Photoelectron Spectra of Indigo Dyes, 3[+]

Photoelectron Spectra and Electronic Structures of a Series of Vinylogous Thioindigoid Compounds

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Dedicated to Professor Martin Klessinger on the occasion of his 65th birthday

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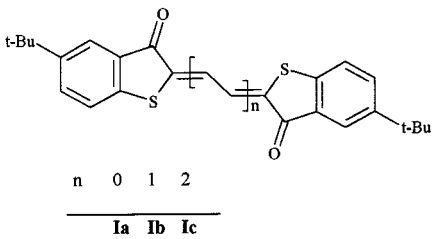
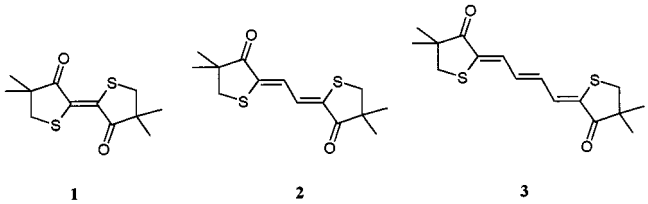
The molecular and the electronic structures of bi(4,4-dimethyl-3-oxotetrahydrothiophen-2-ylidene) (**1**), a compound comprising the basic chromophore of thioindigo dyes, and its two vinylogs **2** and **3** with two and three conjugated central double bonds, respectively, have been analyzed by B3LYP/6–31+G* calculations and UV photoelectron spectroscopy. The calculated structural parameters of **1–3** reveal no systematic variation. The first ionization potentials indicate no, or only a minor, increase in the energy of the highest occupied molecular orbital (HOMO) with the size of the chromophore. These findings are in accord with the corresponding characteristic optical properties of such indigoid compounds. For comparison, substituent effects on highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energies were analyzed by semi-empirical PM3 calculations in a series of α,ω-substituted linear conjugated polyenes. Systems with symmetrical substitution by two donor and two acceptor groups simulate the properties of **1–3**, having rather constant energies for these molecular orbitals and a narrow separation. In addition, the long-wavelength absorption of **1–3**, and probably of other indigoid compounds, is caused by the small overlap density of these molecular orbitals which are largely localized in different parts of the molecule.

Introduction

The unique optical properties of indigoid compounds have lead us to investigate the electronic structures of indigo[1] itself and some other indigo dyes[2] by UV photoelectron (PE) spectroscopy and quantum chemical calculations. A characteristic pattern of indigoids is that vinylogous compounds with several conjugated double bonds instead of the single central double bond of the parent system show no marked variation of the wavelength λ_{max} of their first absorption band.[3–7] As an example, the thioindigoid dyes **Ia–c** have λ_{max} values of 548, 524 and 522 nm (in cyclohexane), respectively.[8] This observation is in striking contrast with the general rule that the extension of a chromophore causes a bathochromic shift of the absorption band.[9][10] In order to elucidate whether this property is also reflected in the electronic structure of such compounds, we have studied the PE spectra of bi(4,4-dimethyl-3-oxotetrahydrothiophen-2-ylidene) (**1**),[11][12] a compound comprising the basic chromophore of thioindigo dyes, and its two vinyl analogs, 4,4,4′,4′-tetramethyl-2,2′-ethanediylidenebis(tetrahydrothiophene)-3,3′-dione (**2**)[12] and 4,4,4′,4′-tetramethyl-2,2′-(2-butene-1,4-diylidene)bis(tetrahydrothiophene)-3,3′-dione (**3**),[12] with two and three conjugated central double bonds, respectively.



Scheme 1. Structures of compounds **Ia–Ic**



Scheme 2. Structures of compounds **1–3**

Syntheses of all three compounds have been described in the literature together with an analysis of their spectroscopic properties.[11][12] The molecular structure of compound **1** has been studied by X-ray diffraction methods.[13] UV/Vis spectra of compounds **1–3** reveal the above-mentioned pattern, characteristic for indigoid compounds: λ_{max} of **2** (446 nm, in cyclohexane) is only a little shorter than

[+] Part 2: Ref.[2] – Part 1: Ref.[1]

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Table 1. Total energy E [au] and selected structure parameters [pm, °] of **1**, **2**, and **3** (B3LYP/6−31+G* results)

