The structures and electronic absorption spectra of substituted phenyldiacetylenes: experimental and theoretical studies

V. I. Baranovski, E. N. Pisarevskaya, O. V. Vinogradova, O. V. Sverdlova, and I. A. Balova*

Department of Chemistry, St. Petersburg State University,
26 Universitetskii prosp., 198504 St. Petersburg, Russian Federation.
Fax: +7 (812) 428 6939. E-mail: baranovs@yandex.ru

The results of experimental and theoretical investigation of the electronic absorption spectra of substituted phenyldiacethylenes are presented. The bands in the experimental spectra were assigned in detail using quantum chemical calculations of the electronic structures and spectra of the molecules. The influence of the interaction of the substituents on the spectral parameters of the systems under study was analyzed.

Key words: quantum chemical calculations, density functional theory, self-consistent reactive field method, polarized continuum model, solvents, electronic absorption spectra.

Compounds containing a conjugated diacetylene system are promising objects for investigation from the viewpoint of the development of fundamental concepts of structural chemistry and for production of biologically active substances[1] and novel materials with unique properties.[2—5]

At present, one of the major and most widely used methods for the synthesis of aryl- and hetaryl-substituted acetylenes is coupling of aryl halides with terminal acetylenes in the presence of the catalyst (Pd/Cu).[6] 1,3-Diynes are hardly accessible and unstable, thus being of limited use in the cross-coupling reactions resulting in 1-aryl-1,3-diacetylenes.

An original method of one-pot synthesis of functional aryl- and hetaryldiynes developed at the Chair of Organic Chemistry, St. Petersburg State University, offers great prospects for obtaining new knowledge about the properties of these compounds and for revealing structure—property correlations when studying their spectral characteristics and chemical transformations.[7—9]

The electronic absorption spectra of phenyldiacetylene (phda) derivatives and the effect of solvent on the position and contours of spectral bands have been studied for several years at the Laboratory of Spectrochemistry (Department of Chemistry, St. Petersburg State University). This work involved the experimental and quantum chemical study of the electronic absorption spectra of solutions of diacetylene derivatives with the general formula $H_2N—Ar—C{\equiv}C—C{\equiv}C—R$ (Fig. 1) in various solvents. The purpose of the work was to study the solvent effect on the molecular structure and spectral parameters (band positions and intensities) of these compounds and to assign the bands in the electronic absorption spectra.

The diacetylene derivatives under study included 2-(dodeca-1,3-diynyl)-4-methylaniline (**1**), 2-(deca-1,3-diynyl)-4-nitroaniline (**2**), 6-bromo-2-(dodeca-1,3-diynyl)-4-methylaniline (**3**), 2-amino-3-(hexadeca-1,3-diynyl)-5-methylpyridine (**4**), and 2-(dodeca-1,3-diynyl)-4-nitro-1-naphthylamine (**5**). The geometric structures of the aryl moieties in molecules **1—5** are shown in Fig. 1.

We also calculated the electronic spectra of nitroaniline and phda in cyclohexane.

The experimental absorption spectra in *n*-hexane and MeCN are shown in Fig. 2. These solvents are transparent at λ = 200—400 nm, have different polarities, and do not react with the compounds under study.

Results and Discussion

The optimized values of selected interatomic distances in the molecules of the compounds under study are listed in Table 1. The changes in the $C—N(NO_2)$, $C—N(NH_2)$, and N—O bond lengths with a change in the medium are most pronounced for the compounds containing the nitro group (**2** and **5**), although the absolute values of these changes are small (0.02—0.035 Å). According to calculations of molecule **5** in the polar solvent (MeCN), the nitro group is rotated about the C—N bond and the oxygen atoms deviate from the ring plane. The changes in the geometric parameters of molecule **3** on going from one medium to another are insignificant. Since the polarities of molecules **1** and **4** are similar to that of molecule **3**, calculations with inclusion of the solvent effect for **1** and **2** were performed only for cyclohexane as the solvent. In addition, this approach is substantiated by insignificant

