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# DFT- AND POST-HF-STUDY ON STRUCTURE AND ELECTRONIC EXCITATION OF ACYCLIC AND CYCLIC SULFUR DIIMIDES

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**A series of representative organic acyclic and cyclic sulfur diimides were studied by Hartree–Fock-plus-correlation *ab initio* quantum chemistry and by density functional theory using Becke's three-parameter functional along with the LYP functional. The widely used formula representation —N=S=N— for these compounds suggests octet expansion of sulfur. This is not confirmed by theory. Although d-polarization functions significantly improve the numerical results, sulfur d-orbitals are hardly occupied. The calculated electronic charge distribution derived by population analysis and by the atoms-in-molecules topological theory favors charge separation resulting in a more or less ylidic structure with —N=S$^+$—N$^-$— and —N$^-$=S$^+$—N— resonance contributors. This structure does not exclude relatively short SN bond lengths. The characteristics of the bonds in the parent structures is preserved in some non-Kekulé-type NSN heterocyles. Strong SN bond charge separations of organyl sulfur diimides are accompanied by short SN bond distances and narrow $S_0/T_1$ and $S_0/S_1$ energy gaps. The experimentally well known naphtho[1,8-*cd*][1,2,6]thiadiazine and the unknown 3,4-dimethylene-1,2,5-thiadiazole belong to this series. The calculations confirm that 1,2,3-thiadiazole is the diaza analog of thiophene rather than the vinylene-bridged sulfur diimide, while more complex heterocycles such as benzo[1,2-*c*; 4,5-*c'*]bis[1,2,5]thiadiazole take an intermediate position between classical and non-classical structures. Two closely related minimum structures are defined on the DFT Born–Oppenheimer energy surface of naphtho[1,8-*cd*; 4,5-*c' d'*]bis[1,2,6]thiadiazine, but so far only one compound is experimentally known. The lowest energy structure is the quinoid form corresponding to the experimentally known compound.**

## INTRODUCTION

The sulfur diimide group —N=S=N— is a constituent element of numerous inorganic compounds.[1] The two free valencies can be linked to various organic fragments giving rise to acyclic and cyclic organyl sulfur diimides. In early studies of organyl sulfur diimides, arguments have been presented in favor of the thiocumulenic structure —N=S=N—.[2] The hypervalency of sulfur may be due to d-orbital participation of sulfur or may be of different origin.[3] Although the inclusion of sulfur d-orbitals in higher coordinated inorganic and organic compounds has been refuted by means of *ab initio* quantum chemical calculations[4–6] recent papers on sulfur diimides adere to the hypervalent description of di-coordinated sulfur.[7] If the hypervalency of sulfur is put into question,[8] the non-polar —N=S=N— bond system has to be replaced by the dipolar resonance contributors —N=S$^+$—N$^-$— and —N$^-$—S$^+$=N—. The structure then appears as zwitterionic or ylidic. A non-hypervalent bonding of sulfur without the above-mentioned SN charge separation suggests spin paired diradical structures.[9]

In principle, the sulfur diimide parent structure, alternatively depicted as HN=S$^+$—NH$^-$ (**1**), is an aza analog of the simplest 'sulfur dimethide' structure, known as thioformaldehyde *S*-methide, $H_2C{=}S^+{-}CH_2^-$. The twofold substitution of the $CH_2$ by the more electronegative nitrogen imparts this compound a higher stability. Actually, sulfur diimides are better known than the nitrogen-free compounds. Aza substitution will alter the nature of the —HC=S$^+$—CH$^-$— group and twofold aza substitution of —HC=S$^+$—CH$^-$— resulting in —N=S$^+$—N$^-$— may transform the donor into an acceptor group.

Sulfur diimide **1** is probably formed in gas phase reactions.[10] Dimethyl sulfur diimide **2** and further aliphatic sulfur diimides could be isolated and are better known than related nitrogen-free compounds.[3] The molecular geometry of **2** has been derived from electron diffraction studies.[11] In agreement with theoretical predictions,[12] the most stable compound is the *E,Z* (*syn,anti*) isomer. The *Z,Z* structure is fixed in cyclic