	1	**1** (X-ray[a])	**2**	**3**
E(M)[b]	−1413.768887		−1491.179784	−1568.591548
S^1-C^2	176.1	173.5(4)	176.2	176.5
C^2-C^3	148.4	148.4(5)	149.5	149.2
C^3-C^4	153.6	151.6(7)	154.0	154.1
C^4-C^5	154.0	152.2(6)	154.0	154.0
S^1-C^5	185.6	183.1(5)	185.2	185.2
C^2-C^9	136.7	137.2(7)	136.4	136.4
C^3-O^6	122.3	121.6(5)	122.0	122.1
C^4-C^7	153.6	151.7(7)	153.6	153.6
C^4-C^8	154.9	154.0(9)	154.9	154.8
C^9-C^{10}	–	–	142.9	143.0
$C^{10}-C^{11}$	–	–	–	136.8
$S^1-C^2-C^3-C^4$	6.8	8.5	4.4	3.7
$C^3-C^2-S^1-C^5$	9.9	10.1	12.3	13.0
$C^3-C^4-C^5-S^1$	30.0	33.1	30.7	31.0
$C^2-C^9-C^{10}-C^{11}$	–	–	180.0	178.8
$E(M^{+\cdot})$[b]	−1413.495198		−1490.914366	−1568.336735

[a] Ref.[13] – [b] M = molecule, $M^{+\cdot}$ = molecular radical cation with the same geometry as M.

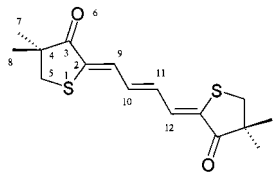
that of **1** (450 nm) while that of **3** (454 nm) is a little longer.[12] The absorption of these vinylogous compounds thus suffers a hypsochromic shift when the chromophore is extended (**1** → **2**). A further extension of the chromophore by an additional C=C double bond (**2** → **3**) leads to a small shift to longer wavelength. On the other hand, the extension of the chromophore is accompanied by a strong increase of the extinction coefficient of the absorption (**1**: 13400, **2**: 31500, **3**: 46800 L mol^{-1} cm^{-1}).[12]

Results and Discussion

Structures

Varying degrees of conjugation in the vinylogous series of compounds **1**−**3** should be reflected in systematic changes of structural parameters. In particular, the bond lengths in the chains O=C−(C=C)$_n$−C=O and S−C−(C=C)$_n$−C−S (n = 1−3) should show such shifts. Since actually only small effects can be expected, it is essential that the structural parameters of all three molecules are accurately determined by the same method. For this purpose we have used the B3LYP method with the basis set 6−31+G*. The molecules were assumed to be centrosymmetric, i.e. the molecular point group C_i was chosen for the calculations. For compound **3** the E configuration at the central C=C bond and the antiperiplanar conformation at the adjoining C−C bonds is confirmed by ^{1}H-NMR spectroscopy. The protons in the chain $=H^9C-CH^{10}=CH^{11}-CH^{12}=$ (cf. Scheme 3) between the two five-membered rings form an AA′MM′ spin system. Analysis of the spectrum by simulation and iteration afforded the following four coupling constants: $^3J_{9,10}$ = 11.88 Hz, $^4J_{9,11}$ = −0.97 Hz, $^5J_{9,12}$ = −0.11 Hz, $^3J_{10,11}$ = 14.56 Hz. Both vicinal couplings (^3J) are thus in the range of dihedral angles of approximately 180°.

Some important calculated structural parameters are summarized in Table 1. For **1** the results of the X-ray analysis[13] are also given. A satisfactory agreement between calculated and experimental parameters can be ascertained. Only very small differences in the respective structural parameters of the three molecules are found, and there are no clear systematic trends in these data. In particular, the bond lengths of **2** and **3** are equal within 0.2 pm. Compared to **1**, the bond lengths of the other two molecules differ by less than 0.9 pm. From the calculated bond lengths, π-bond orders of about 0.80 can be estimated for the formal double bonds $C^2=C^9$ and $C^{10}=C^{11}$, whereas a π-bond order of about 0.45 is obtained for the formal single bonds C^9-C^{10}. The torsional angles given in Table 1 also show very small variations. These findings lead to the conclusion that conjugation in the chromophores does not essentially vary with the size of the vinylogous molecules.



Scheme 3. Atom numbering scheme for compounds **1**−**3**

Photoelectron Spectra and Electronic Structures of 1−3

The electronic structure of indigoid molecules, including that of compound **1**, has been discussed previously.[1][2] In comparison to **1**, compounds **2** and **3** are characterized by one or two additional occupied π-type MOs, respectively. The PE spectra of **1**−**3** are depicted in Figure 1. The PE spectrum of compound **1**[2] is included in Figure 1 in order to show the relationship between these spectra. In Tables 2−4, the relevant ionization potentials (*IP*s) are summarized together with the results of quantum chemical calculations. A correlation diagram of the *IP*s is shown in Figure 2. Although the actual symmetry of the molecules is lower

(see above), the molecular orbitals are classified in terms of the point group C_{2h} since the chromophore, i.e. the central double bond(s), the sulfur atoms and the carbonyl groups, is essentially planar.

