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Hydroxyflavone-containing polymers: theoretical prediction of spectral and nonlinear optical properties

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In order to evaluate spectral and nonlinear optical (NLO) properties of polymers and polymer composites containing natural hydroxyflavones as chain fragments or dopants, a theoretical analysis of absorption spectra of flavones, as well as calculations of values of their first hyperpolarizabilities and bond length alternation coefficients (BLA), were carried out. It has been shown that embedding hydroxyflavone fragments into polymer chains, glycidylation flavone hydroxyl groups, as well as twisting flavone molecules, result in improvement of optical properties of the flavone-containing polymers, namely in widening their transparency range into short-wavelength spectral region. The presence of basic amino-containing hardeners in polymers and polymer composites leads to a partial ionization of the flavone hydroxyl groups and, consequently, narrowing transparency range. The analysis of theoretical values — first hyperpolarizability values and BLA coefficients showed that natural polyhydroxyflavones are perspective chromophores for development of materials having a high NLO activity.

Keywords: hydroxyflavones, flavone-based chromophores, absorption spectra, hyperpolarizability, non-linear optics, polymers and polymer composites.

С целью прогнозирования спектральных и нелинейно-оптических (НЛО) свойств полимеров и полимерных композиций, содержащих в качестве фрагментов цепей или допантов природные гидроксифлавоны, сделан теоретический анализ спектров поглощения последних, а также расчет величин их первой гиперполяризуемости и коэфициентов альтернирования связей (BLA). Показано, что встраивание гидроксифлавонов в полимерные цепи, глицидилирование их гидроксильных групп, а также разуплощение их молекул приводят к расширению их зоны прозрачности в коротковолновую область. Наличие в полимерах и полимерных композициях отвердителей аминного типа приводит к частичной ионизации гидроксигрупп флавонов и последующему сужению зоны прозрачности. Анализ теоретических величин первой гиперполяризуемости и коэффициентов BLA показал, что природные полигидроксифлавоны являются перспективными хромофорами для создания материалов, имеющих высокую NLO активность.

Гідроксифлавон-вміщуючі полімери: теоретична оцінка спектральних та нелінійно-оптичних властивостей. *Д.Мішуров, А.Воронкін, О.Рошаль.*

З метою прогнозування спектральних і нелінійно-оптичних (НЛО) властивостей полімерів і полімерних композицій, що містять природні гідроксифлавони як фрагменти основних полімерних ланцюгів або як допанти, зроблено теоретичний аналіз спектрів поглинання останніх, а також розрахунки величин їх перших гіперполяризовностей і коефіцієнтів альтернування зв'язків (BLA). Показано, що введення гідрокси-флавонів у полімерні ланцюги, гліцидилування їх гідроксильних груп, а також розуплощення їх молекул приводять до розширення їх інтервалу прозорості у короткохвильову область

спектра. Присутність у полімерах та полімерних композиціях твердників амінного типу призводить до часткової іонізації гідроксильних груп флавонів і, таким чином, до звуження зони прозорості. Аналіз теоретичних величин першої гіперполяризовності та коефіцієнтів BLA досліджених хромофорів показав, що природні полігідроксифлавони є перспективними сполуками для створення полімерних матеріалів, що мають високу НЛО активність.

1. Introduction

The development of new polymer materials of high nonlinear optic (NLO) activity for various applications in photonics and optoelectronics is one of important domains of the modern material science [1]. NLO polymer materials can be obtained by several ways. Firstly, NLO polymer composites can result from adding into polymer matrices various organic compounds having high values of the molecular hyperpolarizability (β) [2–10]. Secondly, NLO polymers can be obtained by inclusion of NLO-active chromophores in polymer chains during synthesis of the latter [11–12].

The use of NLO-active chromophores of natural origin such as flavone derivatives for obtaining the NLO-polymers and polymer composites is new and perspective idea. In our recent publications [1, 12, 13], we reported on the synthesis and physico-chemical properties of polymer composites consisting of an epoxide matrix doped by a natural flavone dye — 3,5,7,3′,4′-pentahydroxyflavone (quercetin), as well as of polymers, where this dye is embedded into polymer chains. Obtained polymer systems demonstrated the transparence in a large spectral range, a high NLO activity, and a long chromophore relaxation time after poling procedure [13]. Analysis of experimental data allows us to recommend the use of natural flavonoids for the development of new materials with specified NLO properties.

