

A Joint Theoretical and Experimental Insight into the Electronic Structure of Chromophores Derived from 6*H*,12*H*-5,11-Methanodibenzo[*b,f*][1,5]diazocine

by Vincent Lemaury and Jérôme Cornil

Laboratory for Chemistry of Novel Materials, University of Mons-Hainaut, B-7000 Mons

and

Delphine Didier, Aline Mujawase, and Sergey Sergeev*

Laboratory of Polymer Chemistry, Université Libre de Bruxelles (U.L.B.), CP 206/01,

Boulevard du Triomphe, B-1050 Bruxelles

(phone: +3226505392; fax: +3226505410; e-mail: sserguee@ulb.ac.be)

We report on the synthesis and electronic spectra of the chiral, donor-acceptor (push-pull) chromophores (\pm)-**4** and (\pm)-**5** with a 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine scaffold (Scheme 1 and Fig. 2). The electronic structures of these compounds were investigated at a quantum-chemical level (Figs. 2 and 3). The chemical reactivity of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine ((\pm)-**11**) towards aromatic electrophilic substitution (Scheme 2 and Table) provided additional information about its electronic structure and confirmed nonnegligible delocalization of the lone pair of the bridge-head N-atoms in this heterocyclic system.

Introduction. – Tröger's base (= (\pm)-2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine, (\pm)-**1**; Fig. 1) is a chiral diamine with two stereogenic bridge-head N-atoms. The unusual rigid, V-shaped geometry with the two aromatic rings nearly perpendicular to each other has encouraged many elegant applications of Tröger's base analogs in supramolecular chemistry and molecular recognition. To this end, the 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine scaffold has been transformed to increasingly sophisticated derivatives *via* metal-mediated reactions [1]. Among others, molecular-torsion balances for quantification of weak forces [2], the regio- and stereoselective synthesis of fullerenes with inherently chiral addition patterns [3][4], and chirality transfer in scissor-like heterotopic [Zn(porphyrinato)] assemblies [5] should be mentioned (for recent comprehensive reviews, see [6]).

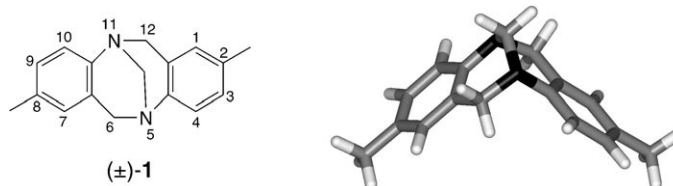


Fig. 1. Tröger's base: Structure and AM1-optimized geometry of the (*S,S*)-enantiomer

Most of the applications reported up to date exploited the folded geometry and the chirality of *Tröger's* base. However, another interesting structural feature, namely the two tertiary-amine functions, was hardly used until now. Due to the presence of two N-atoms, *Tröger's* base can be viewed as a structural analog of *N,N*-dialkylanilines (= *N,N*-dialkylbenzenamines), which have found extensive application in the design of chromophores with nonlinear optical (NLO) properties [7].

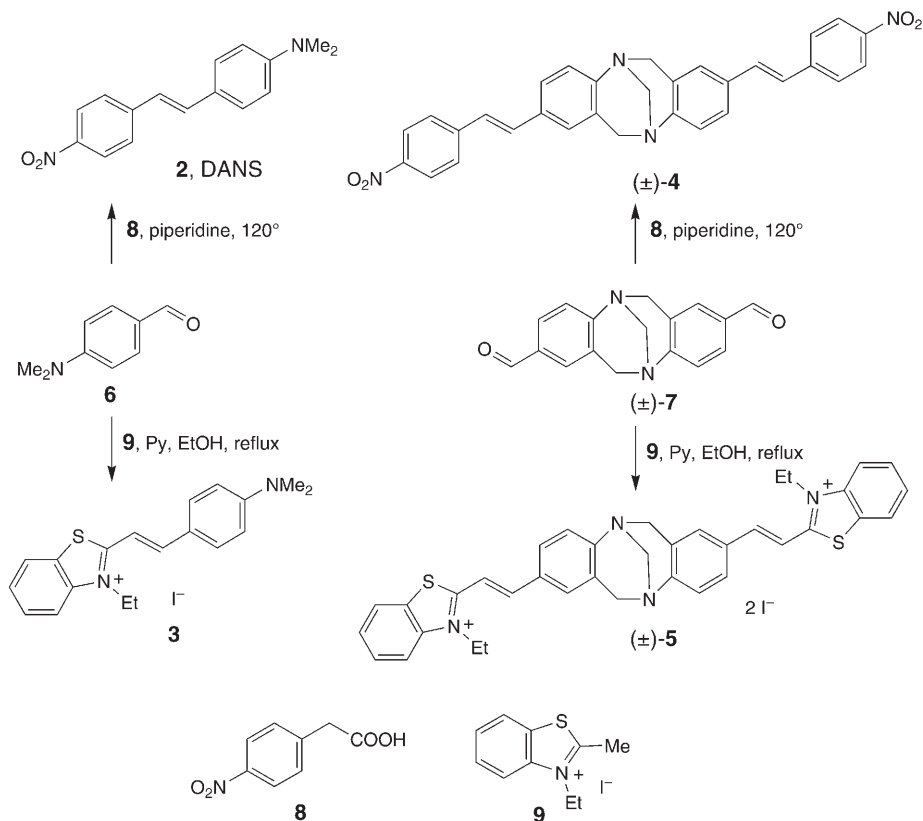
In the course of our own study on chromophores with potential NLO activities, we decided to explore the C_2 -symmetrical V-shaped scaffold of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine that provides a possibility to create two chromophore units within one molecule, their dipole moments being nonantiparallel to each other. The introduction of chirality elements within the conjugated system might prove beneficial for obtaining noncentrosymmetrical crystals. The latter feature constitutes an important prerequisite for the observation of second-order NLO phenomena. An example of V-shaped design of push-pull chromophores is known and is based on axially chiral C_2 -symmetrical binaphthalenol derivatives, which have exhibited high first-order hyperpolarizabilities [8].

