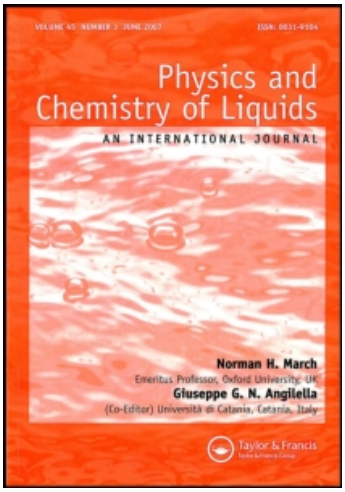

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Structural relationship between photophysical data of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules and number of carbon atoms

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Structural relationship between photophysical data of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules and number of carbon atoms

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A series of star-shaped molecules have been prepared by different methods. These molecules present an important electronic delocalisation between the attractive central ring, i.e. benzene and the three ends π-electron donor groups. These interesting molecules are currently considered because of their wide potential applications. Some of them can act as discotic liquid crystals (DLCs). The 1,3,5-benzene core acts as an effective π-electron center to conjugate with the oligoaryleneethynylene groups of the 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules. Graph theory is an exploration of techniques in discrete mathematics and its results can be applied in various fields of science. Several concepts of graph theory have been found to be useful tools in both *QSAR* and *QSPR*. This theory provides many different methods of characterising chemical structures numerically. In this study, we utilised the number of carbon atoms as a useful structural character (C_n) for relating structure to photophysical properties of the star-shaped molecules **1**–**19**. The interesting results obtained here present the good correlation between the index of C_n, the number of carbon atoms in each of the star-shaped molecular structures that are indicated here, with their photophysical properties. Some of the photophysical data that were communicated in the literature are: quantum yield (Φ_f), fluorescence emission maximum FEM (λ_{em}) and absorbance maximum wavelength AMWL (λ_{abs}). The interesting results of the relationship between 'C_n' and the photophysical data of these star-shaped molecules are presented.

Keywords: star-shaped molecule; photophysical data; molecular topology; quantum yield; number of carbon atoms

1. Introduction

Star-shaped macromolecules, which contain benzene as a core for the star-shape, have been investigated as branched macromolecules and have received significant attention in the elucidation of structure-property relationships [1–9]. Although star polymers constitute a gate group of branched macromolecular structures, the synthesis and study of the properties of star-shaped polymers remains challenging and well defined star polymers are often difficult to prepare in a controlled

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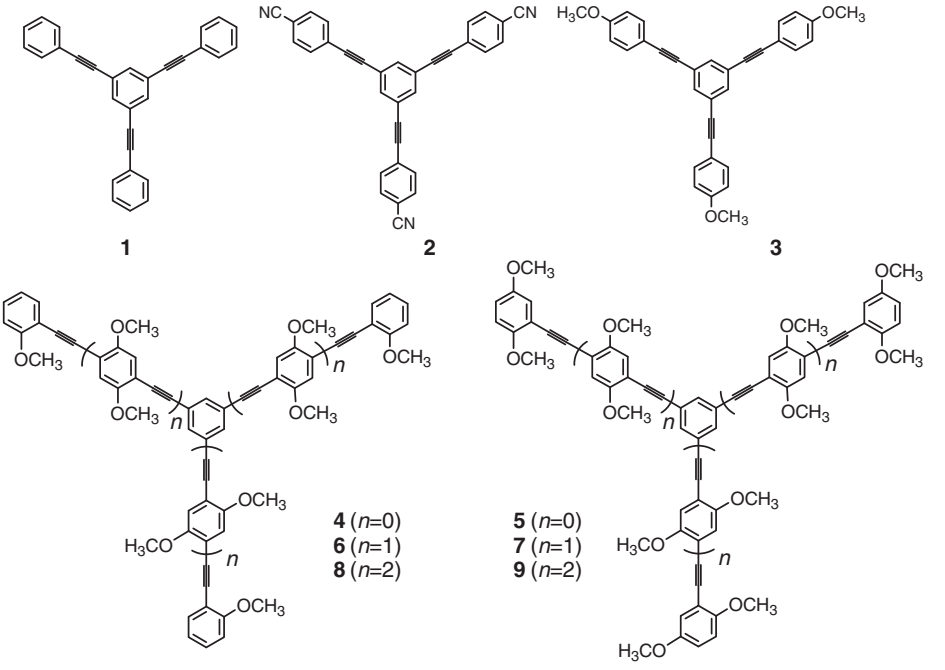
manner [2]. Some types of the molecules, with a trivalent core and three poly π-structures, have attracted much attention and been utilised in different areas of science because of their interesting potential, especially for electronic studies. Because of the properties of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules, they can act as: *discotic liquid crystals* (DLCs), *light-emitting diodes* (LEDs), *field effect transistors* (FETs) and *non linear optics* (NLO) [1]. Study of the electronic properties of these materials with respect to their photophysical properties can be useful and interesting. Especially with respect to their LED character and quantum yield (Φ_f), only a few reports have been reported in the literature [10–12].

