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# Diaryltrisphaeridine Derivatives: Synthesis, Experimental Electrochemical and Photophysical Properties, and Theoretical Studies

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A series of diaryltrisphaeridines have been synthesized by iodination of trisphaeridine and subsequent Suzuki coupling reactions. The photophysical and electrochemical properties of these compounds have been investigated and it has been found that they are dependent on the aryl substituents. In particular, the presence of dimethylamino groups induces a

# Introduction

Polycyclic aromatic compounds that possess extended  $\pi$ conjugation have been extensively used in optical and electronic devices, such as light-emitting diodes, photovoltaic cells, and thin-film transistors, due to their optoelectronic properties.<sup>[1]</sup> As a result, in recent years interest in this kind of compound has risen markedly.<sup>[2]</sup> In the course of our investigations we have developed a new method for the preparation of several polycyclic heteroaromatic compounds<sup>[3]</sup> based on the ring closure of photochemically generated iminyl radicals.<sup>[4]</sup> In particular, we have described an alternative synthesis of alkaloid trisphaeridine ([1,3]dioxolo[4,5-j]phenanthridine, 1).<sup>[3]</sup> The structure of this polycycle (Figure 1) is quite remarkable because the three aromatic rings have different electron densities, which makes them more or less susceptible to electrophilic attack and facilitates regioselective substitution. The ring that is fused to the dioxolo group should have higher reactivity in such reactions. Astonishingly, to the best of our knowledge, examples of trisphaeridine derivatives substituted at both the 7- and 11-positions of the phenanthridine skeleton have not been described to date. This fact is remarkable if one considers that phenanthridine alkaloids exhibit diverse and significant pharmacological and biological activities.<sup>[5]</sup> In particular, trisphaeridine, which is found in the plants of the family Amaryllidaceae, displays excellent antiproliferative effects on both human and mouse cell lines.<sup>[6]</sup> Considering our experience in the synthesis of iodo derivatives,<sup>[7]</sup> we bright-green emission, thus making this compound a promising candidate for fluorescence devices and molecular sensors. Moreover, the green emission disappears on addition of HCl and this material can therefore also be used as a sensor for protons. The results have been rationalized by DFT and TD-DFT theoretical studies.

found it of interest to assess the electrophilic aromatic iodination of trisphaeridine because this approach would open the door to subsequent functionalization and the preparation of compounds with enhanced  $\pi$  conjugation and/or pharmacological activity.



Figure 1. [1,3]Dioxolo[4,5-j]phenanthridine, trisphaeridine.

### **Results and Discussion**

#### **Iodination of Trisphaeridine**

First, we addressed the preparation of the iodo derivatives. The synthesis of 7,11-diiodo-[1,3]dioxolo[4,5-*j*]phenanthridine (**2**) is outlined in Scheme 1. The iodination reaction of trisphaeridine with bis(pyridine)iodonium(I) tetrafluoroborate (Ipy<sub>2</sub>BF<sub>4</sub>) in the presence of CF<sub>3</sub>SO<sub>3</sub>H<sup>[7e]</sup> at room temperature for 14 hours yielded the desired product **2** in 50% yield. The best result was obtained with 4 equiv. of Ipy<sub>2</sub>BF<sub>4</sub>. The use of a smaller proportion of iodinating reagent led to a mixture of mono- and diiodinated compounds along with the starting trisphaeridine. Compound



Scheme 1. Iodination of trisphaeridine.

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**2** is insoluble in chloroform and it was separated from the byproducts by washing with this solvent.

#### Synthesis of Diaryltrisphaeridine Derivatives

Once the iodinated product had been obtained, we proceeded to test various coupling reactions. First, we attempted to couple **2** with 1-ethynylbenzene under Sonogashira reaction conditions.<sup>[8]</sup> Unfortunately, the reaction led to an intractable mixture in which the mono- and disubstituted compounds were detected in very low yields. We next tested the reaction of **2** under Suzuki coupling conditions.<sup>[9]</sup> The optimized reaction conditions allowed the preparation of **3** in 90% yield by heating a solution of **2**, phenylboronic acid (4 equiv.), [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.2 equiv.), and potassium carbonate (2 equiv.) at reflux in dimethoxyethane for 5 days (Scheme 2).



