

# Solvent effects on electronic absorption spectra of donor-substituted 11,11,12,12-tetracyano-9,10-anthraquinodimethanes (TCAQs)

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Solvent effects on the electronic absorption spectra of donor-substituted 11,11,12,12-tetracyano-9,10-anthraquinodimethanes (TCAQs) 1–3 have been investigated in 32 well-selected solvents. These compounds were chosen as model structures for charge-transfer chromophores featuring second- and third-order nonlinear optical properties. The resulting data were evaluated by means of theoretical models and (semi)empirical correlations determining the optical properties related to electron distribution and polarizability. We found that solvent effects on a polar D- $\pi$ -A system do not depend on the donor/acceptor orientation (HOMO/LUMO localization) but especially on the length of the  $\pi$ -system in between. The observed solvent effects are described with high accuracy by the applied theoretical models and linear combinations of physical quantities. Solvent polarization, permanent dipole moment, and molar volume substantially affect the longest-wavelength absorption maxima. Solvent-induced bathochromic shift resulting from the solvent polarity is described with high accuracy by the Born function. On the other hand, hypsochromic effects of the solvent permanent dipole moment are caused due to the slower reorganization of molecular dipoles compared with the rate of excitation. Solvent polarizability shifts the longest-wavelength absorption maxima bathochromically with increasing length of the  $\pi$ -conjugated system. Whereas this effect could be suitably described by the Onsager-induced polarizability, the orientation polarizability was not found to be important. The solvent molar volume as a hypsochromic shift-inducing factor is only relevant if the size of the solute and solvent molecules are comparable. If the size of the solute is considerably larger than that of the solvent molecules, the solvent behaves as a 'shape continuum.' Copyright © 2008 John Wiley & Sons, Ltd.

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## INTRODUCTION

Second- or third-order nonlinear optical properties of organic molecules depend, in general, on the polarizability of the electrons localized in  $\pi$ -bonding molecular orbitals.<sup>[1,2]</sup> The relationship between a molecule's chemical structure and its optical nonlinearity is increasingly being understood through experimental<sup>[3–5]</sup> and theoretical study,<sup>[6–9]</sup> and new predictive chemical models are developed based on linear optical properties. Thus, it is already well established that the second- or third-order optical nonlinearity of organic D- $\pi$ -A push-pull molecules depends on the length of the planar conjugated  $\pi$ -spacer and the electron-donating (D) and electron-withdrawing (A) groups attached.<sup>[10–12]</sup> However, a general description of external factors affecting optical and nonlinear optical properties is more complicated. Investigation of electronic absorption spectra and their dependence on the nature of the solvent used are proper methods for characterizing the properties of D- $\pi$ -A systems. Whereas solvent effects on spectral properties have been investigated in detail for a diverse range of solutes,<sup>[13]</sup> D- $\pi$ -A chromophores as models for molecules featuring second- and third-order NLO properties have not been systematically investigated in this respect. Theoretical studies on

the influence of solvent on solute polarizability and hyperpolarizability have shown that a description of molecular NLO characteristics through the models defining solvent as a dielectric is possible.<sup>[14–30]</sup> However, in order to verify the theoretical conclusions, the application of the models to real systems with suitable and measurable physical quantities is necessary. Solvatochromism of the D- $\pi$ -A systems has been widely studied by electronic absorption or emission spectroscopy<sup>[31–38]</sup> and the observed solvent effects evaluated mainly by means of semi-empirical methods. The observed dependencies are frequently presented in a graphical form only as a plot of two

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variables. Only Spange *et al.*<sup>[33]</sup> utilized empirical correlations and a multiple regression with relevant statistical treatment. A common feature of the above-mentioned work is a lack of different solvents used for the measurement, and last but not the least the unsatisfactory way of statistical evaluation and interpretation of solvent effects.

11,11,12,12-Tetracyano-9,10-antraquinodimethane (TCAQ) derivatives are potent electron acceptors that have been investigated for a variety of applications.<sup>[39–43]</sup> Solvent effects on their electron absorption spectra, however, have not been studied so far. For structurally related 2- and 2,6-(di)arylethynyl-9,10-antraquinones, a close linear correlation of Stokes shifts on the Lippert–Mataga parameter in seven solvents was observed.<sup>[35]</sup> The solvent dependence of the electronic absorption maxima, on the other hand, was not investigated. Szablewski *et al.*<sup>[37]</sup> reported the optical spectra of 2-[4-[amino-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene]-malononitrile ('Ammor,' a TCNQ derivative) measured in eight alcohols and found a good linear correlation of the absorption wavenumber maxima and the Stokes shift on the Lippert–Mataga parameter and the Dimroth–Reichardt parameter  $E_T$ , respectively.