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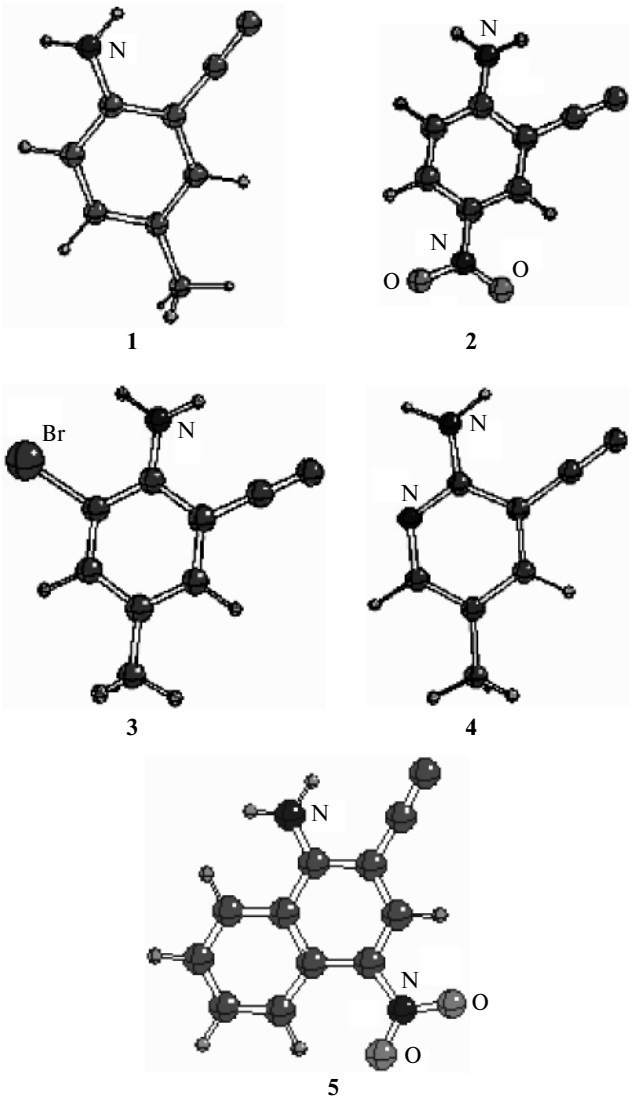

Fig. 1. Geometries of aryl moieties in molecules **1**—**5**.

changes in the spectra of these molecules upon the change in the medium polarity.

The shape of the MOs involved in electron excitation is shown in Fig. 3 for compound **2**. Table 2 illustrates the correspondence between the numbers of the identically or similarly shaped MOs for molecule **2** and other molecules. Figure 3 shows that some MOs are localized on the systems of the triple (MOs 70, 71, and 72) or ordinary (MOs 74 and 75) bonds of the diacetylene moiety and on the aromatic ring π-orbitals. For compounds **2** and **5**, a number of MOs correspond to the oxygen lone pairs (MOs 68 and 69) and to the σ- and π-antibonding MOs of the nitro group (MOs 66 and 73). Among the orbitals of molecule **3**, the φ_{94} MO is σ-antibonding relative to the C—Br bond, while the amino group MOs are not involved in electronic transitions in the region under study.

Table 1. Optimized values of selected interatomic distances (*d*) in molecules **1**—**5** in the gas phase (I) and in cyclohexane (II) and MeCN (III) solutions

Molecule	Bond	*d*/Å		
		I	II	III
1	C—N(NH_2)	—	1.3858	—
	C—C(CH_3)	—	1.5114	—
2	C—N(NH_2)	1.3662	1.3602	1.3472
	C—N(NO_2)	1.4571	1.4506	1.4380
3	C—N(NH_2)	1.3750	1.3757	1.3762
	C—Br	1.9204	1.9214	1.9230
4	C—N(NH_2)	—	1.3567	—
	C—C(CH_3)	—	1.5095	—
5	C—N(NH_2)	1.3509	1.3624	1.3448
	C—N(NO_2)	1.4521	1.4555	1.4414

Table 2. Correspondence between the MO numbers for molecules **1**—**5***

2	**1**	**3**	**4**	**5**
69	—	—	—	89, 90
70	71	88	88	91
71	72	89	87	92
72	73	90	89	93
73	—	—	—	94
74	74	91	90	95
75	75	92	91	97
76	77	93	92	—

* The MO 96 of compound **5** has no analogs in compounds **1**—**4**.