In the early stage of our research, we are interested in simple model systems with two diarylethene chromophore units integrated into the scaffold of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine. In this context, the nature of the electronic structure and optical properties of these systems are worth being investigated, since the analogy between an open-chain molecule and a bicyclic system is not straightforward. We thus undertook theoretical and experimental studies on simple model systems with the aim to estimate delocalization of the lone pair on the N-atoms and its impact on the optical properties.

Results and Discussion. – A structural concept that has been extensively used in the design of second-order NLO chromophores involves an aromatic conjugated π -system end-capped with electron donating (D) and accepting (A) groups (D- π -A or push-pull design). A prototypical and extensively studied molecule is 4-(*N,N*-dimethylamino)-4'-nitrostilbene (= *N,N*-dimethyl-4-[2-(4-nitrophenyl)ethenyl]benzenamine = DANS; **2**). Another system that attracted our attention is the cationic styryl dye **3** which is soluble in polar protic solvents. It is, therefore, interesting for biological applications such as fluorescence imaging since cationic dye molecules are well known to intercalate with DNA [9]. By analogy with **2** and **3**, we designed the bis-chromophore systems (\pm)-**4** and (\pm)-**5** based on the scaffold of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine (*Scheme 1*).

DANS (**2**) was prepared from 4-(dimethylamino)benzaldehyde (**6**) according to the published procedure [10]. Its analog (\pm)-**4** bearing two chromophore units was synthesized from dialdehyde (\pm)-**7** (prepared according to known procedures starting from 4-iodoaniline [3][11]) by the same method. Base-catalyzed *Knoevenagel-Doebner* condensation of (\pm)-**7** with an excess of 4-nitrobenzeneacetic acid (**8**) gave dinitroolefine (\pm)-**4** in a modest yield (25%) after column chromatography.

Styryl dye **3** was synthesized by the *Knoevenagel* condensation of quaternary benzothiazolium salt **9** with aldehyde **6** in the presence of pyridine. For the synthesis of bis-chromophore (\pm)-**5**, the same synthetic procedure was amended: condensation of dialdehyde (\pm)-**7** with 2 equiv. of quaternary salt **9** afforded bis-benzothiazolium

Scheme 1. Synthesis of **2**, **3**, (\pm)-**4**, and (\pm)-**5**. Py = pyridine.

derivative (\pm)-**5**, which was purified by crystallization from EtOH. Both bis-chromophores (\pm)-**4** and (\pm)-**5** were isolated as pure (*E,E*) isomers, as evidenced by the value of the coupling constants $^3J(\text{H,H})$ for the olefinic protons (16.5 Hz for (\pm)-**4** and 15.9 Hz for (\pm)-**5**; cf. 16.2 Hz for **2** and 15.3 Hz for **3**).

The absorption spectra of **2**, **3**, (\pm)-**4**, and (\pm)-**5** are shown in Fig. 2. The lowest-frequency absorption is shifted hypsochromically by 58 nm (0.43 eV) for (\pm)-**4** compared to DANS (**2**) and by 95 nm (0.51 eV) for (\pm)-**5** compared to the styryl dye **3**. The molar absorption coefficients of (\pm)-**4** and (\pm)-**5** are close to twice the corresponding values of **2** and **3**, respectively.

