COMPUTATIONAL DESIGN OF LONG-WAVELENGTH ABSORBING AND EMITTING CARBOSTYRILS

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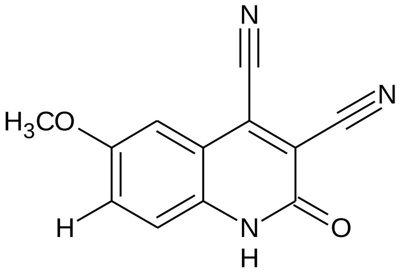
ABSTRACT

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 carbostyriles (quinolone-2(1H)-ones) substituted by electron-donating substituents at positions 6 and 7, are calculated by time-dependent density functional theory (B3LYP) within the Tamm-Dancoff approximation. Bulk solvent effects in DMSO were taken into account by the CPCM solvation model. Particular long-wavelength absorption and emission (λ_{abs}~540 nm, λ_F ~670) is found for derivatives containing an amino group in position 6 and an ether oxygen at C7 (compound **3**). In contrast, considerably shorter wavelength absorption and fluorescence (λ_{abs}~440 nm, λ_F ~530) is calculated for the isomeric compound **4.** Both long wave length absorption and emission and in addition sufficiently large oscillator strengths are predicted for the quinoxaline derivative **5** containing amino groups at C6 and C7.

INTRODUCTION

Carbostyrils [quinolin-2(1H)-ones] derivatives are frequently used as fluorescent sensors in biochemistry, especially as antenna molecules in luminescence energy transfer or FRET systems [1-5]. They also have been used as fluorescent receptor ligands in fluorescence polarization assays [6] or for the determination of bromate in drinking water [7]. With such applications in mind, over the past years a number of studies to optimize the photophysical properties of carbostyrils (wavelength of absorption and emission, Stokes shift, absorption intensities, fluorescence quantum yields) have been published. The most promising carbostyril-based fluorescent dyes so far are 3,4-dicyanoquinolin-2-(1H)-ones substituted in position 6 by electron donor groups, e.g. 3,4-dicyano-6-methoxyquinolin-2-(1H)-one **1** or 3,4-dicyano-6,7-dimethoxyquinolin-2-(1H)-one **2** [8,9].



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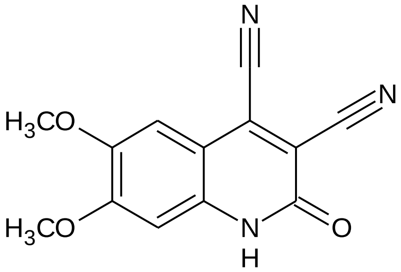

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Interestingly, introduction of a second methoxy group at C7 resulted in a blue shift of both absorption and emission (λ_{abs} = 451, λ_F = 525) compared with **1** (λ_{abs} = 460, λ_F = 545). In contrast, the fluorescence quantum yield was increased (Φ_F = 0.24 in **2** and Φ_F = 0.13 in **1**)

OBJECTIVE OF THE WORK

While introduction of the second cyano group at C3 of the carbostyril moiety, combined with a methoxy group at C6 resulted in unprecedented long wavelength absorptions and emissions of this type of dyes, the fluorescence quantum yields were only modest. In the design of carbostyril-based dyes computational methods have proven quite successful [10]. The aim of the present study is to apply the previously used computational procedure [10] for the design of long wavelength absorbing and emitting carbostyril derivatives with satisfactory absorption intensities and fluorescence quantum yields.

CHOICE OF COMPOUNDS

An obvious modification would be replacement of the methoxy groups by stronger electron donor moieties, for instance dimethylamino groups. However, previous investigations on dimethylamino-substituted carbostyrils indicated a considerably smaller than expected effect of this modification, possibly caused by twisting of the $(CH_3)_2N$ group because of steric hindrance [11]. Indeed, preliminary calculations on 6-dimethylamino-7-methoxy-4-trifluoromethyl carbostyril resulted in a slight twist of the $(CH_3)_2N$ group in the ground state; in the first excited state S_1 a perpendicular arrangement of this moiety – characteristic for an intramolecular charge transfer (TICT) state (Figure 1) with a concomitant zero emission probability (f ~ 0.000) – was found.

