THE ABSORPTION FEATURE OF CONJUGATED COMPOUNDS CONTAINING THE NSN-CHROMOPHORE

J. Fabian[a]; R. Mayer[a]; S. Bleisch[a]

[a] Section of Chemistry, Technical University of Dresden, GDR

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Section of Chemistry, Technical University of Dresden, GDR

The NSN group absorbs at relatively long wavelengths in the uv region. Because of its capability to release or to accept electrons, adjacent groups can produce a pronounced red shift of the color band. Based on the more recently described PPP configuration analysis technique and the MIM–LCI method the color determining electronic transitions of organic sulfdiimides (Sulfurdiimines) has been accounted for in terms of their constituent parts. The calculations revealed that the position of the color band is mainly governed by frontier orbital interactions. Symmetrical junction of the NSN unit with conjugated fragments gives rise to deeply colored heterocyclic compounds, if either their HOMO's or LUMO's have the same symmetry and undergo an effective overlap. This condition is not fulfilled, in general, for compounds which are strongly stabilized in their electronic ground states.

1 INTRODUCTION

The NSN unit represents an interesting substituent group which according to the valence formula —N=S=N— contains a quadrivalent sulfur. Since the calculated NS π-bond orders are, however, in general low, quadrivalency seems mainly to exist from the viewpoint of formal definition and representation.[1] High bond orders were calculated only for few structures and this result does not depend, in essence, on whether sulfur d orbitals are considered or not.

Although some octet expansion of sulfur is not basically excluded, various properties of sulfdiimides are satisfactorily understandable by presuming a σ-bivalent sulfur, which impart some ylid-character to the NS bond. Since high bond orders can exist in spite of large charge separation, this assumption does not necessarily contradict with short NS bond distances found experimentally in non-conjugated sulfdiimides.

Along this reasoning uv/VIS spectral data of diphenyl-sulfdiimides have been discussed in a previous paper.[2] According to Ref. 2 the NSN group should be considered as a four-electron three-center π-system, iso-π-electronic to the allyl anion. Due to the replacement of the methine groups of allyl by electronegative elements the electron releasing strength is weakened, whereas the electron accepting strength is strengthened. Thus the NSN group should display donor as well as acceptor properties. On the other hand, in contrast to the allyl anion, the properties of conjugated sulfdiimides may be strongly dependent upon the nature of the adjacent residues, or of the conjugative bridge which incorporates the NSN group into a heterocyclic structure.

The purpose of this paper is to reveal theoretically the leading principles for the bathochromicity of organic sulfdiimides and to compare predictions and experimental findings. At the first place the chromophoric properties of the NSN group itself is considered along with its response to substituent effect. At the second place, we examined various heterocyclic compounds which, according to theoretical arguments and quantum chemical calculations, should have either long or short wavelength absorptions.

2 THEORETICAL METHODS

The quantum chemical calculations were performed by means of the virtual orbital configuration interaction method in the Pariser–Parr–Pople approximation (PPP method).[3] According to this method the ground state is approximated by a single determinant built up from the N lowest energy molecular orbitals, where N is the number of π-electrons. A basis of single-excited configurations is then

generated by exciting one electron from these occupied orbitals to the virtual, or unoccupied, orbitals and these configurations are then used as a basis to describe molecular excited states. Self consistent field calculations are performed on the ground state to achieve molecular orbitals that are then entered into the configuration interaction calculation of the lowest-energy excited states.