The aim of this work was to study solvent effects on the absorption spectra of three structurally different donor-substituted TCAQ derivatives (Scheme 1, References 44–48) in a large number of well-selected solvents and interpreting the matter of D- $\pi$ -A systems solvation by theoretical models and (semi)empirical correlations. The three TCAQ derivatives vary in the nature and number of electron-donating substituents attached in positions 2 and 6. Compound **1** features one dimethylamino ( $N(CH_3)_2$ ) donor group in position 2, whereas **2** has two  $N(CH_3)_2$  donor groups attached symmetrically on the TCAQ core (point group of symmetry  $C_2$ ). In the third derivative **3**, the  $N(CH_3)_2$  donor group and the TCAQ chromophore are separated by an additional phenyl ring. All of the TCAQ derivatives known to date adopt typical, saddle-like out of plane deformation, which is induced by the steric hindrance between  $C(CN)_2$  moieties and the aromatic core.<sup>[39–43,48]</sup> Thus, the investigated donor-substituted TCAQs **1–3** are geometrically non-centrosymmetric chromophores.

### Methods to evaluate solvent effects in relation to D- $\pi$ -A systems

Several approaches to a quantitative evaluation and interpretation of solvent effects are employed. One of the most used and experimentally verifiable theoretical approaches is based on Onsager's reaction-field theory.<sup>[49]</sup> According to this model (1), the dependence of the absorption wavenumber change of a solute  $\Delta\tilde{\nu}$  at transition from vacuum into a solvent is given by the

following equation:

$$\Delta\tilde{\nu} = \tilde{\nu} - \tilde{\nu}_{\text{vac}} = \left[ A + B + \frac{\mu_g^2 - \mu_e^2}{4\pi h c a^3 \epsilon_0} \right] \left[ \frac{n^2 - 1}{2(n^2 + 1)} \right] + \frac{2\mu_g(\mu_g - \mu_e)}{4\pi h c a^3 \epsilon_0} \left[ \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (1)$$

where  $A$  and  $B$  are the constants dependent on the solute structure,  $\mu_g$  and  $\mu_e$  are the dipole moments of the solute in the ground and excited states, respectively,  $a$  is a spherical cavity radius,  $n$  the refractive index of the solvent, and  $\epsilon$  its relative permittivity. Whereas the first term in Eqn (1) describes the solvent-induced polarization, the second one represents the orientation polarization of a solvent.

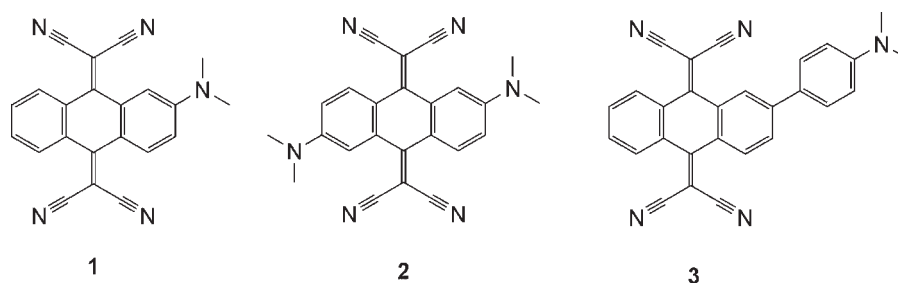
An advantage of the physically defined models is their unambiguous physicochemical interpretation of the results and insight into their underlying physical nature. On the other hand, these models describe the reality only partially and, therefore, additional parameters or their linear combinations in models type (1) are widely applied. Among others, these parameters comprise of a solvent's theoretical characteristics such as HOMO and LUMO energy or the physical quantities obtained from experiments (e.g., boiling point, permanent dipole moment, density, viscosity, or molar volume). The main advantage of these procedures may be seen in the closer correlations obtained, nevertheless, a less explicit physicochemical interpretation of the results remains a limitation.

All of the above-discussed interpretation of solvent effects may fail if hydrogen-bonding interactions between solvent and solute are involved. If such interactions occur, their expression overlaps the solvent polarity and polarizability.<sup>[13]</sup> Hydrogen-bonding interactions are implicitly included in correlations describing solvent effects on the similarity principle. The performed studies have shown that four solvent characteristics are essential for the general description of solvent effects – HBD acidity, HBA basicity, polarity (dipolarity), and polarizability.<sup>[50]</sup> A large number of the correlation equations utilizing empirical parameters are already well known (Reichardt,<sup>[13]</sup> Kamlet, Abboud, and Taft,<sup>[51]</sup> Pytela,<sup>[52]</sup> Catalán and Hopf<sup>[53]</sup>).