The results of calculations and the assignment of transitions in the spectra of compounds **1**—**5** are given in Tables 3—7. The assignment was based on analysis of the contributions of particular transitions to corresponding excitations and on the composition of the MOs involved in the transition. As a rule, only the data for the allowed transitions with a non-zero oscillator strength are presented.

The compounds under study can be divided into two groups in accordance with the patterns of their absorption spectra. The spectra of the molecules containing no nitro groups exhibit two bands in the region 25 000—39 000 cm^{-1}, namely, at 29 000—30 000 cm^{-1} and at ~36 000 cm^{-1}. The latter band possesses a vibronic structure whose components are separated by 2000 cm^{-1}, as in the spectrum of phenyldiacetylene (see further). Based on the results of calculations, these bands were assigned to excitations in the phda moiety. The bands in the shorter-wavelength region are related to higher-energy excitations in this moiety, and for compound **3** they are admixed with transitions from the aromatic ring π-orbitals to the φ_{94} MO, which is σ-antibonding relative

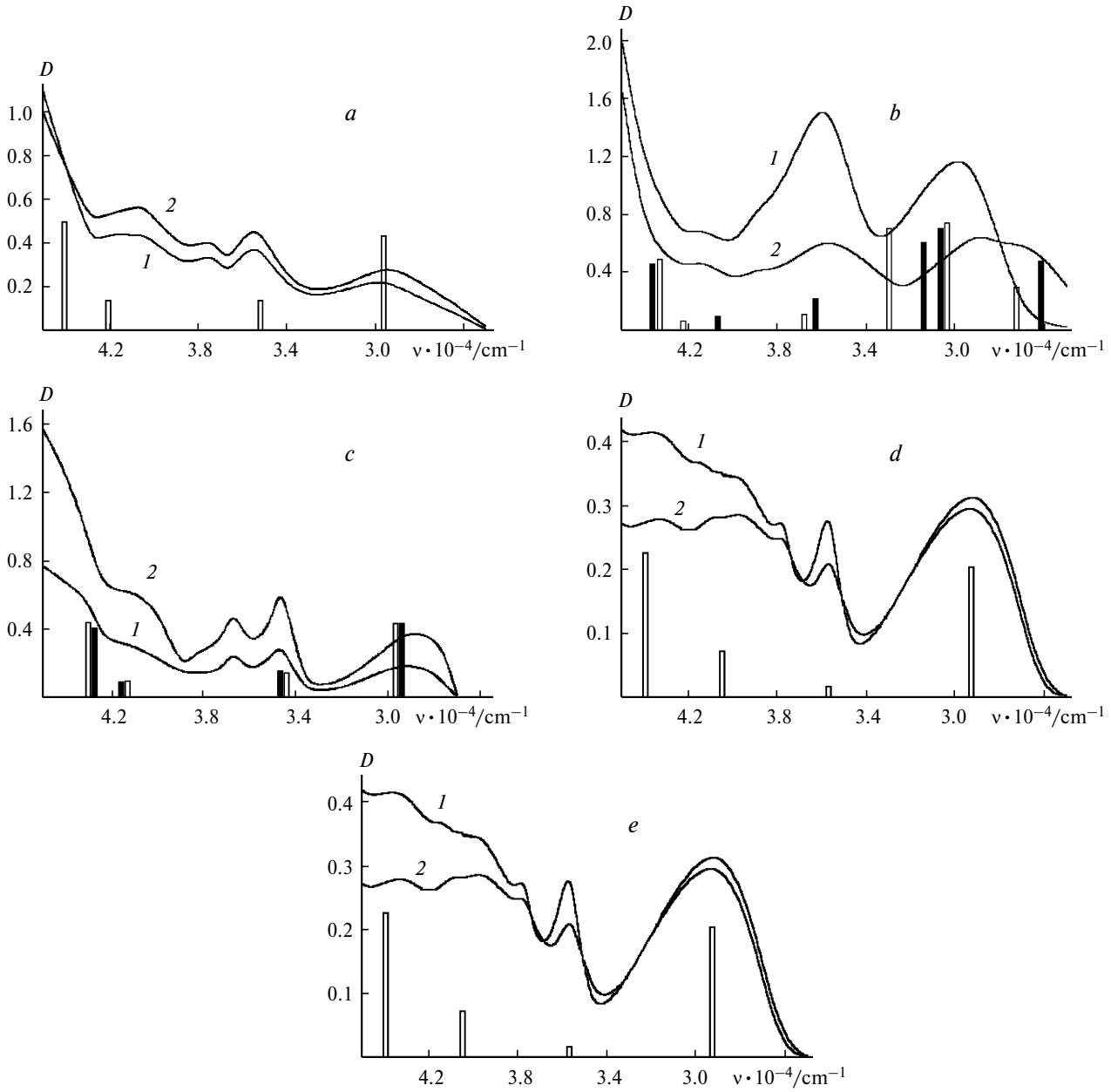

Fig. 2. Experimental spectra of compounds **1**—**5** (*a*—*e*, respectively) in *n*-hexane (*1*) and MeCN (*2*).

to the C—Br bond. The polarity of molecules **1**, **3**, and **4** is low (Table 8), which results in the virtual absence of the solvate shift on going from the nonpolar solvent (cyclohexane) to polar one (MeCN).

According to calculations, the allowance for the solvent effect induces significant changes in the electron density distribution in molecules **1**—**5**, which appear as changes in their dipole moments (see Table 8). The maximum increase in the dipole moments was obtained for the polar molecules **2** and **5**. They have almost equal dipole moments, whose high values are determined by nitroaniline moiety. The interaction with the polar solvent causes the dipole moments to increase by ~40% compared to the gas-phase value and by 25% compared to the nonpolar solvent. The dipole moment of much less polar compound **3** increases by only 13% over the gas-phase value and changes slightly on going from the nonpolar (cyclohexane) to polar (acetonitrile) solvent.

Both the experimental and theoretical spectra of the compounds containing the nitro group exhibit a bathochromic shift of the bands on going from the nonpolar to polar solvent. An obvious explanation is the high polarity of these molecules (see Table 8) and the noticeable changes in the molecular geometry and dipole moments

