

FULL PAPER

The Origin of the Color of 1,2-Dithiins - Interpretation by Kohn-Sham Orbitals

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Abstract According to calculations by time-dependent density-functional theory (TD-DFT) the wine-red color of the half-chair (C_2) 1,2-dithiin (**1**) is mainly due to a one-electron transition between the frontier orbitals. These orbitals are characterized by local two-center CC π bonds. The symmetric HOMO of the twisted structure **1** correlates with the fully delocalized HOMO of the planar reference structure with C_{2v} symmetry. The anti-symmetrical LUMO correlates both with the essentially localized σ^* (SS) of the LUMO and the π^* of the LUMO+1 of the planar compound. Thus the dominating one-electron transition of **1** has some $\pi \rightarrow \sigma^*$ character in the terminology of the planar system with a strong admixture of the anti-bonding combination of the CC bond orbitals to the σ^* -type LUMO. The color of 1,2-dithiins are unique because of the simultaneous presence of a non-coplanar C=C bond system and the SS bond. For the sake of comparison calculations were also performed at *ab initio* levels of theory (TD-RHF, SCI, EOM-CCSD and CASPT2). Although the absorption wavelengths are strongly underestimated by SCI and TD-RHF the order and the nature of the lowest-excited states are the same as those found by TD-DFT. The electron excitation of 1,2-dithiin is compared with that of 1,2-dithiane (**3**). In addition, the structure and the energetics of 1,2-dithiin are compared with 1,4-dithiin (**4**) and thiepin (**5**).

Keywords 1,2-Dithiin, Molecular structure, Electron delocalization, Electronic transition, Time-dependent density-functional theory

Introduction

Many chromophores absorb light mostly due to a single absorption band in the visible region or to the tail into the visible of a UV absorption band. Experimental chemists generally report spectral absorptions with the wavelengths

of maximal absorption (λ_{\max}). The energy at the absorption maximum corresponds approximately to the calculated vertical transition energy. Different quantum chemical models have been developed to calculate electronic transitions at non-empirical levels [1].

A classification of electronic transitions can principally be given by molecular state notations. One component is the molecular symmetry of the ground and the excited state. A clear interpretation of the electronic transitions in terms of molecular substructures (NB-, LE-, and CT-structures) [2] is more difficult or impossible at higher levels of theory. However, as long as the theory is based on MOs, the orbital

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Dedicated to Professor Paul Ragué von Schleyer on the occasion of his 70th birthday

Table 1 Selected bond lengths R (in Å) and dihedral angles θ (in degrees) for 1,2-dithiin (**1**) calculated by RHF [a], DFT [b] and MP2 [c]

	R(C=C)		R(C-C)		R(C-S)		R(S-S)		θ (CSSC)		θ (CCCC)	
	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C ₂	C _{2v}	C ₂
RHF	1.319	1.324	1.472	1.470	1.768	1.774	2.108	2.064	0.0	49.6	0.0	26.1
DFT	1.342	1.348	1.464	1.460	1.772	1.782	2.171	2.110	0.0	49.5	0.0	26.2
MP2	1.342	1.351	1.455	1.448	1.754	1.761	2.122	2.057	0.0	55.1	0.0	29.0
Exp. [d]		1.353		1.451		1.759		2.051		53.9		29.0

[a] RHF/6-31G*, cf. Fig. 2

[b] B3LYP/6-31+G(d,p)

[c] MP2(FC)/6-31G(2df,p)

[d] MW-spectroscopy, see ref [19]