## RESULTS AND DISCUSSION

### Electronic structure

The HOMO of molecule **1** ( $E_{\text{HOMO}} = -8.85$  eV) is positioned on the nitrogen of the  $N(CH_3)_2$  group and partially on the alternating carbon atoms of the aromatic ring (Fig. 1). The energies of the



Scheme 1. Investigated donor-substituted TCAQs

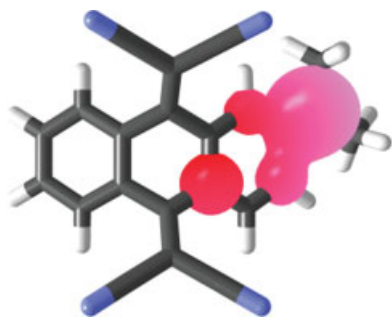


Figure 1. HOMO localization in compound 1

highest occupied MO ( $E_{\text{HOMO}} = -8.70$  eV) and the nearest lower occupied MO ( $E_{\text{HOMO}-1} = -8.72$  eV) for molecule **2** with the optimized geometry including  $C_2$ -symmetry are almost identical and, therefore, we can consider them to degenerate. The degeneration is most likely caused due to the  $C_2$ -symmetry of **2**. The HOMO of molecule **2** is symmetrically localized on the nitrogen atoms of both  $\text{N}(\text{CH}_3)_2$  groups and partially on the carbons in *para*-positions (Figure 1SI in Supporting Information). HOMO of molecule **3** resembles those observed for **1** ( $E_{\text{HOMO}} = -8.40$  eV, Figure 3SI). The LUMO of molecule **1** ( $E_{\text{LUMO}} = -2.18$  eV) is localized on the double bond between the  $\text{C}(\text{CN})_2$  group and the part of the quinoid ring that is next to the  $\text{N}(\text{CH}_3)_2$  group (Fig. 2). Similar to the HOMO of molecule **2**, its LUMO ( $E_{\text{LUMO}} = -1.97$  eV, Figure 2SI) is also symmetrically placed in the TCAQ core. In contrast to the localization of the LUMO of molecule **1**, the LUMO of **3** ( $E_{\text{LUMO}} = -2.24$  eV, Figure 4SI) is localized almost symmetrically as in **2**.

The average second- and third-order polarizabilities  $\beta$  and  $\gamma$  of the investigated molecules **1–3** calculated by MOPAC2007 are  $1.84 \cdot 10^{-29}$  (**1**),  $1.74 \cdot 10^{-29}$  (**2**), and  $3.21 \cdot 10^{-29}$  (**3**) and  $1.14 \cdot 10^{-27}$  (**1**),  $1.91 \cdot 10^{-27}$  (**2**), and  $2.59 \cdot 10^{-27}$  (**3**) esu, respectively. From the values it could be seen that an increase in molecular symmetry and the introduction of two donors caused a second-order polarizability  $\beta$  rather decrease (refer to the above discussion on the HOMO/LUMO localization as well as the UV/Vis spectra of **2** below). On the other hand, despite the smaller interaction between the acceptor and donor in **3** (refer to the HOMO and LUMO localizations in Figures 3SI and 4SI), the larger length of the conjugation path between donor and acceptor caused enhanced hyperpolarizabilities  $\beta$  as well as  $\gamma$ .

### Solvent dependence: experimental data

The dependence of the UV/Vis spectra change on the selected solvents used in the range of wavelengths from 350 to 700 nm for

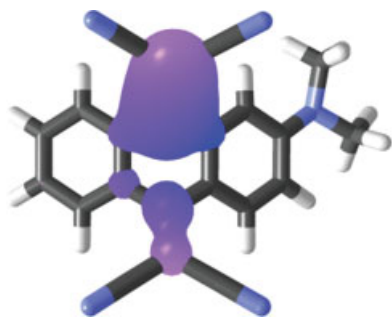


Figure 2. LUMO localization in compound 1

compound **1** is illustrated in Fig. 3 (complete spectra can be seen in Figures 5SI–16SI in Supporting Information). The values of the longest-wavelength absorption maxima  $\lambda_{\text{max}}$  measured in 32 representative solvents for compounds **1–3** are summarized in Table 1. The  $\lambda_{\text{max}}$  values were converted for further evaluation into the wavenumbers  $\tilde{\nu}_{\text{max}}$  having energy dimension. Absence of the possible solute aggregation and its influence on the position of the absorption maxima has been verified by measurements of the UV/Vis spectra for **1–3** in dichloromethane (SI, Figures 17SI–19SI) where the Lambert–Beer law was fully obeyed. Since the solute associates particularly arise in the non-polar solvents, such as dichloromethane, we can justifiably suggest that the observed shifts of the absorption maxima for compounds **1–3** in dependence on the solvent used were not caused by the solute aggregation.

