.

3.3. *Static electric characteristics in gas and solvents*

Static electric characteristics of the studied chromophores in all probable conformations calculated in gas are given in Table 2 along with the statistically averaged values (Table S1). The dipole moment and linear polarizability α_{av} for all chromophores slightly depends on conformation, the only exception being **PP2** for which the range of μ values is from 8.5 to 11.6 D in gas. $\mathbf{Q_{on}}$ chromophore has maximum dipole moment among the studied ones – 17 D; **Q′** and **PP1** have close μ values, the dipole moment for $\mathbf{Q_{Ph}}$ is somewhat smaller. Maximal α_{av} is obtained for $\mathbf{Q_{Ph}}$. The account of the solvent results in a notable growth of μ and α_{av}, which is most pronounced for $\mathbf{Q_{on}}$ in dichloromethane: μ grows by 36 % and α_{av} by 45 %.

Chromophores $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **PP1** are characterized by rather close values of first hyperpolarizability ($\sim 500 \cdot 10^{-30}$ esu); the values are quite moderate [28,29], but they are still greater than β_{tot} for the chromophore with the same vinylene bridge and strong TCF acceptor [29], thus demonstrating the role of macro-acceptor. Chromophore **Q′** has somewhat lower β_{tot} value ($460 \cdot 10^{-30}$ esu); as for **PP2**, it is characterized by β_{tot} ($282 \cdot 10^{-30}$ esu) that is almost half of that for **PP1** due to violated conjugation in macro-acceptor in **PP2** chromophore conditioned by the site of DCV attachment to hetarene moiety (Fig. 1).

The weak dependence of the first hyperpolarizability value on the chromophore conformation was shown earlier by the example of quinoxaline chromophores with TCP acceptor [16] contrary to the case of FTC-based chromophores where a band of values for various conformers amounts to 30 % of the statistical mechanical average [15]. The presented data for chromophores with various macro-acceptors confirm the observation made in [16]: the value for the *cc*-conformer differs within 4, 3 and 1 % compared to that for the most probable *tc*-conformer of $\mathbf{Q_{Ph}}$, $\mathbf{Q_{on}}$ and **PP1** chromophores, correspondingly.

For **Q′** and **PP2** where all four conformers may be realized, the estimations are somewhat different. For **PP2** all four conformers have similar probability and the deviation of β_{tot} for each conformer from the average value does not exceed 5 %; for **Q′** the difference in the first hyperpolarizability values between the value for *tc*- and the most stable *tt*-conformer comprises 10 % and the deviation of β_{tot} for tt-conformer from the average value does not exceed 4 % (Table 2).

Solvent effect on the first hyperpolarizabilities results in the notable growth of chromophores electric characteristics, the corresponding factors being presented in Table 2. Thus average increase of first hyperpolarizability is nearly twofold for dioxane and even higher (from 2.7 to 4.3) in dichloromethane for all studied chromophores except **PP2**

