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Photophysical properties of the symmetrically substituted diarylacetylenes and diarylbuta-1,3diynes

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A series of symmetrically substituted diarylacetylenes and diaryl-1,3butadiynes were prepared and studied with an emphasis on their spectral and photophysical properties. The photophysical characteristics of these compounds were studied in relation to their structures and influence of solvents or temperature. The observed spectral and photophysical properties are explained using potential energy maps in the ground and excited states obtained from density functional theory calculations. The structure-property relationships of all of the compounds are discussed and compared with appropriate diphenylacetylene and diphenyl-1,3-butadiyne derivatives.

Introduction

Asymmetrically substituted acetylene derivatives containing an aromatic or heteroaromatic substituents are fluorescent compounds which have been applied to a variety of purposes. They can be used as polarity-sensitive probes¹, for labelling biological molecule² and intracellular imaging³, as metal or pH sensors⁵⁻⁸, oligonucleotide analogues⁴ swiches^{9,10}, fluorescence electrochemiluminescence materials¹¹⁻¹³ or to synthesize of novel fluorescent probes¹⁴⁻¹⁷. Moreover, so-called pull-push chromophores containing electron donors and acceptors connected by a π -electron bridge $(D-\pi-A)$ show a large nonlinear optical response (NLO) which allows their use in second-order NLO applications $^{\rm 18\mathchar`20}.$ Poly(aryleneethylene)s find wide application as components of light-emitting diodes, solar cells²¹, as well as for the construction of nanoarchitectures²² and molecular machines²³ ²⁶. Buta-1,3-diyne derivatives are less applicable than acetylene derivatives, however, substituted buta-1,3-diynes undergo 1,4-addition reaction in the solid state to give polydiacetylene²⁷ which can be used as a label-free fluorogenic chemosensors²⁸. While asymmetrically substituted derivatives of acetylene and buta-1,3-diyne are fluorescent, their symmetrically substituted phenyl counterparts show very weak or practically no measurable fluorescence at room temperature and their fluorescence quantum yields show

compounds which They can be used biological molec

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[†] Electronic Supplementary Information (ESI) available: [scheme of synthesis and identification data, absorption and emission spectra in 2_MeTHF and acetonitrile, and low temperature luminescence data, fluorescence quantum yield and lifetime, potential of rotation energy in the ground and excited state]. See DOI: 10.1039/x0xx00000x

strong dependence on temperature. This applies in particular to diphenylacetylene (DPA) and diphenyl-1,3-butadiyne and their derivatives containing an electron-donating substituents in position 4, 4` in the phenyl ring $^{29-37}$. These phenomena have been explained by Zgierski and Lim^{38,39} based on theoretical calculations. The authors founded that the excited singlet states of DPA demonstrate the existence of a low energy crossing between the initially excited $\pi\pi^*$ (B_{1u}) state in the linear D_{2h} symmetry and the "non-fluorescent, dark $\pi\sigma^*$ state" $(1^{1}A_{u})$ in the bent C_{2h} symmetry, which, as demonstrated Saltiel and Kumar⁴⁰ is weakly fluorescent state. The state switch from the linear $\pi\pi^*$ state to the bent $\pi\sigma^*$ state accounts for all the unusual photophysical and spectroscopic properties of DPA and its derivatives. The experimental confirmation of the presence of $\pi\sigma^*$ state was a strong $\pi\sigma^* \leftarrow \pi\sigma^*$ absorption at about 700 nm in picosecond transient absorption for different DPA derivatives containing electrondonating substituents and lack of such absorption for electronwithdrawing substituents^{38,39} as it was predicted by theoretical calculations. Moreover, for 1,4-diphenylbuta-1,3-diyne, similarly to DPA, dramatic reduction of the fluorescence quantum yield when the photoexcitation energy becomes higher than about 2000 \mbox{cm}^{-1} above the 1^1B_{1u} state was observed and it was explained assuming the presence of close location of the $1^{1}A_{1u}$ state above $1^{1}B_{1u}$ state³⁵.

A big differences between photophysical properties of DPA and diphenylbuta-1,3-diyne on one side and its nonsymmetrical substituted derivatives containing an polycyclic aromatic/heteroaromatic groups raises the question about the reason for such differences. To find the answer to this question, symmetrical derivatives of acetylene and buta1,3diyne containing polycyclic aromatic substituents were synthetized and its spectral and photophysical properties were examined (Fig. 1). Moreover, there is a lack of the systematic studies of the spectral and photophysical properties of symmetrically substituted diarylacetylene, as well as diarylbuta-1,3-diyne derivatives, and at the same time considerable interest of systems containing divne motif^{41,42}. On the basis of obtained results the similarities and differences between diarylacetylene and diarylbuta-1,3-diyne derivatives are discussed. Moreover, properties of diarylacetylene and diaryl-1,3-butadiyne are compared to published before, properties of DPA and diphenylbuta-1,3-diyne.