At the present time, several hundreds of natural and synthetical flavones are known. On the one hand, this fact provides a great variety of chromophores with large spectrum of NLO activity, but, on the other hand, the search of most appropriate substances is complicated. The optimization and substantial acceleration of the search of necessary flavone chromophores can be achieved when using quantum chemical methods. In particular, calculations of the energies of electronic transitions allow to predict the transparence of polymer materials in different spectral ranges (except for the transparence level due to the light dispersion and depending on synthesis and doping conditions). Theoretical values of dipole moments and hyperpolarizabilities allow to estimate NLO properties of the materials.

The present work is devoted to a theoretical analysis of physico-chemical properties of some flavone derivatives in order to assess the possibility to use them for obtaining new polymeric NLO materials.

2. Theoretical and experimental

The unconstrained geometry optimization of isolated molecules of flavone and flavone derivatives (Fig. 1), calculations of localizations and energies of their molecular orbitals, theoretical absorption spectra and molecular hyperpolarizabilities in the ground singlet electronic state were carried out at the DFT level of theory [14] using the B3LYP functional and cc-pVDZ basis set [15, 16] implemented in the GAUSSIAN 09 program package [17]. When finishing each optimization, the Hessian matrix was calculated and analyzed to assess whether stationary structures had been obtained.

The solvent effect was included in the DFT calculations at the level of the polarized continuum model (PCM) [18, 19] using UAHF radii to obtain the molecular cavity. All the calculations were carried out for acetone medium, because this solvent was used for synthesis of quercetin containing polymer matrices, where the chromophore was built into polymer chains or used as a dopant.

The calculations were carried out on the cluster of the Ukrainian-American Laboratory of Computational Chemistry (UALCC, Kharkiv, Ukraine).

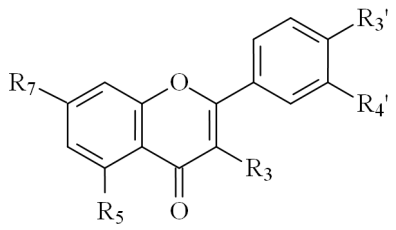
Experimental spectra of free, built-in and doped quercetin were recorded using a Hitachi U3210 spectrophotometer. The treatment of obtained spectra was carried out using the Spectral Data Lab program [20].

Preparation of polymer films with built-in and doped quercetin is described in [1].

3. Results and discussions

3.1 Analysis of UV-Vis spectra of flavone derivatives

It should be noted that NLO polymer materials designed for photonics and optoelectronics purposes have to demonstrate a substantial transparency in a wide spectral range, particularly in UV and visible regions. The transparency range can be predicted using theoretical estimations of long-wavelength band positions of the chromophore.



	R3	R5	R7	R3'	R4'	Name
I	OH					
II		OH				
III			OH			
IV				OH		
V					OH	
VI	OH		OH			
VII	OH				OH	
VIII	OH			OH	OH	
IX	OH	OH	OH			Galangin
X	OH		OH	OH	OH	Fisetin
XI	OH	OH	OH	OH	OH	Quercetin
XII		OH	OH			Chrysin

Fig. 1. Formulae, molecular structures and names of flavone derivatives (all empty cells correspond to hydrogen atoms).

When analyzing the transparency of polymers or polymer composites containing flavone chain fragments or dopants, it is important to consider that pK values of some hydroxyflavones are between 7 and 9 [21, 22]. Consequently, in neutral medium, the flavones can exist as a mixture of neutral and anionic forms. Correspondingly, the positions of absorption bands of both protolytic forms must be taken into account.

In present work, we have analyzed theoretical spectra of the protolytic forms of some wide spread hydroxyflavones. In order to understand spectral behavior of these compounds, we have also obtained spectra of model structures — flavones having one hydroxyl group in different positions. *Neutral forms of flavones.*

The majority of flavones have several absorption bands of complex structure due to four chromophore fragments [23] depicted in the Fig. 2.

Earlier, it was shown that wide and intense long-wavelength absorption band in flavone spectra centered at 330–380 nm is due to several, usually two electronic transitions between orbitals localized on *o*-oxybenzaldehyde (BA) and chromone (CH) fragments of the molecules. Two other transitions occurring between molecular orbitals of the same localization form a wide band centered at 250–290 nm. 3′- and 5-Hydroxy or alkoxyflavones have an additional low-intense absorption band centered at 300–330 nm [23] due to electronic transition between orbitals of phenyl fragment (PH). Moreover, in flavone spectra there is a band of a charge transfer transition with participation of orbitals localized on chromone moiety and side phenyl ring. The position of this band depends substantially on number, position and electron-releasing ability of

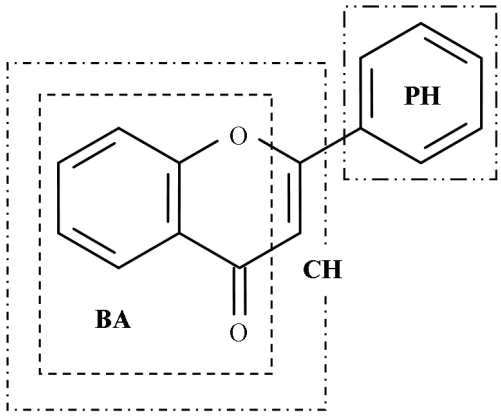


Fig. 2. Localization of chromophore fragments in flavone molecules (based on MO localization and analysis of the configuration interaction for one-electron transitions): BA — *o*-oxybenzaldehyde fragment, CH — chromone fragment, PH — side phenyl ring.

