

Electronic absorption and emission spectra and computational studies of some 2-aryl, 2-styryl, and 2-(4'-aryl)butadienyl quinazolin-4-ones

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Abstract

The relatively less popular group of quinazoline heterocyclic compounds is searched theoretically for compounds with promising classical and nonlinear optical properties, e.g. fluorescence and high (hyper)polarizabilities. Candidates for NLO materials are found among the general series of α -4-(3H)-quinazolonyl- ω -aryl polyenes **1**, **2**, **3** and their fluorescence spectra are registered experimentally. CIS/6-31G* calculations provide no reliable predictions of observed UV/Vis and fluorescence spectra. However, semiempirical CISD PM3 calculations predict fairly well the observed bathochromic effects arising from extension of polyene chains (CH=CH)_n, n=0–2, and donor substitution in the aryl fragments. The observed fluorescence is assigned to planar quinonoid S1 emissive states, while ground S0 state geometries of compounds with n=0 are nonplanar, and with n>0 are planar. We find high TDHF PM3 static polarizabilities for all studied molecules, as well as high hyperpolarizabilities β SHG and γ THG.

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1. Introduction

Organic heterocyclic compounds comprise a vast field for the search of new materials in the fields of both classical and nonlinear optics. Derivatives of quinazoline and quinazolin-4-one are among the relatively less known dyes and/or pigments [1], and even less seems to have been reported on their luminescence properties. To our knowledge, no interest has been shown in the potential application of quinazoline derivatives in the nonlinear optics either. The main direction of the recent publications on quinazoline derivatives is related to their physiological activity [2], and provides quite a few new synthetic routes to the synthesis of potentially interesting compounds along the traditional patterns of electron spectroscopy specimens of

aryl derivatives. As such we choose three series of 2-aryl **1**, 2-arylethylene **2** and 2-arylbutadienyl substituted 4-(3H)-quinazolinones **3**, as shown on Scheme 1 below. Based on structural and theoretical commonsense, one could expect interesting features in the electronic spectra of these compounds, as well as some promising nonlinear optical properties. Once conceived, the idea can be first pursued by theoretical means, and promising results would justify experimental efforts to obtain the envisioned compounds synthetically as well.

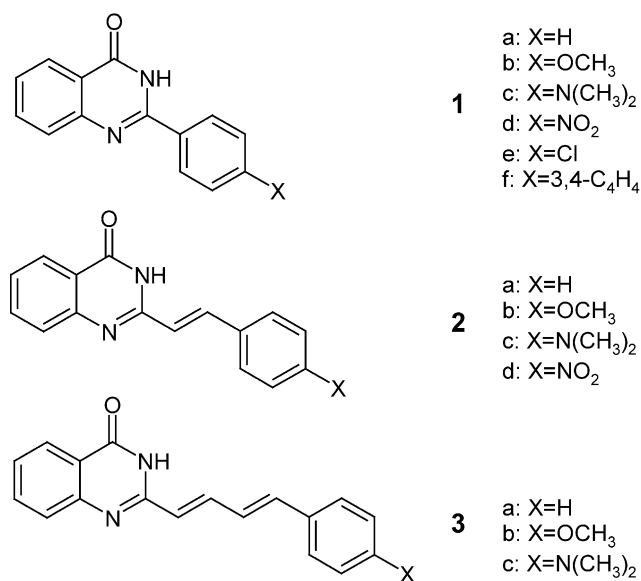
2. Experimental

Synthetic procedures and NMR analytical data on studied 2-aryl-4-(3H)-quinazolinones will be published elsewhere. UV/Vis absorption spectra of studied compounds are registered on a SPECORD UV–Vis Carl Zeiss Jena spectrometer, and fluorescence spectra are recorded

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Scheme 1. The three studies series of 2-substituted 4-(3*H*)-quinazolinones.

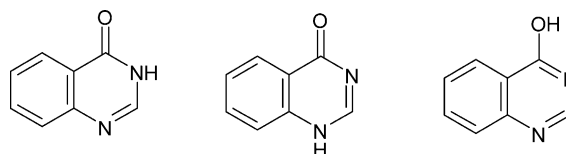
using a MPF-44 Perkin–Elmer spectrofluorimeter. Fluorescence grade solvents, ethylacetate and acetonitrile, are used.