Experimental

Materials and methods

All halogenoarenes: 1-iodonaphtalene (Sigma-Aldrich), 2bromonaphtalene (Fluka AG), 9-bromoanthracene (Fluka), 1bromopyrene (Sigma-Aldrich) and acetylene derivatives: 2-methyl-3-butyn-2-ol (Fluka), trimethylsilylacetylene (Sigma-Aldrich), 1-







4c

5c













Fig. 1 Structure and atom numbering of studied compounds.

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ethynylpyrene (Alfa Aesar) were commercially available and used as received. Symmetrical monoacetylene derivatives (**1c-4c**) were prepared based on the Sonogashira-Hagihara method^{43,44} using a respective halogenoarenes (procedure A and A'), while symmetrically substituted 1,3-butadiyne derivatives (5c-8c) were made based on the Glaser method⁴⁵ (procedure C) (see ESI). The progress of reaction was monitored by means of TLC (Merck plates, Kieselgel 60 F₂₅₄). The products were isolated by means of column chromatography (Merck, Kieselgel 60 (0.040-0.063 mm) and semi-preparative RP-HPLC (Kromasil column, C-8, 5µm, 250 mm long, i.d. 20 mm). The identification of product was based on: ¹H and ¹³C NMR spectra recorded on a Brucker AVANCE III (500 MHz) spectrometer in CDCl₃, mass spectra recorded on a Bruker Paltonics (HCTultra) instrument and Raman spectra recorded on a Bruker FRA-106 instrument (see details in ESI).

Spectroscopy and fluorescence measurements

Absorption spectra were measured using a Perkin-Elmer Lambda-40P spectrophotometer, whereas emission spectra were measured using a FluoroMax-4 (Horriba-Jobin-Yvon) spectrofluorimeter. Low temperature luminescence spectra were obtained using an FL-1013 liquid nitrogen dewar assembly.

Fluorescence quantum yields were calculated using quinine sulphate in 0.5 M H_2SO_4 (QY=0.52±0.02)(for 1,2-di(naphtalen-1-yl)ethyne (1Nac), 1,2-di(naphtalen-2-yl)ethyne (2Nac), 1,4-di(naphtalen-1-yl)buta-1,3-diyne (1Nac2), 1,4-di(naphtalen-1-yl)buta-1,3-diyne (1Nac2), 1,4-di(naphtalen-1-yl)buta-1,3-diyne (Aac), 1,2-di(pyren-1-yl)ethyne (Pac), 1,4-di(anthracen-9-yl)ethyne (Aac), 1,2-di(pyren-1-yl)ethyne (Pac2)) as references and were corrected for different refractive indices of solvents. The fluorescence lifetimes and TRES spectra were measured with a time-correlated single-photon counting fluorescence lifetimes spectrometer FT300 (PicoQuant) using subnanosecond pulsed diodes: PLS-340 (for 1Nac, 2Nac, 1Nac2, 2Nac2) or diode laser LHD 420 (for Aac, Pac, Aac2, Pac2).

Theoretical calculations

All calculations were performed using density functional theory (DFT) within the Turbomole v. 6.4 suite programs on a PC cluster, similarly to published before^{36,37}. The structures of all compounds were prepared and initially optimized using the TmoleX program. Energy-minimized structures were searched for the ground and the lowest excited states using a B3-LYP hybrid functional with def2-TZVP basis set of triple- ζ quality. This procedure was considered satisfactory if the energy difference between optimized cycles was <1*10⁻⁶Hartree for ground state structure optimization. In both

states, a gradient of $<1*10^{-3}$ au was achieved. The low-lying excited states were treated within the adiabatic approximation of timedependent density functional theory (DFT-RPA) using a B3-LYP functional. The geometry optimization of the excited state was performed using grid parameter equal to 4. The convergence of all studied systems was checked by harmonic vibrational analysis. No imaginary frequencies were observed. The rotation energy barriers in the ground and excited states were performed by imposing constraints on the dihedral angle optimizing the energy of molecule. It does not imposed additional constraints such as the symmetry of the molecule. In a similar way the energy of the bent conformation of molecule was calculated imposing the bent angle value and optimizing the remaining part of the molecule; The same functional and bases set were used as in the case of energy optimization.

Results and discussion

Absorption spectra



Fig. 2 Normalized absorption spectra of acetylene and buta-1,3-diyne derivatives in methylcyclohexane (MCH).

