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Rational design of long-wavelength absorbing and emitting carbostyrils aided by time-dependent density functional calculations

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ABSTRACT

We have used computational chemistry methods to aid the rational design of long-wavelength absorbing and emitting organic materials. For this purpose, the vertical electronic transition energies of 3,4-dicyano carbostyrils (quinolone-2(1H)-ones) substituted by electron-donating substituents (methoxy, methylamino, dimethylamino) at positions 6 and 7, are calculated by time-dependent density functional theory (B3LYP) within the Tamm–Dancoff approximation. Bulk solvent effects (DMSO, CH_3CN, H_2O) were taken into account by the CPCM solvation model. Particular long-wavelength absorptions (~540 nm) are predicted for derivatives containing an amino group in position 6 irrespective of whether a 7-methoxy or a 7-amino group is present. In contrast, considerably shorter wavelength absorption (~440 nm) can be expected for 6-methoxy-7-amino substituted 3,4-dicyano carbostyrils. Optimization of the first excited singlet state of 6-dimethylamino substituted carbostyrils leads to a perpendicular arrangement of the $(CH_3)_2N$-group with respect to the heterocyclic ring system accompanied by an extremely low electronic transition energy (1000–1500 nm) with vanishingly small intensity (oscillator strength $f < 0.000$). 6-methoxy-7-amino substituted carbostyrils are predicted to emit at 490–520 nm. An especially long-wavelength fluorescence (~660 nm) is calculated for 6-amino-7-methoxy- as well as 6,7-bis (methylamino)-3,4-dicyanocarbostyril.

1. Introduction

Carbostyrils [quinolin-2(1H)-ones] are frequently used as laser dyes or fluorescence sensors in analytical applications, especially in biochemistry or medicine [1–8]. Most carbostyrils used in these applications are substituted at C7 by a strong electron donor, e.g. an amino or dimethylamino group as in Carbostyril-124 (7-amino-4-methylcarbostyril) and Carbostyril-165 (7-dimethylamino-4-methylcarbostyril). Experimental data for these two compounds (λ_{abs}, λ_F, Φ_F) measured in acetonitrile are 348 nm, 384 nm, 0.30 (Carbostyril-124) and 358, 406, and 0.79 (Carbostyril-165 [1]. However, fairly extensive combined experimental as well as computational studies concerning the rational design of long-wavelength absorbing and emitting carbostyrils [9–14], indicated that significantly improved photophysical properties can be obtained by judiciously choosing the substituents of the carbostyril ring system. Based on these previous investigations, the effects of structural modifications on photophysical properties of carbostyrils can be summarized as follows (Scheme 1): (i) particular long wavelength absorption and emission is found for derivatives bearing an electron acceptor [trifluoromethyl (**1a**, **1b** in Scheme 1 where the relevant experimental data are shown) or cyano (**1c**, **1d**)] in position 4 and an electron-donating group (methoxy) in position 6. (ii) Introduction of a second cyano group in position 3, as in 3,4-dicyano-6-methoxyquinolin-2(1H)-one **1e** results in a profound bathochromic shift. For instance, $\lambda_F = 545$ nm in **1e** compared with $\lambda_F = 461$ nm measured for the mono-cyano derivative 4-cyano-6-methoxyquinolin-2(1H)-one **1c** (iii) An electron-donating group in position 7 has little or even an hypsochromic shift of both absorption and emission. However, absorption intensities (extinction coefficients ε) as well as fluorescence quantum yields Φ_F are usually increased by such substituents, e.g. **1a** vs **1b**, **1c** vs **1d** or **1e** vs **1f** (Scheme 1).

Given these data one might anticipate that further modifications, e.g. change of the electron-donating properties of the substituents in positions 6 and/or 7 of the parent 3,4-dicyano-quinolin-2(1H)-one will further shift the first absorption and fluorescence bands to longer wavelengths or increase absorption intensities and fluorescence quantum yields. In our efforts to designing long wavelength absorbing and emitting carbostyril-based dyes with sufficiently high absorption intensities and fluorescence quantum yields we

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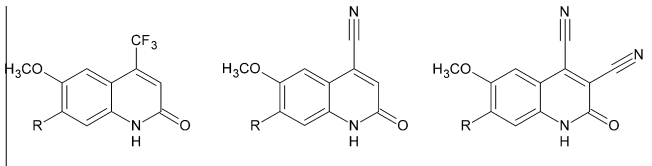

1a,b **1c,d** **1e,f**

	R	λ_{abs} / nm	ε	λ_{Flu} / nm	Φ_F
1a	H	374	5220	450	0.06
1b	CH_3O	368	10400	436	0.45
1c	H	394	5400	461	0.11
1d	CH_3O	390	12400	436	0.61
1e	H	460	4760	545	0.13
1f	CH_3O	451	12270	525	0.24

Scheme 1. Substituent effects on experimental UV/Vis absorption and fluorescence data of selected carbostyrils **1a**–**1f** (experimental data are taken from Ref. [9] for **1a, 1d**; Ref. [11] for **1b**; Ref. [13] for **1a**, **1c**; and Refs. [12,13] for **1e** and **1f**.

considered a series of differently 6,7-disubstituted 3,4-dicyanoquinolin-2(1H)-ones **2**–**10** (Scheme 2). Sincetime-dependent density functional theory [15–19] has become a valuable tool for the calculation of absorption and fluorescence spectra of dye molecules [20–30], we have used this method for a "virtual screening" [30] of these structures.

