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Photoelectron Spectra of Sulfurdiimines and Carbodiimines

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He(I) photoelectron spectra are reported for sulfurdiimines (R–N=S=N–R) and carbodiimines (R–N=C=N–R) with R = CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9. The assignments are based upon the results of calculations on the methyl derivatives using CNDO/2 and Slater X_α methods.

Introduction

Bonding properties and spectroscopic investigations of allyl and allene derivatives directed our attention to the study of cumulated double bond systems such as the sulfurdiimines, R–N=S=N–R and the carbodiimines, R–N=C=N–R, with R = CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9. These double bond systems are particularly interesting as they can behave as ambident ligands in transition metal complexes [1]. The sulfurdiimines for instance may act in principle as σ-(S)-donor, σ-(N)-donor, mono- and bidentate [2] or as η_2- or η_3-donor via the π-electrons of the N=S=N double bond system [3].

The geometry of dimethylsulfurdiimine in the gas phase is known from an electrondiffraction study of Kuyper and Isselman [4]. The methyl groups are directed *cis* and *trans* respectively to the N=S=N part of the molecule, as shown in Fig. 1. The *trans–trans* configuration (see Fig. 3) exists to a lesser extent in the liquid phase and only in equilibrium with *cis–trans* as is known from n.m.r. and infrared data [1]; a rotational barrier of 13 Kcal/mol is calculated for the t-butyl-derivative [1]. The *cis–cis* configuration is excluded because of steric hindrance by the methyl groups. The bond angles and bond distances of dimethyl carbodiimine are taken from the calculated geometry of Williams and Damrauer [5] (see Fig. 2).

The photoelectron spectra of the t-butylcarbo- and sulfurdiimines were observed earlier by Kroner *et al.* [6] together with other bent cumulenes and compared with CNDO/2 calculations based upon optimized structural data. Several sulfur-containing compounds have been studied by Solouki [7] with photoelectron spectroscopy and the results compared with MO calculations.

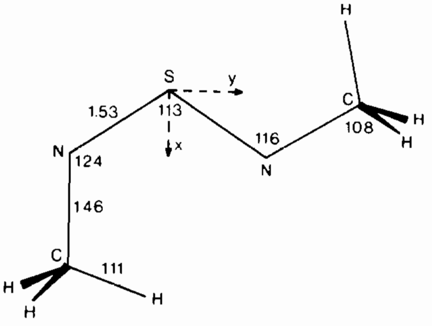

Fig. 1. The geometry of the *cis–trans* dimethylsulfurdiimine. Distances are given in Ångstroms and angles in degrees.

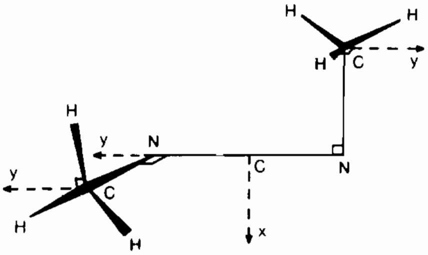

Fig. 2. The calculated geometry of the dimethylcarbodiimine. l(N=C) = 1.26 Å; l(N–CH_3) = 1.40 Å; l(C–H) = 1.09 Å; L(HCH) = 109° 28′.

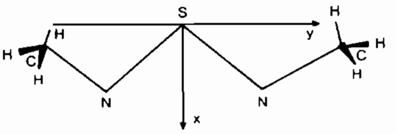

Fig. 3. The geometry of the *trans–trans* dimethylsulfurdiimine.