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Absorption spectra of the studied compounds measured in methylcyclohexane (MCH) are presented in Fig. 2, whereas measured in 2-methyltetrahydrofurane (2-MeTHF) and acetonitrile (MeCN) in Figs 1-8, ESI. All studied compounds, except for 2Nac and 2Nac2, show complicated vibrational structure. Among some of them it can be recognized as vibrations associated with the vibration of the triple bond (about 2000 cm⁻¹) and the ring breathing mode of an aromatic ring (at about 1400 cm⁻¹). However, for acetylene and buta-1,3-diyne derivatives containing 2-naphthyl substituents (2Nac and 2Nac2 and to a lesser extent in the case of 1Nac2) a clear long progression of C=C stretching mode (ca. 2150 cm⁻¹), which is an indication of the large displacement of the C≡C bond upon the electronic excitation, is seen. It is similar to the absorption spectra of simple phenyl derivatives of acetylene and buta-1,3-divne^{30,34-37,46}. The positions of long-wavelength absorption bands measured in MCH are presented in Table 1 ESI. The position of the absorption maximum depends on the size of aromatic substituent. The biggest it is, the more bathochromially shifted spectrum is observed (2Nac<1Nac<Pac<Aac). The introduction of the second acetylene unit does not change the position order in the absorption spectra of studied compounds, albeit it shifts the spectra to the longer wavelengths for about 10 nm (15 nm for 1Nac). However, for 1Nac2 a substantial changes in the shape of absorption spectrum, comparing to that of 1Nac are observed, which pointing to a larger participation of the triple bonds in conjugation between naphthalene substituents. More polar solvent induce small changes in the position of the absorption bands, however, in the case of anthryl derivatives band shape changes (Figs 1-8, ESI). In 2-MeTHF a small bathochromic shift of the absorption spectrum is observed, whereas in MeCN a blue shift for a few nanometers occurs. Simultaneously, with the increase of solvents polarity, vibrating structure is blurred and the ratio of the vibronic band changes. This is particularly evident for anthryl and to a lesser degree for pyrenyl, as well as for di(naphtalen-1-yl) derivatives.

Room temperature fluorescence

The fluorescence spectra of acetylene and buta-1,3-diyne in MCH are presented in Fig. 3, whereas in 2-MeTHF and MeCN in Figs 9-16, ESI. These spectra contain all the characteristic features of the emission spectra of symmetrical derivatives of acetylene and buta-1,3-diyne, as well as phenyleneethylene oligomers^{30,34-37,47-51}. Contrary to the DPA for which two emission band form $1^{1}B_{u}$ and $1^{1}A_{u}$ were observed⁴⁰, for studied compound only one emission band was recorded. The fluorescence spectra are narrow and exhibit clear vibronic bands. Moreover, the optical spectra are characterized by a substantial asymmetry between absorption and fluorescence. These effects have been explained in terms of torsional

disorder and quadratic coupling between the ground and first excited states⁵² or the exciton model developed by Liu et al.^{53,54}. The red shift of the fluorescence maximum depends on the size of substituent for both acetylene and buta-1,3-diyne derivatives in the following order: 2-naphthyl, 1-naphthtyl, pyrenyl and anthryl (Table 1 ESI).



Fig. 3 Normalized fluorescence spectra of acetylene and buta-1,3-diyne derivatives in methylcyclohexane (MCH).

Similarly as for absorption, second acetylenic unit shifts the emission spectrum to the red for about a dozen nanometers for naphthyl and for several nm for anthryl and pyrenyl derivatives (Table 1 ESI). The emission spectra in 2-MeTHF are similar to that in MCH, however, they are shifted by several nm to the red. A greater impact on the shape and position of the emission band has MeCN. The vibrational structure is blurred and for anthryl derivatives it completely disappears. Moreover, emission bands are broader and the ratio of the intensity of the vibrational peaks changes, in comparison to that in 2-MeTHF. Such influence of a polarity of solvent indicates on a fairly large contribution of the emission from the charge transfer excited state. This statement is supported

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by femtosecond time-resolved studies of fluorescence spectra of 1,2-bis(9-anthryl)-acetylene in solvents of different polarity⁵¹. Fluorescence quantum yield of all acetylene and buta-1,3-diyne derivatives in MCH, 2-MeTHF and MeCN are gathered in Table 1. Moreover, in Table 2 ESI fluorescence quantum yields and fluorescence lifetimes measured in five additional non-polar solvents differing in viscosity are presented.

Table 1 Fluorescence quantum yield (ϕ), fluorescence lifetime (τ), pre-exponential factor (α) and quality of fit $\chi 2_R$ of studied compounds in MCH, 2-MeTHF and MeCN.

Compound	Solvent	φ	τ/ns	α	X ² _R
1Nac	MeCN	0.745	1.82	1	0.98
	MeTHF	0.841	1.56	1	0.99
	MCH	0.836	1.69	1	0.95
1Nac2	MeCN	0.083	0.24	1	0.89
	MeTHF	0.165	0.27	1	0.96
	MCH	0.160	0.29	1	0.97
	MeCN	0.109	3.23	0.063	0.95
			0.45	0.937	
2Nac	MeTHF	0.119	4.02	0.067	0.92
ZINAC			0.42	0.933	
	MCH	0.110	4.70	0.060	1.12
			0.48	0.940	
	MeCN	0.004	3.02	0.014	1.14
2Nac2			0.22	0.986	
ZNACZ	MeTHF	0.006	0.23	1	1.15
	MCH	0.010	0.23	1	1.13
	MeCN	0.683	2.63	1	1.14
Aac	MeTHF	0.660	1.75	1	0.97
	MCH	0.634	1.73	1	1.07
Aac2	MeCN	0.199	5.05	0.100	0.89
			1.83	0.900	
	MeTHF	0.200	4.45	0.118	0.98
			1.44	0.882	
	MCH	0.147	3.72	0.153	0.93
			0.91	0.847	
Рас	MeCN	0.920	1.93	1	0.94
	MeTHF	0.986	1.54	1	0.99
	MCH	0.975	1.37	1	1.06
Pac2	MeCN	0.723	1.60	1	1.00
	MeTHF	0.758	1.30	1	0.98
	MCH	0.779	1.14	1	0.97