In 2006, the electronic structures and the photophysical properties of 1,3, 5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1–9** (Figure 1)



No.	*n*
10	2
11	3
12	4
13	5
14	6
15	7
16	8
17	9
18	10
19	11

Figure 1. The structures of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1–9** and the predicted structures **10–19**.

were reported by Yamaguchi *et al.* [1]. In that interesting report, the authors investigated the photophysical properties, light-emitting characteristics and occurrence of π-conjugation between the arms of the star-shaped rigid molecules that comprise a 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1**–**9** and their methoxy derivatives. Some of the quantities that were reported are: quantum yield (Φ_f), fluorescence emission maximum FEM (λ_{em}) and absorbance maximum wavelength AMWL (λ_{abs}).

Graph theory is a sub-discipline of mathematics that is closely related to both topology and combinatory concepts. A graph is a topological concept rather than a geometrical concept of fixed geometry and hence Euclidean metric lengths, angles and 3-D spatial configurations have no importance. Aspects of graph theory have been found to be a useful tool in *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship) [13–18]. The choice of effective, simple structural indices for making good correlations between several data properties is important for the study, extension and prediction of properties for these molecules.

In this study, the structural properties of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1**–**9** were used to derive relationships between the number of carbon atoms (C_n) and photophysical properties such as: quantum yield (Φ_f), FEM (λ_{em}) and AMWL (λ_{abs}). The results were extended for the prediction of photophysical data of **10**–**19**.

2. Graphs and mathematics

All graphing operations were performed using the *Microsoft Office Excel-2003* program. The number of carbon atoms (C_n) was the best and simplest index for this study. Some other indices were examined and the best results and equations to extend the photophysical data were chosen.

3. Discussion

The data for the photophysical values of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1**–**9** and the number of carbon atoms (C_n) are shown in Table 1. The basic structure of these compounds has the $C_{30}H_{18}$ formula and is based on the structure **1**. The units with at least C_8 carbon atoms in structures **4**–**19** were added to each arm of the trivalent benzene cores. The methoxy groups, their position and the acetylene bonds –C≡C– on the aromatic rings can act as bathochromic groups and oxochromes. The substituted benzene can affect all the photophysical properties of these molecules. With respect to the ortho- and meta-positions of the –OMe groups, especially in **9**, it seems to be a more straightforward effect of ortho- and meta-conjugation with benzenes [1]. Because of the cylindrical shape of π-bonds around C≡C (or –CN for **2**), probable rotation around C_{sp}–C_{sp2} has no effect on π-conjugation between acetylene functional groups and benzene rings. The photophysical data that were reported in the literature were measured in $CHCl_3$ and quantum yields are calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4) [1]. By the use of 'Φ_f' some other photophysical data can be calculated [19,20].

Table 1. The experimental selected photophysical data FEM (λ_{em}), AMWL (λ_{abs}) and quantum yield (Φ_f) of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **1–9** [1].

No.	Molecular formula	C_n	Φ_f*	FEM (λ_{em}) (nm)	AMWL (λ_{abs}) (nm)
1	$C_{30}H_{18}$	30	0.15	353	305
2	$C_{33}H_{15}N_3$	33	0.14	357	320
3	$C_{33}H_{24}O_3$	33	0.23	360	316
4	$C_{33}H_{24}O_3$	33	0.24	359	314
5	$C_{36}H_{32}O_6$	36	0.46	384	334
6	$C_{63}H_{56}O_9$	63	0.83	406	377
7	$C_{69}H_{64}O_{12}$	69	0.85	409	380
8	$C_{93}H_{80}O_{15}$	93	0.97	433	405
9	$C_{96}H_{104}O_{18}$	96	0.98	464	426

Note: *The reported photophysical data were measured in $CHCl_3$ and quantum yields were calculated relative to quinine ($\Phi_f = 0.55$ in 0.1 M H_2SO_4) (see [1]).