A general feature of the UV/Vis spectra of TCAQs **1–3** is their intense CT bands, with  $\lambda_{\text{max}}$  appearing between 520 (2.38 eV) and 569 nm (2.18 eV) for compound **1** and 522 (2.38 eV) and 595 nm (2.08 eV) for compound **3**, respectively. Two partially overlapped bands were measured for compounds **2**. Whereas the first and more intensive band has  $\lambda_{\text{max}}$  appearing between 480 (2.58 eV) and 526 nm (2.36 eV), the second one lies about 600 nm (overlapped with the first band). The existence of two bands is most likely given by an interaction between two degenerated transitions from the twofold degenerate HOMO to the nondegenerate LUMO. Despite the saddle-like out of plane deformation seen for all known TCAQs (refer above), the molecular structure of **2** is relatively close to planar and, therefore, we can consider its HOMO and LUMO to be almost centrosymmetric. As a consequence, a transition from the ground to the excited state is accompanied with no dipole moment change and, according to Eqn (1), no solvatochromic effects should be observed. However, the UV/Vis spectrum of **2** features a strong CT from the ground to the excited state. The charge is transported from the  $\text{N}(\text{CH}_3)_2$  donors to the cyano acceptors generating partially positive and negative charges on the donors

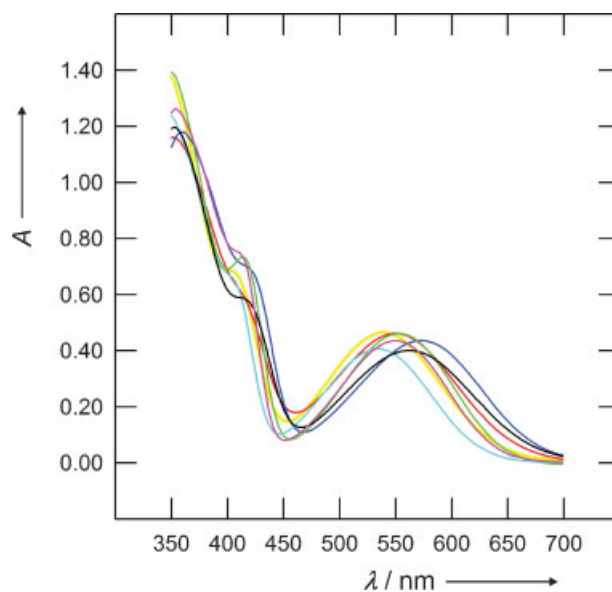


Figure 3. UV/Vis spectra of compound **1** measured in selected solvents: yellow, acetone; red, dimethyl sulfoxide; blue, benzyl alcohol; lime, 1,2-dichloroethane; aqua, 1,4-dioxane; fuchsia, benzene; black, formamide

**Table 1.** The longest-wavelength absorption maxima  $\lambda_{\max}$  of the CT bands measured for TCAQs **1–3** in dependence on the solvent used (listed in ascending order according to solvent  $E_{\text{T}}^{\text{N}}$  values).

Solvent	$E_{\text{T}}^{\text{N}}$	Wavelength, $\lambda_{\max}$ [nm (eV)]		
		<b>1</b>	<b>2</b>	<b>3</b>
Cyclohexane	0.006	522 (2.38)	483 (2.57)	552 (2.25)
Hexane	0.009	520 (2.38)	480 (2.58)	544 (2.28)
Heptane	0.012	521 (2.38)	482 (2.57)	538 (2.30)
Triethylamine	0.043	527 (2.35)	488 (2.54)	503 (2.46)
Tetrachloromethane	0.052	534 (2.32)	494 (2.51)	503 (2.46)
Toluene	0.099	547 (2.27)	506 (2.45)	573 (2.16)
Benzene	0.111	550 (2.25)	508 (2.44)	574 (2.16)
Diethyl ether	0.117	530 (2.34)	490 (2.53)	542 (2.29)
<i>m</i> -Xylene	0.120	546 (2.27)	506 (2.45)	571 (2.17)
1,4-Dioxane	0.164	534 (2.32)	496 (2.50)	543 (2.28)
Bromobenzene	0.182	562 (2.21)	516 (2.40)	595 (2.08)
Chlorobenzene	0.188	558 (2.22)	513 (2.42)	588 (2.11)
Tetrahydrofuran	0.207	539 (2.30)	499 (2.48)	510 (2.43)
Ethyl acetate	0.228	535 (2.32)	496 (2.50)	522 (2.38)
Chloroform	0.259	555 (2.23)	511 (2.43)	582 (2.13)
Pyridine	0.302	557 (2.23)	513 (2.42)	— <sup>a</sup>
Dichloromethane	0.309	554 (2.24)	509 (2.44)	567 (2.19)
Nitrobenzene	0.324	563 (2.20)	518 (2.39)	584 (2.12)
1,2-Dichloroethane	0.327	553 (2.24)	509 (2.44)	570 (2.18)
Butan-2-one	0.327	538 (2.30)	500 (2.48)	529 (2.34)
Benzonitrile	0.333	558 (2.22)	515 (2.41)	— <sup>a</sup>
Acetone	0.355	539 (2.30)	499 (2.48)	536 (2.31)
<i>N,N</i> -Dimethylacetamide	0.377	546 (2.27)	507 (2.45)	535 (2.32)
<i>N,N</i> -Dimethylformamide	0.386	547 (2.27)	507 (2.45)	545 (2.27)
Dimethyl sulfoxide	0.444	553 (2.24)	513 (2.42)	546 (2.27)
Acetonitrile	0.460	542 (2.29)	501 (2.47)	535 (2.32)
Nitromethane	0.481	549 (2.26)	505 (2.46)	542 (2.29)
Propan-2-ol	0.546	543 (2.28)	503 (2.46)	557 (2.23)
Benzyl alcohol	0.608	569 (2.18)	526 (2.36)	594 (2.09)
Ethanol	0.654	544 (2.28)	502 (2.47)	545 (2.27)
Methanol	0.762	541 (2.29)	500 (2.48)	537 (2.31)
Formamide	0.775	562 (2.21)	520 (2.38)	— <sup>a</sup>