Studied compounds have various values of fluorescence quantum yield which depend primarily on the structure of the compound, the size of the substituent and substitution sites, as well as the amount of triple bonds (Table 1). Thus, 1naphthyl derivative of acetylene has much higher fluorescence quantum yield than 2-naphthyl derivative, (about one order of magnitude). As can be seen from the absorption spectrum, this seems to be due to the greater involvement of the triple bond in conjugation with the aromatic system for 2-naphthyl than for 1-naphthyl derivative. Anthryl and pyrenyl derivatives of

acetylene have high fluorescence quantum yield, for pyrenyl derivative the value is closed to 1. However, 1,3-diyne derivatives, except for pyrenyl one, have much lower fluorescence quantum yield than acetylene derivatives (Table 1 and Table 2 ESI). This indicates on the participation of an additional deactivation process of the excited state. The polarity of solvent has minor influence on the fluorescence quantum vield. In acetonitrile it is a bit lower than that in 2-MeTHF or MCH (Table 1). Also, the solvent viscosity does not significantly affect the fluorescence quantum yield (Table 2 ESI). The fluorescence lifetimes of studied compounds are also differentiated as fluorescence guantum yields (Table 1 and Table 1 ESI). The fluorescence intensity decay for 1Nac, 1Nac2, Pac and Pac2 is well described by mono-exponential function. while for 2Nac and 2Nac2 and Aac in viscous solvents by biexponential function. For 1Nac, fluorescence lifetimes are included in the range from 1.82 to 1.46 ns whereas for 1Nac2 are much shorter (about 0.3 ns). 2-Naphthyl derivatives of acetylene buta-1,3-diyne have bi-exponential and fluorescence intensity decay, however, 2Nac2 has a shorter decay time. For 2Nac longer component is about 5 ns while shorter one about 0.5 ns. It is worth to emphasize that contribution of longer fluorescence lifetime seems to depend on solvent viscosity. For solvents with a low viscosity, its contribution to the fluorescence intensity decay is about 4-6% while for viscous solvent increase to several percent (Table 1 ESI). The major component of the fluorescence lifetimes of 2Nac2 (contribution about 94%) is in the range from 0.2 to 0.3 ns, while for the minor component about 3 ns. Due to the very low fluorescence quantum yield of this compound, measured fluorescence lifetimes may be wholly flawed due to Raman scattering and solvent impurities. The fluorescence lifetime of Aac in low viscous solvents is about 2 ns while in viscous solvents the second component (about 0.6 ns) appear with several percent contribution, whereas Aac2 has two fluorescence lifetimes in all studied solvents. The major component (about 90%) is in the range from 0.9 to 1.4 ns while the minor one in the range from 5 to 3.6 ns. For pyrene derivatives of acetylene and buta-1,3-diyne mono-exponential fluorescence intensity decay is recorded. For Pac fluorescence lifetime is about 1.4 ns in non-polar solvents and 1.93 ns in polar acetonitrile, while for Pac2 fluorescence lifetimes are shorter, about 1.2 ns in non-polar solvents and 1.6 ns in acetonitrile. The photophysical and theoretical studies suggest that phenyleneethynylenes exist in planar and several twisted conformations in their ground state due to the nearly free rotation of the arene rings along the molecular axis. On the other hand, their emission spectra are highly structured as a consequence of the planarization of the molecule in the excited state^{47-49,55,56}. The emission properties (fluorescence spectra, fluorescence excitation spectra and fluorescence quantum yield) of 2Nac, 2Nac2 and Aac2 were found to be independent of excitation/observation wavelengths (Figs 4-7 and Figs 17-24 ESI, Table 3, ESI). The bi-exponential

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fluorescence decays can be reasonably explained by the delayed fluorescence caused by thermal repopulation of the second excited state, which was reported for diphenylacethylene derivatives⁵⁷⁻⁵⁹. However, for 2Nac2 and Aac2, contrary to 2Nac, the energy barrier of rotation in the excited state is relatively low (about 16 kJ/mol), Table 5 ESI (for details see Theoretical calculation section,) causing the crossing through the energy barrier several times during the lifetime of the excited state. Thus, the recorded fluorescence excitation/emission spectrum is averaged over emission of different rotamers and fluorescence intensity decay heterogeneous.