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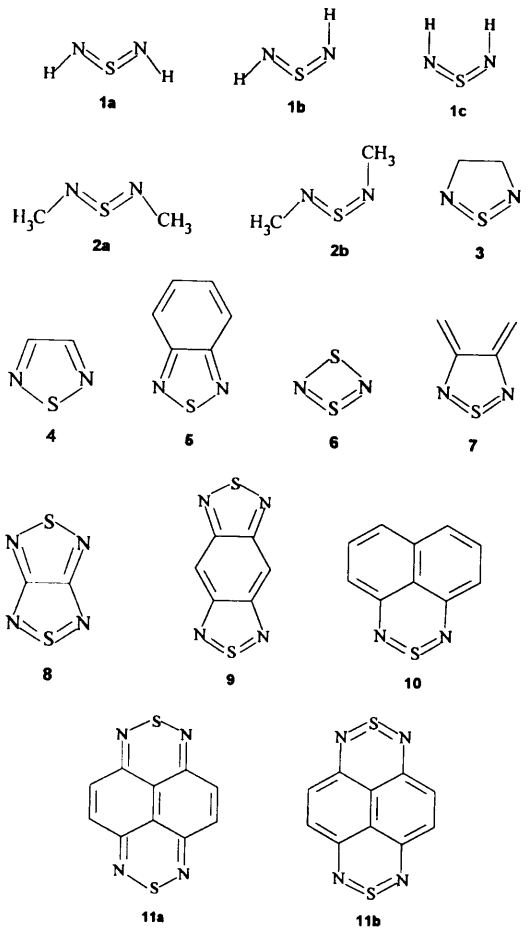
compounds, such as **3**. The conjugated heterocyclic compounds are of different type: the NSN group is contained in a molecular structure of either 'classical' or 'non-classical' type. In the first case classical uncharged valence bond formulae can be written employing atoms in the normal valence states, such as in 1,2,5-thiadiazole (**4**) and benzo[*c*]-1,2,5-thiadiazole (**5**). In the case of **5** the structure then appears to be quinoid. Heterocycles **4** and **5** are well known[1] as diaza-analogous thiophenes. Naphtho[1,8-*cd*;4,5-*c'd'*]bis[1,2,6]thiadiazine (**11a**) may also be represented by a quinoid formula. Little is known about the second series normally presented either as resonance hybrids of several dipolar structures or as a hypervalent structure (non-Kekulé-type structure). Examples of non-classical structures are afforded by the simplest compounds **1**–**3** and more complex heterocyclic compounds **6**–**10**. They either contain the $\sigma$-divalent sulfur in the ylidic or the quadrivalent sulfur in the thiocumulenic bond. For convenience, only hypervalent formulae are presented in this paper for the non-classical structures, and the corresponding class name 'sulfur diimide' is used following a recent recommendation by IUPAC.[13]

Of the series considered, there is some knowledge about heterocyclic compounds with non-classical structures. 1,3,2,4-Dithiadiazete (**6**) has found broad interest as precursor for the polythiazyl $(SN)_x$ polymer, the first non-metallic conductor and polymer with supraconductive properties.[1,14] In contrast to the extensively studied diradicaloid 3,4-dimethylenethiophene,[15] the heteroanalogous compound **7** seems to be unknown. [1,2,5]Thiadiazolo[3,4-*c*][1,2,5]thiadiazole (**8**) has been synthesized[16] and its structure is known from x-ray diffraction measurements.[17] Derivatives of the heterocycle **9** recently received attention as organic narrow gap conductors.[7] Naphtho[1,8-*cd*][1,2,6]thiadiazine (**10**) is easily available as a deep-blue crystalline compound[18] with extraordinary spectral properties.[8,19] UV–visible spectral absorptions of **10** and of other sulfur diimides in solution are well reproduced by Pariser–Parr–Pople calculations.[8,20] As reviewed elsewhere,[21] they are basic chromophores that owe their deep color to the diradicaloid character of the electronic structure. In such cases, theoretical results might be more strongly dependent on the theoretical model. The synthetized quinoid heterocycle **11a**, however, absorbs at considerably shorter wavelengths than **10**.[22]

Most previous *ab initio* theoretical calculations have been performed at the restricted Hartree–Fock level neglecting electron correlation.[1] Calculations at higher levels have only been done for **1**, **2**[12] and **6**[23] To the best of our knowledge, no calculations have been performed by density functional theory for the series considered.

The purpose of this present paper is to examine the molecular and electronic structures of the sulfur diimides **1**–**11** at the correlated level of *ab initio* theory and of density functional theory. Our intention is to




shed light on the nature of the bonding in the non-classical structures and to look for relationships between the structure and the excitation energies to the lowest energy singlet and triplet excited states.

## COMPUTATIONAL

The compounds were investigated by conventional *ab initio* quantum theory[24] and by density functional theory (DFT)[25] using the Gaussian-94 set of codes.[26] *Ab initio* calculations were performed at the beyond-HF level, making use of the many-body perturbation theory truncated at second order [MBPT(2) or MP2] and the quadratic configuration interaction theory including singles and doubles (QCISD),[24,27] keeping the core electrons frozen. Doublet molecules (radicals) and triplet molecules were optimized by the corresponding open-shell programs UMP2 and UQCISD. In general, fully relaxed geometries were obtained by derivative methods. Calculations performed with a

geometry optimized at lower levels of theory are denoted SP for single-point calculations. Unless stated otherwise, the core is fully taken into account. The total energies of the geometry-optimized species provide adiabatic singlet/triplet splitting energies. The lowest vertical singlet–triplet ($S_0/T_1$) and singlet–singlet ($S_0/S_1$) excitation energies were obtained by the configuration interaction method including all singly excited configurations (CIS).[28] The molecular geometries of these calculations are optimum geometries obtained by DFT, which takes into account electron correlation by a correlation functional.[25] The introduction of gradient corrected (non-local) functionals has significantly improved the theoretical predictions.[29,30] DFT includes dynamic and non-dynamic electron correlation to some extent and appears to be the best choice with regards to both efficiency and accuracy. The economy of DFT methods makes them a promising alternative approach to *ab initio* methods. The well approved Hartree–Fock hybrid model Becke3LYP[30] implemented in Gaussian-94 was used throughout this study.