Scheme 2. Synthesis of diphenyltrisphaeridine 3.

In a similar way, more complex diaryltrisphaeridine derivatives **4–8** were synthesized in an effort to explore the influence of phenyl substituents (Figure 2). By using the corresponding arylboronic acid, it was possible to incorporate phenyl (**4**), chloro (**5**), cyano (**6**), methoxy (**7**), or dimethylamino (**8**) substituents into the structure.



Figure 2. Diaryltrisphaeridine derivatives **4–8** (isolated yields are given in parentheses).

#### **Electrochemical Properties**

To elucidate the effect of the substituents on the electrochemical properties, cyclic voltammetry experiments were performed on diaryltrisphaeridines **3–8** in solution in anhydrous  $CH_2Cl_2$  (Table 1). The cyclic voltammograms (CVs) of the compounds **6** and **8** are shown in Figure 3. Compounds **3–7** exhibited irreversible single-electron reduction peaks and oxidation did not occur, which implies a large activation barrier to electron transfer.<sup>[10]</sup> In contrast, **8** exhibited both reduction and oxidation peaks. The reduction potentials ( $E_p^{red}$ ) varied from –0.80 V (vs. Ag/AgCl) for **8**  to -1.20 V for 4, but a correlation between the reduction potentials and the electron-donating or -withdrawing strengths of the substituents was not observed. The intensities are very low in all cases except for compound 6. This

Table 1. Electrochemical properties of diaryltrisphaeridines in solution.  $^{[\mathrm{a},\mathrm{b}]}$ 

Compound	$E_{\rm p}^{\rm red}$ [V]/I [µA/cm <sup>2</sup> ]	$E_{\rm p}^{\rm ox}$ [V]/I [ $\mu$ A/cm <sup>2</sup> ]
3	-0.93/-15	_
4	-1.20/-26	_
5	-0.90/-19	_
6	-1.00/-103	_
7	-1.01/-34	_
8	-0.80/-25	0.98/36

[a] All potentials vs. Ag/AgCl. [b] 1 mM in  $CH_2Cl_2$ , 0.1 M TBAPF<sub>6</sub>. Scan rate: 200 mV/s.



Figure 3. Cyclic voltammograms for the reduction of a) 6 and b) 8, and c) the oxidation of 8 (1 mM in  $CH_2Cl_2$ , 0.1 M TBAPF<sub>6</sub>; scan rate: 200 mV/s).

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can be accounted for by considering the large electron-withdrawing effect of the cyano group, which should stabilize the anion. On the other hand, an oxidation potential was only observed for  $\mathbf{8}$ , which has dimethylamino groups in its structure, and it is reasonable to conclude that the amine nitrogen atoms are responsible for this behavior.

### **Photophysical Properties**

The absorption spectra of 5, 7, and 8 in acetonitrile are shown in Figure 4 (see the Supporting Information for the spectra of 1, 3, 4, and 6) and the absorption maxima and the corresponding molar extinction coefficients for 1 and 3–8 are given in Table 2. The maximum absorption wavelength of trisphaeridine (1; 251 nm) is redshifted by introducing phenyl or biphenyl groups (269 or 294 nm for 3 or 4, respectively), whereas the introduction of substituents onto the phenyl group causes a blueshift of the maximum absorption wavelength of 5 (201 nm), 6 (235 nm), 7 (195 nm), or 8 (200 nm).



Figure 4. Electronic absorption spectra of compounds 5, 7, and 8 in acetonitrile; all the spectra were recorded at a concentration of  $(1-2) \times 10^{-5}$  M.

Table 2. Absorption and emission data for 1 and 3-8.

Compound	$\lambda_{abs} \ [nm]^{[a]}$	$\log(\epsilon/M  \mathrm{cm}^{-1})$	$\lambda_{\rm em} \ [{\rm nm}]^{[a]}$	$arPhi_{ m f}$ [%]
1	251	4.77	371	< 0.1
3	269	4.57	395	15
4	294	4.46	392	18
5	201	5.41	396	12
6	235	4.38	409	16
7	195	4.65	412	20
8	200	4.59	507	40

[a] Absorption and emission maxima.