The spectral characteristics, *i.e.*, the hypsochromic shift of the absorption maxima and increase of the absorption coefficients on going from **2** to (\pm)-**4** or from **3** to (\pm)-**5** were rationalized at a quantum-chemical level. To do so, we first optimized the geometry of the compounds at the semi-empirical *Hartree-Fock* Austin model 1 (AM1) level using the AMPAC package [12]. Semi-empirical *Hartree-Fock* intermediate neglect of differential overlap (INDO) calculations coupled to a single configuration interaction (SCI) scheme were then carried out on the basis of the optimized geometries to simulate the electronic and optical properties [13]; the

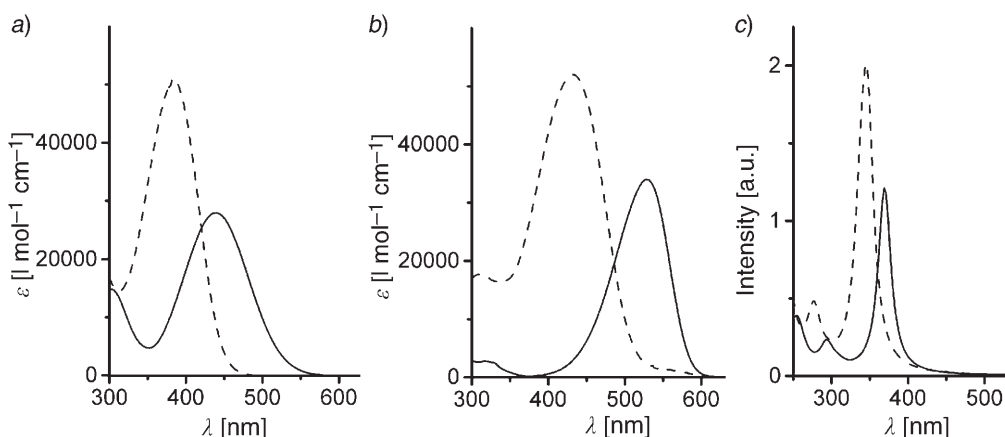


Fig. 2. a) UV/VIS Spectra (CH_2Cl_2) of **2** (—) and (\pm) -**4** (---). b) UV/VIS Spectra (EtOH) of **3** (—) and (\pm) -**5** (---). c) INDO-Simulated absorption spectra of **2** (—) and (S,S) -**4** (---).

configurations in the SCI expansion were generated by promoting a single electron from one of the highest N occupied molecular orbitals to one of the lowest N unoccupied levels (N is, in our case, half the number of π -electrons of the molecule). Although INDO is not the most up-to-date quantum-chemical approach, it remains in our experience the best compromise to describe the optical properties of conjugated systems in general. We have not privileged the time-dependent density-functional-theory (TD-DFT) method which tends to strongly underestimate optical-transition energies when the size of the conjugated backbone becomes too large (see the recent review [14] for a detailed discussion). Here, we focus exclusively on compounds **2** and (\pm) -**4** whose optical properties are not expected to be significantly affected by solvent effects that are neglected here, in contrast to the charged compounds **3** and (\pm) -**5** [15].

The AM1-optimized geometries of **2** and (S,S) -**4** (the (S,S) -enantiomer was arbitrarily chosen for calculations) exhibit a twist angle of *ca.* 40° between the benzene rings. This deviation from planarity results from the fact that the torsion-potential profile of phenylenevinylene segments is flat for moderate torsion angles [16]. The INDO/SCI results show that the molar absorption coefficient of the lowest-optimally allowed transition is increased by *ca.* 70% in (S,S) -**4** compared to **2** (see Fig. 2, c). The lowest-frequency absorption of (S,S) -**4** located at *ca.* 344 nm is composed of two distinct excited states lying very close in energy (338 and 347 nm). The electronic transitions describing these two excited states involve the HOMO – 1, HOMO, LUMO, and LUMO + 1 levels that correspond to the bonding and antibonding combination of the HOMO and LUMO orbitals of compound **2**, respectively.

