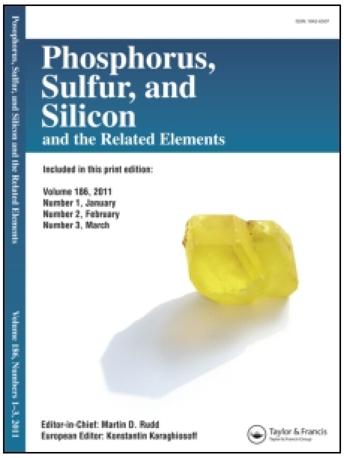

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ON THE ELECTRONIC STRUCTURE OF DIPHENYL-SULFDIIMIDE

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ON THE ELECTRONIC STRUCTURE OF DIPHENYL-SULFDIIMIDE†

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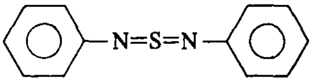
Diphenyl-sulfdiimide (**1**) absorbs at considerably longer wavelengths than the isomeric diphenyl-diazosulfide (**2**). This conspicuous UV-VIS-spectral feature has been examined within the framework of the semi-empirical PPP–method. An explanation could be achieved without taking into account the d orbital expansion of sulfur. "Molecules in molecule"-type calculations revealed the significance of the mixing of the locally excited configurations of the heteroatomic groups with charge transfer configurations. For comparison the spectral data of monophenyl-sulfdiimide (**3**) and *N*-sulfinyl-aniline (**4**) are discussed.

I INTRODUCTION

Diphenyl-sulfdiimide (**1**), now being available by several distinct reaction routes,[1–3] exhibits a deep yellow color. This color results from the intense light absorption in the 400 nm region.[1,2,4,5] In contrast, the iso-π-electronic diphenyl-diazosulfide absorbs strongly only at significantly lower wavelengths ($\approx$330 nm[6,7]). This quite different spectral feature may be caused by different valence states of the sulfur as suggested by formulae **1** and **2**. According to formula **1** diphenyl-sulfdiimide contains a quadrivalent sulfur which is commonly related to a sulfur 3d octet expansion. Without assuming such a 3d participation the molecule must either have the character of a *N*-*S*-ylid (**1a**, **1b**) or of a diradical (**1c**). For the same reason the electronic structures of monophenyl-sulfdiimide (**3**) and *N*-sulfinyl-amine (**4**) may be questioned. In contrast to **1**, **3** and **4** diphenyl-diazosulfide (**2**) can be described unequivocally by a δ-bivalent sulfur.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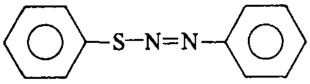
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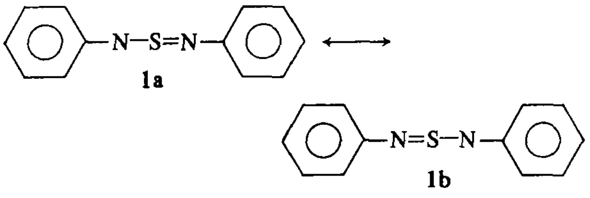
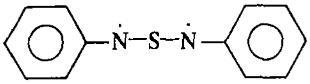

1a ⟷ **1b**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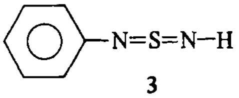
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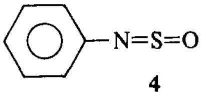
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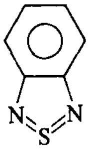
The quadrivalency of sulfur has been discussed for various heterocyclic compounds of the type **5**-**8** and for the thiazyl cations **9** and **10**. In some cases CNDO/2 all-valence electron calculation have been invoked to establish the sulfur 3d participation.[8–12]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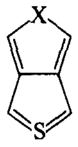
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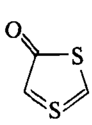
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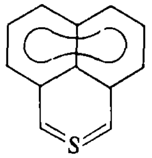
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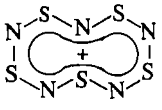
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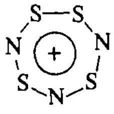
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† Part XXXIX in a series "MO-LCAO calculations on Sulfur-containing π-Electron Systems" (for Part XXXVII see J. Fabian, P. Schönfeld and R. Mayer. In press, *Phosphorus and Sulfur*, (1976)).