The emission spectra of 1 and 3–8 are shown in Figure 5 and the emission maxima and fluorescence quantum yields are given in Table 2. The luminescence of compounds 1 and 3–8 in acetonitrile can be seen in Figure 6. The fluorescence data demonstrate that the introduction of aryl groups strongly affects the quantum efficiencies of the compounds. In fact, the value of  $\Phi_f$  for 1 was determined to be <0.1%, whereas for compounds 3–8  $\Phi_f$  varied from 12 to 40%. Once again, the influence of the dimethylamino moiety should be noted as this shifts the maximum absorption wavelength to 507 nm for 8, that is, around 100 nm higher than those of compounds 3-7, and increases the quantum efficiency to 40%, twice or more than the values obtained for the other diaryltrisphaeridines. This bright-green emission makes trisphaeridine derivative 8 a promising candidate for use in fluorescence devices and molecular sensors.



Figure 5. Emission spectra of 1 and 3–8 in acetonitrile; all the spectra were recorded at a concentration of  $(1-2) \times 10^{-5}$  M. Inset: photo of the luminescence of 8.



Figure 6. Photograph showing the luminescence of compounds 1 and 3–8 in acetonitrile.

### **Theoretical Calculations**

In an effort to understand the experimental results, we performed DFT and time-dependent DFT (TD-DFT) calculations at the B3LYP level of theory with the 6-31G\* basis set<sup>[11,12]</sup> on diaryltrisphaeridines **3–8** to determine the effect that the substitution of **3** has on the HOMO and LUMO energy levels (Table 3). The HOMO and LUMO molecular orbital diagrams of derivatives **3–8** are shown in Figure 7.

Our calculations gave values of -5.69 (HOMO), -1.28 (LUMO), and 4.41 eV (energy gap) for **3**. The presence of extra conjugation (phenyl group, **4**) leads to a slight increase in the energy of the HOMO (-5.66) and lowers the energy of the LUMO (-1.39) to give an energy gap of 4.27 eV. The inclusion of an electron-withdrawing Cl (**5**) or CN (**6**) group significantly lowers the energies of both the

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Compound	$E_{\rm HOMO}  [{\rm eV}]$	$E_{\rm LUMO} [eV]$	$\Delta E [{ m eV}]$
3	-5.69	-1.28	4.41
4	-5.66	-1.39	4.27
5	-5.90	-1.55	4.35
6	-6.20	-2.12	4.08
7	-5.47	-1.17	4.30
8	-4.87	-0.95	3.92

Table 3. Calculated HOMO and LUMO energies for 3-8.<sup>[a]</sup>

[a] Optimized at the B3LYP/6-31G\* level.

HOMO (-5.90 or -6.20, respectively) and the LUMO (-1.55 or -2.12, respectively), which leads to a net decrease in the energy gap of 0.06 or 0.33 eV, respectively. The effect of an electron-donating OMe (7) or NMe<sub>2</sub> (8) group is precisely the opposite in that it significantly raises the energies of both the HOMO (-5.47 or -4.87 eV, respectively) and the LUMO (-1.17 or -0.95 eV, respectively), although the energy gaps are also decreased by 0.11 and 0.49 eV.<sup>[13]</sup> Therefore the presence of NMe<sub>2</sub> decreases the HOMO–LUMO energy gap markedly and this implies that it is easier to promote an electron from the HOMO to the LUMO. These calculations clearly indicate that the inclusion of substituents on the phenyl ring significantly affects the electronic and photophysical properties.

Furthermore, to better illustrate the calculated effect of substituents on the HOMO and LUMO energies, the energy values were plotted against the Hammett substituent constants ( $\sigma_p$ ;<sup>[14]</sup> Figure 8). It can be seen that the HOMO and LUMO energies of **3–8** have a linear correlation with the  $\sigma_p$  of the substituents on the phenyl groups; both have a negative slope. Thus, as mentioned previously, the electron-donating groups cause an increase in orbital energy whereas the electron-withdrawing groups cause a decrease in orbital energy. The correlation coefficients of  $\sigma_p$  with the HOMO and LUMO energies are 0.994 and 0.930, respectively.