3. Computational details

Molecular orbital models of the studied 4(3*H*)-quinazolinone molecules are first optimized using semiempirical PM3 calculations [3], and then refined at the RHF/6-31G* level, usually considered sufficient for routine descriptions of molecular properties [4]. To study the electronic spectra of 4-quinazolinones we apply CIS/6-31G* calculations [5], as well as CISD PM3 semiempirical calculations [6], employing a ‘relaxation cycle’ to account for the different geometries in the ground S0 and the first excited S1 states [7] by explicit optimization with the PRECISE keyword with PM3. This methodology has been used successfully in the interpretation of electronic absorption and emission spectra of heterocyclic compounds [7] in the gas phase and in solvents of varying polarity, in the latter case with the continuum conductor-like screening model of solvation, COSMO [8]. Potential non-linear optical properties of 2-substituted 4-quinazolinones are pursued by calculating polarizability values at the same PM3 semiempirical and RHF/6-31G* levels. We use the standard MOPAC 93 and GAUSSIAN 98 program packages [9,10], with default EF geometry optimization procedures [11]. Polarizabilities are calculated by the time dependent procedures, TDHF, in MOPAC [12].

4. Results and discussion

There are quite a few unsolved problems with quinazolinone and quinazolinone derivatives. We deal first with the prototropic tautomerism of 4-quinazolinone, which could

Scheme 2. The 3*H*, 1*H*, and OH tautomers of 4-quinazolinone.

have in principle 3 isomers—1*H*, 3*H*, and 4-OH, as shown on Scheme 2. Theoretical energies of these species, calculated at the semiempirical PM3 MO, as well as at RHF/6-31G* levels, are listed in Table 1.

At the semiempirical PM3 level, all considered 2-aryl quinazolin-4-ones show preference to the 4-oxo-3*H* tautomer. The 4-oxo-1*H* tautomer has a heat of formation 6–7 kcal mol⁻¹ higher, and the least stable tautomer, 4-hydroxyquinazolinone, has another 1–2 kcal mol⁻¹ higher heat of formation. The same ordering of tautomer stabilities results also from the RHF/6-31G* calculations, with approximately the same energy differences between the three possible isomers.

Additional data, listed in Table 1, include calculated (hyper)polarizabilities of some 2-aryl substituted 4-(3*H*)-quinazolinones, using the time-dependent formulae as implemented in the MOPAC package [12]. Experimental evaluation of these data is not readily available, and comparisons with other computational data from the literature only are possible at the time.

Some values of (hyper)polarizabilities of heterocyclic compounds can be extracted for comparison from recently published studies of Spassova and coworkers [13,14], who have found that the higher the level of calculation of these quantities, the higher their theoretical values. Thus, to estimate the expectations of potential NLO properties of 2-substituted quinazolinone derivatives, we can safely compare orders of magnitude of their calculated semiempirical PM3 values to, e.g. ab initio values, calculated for other heterocyclic compounds and certain benchmark molecules, like 4-nitroaniline. NLO characteristic quantities of the latter compound have been studied both by experiment and a variety of quantum chemical methods [15]. The benchmark values of polarizability α , first hyperpolarizability β SHG (second harmonic generation) and second hyperpolarizability γ THG (third harmonic generation), calculated by TDHF PM3 for 4-nitroaniline, and used in the discussion hereafter, are 74.5; 845.3 at 0.5 eV; and 25,470 at 0.5 eV, respectively. The values given by various ab initio computational schemes for the same quantities are between 40–110 (α) and 950–2800 (β SHG at 1 eV) [14]. Experimental values determined for β in solution are, however, higher by roughly an order of magnitude, in the range of 11–18 $\times 10^3$ [15].

The static PM3 polarizability α of simplest 2-phenyl-4-(3*H*)-quinazolinone, Table 1, is somewhat higher than the value for 4-nitroaniline quoted above and than the ab initio values for a series of thiorodanines [13]. However, the PM3