Other papers, however, have shown, that the CNDO/2 method in the original parametrization[13] highly exaggerates the d effect and, consequently, does not permit a clear-cut decision about an octet expansion.[14] Even in the case of the parent structures **11** and **12** no meaningful judgment could be achieved as to whether or not the inclusion of d orbitals is necessary to explain the electronic transitions.[9]

$(H_3C)H{-}N{=}S{=}N{-}H(CH_3)$ **11**

$H{-}N{=}S{=}O$ **12**

In general, d orbitals do not affect the symmetry of the frontier orbitals and induce only a feeble change of the S—N-bond order[10]. They have been neglected in a study of the isomerization pathway of **12**.[15]

On the other hand, the p model of sulfur has been successfully employed in PPP-type calculation of **5**,[16] **6**,[17] **7**,[18] **8**,[19] **9**,[20] **10**[21] and related structures involving a thiophene like sulfur. Among others, the spectral feature could be reproduced quite well without assuming any d participation.

The purpose of this paper is to elucidate the different spectral properties of **1** and **2**. Taking into account the results mentioned above, we tentatively disregarded the octet expansion and employed the simple p_π-model of sulfur.

II THEORETICAL MODEL

The $\pi \rightarrow \pi^*$ transitions have been calculated by the PPP method.[16] Singly excited configurations Ψ_{ij} were included into the configuration interaction treatment:

$$\Psi = \sum_{ij} c_{ij} \Psi_{ij} \quad \begin{array}{l} i = 1, 2, 3, 4 \\ j = 1', 2', 3', 4' \end{array} \tag{1}$$

In order to achieve a more simple interpretation the "molecules in molecule" (MIM)-method[22] has also been employed. This procedure consists in partitioning the molecular systems in molecular sub-units. This way the state function Ψ are expanded in terms of the no bond configuration Ψ_0, the localized excited (LE) configurations Λ_{kl} and the charge transfer(CT) configurations T_{nm}:

$$\Psi = c_0 \Psi_0 + \sum_{kl} c_{kl} \Lambda_{kl} + \sum_{nm} c_{nn} T_{mn} \tag{2}$$

The sub-units of **1** and **2** are the two benzene moieties and the N—S—N and S—N—N group, resp. Concerning the parameterization, we retain values formerly proposed. Only the resonance integral of the S—N bonds was varied ($0.75 \leqslant k_{SN} \leqslant 0.90$). The calculated spectral data do not strongly depend upon the β_{SN} resonance integral (cf. *vide infra*). A more serious problem, however, concerns the appropriate assumption about the valence state of the heteroatoms. To avoid an arbitrary choice of the ionization potentials as well as to take into account δ charge effects the core charges Z^c have been derived from CNDO/2 calculations (neglecting 3d orbitals) following Eq. (3).

$$Z^c = N_\mu - [q_\mu{}^\delta + 2] \tag{3}$$

where N_μ denotes the nuclear charge and $q_\mu{}^\sigma$ the calculated σ-electron density of the atom μ. Whereas the Z^c values for nitrogen and sulfur of **2** do not deviate significantly from the commonly used fixed values 1 and 2, resp., the corresponding core charges of the heteroatoms in **1** differ more strongly (cf. Table I). In this structure the sulfur atom exhibits an intermediate valence state between that of a thiocarbonyl and that of a thiophene-like sulfur. The same holds for the sulfur atom of **4**.

The atomic parameters U_μ were obtained by means of the Z^c values using Eq. (4).

$$U_\mu = (U_{-X-} - U_{=X}) Z^c + (2U_{=X} - U_{-X-}) \tag{4}$$

The calculated U_μ values are listed in Table I. They are used for the PPP as well as MIM calculations. As only the x-ray study of *p,p'*-dimethyl-**1**[23] and a gas-phase electron diffraction study of methyl-**12**[24] were carried out, the following estimated bond lengths, *r*, have been adopted: $r_{CC} = r_{CN} = r_{NN} = 1.4$ Å, $r_{CS} = 1.7$ Å, $r_{SO} = 1.45$ Å, $r_{SN} = 1.55$ Å. Calculations have been performed on the all-trans and cis-trans configurations. The all-trans configuration of **1** was assumed to be favored in solution.[25] For the sake of simplicity, all angles were adopted to be 120°. Any