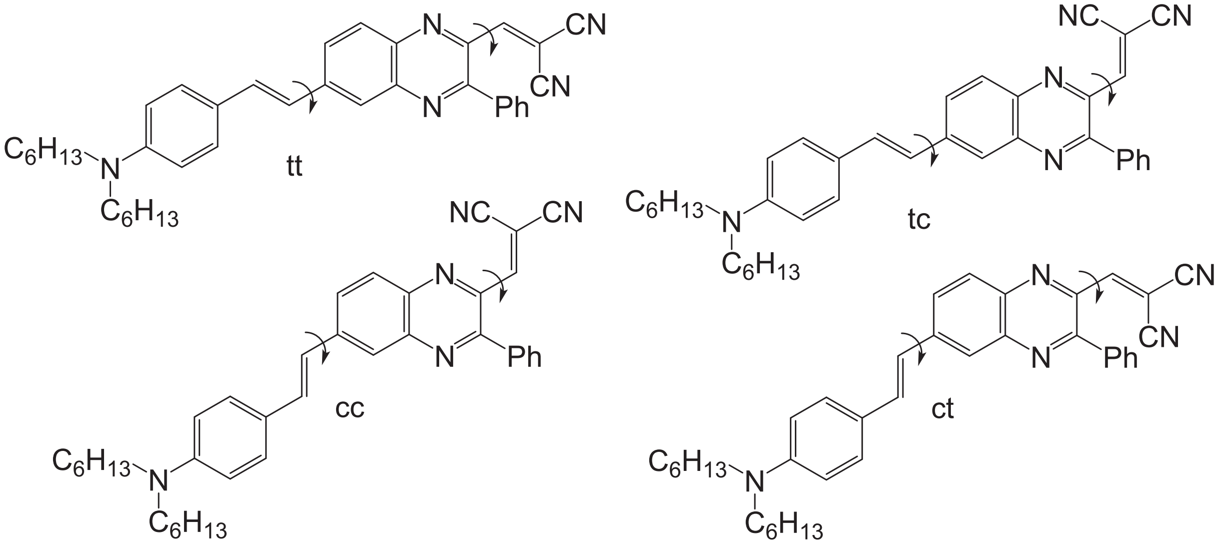

Fig. 2. Possible conformers of $\mathbf{Q_{Ph}}$.

Table 1
Composition of frontier orbitals HOMO, LUMO for the studied chromophores: (D - donor, B – π-electron bridge, A - acceptor)*.

		Q′					Q_{Ph}						Q_{on}					
	ODI		D	B	A		ODI		D	B	A		ODI		D	B	A	
					Het	DCV					Het	DCV					Het	DCV
HOMO	7.5	Comp	65.7	16.2	15.1	3.0	7.5	Comp	66.2	16.0	14.7	3.1	7.4	Comp	65.5	15.0	15.4	4.2
		ODI_F	13.5	50.3	16.1	22.3		ODI_F	13.2	50.9	16.3	22.7		ODI_F	13.7	50.6	12.9	23.1
LUMO	8.0	Comp	4.6	4.9	40.0	50.5	7.2	Comp	4.9	5.0	46.8	43.3	7.2	Comp	5.2	5.6	50.4	38.9
		ODI_F	13.2	56.3	14.0	21.9		ODI_F	13.0	57.1	13.9	21.2		ODI_F	13.2	55.7	15.3	20.8
		PP1					PP2											
	ODI		D	B	A		ODI		D	B	A							
					Het	DCV					Het	DCV						
HOMO	8.1	Comp	70.2	15.0	12.4	2.5	8.2	Comp	70.5	15.5	13.6	0.3						
		ODI_F	13.5	52.2	15.6	22.7		ODI_F	13.4	52.4	13.9	19.8						
LUMO	6.9	Comp	4.7	4.9	50.0	40.4	8.3	Comp	0.7	0.8	51.7	46.8						
		ODI_F	12.9	55.8	13.2	21.0		ODI_F	12.7	47.8	13.7	21.3						

[*] Orbital delocalization index (ODI) is estimated as $ODI_i = 0.01\cdot\sum_A Q_{Ai}^2$, where $\boldsymbol{Q_{Ai}}$ is a composition of atom A in orbital *i*; the ODI a useful indicator of quantifying extent of orbital spatial delocalization [25].