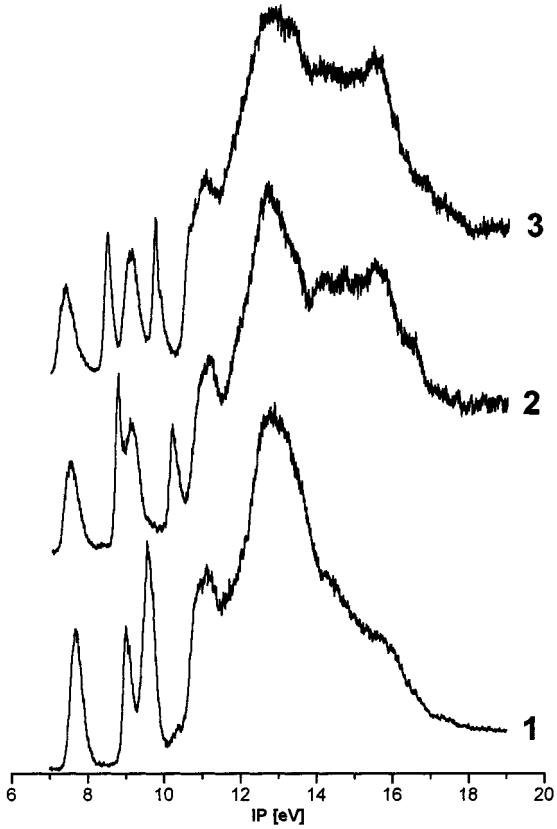


Figure 1. PE spectra of compounds **1**–**3**

Table 2. Ionization potentials *IP* [eV] and orbital energies ε [eV] of **1**

IP_v	PM3 −ε	B3LYP/6−31+G* −ε, IP_v[a]		
	1.07	2.70	π_6	B_g
7.60	8.47	5.75, 7.45	π_5	A_u
8.87	10.01	7.02, 8.72	π_4	B_g
9.42	10.50	7.33, 9.03	n^+(O)	A_g
	11.08	7.63, 10.33	n^-(O)	B_u
10.77	12.11	8.76, 10.46	π_3	A_u
10.96	11.90	9.03, 10.73	n^-(S)	B_u
	11.99	9.12, 10.82	n^+(S)	A_g

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry (see Table 1). Higher *IP*s: $IP_i = -\varepsilon_i + 1.70$ eV (see text).

As a consequence of the semi-empirical method, the orbital energies ε calculated by PM3, are too low by 0.6−1.7 eV, whereas for the B3LYP method they are too high by about 2 eV (Tables 2−4). However, both methods lead to the same assignment of the *IP*s, using Koopmans' theorem $IP_i = -\varepsilon_i$.[14] Much better agreement between experimental and theoretical values can be expected for the first vertical *IP* (IP_{1v}) when the energies of the molecule and the radical cation are calculated by the B3LYP method.

Table 3. Ionization potentials *IP* [eV] and orbital energies ε [eV] of **2**

IP_v	PM3 −ε	B3LYP/6−31+G* −ε, IP_v[a]		
	1.32	2.91	π_7	A_u
7.59	8.46	5.70, 7.22	π_6	B_g
8.80	9.40	6.99, 8.51	π_5	A_u
9.14	10.81	7.15, 8.67	n^+(O)	A_g
	10.98	7.28, 8.80	n^-(O)	B_u
10.21	11.35	8.42, 9.93	π_4	B_g
11.18	11.72	9.05, 10.57	n^+(S)	A_g
	12.00	9.12, 10.67	n^-(S)	B_u

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry (see Table 1). Higher *IP*s: $IP_i = -\varepsilon_i + 1.52$ eV (see text).

Table 4. Ionization potentials *IP* [eV] and orbital energies ε [eV] of **3**

IP	PM3 −ε	B3LYP/6−31+G* −ε, IP_v[a]		
	1.41	2.91	π_8	B_g
7.40	8.39	5.70, 6.93	π_7	A_u
8.46	9.09	6.99, 8.22	π_6	B_g
9.10	10.84	7.15, 8.37	n^+(O)	A_g
	10.89	7.28, 8.51	n^-(O)	B_u
9.72	10.58	8.42, 9.65	π_5	A_u
10.55	11.96	9.05, 10.28	π_4	B_g
11.0	11.76	9.12, 10.35	n^+(S)	A_g
	11.89	9.30, 10.53	n^-(S)	B_u

[a] Calculation of first vertical *IP*: energy difference of molecule and radical cation with identical geometry (see Table 1). Higher *IP*s: $IP_i = -\varepsilon_i + 1.23$ eV (see text).

