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# Experimental and theoretical studies of spectroscopic properties of simple symmetrically substituted diphenylbuta-1,3-diyne derivatives

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## Abstract

A series of symmetrically substituted diphenyl-1,3-butadiyne (DPB) derivatives possessing electron-donating (*N,N*-dimethylamino or methoxy) or electron-accepting (nitrile, ester or aldehyde) groups have been prepared and studied with emphasis on their spectral and photophysical properties. The photophysical characteristics of these compounds have been studied in relation to their structures and influence of solvents or temperature. The observed spectral and photophysical properties are explained with the help of potential energy maps in the ground and excited states obtained from density functional theory (DFT, B3LYP, def2TZVP basis set) calculations. The structure-property relationship of all of the compounds is discussed and compared with appropriate diphenylacetylene derivatives.

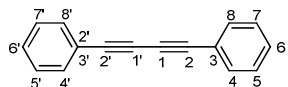
## Introduction

Conjugated organic polymers containing acetylene unit have been the subjects of intense research in recent years<sup>1-3</sup>. In particular, they have been found to be attractive for conventional materials in electronic or photonic devices<sup>4</sup>. Substituted diphenyldiacetylenes undergo 1,4-addition reaction in the solid state to give polydiacetylenes<sup>5-7</sup>. The reaction can be initiated thermally, photochemically or by  $\gamma$ -irradiation. Diphenyldiacetylene derivatives may polymerize to a variety of interesting materials<sup>8</sup>. Rather rigid, the highly conjugated poly(*p*-phenylenethynylene)s are strongly fluorescing<sup>9-15</sup> while diphenylacetylene (tolane) and diphenylbuta-1,3-diyne behave quite differently. One of the most interesting photophysical properties of diphenylacetylene is the loss of fluorescence that occurs following excitation of higher vibronic levels of the  $1B_{1u}$  state under collision-free conditions of a supersonic free jet<sup>16</sup> and in solution<sup>17,18</sup>. It exhibits also a strong temperature dependence of fluorescence quantum yield in solution<sup>19</sup>. These phenomena were explained by Zgierski and Lim<sup>20-22</sup> based on theoretical calculations. They found that while the lowest-energy excited singlet state of diphenylacetylene is the  $B_{1u}$  ( $\pi\pi^*$ ) state in the linear  $D_{2h}$  symmetry, the  $\pi\sigma^*$  state of  $A_u$  symmetry in bent  $C_{2h}$  symmetry is the lowest in energy. The  $\pi\sigma^*$  state was called the dark state because it was thought to be non-fluorescent. However, recently its weak fluorescence was detected by Saltiel and Kumar<sup>23</sup>. This leads to the crossing of the fluorescent  $\pi\pi^*$  state and the  $\pi\sigma^*$

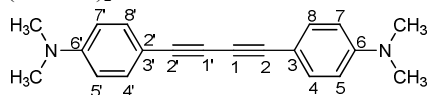
potential energy curve. The transition from the initially excited  $\pi\pi^*$  state to  $\pi\sigma^*$  state requires crossing a small energy barrier which explains the loss of fluorescence in the gas phase at higher excitation energy and the thermally activated quenching of fluorescence in solution. Their calculations also predict that the attachment of an electron-withdrawing group to diphenylacetylene increases the energy of the  $\pi\sigma^*$  state and the  $\pi\pi^* \rightarrow \pi\sigma^*$  state switch is not expected to occur, while the attachment of an electron-donating group to diphenylacetylene enhances the state switch from initially excited  $\pi\pi^*$  to  $\pi\sigma^*$  state. The experimental confirmation of the presence of the  $\pi\sigma^*$  state was strong  $\pi\sigma^* \leftarrow \pi\sigma^*$  absorption at about 700 nm in picosecond transient spectra for different DPA derivatives containing electron-donating substituents and lack of such absorption for electron-withdrawing substituents<sup>17,18,20-22,24-26</sup> as predicted by theoretical calculations. The recent work of Saltiel and Kumar<sup>23</sup> on the photophysics of tolane fully supports theoretical calculations. According to these authors the  $\pi\sigma^*$  state is weakly fluorescent and in glassy media at 77 K the triplet state is much more efficiently populated from the  $1^1B_{2u}$  state, while in solution the  $1^1A_u$  is the precursor of the diphenylacetylene triplet state<sup>17,18</sup>. For 1,4-diphenylbuta-1,3-diyne, as for diphenylacetylene, when the photoexcitation energy becomes higher than about 2000  $\text{cm}^{-1}$  above the  $1^1B_{1u}$  state origin, dramatic reduction of the fluorescence quantum yield was observed in solution<sup>27</sup> and under the collision-free conditions of a supersonic free jet<sup>28</sup>. This can be explained by assuming the presence of close location of the optically forbidden

$^1A_{1u}$  state above  $^1B_{1u}$  state<sup>24,25,27,28</sup>. Moreover, Thulstrup et al.<sup>29</sup> based on linear dichroism in IR and UV range and DFT theoretical calculations concluded that even in cryogenic temperature diphenylbuta-1,3-diyne is highly dynamic molecule. Due to the lack of systematic studies of symmetrically substituted diphenylbuta-1,3-diyne derivatives containing an electron-withdrawing or an electron-donating groups, and at the same time considerable interest of systems containing the diyne motif<sup>30</sup>, we decided to study the spectral and photophysical properties of such derivatives (Fig. 1). Moreover, on the basis of obtained results, the similarities and differences between diphenylacetylene and diphenyldiacetylene derivatives are discussed. Furthermore, the theoretical calculations allowing a relatively full interpretation of experimental results were performed.