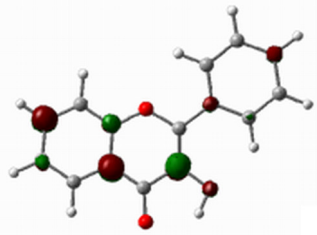
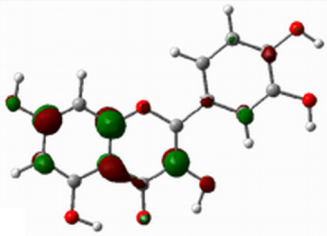
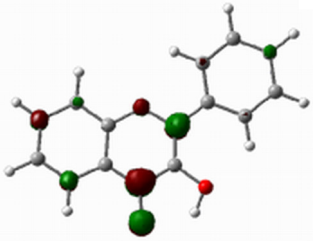
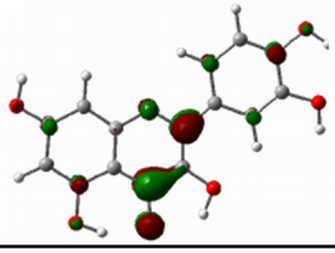
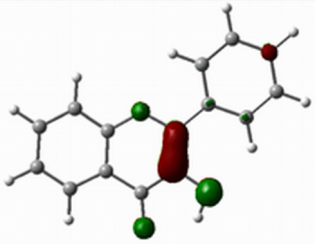
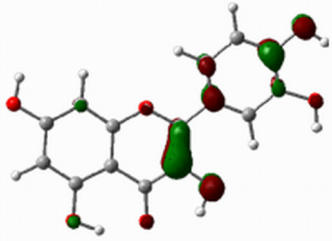
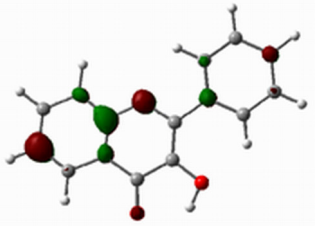
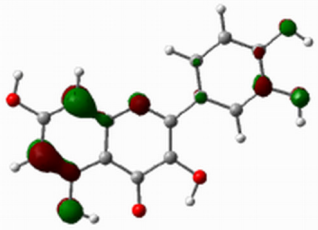
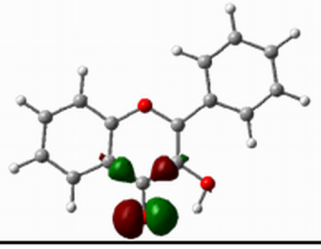
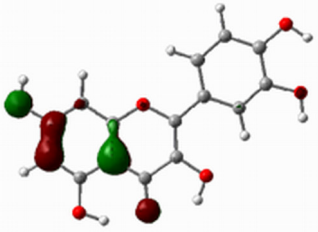
substituents, as well as on torsion angle between the fragments.

Localizations of the molecular orbitals (MO) for a model substance — 3-hydroxyflavone (flavonol) and natural pigment — 3,5,7,3′,4′-pentahydroxyflavone (quercetin) are listed in Table 1. It can be seen that localization character of the MO calculated by DFT method is similar to that obtained in previous publications [23] by semi-empirical methods PPP and CNDO/S.

Table 1 shows that changing number of hydroxyl groups does not result in a substantial changing MO energies and structure, although poly(hydroxyflavones) evidence some higher delocalization onto the side phenyl ring.