<sup>a</sup> Not measurable.

and acceptors, respectively. Formation of such quadrupole as a consequence of the increase in electric moment from the ground to the excited state is the most likely explanation for the solvent effects observed for **2**.<sup>[54–56]</sup> For nonsymmetrical TCAQs **1** and **3** only single CT bands were observed and also the HOMO degeneration was not found using PM6 calculations. The CT character of the longest-wavelength absorptions of compound **1–3** was already confirmed by protonation/neutralization experiment.<sup>[48]</sup>

The measured longest-wavelength absorption maxima  $\lambda_{\max}$  for compounds **1** and **2** clearly shows a red-shift upon going from non-polar solvents such as hexane or heptane to the more polar solvents for example benzene, chloroform or benzyl alcohol. This implies that the excited state must be more polar than the ground state and, therefore, the excited state is being more stabilized moving from less to more polar solvents. This is in full accordance with the observed solvatochromism of known intramolecular push–pull systems.<sup>[31,33,54–56]</sup> On the other hand,

compound **3** is less sensitive to solvent polarity than compounds **1** and **2** and also variation of the solvent effects is less straightforward. Whereas the spectra of **3** in pyridine, benzonitrile, and formamide were not measured due to the low solubility (the CT band of the saturated solution was not detectable), the spectra of **3** in tetrachloromethane, triethylamine, and THF had an anomalous shape and also the positions of the longest-wavelength absorption maxima were considerably different from those predicted by the regression models. Hence, the values for these solvents were omitted from further calculations.

#### Correlations based on the physical models utilizing physical quantities

According to Eqn (1) twofold linear regression of  $\tilde{\nu}_{\max}$  provided for compounds **1–3** relationships (2)–(4) where  $\tilde{\nu}_{\max}$  corresponds to  $\tilde{\nu}$  for the measured absorption maxima in Eqn (1),  $\tilde{\nu}_{\text{vac}}$  is

included in intercept:

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{1}) [\text{cm}^{-1}] \times 10^{-4} &= (21.8 \pm 0.3) - (17.3 \pm 1.6) \left[ \frac{n^2 - 1}{2(n^2 + 1)} \right] \\ &\quad - (1.03 \pm 0.12) \left[ \frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 2} \right] \\ N = 32, s = 0.179, R = 0.917, F(2, 29) &= 76.8 \end{aligned} \quad (2)$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{2}) [\text{cm}^{-1}] \times 10^{-4} &= (23.3 \pm 0.3) - (17.5 \pm 1.6) \left[ \frac{n^2 - 1}{2(n^2 + 1)} \right] \\ &\quad - (1.08 \pm 0.12) \left[ \frac{\varepsilon - 1}{\varepsilon + 1} - \frac{n^2 - 1}{n^2 + 2} \right] \\ N = 32, s = 0.177, R = 0.923, F(2, 29) &= 83.0 \end{aligned} \quad (3)$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{3}) [\text{cm}^{-1}] \times 10^{-4} &= (22.7 \pm 0.6) - (27.5 \pm 3.6) \left[ \frac{n^2 - 1}{2(n^2 + 1)} \right] \\ N = 26, s = 0.378, R = 0.841, F(1, 24) &= 58.1 \end{aligned} \quad (4)$$

Experimental data of compounds **1** and **2** agree very well with the theoretical relation in Eqn (1). The partial correlation coefficient, determining an efficiency of the given variable to explain the data variability, is very similar for both independent variables. This implies that the contribution of induced and orientation solvent polarization is also similar. A negative sign of both regression coefficients implies that the dipole moment of the excited state ( $\mu_e$ ) is larger than the one for the ground state ( $\mu_g$ ). As a consequence, we can suggest a higher stabilization of the excited state and a solvent-induced bathochromic shift. This fully corresponds with the D- $\pi$ -A character of both compounds. In view of the relationship based on Eqn (1), compounds **1** and **2** show a similar behavior that corresponds with the calculated similar hyperpolarizabilities  $\beta$ . This further implies that the HOMO and LUMO symmetry and localization do not play a significant role. For compound **3**, the regression coefficient of the variable explaining orientation polarization is statistically insignificant. The reason could be seen in a small dipole moment of the ground state, in a small difference of the dipole moments of both states, or in a short lifetime of the excited state (a weak stabilization of the excited state in comparison with the ground state). The permanent dipole moment of **3** predicted by MOPAC2007, amounts to 8.46 D. Thus, the most probable explanation is the small difference in the dipole moments of both states. More important is a resulting independence on the environment polarity and, on the contrary, a considerable dependence on the environment polarizability. This fact corresponds with the highest hyperpolarizability  $\beta$  and  $\gamma$  being calculated for **3**.