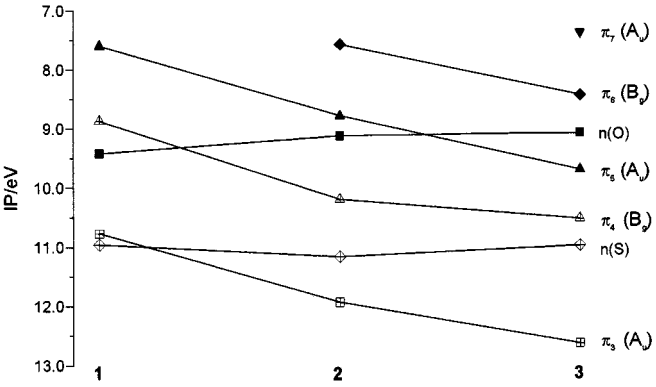


Figure 2. Correlation diagram of *IP* values of compounds **1**–**3**

For IP_{1v}, a single-point calculation was performed for the radical cation ($M^{+\cdot}$) using the molecule's (M) geometry. The corresponding energy values are given in Table 1. We can now correct other ε^{B3LYP} values by the difference Δ = 1.70 eV (compound **1**, Table 2) between −ε(HOMO) and the calculated IP_{1v} in order to obtain higher IP_v values.[15] The corresponding Δ values for **2** and **3** are 1.52 and 1.23 eV, respectively (Tables 3 and 4).

Surprisingly, the B3LYP calculated IP_{1v} values of **1**–**3** vary more (by almost 0.7 eV) than the experimental data (0.2 eV). With increasing size of the molecule, the calculated

IP_{1v} value becomes less accurate, while for the orbital energies, ε, no such variation is noticed; the deviation from Koopmans' approximation, $IP_i = -\varepsilon_i$,[14] is 1.8−2.1 eV for all three molecules. An explanation for this finding might be that the basis set (6−31+G*) used in the calculations was insufficient. We have therefore calculated the IP_{1v} values for **1**−**3** using the basis set 6−311++G** in single-point calculations without further geometry optimization. There were only marginal changes (< 0.04 eV) in MO energies. For **1** we have also optimized the geometry with the expanded basis set, and again only minor changes in structure parameters resulted. Most bond lengths were varied by less than 0.2 pm and the torsional angles by less than 0.5°. For IP_{1v} of **1**, calculated as the energy difference of the structure-optimized molecule and the radical cation with the same geometry, a value of 7.46 eV was obtained that is only 0.01 eV larger than that calculated with the smaller basis set. Therefore, we can conclude that the basis set 6−31+G* is adequate to study the molecules **1**−**3** and we did not find it justified to continue with these lengthy and time-demanding computations for compounds **2** and **3**.

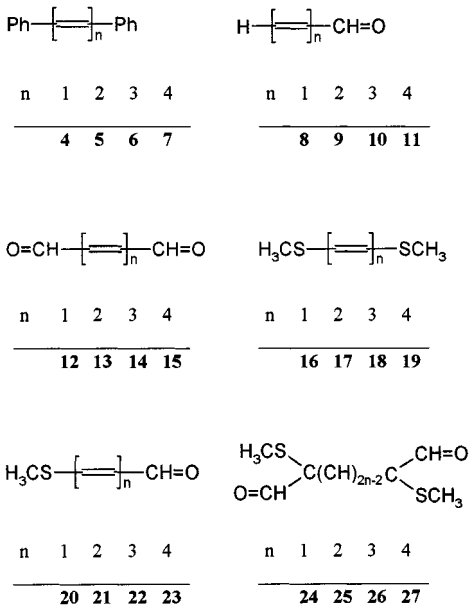
While in compound **1** there are five occupied π-type MOs, compounds **2** and **3** have six and seven such orbitals, respectively. On the other hand, each of these molecules contains two n_π(O) and two n_π(S) orbitals which can be classified as symmetric and antisymmetric combinations of the respective orbitals of the two oxygen and the two sulfur atoms. In indigoid compounds, the two n_π(O) ionizations can differ by up to 0.7 eV.[2] In some cases, however, they form a single, relatively broad ionization band, which prevents the determination of individual *IP* values. This is also the case for the compounds studied here so that no splittings of $IP[n_\pi^+(O)]$ and $IP[n_\pi^-(O)]$ can be given. According to the semi-empirical PM3 results the energy separation of the corresponding orbitals decreases with the length of the conjugated system separating the oxygen atoms. In **1** the two orbitals are split by 0.58 eV, in **2** by 0.50 eV and in **3** by 0.11 eV. The analogous energy separation of the corresponding n_π(S) orbitals is only about 0.02−0.09 eV. The B3LYP results indicate energy splits of 0.1−0.4 eV for the *n*(O) orbitals and 0.02−0.09 eV for the *n*(S) orbitals.