In all the flavones under investigations, the occupied and vacant MO φ_1, and φ_1' are localized on the chromone moiety, and the orbital φ_2 has *o*-oxybenzaldehyde localization. The increase of hydroxyl groups num-

Table 1. Localization of molecular orbitals responsible for electronic transitions in the long-wavelength range of absorption spectra*

	Flavonol	Quercetin
LUMO	 $\varphi_{2'}$ (CH)† -1.01 eV	 $\varphi_{2'}$ (CH) -0.74 eV
	 $\varphi_{1'}$ (CH) -2.20 eV	 $\varphi_{1'}$ (CH) -2.00 eV
HOMO	 φ_1 (CH) -6.02 eV	 φ_1 (CH) -5.62 eV
	 φ_2 (BA) -6.91eV	 φ_2 (BA) -6.26 eV
	 φ_3 (n) -7.17 eV	 φ_3 (BA) -6.74 eV

*Molecular orbitals are localized: BA — on *o*-oxybenzaldehyde part of the chromone fragment; CH — on whole chromone fragment, PH — on the side phenyl ring, *n* — on the carbonyl group. In such table cells the molecular orbital number (φ_i), the type of MO localization (BA, PH, CH, *n*), and MO energies are listed.

ber results in the decrease of the energy of the carbonyl nonbonding orbital that leads to changing its position on the energy diagram — from φ_3 to φ_5. The increase of the quantity of the hydroxyl groups in the side phenyl ring results in the decrease of the PH orbital energy and changing position of this orbital from $\varphi_{4'}$ to $\varphi_{3'}$.

When using the flavones as dopants or fragments of polymer chains, the transparency range of polymers or polymer composites is limited in short-wavelength part of the spectrum by position of flavone long-

Table 2. Theoretical spectral characteristics of model and natural flavones obtained by DFT method (b3lyp/ccPVDZ, solvent — acetone)[1]

	Long-wavelength electronic transitions		
	Ψ_I $\lambda_{abc}(f)$	Ψ_{II} $\lambda_{abs}(f)$	Ψ_{III} $\lambda_{abs}(f)$
I	366 (0.621), $0.58\chi_{1\to1'}$	302 $(0.000)^2$, $0.67\chi_{4\to1'}$	302 (0.223), $0.62\chi_{1\to2'}$
II	365 (0.126), $0.70\chi_{1\to1'}$	313 $(0.000)^2$, $0.69\chi_{4\to1'}$	304 (0.821), $0.62\chi_{2\to1'}$
III	340 $(0.000)^2$, $0.70\chi_{3\to1'}$	322 (0.615), $0.69\chi_{1\to1'}$	303 (0.166), $0.67 chiBR\ RA_{2\to1'}$
IV	343 $(0.000)^2$, $0.69\chi_{3\to1'}$	330 (0.223), $0.69\chi_{1\to1'}$	310 (0.345), $0.68 chiBR\ RA_{2\to1'}$
V	338 $(0.000)^2$, $0.69\chi_{3\to1'}$	333 (0.890), $0.70\chi_{1\to1'}$	295 (0.149), $0.68 chiBR\ RA_{2\to1'}$
VI	367 (0.660), $0.70\chi_{1\to1'}$	302 (0.255), $0.66\chi_{2\to1'}$	297 $(0.000)^2$, $0.69\chi_{5\to1'}$
VII	384 (0.746), $0.70\chi_{1\to1'}$	307 (0.134), $0.68\chi_{2\to1'}$	300 $(0.000)^2$, $0.69\chi_{5\to1'}$
VIII	393 (0.655), $0.70\chi_{1\to1'}$	330 (0.031), $0.69\chi_{2\to1'}$	300 $(0.000)^2$, $0.70\chi_{5\to1'}$
IX	386 (0.517), $0.70\chi_{1\to1'}$	318 (0.299), $0.69\chi_{2\to1'}$	295 (0.111), $0.65\chi_{3\to1'}$
X	388 (0.718), $0.70\chi_{1\to1'}$	323 (0.017), $0.69\chi_{2\to1'}$	296 (0.258), $0.65\chi_{3\to1'}$
XI	396 (0.759), $0.70\chi_{1\to1'}$	338 (0.031), $0.69\chi_{2\to1'}$	301 (0.112), $0.62\chi_{3\to1'}$
XII	361 (0.201), $0.70\chi_{1\to1'}$	312 (0.395), $0.68\chi_{2\to1'}$	308 (0.012), $0.68\chi_{4\to1'}$

* [1] λ_{abs} - maximum of absorption band (nm), f - oscillator strength, μ- dipole moment in the

wavelength band. Consequently, in order to predict the width of the transparency zone, it is necessary, first, to determine energies and nature of long-wavelength electronic transitions occurring between the orbitals of CH, BA and PH localizations.

Parameters of long-wavelength electronic transitions for selected natural and model flavones are listed in Table 2. Positions of hydroxyl groups in model compounds are typical for natural flavones.