Table 1
Tautomers of 2-arylquinazolinones, MO PM3 and RHF/6-31G2 calculations

	ΔH_f (kcal mol ⁻¹)	RHF/6-31G*	α	β	γ
1a-3H	25.95	-719.7941	143.66	255.22	43568
1H	32.15	-719.7779	140.35	579.9	39596
OH	31.72	-719.7837	146.83	556.5	67250
1b-3H	-12.32	-833.6758	161.52	802.2	67888
1H	-6.02		156.09	912.8	47441
OH	-6.59		164.09	1212.6	95779
1c-3H	21.97	-852.8746	183.10	2206.4	163198
1H	28.01	-852.8588	175.41	2183.3	111197
OH	29.75	-852.8635	183.75	2931.7	191281
1d-3H	18.62				
1H	24.85				
OH	22.99				
1e-3H	19.84		160.80	1090.1	111529
1H	25.96		153.69	1299.1	71779
OH	24.93		158.55	1103.8	92928
1f-3H	43.77		192.67	653.4	126326
1H	49.35		184.90	973.1	80280
OH	48.95		190.72	711.3	107772
2a-3H	39.58	-796.6798	179.56	866.9	178512
OH	46.42	-796.6697			
1H	45.08	-796.6659			
2b-3H	1.32				
OH	6.43				
1H	6.88				
2c-3H	35.58	-929.7593	218.24	3491	35,5933
OH	42.62	-929.7480			
1H	41.52	-929.7459			
2d-3H	31.62				
OH	37.44				
1H	37.40				
3a-3H	53.53		217.13	1689.2	369774
1H	59.41		206.77	2067.3	257365
OH	60.40		217.81	2330.5	387251
3b-3H	15.25		237.93	3169.2	480188
1H	20.83		225.91	3376.6	344514
OH	20.48		237.47	3102.7	473362
3c-3H	49.64	-1006.6479	257.0	4841.6	626974
OH	56.67	-1006.6368			
1H	55.54	-1006.6344			

ΔH_f —PM3 heats of formation, kcal mol⁻¹; 6-31G* total energies, a.u.; and (hyper) polarizabilities a.u.* hyper/polarizabilities are calculated using TDHF/PM3 [12].

TDHF values of hyperpolarizabilities β and γ , listed in Table 1, are higher than those of thiorodanines [13] by two to three orders of magnitude. We thus conclude that 2-aryl-polyenyl substituted 4-(3H)-quinazolinones are attractive objects for future studies of NLO properties. An indirect indication of this perspective is given by the fluorescence properties of studied 2-substituted 4-(3H)-quinazolinones, listed in Table 2.

Table 2 presents the calculated PM3 energies of vertical vacuum electronic transitions S0–S1 (absorption) and S1–S0 (emission). It is, however, instructive to consider first the geometry changes incurred to 2-substituted 4-(3H)-quinazolinone molecules by electronic excitation and (vibrational) relaxation to the nearest equilibrium geometry. The equilibrium ground S0 state and first S1 excited state

geometries are given in Fig. 1. As expected, in the ground S0 state, aryl substituents at position 2 of 4-(3H)-quinazolinone in general are nonplanar with respect to the heterocyclic ring, due to torsion around the single C–C bond, connecting the two conjugated fragments. The dihedral angle between the heterocycle and the aromatic ring is in the range 53° (4'-CH₃O, 4'-Me₂N)—50° (phenyl)—15° (4'-Cl). An exception of the PM3 computational scheme is the 2-(4'-nitrophenyl) compound, where the two aromatic rings are coplanar within the limits of error, 2.5°. RHF/6-31G* calculations, like PM3, show that the two aromatic rings of 2-aryl-4-(3H)-quinazolinones are out of each others' plane, although to a somewhat smaller extent—calculated dihedral angles between quinazolinonyl and substituted phenyl rings are in the range of 20–25°.

Table 2

Calculated CISD PM3 gas phase and experimental (ethylacetate, MeCN) electronic spectra of 2-arylsubstituted 4(3*H*)quinazolinones, cm^{-1}

Compound	S0–S1 Absorption	S1–S0 Emission	E_{abs}	E_{fl}	Stoke's shift	
	Calculated	Calculated	Experimental	Experimental	Calculated	Experimental
1a	32,300	25,200	33,000 33,200	– –	7100	–
1b	31,900	22,150			9750	
1c	31,340	24,310	28,700 28,300	24,570 23,470	7030	4130 4830
1e	30,210	28,620	32,500 32,500	23,640	1590	8860
1f	29,706	23,216	32,100 32,200	– –	6490	– –
2a	29,000	21,730	31,500 31,500	24,095 23,695	7270	7400 7800
2b	28,112	21,686	28,800 28,700	23,310 23,250	6426	5500 5450
2c	26,708	21,433	25,300 24,900	20,700 19,650	5280	4600 5250
3a	27,885	19,490				8395
3c	26,027	19,128	24,300 24,100	18,520 17,300	6900	5780 6800

The estimated accuracy of experimental spectra is $\pm 200 \text{ cm}^{-1}$.