In order to give a simple and pictorial interpretation of the theoretical results in terms of molecular fragments or topological equivalent π-systems, calculated state wave functions were subjected to the so-called configuration analysis (CA) as described by Baba, Suzuki and Takemura.[4,5] This analysis is performed by additionally calculating the state wave functions of reference systems and projecting the state wave functions of the concerned system upon the wave functions of the reference systems. In the case of a composite molecule approach the reference states are the zero-order no-bond (NB) ground state, locally excited (LE) states and charge transfer (CT) states, in which an electron is transferred from one fragment to another one. As far as only a limited number of electronic configurations is considered, the description of delocalized wave functions in term of the localized ones is more or less incomplete. The sum of the squared coefficients of the configuration interaction expansion (r_M), resulting from projection, is consequently lower than unity. Having confirmed the appropriateness of the chosen "building unit" model the genesis of the term levels can be successfully traced back by composite molecule approaches, such as by the MIM–LCI method.[3,6] As discussed by one of the authors (J.F.) in detail elsewhere,[7,8] low-energy excited electronic states may result from an effective mixing of proper LE and CT configurations. This interaction necessitates large expansion coefficients in the localized orbitals of each fragment at the points of interaction. This effect, however, may be weakened or even overcompensated by a strong mixing between CT configurations and the NB ground state. This mixing becomes large with an efficient overlap between donor and acceptor orbitals. Thus qualitative predictions can be given by inspecting key orbital interactions only. If the combined molecule possesses a higher symmetry, the knowledge of the symmetry of the corresponding fragment orbitals may be sufficient to make predictions. The absorption behavior of simple sulfur heterocycles has been discussed most recently from this point of view.[9]

Concerning the numerical calculations we em-

ployed the conventional version of the PPP procedure: The core charge were defined by integer values ($Z_S = 2$, $Z_N = 1$), permitting the formerly used parametrization to be retained (see Ref. 2) ($U_C = -11.42$ eV; $U_N = -14.16$ eV; $U_S = -20.0$ eV; $\gamma_{CC} = \gamma_{SS} = 10.84$ eV; $\gamma_{NN} = 12.81$ eV; $\beta_{CC} = -2.318$ eV; $\beta_{NS} = 0.8\ \beta_{CC}$; $\beta_{CN} = 0.85\ \beta_{CC}$). Furthermore, idealized geometries and C_{2v}-symmetry were presumed. MIM/LCI calculations were carried out in the same parametrization. All singly-excited configurations up to a maximum of 16 were included into the CI calculation. These configurations were constructed from the four highest occupied and four lowest empty orbitals. The number of the configurations considered in PPP–CA calculations are given in the captions of Figures 1 and 3 in context with the theoretical results.

3   RESULTS AND DISCUSSION

Chromophoric Properties of the NSN Group

According to the PPP calculations the NSN group should absorb in the near ultraviolet. An absorption has been actually found in this region for the aliphatic sulfdiimides (1) to (3) (cf. Table I). The assignment of the absorption band at about 270 nm to the transition agrees with the results of CNDO/S calculations of (1).[11,12] $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions are predicted at longer and shorter wavelengths, respectively.[11] The PPP calculations of the NSN group suggest that the absorption arises from a nearly pure $1 \rightarrow 1'$ transition. Furthermore, the NSN group should act as donor group if joined to benzene. According to the examination of the photoelectron spectra of (1) to (3) the ionization from the highest occupied non-bonding π MO accounts for the low ionization potentials of aliphatic sulfurdiimides, ranging from 8.6 to 9.3 eV.[16,17] These ionization potentials are more similar to those of the H_2S (10.43 eV[18]) or dimethylsulfide (8.67 eV[18]) than to the π-type ionization potential of azomethane (11.84 eV[19]). Consequently, the NSN group exhibits donor properties in diphenyl-sulfdiimide (4a) in the electronic ground state, as suggested by our former PPP calculations.[2] This conclusion is in line with nmr spectral data.[20] The ^{13}C chemical shifts clearly show the donor-type substituent effect of the NSN group,

1   2 a: n=1   3
                        b: n=2

X—⬡—N=S=N—⬡—Y

4 a: X,Y = H
   b: X,Y = NMe₂
   c: X,Y = NO₂
   d: X = NMe₂, Y = NO₂
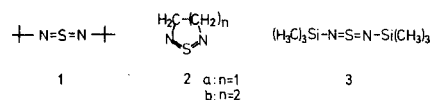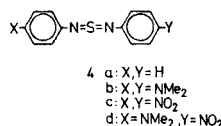
giving rise to a higher electron shielding at the carbon atom in *para*-position of (**4a**) compared to that of benzene, in sharp contrast to the effect of the azo group.