As shown in Figure 7, in 3-6 the HOMO orbital is located mainly on the phenanthridine skeleton, whereas the density of the LUMO orbitals is distributed throughout almost the entire structure. The presence of methoxy groups in 7 leads to a distribution of the HOMO density throughout the structure and removes part of the LUMO density from the phenanthridine skeleton. This effect is enhanced in 8, in which the dimethylamino groups cause the HOMO orbital to be mainly located on the dimethylaminophenyl moiety and the majority of the density of the LUMO resides on the phenanthridine skeleton, which indicates that the low-lying transition involves redistribution of charge from the nitrogen lone-pair to the phenanthridine skeleton. Such a charge transfer should account for the different electrochemical and photophysical properties of 8 observed experimentally.

The involvement of frontier orbitals in the photoluminescent properties of **8** was confirmed by TD-DFT calculations. The most significant theoretical excitations, oscillator strengths (intensity), and orbital contributions are shown in Table 4 (see the Supporting Information for the calculated values for 3–7). The calculated  $\pi$ – $\pi$ \* S<sub>0</sub>→S<sub>1</sub> excitation has an oscillator strength *f* of 0.24 with a  $\lambda_{calcd}$  of 364 nm. The



Figure 7. HOMO and LUMO molecular orbital diagrams of compounds **3–8** calculated at the B3LYP/6-31G\* level of theory.

most important contribution to this excitation is provided by the transition between the HOMO (122) and LUMO

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Figure 8. Correlation of a) the HOMO and b) the LUMO energies with the Hammett constants  $\sigma_p$ .

(123), which clearly matches the charge transfer. The calculated excitation centered at 337 nm (f = 0.20) also has a high involvement of the HOMO and LUMO orbitals (HOMO-2 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1).

Table 4. Singlet excitations for 8 calculated by TD-DFT.

$\lambda_{\text{calcd.}}$ [nm]	f [a]	Contributions <sup>[b]</sup>
364	0.24	$122 \rightarrow 123 (45)$
337	0.20	$120 \rightarrow 123 (10); 122 \rightarrow 124 (31)$
275	0.37	$119 \rightarrow 123 \ (15); \ 120 \rightarrow 124 \ (14); \ 122 \rightarrow 126 \ (6)$
264	0.23	$119 \rightarrow 124 \ (12); \ 122 \rightarrow 125 \ (7); \ 122 \rightarrow 127 \ (10)$
238	0.32	$114 \rightarrow 123$ (7); $120 \rightarrow 127$ (13); $122 \rightarrow 128$ (6)

[a] Oscillator strength. Only the main intensities ( $\geq 0.20$ ) are shown. [b] Value is [coeff]<sup>2</sup>×100. Only the main contributions ( $\geq 5$ ) are shown.

#### **Proton Sensor**

Given that the electronic characteristics of the dimethylamino group on the phenyl ring confer a special luminescent behavior, blocking of the nitrogen atom electron pair should have a noticeable effect on the luminescence. With this in mind, a series of luminescence assays were carried out on 8 in the presence of varying amounts of HCl. The results are shown in Figure 9. It can be seen that the presence of 0.4 equiv. of HCl reduces the luminescence by approximately half, whereas the luminescence virtually disappears upon the addition of 0.8 equiv. of HCl, which indicates that 8 could be used for the detection of protons. Interestingly, 1 equiv. of HCl seems to be sufficient to block the emission at 507 nm. To obtain a greater understanding of the protonated species, we also performed a series of DFT calculations on 8 with a proton added to each of the nitrogen atoms. In the most stable structure the proton was located on the phenanthridine nitrogen (9). TD-DFT calculations showed an excitation from the HOMO-1 to the LUMO+2 (f = 0.25) with a  $\lambda_{calcd.}$  of 313 nm (Figure 10).



Figure 9. Emission spectra of **8** in acetonitrile in the presence of 0.0, 0.4, and 0.8 equiv. of HCl.



Figure 10. HOMO-1 and LUMO+2 molecular orbitals (B3LYP/ 6-31G\*) and single-excitation calculations (TD-DFT/6-31G\*) for model compound 9.

The results suggest that the phenanthridine unit must be the fluorophore whereas the presence of the different substituents modulates the intensity and wavelength of the emission band.