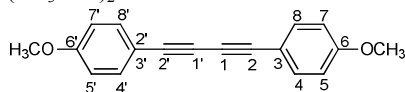
#### DPB



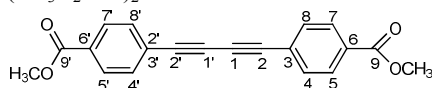
#### (DMAPh)<sub>2</sub>DA



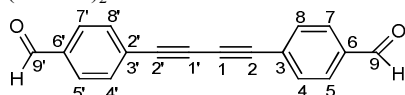
#### (CH<sub>3</sub>Oph)<sub>2</sub>DA



#### (CH<sub>3</sub>O<sub>2</sub>Cph)<sub>2</sub>DA



#### (OHCPH)<sub>2</sub>DA



#### (NCPh)<sub>2</sub>DA

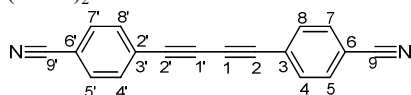


Fig. 1 Structure and atom numbering of compounds studied.

## Materials and methods

### Absorption and fluorescence measurements

Absorption spectra were measured using a Perkin-Elmer Lambda-40P spectrophotometer whereas emission spectra were measured using a FluoroMax-4 (Horiba Jobin-Yvon) spectrofluorimeter. Low temperature luminescence spectra were obtained using FL-1013 liquid nitrogen dewar assembly. Fluorescence quantum yields were calculated using quinine sulphate in 0.05 M H<sub>2</sub>SO<sub>4</sub> (QY=0.53±0.02)<sup>31</sup> as reference and were corrected for different refractive indices of solvents. The fluorescence lifetimes were

measured with a time-correlated single-photon counting FT300 PicoQuant fluorescence lifetimes spectrometer using PLS-340 sub-nanosecond pulsed diode.

### Theoretical calculations

All calculations were performed using density functional theory (DFT) within Turbomole v. 6.4 suite programs on a PC cluster. The structures of all compounds were prepared and initially optimized using TmoleX program. Energy-minimum structures were searched for the ground and the lowest excited states using a B3-LYP hybrid functional with def2-TZVP basis set of triple- $\zeta$  quality. This procedure was considered satisfactory if the energy difference between optimized cycles was  $<1 \times 10^{-6}$  Hartree for the ground state structure optimization and  $<1 \times 10^{-7}$  Hartree for the excited state structure optimization. In both states a gradient of  $<1 \times 10^{-3}$  au was achieved. The low-lying excited states were treated within the adiabatic approximation of time-dependent density functional theory (DFT-RPA) using B3-LYP functional. The geometry optimization of excited state was performed using a grid parameter equal to 4. The convergence of all systems studied was checked by the harmonic vibrational analysis. No imaginary frequencies were observed. The rotation energy barriers in the ground and the excited states were performed by imposing constraints on the dihedral angle and optimizing the energy of molecule varying all other degrees of freedom. No additional constraints such as the symmetry of the molecule have been imposed. In a similar way the energy of bent conformation of molecule was calculated constraining the bent angle value and optimizing the remaining part of molecule. The same functional and basis set was used as in the case of energy optimization.

### Crystal structure determination

Single-crystal specimens of the title compounds were selected for the X-ray diffraction experiment at T = 295 K. Diffraction data were collected on an Oxford Diffraction Gemini R ULTRA Ruby CCD diffractometer with MoK $\alpha$  ( $\lambda=0.71073$  Å) radiation. The lattice parameters were obtained by least-squares fit to the optimized setting angles of the collected reflections by means of CrysAlis CCD<sup>32</sup>. The structural determination was carried out using the SHELX package. The structures were solved by direct methods, with refinements being carried out by full-matrix least-squares on F<sub>2</sub> using the SHELXL-97 program<sup>33</sup>. All H-atoms bound to aromatic C-atoms were placed geometrically and refined using a riding model with C–H=0.93–0.97 Å and Uiso(H)=1.2–1.5Ueq(C). All H-atoms bound to N(O)-atoms were located on a difference Fourier map and refined freely with Uiso(H) = 1.5Ueq(N). All the interactions demonstrated were found using the PLATON program<sup>34</sup>. The molecular graphics were prepared using the ORTEPII<sup>35</sup>, PLUTO-78<sup>36</sup> and Mercury<sup>37</sup> programs.

### Synthesis

General scheme of synthesis of diphenylbuta-1,3-diyne derivatives is shown in Scheme 1 ESI. Methyl-4-iodobenzoate, 4-iodobenzonitrile, 4-((trimethylsilyl)ethynyl)-benzaldehyde, phenylacetylene, 4-ethynylanisole, 4-ethynyl-N,N-dimethylaniline, ethynyltrimethylsilane, bis(triphenylphosphine)palladium(II) dichloride (Sigma Aldrich), 2-methyl-3-butyn-2-ol (Fluka) were commercially available and used without further purification. The progress of all reaction performed was checked by means of TLC (Merck plates, Kieselgel 60 F<sub>254</sub>). 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, 5  $\mu\text{m}$ , 250 mm long, i.d. 20 mm). The identification of the product was based on:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra recorded on Bruker AVANCE III (500 MHz) spectrometer in  $\text{CDCl}_3$ , mass spectra recorded on Bruker Daltonics (HCTultra) instrument, Raman spectra recorded on Raman FRA-106 instrument and crystallography structures (see ESI for details).

## General procedure

Protected acetylene derivatives were synthesized according to Sonogashira-Hagihara procedure<sup>38-41</sup>. Synthesis of symmetrically substituted diphenylbuta-1,3-diyne and its derivatives [1,4-diphenylbuta-1,3-diyne (DPB), 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (( $\text{CH}_3\text{OPh}$ )<sub>2</sub>DA), dimethyl 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzoate (( $\text{CH}_3\text{O}_2\text{CPh}$ )<sub>2</sub>DA), 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzaldehyde (( $\text{OHCPH}$ )<sub>2</sub>DA), 4,4'-(buta-1,3-diyne-1,4-diyl)dibenzonitrile (( $\text{NCPH}$ )<sub>2</sub>DA) (4,4'-(buta-1,3-diyne-1,4-diyl)bis(*N,N*-dimethylaniline) (( $\text{DMAPh}$ )<sub>2</sub>DA) were based on Glaser<sup>42,43</sup> or Eglinton<sup>44,45</sup> methods (for details see ESI).