However, the substituent effect of the NSN group in the lowest excited state seems to be more complicated. The results of the MIM–LCI calculation of (**4a**) performed in our previous paper[2] and the results of the PPP–CA calculation presented in Figure 1 show consistently that both the NSN-to-benzene and the benzene-to-NSN CT transfer are involved in the lowest-energy transition. Thus the yellow color of (**4a**) results from an effective mixing of the LE configuration of the NSN moiety with the above-mentioned CT configurations. Spectral substituent effects on (**4a**) depends both upon the change in CT transition energy arising from substitution and the size of the expansion coefficients at the points of interaction. Since the expansion coefficients at the nitrogen atoms are larger in the HOMO than in the LUMO of the NSN group, in the case of a comparable energetics the aryl-to-NSN CT con-

figuration mixes stronger with the LE configuration of the NSN group than the NSN-to-aryl CT configuration does. Thus a deeper color may be generated rather by attaching donor than acceptor substituents in *para*-position. This conclusion agrees with the results of the PPP–CA calculations of (**4b**) and (**4c**) which are depicted in Figure 1, in which calculated transition energies and intensities are presented in a bar-graph format. The weights of the preponderant configurations of the configuration interaction expansion are illustrated by cycles. Whereas the locally excited state dominates in the CI expansion of (**4a**), locally and charge transfer excited state contribute comparably to the lowest excited state of (**4b**). Closely similar results have been obtained by LHM calculations. The values obtained in the PPP calculation matches the experimental values quite well (cf. Table I). Compound (**4b**) absorbs at longer wavelengths than (**4c**) and only a slight spectral shift occurs in passing (**4b**) to (**4d**).[13] As far as the spectral substituent effect on diphenyl-sulfdiimide is considered, the results show (**4a**) to be stronger related to azobenzene than to diphenylsulfide. According to color-structure relationship derived for azobenzenes,[8] blue or even green diphenyl-sulfdiimides could be produced by appropriate multiple donor substitution.

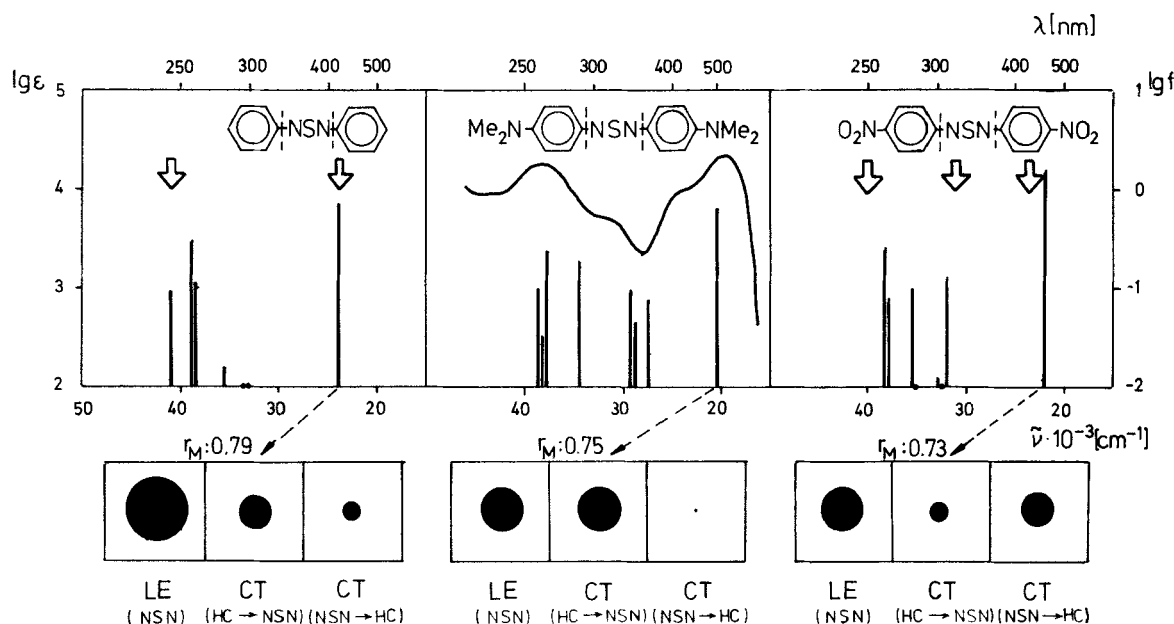FIGURE 1 Spectral absorption curves or experimental absorption maxima (arrow) of diphenyl-sulfdiimides and results of the PPP–CA calculations. The configuration analysis was performed with respect to composite molecules (25 configurations), built up from the NSN group and benzenoid fragments (**4a** in cyclohexane,[21] **4b** in cyclohexane, **4c** in hexane[14] and dioxane,[15] respectively).