Figure 2 clearly reveals an inverse behaviour of π and *n* *IP*s. While the respective π *IP*s *increase* with the size of the molecules, the *n*(O) and the *n*(S) ionizations *decrease*. In the diagram, *IP*s related to MOs of the same symmetry and the same number of nodes are connected. The stabilization of a certain π-MO caused by the extension of the chromophore is approximately equal to the energy difference of two neighboring π-MOs so that so following relation holds: $-\varepsilon[\pi_i(n)] \approx -\varepsilon[\pi_{i+1}(n+1)]$, *n* indicates the number of central double bonds and coincides with the numbers of **1**−**3**. Since neighboring π-MOs differ by one in the number of nodes, the stabilization of a certain π-MO caused by the introduction of an additional C=C double bond is compensated when an additional node is introduced. The following data may serve to illustrate this relation: $IP[\pi_4(\mathbf{1})] = 8.87 \approx IP[\pi_5(\mathbf{2})] = 8.80 \approx IP[\pi_6(\mathbf{3})] = 8.46$ eV. That this relationships is followed particularly well for the HOMO energies and the first *IP*s of **1**−**3** has already been pointed out. Inspection of the PM3-calculated orbital energies reveals that this relation also holds for the unoccupied (virtual) π-MOs; only for the lowest occupied orbitals ($\pi_1-\pi_3$) does it fail. Destabilization of *n*(O) and *n*(S) orbitals with increasing size of the molecules can be attributed to *n*/σ interactions, i.e. to delocalization of these orbitals.

With respect to the wavelength of the first absorption maximum of **1**−**3**, the first *IP* (IP_1) of these compounds is most important. **1** and **2** have the same IP_1 (the difference of 0.01 eV, Tables 2 and 3, falls within the accuracy of the measurement, see Experimental Section). On the other hand, in compound **3** IP_1 is lowered by 0.19 eV relative to its position in **1** and **2**. These values may be compared with the first *IP*s of ethene (10.51 eV[16]), 1,3-butadiene (9.09 eV[16]) and 1,3,5-hexatriene (8.29 eV[17]). They exhibit the well-known pattern of increasing HOMO energy in conjugated polyenes which are accompanied by decreasing HOMO−LUMO excitation energies.[9][10] As another series of compounds showing the effect of the length of a conjugated system, the α,ω-diphenylpolyenes[18][19] **4** (IP_1 = 7.93 eV), **5** (7.54 eV), **6** (7.27 eV) and **7** (7.19 eV) may be considered. Here the decrease of the energy values is much smaller than in the unsubstituted polyenes and convergence to a constant value (approximately 7.1 eV) at long chain length is observed. In polyene aldehydes[18] the decrease of the *IP* related to the highest occupied π-MO, **8** (10.35 eV), **9** (9.22 eV) and **10** (8.42 eV), suggests that a constant value might be reached after a few further steps. The best series to compare with **1**−**3** would be dicarbonyl compounds like the dialdehydes glyoxal (**12**) (IP_1 = 10.60 eV[16]), fumaraldehyde (**13**), muconaldehyde (**14**) and deca-2,4,6,8-tetraenedial (**15**), and the dithioethers **16**−**19**. However, with only a few exceptions the corresponding *IP* values are unknown whilst to our knowledge, data of other similar series of α,ω-disubstituted polyenes are not available. Therefore, the only complete series is that of the diphenylpolyenes which leads to the question why in the thioindigoid series **1**−**3** the constant value is already reached in the first member.