To the contrast of the ground S0 state results, the CISD PM3 geometries, calculated for the excited S1 states of 2-aryl-4-(3*H*)-quinazolinones, have coplanar heterocyclic and aromatic rings. It is important to note as well, that in the first excited S1 state the order of stability of quinazolinone tautomers is preserved with most substituents, and even reinforced by larger energy differences between the prototropic isomers. There are, possibly, important exceptions from the rule: for example, quinazolines with 4'-CH₃O- and 4'-(CH₃)₂N-

phenyl substituents in position 2 have PM3 values of heats of formation in the S1 state of 66.6 (3*H*), 77.3 (4-OH), and 98.1 (1*H*) kcal mol^{-1} (4'-CH₃O), while for 4'-(CH₃)₂N the values are 98.3 (3*H*), 105.4 (4-OH), and 113.0 (1*H*—may not be completely optimized) kcal mol^{-1} . However, attempted PM3 CISD optimizations of the S1 state for the latter 4'-(CH₃)₂N-phenyl-4-(1*H*)quinazolinone molecule tend to converge into a low-lying and severely bent T1 state, with heat of formation 86.1 kcal mol^{-1} .

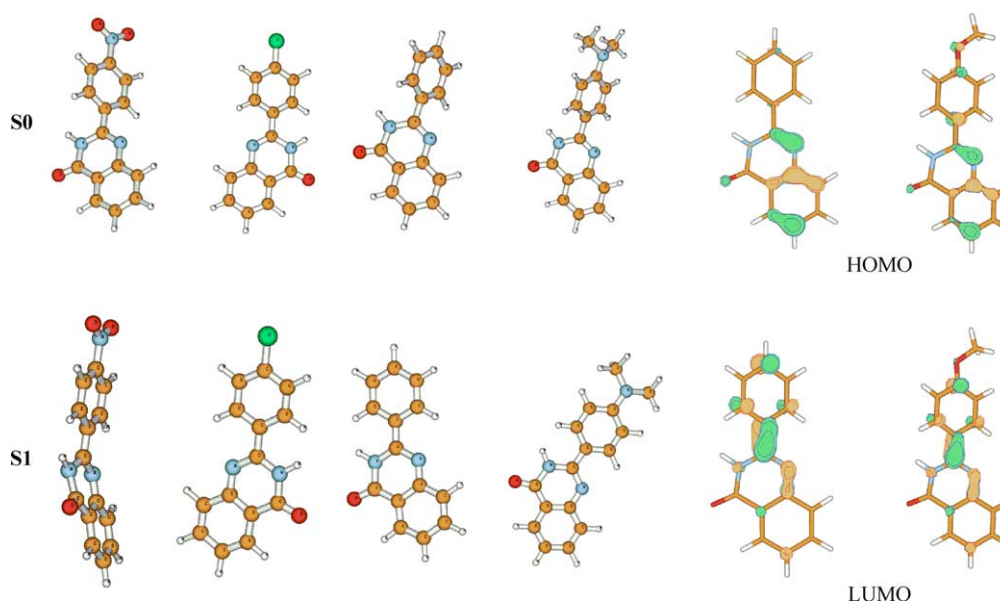


Fig. 1. PM3 ground state S0 and CISD PM3 excited state S1 geometries, HOMO and LUMO (RHF/6-31G*) of 2-aryl-4(3*H*)quinazolinones.