TABLE I
Parameters employed in PPP type calculation[a]

Compound	Atom	Z^c	U in eV
1	S	1.5087	−16.315
	N	1.1546	−15.547
2	S[b]	1.8835	−19.126
	N_1	0.9533	−13.741
	N_2	0.9863	−14.037
3	S	1.5490	−16.618
	N	1.0031	−14.188
	O	1.3573	−20.814

[a] $U_{=S}$: −12.5 eV, U_{-S-}: −20 eV, $\gamma_{SS} = 10.84$ eV $U_{=N}$: −14.16 eV, U_{-N}: −23.13 eV, $\gamma_{NN} = 19.28$ eV $\beta_{CS} = 0.7\ \beta_{CC}$, $\beta_{CO} = 1.2\ \beta_{CC}$; $\beta_{CC} = -2.318$ eV. The Z^c- and U-value were calculated by Eqs. (3) and (4), resp.

[b] $H_5C_6{-}S{-}N_1{=}N_2{-}C_6H_5$.

deviations of the benzene moieties from planarity were neglected.

III RESULTS AND DISCUSSION

The CNDO/2 all-valence electron densities indicate a pronounced different electron distribution between **1** and **2**. The electron densities within the heteroatomic substituent group are more ylid like in the case **1** (and **3**) (cf. Figure 1), but the N—S bond energies display a considerable double bond fixation. As the π-molecular diagram reveals the same pattern (Figure 1) the electronic structure of diphenyl-sulfdiimide may be expressed by the limiting formulae **1a** and **1b** rather than by **1**. Beyond this, the NSN, SNN as well as the NSO-substituent groups in the ground state act as a weak π-electron donor. Consequently, the *o*- and *p*-positions of the benzenes bear negative charges.

The π → π*-transition energies, which we have calculated on the basis of this electronic structure, agree well with the experimental data (cf. Table II). The pronounced longer wavelength absorption of **1** compared to **2** and **3** is, thus, correctly reproduced. The result does not depend upon the parametrization within a range of reasonable values and are only smoothly changed in passing from the all-trans to the cis-trans configuration. The very similar spectral data obtained by means of the MIM procedures (Table II) encouraged us to use this method for an interpretation of the nature of the long wavelength absorptions. The most important excited configurations involved in the configuration-interaction matrices are the LE configurations of the heteroatomic group X and the CT configurations (Figure 2). As shown in Table III the lowest energy state of **1** and **2** is mainly represented by mixing LE(X) and CT(X → benzene). Based on these configurations the higher absorption wavelength of **1**, in comparison to **2**, results from the lower excitation and ionization energy of the NSN compared to the SNN moiety. A qualitative idea about the interrelations of these energies is already accessible within the HMO approach, starting from the molecular orbitals of the triaza-trimethinium anion (triazenium anion) (Figure 3). As the highest occupied molecular orbital (HOMO) possesses a nodal plane which bisects the NNN angle, only sulfur in the 1(3) position lowers the HOMO-energy level ($\alpha_{\ddot{S}} > \alpha_{\dot{N}}$). On the other hand, as can be derived from the expansion coefficients heteroatomic substitution decreases the energy of the lowest free molecular orbital (LFMO) preferably in the 2 position. Consequently, the energy necessary to excite as well as to remove an electron is lower for the NSN than for the SNN group. This conclusion is retained if a lower resonance integral for the N—S in comparison to the N—N bond is taken into account.

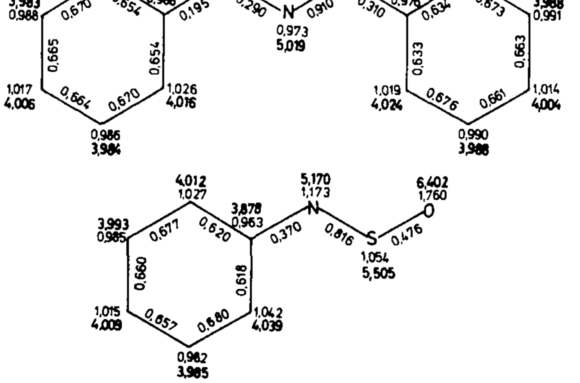
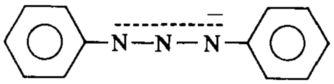


FIGURE 1 CNDO/2 all valence electron densities, π-electron densities (in parentheses) and π-bond orders of **1**, **2** and **3**.