Experimental

The pure compounds R–N=S=N–R were obtained by the method of Kuyper and Vrieze [1] and the R–N=S=N–R samples by the methods of

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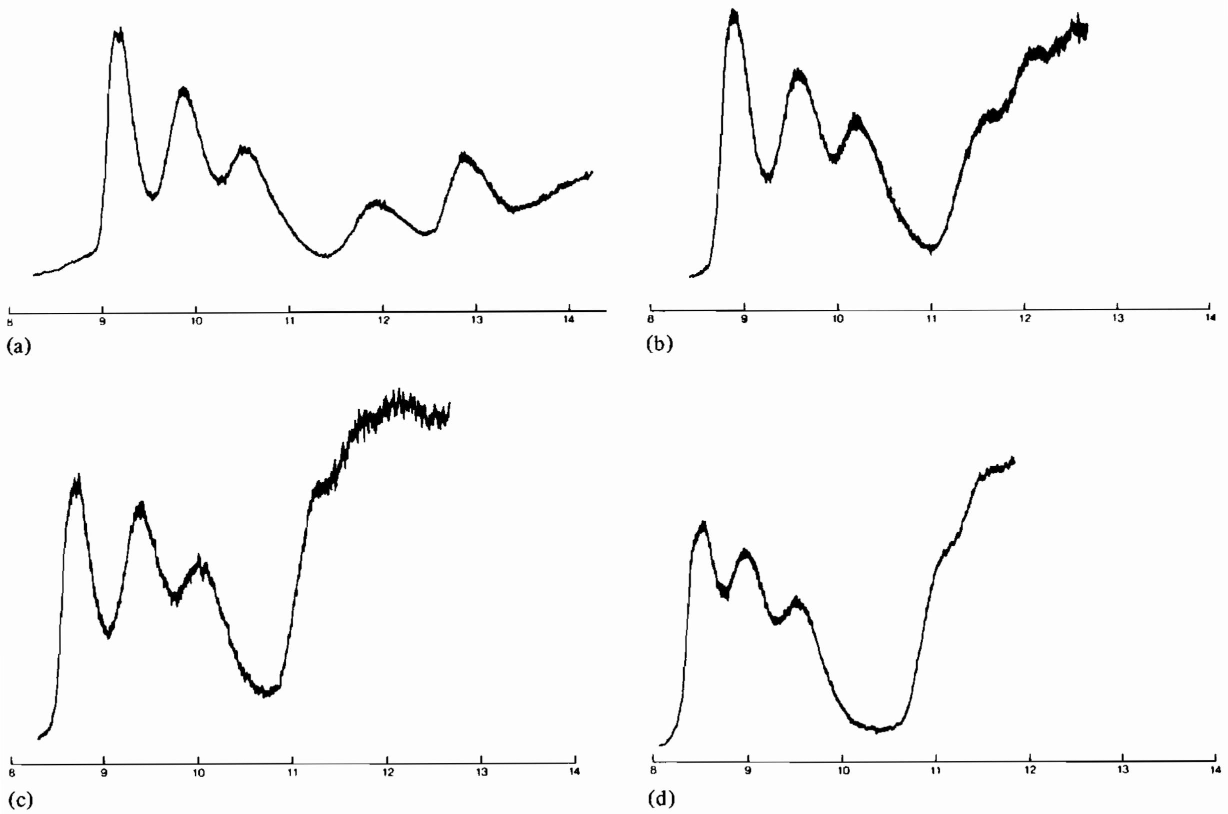


Fig. 4. (a) Photoelectron spectrum of dimethylsulfurdiimine. (b) Photoelectron spectrum of diethylsufurdiimine. (c) Photoelectron spectrum of diisopropylsulfurdiimine. (d) Photoelectron spectrum of ditertiarybutylsulfurdiimine.

Rapi and Sbrana [8], for R = CH_3 and Schmidt and Striewsky [9] for R = C_2H_5, i-C_3H_7 and t-C_4H_9. All the samples were purified by distillation except CH_3–N=C=N–CH_3, which was obtained by preparative gas chromatography as described in ref. 8. All samples are fairly stable, though they tend to polymerise when exposed to air.