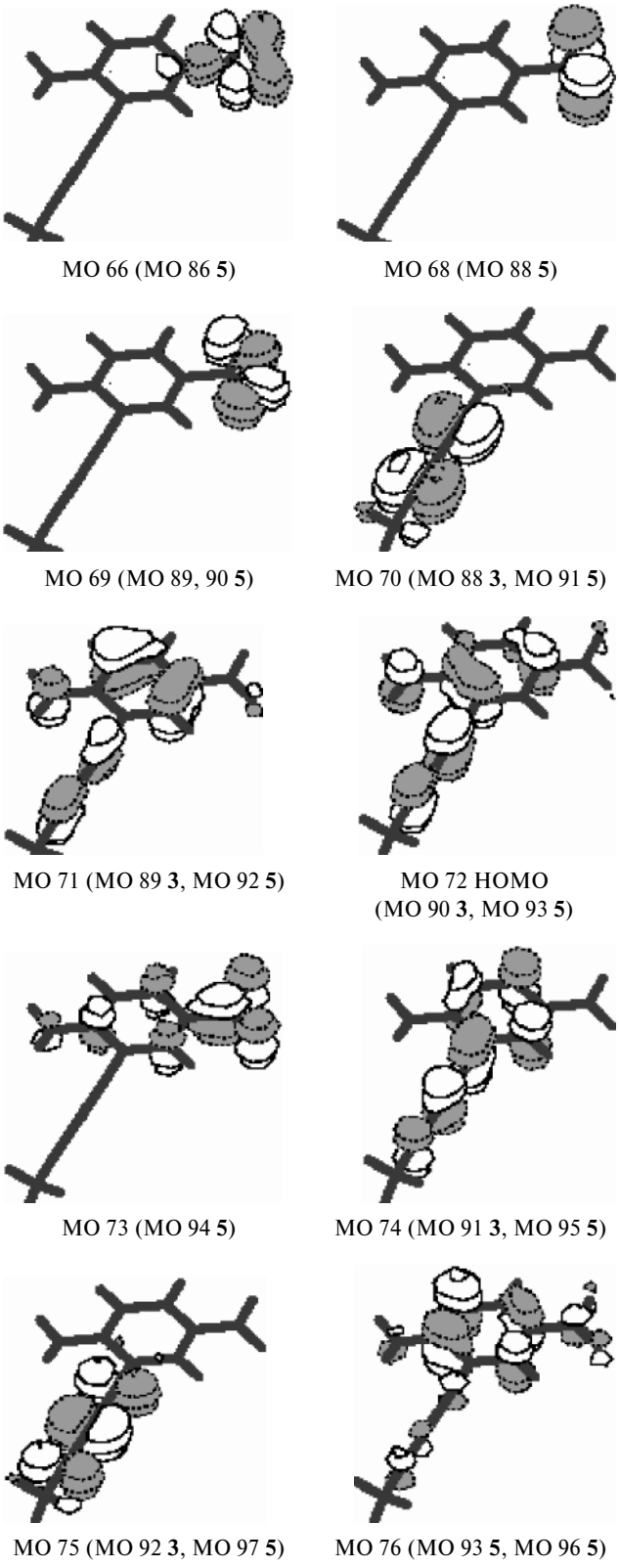

Fig. 3. Molecular orbitals of compound **2**.

upon the change in the medium polarity. Not only transitions localized within the phda moiety which are characteristic of the first group of compounds, but also transitions corresponding to charge transfer from the aromatic ring and diacetylene moiety to the nitro group antibonding

Table 3. Character, energies (E), and oscillator strengths (f) of the transitions in the spectrum of compound **1** in cyclohexane

Transition	E/cm^{-1}	f
73 → 74	29865	0.41
73 → 75	32213	0.0001
71 → 74	34169	0.0003
72 → 74	35125	0.13
72 → 75	39713	0.0

Table 4. Character, energies (E), and oscillator strengths (f) of the transitions in the spectrum of compound **2** in acetonitrile (I) and cyclohexane (II)

Transition	E/cm^{-1}		f	
	I	II	I	II
72 → 73	26028	27280	0.24	0.18
72 → 74	30561	30779	0.35	0.39
71 → 73	31418	32975	0.30	0.37
71 → 74	36298	36445	0.11	0.06
68 → 73	40866	42230	0.04	0.03
72 → 76	43511	43230	0.23	0.25
68 → 74, 70 → 75, 72 → 76, 72 → 77	45506	45391	0.80	0.79

Table 5. Character, energies (E), and oscillator strengths (f) of the transitions in the spectrum of compound **3** in acetonitrile (I) and cyclohexane (II)

Transition	E/cm^{-1}		f	
	I	II	I	II
90 → 91	29433	29529	0.41	0.43
89 → 91	34406	34399	0.16	0.15
90 → 93	41760	41724	0.09	0.09
88 → 92, 90 → 95, 87 → 91, 89 → 91	42910	42840	0.42	0.45
87 → 91, 90 → 95	45422	45297	0.12	0.11
89 → 93	46969	46846	0.84	0.01

Table 6. Character, energies (E), and oscillator strengths (f) of the transitions in the spectrum of compound **4** in cyclohexane