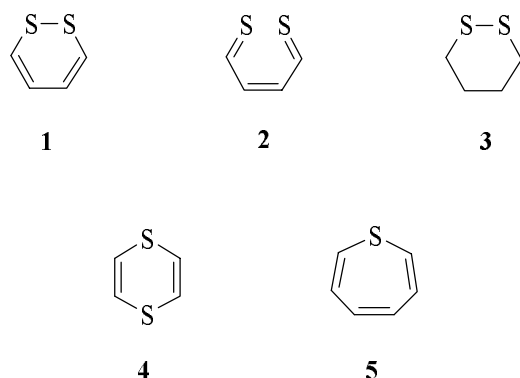
concept in molecular spectroscopy is valuable [3]. The transitions between electronic states may be interpreted, in an approximate way, in terms of one-electron transitions. This concept is also applicable for the Hohenberg-Kohn-Sham density-functional theory based on Kohn-Sham (KS) orbitals [4]. Thus electronic excitations calculated by time-dependent density-functional theory (TD-DFT) can be analyzed in terms of the KS one-electron transitions in notations first introduced by Kasha [5], such as $\pi \rightarrow \pi^*$, $n(\sigma) \rightarrow \pi$, $\pi \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$ etc. However, this one-electron notation is only strictly applicable for molecules with a plane of symmetry. If the molecule is not planar this classification is not valid. Then the one-electron transitions can no longer be described in the terms mentioned above. In these cases a pictorial presentation of the MOs becomes important and essential for understanding. Fortunately, useful programs for depicting MOs are now available, e.g. MOLDEEN [6]. This program is used in conjunction with calculations using the GAUSSIAN program package [7].

To illustrate the analysis of the nature of electronic transitions with the help of graphical representations, the twisted 1,2-dithiin (**1**) is an informative example (cf. Scheme 1). The parent compound was synthesized by Schroth et al. [8] and progress in 1,2-dithiin chemistry has been reviewed recently [9]. These heterocycles attract much current interest because

of their antibacterial, antiviral, antibiotic and anti HIV activities [10]. Except for dibenzo[ce][1,2]dithiin and some related more highly annulated compounds, 1,2-dithiins display an absorption band of medium intensity in the visible region between about 400 and 500 nm with molar absorption coefficients of about 100 cm² mmol⁻¹ at the absorption maximum. Consequently, the compounds are yellow to violet in color [9b,10b]. The color of 1,2-dithiins led to some confusion in the past. At first glance, the observed color suggests a dithione rather than a cyclic disulfide structure. Thus, the question was asked whether the open-chain valence isomer (Z)-2-enedithione **2** or its rotamers were responsible for the color. The possibility of the presence of the triplet of **1** giving rise to the color has also been considered [11]. Experimental [12] and theoretical results [13], however, have unequivocally confirmed the cyclic 1,2-dithiin structure. Without doubt, the origin of the color is due to the cyclic disulfide structure. In contrast to the wine-red colored 1,2-dithiin (absorption maximum at about 460 nm) the saturated 1,2-dithiane (**3**) is colorless (290 nm) [14] as is the isomeric 1,4-dithiin (**4**) (270 nm) [15]. Huisgen regarded the light absorption of **1** as an enigma because "it conflicted with the chemical intuition for a cyclic conjugated disulfide" [16]. According to Schroth, the color of 1,2-dithiin "presents even today a theoretical challenge with respect to the non-planar structure and the absence of any classical chromophore" [17].

The cyclic half-chair structure of **1** was first predicted by MP2 calculations [18]. The calculated geometrical parameters are in excellent agreement with the recent results of microwave spectroscopy [19]. Based on the MP2 structure, the lowest energy transitions were first calculated by the multi-configurational approach known as CIPSI [20]. The results of this study were promising and proved to be essentially correct in view of our recent studies using other theoretical models. However, the pictorial representation of the results was limited that time.