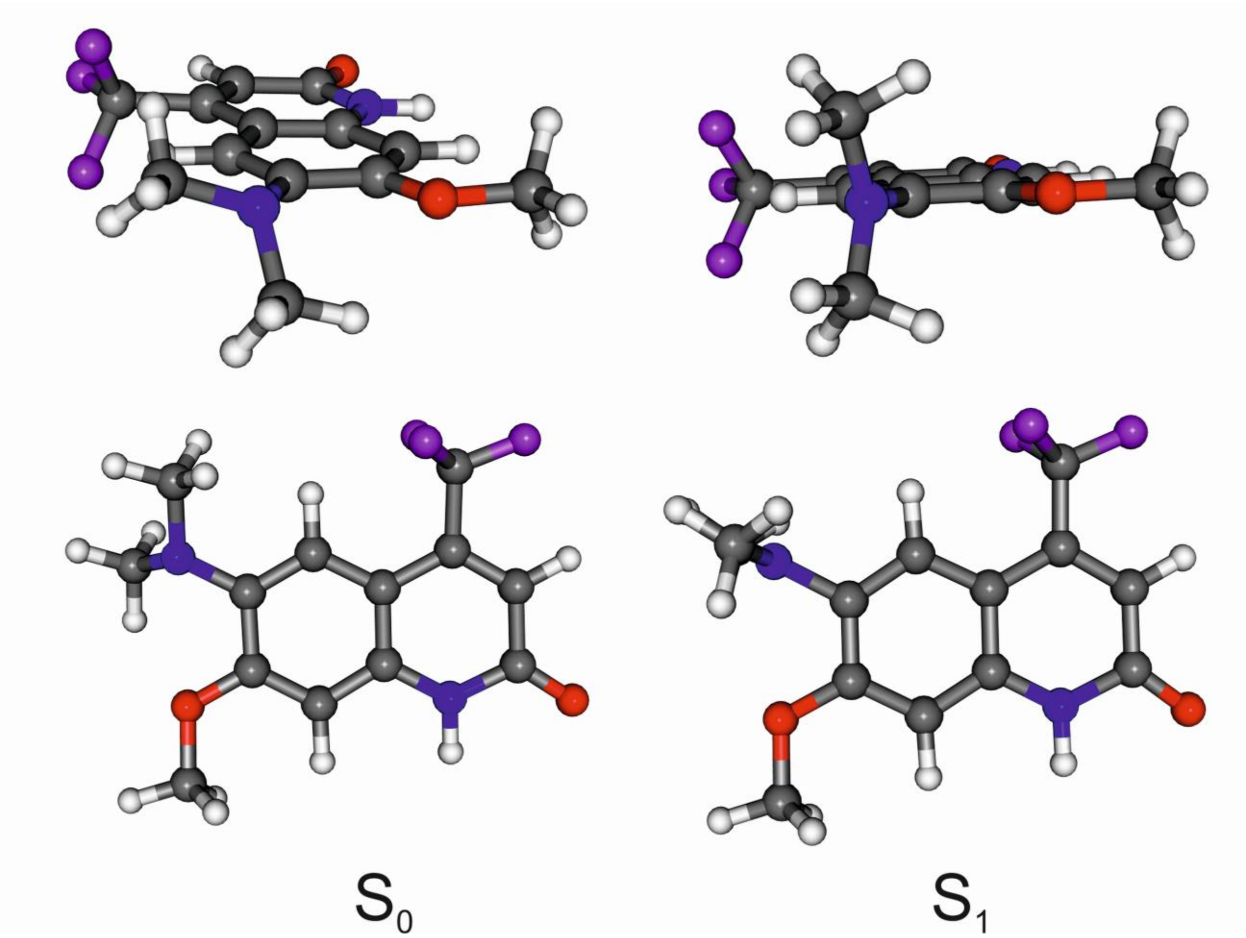
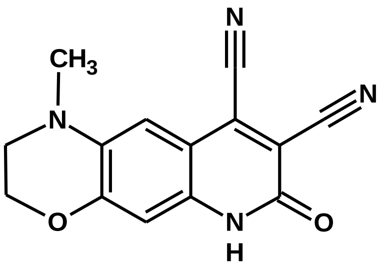


Figure 1 Optimized structures of 6-dimethylamino-7-methoxy-4-trifluoromethylcarbostyril in the S$_0$ (left) and S$_1$ (right) states.

Consequently, we decided to use derivatives with largely fixed torsional angles of the substituents by incorporation into a cyclic system, compounds **3** – **5**.