The hypsochromic shift of the lowest frequency absorption observed in the experimental spectra on going from **2** to (S,S) -**4** is also reproduced by our simulations (Fig. 2) though being underestimated (25 nm vs. 58 nm, resp.). Note that similar shifts are obtained when the two chromophores are constrained to be planar. This shift originates from a large stabilization of the HOMO orbital in (S,S) -**4** (–7.90 eV) compared to **2** (–7.32 eV) (see Fig. 3). In contrast, the LUMO level is slightly

stabilized when going from **2** (-1.39 eV) to (*S,S*)-**4** (-1.53 eV). To shed light into the large stabilization of the HOMO orbital, we first compared the electronic structure of compound **2** to that of the model compound (*S,S*)-**10** with only one styryl chromophore unit (see Fig. 3). The stabilization of the HOMO orbital by *ca.* 0.4 eV on going from **2** to (*S,S*)-**10** results from the fact that the methano bridge of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine implies a change in the orientation of the p_z orbital of the N-atom of the amino group with respect to the benzene ring. In molecule **2**, the p_z orbital of the N-atom of the amino group is fully conjugated with the p_z orbitals of the adjacent ring, whereas the conjugation is reduced in (*S,S*)-**10** due to the geometric constraints induced by the bridge. Since the p_z orbital of the N-atom of the amino group significantly contributes to the HOMO level, this reduction of conjugation is at the origin of the large stabilization of the HOMO level. The fact that the LUMO level is not significantly modified on going from **2** to (*S,S*)-**10** is explained by the localization of this orbital at the terminal NO_2 groups (see Fig. 3 for the graphical representation of the HOMO/LUMO levels of **2**, (*S,S*)-**4**, and (*S,S*)-**10**). The HOMO level is further stabilized by *ca.* 0.15 eV on going from (*S,S*)-**10** to (*S,S*)-**4**. This weaker contribution to the HOMO shift is attributed to changes in the amplitude of the electrostatic interactions when the second polar chromophore moiety is introduced into the 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine scaffold. The very small splitting calculated between the highest two occupied and lowest two unoccupied levels (0.06 eV and 0.003 eV, resp.) in (*S,S*)-**4** points to a weak electronic coupling between the two chromophore units within the molecule. Thus, such systems do not allow for a

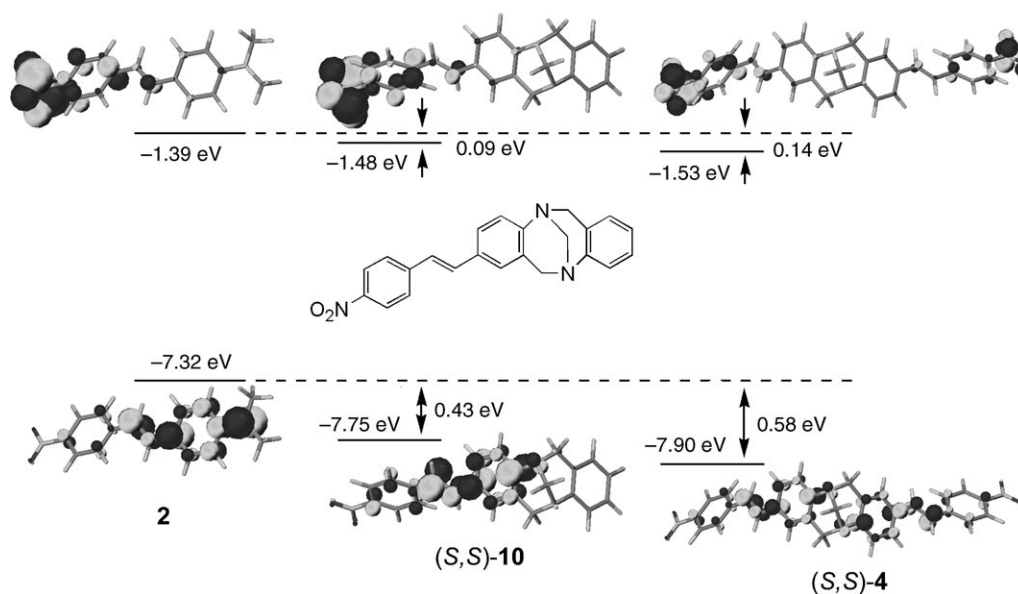
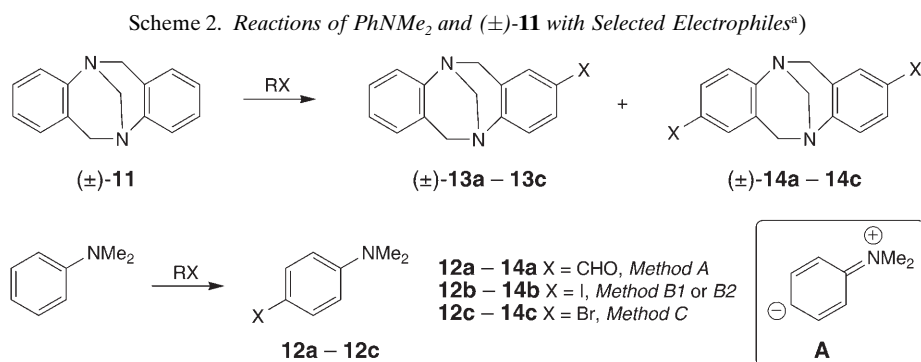