Fig. 4 The normalized emission spectra of 2Nac in methylcyclohexane recorded for different excitation wavelengths. The shoulder in the spectrum recorded at λ_{ex} =330 nm is caused by scattered light.



Fig. 5 The normalized fluorescence excitation spectra of 2Nac in methylcyclohexane recorded for different observation wavelengths.



Fig. 6 The normalized emission spectra of Aac2 in methylcyclohexane recorded for different excitation wavelengths. The shoulder in the spectrum recorded at λ_{ex} =465 nm is caused by scattered light.



Fig. 7 The normalized fluorescence excitation spectra of 2Nac in methylcyclohexane recorded for different observation wavelengths. The shoulder in the spectrum recorded at λ_{obs} =475 nm is caused by scattered light

For compounds having a mono-exponential fluorescence intensity decay, it is possible to calculate the radiative (k_r) and non-radiative (k_{nr}) rate constants, according to equations: $k_r = \phi / \tau$ and $k_{nr} = (1 - \phi) / \tau$, where ϕ is the fluorescence quantum yield and τ is fluorescence lifetime. For 1Nac, 2Nac2, Aac, Pac and Pac2 the corresponding rate constants for the three solvents used (MeCN, 2-MeTHF and MCH) are summarized in Table 4 ESI. The fluorescence rate constant is very similar for all above-mentioned derivatives in the nonpolar 2-MeTHF and MCH while a little lower in MeCN. In contrast, there is a big difference in the k_{nr} rate constant between acetylene and buta-1,3-diyne derivatives.

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radiative rate constant for buta-1,3-divne is one order higher than that for appropriate acetylene derivative. This indicates on the additional deactivation channel of the excited state, probably related with the greater conformational freedom. Also, values of the fluorescence rate constant in acetonitrile, smaller than in nonpolar solvents, seem to confirm that the emission of anthryl and pyrenyl derivatives of acetylene and 1,3-divne in this solvent comes from the charge-transfer (CT) state. Presented in Figs 25-28, ESI time-resolved emission spectra (TRES) for anthryl and pyrenyl derivatives show the bathochromic evolution of the fluorescence in a short time after excitation. Such a process has been observed for 1,2bis(9-anthryl)acetylene by Gutierez-Arzuluz et al.⁵¹. These authors demonstrated on the basis of femtosecond fluorescence up-conversion experiments that in acetonitrile spectral shift is biphasic, with first sub-picosecond decay time dictated by solvent response and a much slower one, about 37 ps, connected with the relaxation of the excited state structure leading to a change in the relative orientation of the two anthracenic end group which allows for further stabilization of the CT state. Thus, before the system is able to relax to the full CT state, an initial equilibrium between the local excited state and partial charge-transfer excited state takes place. It seems that the process of solvent-mediated symmetry reduction in the excited state, also takes place for anthryl derivative of buta-1,3-diyne as well as pyrenyl derivative of acetylene and buta-1,3-diyne and to some extent for the naphthyl derivatives of acetylene. The broad structureless fluorescence spectra of anthryl derivatives in MeCN suggests the possibility of the formation of orthogonal twisted-internal charge transfer (TICT) state⁵¹. The dependence of fluorescence decay times on the observation wavelengths found for Aac2 (Table 2) suggests the relatively slow conformation changes.

Table 2 Fluorescence lifetime (τ), pre-exponential factor (α) and quality of fit (χ^2_{R}) of Aac and Aac2 in acetonitrile determined for different observation wavelengths.

Observation		λ_{exc} = 420 /nm	
wavelength /nm	τ/ns	α	X ² _R
405	5.05	0.10	
495	1.83	0.90	1.10
F 4F	5.40	0.04	
515	1.88	0.94	0.97
520	6.06	0.007	
530	1.87	0.993	0.99
560	1.87	1	1.09
575	1.87	1	1.03
		Aac	
460	2.65	1	1.11
475	2.62	1	1.12
500	2.65	1	1.12
530	2.64	1	1.03
570	2.63	1	1.08

This may indicate on the transformation to orthogonal TICT state, all the more, that the energy barrier of rotation decreases with increasing the solvent polarity⁵⁰. A such dependence is not determined for Aac (Table 2). However, according to Gutierez-Arzuluz et al.⁵¹ the relative orientation of the two anthracenic groups of the Aac molecule occurs rapidly over time of about 40 ps, shorter than the resolving power of our instrument. Based on measurements of the fluorescence quantum yield, it is difficult to conclude about the influence of the solvent viscosity on the photophysical properties, however, the measurements of the fluorescence intensity decay indicate that the 2-naphthyl and 9-anthryl derivatives of acetylene can be used as molecular rotor to study the solvent viscosity (particularly for viscous solvents at

Low temperature luminescence

lower temperature⁵⁴).