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# Conclusions

We have prepared a series of diaryltrisphaeridines by iodination of trisphaeridine and subsequent Suzuki coupling reaction. These compounds were investigated by photophysical and electrochemical methods. The properties of the materials depend on the aryl substituent. In particular, the presence of dimethylamino moieties induces a brightgreen emission, which makes this a promising compound for use in fluorescence devices and molecular sensors. Moreover, the green emission disappears on addition of HCl and this material can therefore also be used as a proton sensor. The results have been rationalized by DFT and TD-DFT theoretical studies.

### **Experimental Section**

**7,11-Diiodo[1,3]dioxolo[4,5-/]phenanthridine** (2): Bis(pyridine)iodonium(I) tetrafluoroborate (Ipy<sub>2</sub>BF<sub>4</sub>; 17 mmol, 6.5 g) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) in an oven-dried flask at room temperature under argon. Trisphaeridine (1; 4.4 mmol, 0.9 g) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> in another flask under argon and this solution was added to the Ipy<sub>2</sub>BF<sub>4</sub> solution. A solution of CF<sub>3</sub>SO<sub>3</sub>H (35 mmol, 3.1 mL) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added over a period of 3 min to the magnetically stirred mixture. Finally, the reaction mixture was stirred overnight at room temperature. The reaction was treated with aqueous sodium thiosulfate, extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed under reduced pressure, the residue was washed with chloroform, and the resulting solid was filtered off to give compound **2** as a brown solid.

General Procedure for the Preparation of Diaryltrisphaeridines: The diiodinated trisphaeridine 2 (0.2 mmol, 0.1 g) and tetrakis(triphenylphosphane)palladium(0) (0.05 mmol, 50 mg) were dissolved in 1,2-dimethoxyethane (50 mL) and the mixture was stirred for 20 min at room temperature. A solution of potassium carbonate (0.7 mmol, 0.1 g) and phenylboronic acid (0.9 mmol, 0.1 g) in water (8 mL) was then added and the resulting mixture was heated at 92 °C for 3–7 d. The mixture was extracted with diethyl ether ( $3 \times 50 \text{ mL}$ ) and the organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and evaporated under reduced pressure. The resulting diaryltrisphaerid-ine was purified by column chromatography (silica gel, hexane/EtOAc, 7:3). The coupling reaction should be repeated twice for the complete conversion of 2 into diaryltrisphaeridines 5–8.

**Supporting Information** (see footnote on the first page of this article): Complete experimental procedures, characterization data for new compounds, and Cartesian coordinates and single-excitation calculations for the geometries discussed in the text.

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U. Scherf (Eds.), Organic Light Emitting Devices: Synthesis Properties and Applications, Wiley-VCH, Weinheim, 2006; d) L. Barsanti, V. Evangelista, P. Gualtieri, V. Passarelli, S. Vestri (Eds.), Molecular Electronics: Bio-Sensors and Bio-Computers NATO Science Series II: Mathematics, Physics, Chemistry, vol. 96, Plenum Press, New York, 2003; e) K. Mullen, G. Wegner (Eds.), Electronic Materials: The Oligomer Approach, Wiley-VCH, Weinheim, Germany, 1998.