A quantitative interpretation of solvent effects could also involve a multiple regression with the linear combination of two, three, and four (no more) independent variables. The following quantities or their functions were used as the best independent variables:

(i)  $\frac{\varepsilon - 1}{\varepsilon + 2}$ ; (ii)  $\frac{n^2 - 1}{n^2 + 2}$ ; (iii)  $\frac{1}{\varepsilon}$  (Reference 57); (iv)  $\frac{\varepsilon}{2\varepsilon + 1}$  (References 58,59); (v) solvent HOMO and LUMO; (vi)  $\mu$  (solvent permanent dipole moment); and (vii)  $V_m$  (solvent molar volume).

The following relationships of the explanatory variable were found as statistically and physicochemical the best ones (listed in descending order according to the given partial correlation

coefficient):

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{1}) [\text{cm}^{-1}] \times 10^{-4} &= (20.1 \pm 0.2) - (10.0 \pm 0.7) \left[ \frac{n^2 - 1}{n^2 + 2} \right] \\ &\quad + (1.78 \pm 0.30) \frac{1}{\varepsilon} \pm (3.08 + 1.03) 10^{-2} \mu + (4.34 + 1.24) 10^{-3} V_m \\ N = 32, s = 0.119, R = 0.967, F(4, 27) &= 97.4 \end{aligned} \quad (5)$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{2}) [\text{cm}^{-1}] \times 10^{-4} &= (21.6 \pm 0.2) - (10.0 \pm 0.7) \left[ \frac{n^2 - 1}{n^2 + 2} \right] \\ &\quad + (1.71 \pm 0.33) \frac{1}{\varepsilon} \pm (2.47 + 1.12) 10^{-2} \mu + (4.40 \pm 1.35) 10^{-3} V_m \\ N = 32, s = 0.129, R = 0.963, F(4, 27) &= 85.3 \end{aligned} \quad (6)$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{3}) [\text{cm}^{-1}] \times 10^{-4} &= (21.2 \pm 0.4) - (17.2 \pm 1.5) \left[ \frac{n^2 - 1}{n^2 + 2} \right] \\ &\quad + (1.23 \pm 0.73) 10^{-1} \mu + (2.61 + 0.60) \frac{1}{\varepsilon} \\ N = 26, s = 0.267, R = 0.931, F(3, 22) &= 47.5 \end{aligned} \quad (7)$$

The relationships in Eqns (5)–(7) are closer than relations based on Eqn (1). The main reason lies probably in a higher number of regression variables. In all of the equations a dominant explanatory variable is the term describing solvent-induced polarization. Similar to Eqns (2)–(4), the respective regression coefficients are consistent for compounds **1** and **2** whereas the regression coefficient is higher for compound **3** (refer to the above discussion).

It is worthwhile to notice that the Born function<sup>[57]</sup> of the relative permittivity  $1/\varepsilon$  has been found as the most effective description of the environment polarity. This function is the oldest and simplest description of an interaction between solute and solvent. The positive sign of the  $1/\varepsilon$  function implies that the increasing solvent polarity leads to a bathochromic shift. This relation could be explained as an electrostatic stabilization of the point charges on acceptors and donors in the excited state.

Similarly, a dependence on the solvent permanent dipole moment may be interpreted as a stabilizing dipole–dipole interaction. The positive sign of this quantity means higher stabilization of the ground state and resulting hypsochromic shift. Since an excitation is much faster than the reorganization of molecular dipoles, a relative equilibrium orientation of the solute and solvent molecules in the excited state resembles those in the ground state. Hence, stabilization of the ground state due to the dipole–dipole interaction is higher than the excited state.

The dependence on the Born function and the dipole moment for the larger molecule **3** is higher than for molecules **1** and **2** which is presumably caused due to a better solvent aggregation around the isolated charges on the acceptor and donor moieties of **3**. A dependence on the solvent molar volume has been seen only for compounds **1** and **2**. This is probably caused by the size and shape of the solute molecule. If the solute molecule **3** is considerably larger than the solvent molecules, the molecular size of the solvent vanishes, and the solvent molar volume is macroscopically insignificant.