In order to check the influence of the environment stiffness on the fluorescence fluorescence intensity, the luminescence spectra of the studied compounds were measured in glass of MCH and 2-MeTHF. As the measurements at liquid nitrogen temperature in 2-MeTHF gave the same results as in MCH, they are not presented here. Luminescence, fluorescence excitation and room temperature fluorescence spectra of 1naphthyl and 2-naphthyl acetylene and buta-1,3-diyne derivatives in MCH are presented in Figs 8-11, while for anthryl and pyrenyl derivatives in Figs 29-32, ESI.



Fig. 8 The normalized emission (solid red line), and excitation (solid green line) spectrum measured at 77 K and fluorescence spectrum measured at room temperature (black solid line) of 1Nac in methylcyclohexane. Published on 13 November 2015. Downloaded by Mount Allison University on 20/11/2015 09:18:57.

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Fig. 9 The normalized emission (solid red line), and excitation (solid green line) spectrum measured at 77 K and fluorescence spectrum measured at room temperature (black solid line) of 2Nac in methylcyclohexane.

Fluorescence spectra measured at 77 K have a richer vibrational structure than those recorded at room temperature and are red-shifted for a few nanometers. Furthermore, they exhibit very small Stokes' shift. In contrast to the room temperature results, for all studied compounds, except pyrenyl derivatives, almost mirror symmetric images between the fluorescence and fluorescence excitation spectra are recognizable at 77 K. The lack of mirror symmetry between fluorescence and



Fig. 10 The normalized emission (solid red line), and excitation (solid green line) spectrum measured at 77 K and fluorescence spectrum measured at room temperature (black solid line) of 1Nac2 in methylcyclohexane.

Fig. 11 The normalized emission (solid red line), and excitation (solid green line) spectrum measured at 77 K and fluorescence spectrum measured at room temperature (black solid line) of 2Nac2 in methylcyclohexane.

fluorescence excitation spectra for pyrenyl derivative indicates that long absorption band is a superposition of at least two absorption transitions. The mirror symmetry indicates on a hindered ring torsion in the MCH organic glass. It is worth mentioning that for 2-naphtyl derivatives only a very weak phosphorescence is detected indicating a low intersystem crossing rate constant in both acetylene and buta-1,3-diyne derivatives. For all the studied compounds, the room temperature fluorescence intensity is less intense than that recorded at 77 K. The exception are pyrene derivatives (Pac and Pac2, Figs 31 and 32, ESI) for which room temperature fluorescence is much more intense, probably because of solubility at low temperature. It should be noted that for compounds with high or moderate value of the fluorescence quantum yield (acetylene derivatives), the increase of fluorescence intensity with decreasing temperature is relatively small, contrary to buta-1,3-divne derivatives (Figs 8-11). Thus, the measurements in stiff organic glasses confirm the greater conformational freedom of buta-1,3-diyne derivatives in comparison to acetylene derivatives⁵⁶.

Theoretical calculations

To understand the influence of the substituents dimension on torsional motions of acetylene and buta-1,3-diyne derivatives, we studied the torsional potential in both the ground and excited states within the framework of the local mode approximation using a DFT method. Figs 33-38, ESI show DFTbased torsional potentials for 1Nac, 2Nac, Aac, 1Nac2, 2Nac2 and Aac2 in the ground and excited states. The torsional potential in the ground state is well approximated by a simple periodic potential of the form: Published on 13 November 2015. Downloaded by Mount Allison University on 20/11/2015 09:18:57

where: V_{max} is the barrier height of the torsional potential and θ is the ring-to-ring torsional angle. The above equation well describes the torsional potential in the ground state, while poorly in the excited state, in which the approximation by Gauss or Lorentz function is much better (Fig 38 ESI). The energy barrier of rotation in the excited state is much higher than in the ground state indicating a hampered rotation of polyaromatic hydrocarbon units in the excited state, which is attributed to the breaking of the cylindrical structure of the electron density along the axis of symmetry⁶¹ and the adoption of the partial cummulene-like structure⁵⁵. For this reason, the rotation energy barrier for 1- and 2-naphthalene derivatives in the excited state is high (close to 40 kJ / mol) contrary to diphenylbutadiyne for which the rotation energy barrier is low $(\Delta E^{3} kJ/mol)$. Therefore replacement of the phenyl group with naphthyl groups eliminates an energy minimum at the orthogonal geometry in the excited state observed for diphenylbuta-1,3-diyne⁶². For 1Nac in the ground and excited states, the most stable is trans conformation, while cis conformer is non-planar (the ring-to-ring torsional angle is about 27 degrees) and less stable for about 0.5 kJmol⁻¹ (Fig. 33 ESI). Due to the lack of steric hindrance for the acetylene and diacetylene derivatives, the place of substitution in the naphthalene does not differentiate the rotation energy barrier as it does for ethylene derivatives⁶³. Theoretical calculations at the density functional level of theory indicate that in the ground and excited state anthryl derivative of acetylene is not fully planar. An angle between the two anthryl unit of about 38 degrees exists in the ground state, with the flat maximum at 90 degrees, in accordance with the data published by Gutierez-Arzaluz et al.⁵⁰. However, in the excited state this dihedral angle decreases to a value of 20 degrees (Fig. 35 ESI). For all studied buta-1,3-diyne derivatives in the both ground and excited states the most stable are linear planar conformations (Figs 36-38 ESI). The barrier heights of the torsional potential calculated using the equation (1), for all the studied compounds, are gathered in Table 5, ESI. For acetylene derivatives the energy barriers of rotation in the ground state of are slightly higher than these for buta-1,3-diyne derivatives comparable to the and are values for diphenylacethylene^{29,36,37,64} and its symmetrically substituted derivatives³⁶. Lower values of rotational energy barriers obtained for 1,3-diyne are in the conformity with the statement that the insertion of extra –C≡C- unit decreases the barrier by 40-70%⁶¹. The rotational energy barriers calculated for the polycyclic aromatic hydrocarbon derivatives of buta-1,3-diyne are comparable with the data obtained for diphenylbuta-1,3-diyne^{29,37,46} and its derivatives³⁷. Moreover, the value of the energy barrier of rotation determined experimentally for covalently-linked multi-porphyrin arrays⁶⁵