- [2] See, for example: a) D. T. Chae, A. G. Fix, B. D. Rose, C. D. Weber, S. Nobusue, C. E. Stockwell, L. N. Zakharov, M. C. Lonergan, M. M. Haley, *Angew. Chem. Int. Ed.* 2011, 50, 11103; b) D. T. Chase, B. S. Young, M. M. Haley, *J. Org. Chem.* 2011, 76, 4043; c) C. B. Nielsen, T. Brock-Nannestad, T. K. Reenberg, P. Hammershøj, J. B. Christensen, J. W. Stouwdam, M. Pittelkow, *Chem. Eur. J.* 2010, *16*, 13030; d) C.-S. Li, Y.-H. Tsai, W.-C. Lee, W.-J. Kuo, *J. Org. Chem.* 2010, *75*, 4004.
- [3] R. Alonso, A. Caballero, P. J. Campos, M. A. Rodríguez, *Tetra-hedron* 2010, 66, 8828.
- [4] a) R. Alonso, P. J. Campos, M. A. Rodríguez, D. Sampedro, J. Org. Chem. 2008, 73, 2234; b) R. Alonso, P. J. Campos, B. García, M. A. Rodríguez, Org. Lett. 2006, 8, 3521.
- a) Z. Jin, Nat. Prod. Rep. 2011, 28, 1126, and references cited [5] therein; b) J. Marco-Contelles, M. C. Carreiras, C. Rodríguez, M. Villarroya, A. G. García, Chem. Rev. 2006, 106, 116; c) E. E. Elgorashi, G. I. Stafford, J. Van Staden, Plant Methods 2004, 70, 260; d) B. Sener, I. Orhan, J. Satayavivad, Phytother. Res. 2003, 17, 1220; e) S. Amos, L. Binda, P. Akah, C. Wambebe, K. Gamaniel, Fitoterapia 2003, 74, 23; f) G. Schmeda-Hirschmann, J. A. Rodríguez, J. I. Loyola, L. Astudillo, J. Bastida, F. Viladomat, C. Codina, Pharm. Pharmacol. Commun. 2000, 6, 309; g) M. Tanker, G. Citoglu, B. Gumusel, B. Sener, Int. J. Pharmacogn. 1996, 34, 194; h) B. Gabrielsen, T. P. Monath, J. W. Huggins, D. F. Fefauver, G. R. Pettit, G. Groszek, M. Hollingshead, J. J. Kirsi, W. M. Shannon, E. M. Schubert, J. Dare, B. Ugarkar, M. A. Ussery, M. J. Phelan, J. Nat. Prod. 1992, 55, 1569.
- [6] I. Zupkó, B. Réthy, J. Hohmann, J. Molnár, I. Ocsovszki, G. Falkay, *in vivo* 2009, 23, 41.
- [7] a) P. J. Campos, B. García, M. A. Rodríguez, *Tetrahedron Lett.*2002, 43, 6111; b) P. J. Campos, B. García, M. A. Rodríguez, *Tetrahedron Lett.*2000, 41, 979; c) P. J. Campos, J. Arranz, M. A. Rodríguez, *Tetrahedron Lett.*1997, 38, 8397; d) P. J. Campos, C.-Q. Tan, M. A. Rodríguez, *Tetrahedron Lett.*1995, 36, 5257; e) J. Barluenga, J. M. González, M. A. García-Martín, P. J. Campos, G. Asensio, J. Org. Chem.
  1990, 55, 3104; g) J. Barluenga, M. A. Rodríguez, P. J. Campos, G. Asensio, J. Arcanzo, G. Asensio, J. Am. Chem. Soc.
  1988, 110, 5567.
- [8] a) K. Sonogashira, J. Organomet. Chem. 2002, 653, 46; b) J. A. Hur, S. Y. Bae, K. H. Kim, T. W. Wan, M. J. Cho, D. H. Choi, Org. Lett. 2011, 13, 1948.
- [9] A. Suzuki, J. Organomet. Chem. 1999, 576, 147.
- [10] See, for example: P. Zanello, *Inorganic Electrochemistry: Theory, Practice and Application*, Royal Society of Chemistry, Cambridge, 2003.
- [11] All calculations were carried out by using the Gaussian 03 program package. The geometry was fully optimized in the ground state without any symmetry constraint for all model compounds at the B3LYP/6-31G\* level of theory. Subsequent calculations of the orbitals were performed.
- [12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P.

a) P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* 2010, *110*, 268;
 b) T. J. J. Müller, U. H. F. Bunz (Eds.), *Functional Organic Materials*, Wiley-VCH, Weinheim, Germany, 2007; c) K. Mullen,

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Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W.

Gaussian, Inc., Wallingford, CT, 2004.

Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision C.02,

- [13] A similar effect on the energy of the frontier orbitals depending on the type of substituent has been observed in other unsaturated systems, see, for example: I. Fleming, *Frontier Orbitals* and Organic Chemical Reactions, Wiley, Chichester, UK, 1976.
- [14] C. Hansch, A. Leo, R. W. Taft, Chem. Rev. 1991, 91, 165. Received: August 3, 2012

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### **Diaryltrisphaeridine Derivatives**

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Diaryltrisphaeridine Derivatives: Synthesis, Experimental Electrochemical and Photophysical Properties, and Theoretical Studies

**Keywords:** Heterocycles / Alkaloids / Luminescence / Sensors / Electrochemistry / Density functional theory