HOMO and LUMO Energies of Conjugated Polyenes

Since the desired experimental data (*IP* values) are not available we have performed model calculations on some α,ω-di- and α,α,ω,ω-tetrasubstituted linear polyenes in order to elucidate the influence of donor and/or acceptor substituents on the energies of HOMOs and LUMOs. In general, it is assumed that donor groups (X) destabilize π and π*-MOs whereas the inverse holds for acceptor groups (Z).[20] For reference, the series of unsubstituted polyenes (from ethene to octatetraene) is included. The groups SCH_3 and CH=O were chosen as donor (X) and acceptor (Z) substituents, respectively, in order to simulate the environment of the central double-bond system in **1**−**3**. In the calculations, the substituents were kept coplanar with the polyene system in order to facilitate optimal interaction. The results are summarized in Table 5.



Scheme 4. Structures of compounds **4−27**

Table 5. LUMO and HOMO energies [eV] of α,ω-di- and α,α,ω,ω-tetrasubstituted polyenes (PM3 results)

[a]	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$H(CH{=}CH)_nH$				
LUMO	3.88	0.26	−0.25	−0.56
HOMO	−10.64	−9.47	−8.90	−8.58
$X(CH{=}CH)_nX$				
LUMO	−0.12	−0.28	−0.62	−0.83
HOMO	−8.23	−8.13	−8.07	−8.03
$Z(CH{=}CH)_nZ$				
LUMO	−1.11	−1.33	−1.44	−1.49
HOMO	−10.92	−10.18	−9.55	−9.15
$X(CH{=}CH)_nZ$				
LUMO	−0.46	−0.86	−1.07	−1.19
HOMO	−9.07	−8.73	−8.52	−8.38
$XZC(CH)_{2n-2}ZX$[b]				
LUMO	−1.36	−1.51	−1.56	−1.57
HOMO	−8.64	−8.51	−8.40	−8.33

[a] $X = S{-}CH_3$, $Z = CHO$. − [b] Planar molecules.

As expected, in all cases the splitting of the HOMO and LUMO energies decreases with the chain length. However, in all substituted molecules the splitting is smaller than in the unsubstituted parent hydrocarbons. In the series $Z(CH{=}CH)_nZ$ of disubstituted molecules with Z = CHO (**12−15**), the HOMO energies are much more affected than the LUMO energies, while the reverse holds for the molecules $X(CH{=}CH)_nX$ with $X = S{-}CH_3$ (**16−19**). The merocyanine-like molecules $X(CH{=}CH)_nZ$ (**20−23**), substituted with one donor (X) and one acceptor group (Z), are noteworthy because the HOMO and the LUMO energies show the same variation with the chain length. And, finally, in the tetrasubstituted molecules $ZXC(CH)_{2n-2}CXZ$ (**24−27**) both the HOMO and the LUMO energies remain rather constant, i.e. the HOMOs follow those of the donor- and the LUMOs follow those of the acceptor-disubstituted molecules. The tetrasubstituted molecules which can be classified as push-pull or captodative systems are thus good models for the vinylogous indigoid compounds **1−3**.

Electronic Structure and Light Absorption of Indigoid Compounds

The fact that the central extension of the chromophore in the compounds **2** and **3**, compared to **1**, has no, or only a minor effect on the first *IP*, makes these compounds clearly different from ordinary conjugated systems and is in accordance with their optical properties.[12] The HOMO of indigoid compounds to which IP_1 is related, has an exceptionally high energy owing to the destabilizing effect of the two donor groups connected to the central C=C double bond.[2] Similarly, the energy of the LUMO is low because of the stabilizing effect of the two carbonyl groups. The energy gap between HOMO and LUMO thus becomes rather narrow and the energy of the transition to the first excited state is low. Oxidation and reduction should be easily feasible for all three compounds.

The HOMOs and LUMOs of compounds **1−3**, as calculated by the PM3 method, are depicted in Figure 3. In all three compounds, the HOMO has largest coefficients on the two sulfur atoms so that the insertion of additional C=C groups has only a minor effect on the MO energy. So, the HOMO energy, as calculated by PM3, increases only by about 0.1 eV in the series **1** → **3** whilst the LUMO energy decreases by about 0.3 eV. The corresponding B3LYP values are 0.4 eV for the HOMO and 0.2 eV for the LUMO energies.