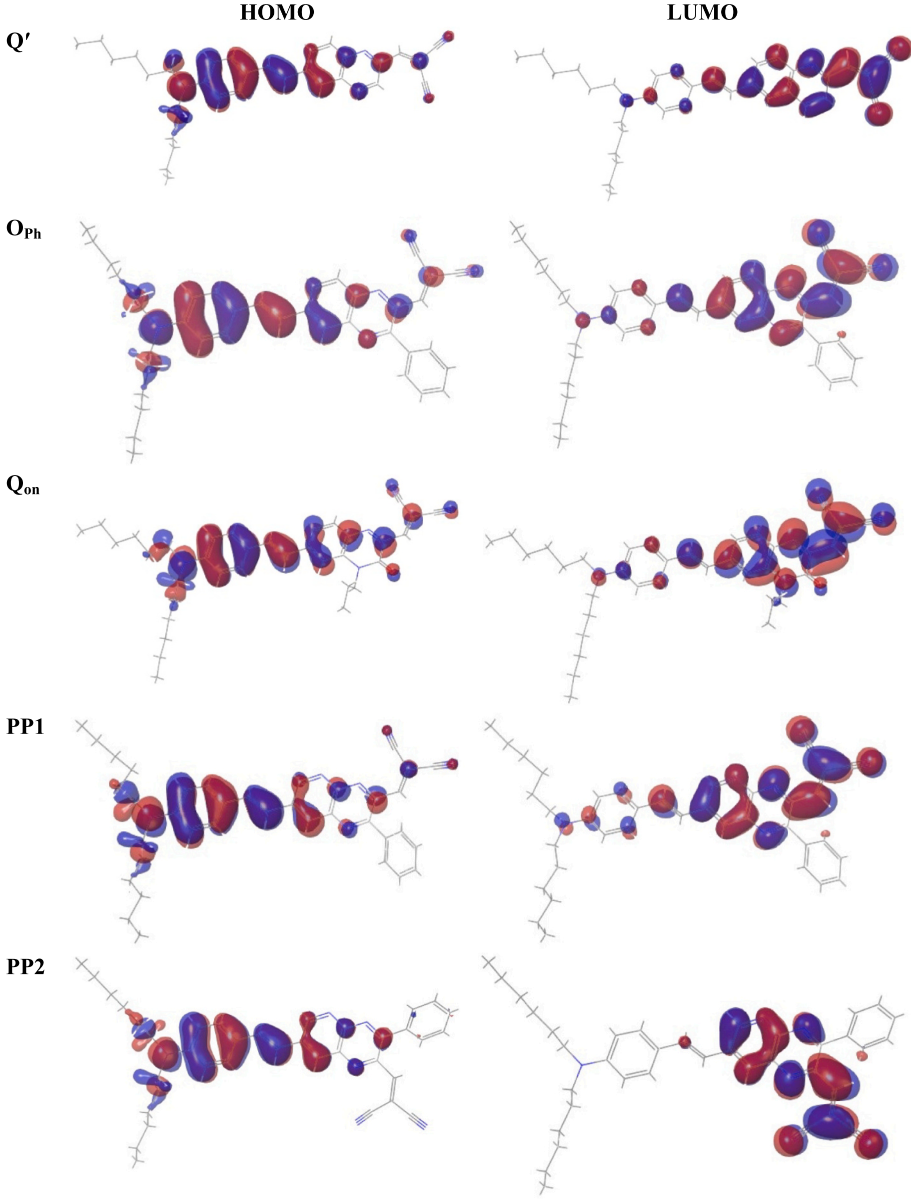

Fig. 3. Frontier molecular orbitals for chromophores **Q′**, $\mathbf{O_{Ph}}$, $\mathbf{Q_{on}}$, **PP1** and **PP2** (most stable conformers).

Table 2
Static electric characteristics of the studied chromophores: dipole moment in D, average polarizability in 10^{-24} esu, first hyperpolarizability in 10^{-30} esu, and corresponding ratios.

	Characteristics	Q′				Q_{Ph}		Q_{on}	
		Conformer				Conformer		Conformer	
		tc	*cc*	*tt*	*ct*	*tc*	*cc*	*tc*	*cc*
Gas	μ	13.7	14.0	14.2	13.9	12.9	12.9	16.4	17.0
	α_{av} (0)	85.6	85.3	87.6	86.8	99.1	97.9	94.7	94.4
	β_{tot} (0)	432.1	432.7	476.8	467.0	518.8	498.0	520.9	537.4
	$\beta_{av}(0)$		460.2			514.2		525.5	
Dioxane	μ			15.5		14.5		19.7	
	α_{av} (0)			100.8		115.4		114.4	
	β_{tot} (0)			830.9		970.0		1167.7	
	$\alpha_{av}^{sol}/\alpha_{av}^{gas}$			1.15		1.16		1.21	
	$\beta_{tot}^{sol}/\beta_{tot}^{gas}$			1.74		1.87		2.24	
Dichloro methane	μ			16.6		15.8		22.3	
	α_{av} (0)			115.0		133.6		136.9	
	β_{tot} (0)			1263.2		1605.4		2224.4	
	$\alpha_{av}^{sol}/\alpha_{av}^{gas}$			1.31		1.35		1.45	
	$\beta_{tot}^{sol}/\beta_{tot}^{gas}$			2.65		3.09		4.27	