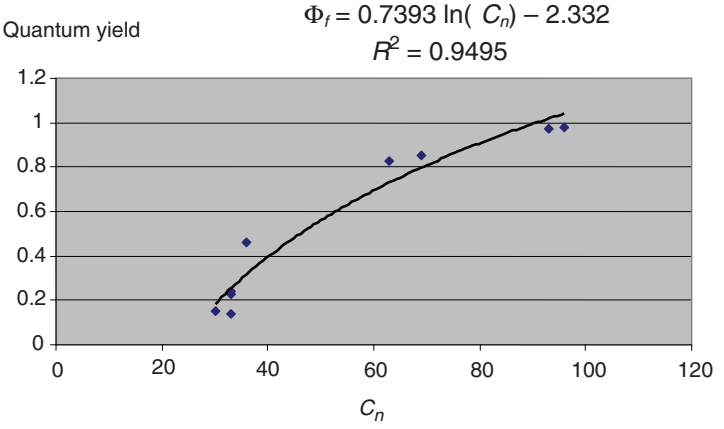


Figure 2. The curve of the relationship between the values of quantum yield (Φ_f) *vs.* the C_n (number of carbon atoms) for **1–9**.

In the molecular formula of **10–19**, it can be seen that each structure (with D_{3h} point group) is different from the next one for $C_{24}H_{12}$. The common structural molecular formula for **1** and **10–19** is $C_{2n-6}H_n$.

Figures 2 to 4 show the 2-D diagrams of the relationship between the main values that were listed in Table 1.

Figure 2 shows the curve of the relationship between the values of quantum yield (Φ_f) *versus* C_n (number of carbon atoms) for **1–9**. Equation (4) describes Figure 3 and shows the *Nieperian* logarithmic behaviour of the relationship between C_n and Φ_f. With this equation it is possible to achieve a good approximation for extending the determination of the Φ_f. The *R*-squared value (R^2) for this graph is 0.949.

$$\Phi_f = 0.7393[\ln(C_n)] - 2.332 \quad (1)$$

Equation (1) affords a good approximation for calculation of Φ_f for **10–19**. The calculated values are shown in Table 2.

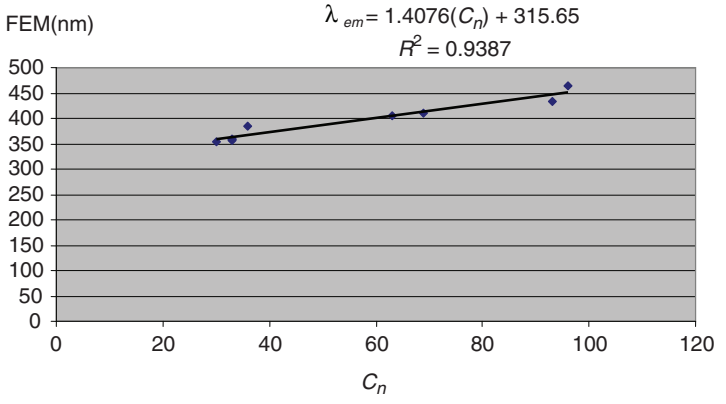


Figure 3. The curve of the relationship between the values of FEM (λ_{em}) *vs*. the number of carbon atoms (C_n) for **1**–**9**.

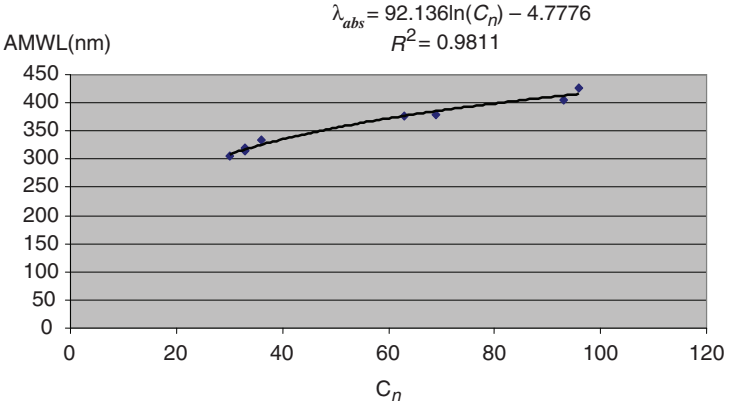


Figure 4. The curve of the relationship between the values of AMWL (λ_{abs}) *vs*. the number of carbon atoms (C_n) for **1**–**9**.