Fig. 3. Energy diagram and shape of the HOMO and LUMO orbitals in **2**, (*S,S*)-**10**, and (*S,S*)-**4**. The size and color of the circles describe the amplitude and sign of the LCAO (linear combination of atomic orbitals) coefficients associated with the π -atomic orbitals.

delocalization of molecular orbitals along the conjugated backbone *via* ‘ π - σ - π through-bond coupling’, as it has been shown for bis-chromophore systems with 1,3-bis(methylene)cyclobutane or cyclodiborazane cores [17].

Additional experimental information on the electronic structure of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine can be obtained from its reactivity in electrophilic substitution reactions. Indeed, *N,N*-dialkylanilines are highly reactive towards various electrophiles and often give exclusively the products of substitution in the *para*-position with respect to the dialkylamino group. We applied to (\pm)-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine ((\pm)-**11**) some electrophilic substitutions that are well known for *N,N*-dialkylanilines (Scheme 2). The results of these experiments with PhNMe₂ to give substituted anilines **12** and with (\pm)-**11** to give products of single or two-fold substitution (\pm)-**13** and (\pm)-**14**, respectively, are summarized in the Table. They clearly show a much lower reactivity of (\pm)-**11** vs. PhNMe₂. For instance, a *Vilsmeier–Haack* formylation of PhNMe₂ gave 70% of aldehyde **12a**. On the contrary, with (\pm)-**11**, no formylation took place under identical conditions. A recently described mild iodination



^{a)} For conditions and yields, see Table.

Table. Reactions of PhNMe₂ and (\pm)-**11** with Selected Electrophiles. See also Scheme 2.

Method	Conditions ^{a)}	X	12 ([%] ^{b)} from PhNMe ₂	(\pm)- 13 ([%] ^{b)} from (\pm)- 11	(\pm)- 14 ([%] ^{b)} from (\pm)- 11
A	DMF, POCl ₃ , 2 h, 100°	CHO	12a (70) [18]	(\pm)- 13a (0)	(\pm)- 14a (0)
B1	I ₂ , dioxane/pyridine, 1 h, r.t.	I	12b (98) [19]	(\pm)- 13b (0)	(\pm)- 14b (0)
B2	ICl (1.1 equiv.), In(OTf) ₃ (0.5 equiv.), MeCN, 1 h, r.t.	I	12b (98) [20]	–	–
B2	ICl (2.2 equiv.), In(OTf) ₃ (1 equiv.), MeCN, 24 h, r.t.	I	–	(\pm)- 13b (23)	(\pm)- 14b (traces)
C	NBS (1 equiv.), DMF, 12 h, r.t.	Br	12c (91) ^{c)}	–	–
C	NBS (2 equiv.), DMF, 18 h, r.t.	Br	–	(\pm)- 13c (30)	(\pm)- 14c (30)
C	NBS (2.5 equiv.), DMF, 18 h, 80°	Br	–	(\pm)- 13c (25)	(\pm)- 14c (56)

^{a)} DMF = *N,N*-Dimethylformamide, TfO = trifluoromethanesulfonate, and NBS = *N*-bromosuccinimide. ^{b)} Isolated yield of analytically pure products. ^{c)} Prepared according to the published general procedure for the bromination of *N,N*-dialkylanilines [21].

of PhNMe₂ with molecular I₂ in dioxane/pyridine gave a nearly quantitative yield of the *para*-iodo derivative **12b**, while the starting material was quantitatively recovered in the case of (±)-**11**. Thus, the aromatic rings of the 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]-diazocine system appear to be inert towards less reactive electrophiles.

However, some other transformations demonstrated the feasibility of electrophilic substitution of (±)-**11**. For example, bromination of PhNMe₂ with *N*-bromosuccinimide (NBS) gave nearly quantitative yields of 4-bromoaniline (**12c**). When (±)-**11** was treated with 2 equiv. of NBS in DMF, 30% of bromide (±)-**13c** together with 30% of dibromide (±)-**14c** and *ca.* 10% of the starting material were isolated after 18 h at room temperature. When this reaction was performed at elevated temperature and with excess of NBS, the yield of the product of two-fold substitution (±)-**14c** was increased to 57%, while the yield of bromide (±)-**13c** was decreased to 25%, and no starting material was isolated. In addition, iodination of (±)-**11** with ICl in the presence of In(OTf)₃ as an activating *Lewis* acid proceeded much slower and with lower yield compared to PhNMe₂.