The aim of this study was to calculate the lowest-energy transitions responsible for the color band by the TD-DFT method and to use KS-orbitals for interpretation of the results. In the search for an interpretation of the one-electron transitions, the relevant MOs of twisted **1** are related to those of the planar structure and of the corresponding saturated

**Scheme 1** Formulas

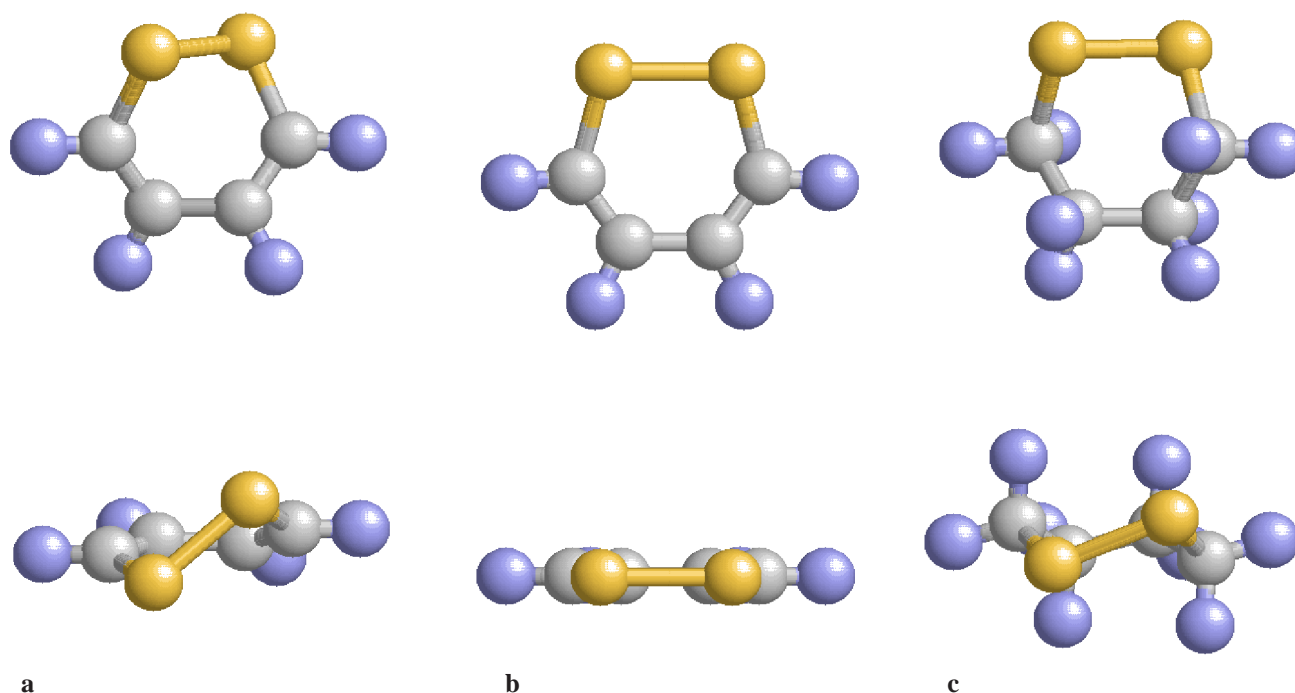


Figure 1 DFT-optimized molecular structures shown in 3D-representations: (a) 1,2-Dithiin **1** (C_2); (b) 1,2-Dithiin **1** (C_{2v}); (c) Tetrahydro-1,2-dithian **3** (C_2)

disulfide. For the sake of comparison, the results of *ab initio* calculations were also performed and are discussed.

Results and discussion

The structure of 1,2-dithiin

The structure of the compounds studied are shown in Figure 1. The cyclic disulfides **1** and **3** have C_2 -symmetry. The two-fold axis passes through the middle of the CC and SS single bonds, which are opposite to each other in the six-membered ring.