In Figure 3, there is a good linear relationship between the values of the FEM (λ_{em}) of **1**–**9** and the number of carbon atoms (C_n). By this equation, it is possible to achieve a good approximation for extending the determination of FEM in 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules like **10**–**19**. The *R*-squared value (R^2) for this graph is equal to 0.939.

$$\lambda_{em} = 1.4076(C_n) + 315.65 \quad (2)$$

Equation (2), that is relevant to Figure 3, is a simple linear equation for the relationship between C_n and λ_{em}. This equation was extended for the approximation of the FEM (λ_{em}) in **10**–**19**. The calculated values are shown in Table 2.

Figure 4 shows a curve for the relationship between the values of calculated AMWL (λ_{abs}) *versus* the number of carbon atoms (C_n) for **1**–**9**. Equation (4) is relevant to Figure 3. As in Equation (1) shown in Figure 2, one can see the *Nieperian* logarithmic behaviour of this relationship. By this equation it is possible to achieve a good approximation for extending the determination of the AMWL (λ_{abs}) for

Table 2. The calculated selected photophysical data FEM (λ_{em}), absorbance maximum wavelength AMWL (λ_{abs}) and quantum yield (Φ_f) of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules **10**–**19**[a].

No.	Molecular formula[b]	C_n	Φ_f[c]	FEM (λ_{em}) (nm)	AMWL (λ_{abs}) (nm)
8	$C_{93}H_{80}O_{15}$	93	0.97[0.95]	433[430]	405[403]
9	$C_{96}H_{104}O_{18}$	96	0.98[0.96]	464[467]	426[428]
10	$C_{54}H_{30}$	54	0.62	391.66	362.75
11	$C_{78}H_{42}$	78	0.89	425.44	396.63
12	$C_{102}H_{54}$	102	(1.09)	459.22	421.35
13	$C_{126}H_{66}$	126	(1.24)	493.01	440.82
14	$C_{150}H_{78}$	150	(1.37)	526.79	456.88
15	$C_{174}H_{90}$	174	(1.48)	560.57	470.56
16	$C_{198}H_{102}$	198	(1.58)	594.35	482.46
17	$C_{222}H_{114}$	222	(1.66)	628.14	493.00
18	$C_{248}H_{126}$	248	(1.74)	664.73	503.21
19	$C_{272}H_{138}$	272	(1.81)	698.52	511.72

Notes: [a]For calculation of the photophysical values, Equations (1)–(6) were used for **10**–**19**.
[b]The common structural formula for **1** and **10**–**19** is: $C_{2n-6}H_n$.
[c]The values of Φ_f for **10**–**19** shown in parentheses are the mathematical calculations and there were not any experimental results for their comparison, Equation (4).

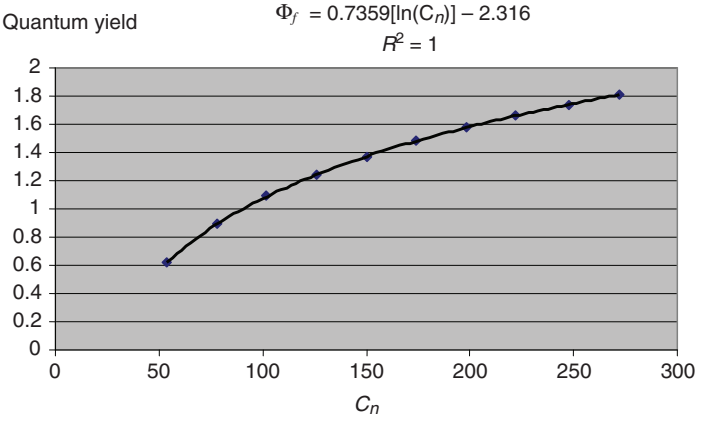


Figure 5. The curve of the relationship between the values of quantum yield (Φ_f) *vs.* the C_n (number of carbon atoms) for **10**–**19**.

1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules (D_{3h}, $C_{2n-6}H_n$). The *R*-squared value (R^2) for this graph is 0.981.

$$\lambda_{abs} = 92.136[\ln(C_n)] - 4.7776. \quad (3)$$

The predicted values of quantum yield (Φ_f) for 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules (**10**–**19**) were calculated by the use of Equation (1) (Table 2 and Figure 5). In Figure 5, the line of best fit is curved between C_n and Φ_f for **10**–**19**. The use of Equation (1) affords a good approximation for calculating (Φ_f) in **10**–**19**. The *R*-squared value (R^2) for this graph is equal to 1.000.