In order to clarify the electron distribution and nature of bonding, the widely used Mulliken population analysis (MPA)[24] was performed. Partial $\pi$-charges are derived from the gross orbital population of the $\pi$-type functions presuming core charges of 1 for carbon and nitrogen and 2 for sulfur. The basis set dependence of the MPA is reduced in the Weinhold–Reed natural population analysis (NPA) that refers to a set of orthogonal basis functions.[31] Finally atomic charges are calculated from charge densities by Bader's 'atoms-in-molecules' (AIM) method.[32,33] The topology of charge distribution is used in this method to define atomic regions. Numerical integration of the charge density within the atomic region and the consideration of the local nuclear charge provide the charge of a non-spherical atom.

The split valence DZ basis sets 3–21G, 3–21G(*) and 6–31G* were employed in the MP2 and DFT calculations and the basis set 6–31 + G* in CIS calculations. The augmentation of the basis set by plus functions (+) is motivated by the necessary extension of the virtual orbital space for the CI calculation. The extended basis set reduces the transition energies of the chromophores. Calculations of some parent structures were done at the computationally more demanding QCISD level of theory, employing the more extended basis set 6–31 + G(d, p). For the sake of comparison, UV/visible spectral data were also calculated by the semi-empirical PM3-PECI method using VAMP.[34] Whereas CIS and $\pi$CIS imply full configuration interaction of mono-excited configurations, the PECI method[35] includes a limited number of mono- and di-excited configurations (singles-plus-pair-doubles). In the latter case the five highest occupied and the five lowest empty molecular orbitals are considered (PECI = 10).

## RESULTS AND DISCUSSION

### d-Orbital effect

The effect of the sulfur d-orbitals is demonstrated by calculations with Pople's small DZ valence basis sets 3–21G and 3–21G(*). The former includes d-functions at sulfur and has proven to be the better one.[36] Examination of the Mulliken gross electron population of the non-classical structure **1** and the classical structure **4** revealed low occupancies of d-type functions. The occupation numbers amount to 0·11 and 0·14, respectively. That is only about one tenth of the expectation value for sulfur $sp^3d$ hybridization. Although the d-functions obviously act as polarization functions rather than as d-orbitals of the valence shell, the effect of these functions is large. As shown in Table 1, the SN bonds are shortened by 0·12 Å and the shorter distance is the only reasonable one (see below). Also, the charge separation of the SN bond is obviously altered. Surprisingly, all compounds undergo a slight decrease in the positive charge at sulfur only according to MPA. A strong increase in charge separation is found on going from MPA to NPA. The MPA charge separation is reduced with d-functions while the NPA charges increase. This discrepancy initiated an additional analysis of the charge alteration upon basis set expansion by AIM. The parent compound **1** (*EE*) was taken as an example. The calculation has revealed that the AIM calculations support the change predicted by NPA. The change is very large for the 'hypervalent' compound considered. When d-effects are included, the positive charge at sulfur increases from +0·79 to +1·59 and the negative charge decreases from −0·69 to −1·12. All calculated data discussed in the following were obtained by basis sets that include polarization functions.

At any rate, the calculated d-orbital occupation furnishes no evidence for hypervalent structures. Any discussion in terms of hypervalency needs a clear definition.[37] Hypervalency plays a different role in a semi-empirical approach than in an *ab initio* theoretical approximation. In the latter case, the atom-centered molecular wavefunctions require some functions higher in order than s- and p-functions to gain higher flexibility in describing the bond. Such polarization functions have to be distinguished from valence type d-orbitials.[5] Moreover, it has been discussed in early papers as to whether hypervalency might be compatible with s,p-shells only in particular cases. According to Ref. 38, valence formation is subjected to the 'free democracy principle.' In that case, valency cannot be adequately mirrored in valence formulae. Calculations by the spin-coupled VB theory (GVB) do not exclude hypervalent structures even for compounds with first-row elements. According to such calculations, ozone may actually be written as O=O=O and diazomethane as