The singlet excitation energy $\Delta E_{i\rightarrow k}$ of an electronic transition can be expressed as Equation 1 in which ε_k and ε_i are the energies of the two involved orbitals, J_{ik} is the Coulomb and K_{ik} the exchange integral.[9][10] Since both J_{ik} and K_{ik} are positive and K_{ik} is generally much smaller than J_{ik}, the excitation energy is smaller than the MO energy difference $\Delta\varepsilon_{ik}$.

$$\Delta E_{i\rightarrow k} = \varepsilon_k - \varepsilon_i - J_{ik} + 2K_{ik} = \Delta\varepsilon_{ik} - J_{ik} + 2K_{ik} \quad (1)$$

Although the assumption that the HOMO−LUMO energy gap $\Delta\varepsilon$ might serve as an approximation for the electronic excitation energy ΔE is thus far too simple it has been shown that these two properties are linearly correlated in certain classes of compounds.[9][10] Regression analysis of the λ_{max} data and PM3-calculated $\Delta\varepsilon$ values of polyenes $H{-}(CH{=}CH)_n{-}H$ with $n = 1{-}8$ reveals the linear correlation $\Delta\varepsilon = 1.08\ \Delta E + 3.66$ (eV) with a correlation coefficient of $r = 0.999$.

In Table 6, the experimental excitation energies ΔE of **1−3** for the first absorption[12] are summarized together with the corresponding results of PM3 calculations and the energy differences of the HOMOs and LUMOs of these molecules. The data indicate that, as expected, the $\Delta\varepsilon$ values calculated by the PM3 method are considerably larger than the experimental ΔE values. However, the B3LYP method affords data that are surprisingly close to the experimental ones. On the other hand, the PM3-calculated ΔE values are

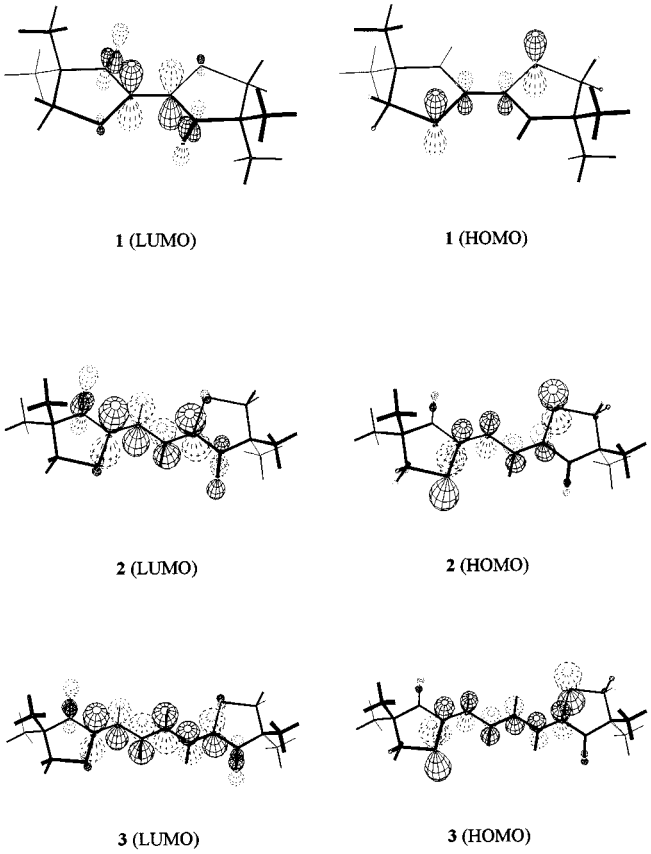


Figure 3. HOMO and LUMO of compounds **1**−**3** (PM3 results)

too large by about 20−40%. Analysis of the data reveals that there is no linear correlation between calculated and experimental values (*r* values are between 0.14 and 0.20). It has, however, to be taken into account that the experimental ΔE values vary only by 0.06 eV (2%) so that all theoretical methods are probably inadequate to reproduce the observed trend correctly.

Table 6. Experimental and calculated excitation energies ΔE [eV] and HOMO−LUMO energy differences $\Delta\varepsilon$ [eV] of compounds **1**−**3**

	ΔE (exp.)[a]	ΔE (PM3)[b]	$\Delta\varepsilon$ (PM3)	$\Delta\varepsilon$ (B3LYP)[c]
1	2.76	3.34	7.40	3.05
2	2.80	3.68	7.14	2.79
3	2.74	3.85	6.98	2.79

[a] Ref.[12] − [b] Vertical transition. − [c] Basis set: 6−31+G*.

When for indigoid compounds **1**−**3**, $\Delta E_{i\rightarrow k}$ and $\Delta\varepsilon_{ik}$ vary little with the extension of the central π electron system then also the other two parameters of Equation 1 should be rather the same. For K_{ik} a small value can be expected since HOMOs and LUMOs are largely localized in different parts of the molecules[6,9,10] (Figure 3). In addition, for neighboring C atoms in the chain between the rings of **1**−**3** the orbital coefficients in these MOs have either the same or opposite signs which results in vanishing contributions to the overlap integral of these parts of the molecules. The close similarity of the HOMOs and the LUMOs of **1**−**3** also causes the Coulomb integral J_{ik} to have similar values. A narrow energy gap of HOMO and LUMO, their small overlap density leading to small K_{ik} and little variation in J_{ik} can thus be considered as the origin of the long-wavelength absorption of **1**−**3** and likely of other indigoid compounds.