The analysis of the configuration interaction showed that electronic transitions, which form long-wavelength absorption bands of flavones, can be described as one-electron transitions between orbitals CH → CH (Ψ_{II} for ***I–II*** and Ψ_I for ***III–XII***) and BA → CH (Ψ_{III} for ***I–II***; Ψ_{II} and Ψ_{III} for ***III–XII***). In addition, long-wavelength band includes a forbidden $n \to \pi^*$ transition of the carbonyl group. In the case of mono(hydroxyflavones), this is a transition Ψ_I or Ψ_{II}. When increasing number of hydroxyl groups, the energy of the n-orbital decreases, which results in a hypsochrome shift of the $n \to \pi^*$ transition from 330–340 to 295–305 nm.

The position of absorption band maximum depends generally on the energy of the long-wavelength transition CH → CH, which is, in its turn, determined by the energy of the occupied orbital Ψ_1. The increase of hydroxyl group quantity in the chromone fragment, particularly, the addition of 3-hydroxyl group, results in increase of the Ψ_1 energy and decrease of the energy of correponding Ψ_I transition. In the result, the long-wavelength band undergoes the bathochromic shift from 340–350 to 385 nm.

Furthermore, as it was already noted, the presence of hydroxyl groups in the side phenyl ring leads to partial delocalization of CH orbital onto this ring, which results in an additional increase of φ_1 orbital energy, decrease of the energy of the long-wavelength transition, and bathochromic shift of the absorption band. Thus, in cases of compounds X and XI this band is shifted to 390–400 nm.

It is evident that widening of the transparency range is possible when shifting long-wavelength absorption band to short-wavelength region of the spectrum. According to the data listed in Table 2, the widest transparency range must be in the case of flavones having a small number of hydroxyl groups in the chromone moiety (with no hydroxyl groups in the side phenyl ring). Thus, among the natural flavones under investigations, 5,7- and 3,7-dihydroxyflavones (***VI*** and ***XII***) have the most appropriated spectral characteristics.

Ionized flavones.

To make a correct estimation of the transparence zone range, it is important to take into account a fact that the synthesis of polymer chains is carried out in media whose pH differs from the neutral one. Thus, the building of polymer chains into epoxide polymer matrix occurs in the presence of a basic hardener containing amino groups. The medium in the polymer matrix formed is therefore basic, too.

As it was noted above, pK_a values of some flavone hydroxyl groups are in the range 7–9, that is why, some part of doped flavone molecules or the flavone fragments in polymer chains can be in ionized state (to be an anion). Taking into account sterical hindrances due to rigidity of three-dimensional polymer network, one can assume that the distribution of anionic forms of different structure would hardly correspond to their thermodynamic stabilities, and depends on relative positions of the chromophore fragments, amino groups in polymer chains and free hardener molecules.

In order to estimate the influence of the ionization on spectral properties of flavones, we calculated spectral parameters of long-wavelength electronic transitions of quercetin anions. Obtained results are listed in Table 3.

The analysis of MO energies for the neutral and ionized quercetin shows that appearance of the negative charge results in a substantial decrease of energies of all the MOs. Unlike the neutral flavones, whose HOMO are localized on chromone moiety only, quercetin anions ***XIb*** and ***XIc*** have HOMO of BA type, and orbitals of ***XId*** and ***XIe*** anions are localized on side phenyl ring. LUMO of anions ***XIa***, ***XId*** and ***XIe*** are similar to those of neutral molecules, however the dissociation of 5- and 7-hydroxyl groups result in formation of LUMO of the cinnamoyl localization, typical for chalcones and cinnamoyl pyrones [24]. Since all the long-wavelength transitions can be considered as the one-configuration ones, the comparison of MO localizations allows to conclude that the excitation of 3-hydroxyl anions (XI*a*) is accompanied by redistribution of the electronic density inside chromone moiety, anions with ionized 5- and 7-hydroxyl groups have long-wavelength transition with charge transfer onto the side phenyl ring, and anions with dissociated 3′ and 4′-hydroxyl groups have charge-transfer transition in opposite direction — from phenyl ring to chromone.

The data in Table 3 show that, independently on MO localization, the energy gap between HOMO and LUMO in the anions is always lower than that in the neutral molecule. Therefore, independently on the position of ionized hydroxyl group, the anion formation results in a bathochromic shift of long-wavelength absorption band. Such a spectral effect can also be interpreted as increasing electron-releasing ability of hydroxyl groups after their ionization. A value of this shift is in the range from 2525 cm^{-1} (anion ***XIc***) to 5255 cm^{-1} (anion ***XIe***).

The substitution of hydrogen atoms of the hydroxyl groups by acyl or glycidyl fragments [1] would result, inversely, in decreasing electron-realizing ability, and, correspondingly, in the opposite spectral effect — the hypsochromic shift of long-wavelength band.