	Characteristics	PP1		PP2			
		Conformer		Conformer			
		tc	*cc*	*tc*	*cc*	*tt*	*ct*
Gas	μ	14.2	15.0	9.0	8.5	11.6	11.5
	α_{av} (0)	97.3	97.0	94.8	94.0	93.4	93.3
	β_{tot} (0)	496.3	501.6	291.1	299.8	268.8	276.3
	$\beta_{av}(0)$	498.5		281.5			
Dioxane	μ	16.2		9.9	9.2	12.8	12.8
	α_{av} (0)	114.5		107.3	106.9	105.9	105.8
	β_{tot} (0)	992.2		460.9	473.6	428.4	441.3
	$\alpha_{av}^{sol}/\alpha_{av}^{gas}$	1.18		1.13	1.14	1.13	1.13
	$\beta_{tot}^{sol}/\beta_{tot}^{gas}$	2.0		1. 58	1.58	1.59	1.60
Dichloro methane	μ	18.0		10.4	9.6		
	α_{av} (0)	134.0		121.1	120.9		
	β_{tot} (0)	1773.6		645.9	665.1		
	$\alpha_{av}^{sol}/\alpha_{av}^{gas}$	1.38		1.28	1.29		
	$\beta_{tot}^{sol}/\beta_{tot}^{gas}$	3.57		2.22	2.22		

for which β_{tot} grows by 1.6 and 2.2, respectively.

3.4. *Dynamic electric characteristics in gas and solvents*

Since chromophores in a material intended for optoelectronic applications are exposed to an electromagnetic field of a certain frequency, it makes sense to study their characteristics not only in the static limit, but also in the dynamic mode. The values of molecular (hyper)polarizabilities, $\alpha_{av}(\omega)$, $\beta_{tot}(\omega)$ and $\beta_{tot}(2\omega)$ for the studied chromophores were calculated in gas, dioxane and dichloromethane at 1907 nm to avoid resonance enhancement of the first hyperpolarizability at the harmonic frequency (Table 3), since it was shown in [14] that all studied chromophores absorb in the range from 504 to 573 nm in 1,4-dioxane and from 531 to 620 nm in dichloromethane, all calculations are performed far from resonance frequency.

The presented data demonstrate that the tendency in the change of polarizability values, $\alpha_{av}(\omega)$, observed for the static case (**Q′** < $\mathbf{Q_{Ph}}$ < **PP1** < $\mathbf{Q_{on}}$) also holds in the dynamic case, the values staying almost unchanged for all chromophores. Similar situation takes place for $\beta_{tot}(\omega)$: insignificant $\beta_{tot}(\omega)/\beta_{tot}(0)$ growth can be seen in the range of 1.12 to 1.14. As for $\beta_{tot}(2\omega)$, the growth of the values is much more pronounced: maximal growth is obtained for $\mathbf{Q_{on}}$ (1.53 times) (Table 3), and it correlates with the macro-acceptor strength increase.

The trends in the change of dynamic electric characteristics observed as a result of solvent effect are also similar to those described for the static case (Table 2): polarizability values are slightly higher than gas values for both solvents. The changes in $\beta_{tot}(\omega)$ are in the range 1.74–2.2 times for dioxane and 2.17–3.33 for dichloromethane; for $\beta_{tot}(2\omega)$ they fall in the range 1.80–2.47 in dioxane and 2.07–3.33 in dichloromethane, in both cases the ratio increases in a series **Q′** < $\mathbf{Q_{Ph}}$ < **PP1** < $\mathbf{Q_{on}}$. The $\beta_{tot}(2\omega)/\beta_{tot}(0)$ ratio in solvents increase moderately (up to 1.7 in dioxane and 1.2 in dichloromethane); the $\alpha_{av}(\omega)/\alpha_{av}(0)$ and $\beta_{tot}(\omega)/\beta_{tot}(0)$ ratios are close to unity in dioxane, however, in dichloromethane they are slightly lower due to the permittivity dispersion in this case ($\varepsilon_\infty = 2.02$) [30]. Thus, first hyperpolarizability values calculated at second harmonic frequency are rather high, the macro-acceptor containing quinoxalinone moiety may be considered most promising for future research.