Selected geometrical data for 1,2-dithiin (**1**) are collected in Table 1. The results of the MP2 calculations appear most definitive. The geometrical data calculated with the 6-31G(2df,p) basis set does not show much improvement over those formerly obtained with 6-31G(d) [18]. The more extended 6-31G(2df,p) basis set is taken mainly to get more reliable relative energies. DFT B3LYP/6-31+G(d,p) calculations overestimate CS and SS bond lengths. This is a well-known systematic error of DFT in calculations of compounds with third row elements [21]. Although bond lengths in sulfur-containing compounds calculated using this method are improved with more extended basis sets with additional d- and f- polarization functions [22] or by replacing the B3LYP functional with B3P86 [23], the relatively small effect of the mo-

lecular geometry on the absorption wavelength justifies the neglect of additional structural data.

According to DFT as well as *ab initio* calculations, the CC bond length alternation of the planar C_{2v} structure of **1** is increased and the CS and SS bonds are lengthened relative to the half-chair C_2 structure (cf. Table 2). Frequency calculations confirmed that the planar structure is a transition state for ring inversion. Ring inversion is illustrated in Figure 2 using the intrinsic reaction co-ordinate reaction path. Simulation of the structural change shows that the sulfur atoms are those most strongly involved in this transformation.

In spite of the large change in geometry of **1** the barrier to inversion is relatively low and amounts to 8.7 kcal mol⁻¹ at the more reliable MP2/6-31G(2df,p) level. The experimental ΔG^\ddagger value of 3,6-bis(acetoxymethyl)-1,2-dithiin is about 8.0 kcal mol⁻¹ [24]. The barriers for ring inversion of 1,4-dithiin and thiepin are also less than 10 kcal mol⁻¹. The DFT calculations probably underestimate the activation energy for inversion.

The planar structure is an anti-aromatic 8π system. The anti-aromatic electron delocalization is confirmed by the nucleus-independent chemical shift (NICS) analysis introduced by Schleyer et al. [25]. NICS is the negative isotropic chemical shielding at the geometrical center of the ring. NICS values are usually calculated for molecules in the electronic ground state but may be also informative for transition structures of chemical reactions [26]. The NICS value of the twisted 1,2-dithiin is about zero (-0.3 ppm), indicating that this compound is neither aromatic nor anti-aromatic but rather non-

Table 2 Barriers to ring inversion (ΔE^\ddagger) in kcal mol⁻¹ and nucleus-independent chemical shifts (NICS) in ppm of some sulfur-containing heterocycles

Compound	ΔE^\ddagger [a]		NICS [b]	
	DFT [c]	MP2 [d]	gauche	planar
1,2-dithiin (1)	5.2	8.7	-0.3	4.9
1,4-dithiin (4)	2.8	4.9	-4.3	5.4
thiepin (5)	5.8	9.2	-1.3	12.6

[a] Very low barriers for **4** were found at lower levels of theory, see ref [42]. According to ref [43] the barrier of **5** amounts to 7.6 kcal mol⁻¹ (QCISD(T)//MP2/6-31G(d))

[b] GIAO RHF/6-31+G(d)//B3LYP/6-31+G(d)

[c] B3LYP/6-31+G(d,p)

[d] MP2(FC)/6-31G(2df,p)

aromatic. However, the NICS value of planar **1** (C_{2v}) is noticeably larger (5.3 ppm). This value corresponds to an electronic structure of anti-aromatic character. The loss of anti-aromatic character in passing from the planar to the twisted 1,2-dithiin agrees with the recent discussion of anti-aromaticity in terms of energy [27]. The NICS value of the planar cyclooctatetraene transition structure calculated by Schleyer et al., using the same approximation, is considerably higher than that of planar 1,2-dithiin (30.1 ppm) [25]. This value indicates the strongly anti-aromatic character of the planar 8π hydrocarbon. For comparison the NICS values of the corresponding planar transition structures involved in ring inversion of the boat-shaped 1,4-dithiin (**4**) and thiepin (**5**) were also calculated. The results are listed in Table 2. Again, the planar structures appear to be anti-aromatic and the more stable puckered heterocycles as non-aromatic. The

non-aromatic character of **4** is in agreement with the conformational criterion of aromaticity and anti-aromaticity [28].