The results of the reactions between (±)-**11** and different electrophiles establish the much lower reactivity of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine compared to that of *N,N*-dialkylanilines. At the same time, these results suggest that the impact of a resonance structure such as **A-11** (Scheme 2) in (±)-**11** is small but not negligible. Indeed, aromatic electrophilic substitution, if any, occurs exclusively at C(2) and C(8) of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine, *i.e.*, in the *para*-position to the N-atom, and no isomeric products were isolated. In addition, (±)-**11** demonstrates a higher reactivity towards electrophiles compared to benzene, which does not give products of substitution with NBS and requires catalysis with *Lewis* acids and higher temperatures to obtain products of electrophilic bromination [22]. Thus, the data on the chemical reactivity of (±)-**11** in reactions with various electrophiles are consistent with the results of the calculations that predict, on the HOMO level, smaller LCAO coefficients on the N-atoms of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine derivatives than on those of PhNMe₂-derived analogs, but which are by no means negligible.

Conclusions. – In summary, we have reported the synthesis of chiral, donor-acceptor (push-pull) chromophores with a 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine scaffold. Theoretical calculations demonstrate a significant stabilization of the HOMO level resulting in a pronounced hypsochromic shift of the lowest-frequency absorption, compared to similar chromophores derived from PhNMe₂. The theoretical results and the spectral studies in combination with the data on the chemical reactivity of 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine towards aromatic electrophilic substitution confirms the nonnegligible delocalization of the lone pair of the bridge-head N-atoms in this heterocyclic system. We are currently working on the synthesis of novel chromophores with a 6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine scaffold as well as on the studies of their nonlinear optical properties.

S. S. is indebted to Prof. Y. Geerts, Université Libre de Bruxelles, for the opportunity to conduct an independent research program in his laboratory and for generous financial support. We thank Prof. R. Flammang and co-workers, Université Mons-Hainaut, for the measurement of mass spectra. The work in Mons was supported by the *Belgian Federal Government 'Interuniversity Attraction Pole in Supra-*

molecular Chemistry and Catalysis, PAI 5/3', and the Belgian National Fund for Scientific Research (FNRS/FRFC). J. C. is an FNRS Research Associate.

Experimental Part

General. All chemicals were purchased from Aldrich, Acros, or TCI and used without further purification unless stated otherwise. THF was refluxed over Na and benzophenone until a blue-violet color persisted and distilled directly into the reaction flask. The following compounds were prepared according to previously published procedures: **2** [10], (\pm)-**7** [3], and (\pm)-**11** [23] (we found our recently published procedure for the synthesis of (\pm)-**11** more convenient than the method of Kaupp *et al.* [24]). Column chromatography (CC): silica gel 60 (Macherey-Nagel, particle size 0.04–0.063 mm). TLC: precoated silica gel 60 F_{254} plates (Merck). UV/VIS Spectra: Agilent 8453-UV/VIS-NIR spectrophotometer; 1 cm cell at r.t.; λ_{\max} (ϵ_{\max} [M⁻¹ cm⁻¹]) in nm. ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) Spectra: Bruker Avance-300 spectrometer; CDCl₃ solns.; chemical shifts δ in ppm rel. to Me₄Si, coupling constants J in Hz. MS: Waters AutoSpec-6F instrument for EI and Waters QToF-2 instrument for ESI; in m/z with the lowest isotope mass. The analytical data of **12c** were identical to those of the authentic material purchased from Aldrich; the data of **13b,c** [23] and **14b,c** [11] were identical to those previously published.

2-[*(1E)*-2-[4-(Dimethylamino)phenyl]ethenyl]-3-ethylbenzothiazol-3-ium Iodide (**3**). A stirred mixture of (4-dimethylamino)benzaldehyde (**6**; 0.447 g, 3.00 mmol), 3-ethyl-2-methylbenzothiazol-3-ium iodide (**9**; 0.806 g, 2.64 mmol), pyridine (0.35 ml), and EtOH (35 ml) was heated to reflux for 18 h. The mixture was then allowed to reach r.t., and the resulting solid was filtered, washed with cold EtOH, and dried. Crystallization from EtOH (40 ml) afforded pure **3**·EtOH (1.09 g, 86%). Crystalline maroon solid. UV/VIS (EtOH): 528 (34000). ¹H-NMR (300 MHz, (CD₃)₂SO, 25°): 1.44 (*t*, J = 7.1, 3 H); 3.12 (*s*, 6 H); 4.84 (*q*, J = 6.9, 2 H); 6.84 (*d*, J = 9.3, 2 H); 7.62 (*d*, J = 15.3, 1 H); 7.64–7.82 (*m*, 2 H); 7.94 (*d*, J = 8.7, 2 H); 8.09 (*d*, J = 15.3, 1 H); 8.14 (*d*, J = 8.4, 1 H); 8.31 (*d*, J = 7.8, 1 H). ¹³C-NMR (75 MHz, (CD₃)₂SO, 25°): 13.7; 40.3; 43.4; 105.4; 111.8; 115.6; 121.3; 123.9; 127.1; 127.3; 128.8; 132.9; 140.7; 150.6; 153.4; 170.7. ESI-MS: 309.2 (M^+ , C₁₆H₂₁N₂S⁺; calc. 309.1).