Table 1. Sulfur-nitrogen bond lengths $r_{SN}$ in Å, MPA and NPA atomic charges at nitrogen ($q_N$) and sulfur ($q_S$) for selected organyl sulfur diimides with and without consideration of d-functions using Becke3LYP/3-21G and Becke3LYP/3-21G(*) (differences in bond lengths and charges are given as $\Delta r_{SN}$, $\Delta q_N$ and $\Delta q_S$)

| | $r_{SN}$ | | |
|---|---|---|---|
| Compound | 3-21G | 3-21G(*) | $\Delta r_{SN}$ |
| **1a** (*EE*) | 1·69 | 1·56 | 0·13 |
| **3** | 1·69 | 1·58 | 0·11 |
| **4** | 1·80 | 1·68 | 0·12 |
| **7** | 1·72 | 1·60 | 0·12 |

| | | 3-21G | | 3-21G(*) | | | |
|---|---|---|---|---|---|---|---|
| | | $q_N$ | $q_S$ | $q_N$ | $q_S$ | $\Delta q_N$ | $\Delta q_S$ |
| **1a** (*EE*) | | −0·63 | 0·71 | −0·58 | 0·60 | 0·05 | 0·11 |
| **3** | MPA | −0·55 | 0·78 | −0·48 | 0·68 | 0·07 | 0·10 |
| **4** | | −0·53 | 0·56 | −0·50 | 0·56 | 0·03 | 0·00 |
| **7** | | −0·62 | 0·76 | −0·54 | 0·69 | 0·08 | 0·07 |
| **1a** (*EE*) | | −0·72 | 0·77 | −0·89 | 1·06 | −0·17 | −0·29 |
| **3** | NPA | −0·56 | 0·83 | −0·70 | 1·09 | −0·14 | −0·26 |
| **4** | | −0·46 | 0·55 | −0·57 | 0·79 | −0·11 | −0·24 |
| **7** | | −0·53 | 0·80 | −0·66 | 1·06 | −0·13 | −0·26 |

$H_2C{=}N{\equiv}N$[39] rather than using dipolar resonance structures.

## Molecular geometry

Selected geometric parameters obtained by DFT calculations are shown in Figure 1 and SN bond lengths are listed in Table 2. The SN bonds of the parent structures **1**–**3** calculated at about 1·56 Å are remarkably short even if compared with the SN double bond in H—N=S. At the highest level of theory employed in this study (QCISD/6-31+G**), the SN bond length of H—N=S amounts to 1·59 Å, i.e. the length of the SN bonds in —N=S=N— of **1** and some derivatives are 0·03 Å shorter than in H—N=S. In the heterocyclic compounds the SN bond length differs over a wide range. Involved in a conjugated system such as 1,2,5-thiadiazole (**4**) and, to a lesser extent, in the 'quinoid' structures **5** and **11a**, the SN bond is longer than in the parent compound (1·65–1·68 Å), consistent with =N—S—N= subunits. In agreement with this structure, the two nitrogen atoms of the NSN fragment are strongly bound to the adjacent carbon atoms of the hydrocarbon fragment. This is documented for compound **4**, displaying CN bond lengths of about 1·32 Å. As suggested by the resonance formulae, 'di-heterocyclic' structures such as **8** and **9** take an intermediate position, exhibiting both the =N—S—N= and —N=S=N— structural unit. In sharp contrast to the above-mentioned compounds, in the cases of **7** and **10** the calculated SN bonds are nearly as short as in the parent structures **2** and **3** (about 1·58 Å) while the CN bonds are unusually long (about 1·40 Å). 1,3,2,4-Dithiadiazete (**6**) is an exceptional case. The NSN unit is bridged by sulfur. Thus the NSN group appears twice. The SN bond length becomes as large as 1·67 Å. The predicted geometric parameters of MP2 calculations show the same order as the DFT calculations. Interestingly, the SN bond lengths of the DFT calculations are on average 0·016 Å shorter than those of MP2 calculations, except in the case of **4** and **5**. In general, bond lengths are predicted larger by DFT employing the Becke3LYP functional than by MP2 with the same basis set. There is one remarkable exceptional structure. As expected, and in agreement with an x-ray diffraction study,[22] **11a** in its lowest energy DFT optimum geometry is a quinoid structure, but an additional non-classical ylidic structure **11b** is predicted in this approximation (cf. Figure 1). Whether both closely related optimum structures remain minima at the beyond-Hartree–Fock *ab initio* level has not yet been verified. Unfortunately, calculations on **11** are at present not feasible at higher levels of correlated *ab initio* quantum chemistry. Cases of isomerism between planar molecules of the same connectivity and symmetry seem to be rare. The extensively discussed 'bond stretch isomerism' ('distortional isomerism') of some inorganic compounds proved to be wrong or at least suspect.[40]

Some experimental structural data for **2**,[11] **6**,[41] **8**,[17] and **11**[22] and of compounds of more or less classical structure such as **4**,[42] **5**[43] and dibromo-**9**[7] are available for comparison. The experimental data (cf. Figure 1)