TABLE I

Calculated and experimental spectral data of organic sulfdiimides

Calculated values (PPP-approximation)		Experimental values		
λ[nm] (lgf)	P	λ[nm] (lgε)		Solvent
(1) ⎫		274	(3.40)	Gᵃ
		278		b
(2a) ⎬ 255 (−0.02)	⊥	257	(2.74)	Eᶜ
(2b) ⎪		277.5	(3.61)	Eᵈ
(3) ⎭		274	(4.01)	. CHᵉ
(4b) 485 (0.23)	⊥	510	(4.35)	CHᶠ
360 (−1.19)	‖			
341 (−1.34)	⊥			
341 (−0.98)	‖	307s	(3.74)	
288 (−0.77)	⊥			
262 (−0.60)	‖			
262 (−1.17)	‖	263	(4.25)	
260 (−0.96)	‖			
(4c) 448 (0.24)	⊥	425		Hᵍ
313 (−0.90)	‖	325		
307 (−2.31)	⊥			
306 (−1.86)	‖			
284 (−3.70)	⊥			
281 (−0.97)	‖			
261 (−1.12)	⊥			
259 (−0.63)	‖	250	(4.42)	Dʰ
(4d) 503 (0.19)		531	(4.40)	Bⁱ
339 (−0.68)				
330 (−1.16)				
323 (−0.85)				
308 (−2.08)				
276 (−0.85)				
267 (−0.71)				
244 (−2.21)				
(6) 309 (−0.52)	⊥	⎧311 (4.15)⎫		CHᵉ
301 (−0.89)	‖	⎨304 (4.15)⎬		
242 (−1.48)	⊥	⎩299 (4.09)⎭		
229 (−0.08)	‖	223	(4.15)	
(7) 661 (−1.00)	⊥	645	(2.70)	
352 (−0.67)	‖	347	(3.95)	
342 (−0.83)	⊥			
328 (−1.80)	‖	332	(3.95)	CHᵉ
262 (−0.74)	⊥			
256 (−0.12)	‖			
235 (−1.22)	⊥			
224 (0.06)	⊥	235	(4.75)	
(11) 806 (−0.83)	⊥			
248 (−0.46)	‖			
(13) 461 (−0.62)	⊥			
253 (−0.57)	⊥			

ᵃ Calculated frontier orbital energies in eV (HOMO/LUMO):
(1) to (3) (HN=S=NH) −9.02/−2.68, (4a) −8.52/−3.47,
(4b) −7.39/−2.84, (4c) −9.17/−4.27, (4d) −8.13/3.61,
(6) −9.21/−2.65, (7) −7.98/−3.41, (11) −6.11/−1.71,
(13) −9.96/−4.37.
ᵇ Ref. 11.
ᶜ Ref. 12.
ᵈ Ref. 10.