To summarize, the ratio of polarizability values in solvent with respect to gas values for the studied chromophores grows both in static and dynamic cases with the increase of the number of nitrogen atoms in azine fragment: **Q′**, $\mathbf{Q_{Ph}}$, **PP1** (1.15; 1.16; 1.18 и 1.14; 1.16; 1.17 in dioxane for static and dynamic cases, respectively; Tables 1,2), what correlates with π-deficiency increase of hetarene fragment. The same tendency is true for more polar dichloromethane: **Q′**, $\mathbf{Q_{Ph}}$, **PP1** (1.31; 1.35; 1.38 и 1.16; 1.19; 1.22) for static and dynamic cases, respectively; Tables 2, 3.

Even more pronounced ratio growth occurs for $\mathbf{Q_{on}}$ (1.21 and 1.21 for dioxane in static and dynamic cases); for $\mathbf{Q_{on}}$ in dichlormetane these ratios are 1.45 and 1.27 in static and dynamic cases. The correlation of the growth of the ratio of polarizabilities in the gas phase and solvent with the increase in the number of heteroatoms in azine is also preserved in this case (an oxygen atom is added), but the quinoxalin-2-one fragment in $\mathbf{Q_{on}}$ is a less π-deficient one than the pyridopyrazine and even quinoxaline due to the presence of pyrrole type heteroatom. That is, the correlation between the pointed ratio and azine fragment π-deficiency

Table 3
Dynamic electric characteristics of the chromophores: average polarizability, α_{av} (10^{-24} esu), first hyperpolarizability, β_{tot} (10^{-30} esu), calculated in gas, dioxane and dichloromethane, and corresponding ratios.

	Q′	Q_{Ph}	Q_{on}	PP1	PP2
Gas					
$\alpha_{av}(\omega)$	89.3	101.0	96.7	99.1	95.8
$\beta_{tot}(\omega)$	535.2	588.8	594.1	563.0	322.7
$\beta_{tot}(2\omega)$	689.9	781.3	798.2	745.4	405.1
$\alpha_{av}(\omega)/\alpha_{av}(0)$	1.02	1.02	1.02	1.02	1.01
$\beta_{tot}(\omega)/\beta_{tot}(0)$	1.12	1.13	1.14	1.13	1.12
$\beta_{tot}(2\omega)/\beta_{tot}(0)$	1.45	1.51	1.53	1.50	1.39
Dioxane					
$\alpha_{av}(\omega)$	102.1	117.0	117.0	116.2	108.0
$\beta_{tot}(\omega)$	930.6	1103.7	1103.7	1132.0	509.6
$\beta_{tot}(2\omega)$	1244.6	1543.5	1543.5	1594.7	659.1
$\alpha_{av}^{sol}(\omega)/\alpha_{av}^{gas}(\omega)$	1.14	1.16	1.21	1.17	1.13
$\beta_{tot}^{sol}(\omega)/\beta_{tot}^{gas}(\omega)$	1.74	1.87	2.27	2.01	1.58
$\beta_{tot}^{sol}(2\omega)/\beta_{tot}^{gas}(2\omega)$	1.80	1.98	2.47	2.14	1.63
$\alpha_{av}^{sol}(\omega)/\alpha_{av}^{sol}(0)$	1.1	1.2	1.02	1.01	1.01
$\beta_{tot}^{sol}(\omega)/\beta_{tot}^{sol}(0)$	1.1	1.14	1.15	1.14	1.11
$\beta_{tot}^{sol}(2\omega)/\beta_{tot}^{sol}(0)$	1.50	1.59	1.69	1.61	1.43
Dichloromethane					
$\alpha_{av}(\omega)$	103.8	120.2	122.9	120.8	108.9
$\beta_{tot}(\omega)$	1163.0	1480.3	1976.9	1638.7	606.2
$\beta_{tot}(2\omega)$	1428.8	1911.4	2654.7	2162.2	730.6
$\alpha_{av}^{sol}(\omega)/\alpha_{av}^{gas}(\omega)$	1.16	1.19	1.27	1.22	1.14
$\beta_{tot}^{sol}(\omega)/\beta_{tot}^{gas}(\omega)$	2.17	2.51	3.33	2.91	1.87
$\beta_{tot}^{sol}(2\omega)/\beta_{tot}^{gas}(2\omega)$	2.07	2.17	3.33	2.90	1.79
$\alpha_{av}^{sol}(\omega)/\alpha_{av}^{sol}(0)$	0.90	0.90	0.90	0.90	0.90
$\beta_{tot}^{sol}(\omega)/\beta_{tot}^{sol}(0)$	0.92	0.92	0.89	0.92	0.94
$\beta_{tot}^{sol}(2\omega)/\beta_{tot}^{sol}(0)$	1.13	1.19	1.19	1.22	1.13