These compounds have been chosen such to cover different electron-donating properties of the substituents (methoxy vs amino-derivatives), possible intramolecular hydrogen bonding between these substituents (monomethylamino groups), and steric hindrance or lack thereof (dimethylamino groups vs incorporation of the substituents into a six-membered ring). Recently we have calculated the electronic excitation energies (absorption and fluorescence) of **1e** and **1f** by various density functionals (B3LYP, CAM-B3LYP, PBE0, LC-PBE, M06-2X, and B2PLYP) using both the time-dependent density functional (TDDFT) and Tamm–Dancoff approximation (TDA) [14]. The solvent DMSO had been included by both, explicit solvent molecules and the linear response (LR) approach in non-equilibrium. Closest agreement with experimental data was obtained with the TDA-B3LYP procedure. Consequently, TDA-B3LYP calculations combined with the non-equilibrium LR approach for solvation has primarily been used in the present investigation[1]. For some selected compounds in addition the state-specific solvation model and also the TDDFT procedure has been applied.

2. Computational details

All structures were completely optimized in the ground (S_0) and first electronic excited singlet state (S_1) using the B3LYP hybrid density functional [31,32] in combination with the def2-TZVP basis set [33] in the gas phase. Bulk solvent effects (DMSO, CH_3CN, H_2O) were treated by the CPCM solvation model [34,35] using the linear response (LR) approach (non-equilibrium solvation) in combination with the gas-phase optimized S_0 and S_1 geometries. No optimization in the respective solvent has been done. To check this protocol, test calculations on compounds **1e**, **7**, and **13** using the state-specific (SS) solvation model [36–38] have also been performed. Since in the LR calculations only gas-phase optimized geometries were used, the SS calculations were also based on these structures. In addition, the S_0 as well as the S_1 state of **1e** were optimized in DMSO, those of **13** in DMSO, EtOH, and $CHCl_3$. Excitation energies within the SS model were obtained by TDDFT rather than TDA. The local vs intramolecular charge transfer character of the individual electronic excited states was characterized by the Λ-diagnostic [39,40] describing the overlap of the orbitals involved in the electronic transition. The TDA approximation, i.e. the CIS-like variant of time-dependent density functional theory [16–19], was used for calculating excitation energies. Programs used were ORCA [41,42] for geometry optimization and GAMESS [43,44] for TDA calculations. State-specific solvation calculations were done with Gaussian 09 [45]. TightSCF and Grid4 was used for geometry optimization; the DFT grid applied in the TDA calculations was NRAD = 96, NLEB = 302. Otherwise default settings were used. Visualization was done with MOLDEN [46] and MOLEKEL [47].

3. Results and discussion

In the first part of the study the LR approach for solvation has been applied. First, calculated electronic transition energies using ground state geometries, i.e. absorption wavelengths λ_{abs}, oscillator strengths, and Λ-diagnostics of compounds **2**–**10** in DMSO are summarized in Table 1. Also presented there are the orbital compositions of S_1 and S_2. For comparison purposes the data for **1e** and **1f** [12–14] are also included. Second, the analogous data obtained when using S_1 geometries, i.e. fluorescence spectra, are presented in Table 2, followed by a brief discussion of solvent effects (CH_3CN, H_2O). Third, comparison with experimental results [11] obtained for some analogous compounds (Scheme 3 in Section 3.4), namely 7-methoxy-6-(methylamino)-4-(trifluoromethyl) quinolin-2(1H)-one (**11**), 6-(dimethylamino)-7-methoxy-4-(trifluoromethyl)quinolin-2(1H)-one (**12**), and 1,4-dimethyl-9-(trifluoromethyl)-1,3,4,6-tetrahydropyrido[2,3-g]quinoxalin-7(2H)-one (**13**) is made. Comparison of the LR results with the SS approach for solvation has been performed for selected carbostyrils **1e**, **7** and **13**. Finally, in Section 3.5 electronic transition energies ΔE_{abs} and ΔE_{em} of selected derivatives obtained by TDA are compared with those resulting from the TDDFT procedure.

For compound **4** two conformations differing in the twists of the methylamino groups with respect to the heterocyclic ring system were calculated (see Fig. 1). In **4a** the two torsional angles τ_1(C5–C6–N–CH_3) and τ_2(C8–C7–N–CH_3) are $\tau_1 = 11^o$ and $\tau_2 = 113^o$; in **4b** $\tau_1 = 96^o$ and $\tau_2 = 8^o$. In the ground state isomer **4b** is more stable than **4a** by 3.2 kcal mol^{-1}. Excitation into S_1 reverses this stability order, and **4a** is more stable than **4b** by 4.5 kcal mol^{-1}. In principle, for **10** also two such conformations are possible. However, upon optimization only one was obtained with $\tau_1 = -18^o$ and $\tau_2 = -13^o$ (for measuring τ_1 and τ_2 the two methyl groups pointing away from each other were used).

3.1. Absorption spectra

For all compounds two long-wavelength absorption bands in the visible region (430–545 nm and 350–430 nm) with significant oscillator strengths are predicted. The first transition is the stronger one in compounds **2**, **4b**, **6**, and **8**. While the presence of an amino in position 7 does not in all cases lead to a greater intensity of the first absorption band, see for instance **6** vs **7** or compound **10**, it appears to be a necessary requirement for especially strong long-wavelength absorption. This is further corroborated

[1] Some preliminary results of this investigation have been presented at "The 18th International Electronic Conference on Synthetic Organic Chemistry (ECSOC)", Nov 1–30, 2014, cited as (Kelterer, A.; Fabian, W.; Uray, G. Computational Design of Long-Wavelength Absorbing and Emitting Carbostyrils. In Proceedings of the 18th Int. Electron. Conf. Synth. Org. Chem., 1–30 November 2014; Sciforum Electronic Conference Series, Vol. 18, 2014 , e011; doi: http://dx.doi.org/10.3390/ecsoc-18-e011).