Returning to optical properties of polymers, one can conclude that the presence of some quantity of the ionized flavone in polymeric matrix leads to narrowing its transparency zone. And vice versa, when carrying out glycidylation or acylation of hydroxyl groups, the transparency zone would expand.

Influence of sterical effects

As noted above, in polyhydroxy flavones, the molecular orbitals of CH type are partially delocalized on the side phenyl ring (for example, the MO φ_1 and $\varphi_{1'}$ of quercetin in Table 1). The energies of such orbitals and, correspondingly, the energies of electronic transitions depend on the degree of conjugation between the chromone and phenyl fragments. The degree of conjugation, in its turn, depends on the torsion angle between these fragments — θ. The geometry optimization of flavone derivatives showed that values of the torsion angle are in the range 0 and 10°, that is, the conjugation can be considered as maximal. However, the etherification (for example, glycidilation) of 3-hydroxyl group can result in appearance of sterical hindrances that lead to substantial increase of the torsion angle. Moreover, when flavone fragments are built into polymer chains, optimal conformations of the chains can be sometimes achieved at high values of θ, i.e. when flavone molecules are twisted.

Changing spectral parameters of quercetin when increasing the inter-fragmental torsion angle are listed in Table 4.

The data in Table 4 show that the twisting of free flavone molecules or flavone fragments in polymer chains result in decrease of the HOMO energy and increase of

Table 3. Spectral properties of long-wavelength electronic transitions of quercetin anions

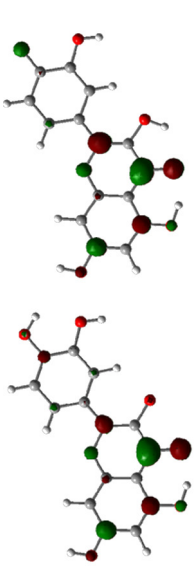
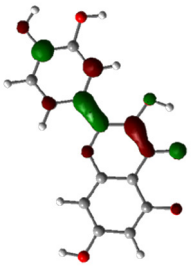
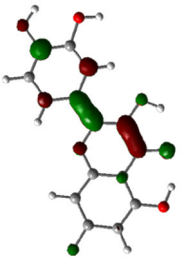
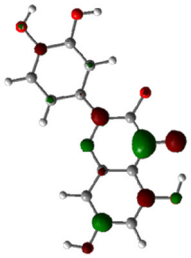
	XIa	*XIb*	*XIc*	*XId*	*XIe*
R_3	O^-	OH	OH	OH	OH
R_5	OH	O^-	OH	OH	OH
R_7	OH	OH	O^-	OH	OH
$R_{3'}$	OH	OH	OH	O^-	OH
$R_{4'}$	OH	OH	OH	OH	O^-
λ_{abs} (*f*)	490 (0.579)	448 (0.251)	440 (0.493)	578 (0.199)	500 (0.974)
C.I.	$0.71\chi_{1\to1'}$	$0.70\chi_{1\to1'}$	$0.70\chi_{1\to1'}$	$0.71\chi_{1\to1'}$	$0.70\chi_{1\to1'}$
LUMO					
E_{LUMO}, eV	-1.12	-1.10	-1.31	-1.58	-1.36
HOMO					
E_{HOMO}, eV	-4.05	-4.46	-4.65	-4.18	-4.15
ΔE_{MO}, eV	2.93	3.36	3.33	2.59	2.81
Transition	CH→CH	BA→CN	BA→CN	PH→CH	PH→CH

Table 4. Dependences of quercetin spectral parameters on the torsional angle (Θ) between the chromone fragment and side phenyl ring*

Θ°	0	15	30	45	60
$\lambda_{abs}(f)$	396 (0.759)	394 (0.741)	388 (0.689)	377 (0.602)	364 (0.475)
C.I.	$0.70_{\chi 1\rightarrow 1'}$	$0.70_{\chi 1\rightarrow 1'}$	$0.70_{\chi 1->Bs\ sA\ 1'}$	$0.70_{\chi 1\rightarrow 1'}$	$0.70_{\chi 1\rightarrow 1'}$
E_{HOMO}, eV	−5.62	−5.63	−5.65	−5.71	−5.79
E_{LUMO}, eV	−2.00	−1.98	−1.94	−1.87	−1.81
ΔE_{MO}, eV	3.62	3.64	3.72	3.83	3.98
μ, D	3.89	4.00	4.20	4.48	4.79

* parameter designations are given in footnotes of Tables 1–3.

the LUMO energy, that leads to increase of the energetic gap between MO and increase of the transition energy. Thus, when rotating the phenyl fragment through an angle from 0 to 60°, the hypsochromic shift ~ 2200 cm^{-1} — from 396 to 364 nm can be expected. Wherein, the oscillator strength of the transition decreases twice, thus the hypsochromic shift is accompanied by decrease of long-wavelength band intensity.