holds only partially. However, the mentioned ratio correlates well with a decrease in the aromaticity of the azine fragment, which is greatest in quinoline and least in quinoxalin-2-one and pyridopyrazine. In experimental studies, it is manifested in bathochromic shift of λ_{max} (504, 546, 556 and 573 nm in dioxane) and growth of solvatochromic shift $\Delta\lambda$ (chloroform-dioxane) in the UV–vis spectra: 32, 46, 63, 54 nm for **Q′**, **Q_{Ph}**, **PP1**, **Q_{on}**, correspondingly [14].

The same tendency holds for the first hyperpolarizability values, in this case it is manifested even stronger: for the chromophores **Q′**, **Q_{Ph}**, **PP1**, **Q_{on}**, the ratios of the values of β_{tot} in dioxane/dichloromethane and gas calculated for static and dynamic cases are: 1.74/2.65; 1.87/3.09; 2.0/3.57; 2.24/4.27 and 1.80/2.07; 1.98/2.17; 2.14/2.90; 2.47/3.37, respectively. Thus, for tuning the structure of effective chromophores, the inclusion of hetarene fragments with reduced aromaticity in the macro-acceptor is promising.

4. Conclusions

Here we continue the study of chromophores with macro-acceptors, composed of fused azine moieties (quinoline, quinoxaline, quinoxalinone, pyridopyrazine) and malononitrile one. For all studied chromophores, except **Q′**, containing quinoline hetarene moiety, two conformations are realized: *tc* and *cc* ones with *cis*-arrangement of double bonds within macro-acceptor; according to the estimation of Boltzmann probability, *tc*-conformer is shown to be the most favorable for **Q_{Ph}**, **Q_{on}** and **PP1**. The increase of the first hyperpolarizability values for the studied chromophores is in line with the analysis of HOMO/LUMO composition demonstrating effective charge transfer along the chromophore skeleton. The calculations of electric properties performed for various conformers of the studied chromophores demonstrate very small dependence of the (hyper)polarizability values on chromophore conformation. This result is important for possible application of such chromophores as molecular sources of materials nonlinear response. The dynamic first hyperpolarizabilities calculated at 1907 nm demonstrate moderate increase of $\beta(\omega)$ and notable enhancement at the harmonic frequency (by 1.5 times). Solvent effect on the electric properties of the studied chromophores is considered both for static and dynamic cases in dioxane and dichloromethane; similar tendencies are obtained in the change of polarizability and first hyperpolarizabilities: the values increase in a series **Q′ < Q_{Ph} < PP1 < Q_{on}.** It is noteworthy that the increase of the corresponding ratios in this series correlates with a decrease in the aromaticity of the azine moieties of macro-acceptor. Finally, in the case of **Q_{on}** first hyperpolarizability growth is most pronounced, demonstrating the highest value for $\beta_{tot}(0)$ and $\beta_{tot}(2\omega)$ in dioxane/dichloromethane by 2.24/4.27 and 2.47/3.33 times greater than in gas for the static and dynamic cases, respectively; the presented data give grounds to consider the chromophores with macro-acceptors promising for future research.

CRediT authorship contribution statement

Alina I. Levitskaya: Software, Investigation, Formal analysis, Data curation. **Olga D. Fominykh:** Validation, Formal analysis, Conceptualization. **Alexey A. Kalinin:** Writing – original draft, Investigation, Conceptualization. **Marina Yu. Balakina:** Writing – original draft, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.comptc.2025.115203.

Data availability

Data will be made available on request.

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