## Results and discussion

### Absorption spectra

Absorption spectra of diphenylbuta-1,3-diyne derivatives in methylcyclohexane (MCH) are presented in Fig. 2, while in 2-methyltetrahydrofuran (MeTHF) and acetonitrile (MeCN) in Figs 1 and 2 ESI. Moreover, in Table 1 ESI the molar decadic absorption coefficients for all studied compounds in all solvents used are presented.

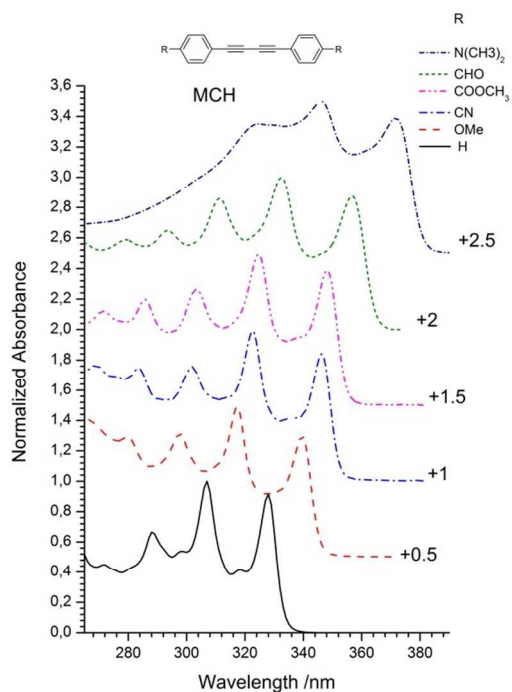


Fig. 2 Absorption spectra of diphenylbuta-1,3-diyne derivatives in methylcyclohexane (MCH).

Absorption spectrum of diphenylbuta-1,3-diyne (DPB) measured in MCH is consistent with the spectrum of this compound published by Nagano et al.<sup>27</sup> and Hirata et al.<sup>24</sup>. The long wavelength absorption band is connected with the transition between the ground  $S_0$  and  $1^1\text{B}_{1u}$  state<sup>27</sup>. It has a clear vibronic structure with the most prominent vibrational mode of the  $\text{C}\equiv\text{C}$  stretching (Table 1) and additional vibrational mode about  $1000\text{ cm}^{-1}$  corresponding to phenyl ring vibration<sup>27</sup>. However, the vibronic band of the phenyl group is weaker than that in diphenylacetylene. Furthermore, the 0-0 vibronic band of DPB is red shifted for about 30 nm compared to the spectrum of diphenylacetylene measured in the same solvent<sup>21,27,46</sup>.

Table 1 The position of long wavelength vibronic absorption band and the main vibrational mode of DPB derivatives in MCH.

derivative	$\lambda$ / nm	$\nu_{\text{C}\equiv\text{C}}$ / $\text{cm}^{-1}$
-H	328	2097
-OMe	339.5	2050
-CN	346.5	2120
-COOMe	348	2080
-CHO	357	2040
-DMA	372	2020

The substituents in the 4 and 4' position in the phenyl ring of DPB causes the long-wavelength shift of absorption spectrum and results in a slight broadening of vibronic bands, hiding a weak vibronic band associated with the phenyl ring vibrations (Figs 2 and 1,2 ESI, Table 1). However, a significant broadening of vibrational structure is recorded for ( $\text{DMAPh}$ )<sub>2</sub>DA. The differences in the position of the 0-0 vibronic transition between corresponding derivatives of diphenylbuta-1,3-diyne and diphenylacetylene are in the range of 20 to 30 nm<sup>46</sup>. The influence of solvent polarity on the position of the absorption bands is similar as in the case of diphenylacetylene derivatives<sup>46</sup>. Only for ( $\text{DMAPh}$ )<sub>2</sub>DA derivative, the absorption band in MeTHF shifts to the red for about 10 nm, whereas the position of the absorption band for the rest of derivatives is practically not altered. Moreover, in acetonitrile a small blue-shift (about 2-3 nm) is observed for all investigated derivatives (Table 2 ESI).

### Fluorescence at room temperature

Fluorescence spectra of ( $\text{CH}_3\text{O}_2\text{CPh}$ )<sub>2</sub>DA (Fig. 3) and ( $\text{NCPH}$ )<sub>2</sub>DA (Fig. 3 ESI) are located in the range from 340 nm to 500 nm and have a typical for arylacetylene<sup>21,27,46</sup> emission band shape showing rich vibrational structure with an intense 0-0 transition. The vibrational bands at about  $1100\text{ cm}^{-1}$  obviously appeared, in addition to the progression of  $2100\text{-}2180\text{ cm}^{-1}$ . In acetonitrile, the fluorescence spectrum is a little shifted to the red and has a more blurred vibrational structure compared to MCH and MeTHF. The lack of measurable fluorescence for mono- and dimethoxy-DPB was also stated by Hirata et al.<sup>24</sup>. As in the case of diphenylacetylene derivatives lack of a mirror symmetry between absorption and emission spectra is observed for diphenylbuta-1,3-diyne derivatives. This phenomena have been explained in terms of torsional disorder and quadratic coupling between the ground and the first excited state<sup>47</sup> or the exciton model developed by Liu et al.<sup>48,49</sup>. The absorption and fluorescence excitation spectra of ( $\text{CH}_3\text{O}_2\text{CPh}$ )<sub>2</sub>DA and ( $\text{NCPH}$ )<sub>2</sub>DA in all studied solvents (Fig. 4 and Figs 4-8 ESI),

contrary to unsubstituted DPB<sup>27</sup> and DPA, overlap with each other, similarly as for corresponding diphenylacetylene derivatives<sup>24,46</sup>.