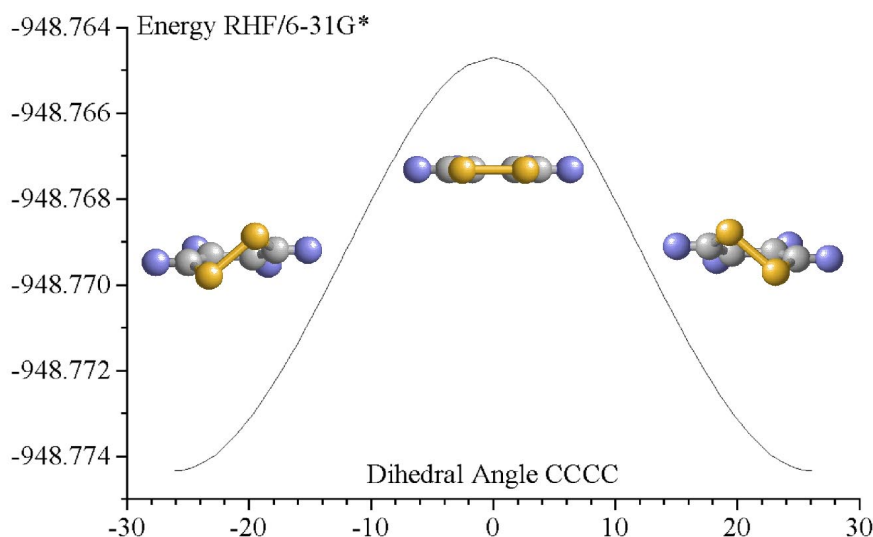
Results of TD-DFT calculations

The TD-DFT method involves a linear response theory approach which focuses on the computation of discrete transition energies rather than on the computation of two states explicitly and independently [4]. The TD-DFT program [29] is included in GAUSSIAN 98 [7]. Correct oscillator strengths (f) are calculated only from version A7 of G98 [30]. The f -values listed in Table 3 are based on the calculated transition dipole lengths.

There are few TD-DFT calculated spectral data for organic compounds published yet [31]. Calculations involving a series of about 60 sulfur organic compounds has recently led to very promising results achieved with relatively low computational effort [22, 32]. Surprisingly the spectral data are not very dependent on the functional and on the basis set. Becke's hybrid B3LYP functional [33] was employed in the TD-KS calculations in this study in conjunction with the 6-31+G(d) basis set. As shown in Table 3 the TD-DFT calculation provided a long wavelength absorption. 1,2-Dithiin is excited from the ground state of A symmetry to the lowest-energy excited state of B symmetry and to two higher-excited states of A and B symmetry. The lowest energy B \leftarrow A transition is polarized perpendicular to the molecular axis. The lowest energy transition clearly causes the color. The higher-energy transitions obviously give rise to the near UV absorption. In the case of the TD-DFT calculation the first two higher-energy transitions are close in energy.

The dominant one-electron transitions of twisted and planar 1,2-dithiin are depicted in Figure 3. As shown in the correlation diagram, the HOMO and LUMO of the twisted

Figure 2 Reaction path (intrinsic reaction coordinate) and visualization of the inversion of the half-chair conformer of 1,2-dithiin through the planar transition state