ARTICLE are also lower than that for diphenylacetylene. The DFT method gives overestimated values of the energy barrier of rotation⁵⁶. However, the experimentally determined

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rotation⁵⁶. However, the experimentally determined magnitude of the rotational barrier is found to be the 40% larger than that in a gas phase²⁹, thus they may be close to the barrier of rotation in low viscous solvent, especially for polyaromatic hydrocarbon substituents. The rate constant of the conversion through the energy barrier during the rotation $(k_{c\rightarrow t})$ can be calculated on the basis of transition-state theory for unimolecular reaction using the equation:

$$k_{c \to t} = \frac{\kappa kT}{h} * e * \exp(\Delta S / R) * \exp(-\Delta E_a / RT)$$
 (2)

where: k is the Boltzmann constant, T is the absolute temperature, h is Planck's constant, R is the gas constant, ΔS is the entropy change, and ΔE_{a} is the energy of activation. It is difficult to assign a value to the transmission coefficient, κ , which incorporates all correction factors and uncertainties. We chose $\kappa\text{=}0.4$ as for ring inversion 66 and $\Delta S\text{=}0$ and for these values the rate constant and rotamer lifetime were calculated. Rate constant of barrier crossing for the energy barrier of rotation in the ground state at room temperature (300 K), gathered in Table 4 ESI, are high and rotamer lifetimes are as short as tens of femtoseconds, which is tantamount with the free rotation in the ground state. The energy barriers of rotation in the excited state (Table 5, ESI) for acetylene derivatives are in the range from 40 kJmol⁻¹ to 30 kJmol⁻¹ therefore similar to these for symmetrically substituted derivatives³⁶ diphnenylacetylene or 1.4bis(phenylethynyl)benzene^{55,56}. Moreover, the energy barrier of rotation in the excited state for studied buta-1,3-diyne derivatives are about 10 kJmol⁻¹ lower than that for acetylene derivatives (Table 5 ESI) and much lower than that for symmetrically substituted diphenyl derivatives of buta-1,3diyne³⁷. The calculated rate constant of rotation for acetylene derivatives are low and rotamer lifetimes are long, a hundred of nanosecond for naphthyl derivatives and about 20 ns for anthryl derivative (Table 5 ESI). Thus, during the fluorescence lifetime there is no rotation of aryl substituents in the excited state. However, lower energy barrier of rotation for buta-1,3diyne causing that rotamer lifetime for naphthyl derivatives are about 100 ps, while for anthryl derivative about 800 ps, which are comparable to the fluorescence lifetime. Accordingly, rotation in the excited state may provide to appear an additional radiationless channel for excited state deactivation. However, as in the case of the ground state, the energy barrier of rotation in the excited state seems to be overestimated. However, taking into account the size of the substituents and the viscosity of the solvent with a high degree of probability it can be assumed that during the lifetime of the excited state the acetylene derivatives do not change their conformation contrary to the buta-1,3-diyne derivatives.

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A low value of rotation barriers in the ground state and at the same time large its high value in the excited state should cause that in the ground state the two conformers of 1Nac and 2Nac should be almost equally populated and should be distinct isomers in the excited state. Because two conformers belong to different symmetry groups and should have different electronic transition and consequently the different absorption and emission spectra as in the case of trans-1,2-di(2naphthyl)ethane^{67,68}. However, theoretically calculated, using TD DFT method, the vertical transitions in absorption and emission for fully optimized structure for both conformers (cis and trans) of 1Nac and 2Nac reveal a great coincidence of the vertical transition in absorption and emission of the rotamers (Table 3). Moreover, the value of the angle between long axis of molecule and transition dipole moment for both rotamers differs slightly (Figs 39-42 ESI). Thus, our earlier statement that fluorescence and fluorescence excitation spectra are excitation and monitoring wavelength independent is fully consistent with the calculations.