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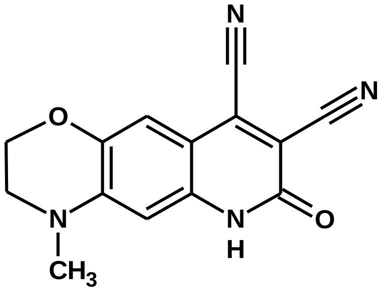

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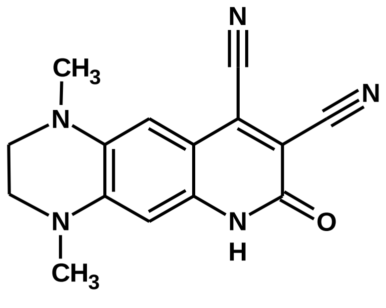

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RESULTS AND DISCUSSION

Calculated vertical transition energies (absorption wavelengths λ_{abs} and oscillator strengths f) in DMSO as solvent for compounds **3** – **5** are summarized in Table 1.

According to the calculations, two electronic transitions in the visible region should be observable with significant oscillator strengths. The first one is dominated by the HOMO → LUMO, the second one by the HOMO-1 → LUMO excitation. With respect to the positional isomers **3** and **4**, derivative **3** with the stronger electron donor in position 6 is predicted to absorb at significantly longer wavelengths than compound **4**. On the other hand, for this latter derivative a substantially larger oscillator strength f is obtained. Hence, increasing the donor strength of the substituent at C6 should result in a bathochromic shift, while increasing that of the C7-substituent leads to hypso- and hyperchromic shifts. Increasing the donor strength at both positions, compound **5**, leads to a still sufficiently red shifted absorption with intermediate intensity.

Table 1 Calculated (CPCM-B3LYP/TZVP) vertical $S_0 \rightarrow S_i$ transition energies (absorption wavelengths λ_{abs} and oscillator strengths f) in DMSO as solvent for compounds **3** – **5**

	λ_{abs} / nm	f	HOMO → LUMO	HOMO-1 → LUMO
3	542	0.207	-0.965	-0.209
	362	0.441	-0.186	0.940
4	444	0.599	0.908	0.360
	405	0.243	-0.346	0.920
5	525	0.350	0.919	-0.351
	362	0.441	-0.186	0.940

The analogous data obtained by using S_1 – optimized geometries, i.e. fluorescence wavelengths λ_F, are presented in Table 2. Similar to absorption, particular long wavelength emission is predicted for the carbostyril derivative bearing the stronger electron donor at C6 (**3,** λ_F = 671 nm) whereas a larger oscillator strength but shorter wavelength emission are calculated for **4**. For compound **5** emission at almost the same wavelength as predicted for **3** is obtained **(**λ_F = 660 nm) but with a significantly larger oscillator strength.

Table 2 Calculated (CPCM-B3LYP/TZVP) vertical $S_1 \rightarrow S_0$ transition energies (fluorescence wavelengths λ_F and oscillator strengths f) in DMSO as solvent for compounds **3** – **5**.

	λ_F / nm	f	HOMO → LUMO	HOMO-1 → LUMO
3	671	0.175	-0.972	-0.172
4	534	0.309	-0.904	0.386
5	660	0.242	-0.951	-0.257

CONCLUSION

Time-dependent density functional theory (TDA-B3LYP/TZVPP) has been used to calculate the vertical electronic transition energies $S_0 \rightarrow S_i$ (absorption) and $S_1 \rightarrow S_0$ (fluorescence) for 3,4-dicyanocarbostyrils substituted at C6 and C7 by electron donor groups of different donating power. A stronger donor at C6 leads to a substantial bathochromic shift of both absorption as well as emission. Increasing the donor strength of the C7-substituent results in hypso- but also hyperchromic shifts. The most promising candidate with respect to both wavelengths and intensities of absorption and emission appears to be the quinoxaline derivative **5**.

COMPUTATIONAL DETAILS

Geometries in the ground and first electronic singlet state were optimized by B3LYP/TZVP [12-14], followed by time-dependent density functional calculations [15,16] in the Tamm-Dancoff approximation (TDA-B3LYP/TZVP). Bulk solvent effects were included by the CPCM procedure [17,18]. Programs used were ORCA [19,20], GAMESS [21,22], MOLDEN [23], and MOLEKEL [24].

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