(\pm)-2,8-Bis[*(1E)*-2-(4-nitrophenyl)ethenyl]-6H,12H-5,11-methanodibenzo[*b,f*][1,5]diazocine ((\pm)-**4**). A mixture of aldehyde (\pm)-**7** (0.278 g, 0.5 mmol), 4-nitrobenzeneacetic acid (**8**; 0.543 g, 3 mmol), and piperidine (0.30 ml, 3 mmol) was heated for 20 h at 120° (bath temp.). The mixture was allowed to reach r.t. and then dissolved in CH₂Cl₂ (20 ml). The resulting soln. was subjected to CC (SiO₂, CH₂Cl₂/AcOEt 5:1); pure (\pm)-**4** (108 mg, 21%). Orange solid. UV/VIS (EtOH): 382 (51000). ¹H-NMR (300 MHz, CDCl₃, 25°): 4.24 (*d*, J = 16.8, 2 H); 4.34 (*s*, 2 H); 4.75 (*d*, J = 16.8, 2 H); 6.98 (*d*, J = 16.5, 2 CH=CH); 7.09–7.19 (*m*, 6 H); 7.37 (*dd*, J = 8.4, 1.8, 2 H); 7.54 (*d*, J = 8.7, 4 H); 8.17 (*d*, J = 8.7, 4 H). ¹³C-NMR (75 MHz, CDCl₃, 25°): 58.7 (2 C); 66.9 (1 C); 124.2 (4 C); 125.4 (2 C); 125.5 (2 C); 125.8 (2 C); 126.1 (2 C); 126.6 (4 C); 128.2 (2 C); 132.2 (2 C); 132.6 (2 C); 143.9 (2 C); 146.6 (2 C); 148.8 (2 C). HR-EI-MS: 516.1766 (M^+ , C₃₁H₂₄N₄O₄⁺; calc. 516.1798).

(\pm)-2,2'-[6H,12H-5,11-methanodibenzo[*b,f*][1,5]diazocin-2,8-diyl-di-(*1E*)-ethene-2,1-diyl]bis[3-ethylbenzothiazol-3-ium] Diiodide ((\pm)-**5**). As described for **3**, with (\pm)-**7** (0.139 g, 0.499 mmol), **9** (0.308 g, 1.01 mmol), pyridine (0.14 ml), and EtOH (15 ml); pure (\pm)-**5** (0.225 g, 53%). Crystalline orange solid. UV/VIS (EtOH): 433 (52000). ¹H-NMR (300 MHz, (CD₃)₂SO, 25°): 1.44 (*t*, J = 7.1, 6 H); 4.32–4.41 (*m*, 4 H); 4.84 (*d*, J = 16.5, 2 H); 4.93 (*q*, J = 7.1, 4 H); 7.39 (*d*, J = 8.7, 2 H); 7.72–7.96 (*m*, 10 H); 8.13 (*d*, J = 15.9, 2 CH=CH); 8.28 (*d*, J = 8.7, 2 H); 8.42 (*d*, J = 6.9, 2 H). ¹³C-NMR (75 MHz, (CD₃)₂SO, 25°): 14.1 (2 C); 44.3 (2 C); 58.1 (2 C); 65.8 (1 C); 111.7 (2 C); 116.5 (2 C); 124.3 (2 C); 125.3 (2 C); 128.0 (2 C); 128.2 (2 C); 128.9 (2 C); 129.0 (4 C); 129.2 (2 C); 129.4 (2 C); 140.8 (2 C); 148.8 (2 C); 152.4 (2 C); 171.4 (2 C). HR-ESI-MS: 299.1111 (M^{2+} , C₃₇H₃₄N₄S₂²⁺; calc. 299.1107).

REFERENCES

- [1] U. Kiehne, T. Weilandt, A. Lützen, *Org. Lett.* **2007**, *9*, 1283; D. Didier, S. Sergeev, *Tetrahedron* **2007**, *63*, 3864; S. P. Bew, L. Gentil, V. Scholier, S. V. Sharma, *Chem. Commun.* **2007**, 389; U. Kiehne, A.