In this connection it is worth noting that intense wave-length absorption is well known for the polymethine-like structures. Whereas data about the 1,3-diphenyl-triazeniumion **13** are not available as yet the parent hydrocarbon **14** was found to absorb at 535 nm.[26] Hence, the yellow color of **1** can be related to the presence of a polymethinic chromophore which undergoes a strong coupling with degenerate CT configurations.



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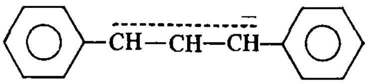

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The comparison of the calculated spectral data of **1** and **3** (and **4**) shows clearly the significance of the presence of two phenyl substituents. In order to

TABLE II
Experimental and theoretical absorption wavelengths ($\lambda_{max} > 200$ nm)

Structure	Method	β_{SN} β_{SO}	λ_{max}(lg f) and (lg ϵ), resp.
all-trans −1	PPP[d]	0.9	378(0.17) 292(−1.70) 291(−1.35) 249(−1.93) 244(−0.95) 239(−0.53) 237(−0.53)
		0.85	388(0.17) 293(−1.39) 293(−1.76) 255(−1.67) 245(−1.05) 243(−0.93) 241(−0.52)
		0.80	398(0.15) 294(−1.54) 294(−1.85) 261(−1.65) 247(−0.94) 245(−1.23) 245(−0.49)
		0.75	410(0.15) 296(−1.54) 295(−1.97) 268(−1.67) 251(−0.96) 249(−0.59) 245(−0.92)
	MIM[e]	0.80	409(0.18 314(−1.77) 314(−1.53) 285(−0.79) 256(−2.52) 253(−1.54) 252(−1.20) 226(−2.23) 215(−1.47) 215(−1.25)
cis-trans −1	PPP	0.80	408(0.00) 300(−1.69) 295(−1.86) 265(−0.99) 255(−0.59) 248(−1.67) 245 (−0.53)
exp. values[a]			414(4.20) 355s(3.93) 291s(3.43) 262s(3.66) 246s(3.86) 245(13.89) 221(3.96)
trans −2	PPP	0.9	304(0.05) 272(−2.10) 268(−2.20) 238(−0.99) 216(−0.57) 215(−0.98) 209(−0.40)
		0.85	306(0.04) 272(−2.07) 267(−2.35) 237(−0.97) 217(−1.16) 215(−0.51) 208(−0.38)
		0.80	307(0.02) 272(−2.03) 267(−2.52) 237(−0.96) 219(−1.39) 216(−0.46) 207(−0.37)
		0.75	309(0.01) 272(−2.73) 267(−2.73) 236(−0.94) 222(−1.33) 216(−0.46) 207(−0.36)
	MIM[e]	0.80	308(0.04) 285(−1.95) 277(−3.39) 256(−0.78) 229(−1.12) 223(−0.80) 214(−1.56) 206(−2.31) 201(−0.70)
cis-trans −2		0.80	315(−0.12) 272(−1.64) 272(−1.93) 239(−0.77) 224(−0.63) 222(−0.88) 208(−0.45)
exp. values[b]			333(4.09) 260(4.08)
trans −3	PPP[f]	0.8	331(0.07) 299(−1.54) 241(−1.67) 237(−0.78) 216(−0.85) 206(−4.91)
	MIM[e]	0.8	346(0.08) 308(−1.62) 248(−1.27) 241(−1.25) 211(−0.85) 209(−1.29)
cis-trans −3			346(−0.17) 296(−1.67) 236(−1.60) 231(−0.78) 218(−1.28) 202(−1.86)
exp. values			
trans −4	PPP	0.80	335(0.00) 300(−2.12) 247(−1.07) 244(−0.79) 215(−1.35) 201(−1.03)
	MIM[e]		348(0.00) 299(−2.30) 251(−1.09) 230(−0.77) 212(−1.33) 204(−0.91)
cis-trans −4		0.80	351(−0.24) 310(−1.43) 256(−2.04) 247(−0.72) 214(−0.88) 204(−0.87)
exp. values[c]			320(4.00) 238(3.82) 233(3.85)

[a] Ref. 4 , in cyclohexane.

[b] Ref. 6 , in dioxan.