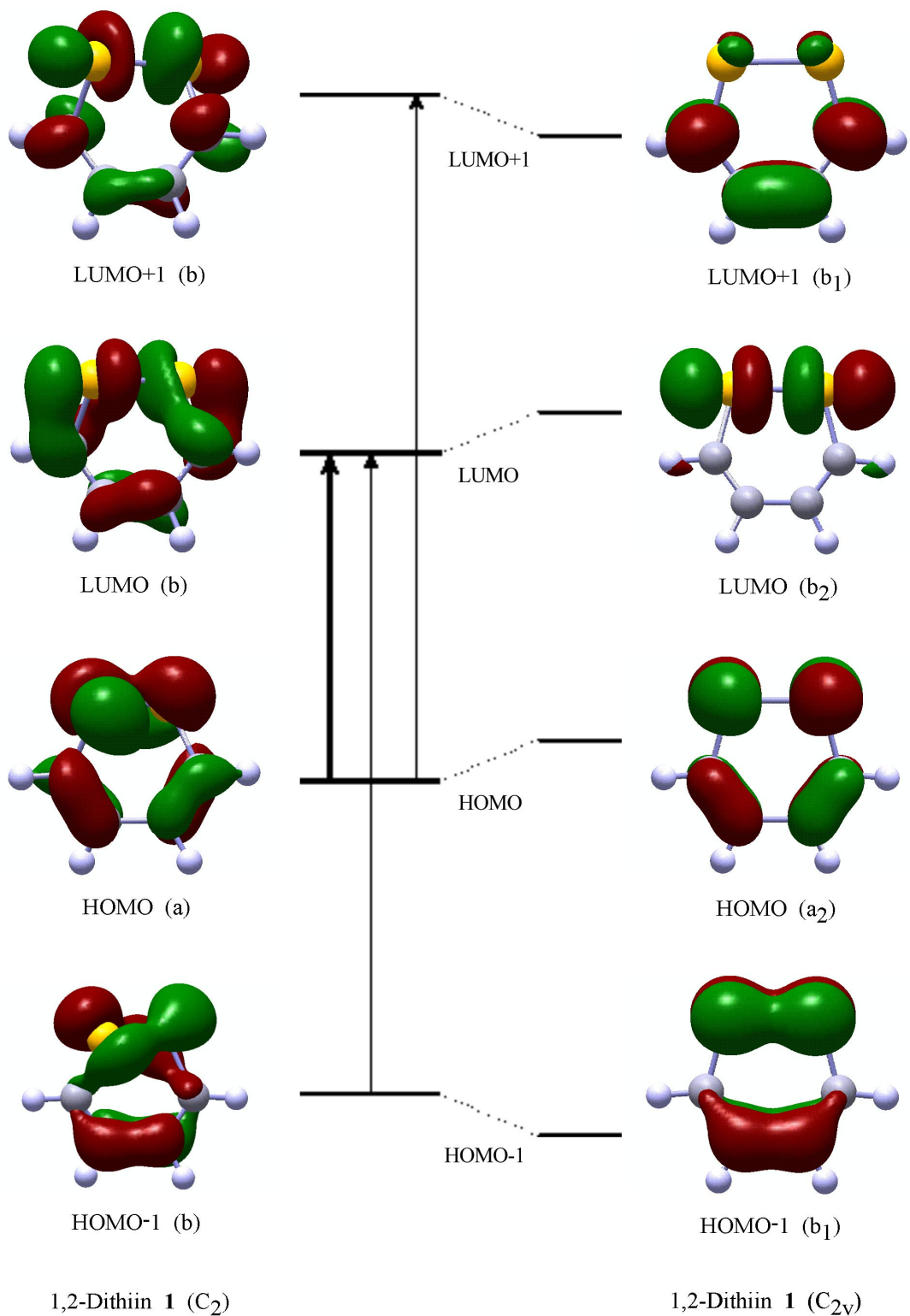


Figure 3 Qualitative MO correlation diagram between HOMO+1, HOMO, LUMO and LUMO+1 of the twisted 1,2-dithiin (C₂) and the planar 1,2-dithiin (C_{2v}) and pictorial representation of the molecular orbitals. Symmetry of the MOs in parenthesis

Table 3 Lowest-energy transitions of the twisted 1,2-dithiin (C_2) calculated by different theoretical models