The photoelectron spectra were recorded on a Perkin–Elmer PS-18 instrument, equipped with a 584 Å (21.21 eV) He discharge source. Because all the samples are liquids, we used a volatile sample inlet system with a continuous gasflow of 0.2 torr.

The spectra were obtained with a maximum count rate of 10^4 cps and calibrated with a mixture of Ar and Xe; the resolution was about 30 meV.

Computational

For the calculations we used two different methods: first a Slater X_α method provided by Baerends *et al.* [10], involving an averaged X_α exchange instead of the non-local exchange operator in the Hartree Fock method and including a population analysis [11] and corrections for the deviations from Koopmans' theorem. These corrections consist of calculating ionisation potentials using a transition state in which the molecule under study has lost one half of an electron.

Secondly we used the CNDO/2 method as described by Pople and Beveridge [12] including d-orbitals on the sulfur atom.

Results and Discussion

The He(I) photoelectron spectra of R–N=S=N–R and R–N=C=N–R (R = CH_3, C_2H_5, i-C_3H_7 and t-C_4H_9) are shown in Figs. 4 and 5.

The spectra of the N=S=N compounds nearly all have the same shape, *i.e.* three distinct peaks separated from a series of poorly resolved bands. The dimethyl derivative shows five well resolved peaks.

In view of assignments made for related molecules such as SO_2 [13], H_2S [13], SSO [14], $(R_2N)_2SO$ [17] and $F_2S(NH)_2$ [18] we expect that the maxima on the low energy side of the spectra represent the removal of electrons from orbitals with π-character and from orbitals representing lone pairs on the nitrogen and the sulfur atoms. For the relative ordering of the lone pair and π-type orbitals we have to rely on the calculations performed and