Transition	E/cm^{-1}	f
89 → 90	29017	0.43
89 → 91	31628	0.001
87 → 90	35742	0.015
86 → 90	38882	0.002
89 → 92	40537	0.15
87 → 91	40858	0.008
88 → 91, 89 → 93	44078	0.490

Table 7. Character, energies (E), and oscillator strengths (f) of the transitions in the spectrum of compound **5**

Transition	E/cm^{-1}	f
	Acetonitrile	
93 → 94	24131	0.24
93 → 95	28675	0.26
89 → 94, 92 → 94	29703	0.20
92 → 94, 89 → 94, 93 → 95	30086	0.22
93 → 96	33254	0.01
90 → 94	34464	0.09
92 → 95	35747	0.16
84 → 94, 86 → 94	36059	0.02
88 → 94, 89 → 94	38393	0.07
90 → 95, 92 → 96	40826	0.03
93 → 98, 92 → 96	41480	0.09
90 → 96, 91 → 97, 92 → 96, 89 → 95	42834	1.08
91 → 96	43580	0.01
89 → 95, 92 → 96	43911	0.09
88 → 95, 92 → 96	44696	0.02
	Cyclohexane	
93 → 94	24911	0.22
93 → 95	28849	0.35
92 → 94, 93 → 95	30819	0.46
93 → 96	33843	0.02
90 → 94	35924	0.22
88 → 94	39267	0.06
90 → 95, 92 → 96, 92 → 97	41419	0.07
93 → 98, 92 → 95 91 → 97	41548	0.16
90 → 95, 88 → 95 91 → 97, 92 → 96	43081	0.99
88 → 95, 96 → 92 86 → 94	44443	0.06
86 → 94, 88 → 95	45276	0.14

Table 8. Calculated dipole moments (μ) of molecules **1**—**5** in the gas phase and in cyclohexane and MeCN solutions

Molecule	μ/D		
	Gas phase	Cyclohexane	Acetonitrile
1	—	2.304	—
2	8.034	9.158	11.369
3	2.386	2.519	2.695
4	—	2.200	—
5	7.815	9.132	11.537

π-orbital (see Fig. 3, MO 73) and low-intensity transitions localized within the nitro group manifest themselves. The shorter-wavelength transitions are of mixed character.

It seems reasonable to consider the compounds under study as phda derivatives and to analyze their spectra on the basis of the spectral properties of this molecule.

The electronic absorption spectrum of phda[10] was measured in two solvents, MeOH and MeCN. The absorption band has a clearly defined vibrational structure, which includes five vibronic components separated by 2020 cm^{-1} on the average, which corresponds to the stretching vibration of the diacetylene group. The oscillator strength (1.025 in MeCN, 0.57 in MeOH) corresponds to the allowed electronic transition. The most intense band corresponds to the 0—1 transition, indicating a large shift of the potential energy minimum upon the excitation of the molecule.

The results of the calculation of the electronic absorption spectrum of phda are given in Table 9. The first three excited states correspond to excitations within the diacetylene fragment accompanied by charge transfer from the triple to the ordinary bonds. The fourth transition corresponds to excitations involving the phenyl ring π-orbitals.

In the experimental spectrum of phda, the longest-wavelength band corresponding to the transition between the orbitals localized on the systems of triple and ordinary bonds is separated from the nearest shorter-wavelength band by an interval of ~1.5 eV. We calculated the band shape for the allowed long-wavelength transition, optimized the molecular geometries in the lowest singlet and triplet states, and calculated the ground-state vibrational spectrum. Then we calculated the band shape by the wave packet dynamics method.[11—13] The excited-state energy was accepted to be equal to the energy of the first allowed transition in the spectrum obtained from DT DFT calculations (34 482 cm^{-1}). This spectrum shows a well-defined vibrational structure. Five vibronic components are separated by 2100 cm^{-1} from one another, which corresponds to the stretching vibration of the diacetylene group (see above). The 0—0 transition is at ~35 200 cm^{-1} in the experiment and at 34 600 cm^{-1} in the calculated spectrum. Thus, the error in calculation of the excited state energy (transition 0—0) is ~1000 cm^{-1}.