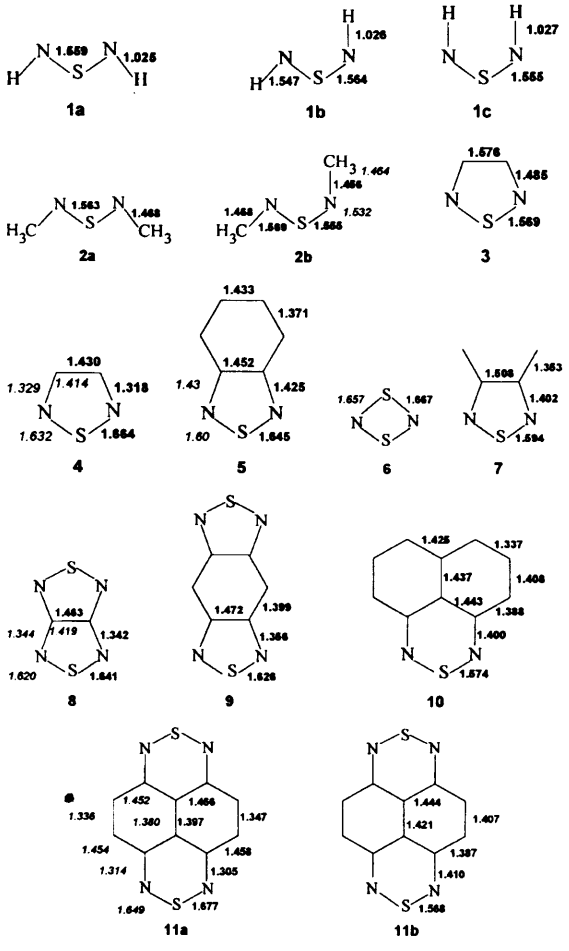


Figure 1. Selected bond lengths of **1–11** calculated at the DFT/6–31G* level (experimental data for **2b**,[11] **4**,[42a] **5**,[43] **6**,[41] **8**[17] and **11a**,[22] numbers in italics). For additional experimental data, see Ref. 51

actually comprise a wide range of SN bond lengths from 1·53 Å (electron diffraction of **2**) via 1·63 Å (electron diffraction and x-ray study of **4**) to 1·65 Å (x-ray study of **11a**). In all cases bond lengths predicted by DFT (and also MP2) were slightly longer. The calculated bond lengths refer to isolated molecules whereas they are more or less distorted in the crystal. The experimental deviations also prevent any closer comparison between theory and experiment.

## Electron distribution

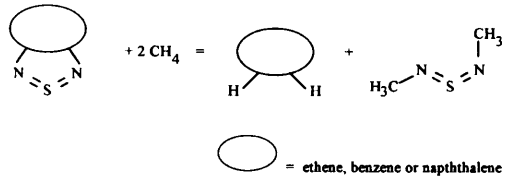
The peculiarity of the SN bond is displayed by the SN bond length and the charge separation of this bond. This is exemplified in Figure 2 with charges calculated for **10** by different theoretical models. The short SN bond of **10** is obviously more or less ylidic. In consideration of the whole molecule, the NSN group is an acceptor group. Although four electrons of the three atoms contribute to the $\pi$-system of NSN, this group has only a very low $\pi$-donor character in the conjugated $\pi$-electronic system of the heterocycle. The total charges differ strongly since MPA belongs to a spherical atom whereas AIM defines a non-spherical atom. As is well known, AIM charges are therefore extremely large.[6]

The total atomic charges at nitrogen and sulfur obtained by DFT calculations are compared in Table 2 for the whole series considered. If the SN bonds are short, such as in **7** and **10**, the charge separation is obviously large. These are compounds of non-classical structure. In the case of long SN bonds, in both classical structures **4** and **5** smaller charges at the heteroatoms are obtained. As shown by the comparison of charges obtained by different models, this conclusion does not depend on how the atomic charges are obtained. The absolute values differ considerably while the general pattern remains. For each compound the charge separation increases in the order MPA < NPA < AIM.

## Stabilization energy

The molecular geometry and the electron distribution indicate clearly that the NSN unit is distinctly bound to the hydrocarbon fragment in forming heterocyclic rings. The NSN group appears greatly isolated from naphthalene in **10** but is strongly fused with ethylene in **4**. Heterocycles such as **5**, **8** and **9** take an intermediate position.

This feature has been confirmed by calculating the energies of 'isodesmic reactions.' Isodesmic reactions consider transformations in which the number of bonds of each formal type is conserved and only the relationship among the bonds is altered.[24] Along these lines, correlation energy contributions inherent in individual bonds are largely cancelled. In the following analysis, isodesmic 'methyl stabilization' energies have been calculated by the reaction shown in equation (**1**).




The relative energies were calculated by the DFT Becke3LYP/6–31G* model.

According to the calculated energies, the stability of the organyl sulfur diimides decreases in the sequence **4**(62·4) > **5**(47·5) > **9** > (36·6) > **10**(24·7 kcal mol$^{-1}$. This sequence clearly shows a transition from classical to non-classical structures that are less stabilized.