### Correlations based on the similarity principle employing empirical parameters

The parameters  $E_T^N$  (Reference 13) and SP (Reference 53), equation with the parameters  $\alpha$ ,  $\beta$ , and  $\pi^*$  (Reference 51), and the equation with the statistically adjusted parameters PAC, PBC, and PBC (Reference 52) were used for an evaluation of the solvent effects on the longest-wavelength absorption maxima for compounds **1–3**. Statistically significant dependencies on the Reichardt parameter  $E_T^N$  were found only for compound **1** and **2** but the correlations were not close ( $r_1 = 0.520$  and  $r_2 = 0.548$ , respectively). Better correlations were gained for all studied compounds using the parameters SP introduced by Catalán and Hopf ( $r_1 = 0.785$ ,  $r_2 = 0.783$ ,  $r_3 = 0.594$ ). This implies that the solvent polarizability is more significant factor than polarity, however, a description of the observed solvent effect by only one parameter is insufficient. Equation with the parameters  $\alpha$ ,  $\beta$ , and  $\pi^*$  provided the following relationships:

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{1}) [\text{cm}^{-1}] \times 10^{-4} &= (19.1 \pm 0.1) - (0.269 \pm 0.121) \alpha \\ &+ (0.415 \pm 0.122) \beta - (1.35 \pm 0.11) \pi^* \quad (8) \\ N = 29, s = 0.173, R = 0.925, F(3, 25) &= 49.5 \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{2}) [\text{cm}^{-1}] \times 10^{-4} &= (20.7 \pm 0.1) - (1.33 \pm 0.12) \pi^* \quad (9) \\ N = 32, s = 0.194, R = 0.903, F(1, 30) &= 132 \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{3}) [\text{cm}^{-1}] \times 10^{-4} &= (18.3 \pm 0.3) + (1.39 \pm 0.41) \\ &\times \beta - (1.22 \pm 0.41) \pi^* \quad (10) \\ N = 24, s = 0.560, R = 0.647, F(2, 21) &= 7.54 \end{aligned}$$

The tightness of the correlation is worse than those observed for the linear additive relation of physical quantities. According to the partial regression coefficient, parameter  $\pi^*$  is a dominant explanatory variable in Eqns (8) and (9). In Eqn (10), its significance is comparable with parameter  $\beta$ . The significance of the parameters describing specific hydrogen-bonding interaction ( $\alpha$  and  $\beta$ ) is lower and, therefore, these interactions are apparently not involved. The regression coefficient sign for parameter  $\pi^*$  is negative and, in view of the complex character of this parameter, we can rather assume a more substantial effect of the solvent polarizability than of solvent polarity. A negative sign of the regression coefficient for parameter  $\alpha$  in Eqn (10) indicates a bathochromic shift caused presumably due to a hydrogen bond on the acceptor moiety of **1**. On the other hand, a positive sign of the regression coefficient for parameter  $\beta$  in Eqns (8) and (10) indicates a hypsochromic shift caused presumably by a nucleophilic interaction of the solvent molecules with the electron-withdrawing molecule moieties. The basic character of the solvent cannot be considered due to the absence of acidic hydrogens in **1** and **3**, respectively.

Calculations with parameters PAC, PBC, and PBC led to the following relationships:

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{1}) [\text{cm}^{-1}] \times 10^{-4} &= (19.1 \pm 0.1) \\ &+ (0.598 \pm 0.167) \text{PBC} - (2.04 \pm 0.18) \text{PPC} \quad (11) \\ N = 32, s = 0.173, R = 0.923, F(2, 29) &= 83.3 \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{2}) [\text{cm}^{-1}] \times 10^{-4} &= (20.7 \pm 0.1) \\ &+ (0.429 \pm 0.177) \text{PBC} - (1.97 \pm 0.19) \text{PPC} \quad (12) \\ N = 32, s = 0.184, R = 0.916, F(2, 29) &= 75.9 \end{aligned}$$

$$\begin{aligned} \tilde{\nu}_{\max}(\mathbf{3}) [\text{cm}^{-1}] \times 10^{-4} &= (18.4 \pm 0.2) + (2.85 \pm 0.40) \\ &\times \text{PBC} - (3.35 \pm 0.48) \text{PPC} \quad (13) \\ N = 26, s = 0.382, R = 0.845, F(2, 23) &= 28.7 \end{aligned}$$

These correlations are slightly closer than those for Eqns (8)–(10) but the results are more consistent. Whereas Eqns (11) and (12) apply the parameter PPC describing the solvent polarity and polarizability as a major explanatory variable, in Eqn (13), its significance is comparable with parameter PBC describing basicity in the interaction with solvent polarity. The results and their interpretation are analogous with those deduced from the correlations given by Eqns (8)–(10). It is also worthwhile to notice that the values of the regression coefficient for parameter PPC have the same trend as the calculated average second-order polarizabilities (hyperpolarizabilities)  $\beta$ .