As mentioned above, for all the compounds under study the region 20 000—40 000 cm^{-1} is characterized of three types of the excited states. These are the states corresponding to excitations in the NO_2 group and to the charge-transfer transitions from the phda (or naphthalene-diacetylene) moiety to the antibonding π-orbital of the nitro group (see Fig. 3). Some of these transitions are not presented in Tables 3—7, because they are forbidden or

Table 9. Theoretical absorption spectrum of phenyldiacetylene

ΔE/eV	f	Transition
4.1665	0	$9b_2 \rightarrow 5b_1$
4.275	0.276	$4b_1 \rightarrow 5b_1$, $9b_2 \rightarrow 10b_2$
4.4290	0	$4b_1 \rightarrow 10b_2$
4.8280	0.001	$1a_2 \rightarrow 5b_1$, $4b_1 \rightarrow 2a_2$

of low intensity. An analysis of these transitions allows one to conclude about the interaction of different substituents in molecules **1**—**5**.

The molecules of all compounds under study differ from the phda molecule in that they contain a typical auxochrome, *i.e.*, amino group linked to the aromatic ring. In the spectrum of compound **1**, the long-wavelength band undergoes a noticeable bathochromic shift (5000 cm^{-1}) relative to the corresponding band in the phda spectrum. Compounds **2**—**5** can be considered as derivatives of compound **1**. Molecules **2** and **5** contain the nitroo group in *para*-position to the amino group, and molecule **3** contains the bromine atom in *ortho*-position to the amino group. There is one more aromatic ring in molecule **5**. The nature of the aromatic ring changes from benzene to pyridine in compound **4**. They may cause a bathochromic shift of the band corresponding to the longest-wavelength transition within the phda moiety. As compared to the spectra of compound **1**, the position of the long-wavelength band in the spectra of the diacetylene derivatives of aniline **2** and **3** and aminopyridine **4** changes insignificantly. The maximum bathochromic shift of the band is observed for compound **5** containing the naphthalene moiety and the more extended π-system. Probably, the polar solvent favors stabilization of the charge-transfer excited state of compounds **2** and **5**, which noticeably affects the positions and intensities of the long-wavelength bands in the experimental spectra.

The first allowed transition in the electronic spectrum of phda (34 482 cm^{-1}) was characterized above and corresponds to the excitation from the ∂-orbital localized on the aromatic ring and triple bonds of diacetylene (π^v) to the MO localized on the ring and ordinary bonds of diacetylene (π^{*v}). Transitions of similar character in molecules **1**—**5** have close energies, which reflects their same-type character.

The $\pi^v \rightarrow \pi^{*h}$ and $\pi^h \rightarrow \pi^{*v}$ excitations (π^h are the diacetylene orbitals lying in the plane of the phda moiety, see Fig. 3) were attributed to the forbidden or almost forbidden transitions. The energies of these transitions are listed in Table 10. The allowed $\pi^v \rightarrow \pi^{*v}$ transitions are appreciably shifted to the long-wavelength region, the effect being almost unnoticeable for the $\pi^h \rightarrow \pi^{*v}$ transitions. The inclusion of substituents in the phda aromatic ring is analogous to the influence of the amino group on the spectrum of nitrobenzene.

According to calculations, the addition of the phda moiety to nitroaniline (**2**) or to 1-amino-4-nitronaphthalene (**5**) also induces a shift of the charge-transfer transition phda → NO_2 to the long-wavelength region (30 758, 27 280, and 24 911 cm^{-1} for nitroaniline, **2**, and **5**, respectively). At the same time, a hypsochromic shift is observed for the charge-transfer transition from the lone electron pair of the O atoms (see Fig. 3, MO 69) to the π*-orbital of the NO_2 group: 30 925, 42 230, and 39 267 cm^{-1} for nitroaniline, **2**, and **5**, respectively. Traditionally, these effects are explained by the configuration interactionss in compounds containing several optically active substituents.