Table 2. Sulfur–nitrogen bond lengths $r_{SN}$ in Å and Mulliken total atomic charges at nitrogen ($q_N$) and sulfur ($q_S$) of sulfur diimides at the DFT and MP2 level with 6–31G* basis set[a]

| Compound | $r_{SN}$ | | DFT | | $E_{tot}$ | |
|---|---|---|---|---|---|---|
| | DFT | MP2 | $q_N$ | $q_S$ | DFT | MP2 |
| **1a** (*EE*) | 1·559 | 1·571 | −0·622 | +0·600 | −508·80071 | −507·94801 |
| **1b** (*EZ*) | 1·564[c] | 1·575[c] | −0·669 | +0·647 | −508·80837 | −507·95608 |
| **1c** (*ZZ*) | 1·555 | 1·567 | −0·641 | +0·654 | −508·81030 | −507·95857 |
| **2a** (*EE*) | 1·563 | 1·581 | −0·468 | +0·619 | −587·41475 | −586·27365 |
| **2b** (*EZ*) | 1·555[d] | 1·575[d] | −0·521[d] | +0·639 | −587·42927 | −586·28996 |
| **3** | 1·569 | 1·588 | −0·496 | +0·672 | −586·22498 | −585·12760 |
| **4** | 1·664 | 1·645 | −0·455 | +0·541 | −585·07945 | −584·01153 |
| **5** | 1·645 | 1·635 | −0·554 | +0·572 | −738·71693 | −737·13517 |
| **6** | 1·667 | 1·684 | −0·580 | +0·580 | −905·76534 | −904·41992 |
| **7** | 1·594 | 1·620 | −0·533 | +0·660 | −662·41938 | −661·05987 |
| **8** | 1·641 | 1·652 | −0·520 | +0·639 | −1091·51995 | −1089·63937 |
| **9** | 1·626 | 1·637 | −0·554 | +0·625 | −1245·16769 | −1242·80348 |
| **10** | 1·574 | 1·597 | −0·557 | +0·652 | −892·32453 | −890·25837 |
| **11a** | 1·677 | — | −0·579 | +0·489 | −1398·78657 | — |
| **11b** | 1·568 | — | −0·561 | +0·664 | −1398·74755 | — |

[a] MP2 (frozen) rather than MP2 (full) for **5** and **7**–**10**.
[b] Total energies in hartree. 1hartree = 627·51 kcal mol$^{-1}$.
[c] The second S—N bond is calculated as 1·547 (DFT) and 1·558 Å (MP2), respectively.
[d] The second S—N bond is calculated as 1·569 (DFT) and 1·568 Å (MP2), respectively. Charge at second nitrogen is −0·468.

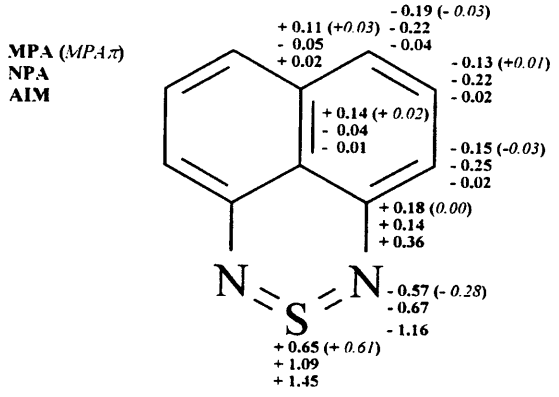


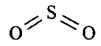
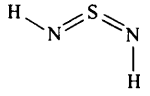
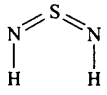
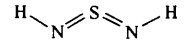
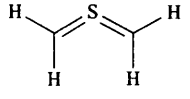

Figure 2. Atomic charges and charge distribution of naphtho[1,8-*cd*][1,2,6]thiadiazine (**10**) according to the MPA (top, π-charges in parentheses), NPA (middle) and AIM calculations (bottom).

## $S_0/T_1$ splitting and electronic excitation

The singlet/triplet ($S_0/T_1$) gap is a well known indicator of the diradical behavior of closed-shell structures.[44] The adiabatic $S_0/T_1$ splitting energies obtained by the energy differences are presented in Tables 3 and 4. Although these energies are more or less subject to error, they do not depend too much of the level of theory employed (cf. Table 3). Thus the DFT results encourage calculations on larger compounds. The principal conclusion appears to be reliable and informative: the $S_0/T_1$ splitting is considerably higher[45] when the terminal methide groups of thioformaldehyde *S*-methide ($H_2C{=}S^+{-}CH_2^-$) are replaced by the more electronegative NH group or by oxygen, providing the sulfur diimide parent structure **1** or sulfur dioxide (cf. Table 3). If a limiting value for the $S_0/T_1$ gap of about 25 kcal mol$^{-1}$ is accepted to discriminate between diradicaloid and non-diradicaloid species,[44] the latter compounds are clearly far from being diradicaloid. However, according to the results of DFT calculations collected in Table 4, the $S_0/T_1$ energy gap of some derivatives of sulfur diimides can also be low when the NSN group is non-classically linked to a hydrocarbon fragment. According to the $S_0/T_1$ splitting energies, **7**, **10** and **11a** appear to be diradicaloid and **9** is in the borderline region. According to the DFT/6–31G* calculations, the energy gap decreases in the sequence **4**(97·2) > **5**(50·0) > **9**(20·1) > **10**(7·9 kcal mol$^{-1}$). Remarkably, this is the same order as found for stabilization energies according to equation (1).