### CONCLUSION

It has been shown that study of solvent effects on absorption (and eventually emission) spectra of D- $\pi$ -A push-pull systems may be a suitable method for determining their optical properties related to electron distribution and polarizability. Correlations resulting from the theoretical models and empirical parameters were statistically comparable to our experimental data. According to the analysis of these relationships, we can conclude that a polar D- $\pi$ -A system is more stabilized in the excited state than in the less polar ground state. The same result may also be simply deduced from the measured positions of  $\lambda_{\max}$  moving from less to more polar and polarizable solvents. Solvent effects do not depend on the orientation of acceptors and donors attached to the  $\pi$ -system and, therefore, also not on the HOMO and LUMO localizations. A crucial factor is the length of the  $\pi$ -system in between. Theoretical physical models and linear combinations of physical quantities are the most suited for the interpretation of solvent effects because they enable a more straightforward physico-chemical interpretation of the results obtained. The following solvent properties have been found as the most considerable factors affecting the position of the longest-wavelength absorption maxima: polarization, permanent dipole moment, and molar volume. A minor effect of specific hydrogen-bonding interaction has also been observed. Bathochromic shifts of the CT band with increasing solvent polarity as a result of the excited state stabilization has been most accurately described by the Born function where the electrostatic stabilization could be elucidated as a solvent interaction with the charged terminal acceptor and donor groups. A permanent dipole moment has, on contrary, a hypsochromic effect due to the slower reorganization of molecular dipoles compared with the rate of excitation. Solvent polarizability affects the entire solute polarizability having a bathochromic shift. This effect becomes stronger with increasing the length of the  $\pi$ -conjugated system between acceptor and donor. Whereas the effect of the solvent polarizability has been the most accurately described by the Onsager-induced polarizability, the orientation polarizability has not been significant. Solvent molar volume as a hypsochromic factor has an impact only if the solute size is comparable with the solvent size. If the solute size is considerably larger than the size of the solvent molecules, the solvents behave as a 'shape continuum' and the solvent molar volume becomes insignificant.

### EXPERIMENTAL SECTION

The complete synthesis and full spectral characterization of compounds **1–3** has been reported previously.<sup>[48]</sup> Solvents used

for the solvatochromism study were chosen according to their specific difference (HBD acidity, HBA basicity, polarity (dipolarity), polarizability and their combinations).<sup>[60]</sup> Solvents were reagent-grade and were purified by the following methods: (i) hexane, heptane, and cyclohexane were simply distilled and stored over molecular sieves (4 Å); (ii) tetrachloromethane, chloroform, dichloromethane, 1,2-dichloroethane, bromobenzene, chlorobenzene, ethylacetate, benzyl alcohol, 2-butanone, propan-2-ol, and acetone were washed with aq. K<sub>2</sub>CO<sub>3</sub> (sat.), dried (MgSO<sub>4</sub>), (vacuum) distilled, and stored over molecular sieves (4 Å); (iii) dioxane, diethylether, and THF were freshly distilled from sodium benzophenone ketyl; (iv) benzene, *m*-xylene, toluene, triethylamine, benzonitrile, acetonitrile, nitromethane, nitrobenzene, and formamide were pre-dried using molecular sieves (4 Å) and vacuum-distilled; (v) ethanol and methanol were dried with Na and distilled; (vi) pyridine was washed with aq. KOH, dried (MgSO<sub>4</sub>), and distilled; (vii) spectral *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide were dried using molecular sieves (4 Å). The measured solution of compounds **1–3** had a concentration of 6.10<sup>-5</sup> mol/L. Absorbance was in the range from 0.1 to 0.5. If the compound was not completely dissolved a filtered saturated solution was measured instead. Electron absorption spectra were recorded on a Hewlett–Packard 8453 spectrophotometer in the range of wavelengths from 200 to 800 nm with an accuracy of 1 nm. In order to verify the concentration independency of the absorption maxima position and that the Lambert–Beer law is fully obeyed spectra of TCAQs **1–3** at different concentrations ranging from 6.45.10<sup>-5</sup> to 6.45.10<sup>-6</sup> M were measured (as shown in SI, Figures 17SI–19SI). The longest-wavelength absorption maxima have been numerically determined from the obtained smoothed dependencies of absorbance on wavelength.

Initial geometries of the compounds **1–3** have been calculated by PM3 method (ArgusLab, Reference 61, internal parametrization used) and subsequently optimized by the PM6 method (MOPAC2007, Reference 62, internal parametrization used). Employing MOPAC2007, the following characteristics were further calculated: HOMO and LUMO energies, isotropic polarizability  $\alpha$ , and average second- and third-order polarizabilities  $\beta$  and  $\gamma$ . Experimental data were examined by multivariate graphical display methods and subsequently treated by multiple linear regressions (including *t*-test, *F*-test, assessing multicollinearity, residual analysis). Residuals in all of the presented regressions had Normal distribution, and outliers were not detected. The Program OPstat<sup>[63]</sup> was employed for all statistical calculations.

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