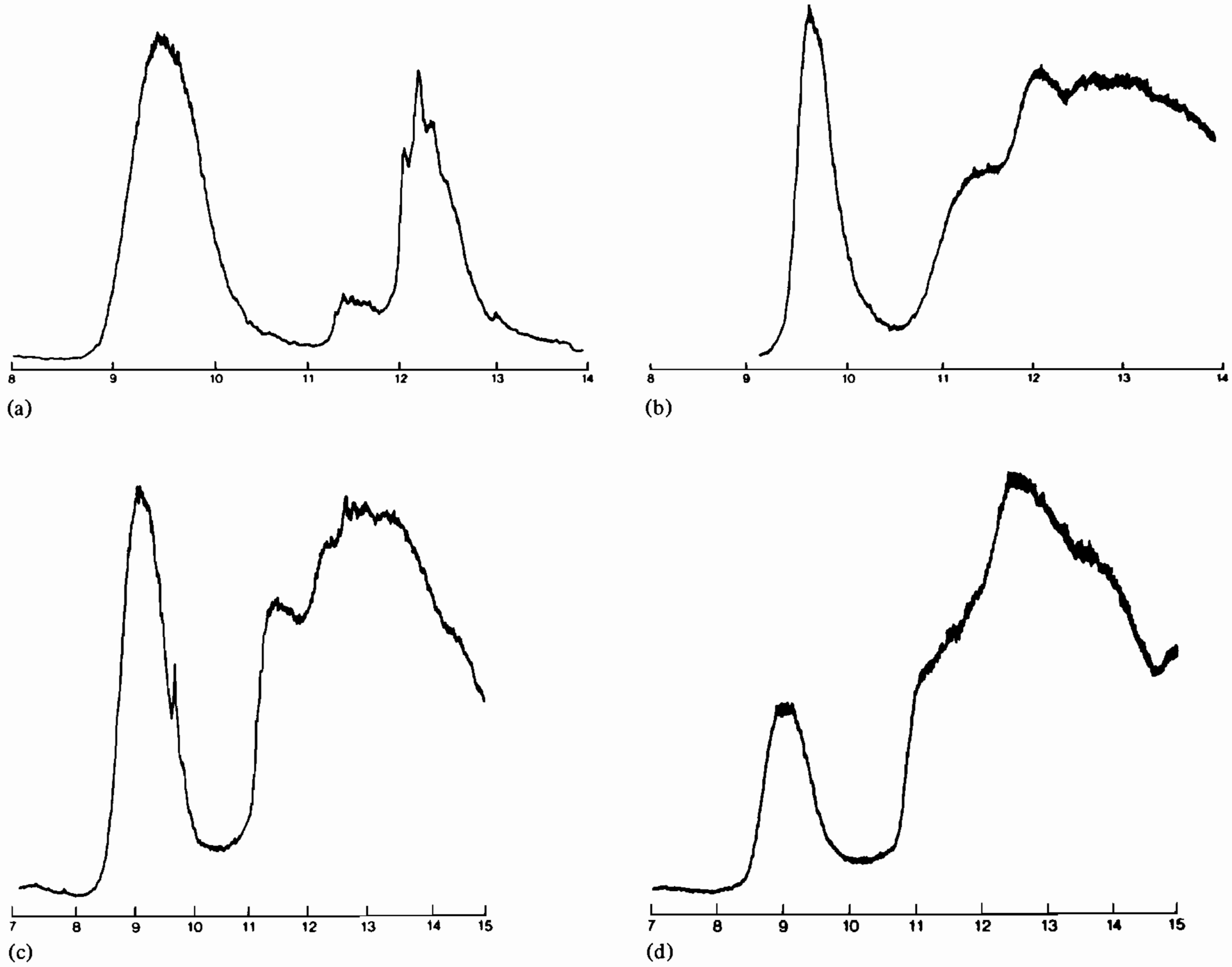


Fig. 5. (a) Photoelectron spectrum of dimethylcarbodiimine. (b) Photoelectron spectrum of diethylcarbodiimine. (c) Photoelectron spectrum of diisopropylcarbodiimine. The sharp maximum at 9.8 eV is due to an impurity. (d) Photoelectron spectrum of ditertiarybutylcarbodiimine.

comparison with related molecules [13–18], for no vibrational fine structure has been observed.

The spectra of the carbodiimines also show the same features, one distinct peak clearly separated from the rest of the ionisations (Fig. 5). Table I gives the experimental ionisation potentials and the calculated energy levels as well as the values found by Kroner *et al.* [6] for the t-butyl derivatives; in the CNDO/2 program no corrections have been made for rearrangements upon ionisation.

The discrepancy between experimentally determined IP's and the Slater X_α values may be due to the lack of consideration of d-orbitals on sulfur in the calculations and for the carbodiimines to the lack of an experimentally determined geometry of the molecules.

Both Slater X_α and CNDO/2 give the same ordering of π and lone pair levels. For the sulfurdiimines the first band is the ionisation from a mostly π-type orbital involving a d_{yz} orbital on sulfur and p_z orbitals on the nitrogen atoms. The next two bands are due to ionisations from lone pair orbitals, the first a symmetrical combination of the lone pairs on the sulfur and nitrogen atoms, the second an asymmetrical combination of the lone pairs on the nitrogen atoms with no contribution of the sulfur lone pair.

The fourth band, a shoulder just visible on the ionisations of the σ-skeleton – except in the dimethyl derivative where it is well resolved – represents a π-type orbital located on the –NSN– part of the molecule, involving p_z-orbitals. This assignment is in agreement with the results of Solouki [7] for $F_2S{=}N{-}CH_3$ (see Table II).

Comparison of the results from the calculations made on the *cis–trans* species with those on the *trans–trans* isomer (Table I) shows hardly any difference in energy levels, and no differences in orbital character or in the level ordering.