A low $S_0/T_1$ energy gap has also been calculated for the nitrogen-free analogs of **7** and **10**, i.e. 3,4-dimethylenethiophene and naphtho[1,8-*cd*]thiapyran.[46] Figure 3 illustrates the changes in bond length, charge distribution and $S_0/T_1$ splitting energies by comparison of compounds **1b**, **2b**, **3**, **4**, **8** and **10**. The low splitting energy of **10** is accompanied by a short SN bond length. In contrast, the classical 1,2,5-thiadiazole (**4**) shows an extremely large $S_0/T_1$ gap and a large SN bond length. Concomitantly, the charge separation of the SN bond is minimal.

Table 3. $S_0/T_1$ splitting energies (kcal mol$^{-1}$) of parent sulfur diimides and related compounds at optimum geometries at different levels of theory

| Compound | Becke3LYP/6–31G* | MP2 (full)/6–31G*QCISD/6–31 + G** | |
|---|---|---|---|
|  | 60.4 | 71.9 | 65.9 |
|  | 68.9 | 87.6 | 70.8 |
|  | 63.9 | 76.4 | 67.6 |
|  | 60.1 | 71.5 | 66.6 |
|  | 20.6 | 24.5 | 17.6 |

The results of the CIS method provide a qualitatively similar trend (cf. Table 5). Since the excited states are defined by configuration interaction whereas the RHF singlet ground states are unchanged, the (vertical) $S_0/T_1$ splitting is too low in this approximation. In the case of **7** with the lowest singlet/triplet gap (cf. Table 4), a triplet molecule is even wrongly predicted for that reason.

The vertical lowest $S_0/T_1$ excitation energies that determine the position of the color band of ylidic sulfur diimides are surprisingly well predicted for non-classical compounds such as **10** (cf. Table 5). This is in line

Table 4. DFT (Becke3LYP/6–31G*) $S_0/T_1$ splitting energies

| Compound | $\Delta E$ ($S_0/T_1$) (eV) | $\Delta E$ ($S_0/T_1$) (kcal mol$^{-1}$) | $E_{tot}$ ($T_1$) (hartree) |
|---|---|---|---|
| **1a** (*EE*) | 2·61 | 60·1 | −508·70497 |
| **1b** (*EZ*) | 2·99 | 68·9 | −508·69864 |
| **1c** (*ZZ*) | 2·77 | 63·9 | −508·70840 |
| **2a** (*EE*) | 2·25 | 51·8 | −587·33224 |
| **2b** (*EZ*) | 1·23 | 28·3 | −587·38416 |
| **3** | 0·97 | 22·4 | −586·18935 |
| **4** | 4·22 | 97·2 | −584·93667 |
| **5** | 2·17 | 50·0 | −738·63722 |
| **6** | 1·96 | 45·2 | −905·69331 |
| **7** | 0·19 | 4·4 | −662·41239 |
| **8** | 3·17 | 73·0 | −1091·40357 |
| **9** | 0·87 | 20·1 | −1245·13555 |
| **10** | 0·34 | 7·9 | −892·31193 |
| **11a** | 0·57 | 13·2 | −1398·76541 |

Table 5. Lowest energy vertical singlet–singlet and singlet–triplet transitions of diorganyl sulfur diimides obtained by *ab initio* CIS/6–31 + G* and by all valence electron PECI calculations (PM3 method)[a] based on DFT(Becke3LYP)/6–31G* optimum geometries

| Compound | $S_1 \leftarrow S_0$[b] eV | nm | $f$ | $T_1 \leftarrow S_0$ (eV) |
|---|---|---|---|---|
| **1a** (*EE*) | 4·98 | 249 | 0·24 | 1·26 |
| **1b** (*EZ*) | 5·20 | 238 | 0·27 | 1·51 |
| **1c** (*ZZ*) | 5·34 | 232 | 0·25 | 1·82 |
| **2a** (*EE*) | 4·17 | 297 | 0·33 | 0·63 |
| **2b** (*EZ*) | 4·66 | 266 | 0·32 | 1·07 |
| **3** | 4·32 | 287 | 0·18 | 0·87 |
| **4** | 6·15 | 202 | 0·27 | 3·45 |
| **5** | 4·65 | 266 | 0·15 | 2·01 |
| **7** | 2·82 | 439 | 0·29 | −0·05 |
| **8** | 4·18 | 297 | 0·16 | 1·30 |
| **9** | 3·03 | 409 | 0·21 | — |
| **10** | 2·19 | 566 | 0·05 | 0·04 |

[a] Wavelength of the lowest energy $\pi \rightarrow \pi^*$ ($B_2 \leftarrow A_1$) transitions in nm (with oscillator strengths in parentheses) according to all-valence electron PECI calculations (PM3, PECI = 10): **1** (*EZ*), 335 (0·02), **2** (*EZ*), 363 (0·04); **3**, 371 (0·04); **4**, 256 (0·05); **5**, 341 (0·09); **7**, 450 (0·15); **8**, 373 (0·07); **9** 433 (0·21); **10**, 655 (0·04). The transitions are polarized perpendicular to the twofold axis. Experimental lowest energy absorption wavelengths: **3**, 257; **4**, 254; **5**, 311; **8**, 317; **10**, 642 nm.