Increase of the torsion angle results also in growth of flavone dipole moments that can leads to increase of the solvatochromism and NLO properties of polymer materials doped or modified by these chromophores.

Fig. 3 shows experimental absorption spectra of quercetin in acetone (a) (acetone solutions are usually used for doping or modifying polymer matrices by flavones), of epoxy resin doped by quercetin (b), and of a polymer where quercetin molecules are built into polymer chains (*c*).

Comparison of the experimental and theoretical spectra shows that calculated energies of electronic transitions are lower by 0.3 eV, but, generally, predicted spectral behavior of flavones agrees well with experimental data.

It can be seen that long-wavelength band in the absorption spectrum of quercetin in acetone solution (*a*) has minimal half-width equal to 3560 cm^{-1}.

In the case of epoxy resin doped by quercetin (spectrum *b*), all the hydroxyl groups of quercetin can potentially be ionized by basic molecules of the hardener. This could result in formation of a mixture of different anionic forms. Indeed, in spectrum (*b*), besides the absorption band of neutral quercetin, long-wavelength shoulder at 410–440 nm is also seen. Absorption band half-width of the neutral form of quercetin in epoxide polymer matrix is equal to 4960 cm^{-1} that is substantially greater than in acetone solutions or in acetone solutions

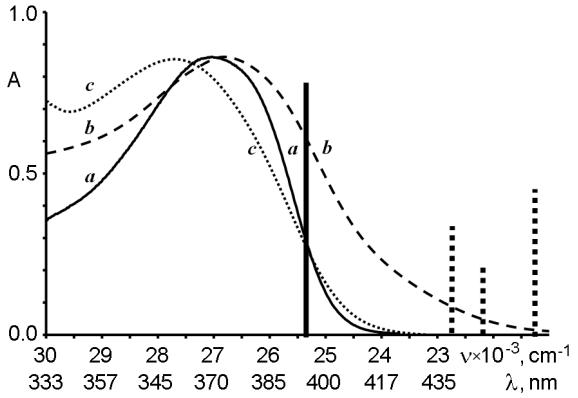


Fig. 3. Experimental and theoretical absorption spectra. Experimental spectra: *a* — solution of quercetin in acetone, *b* — polymer matrix doped by quecetine, c — polymeric matrix with quercetin fragments embedded in polymeric chains. Theoretical spectra: solid column — neutral quercetin, dotted columns — quercetine anionic forms ***XIa–XIc***.

containing epoxy oligomer. This phenomenon is probably due to the fact that hydrogen bonds between quercetin and polymer matrix are stronger than those between quercetin and solvent or oligomer molecules.

It should be noted that, in the polymer matrix, quercetin molecules are located in cavities of a three-dimensional polymer network retaining quite significant mobility. Therefore, we can assume that quercetin molecules in the polymer are in a thermodynamically favorable flat state.

Absorption spectrum (*c*) is obtained for a network epoxy polymer, where quercetin fragments are built into polymer chain. Such a polymer was obtained by the polycondensation with 7,4′-diglycidyloxy quercetin, where hydrogen atoms of the most acidic hydroxyl groups are substituted by glycidyl groups. The etherification of 7- and

4′-hydroxyl groups substantially decreases probability of the quercetin anion formation and has to result in hypsochromic shift of the absorption band due to decreasing electron-releasing properties of substituents. These effects are clearly seen in Fig. 2: the anion shoulder in the spectrum (*c*) is absent, and the long-wavelength band undergoes a blue shift.

Further broadening of the absorption band up to 5080 cm^{-1} (in comparison with spectra (*a*) and (*b*)) can be explained by another way. Owing to sterical effects in polymer chains, which are rigid due to their covalent cross-linking and hydrogen bonding, quercetin fragments can be twisted and exist as a large set of rotamers having various conjugation grades between the chromone moiety and the side phenyl ring. Thus, the broadening of the absorption band can be due to the interference of absorption of the various rotamers.

3.2. NLO properties of flavone derivatives

It is known that one of conditions necessary for substantial NLO activity is a large value of the first hyperpolarizability — β. This last depends on polarity of a molecule, on a size of its π-system, on the structural peculiarities such as planarity of the molecule or relative positions of electron releasing and electron withdrawing substituents. According to two-state theoretical approximation [25], first hyperpolarizability β_{tot} depends on the difference of the dipole moments in the ground and excited states — μ_{exc} and μ_{gr}, the difference of the energies of these states — E_{ge}, transition dipole moment — μ_{ge} and can be expressed by an equation:

$$\beta_{tot} \approx (\mu_{exc} - \mu_{gr}) \cdot \frac{\mu_{ge}^2}{E_{ge}^2}.$$

We have also characterized first hyperpolarizability using β_{zzz} — the hyperpolarizability tensor element coincident with the molecular symmetry axis and depending on the wavelength of the incident light and the dielectric permittivity of the medium. β_{zzz} has to be approximately proportional to β_{tot} values.