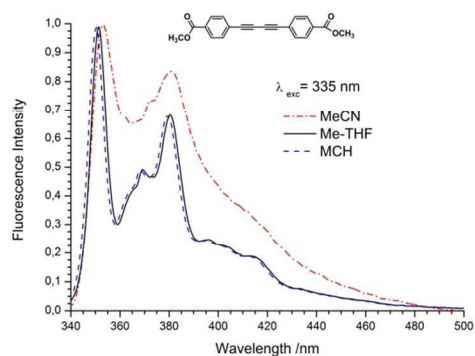


Fig. 3 Emission spectra of  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$  in acetonitrile (red dash-dot line), 2-methyltetrahydrofuran (black solid line) and methylcyclohexane (blue dashed line).

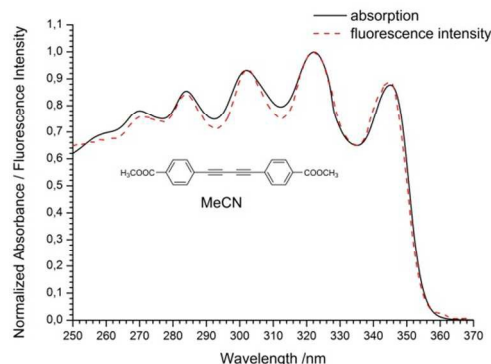


Fig. 4 Absorption (black solid line) and fluorescence excitation spectrum (red dashed line) of  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$  in acetonitrile.

This indicates that there is no additional deactivation channel of the excited state for excitation energy higher than several thousand  $\text{cm}^{-1}$  than 0-0 transition connected with the transition to the  $\sigma\pi^*$  state<sup>18-20,46</sup>. Because of the fact that  $(\text{CH}_3\text{OPh})_2\text{DA}$  and  $(\text{DMAPh})_2\text{DA}$  are not fluorescent, it is not possible to assess whether the transition to the  $\sigma\pi^*$  state occurs for these DPB derivatives, as observed for diphenylacetylene derivatives possessing electron-donating substituent(s)<sup>20,22,46</sup>. The fluorescence quantum yields of diphenylbuta-1,3-diyne derivatives are low (Table 2). For  $(\text{NCPH})_2\text{DA}$  and  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$ , they are one order lower than for corresponding derivatives of phenylacetylene<sup>46</sup>. Moreover, the nitrile derivative has about three times higher fluorescence quantum yield than the ester. The rest of diphenylbuta-1,3-diyne derivatives studied showed so weak fluorescence that we could not distinguish it from the tailing part of the stray light or Raman scattering of the solvent.

Table 2. Fluorescence quantum yields of  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$  and  $(\text{NCPH})_2\text{DA}$  in selected solvents.

Compound	Solvent	$\phi$
$(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$	MeCN	0.009
	cyclohexane	0.014
	$\text{C}_6\text{H}_{14}$	0.016
	$\text{C}_{16}\text{H}_{34}$	0.017
	MCH	0.014
	MeTHF	0.014
$(\text{NCPH})_2\text{DA}$	MeCN	0.028
	cyclohexane	0.044
	$\text{C}_6\text{H}_{14}$	0.041
	$\text{C}_{16}\text{H}_{34}$	0.043
	MCH	0.040
	MeTHF	0.035

Fluorescence intensity decays were measured for  $(\text{NCPH})_2\text{DA}$  and  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$ . However, for  $(\text{CH}_3\text{O}_2\text{CPh})_2\text{DA}$  the fluorescence lifetimes in studied solvents were shorter than resolving power of our apparatus ( $<100$  ps). Thus, only for  $(\text{NCPH})_2\text{DA}$  derivative fluorescence lifetimes are presented in Table 3. In all solvents studied bi-exponential fluorescence intensity decay was recorded. The shorter average fluorescence lifetime is observed in acetonitrile solution (574 ps) and MeTHF (610 ps) whereas the longer in MCH (1.271 ns) and hexadecane (1.069 ns). Bi-exponential fluorescence intensity decay could be a result of the equilibrium between  $S_1$  and  $S_2$  states as suggested by Hirata et al.<sup>25</sup> based on picosecond transient absorption spectroscopy or the presence of two non-equilibrating conformers. However, the lack of dependence of fluorescence spectra, fluorescence quantum yield on excitation wavelength and fluorescence excitation spectra on monitoring wavelength<sup>50</sup> indicate on the equilibrium between  $S_1$  and  $S_2$  states in MCH, MeTHF as well as in MeCN (exemplary data for ester are given in Figs 9,10 ESI). Thus, broader emission spectra in acetonitrile than in nonpolar solvents seem to be caused by the presence of the charge transfer structures induced by dipole solvent but not due to the presence of conformers.

The effect of solvent viscosity on the photophysical properties of  $(\text{NCPH})_2\text{DA}$  was also examined. However, the small difference between fluorescence quantum yield measured and fluorescence lifetime of  $(\text{NCPH})_2\text{DA}$  in hexane and hexadecane does not allow to clearly state on influence of the viscosity on photophysics of this DPB derivative.

Table 3. Fluorescence lifetimes ( $\tau$ ), pre-exponential factors ( $\alpha$ ) and quality of fit ( $\chi^2_R$ ) of (NCPH)<sub>2</sub>DA in selected solvents observed at 350 nm. Excitation wavelength 336 nm.