Exp. [a]	Transition	TD-DFT [b,c]	TD-RHF [b]	CASPT2 [c,d]	CIPSI [e]	EOM-CCSD [c,f]	SCI [b]
λ_{\max} (log ϵ)					λ (f)		
452 (1.95)	B \leftarrow A	488 (0.003)	357 (0.007)	538 (0.001)	405 (0.002)	391 (< 0.001)	345 (0.008)
279 (3.30)	A \leftarrow A	284 (0.031)	243 (0.03)	334 (0.025)	246 (0.064)	254 (0.003)	220 (0.048)
248 (3.18)	B \leftarrow A	260 (0.025)	223 (0.05)	296 (0.032)	239 (0.048)	223 (0.013)	235 (0.036)

[a] measured in CH_2Cl_2 , ref [44]; 451 nm (log ϵ 2.88) in cyclohexane, ref [8]

[b] Calculated with the MW geometry, ref [19]

[c] an additional weak transition (B \leftarrow A) of very low intensity in the NUV region is omitted

[d] B3LYP/6-31G(d) optimum geometry; small ANO basis set (without f-type functions), with a more extended ANO basis set second transition shifted to longer wavelengths

[e] MP2/6-31G(d) optimum geometry, ref [18]

[f] 6-31G(d) basis set

1,2-dithiin are shifted to higher energies in going from the puckered to the planar structure. The HOMO-LUMO gap is decreased. The one-electron transition from the HOMO to the LUMO of **1** mainly contributes to the lowest-energy electronic transition (about 40%). This holds both for the twisted and planar 1,2-dithiin. The MOs of the planar reference structure can easily be classified. The HOMO is a π -type orbital while the LUMO is essentially of the σ (SS)*-type. The transition next higher in energy occurs from the HOMO to the LUMO+1. This is a π - π^* -transition. Twisting of **1** in passing from the C_{2v} - to the C_2 -symmetry causes a strong change in the HOMO from a fully π -delocalized MO to an orbital which displays localized π -type overlaps. Although the π -notation is no longer valid for the non-planar compound, the HOMO π -orbital of the planar compound may be considered as perturbed in the non-planar compound and therefore is designated by $\tilde{\pi}$ in the following discussion. The energy of the LUMO changes more relative to the planar reference compound. The σ^* (SS)-character is no longer dominant in the LUMO of the twisted structure. Because of the reduced symmetry in the twisted structure and the σ/π -mixing of the reference orbitals the LUMO of **1** gains π^* -character. Thus the mixing of the MOs results in the lowest energy transition of the twisted 1,2-dithiin both $\tilde{\pi} \rightarrow \tilde{\pi}^*$ and $\tilde{\pi} \rightarrow \sigma^*$ character.

This interpretation is supported by the change of the bond orders on excitation. The Wiberg SS bond index [34] of the twisted 1,2-dithiin calculated by Weinhold's NBO program package [35] decreases on excitation from 1.02 to 0.73, and that of the planar compound from 0.98 to 0.50. The node at the SS bond of the LUMO obviously is reflected in the reduced SS bond strength of the lowest excited state.

If the frontier orbitals of the twisted 1,2-dithiin (**1**) and the twisted 1,2-dithiane (**3**) are compared, the delocalized frontier MO of 1,2-dithiin is related to the mainly localized

MOs of the saturated cyclic disulfide (see Figure 4). The HOMO in the last case is the symmetrical combination of two sulfur orbitals of the planar structure generally denoted as n_{SS+} . The LUMO is the anti-symmetrical combination of the $p\sigma$ -orbitals of adjacent sulfur atoms directed towards each other denoted by $\sigma(SS)^*$. This is an accepted theoretical model of organic disulfides [36]. Thus the lowest energy transition of **1** is, therefore, also related to lowest-energy transition of the type $n_{SS+} \rightarrow \sigma(SS)^*$ of the twisted 1,2-dithiane.