The π-electron system of the basic indigo chromophore can formally be obtained by joining two identical fragments. The coupling of two radical centres thus affords one bonding (HOMO) and one antibonding (LUMO) π MO. It has been pointed out by Klessinger[5] that the small HOMO−LUMO energy gap of indigoid compounds, and thus their long-wavelength absorption, results from a pronounced delocalization of the unpaired electron in the radical fragments due to captodative radical stabilization.[21]

Experimental Section

General: The ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker DRX500 (AVANCE) spectrometer. The following frequencies were used: 500.13 MHz (^{1}H), and 125.76 MHz (^{13}C). The spectra were measured as solutions in a 5-mm tube at room temperature with the solvent $CDCl_3$. The chemical shifts are reported in units of parts per million (δ) relative to tetramethylsilane (^{1}H, ^{13}C) as internal standard. Coupling constants *J* are given in Hz. For spectral simulations the program WINDAISY of Bruker was used. − Infrared (IR) spectra were recorded with a BioRad FTS 135 Fourier transform IR spectrometer. Only the most significant absorptions are given. − Electron impact mass spectra (MS) were obtained with a Hewlett Packard HP 5971A MSD instrument (70 eV). The intensities are reported as a percentage relative to the base peak after the corresponding *m*/*z* value. For high-resolution measurements a Fisons VG Prospec 3000 (70 eV) instrument was used. − PE spectra were recorded with a UPG200 spectrometer of Leybold−Heraeus equipped with an He(I) radiation source (21.21 eV). The energy scale was calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ± 0.03 eV for ionization energies; for broad and overlapping signals it was only ± 0.1 eV. Samples were heated in order to reach sufficient vapour pressure: **1** 190°C, **2** 230°C, **3** 250°C. − Semi-empirical PM3[22] calculations were performed with the MOPAC93[23] program package, B3LYP[24−27] calculations with the program GAUSSIAN 94.[28] If not stated otherwise, geometries were fully optimized at the respective levels of theory. MOs were plotted by using the program PERVAL.[29] − Compounds **1**,[11] **2**[12] and **3**[12] were synthesized as described in the literature. Of the latter two compounds some spectra were measured for their characterization.

4,4,4′,4′-Tetramethyl-2,2′-ethanediylidenebis(tetrahydrothiophene)-3,3′-dione (2): ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 12 H, CH_3), 2.99 (s, 4 H, CH_2), 7.01 (s, 2 H, CH). − ^{13}C NMR ($CDCl_3$): δ = 24.28 (CH_3), 39.87 (CH_2), 46.07 (>C<), 122.35 (CH), 140.29 (>C=), 204.92 (>C=O). − IR (KBr): $\tilde{\nu}$ = 3368 cm^{-1} (2 C=O), 2966 (C=O), 1538 (C=C), 1464, 1270, 1074, 1001, 875, 821, 748. − MS EI(70 eV); *m*/*z* (%): 282 (54) [M^+], 198 (100), 183 (25), 142 (15), 114 (41). − HR-MS; $C_{14}H_{18}O_2S_2$ [M^+]: calcd. 282.0748; found 282.0739.

4,4,4′,4′-Tetramethyl-2,2′-(2-butene-1,4-diylidene)bis(tetrahydrothiophene)-3,3′-dione (3): ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 12 H, CH_3), 2.99 (s, 4 H, CH_2), 6.61−6.67 (m, 2 H, CH), 7.03−7.09 (m,

2 H, CH). The multiplets centred at δ = 6.64 and δ = 7.06 belong to an AA′MM′ system. – ^{13}C NMR ($CDCl_3$): δ = 24.26 (CH_3), 39.88 (CH_2), 46.05 (>C<), 126.17 (CH), 135.33 (CH), 135.88 (>C=), 205.17 (>C=O). – IR (KBr): $\tilde{\nu}$ = 3375 cm^{-1} (2 C=O), 2974 (C–H), 1696 (C=O), 1574 (C=C), 1278, 1243, 1077, 973, 664. – MS EI(70 eV); *m/z* (%): 308 (100) [M^+], 293 (32), 224 (30), 140 (76), 96 (20). – HR-MS; $C_{16}H_{20}O_2S_2$ [M^+]: calcd. 308.0905; found 308.0899.

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