Heterocyclic Sulfdiimides

Another way of modifying the sulfdiimide structure consists in introducing the NSN unit into cyclic π-electron systems. The five-membered 1,2,5-thiadiazoles, such as (5) and (6) belong to them. However, in contrast to the acyclic diaryl-sulfdiimides they are colorless. Whereas (5) can be regarded as 2,5-diaza-thiophene (5b) as cyclic sulfdiimide (5a),[22] in good agreement with the experimentally derived molecular structure, an alternative description of (6a) requires necessarily the quinoid structure (6b). On the other hand, heterocyclic sulfdiimides can also be colored. This has been demonstrated with naphthol[1,8-cd][1,2,6]thiadiazine, which absorbs even at 642 nm with low intensity.[23]
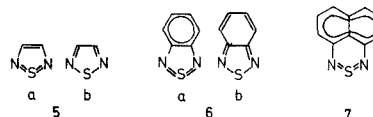
To rationalize these facts and to disclose the origin, we return to the composite molecule treatment mentioned above, starting from the NSN unit and the remaining hydrocarbon fragments. Both constituent parts encompass a common symmetry plane perpendicular to the ring and containing a twofold axis (C_{2v}-symmetry). Thus the molecular orbitals of the fragments can be classified as being either symmetric or antisymmetric with respect to this plane. The highest occupied non-bonding orbital of the NSN moiety is antisymmetric and the LUMO is symmetric. Then the lowest excited state has B_2-symmetry. The electronic transition from the A_1 ground state to the excited B_2 state is polarized perpendicular to the plane of symmetry. The LE state only mixes with CT states which display the same symmetry behavior. If the lowest energy CT state has the same symmetry as the LE state the resultant first excited state is lowered in energy (case I). If, however, the CT transition occurs between MO's of the same symmetry, the resultant excited state has A_1-symmetry alike the ground state. This CT state combines then with the ground state, but not with the lowest excited state of the NSN group. In the consequence the ground state is

ᵉ This paper.
ᶠ This paper; $\lambda_{max} = 532$ (4.50) in benzene[13].
ᵍ Ref. 14.
ʰ Ref. 15.
ⁱ Ref. 13.
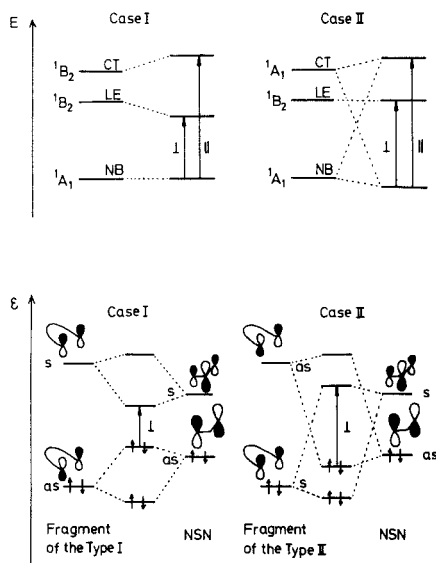Abbreviations: B benzene, CH cyclohexane, D dioxane, E ethanol, G gaseous phase, H hexane.

FIGURE 2   Construction of term level diagrams (upper part) and orbital interaction diagrams (lower part) of C_{2v}-symmetrical, cyclic sulfdiimides from the corresponding wavefunctions of the constituent parts.

depressed and the CT excited state is raised in energy (case II). Whereas in the first discussed case the energy gap between the lowest energy π-states is lowered, the energy gap is enlarged in the last mentioned case. Thus either bathochromic or hypsochromic shift occurs. This relationship has been demonstrated in Figure 2 (upper part).

As far as only the lowest energy transitions between the molecular fragments are considered, conclusions can be readily drawn only by inspecting the symmetry of the frontier orbitals: Along the above reasoning ground state stabilization, and, consequently, relatively short wavelength absorption are expected, if the HOMO of the first and LUMO of the second fragments (or *vice versa*) show the same symmetry behaviour with respect to the mirror plane. Excited state stabilization and relatively long

TABLE II

Molecular fragments of symmetrically-bivalent joined sulfdiimides classified according to the symmetry behavior of their frontier orbitals in respect to the mirror plane

wavelength absorption are anticipated, however, if either the HOMO's and LUMO's display the same symmetry behavior. Both cases are shown in a schematic fashion in the lower part of Figure 2, in which orbitals of the fragments are indicated on the left in each case and those of the NSN group on the right, and in the middle of their allowed combinations. The resultant 1 → 1' transitions differ in energy, but in both cases the respective electronic transition moments are aligned perpendicular to the symmetry plane.