- Lützen, *Synthesis* **2004**, 1687; F. Hof, M. Schär, D. M. Scofield, F. Fischer, F. Diederich, S. Sergeev, *Helv. Chim. Acta* **2005**, 88, 2333; C. Solano, D. Svensson, Z. Olomi, J. Jensen, O. F. Wendt, K. Wärnmark, *Eur. J. Org. Chem.* **2005**, 3510; J. Jensen, J. Tejler, K. Wärnmark, *J. Org. Chem.* **2002**, 67, 6008; T. Mas, C. Pardo, J. Elguero, *Helv. Chim. Acta* **2005**, 88, 1199.
- [2] S. Paliwal, S. Geib, C. S. Wilcox, *J. Am. Chem. Soc.* **1994**, 116, 4497; E.-i. Kim, S. Paliwal, C. S. Wilcox, *J. Am. Chem. Soc.* **1998**, 120, 11192; F. Hof, D. M. Scofield, W. B. Schweizer, F. Diederich, *Angew. Chem., Int. Ed.* **2004**, 43, 5056.
- [3] S. Sergeev, M. Schär, P. Seiler, O. Lukyanova, L. Echegoyen, F. Diederich, *Chem.–Eur. J.* **2005**, 11, 2284.
- [4] W. W. H. Wong, F. Diederich, *Chem.–Eur. J.* **2006**, 12, 3463; S. Sergeev, F. Diederich, *Angew. Chem., Int. Ed.* **2004**, 43, 1738.
- [5] Y. Kubo, T. Ohno, J.-i. Yamanaka, S. Tokita, T. Iida, Y. Ishimaru, *J. Am. Chem. Soc.* **2001**, 123, 12700.
- [6] B. Dolensky, J. Elguero, V. Král, C. Pardo, M. Valík, *Adv. Heterocycl. Chem.* **2007**, 93, 1; M. Valík, R. M. Strongin, V. Král, *Supramol. Chem.* **2005**, 17, 347.
- [7] S. R. Marder, *Chem. Commun.* **2006**, 131.
- [8] H.-J. Deussen, C. Boutton, N. Thorup, T. Geisler, E. Hendrickx, K. Bechgaard, A. Persoons, T. Bjornholm, *Chem.–Eur. J.* **1998**, 4, 240.
- [9] H. Ihmels, D. Otto, *Top. Curr. Chem.* **2005**, 258, 161.
- [10] G.-D. Peng, A. D. Q. Li, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, 39, 1794.
- [11] J. Jensen, K. Wärnmark, *Synthesis* **2001**, 1873.
- [12] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, 107, 3902; AMPAC version 6.55, Semichem, Inc., Shawnee, Kansas, USA, 1997.
- [13] J. Ridley, M. Zerner, *Theor. Chim. Acta* **1973**, 32, 111.
- [14] J. Gierschner, J. Cornil, H.-J. Egelhaaf, *Adv. Mater.* **2007**, 19, 173.
- [15] L. C. T. Shoute, H. Y. Woo, D. Vak, G. C. Bazan, A. Myers Kelley, *J. Chem. Phys.* **2006**, 125, 054506; J. Kabatc, B. Jedrzejewska, P. Orlinski, J. Paczkowski, *Spectrochim. Acta, Part A* **2005**, 62, 115.
- [16] O. Lhost, J. L. Bredas, *J. Chem. Phys.* **1992**, 96, 5279.
- [17] A. Hayek, J.-F. Nicoud, F. Bolze, C. Bourgogne, P. L. Baldeck, *Angew. Chem., Int. Ed.* **2006**, 45, 6466.
- [18] E. E. Campaigne, W. L. Archer, *J. Am. Chem. Soc.* **1953**, 75, 989.
- [19] C. Monnereau, E. Blart, F. Odobel, *Tetrahedron Lett.* **2005**, 46, 5421.
- [20] R. Johnsson, A. Meijer, U. Ellervik, *Tetrahedron* **2005**, 61, 11657.
- [21] K. Staub, G. A. Levina, S. Barlow, T. C. Kowalczyk, H. S. Lackritz, M. Barzoukas, A. Fort, S. R. Marder, *J. Mater. Chem.* **2003**, 13, 825.
- [22] L. Horner, E. H. Winkelmann, *Angew. Chem.* **1959**, 71, 349.
- [23] D. Didier, S. Sergeev, *Eur. J. Org. Chem.* **2007**, 3905.
- [24] G. Kaupp, J. Schmeyers, J. Boy, *J. Prakt. Chem.* **2000**, 342, 269.

Received June 5, 2007