Table 10. Calculated energies (E) of transitions caused by excitations within the phda moiety (experimental values are given in parentheses)*

Compound	E/cm^{-1}		
	$\pi^v \rightarrow \pi^{*v}$	$\pi^v \rightarrow \pi^{*h}$	$\pi^h \rightarrow \pi^{*v}$
phda	34482 (34500)	35827	33607
1	29865 (29500)	32213	34169
2	30780 (29000)	33838	33159
3	29529 (28500)	32249	33620
4	29017 (29000)	31628	32925
5	28849 (27500)	32255	33948

* Shown are the symmetries of the orbitals within the diacetylene moiety relative to the bond line (local point symmetry group $C_{\infty v}$).

Thus, this work is a combined experimental and theoretical study of the electronic spectra of the molecules in which the aromatic ring (rings) contains a number of spectrally active substituents. The use of quantum chemical methods for calculations of the electronic structures and spectra of the molecules under study makes it possible to perform complete assignment of bands in the experimental spectra and to elucidate the effect of the interaction of the substituents on the spectral characteristics of the systems in question. Good agreement between the experimental and calculated data confirms that the TD DFT method allows one to calculate both the transition energies in complex organic molecules and the spectral band shifts caused by polar and nonpolar solvents.

Experimental

Compounds **1**—**5** were synthesized following published procedures.[8,9] Their structures were proved by physicochemical methods. Solvents were prepared by standard methods. The purity of the solvents was monitored spectrophotometrically. The absence of absorption of the solvents in the region under study was determined spectroscopically.

Hexane (commercial product) was refluxed over sodium, then distilled from a flask with a dephlegmator over sodium, and stored in a vacuum desiccator. Acetonitrile (commercial product) was refluxed for 5 h over phosphorus pentoxide, distilled off, and distilled again from a flask with a dephlegmator over potash.

Weighed samples of substances (0.4—0.6 mg) were taken using an analytical microbalance (accuracy ±0.05 mg); the concentrations in hexane solutions were $9.8 \cdot 10^{-5}$ (**1**), $9 \cdot 10^{-5}$ (**2**), $6.01 \cdot 10^{-5}$ (**3**), $1.06 \cdot 10^{-5}$ (**4**), and $5.2 \cdot 10^{-5}$ mol L^{-1} (**5**), and those in acetonitrile solutions were $1.04 \cdot 10^{-5}$ (**1**), $8.8 \cdot 10^{-5}$ (**2**), $1.1 \cdot 10^{-5}$ (**3**), $1.28 \cdot 10^{-5}$ (**4**), and $6.8 \cdot 10^{-5}$ mol L^{-1} (**5**). Electronic absorption spectra were obtained on a Specord M-40 spectrophotometer in the interval λ = 230—400 nm at a layer thickness of 1 cm.

Density functional calculations were performed with the B3LYP hybrid functional[14] in the 6-31G* basis set using the GAUSSIAN03 program[15] with geometry optimization in the gas phase and inclusion of solvent (MeCN and cyclohexane) effects in the framework of the polarizable continuum model (PCM).[16] In the PCM, a molecule in a solvent is surrounded by a cavity formed by spheres centered on each atom and by the regions of the external space inaccessible to the solvent molecules. In the calculations, *n*-hexane was replaced by cyclohexane, whose dielectric constant is similar to that of *n*-hexane (1.90). The main parameters of the model are the dielectric constant of the solvent (2.023 for cyclohexane and 36.64 for acetonitrile; the default values for the GAUSSIAN program, the radius of the solvent molecule, and the radii of the spheres surrounding the atoms of the solute molecules.

The spectra were calculated by the TD DFT method.[17] The wave function of this method is analogous to that of the configuration interaction method in the approximation of singly excited configurations with partial inclusion of correlation effects in the excited state. For N- and O-containing organic compounds, the errors in calculation of the transition energies are several tenths of electron-volts.[18,19] Considerable errors can be expected in calculations of the oscillator strength.

The calculations were performed at the Petrodvorets Telecommunication Center of the St. Petersburg State University.

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