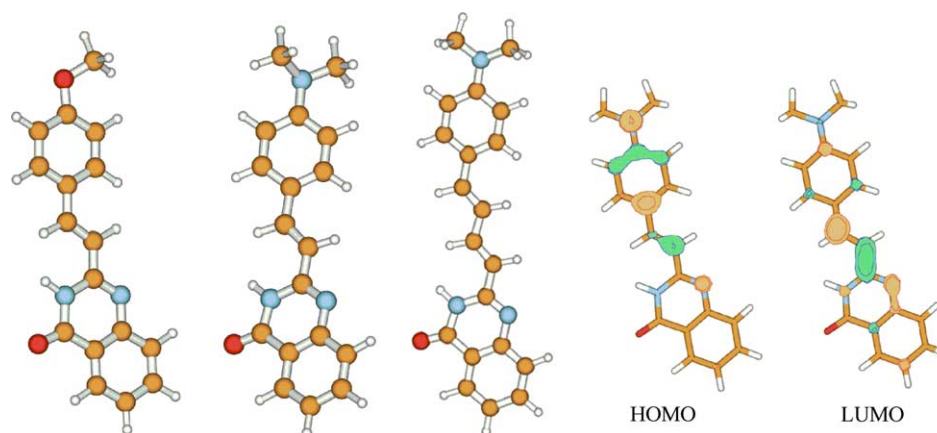


Fig. 2. PM3 ground state S0 and CISD PM3 excited state S1 geometries, HOMO and LUMO (RHF/6-31G*) of α -[2-4(3H)quinazolonyl]- ω -aryl polyenes.

As shown on Fig. 1, excited S1 geometries of 2-aryl-4-(3H)-quinazolinones are mostly planar, evidently due to the quinonoid structure of the excited state. There are exceptions in the S1 geometry of the 4'-nitro-compound **1d**, where the aromatic rings are out of each others' planes as well. Knowing already the quinonoid electronic structure of the excited S1 state, we interpret this result as the manifestation of some singlet–triplet instability, observed also with the other extreme of 2-aryl substituted 4-quinazolinones, 4'-dimethylamino **1c**, vide supra. The less stable 1H-prototropic tautomers of **1b** and **1c** tend to lose planarity in the S1 state and possibly also lose their singlet–triplet stability.

Geometries of α -[2-4-(3H)-quinazolonyl]- ω -aryl polyenes **2** and **3** in the ground S0 and excited S1 electronic states are planar and considerably closer to each other than those of corresponding ground and excited states of 2-aryl-4-(3H)-quinazolinones, Fig. 2. Frontier orbitals of these polyenic systems are dominated by the large conjugated substituents, and once again show quinonoid character of the excited S1 state.

Semiempirical CISD calculations at the NDDO level are usually sufficient to provide the rational basis to the understanding of electronic absorption and emission spectra [7 and references therein]. Prior to directly considering the interpretation of experimental spectra, Table 2, we attempt to acquire additional data from CIS/6-31G* calculations of selected 2-substituted 4-(3H)-quinazolinones. At the corresponding optimized CIS/6-31G* geometry, calculated first excitation energies do not reproduce observed trends of substituent effects in either 2-aryl 4-(3H)-quinazolinone or α -[2-4-(3H)-quinazolonyl]- ω -aryl ethylene series, and only fairly predict bathochromic shifts of spectral maxima due to the extension of conjugated π -electronic systems, Table 3, entries **1a** and **2a**. However, predicted substituent effects for charge transfer and π -extension effects are much smaller than observed, see entries **1c** and **2c** with the donor Me₂N substituent.

The rather discouraging CIS/6-31G* results on electronic transition energies of studied 2-substituted 4(3H)quinazolinones leave us with the satisfactory predictions of CISD PM3 calculations, Table 2, where theoretical absorption and fluorescence maxima deviate from experiment by not more than 2500 cm⁻¹, or 0.3 eV. This allows us to assign the observed fluorescence of 4(3H)quinazolinones to a planar conjugated quinonoid S1 state, Figs. 1 and 2, augmented by considerable excited state charge transfer. This deduction is supported by the significant bathochromic effect of polar solvent CH₃CN on the fluorescence maxima, Table 2, while absorption maxima show practically no effect of the change of ethyl acetate ($\epsilon=6.02$) to acetonitrile ($\epsilon=37.5$). The experimental failure to observe fluorescence for 2-aryl-4-(3H)-quinazolinones with no donor substituent in the aryl fragment, e.g. **1a** and **1f**, Table 2, also supports the above conclusion. The reported spectroscopic and theoretical results are thus a good prerequisite to further detailed studies of photophysics and photochemistry, as well as of nonlinear optical properties of 2-aryl-4-(3H)-quinazolinones.

Table 3
CIS/6-31G* gas phase and experimental excitation energies, cm⁻¹, of selected 2-aryl 4-(3H)-quinazolinones

	CIS/6-31G* (cm ⁻¹)	Absorption	Fluorescence
1a	34,976	Exp. 33,000	Fl. –
1b	35,338	Exp.	Fl.
1c	34,883	Exp. 28,700	Fl. 24,570
2a	32,401	Exp. 31,500	Fl. 24,095
2c ^a	30,985	Exp. 25,300	Fl. 20,700

^a CIS/6-31G calculation.

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