As the HOMO of the NSN group is symmetric and the LUMO is antisymmetric, two series of fragments can be clearly distinguished: The series I comprises fragments with the same and the series II fragments with the inverse symmetry pattern of their frontier orbitals with respect to those of the NSN group (according to cases I and II in Figure 2). Some examples are given in Table II.

It has been actually found that not only (5) but also (8),[24] (9) and (10)[25] are colorless compounds. They belong to ground state stabilized structures derived from fragments of type II. Less is known about the energetically unfavored and probably colored sulfdiimides containing the fragments of type I. The compound S_3N_2 (11) appears to be not yet known, but the (probably no coplanar) (12) exhibits a wine-red color (λ_{max}: 432 nm).[26] Attempts failed to synthesize (10)[23] and (13). Bis(trimethylsilyl)sulfdiimide reacts with oxalylchloride, but a colored product could not be isolated from the orange solution.

An additional comment deserves the electronic structure of (6) and (7). 2,1,3-Benzothiadiazole (6) contains a benzene subunit which possesses degenerate frontier orbitals. However, they differ in the size of their coefficients in the linked positions. The HOMO and LUMO with the higher coefficients mainly determines the interfragmental overlap. These orbitals justify to attribute the benzene moiety to fragments of the type II which cause relatively short wavelength absorptions. In naphtho[1,8-cd][1,2,6]thiadiazine, on the other hand, both the HOMO and LUMO of the naphthalene subunit is antisymmetric to the symmetry plane. Due to the mixing-in of naphthalene-to-NSN CT configurations the ground as well as the lowest excited state undergo some stabilization. For energetic reasons,
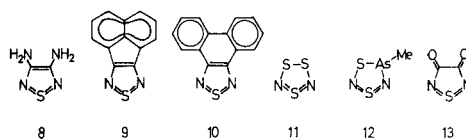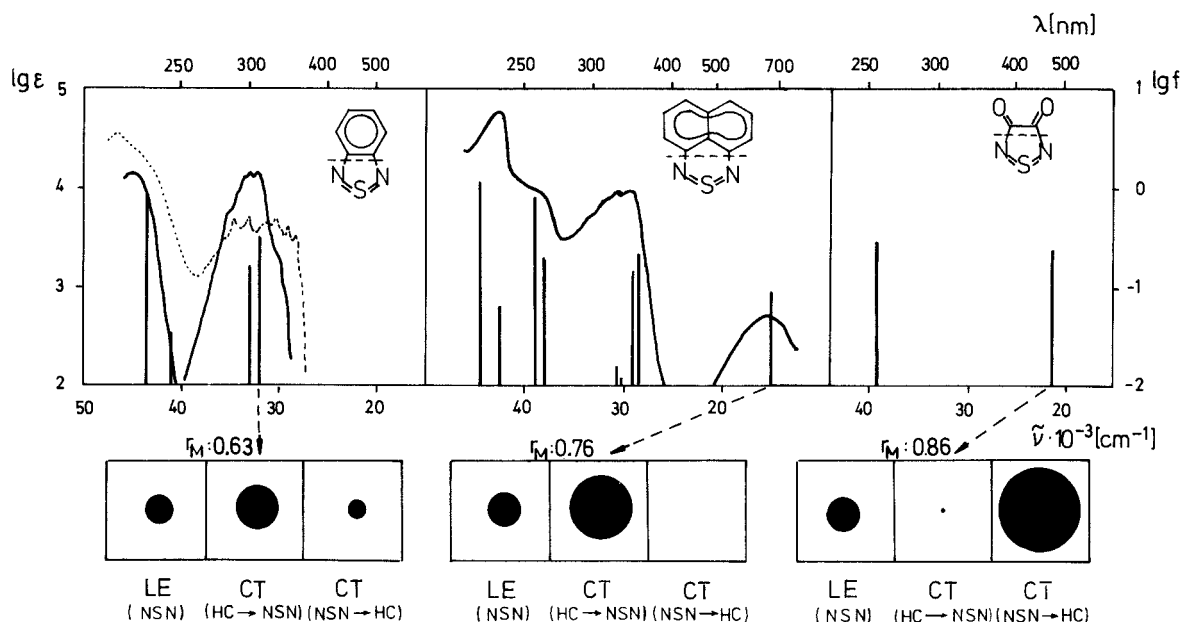
FIGURE 3   Spectral absorption curves of cyclic sulfdiimides and results of PPP–CA calculations. The configuration analysis was performed with respect to composite molecules, built up from the NSN group and the conjugative bridge. The number of reference configurations are 20 for (6), 36 for (7) and 12 for (13) (spectra: 6 and 7 in cyclohexane, dotted curve: benzo[c]thiophene in cyclohexane).