[c] In cyclohexane, cf. Ref. 27: 321(3.97) 235(3.80), cf. also Ref. 28.

[d] With parametrization of thiocarbonyl sulfur[29] ($U_S = -12.5$eV, $\gamma_{SS} = 9.8$eV, $Z_S = 1$, $\beta_{NS} = 0.85\beta_{CC}$): 444(0.15) 360(−1.60) 359(−1.19 282(−0.89) 240(−1.66) 227(−1.34) 226(−0.94; with parametrization of sulfide sulfur[30] ($U_S = -20$eV, $\gamma_{SS} = 10.84$eV, $Z_S = 2$, $\beta_{NS} = 0.85\beta_{CC}$): 411(0.19) 311(−2.64) 301(−2.91) 281(−1.78) 260(−0.93) 258(−0.51) 242(−1.02).

[e] The ground state depression energy has been neglected.

[f] The same parameters as used for 1.

TABLE III
MIM configurations mainly contributing to the lowest excited state

Compound	MIM configurations		
	LE(X)	CT (X →B)	CT(B →X)
1 (X = NSN)	36.8%	34.1%	15.3%
2 (X = SNN)	43.9%	27.8%	14.0%
3 (X = NSN)	37.3%	34.7%	15.6%
4 (X = NSO)	33.0%	11.6%	43.0%

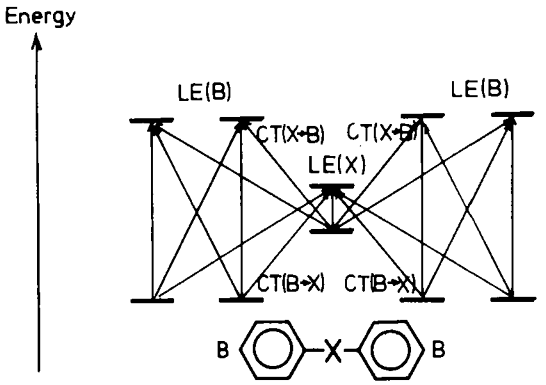

FIGURE 2 Most important LE and CT configurations (ϕ = phenyl, X = heteroatomic group).

rationalize this effect the interaction between the LE configuration of the NSN group and the CT configuration NSN → benzene were considered and the results illustrated in Figure 4. The low first excited energy level is due to the splitting caused by the CT configurations of the second benzene fragment.

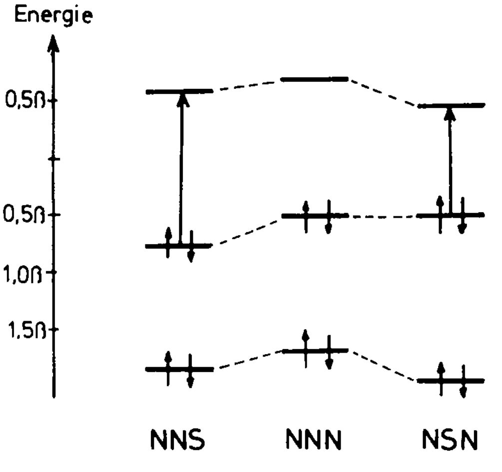

FIGURE 3 Hückel-molecular orbitals of NNN⁻and their shift by heteroatomic substitution ($\beta_{SN} = \beta_{NN}$).

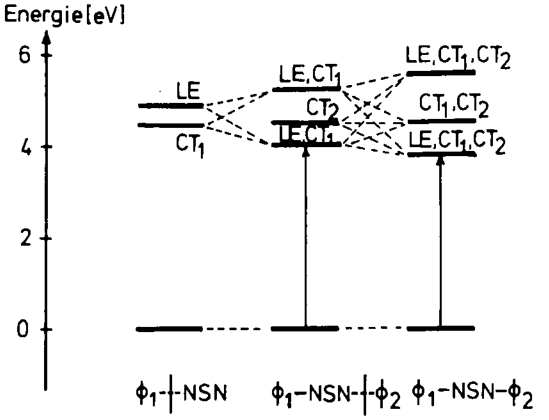

FIGURE 4 Splitting of the term levels by interaction of the lowest energy LE and CT configurations of **1**.

In summary, we found that the peculiar properties of **1** are not unusual and can be sufficiently interpreted without invoking sulfur 3d orbitals.

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