$$\Phi_f = 0.7359[\ln(C_n)] - 2.316. \quad (4)$$

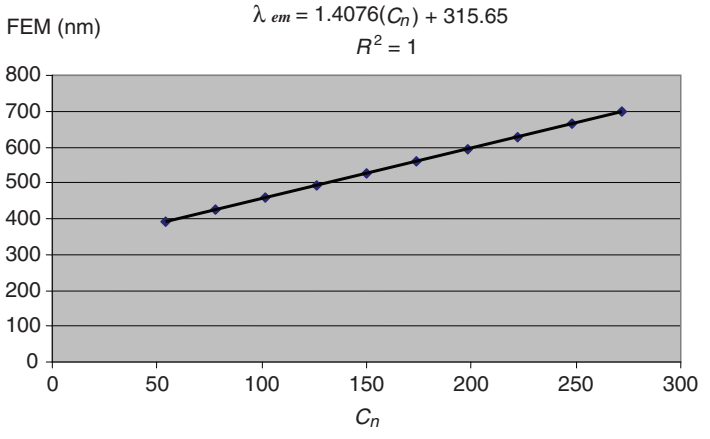


Figure 6. The linear relationship between the FEM (λ_{em}) values *vs.* the number of carbon atoms (C_n) for **10**–**19**.

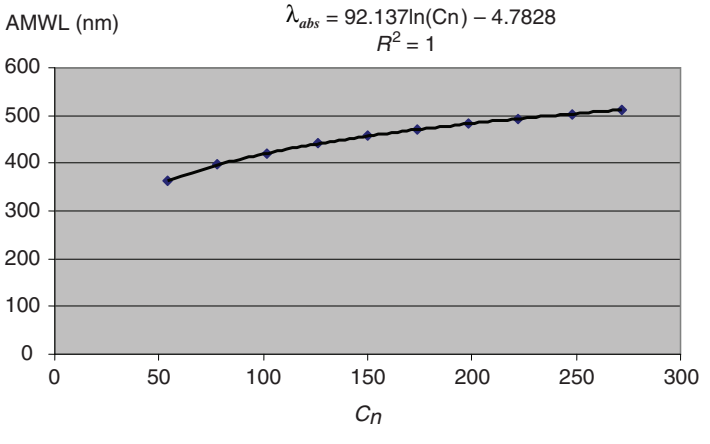


Figure 7. The curve of the relationship between the values of absorbance maximum wavelength AMWL (λ_{abs}) *vs.* the number of carbon atoms (C_n) for **10**–**19**.

The values of Φ_f for **10**–**19** that were shown in Table 2 are mathematical calculations and there were not any experimental results for their comparison.

There is a very good linear relationship between the number of carbon atoms (C_n) and the FEM (λ_{em}) of **10**–**19**. This relationship was shown in Figure 6 and Equation (5). The *R*-squared value (R^2) for this graph is equal to 1.000.

$$\lambda_{em} = 1.4076(C_n) + 315.65. \quad (5)$$

Similar to Figure 4, the line of best fit is curved in Figure 7. Equation (6) is relevant to Figure 7 and shows the *Nieperian* logarithmic behaviour of the relationship between C_n and calculated AMWL (λ_{abs}). By this equation it is possible to achieve a good approximation for the determination of the λ_{abs} of **10**–**19**. The *R*-squared value (R^2) for this graph is 1.000.

$$\lambda_{abs} = 92.137[\ln(C_n)] - 4.7828. \quad (6)$$

By the use of Equations (4)–(6) we can achieve a model to approximate the values of photophysical data including quantum yield (Φ_f), FEM (λ_{em}) and AMWL (λ_{abs}) for compounds **10**–**19** with D_{3h} point group and $C_{2n-6}H_n$ molecular formula. The number of carbon atoms of these molecules is a very good characteristic for determining the quantitative relationship between the structures and photophysical data of 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules (**10**–**19**).

4. Conclusion

The star-shaped molecules present important electronic delocalisation between the attractive central ring, i.e. benzene and the three end π-electron donor groups. The 1,3,5-benzene core acts as an effective π-electron centre to conjugate with the oligoaryleneethynylene groups of the 1,3,5-trisubstituted oligoaryleneethynylene benzene star-shaped molecules (**1**–**19**). These interesting molecules are currently considered because of their wide potential application. This work attempted to derive the relationships between the number of carbon atoms (C_n) and photophysical properties such as: quantum yield (Φ_f), FEM (λ_{em}) and AMWL (λ_{abs}) of **1**–**19**. By the use of the model and the related equations, it is possible to calculate some of the photophysical data for these molecules in a simple manner and with good approximation.

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