however, the excited state stabilization is by far the larger. For this reason a pronounced red shift occurs. The situation is therefore somewhat similar to that encountered with fragments of type I.

The quite distinct color properties of cyclic sulfdiimides in dependence on the nature of the coupled fragment is supported by PPP-type calculations. For brevity, only a few data are listed in Table I. The calculated long-wavelength absorption of (7) matches the experimental value quite well. The low absorption intensities reflect the high CT character of the lowest excited state. The results of PPP–CA calculations are illustrated in Figure 3. They support the predominance of the naphthalene-to-NSN charge transfer in the lowest excited state of (7). In contrast, to (7), the inverse transfer dominates in (13) for energetic reasons. The same conclusion can be drawn from the LHM calculations which are not presented for sake of brevity.

Strongly different positions of the longest-wavelength absorption have been calculated for the iso-π-electronic (11) and (13) (cf. Table I). For reasons discussed above the NSN group acts favorably as acceptor group upon electronic excitation. Thus union with the donor fragment SS generates significantly longer absorption wavelengths than union with acceptor fragment CO—CO.

The numerical data tabulated in Table I should, however, not be overestimated for two reasons: First, the parametrization employed was not optimized for the structures considered. Secondly, compounds with weak ground state stabilization must not be coplanar. Even the NSN group itself may depart from planarity, such as discussed for (2b) in context with photoelectron spectra.[17] X-ray studies evidence, however, the planarity of the NSN subunit in a non-planar sulfdiimide.[27]

The r_M-values of the configuration analyses presented in Figure 3 indicate a high appropriateness of the composite molecule model in case I (fragments of type I), but a rather bad representation in case II. In the latter case alternative models may be invoked for rationalizing the absorption feature, such as for (5), (6) and (8)–(10). PPP–CA calculation of (6) carried out with respect to a ortho-quinone diimide bridged by sulfur reveals that this reference state is not favored over the benzene-sulfdiimide representation (cf. Table III). This outcome, in turn, supports the pronounced stabilization of the zero-order no-bond ground state which corresponds to a highly delocalized π-electron system. Consequently (6) is more favorably referenced against benzo[c]thiophene, which actually displays a closely similar absorption spectrum (cf.

TABLE III

Alternative reference structures in describing the electronic states of 2,1,3-benzothiadiazol and results of CA calculations


	Ψ_0	Ψ_1	Ψ_2	Ψ_3	Ψ_4
	0.87	0.63	0.52	0.59	0.61
	0.91	0.66	0.56	0.58	0.55
	0.99	0.98	0.98	0.98	0.98

Figure 3). The slight blue shift in passing from the thiophene to (6) is readily understandable by Dewar's first-order perturbation theory[28] taking into account the higher electronegativity of =N— in comparison to =C— and the descent of electron density in the substituted positions of the thiophene upon excitation. Another well-known approach for interpreting the spectra of fused 1,2,5-thiadiazoles consists in replacing the sulfur atom by a double bond giving rise to iso-π-electronic 1,4-pyrazines.[29]

In summary, the distinct color properties of sulfdiimides can be satisfactorily accounted for in terms of either isoconjugated structures of composite molecule structures by means of perturbation theoretical arguments.

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