Solvent	$\tau$ /ns	$\alpha$	$\chi^2_R$
MeCN	0.821	0.197	1.11
	0.106	0.803	
cyclohexane	1.414	0.219	1.05
	0.381	0.781	
C <sub>6</sub> H <sub>14</sub>	1.060	0.382	1.08
	0.252	0.618	
(NCPH) <sub>2</sub> DA	1.706	0.208	1.07
	0.539	0.792	
MCH	1.453	0.320	1.15
	0.107	0.680	
MeTHF	0.689	0.525	1.11
	0.123	0.475	

## Luminescence at 77K

In methylcyclohexane at 77K diphenylbuta-1,3-diyne shows a weak fluorescence and strong phosphorescence<sup>27</sup>. Moreover, the lack of agreement between the fluorescence and the phosphorescence excitation spectrum was observed. In order to verify whether studied compounds form the triplet state efficiently and to identify from which state intersystem crossing occurs for all studied compounds, the emission and excitation spectra in MCH and MeTHF were measured at liquid nitrogen temperature. Overlapped luminescence and fluorescence and phosphorescence excitation spectra for (DMAPH)<sub>2</sub>DA and (CH<sub>3</sub>O<sub>2</sub>CPh)<sub>2</sub>DA in MeTHF at 77 K and fluorescence at room temperature (both were measured at the same fluorimeter settings) are presented in Figs 5 and 6, while for the rest of compounds studied in both solvents used are presented in Figs 11-18 ESI. All compounds studied shown measurable luminescence, except for (OHCPH)<sub>2</sub>DA which does not show measurable emission in both solvents used. For (CH<sub>3</sub>O<sub>2</sub>Ph)<sub>2</sub>DA only strong phosphorescence with origin at 500 nm was recorded (Figs 14,15 ESI). The rest of studied compounds show both fluorescence and phosphorescence. The luminescence spectrum of the parent compound (DPB) in MCH solvent (Fig. 11 ESI) is the same as published by Nagano et al.<sup>27</sup>. Also in MeTHF (Fig. 12 ESI) a weak fluorescence (origin at 330 nm) and strong phosphorescence (origin at 490 nm) with very clear vibrational structure is observed.

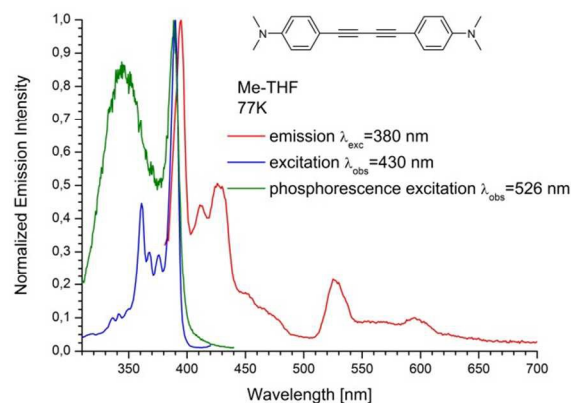


Fig. 5 Emission (solid red line), and excitation (solid blue line) and phosphorescence excitation (green solid line) spectrum of (DMAPH)<sub>2</sub>DA in MeTHF measured at 77 K

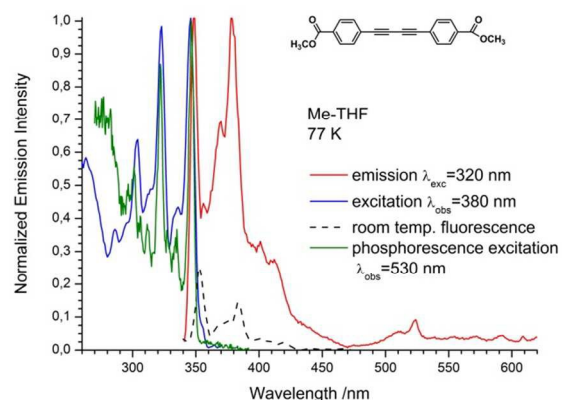


Fig. 6 Emission (solid red line), and excitation (solid blue line) and phosphorescence excitation (green solid line) spectrum of (CH<sub>3</sub>O<sub>2</sub>CPh)<sub>2</sub>DA in MeTHF measured at 77 K and room temperature fluorescence spectrum (black dashed line).

For DPB the fluorescence to phosphorescence intensity ratio measured at 0-0 transition indicates that in MeTHF phosphorescence is much more intense than in MCH (1:14 and 1:5.1, respectively). A greater phosphorescence intensity in MeTHF than MCH was also observed for diphenylacetylene derivatives<sup>46</sup>. The remaining studied compounds show intense fluorescence and weak phosphorescence which is more intensive in MeTHF than that in MCH. In contrast to the room temperature results, almost the mirror symmetry image of fluorescence excitation spectra and fluorescence spectra, though sometimes they are distorted by tailing part of the stray light or Raman scattering of the solvent, may indicate on the hindered rotation of phenyl rings in the excited state in organic glass like in the case of diphenylacetylene derivatives<sup>19,46</sup>. Furthermore, strong dependence of fluorescence intensity on the temperature, especially for DPB derivatives with an electron-donating substituents, should be emphasized. For (CH<sub>3</sub>O<sub>2</sub>Ph)<sub>2</sub>DA, similarly to unsubstituted DPB, only phosphorescence is observed, whereas for (DMAPH)<sub>2</sub>DA both fluorescence and phosphorescence spectra were recorded. In contrast, derivatives of DPB with an electron-accepting substituents