What makes the chromophore of 1,2-dithiin unique? This is certainly the presence of a perturbed π -system in the HOMO of the twisted **1** including the two sulfur atoms while the LUMO, on the other hand, consists of the perturbed π^* -system of the carbon fragment and the $\sigma(SS)^*$. The consequence is a low HOMO-LUMO gap of the KS orbitals and a considerable increase of the gap in going from twisted **1** relative to twisted **3**. The HOMO-LUMO gap in **1** amounts to about 3.4 eV whereas that in **3** is 5.1 eV. The HOMO of **1** is lower and the LUMO higher in energy with respect to the unsaturated compound (see Figure 4). Therefore, the first ionization energy of **1** should be lower than for **3** and, in particular, the electron affinity should be larger than that in **3**. According to the first ionization energies determined by photoelectron spectra the first ionization energy of **1** (8.16 eV) [37] actually increases in going from **1** to **3** (8.37 eV) [38].

The relative low transition probability of the color-determining lowest-energy transition is due to the weak spatial overlap between the frontier orbitals of **1**, which are of different symmetry. This can be most easily understood considering the planar reference compound (see Table 2). In the planar compound the lowest energy electronic transition occurs from the HOMO of a_2 - to the LUMO of b_2 -symmetry. The transition between the ground and excited state is $B_1 \leftarrow A_1$ and consequently forbidden by symmetry. When going from the planar **1** (C_{2v}) to the twisted **1** (C_2), the forbidden lowest-

in the same assignment of the transition as in TD-DFT calculations. TD-DFT results are clearly superior over those of the TD-RHF *ab initio* method. The main reason for longer wavelength absorption of **1** with TD-DFT relative to TD-RHF and SCI is, obviously, the low HOMO-LUMO gap of the KS orbitals. It amounts to 3.6 eV; whereas, the gap is 9.7 eV for the RHF frontier orbitals.

Like CIS the more refined EOM-CCSD method [1b] is based on RHF orbitals but takes into account electron correlation by the coupled cluster method. Calculations of larger compounds are not practical with the ACES II package [41]. The need for more extended basis sets exceeds the memory limits for the compounds considered in this study. The calculation with the double-zeta valence basis set resulted in an absorption at about 400 nm, which is 60 nm blue-shifted from the experimental result. Again, the lowest-energy term levels are the same as those found by the other theoretical models. However, the electronic transitions cannot be interpreted by the EOM-CCSD calculation with the ACES II program.

Conclusions

TD-KS and *ab initio* calculations have essentially confirmed the results of the former CIPSI study. According to the calculations the color band of the half chair (C_2) 1,2-dithiin is due to the lowest energy excitation to an electronic state of B-symmetry. The transition is predominantly of HOMO-LUMO character. According to the graphical representation of the HOMO and LUMO, the twisted 1,2-dithiin exhibits frontier orbitals with local two-center π -bonds. Reference to the planar 1,2-dithiin facilitated the interpretation of the composition of the frontier orbitals. The symmetric HOMO is a distorted π -MO of the planar compound. The anti-symmetric LUMO, however, is related to the two unoccupied MOs of the planar compound: the lowest π^* -type orbital and the anti-bonding SS bond orbital. The presence of the perturbed conjugated system and the disulfide bond brings about the unique chromophoric system of 1,2-dithiin with a low HOMO-LUMO gap. The chromophore of the *gauche* 1,2-dithiin differs from that of *gauche* 1,2-dithiane in that the frontier orbitals of the former are delocalized, whereas, the MOs of the latter are more localized. The planar 1,2-dithiin is the transition structure for inversion characterized by one imaginary frequency and by a positive NICS value indicating anti-aromatic electron delocalization.

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Supplementary material available Optimized structures **1** (C_2), **1** (C_{2v}) and **3** in XYZ and VRML format, animation of the ring inversion of **1** in XYZ and GIF format, frontier orbitals of **1** (C_2), **1** (C_{2v}) and **3** as enlarged JPEG and VRML.

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