[b] $\pi \rightarrow \pi^*$ transitions; in the case of compounds **1–3** a low-intensity $\sigma \rightarrow \pi^*$ transition is calculated between 250 and 310 nm at longer wavelengths than the $\pi \rightarrow \pi^*$ transition.

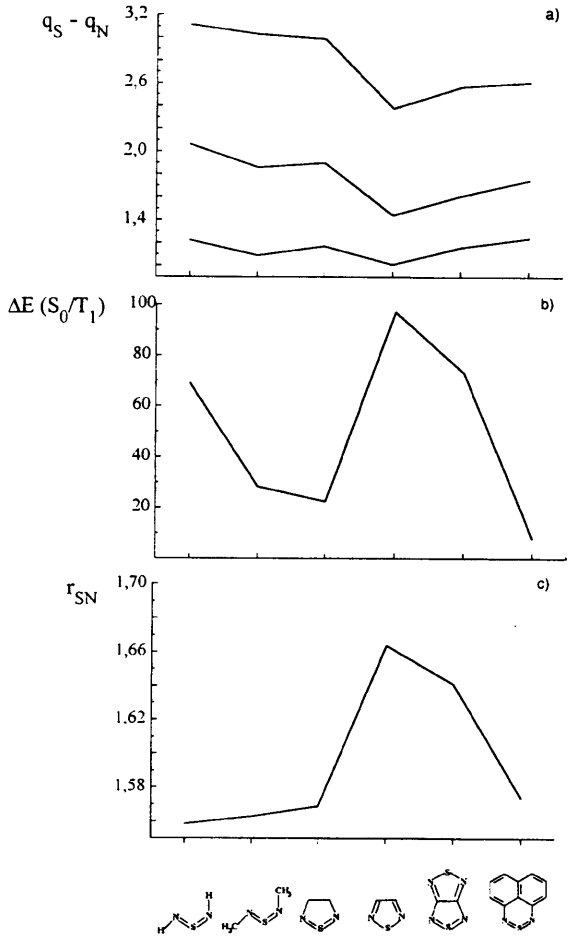



Figure 3. (a) Change in charge separation, difference in the total atomic charges, (b) SN bond lengths (in Å) and (c) $S_0/T_1$ splitting energies (in kcal mol$^{-1}$) of sulfur diimides

with previous results on thiocarbonyl *S*-methides calculated in the same approximation.[45-47] In contrast, the excitation energies of typical dye classical chromophores, such as polymethine, are much too high. The exceptionally good agreement is obviously due to the fact that the ground-state energies of diradicaloid compounds are underestimated to a similar extent as the lowest excited-state energy.

The *ab initio* theoretical result supports early assignment of the color band to $\pi \rightarrow \pi^*$ transitions. Inspection of the pertinant MO coefficients of the CI matrix allows a cross-classification of the states involved in the electron excitation. According to the *ab initio* CIS calculations, the color band is due to an allowed $\pi \rightarrow \pi^*$ transition which is polarized perpendicular to the twofold axis for all molecules of $C_{2v}$ symmetry ($B_2 \leftarrow A_1$ transitions), except for **4**. This result justifies the previous prediction of the position of the color band of **10** by semi-empirical PPP calculations.[8] The only slightly more expensive PM3/PECI-all-valence electron calculations gave similar predictions (cf. footnote to Table 5). According to both *ab initio* and semi-empirical calculations, naphtho[1,8-*cd*][1,2,6]thiadiazine (**10**) proved to be the most bathochromic compound of the series considered (about 600 nm). The experimental absorption wavelength of the color band of **10** is 642 nm.[18]

## CONCLUSION

At first sight, the data presented and discussed above display a contradictory picture about the electronic structure of the sulfur diimide and the nature of the NSN bond. The short SN bond length may suggest a thiocumulenic structure whereas the pronounced charge separation favors an ylidic type of bond with a lower double bond character. However, the results no longer appear controversial when Coulomb contraction is considered in polar bonds. This effect has recently been discussed for short CO bonds encountered in zwitterionic olate structures.[48] These bonds display the same type of strong charge separation.

Ylidic structures may also have some diradicaloid character. As detailed by Salem and Rowland[49] and reviewed elsewhere,[50] the ylidic and diradical structures are two parts in the more general theoretical description of some molecular structures.

Valence formulae have a large intuitive power. The mesomeric formulae of compounds such as **7** and **10** indicate surprisingly well the main characteristics of the electronic structure confirmed by numerical results. Whereas the NSN bond appears strongly isolated in the above-mentioned non-classical compounds, it merges with the hydrocarbon fragment in the classical compounds **4** and **5**. The main classification is obviously controlled by topology and by the conjugated system that is only displayed in the resonance structures.

Sulfur diimides of non-classical structure are distinguished from those of classical structure by shorter SN bond lengths, lower $S_0/T_1$ energy gaps and first absorption bands at long wavelengths.

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