Table 3 Vertical transition in absorption and emission (in nm) and oscillator strength (f) for the two rotamers of dinaphthylacetylene isomers (1Nac and 2Nac) calculated using TD DFT method (B3LYP, def2TZVP basis set).

1	1Nc cis 1Nac trans		2Nac cis		2Nac trans		
abs	f	abs	f	abs	f	abs	f
377	0.625	378	0.655	350	0.92	351	1.01
328	0.3*10 ⁻⁴	326	0.2*10 ⁻⁵	329	0.1*10 ⁻⁴	329	0.6*10 ⁻⁶
310	0.5*10 ⁻³	309	0.510 ⁻⁶	317	0.2*10 ⁻³	318	0.2*10 ⁻²
299	0.2*10 ⁻⁵	300	0.3*10 ⁻⁴	303	0.11	304	1.0*10 ⁻³
299	0.9*10 ⁻⁴	299	0.6*10 ⁻⁶	284	0.56	285	0.60
emission							
427	0.71	427	0.74	391	1.08	390	1.20

According to Zgierski et al.^{38,39} and Wierzbicka et al.³⁶ low fluorescence quantum yield of DPA and its derivatives and its strong dependence on temperature is caused by the state switch from initially excited linear fluorescing $\pi\pi^*$ to the bent $\sigma\pi^*$ state. The same phenomenon seems to occur for buta-1,3diyne and its symmetrically substituted derivatives containing electron-donating substituents³⁷. Similar calculations to those described in the above cited works³⁶⁻³⁹ were carried out to check the influence of the bending of C_{Ar}-C=C angle on the potential energy of the excited state, for naphthyl derivatives of acetylene and buta-1,3-diyne. For other studied derivatives (anthryl and pyrenyl substituent) such a calculations were not performed due to the cost.



Fig. 12 The potential-energy profiles of CPh-C≡C bending angle in the excited state for 1Nac (red dashed line) and 2Nac (black solid line).

As shown in Fig. 12 for the naphthyl derivatives of acetylene large excess of the excitation energy is needed to achieve the $\sigma\pi^*/\pi\pi^*$ states intersection (about 36 kJmol⁻¹ at bending angle equal to 135 degrees and 42 kJmol⁻¹ at bending angle equal to 145 degrees for 2Nac and 1Nac, respectively). Moreover, the $\sigma\pi^*$ is less stable than linear $\pi\pi^*$ for about 18 kJmol⁻¹ for 2Nac and 40 kJmol⁻¹ for 1Nac. Other results were obtained for buta-1,3-diyne derivatives. In this case, the presence of two acetylene units causes that there are two possible bending of the molecule. One comprising atoms C_{Ar}-C=C, like in acetylene derivative, and the second one containing C=C-C atoms. The results of calculations are presented in Fig. 13.



Fig. 13 The potential-energy profiles of CPh-C=C (solid lines) and C-C=C (dashed line) bending angle in the excited state for 1Nac2 (black solid line and blue dashed line) and 2Nac2 (red solid line and green dashed line).

Bending of the molecule at the site comprising atoms C=C-C atoms is less favourable energetically. The potential energy of bending curve is increasing without a clear minimum for both 1Nac2 2Nac2. However, bending containing C_{Ar}-C=C leads to the $\sigma\pi^*/\pi\pi^*$ states intersection for a bending angle about 160

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degrees with the energy barrier about 11 kJmol⁻¹ for 1Nac2 and 9 kJmol⁻¹ for 2Nac2. Moreover, for 1Nac2 the shallow minimum at bending angle about 135 degrees is observed and $\sigma\pi^*$ state is less stable than linear $\pi\pi^*$ state for about 7 kJmol⁻¹, while for 2Nac2 $\sigma\pi^*$ is a little more stable (1.7 kJmol⁻¹). Thus, theoretical calculations explain the differences in the photophysics between acetylene and buta-1,3-diyne derivatives of polycyclic aromatic hydrocarbon derivatives.

Conclusions

The polycyclic aromatic hydrocarbon derivatives of acetylene possess high fluorescence quantum yields and the weak dependence of fluorescence intensity on temperature. This is due to stiffening of the molecule in the excited state as a result of a strong electron coupling between the polycyclic aromatic substituents. As a consequence the bending of molecule leading to a $\sigma\pi^*$ state is highly energetically unfavourable which is confirmed by theoretical calculations. Thus, they do not show any anomalous dynamic behaviour but act as a usual aromatic compounds. In the case of buta-1,3-diyne derivatives the size of substituent has influence on their photophysical behaviour. For big substituents like pyrenyl and to some extent anhthryl, buta-1,3-diacetylene derivatives behave appropriate acetylene derivatives. However, bicyclic aromatic substituents (naphthyl) exhibit all the characteristics of the phenyl derivative of buta-1,3-diyne or acetylene. For 1- and 2naphthyl isomers and 9-anthracene derivatives of acetylene derivatives fluorescence and fluorescence excitation spectra are excitation and monitoring wavelength independent because of coincidence of absoeption and emission spectra of the rotamers.

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