show moderate temperature dependence of fluorescence. The phosphorescence excitation spectra of DPB and (CH<sub>3</sub>OPh)<sub>2</sub>DA in both solvents used possess a clear vibrational structure similar to the vibration absorption spectra (Figs 11,12,14,15 ESI). Moreover, the phosphorescence excitation spectra of (CH<sub>3</sub>O<sub>2</sub>CPh)<sub>2</sub>DA (Fig. 6) and (NCPh)<sub>2</sub>DA (Fig. 17 ESI) in glassy MeTHF are very similar to the fluorescence excitation spectra, while for (DMAPh)<sub>2</sub>DA phosphorescence and fluorescence excitation spectra are clearly different (Fig. 5). For DPB, Nagano et al.<sup>51-53</sup> showed that the intersystem crossing takes place from 1<sup>1</sup>B<sub>1u</sub> state to the <sup>3</sup>A<sub>u</sub> state. The presented above results suggest a similar mechanism of the triplet state population for (CH<sub>3</sub>OPh)<sub>2</sub>DA, (CH<sub>3</sub>O<sub>2</sub>CPh)<sub>2</sub>DA and (NCPh)<sub>2</sub>DA. On the other hand, inconformity of the fluorescence and phosphorescence excitation spectra of (DMAPh)<sub>2</sub>DA suggests a mechanism postulated by Saltiel and Kumar<sup>23</sup> for diphenylacetylene in which (1<sup>1</sup>B<sub>2u</sub>) is the precursor of the triplet state.

### Theoretical calculations

The optimized ground and excited states structures were calculated using DFT method. The optimized ground state structures are planar, consistent with the crystallographic structure for all compounds studied. The exception is (CH<sub>3</sub>OPh)<sub>2</sub>DA for which the phenyl rings in the crystal structure are mutually perpendicular (see crystal structure in ESI). This difference in the stability between calculated and crystal structure planar and orthogonal conformers of (CH<sub>3</sub>OPh)<sub>2</sub>DA is due to the fact that the calculations relate to the isolated molecules in the gas phase while in the crystal intermolecular interactions stabilize the orthogonal conformer to optimized packing. This indicates that the energy involved for such distortions is small. The higher energy barrier of rotation in the excited state than in the ground state is attributed to the breaking of the cylindrical structure of the electron density along the axis of symmetry<sup>58</sup> and the adoption of the partial cummulene-like structure<sup>54</sup>. The calculated lengths of single and triple bonds with that of the crystal structure are gathered in Table 4 ESI. The bonds lengths of buta-1,3-diyne unit obtained for the optimized structure using quantum chemical calculations are slightly longer than that of crystal structure. They are also longer than values for unsubstituted buta-1,3-diyne obtained by *ab initio* calculations at the highest possible level<sup>55</sup>. The torsional potentials in both the ground and excited states within the framework of the local mode approximation using DFT method were also calculated. Figs 19-21 ESI present DFT-based torsional potential for DPB, (CH<sub>3</sub>OPh)<sub>2</sub>DA and (OHPH)<sub>2</sub>DA, respectively, for the ground and excited states. Because the torsional potentials for (CH<sub>3</sub>O<sub>2</sub>CPh)<sub>2</sub>DA, (NCPh)<sub>2</sub>DA and (DMAPh)<sub>2</sub>DA have the same shape as for (OHPH)<sub>2</sub>DA they are not presented. The torsional potential in the ground state is well approximated by a simple periodic potential of the form:

$$V(\Theta) = \frac{V_{\max}}{2} (1 - \cos 2\Theta) \quad (1)$$

where:  $V_{\max}$  is the barrier of the torsional potential and  $\theta$  is the ring to ring torsional angle. The magnitude of the 2-fold rotational barrier calculated for the ground state using above equation are gathered in Table 3 ESI. The energy barriers of rotation in the ground state are very low, in the range of 1 kJ/mol for (CH<sub>3</sub>OPh)<sub>2</sub>DA to 1.6 kJ/mol for (OHPH)<sub>2</sub>DA (lower than RT value at room temperature ~2.5 kJ). For DPB the barrier of rotation in the ground state is comparable to that calculated by Thulstrup et al.<sup>29</sup> (~1.3 kJ/mol) and Sebre and Zwier<sup>28</sup> (~1kJ/mol). There is a small influence of type of substituents on height of the rotation barrier in the ground state. A little higher

torsional barriers were obtained for derivatives with an electron withdrawing substituents. Contrary to Graeves et al.<sup>56</sup> who considers that the DFT derived potentials cannot be used to describe the torsional motions, Fujiwara et al.<sup>57</sup> believe that the DFT method can be used to calculate the rotational barrier despite the fact that it overestimates barriers of rotation in relation to *ab initio* methods and experimental values. However, taking into account that the experimentally determined magnitude of rotational barrier is found to be the 40% larger than that in the gas phase<sup>16</sup> they may be close to the barrier of rotation in low viscous solvent. Thus, obtained results indicate free rotation of the phenyl rings of diphenylbuta-1,3-diyne derivatives in the ground state. A large conformational freedom for DPB in the ground state, even at cryogenic temperatures, was stated by Thulstrup et al.<sup>29</sup>. The calculated height of the rotational barriers of DPB and its derivatives are substantially lower than that for diphenylacetylene<sup>46</sup>. Moreover, the magnitude of rotational barriers obtained experimentally for covalently-linked multi-porphyrin arrays<sup>58</sup> are also lower than that of diphenylacetylene. Similarly to the ground state, in the excited state the lowest energy optimized structures are also planar for all compounds studied. The bond lengths of buta-1,3-diyne unit have changed upon excitation in such a way that the triple bonds lengthen while single bonds shorten (Table 4 ESI). The torsional potential calculated for the fluorescent 1<sup>1</sup>B<sub>u</sub> state reveals that for parent compound (DPB) the magnitude of the 4-fold rotational barrier for the linear  $\pi\pi^*$  is low (~2.7 kJ/mol, Fig. 19 ESI) and lower than 2-fold rotational barrier in the S<sub>1</sub> (6.4 kJ/mol) and S<sub>2</sub> states (~10.7 kJ/mol) calculated by Sebre and Zwier<sup>28</sup>. Despite the fact that for DPB a close energetic proximity between planar and orthogonal conformers exists, a fluorescent state planar 1<sup>1</sup>B<sub>1u</sub> is assigned<sup>27</sup>. For the rest of studied compounds torsional potential function shows 2-fold rotational barrier, with the proviso that for (CH<sub>3</sub>OPh)<sub>2</sub>DA a small recess for 90 degrees is present (Fig 21 ESI). However, the magnitude of rotational barrier ( $\Delta E$ ) of DPB derivatives is relatively low, much lower than that for diphenylacetylene derivatives<sup>46</sup> and does not exceed ~7 kJ/mol which may be the reason of a large conformational freedom as was stated by Thulstrup et al.<sup>29</sup>. The rate constant of the conversion through the energy barrier during the rotation ( $k_{c \rightarrow t}$ ) can be calculated on the basis of the transition-state theory using the equation:

$$k_{c \rightarrow t} = \frac{\kappa k T}{h} * e * \exp(\Delta S) \exp(-\Delta E_a / RT) \quad (2)$$

where:  $k$  is Boltzmann constant,  $T$  is the absolute temperature,  $h$  is Planck's constant,  $R$  is gas constant,  $\Delta S$  is the entropy change, and  $\Delta E_a$  is the energy of activation. It is difficult to assign a value to the transmission coefficient,  $\kappa$ , which incorporates all correction factors and uncertainties. We chose,  $\kappa=0.4$  as for ring inversion<sup>59</sup> and  $\Delta S=0$  and for these values the rate constant and rotamer lifetime were calculated. The rate of rotamer interconversion in the excited state calculated according to the Eq. (2) for  $\Delta E=7$  kJ/mol is high (~9\*10<sup>9</sup> s<sup>-1</sup>) and the rotamer lifetime ~110 ps. Thus, rotation in the excited state may provide an additional radiationless channel of the excited state deactivation which may explains the order of magnitude lower fluorescence quantum yields of DPB derivatives compared to DPA derivatives. The question is whether the lack of measurable fluorescence at room temperature for DPB derivative possessing an electron-donating substituent(s) and strong dependence of its fluorescence intensity on temperature are caused by a change of nature of the lowest excited state resulting from the bending angle of buta-1,3-diyne unit, like for diphenylacetylene and its derivatives.

As shown for diphenylacetylene and its derivatives<sup>20-23,46</sup> for derivatives containing an electro-donating substituent bending of  $C_{Ph}-C\equiv C$  angle causes that the lowest excited state is the  $\sigma\pi^*$  (weakly fluorescing state), while for derivatives containing an electron-accepting substituents it is  $\pi\pi^*$  (strong fluorescing state). The same phenomenon seems to occur for buta-1,3-diyne derivatives. The potential-energy profile of the low-lying electronic state calculated for DPB,  $(CH_3OPh)_2DA$  and  $(DMAPh)_2DA$  as a function of  $C_{Ph}-C\equiv C$  bending angle for the optimized excited-state geometry reveals state crossing. Starting from the linear buta-1,3-diyne unit of  $(CH_3OPh)_2DA$  at  $D_{2h}$  conformation and changing (lowering) the bending angle up to the value of approximately 160-165 degrees causes the increase of  $\pi\pi^*$  state energy (Fig. 7). However, further bending of the molecule causes the energy decrease associated with the transition to the  $\sigma\pi^*$  state (Figs 22,23 ESI). The same potential-energy profiles were obtained for DPB and  $(DMAPh)_2DA$ . The energies of activations of state crossing estimated from the curves crossing are low (4.4 kJ/mol, 8.8 kJ/mol and 11.5 kJ/mol for DPB,  $(CH_3OPh)_2DA$  and  $(DMAPh)_2DA$ , respectively). The lowest energy of the  $\sigma\pi^*$  state is reached for the  $C_{Ph}-C\equiv C$  bending angle at about 136 degrees ( $C_{2v}$  conformation of buta-1,3-diyne unit (Fig. 7)) and therefore at smaller bending angle than for DPA derivatives<sup>20-22,46</sup>. The stabilization energy calculated as the difference between the energy for linear structure of  $\pi\pi^*$  state (taken as the zero energy) and the lowest energy of the  $\sigma\pi^*$  state are -18.7 kJ/mol, -32.6 kJ/mol and -30.6 kJ/mol for DPB,  $(CH_3OPh)_2DA$  and  $(DMAPh)_2DA$ , respectively. The results obtained by us are in contradiction with the results published by Sebree and Zwier<sup>28</sup>. Their results predict a state crossing about 16.7 kJ/mol ( $\sim 1400\text{ cm}^{-1}$ ) above the  $1^1B_{1u}$  minimum with the  $A_u$  minimum being approximately 10.2 kJ/mol ( $850\text{ cm}^{-1}$ ) higher than the  $B_{1u}$  optimized geometry. However, the potential energy profile for the  $A_u$  state were done with a  $C_{2h}$  symmetry constrain which significantly increases the energy compared to the calculations without imposing symmetry<sup>60</sup>. Additionally, the  $B_{1u}$  potential energy profile was obtained on the  $A_u$  surface. The dependence of potential energy function on the bending angle calculated for an electron-accepting derivatives of buta-1,3-diyne is shown in Fig. 8. Initially, the bending of the molecule causes the energy increase and after crossing a small barrier (about 5 kJ/mol at the bending angle equal to 165 degrees) reaches shallow minimum (-1.2 kJ/mol for  $(CH_3O_2CPh)_2DA$ , -2.8 kJ/mol for  $(NCPH)_2DA$ ) for which molecule has a "scorpion like" structure (Figs 24,25 ESI). However, there is no state crossing, but the potential energy curve corresponds to the  $\pi\pi^*$  (Fig. 8). In diphenylbuta-1,3-diyne, apart from the  $C_{Ph}-C\equiv C$  angle, there is possibility to bent molecule at  $C\equiv C-C\equiv C$  angle. Calculated potential energy profile for an electron-accepting DPB derivatives has a similar shape as for  $C_{Ph}-C\equiv C$  angle but higher energy (Fig. 8).