Calculated dipole moments β_{tot} and β_{zzz} are listed in Table 5. It was found that β_{zzz} values calculated by DFT method have a good correlation ($R = 0.83$) with β_{tot} values obtained according to the equation mentioned above. It also can be seen that maximal absolute values of first hyperpolarizability are expected for natural flavones ***VI*** and ***XI***.

Another parameter which allows to approximately predict NLO properties of organic molecules is a Bond-Length Alternation (BLA) number. Since hyperpolarizability is typical for π-conjugated systems, the degree of conjugation can be characterized by length alternation of bonds having high and low π-orders [26]. BLA can also be used to estimate the amount of polarization in conjugated molecule. BLA parameter is equal to $\Delta\overline{L}$ which is an average of the differences in the length between adjacent carbon-carbon "single" and "double" bonds $\Delta L = L_{single} - L_{double}$.

As it was shown in [26–29], substances demonstrating high NLO activity, for example stilbenes with electron releasing and withdrawing substituents or diphenyl polyenes, have BLA parameters larger than 0.1 Å. In the case of flavones, the highest BLA parameters are typical for 3,4′-dihydroxyl derivatives and reach 0.028–0.034 Å. This last fact proves that the natural flavones can be used for creation of new NLO materials. It is worth to note that 3,5,7,3′,4′-pentahydroxyflavone — quercetin has maximal parameters of β_{tot}, β_{zzz} and BLA and would demonstrate most pronounced NLO activity.

It is worth noting that the comparison of BLA parameters with first hyperpolarizability values β_{tot} and β_{zzz} has evidenced the linear correlation between them. Thus, correlation coefficients between BLA and β_{tot}, as well as between BLA and β_{zzz} are 0.74–0.76.

4. Conclusions

Summarizing results presented in this work we can draw several conclusions.

First, it can be seen that quantum chemical calculations give enough plausible information about spectral properties of flavones and their derivative. Obtained data can be useful not only for the prediction of optical properties of flavone-containing polymers and polymer composites (for example, the transparency range), but also for the explanation of the interaction between flavones and their polymer environment.

Second, calculations of β/β_{zzz} or non-direct estimations of NLO ability using BLA parameters show that the natural poly(hydroxyflavones) can potentially be used as chromophores for creation of various polymers and polymer composites having NLO properties. The most appropriate flavone with regard to its availability and maximal NLO ability is apparently quercetin.

Aknowlegments. The authors gratefully acknowledge Professor K.Krzyminski from University of Gdansk for assistance with testing

Table 5. Physico-chemical parameters of flavone derivatives

	E_{ge}, eV	μ_{gr}, D	μ_{exc}, D	μ_{ge}, D	$\beta_{tot}\cdot10^{-30}$ esu	$\beta_{zzz}\cdot10^{-30}$ esu	BLA, Å
I	3.38	4.00	5.00	7.51	4.94	2.73	0.022
II	3.39	6.40	9.23	1.51	0.56	−12.36	0.004
III	3.64*	4.60	4.13	0.00	–	0.66	0.014
IV	3.61*	7.08	1.50	0.00	–	−6.74	0.006
V	3.67*	7.70	2.41	0.00	–	−7.53	0.023
VI	3.38	4.41	3.67	7.97	−4.11	−11.22	0.023
VII	3.23	6.05	10.63	9.43	39.04	4.00	0.030
VIII	3.15	7.42	14.82	8.48	53.63	−7.62	0.028
IX	3.22	2.76	5.10	6.57	9.74	−0.37	0.021
X	3.20	6.80	11.55	9.17	39.01	0.84	0.030
XI	3.13	3.89	8.78	9.91	49.02	12.81	0.034
XII	3.43	4.78	10.11	2.40	2.61	−3.76	0.007

*Long-wavelength electron transitions of ***III***, ***IV*** and ***V*** are forbidden because they are of $n\pi^*$ nature, and their μ_{ge} and, correspondingly, β values are equal to zero.

the structures of the glycidyl ethers. The Ukrainian-American Laboratory of Computational Chemistry (UALCC, Kharkiv, Ukraine) is also gratefully acknowledged. This project is supported by grants of Ministry of Education and Science of Ukraine 0116U000835.

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