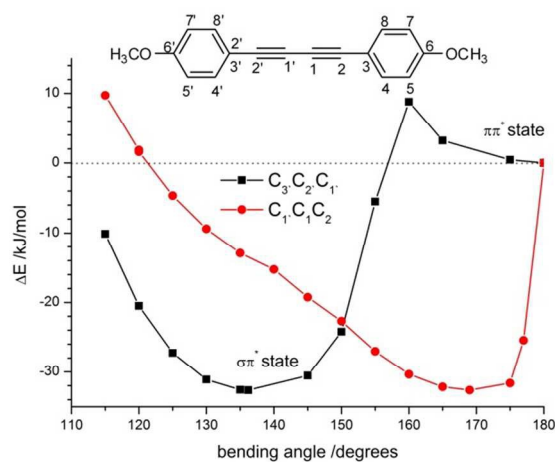


Fig. 7. The potential-energy profiles as a function of  $C_{Ph}-C\equiv C$  (black line) and  $C-C\equiv C$  (red line) bending angle for  $(CH_3OPh)_2DA$ .

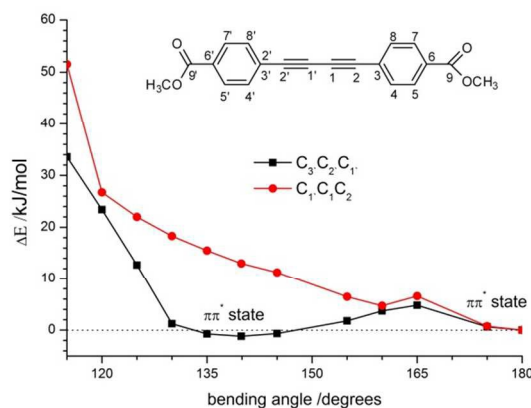


Fig. 8 The potential-energy profiles as a function of  $C_{Ph}-C\equiv C$  (black line) and  $C-C\equiv C$  (red line) bending angle for  $(CH_3O_2CPh)_2DA$ .

However, for DPB and its derivatives possessing an electron-donating substituents the small (a few degrees) change of the  $C\equiv C-C\equiv C$  angle causes the change of  $C_{Ph}-C\equiv C$  angle to the value of 136 degrees which corresponds to the bending angle for the lowest energy conformation for the  $\sigma\pi^*$  state. Further bending of the molecule results in a systematic energy increase (Figs 7,8). Thus, diphenylbuta-1,3-diyne excited state behaves just like acetylene derivatives and the bending of  $C_{Ph}-C\equiv C-C\equiv C$  angle determines the potential energy profile of the lowest excited state.

## Conclusions

Synthesized novel symmetrically substituted diphenylbuta-1,3-diyne derivatives containing an electron-donating or an electron-accepting substituents and their spectral and photophysical properties were studied. Substituents introduced into the molecule do not change the nature of electronic transitions in comparison to the parent molecule. Substituents, especially  $N,N$ -dimethylamino group, cause bathochromic shift of the absorption spectra and simultaneously blurring of their vibrational structure. Due to the symmetry of the compounds a solvatochromic effect is not observed. The fluorescence



quantum yields of diphenylbuta-1,3-diyne derivatives studied are substantially lower than these of diphenylacetylene derivatives and can be explained by assuming a large conformational flexibility of those compounds associated with rotation around a single bond. The rotation of phenyl ring in DPB derivatives is free in the ground state, but somewhat hindered in the excited state. This finding provides rationale for well-known temperature dependence of the spectral shape of absorption and lack of mirror symmetry relationship between the absorption and fluorescence spectra at elevated temperature. Furthermore, the results provide evidence that for diphenylbuta-1,3-diyne derivatives containing an electron-donating substituents the lack of measurable fluorescence at room temperature and its strong dependence on temperature can be attributed to the  $\pi\pi^*$ - $\sigma\pi^*$  intersection, similarly to the diphenylacetylene derivatives. The absence of low-energy crossing between the fluorescent  $\pi\pi^*$  state and the  $\sigma\pi^*$  state in the diphenylbuta-1,3-diyne derivatives containing an electron-accepting substituents, predicted by the calculations, is consistent with a larger fluorescence quantum yield and the absence of significant thermal quenching of emission, as the absence of the spectral feature that can be assigned to  $\sigma\pi^*$ - $\sigma\pi^*$  transition in picosecond transient absorption.

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#### Notes and references

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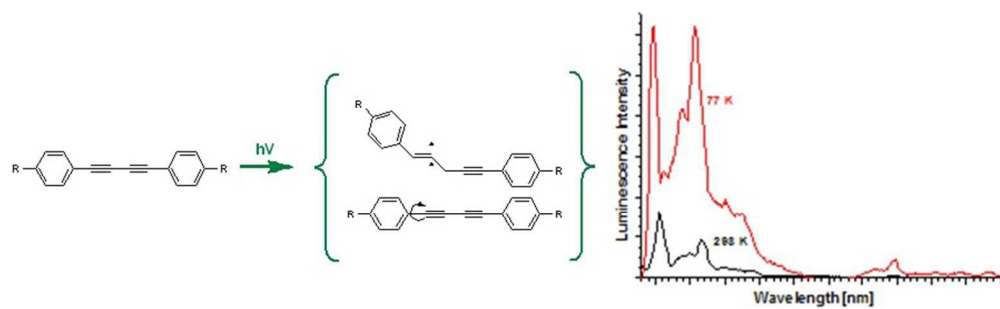
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