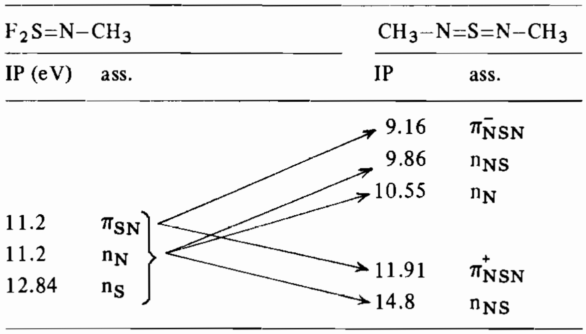
The symmetrical species (see Fig. 3) has C_{2v} symmetry and we can give the first π-type orbital an A_2

TABLE I. Ionisation Energies IE_n and Eigenvalues ϵ_J (eV).

RNSNR	Calculated ϵ_J			Observed IE_n				
Assignment *trans–trans* species	CNDO/2 *cis–trans* $R = CH_3$	CNDO/2 *trans–trans* $R = CH_3$	Slater X_α $R = CH_3$	$R = CH_3$	$R = C_2H_5$	$R = i\text{-}C_3H_7$	$R = t\text{-}C_4H_9$	Ref. 6
A_2	12.37	12.25	8.2	9.16	8.90	8.75	8.61	8.65
A_1	13.37	13.03	8.8	9.86	9.62	9.43	9.06	9.01
B_1	13.58	14.15	9.4	10.55	10.26	10.05	9.57	9.60
B_2	14.81	14.90	11.9	11.91	11.62	11.34	11.10	11.1
B_1	16.45	16.84	12.2	12.85	~12.2	~11.7	~11.6	–

RNCNR	Calculated ϵ_J		Observed IE_n				
Assignment	CNDO/2 $R = CH_3$	Slater X_α $R = CH_3$	$R = CH_3$	$R = C_2H_5$	$R = i\text{-}C_3H_7$	$R = t\text{-}C_4H_9$	Ref. 6
B	11.85	9.5	9.50	9.60	9.05	9.00	8.94
A	12.45	10.1					
B	14.99	10.6	11.55	11.23	11.42	11.19	–
A	15.69	10.9	12.26	12.02	12.20	12.56	–

TABLE II. Solouki's Calculations [7].



$F_2S{=}N{-}CH_3$ IP (eV)	ass.	$CH_3{-}N{=}S{=}N{-}CH_3$ IP	ass.
		9.16	$\bar{\pi}_{NSN}$
		9.86	n_{NS}
		10.55	n_N
11.2	π_{SN}		
11.2	n_N		
12.84	n_S		
		11.91	$\overset{+}{\pi}_{NSN}$
		14.8	n_{NS}

notation, the following lone pairs an A_1 and B_1 and the second π-type orbital transforms as B_2. The lowest lying empty orbital is of B_2 symmetry and has a strong π*-character.

In the spectra of the carbodiimines the first maximum consists of two bands, representing two orbitals located on the –NCN– part of the molecule both with π-type and lone pair character from the nitrogen atoms. The molecule has C_2 symmetry and the molecular orbital calculated to have the lowest ionisation potential transforms as a B, the second orbital as an A species. Throughout both series of molecules the spectra have the same features with only small shifts.

The sulfurdiimine spectra show a shift to lower ionisation energy for each of the first four maxima going from R = methyl to R = t-butyl. This is not remarkable since an electron releasing substituent tends to enlarge the electron density in the NSN part

TABLE III. Orbital Population and Total Charge in the CNDO/2 Program.[a]

Atom	Orbital	Population	Tot. Charge
CH_3NSNCH_3			
S	3s	1.78	
	$3p_x$	1.07	+0.21
	$3p_y$	0.81	
	$3p_z$	0.86	
	$3d_{z^2}$	0.08	
	$3d_{x^2-y^2}$	0.10	
	$3d_{xy}$	0.49	
	$3d_{yz}$	0.32	
	$3d_{xz}$	0.26	
N	2s	1.49	
	$2p_x$	1.24	–0.20
	$2p_y$	1.20	
	$2p_z$	1.26	
C	2s	1.03	
	$2p_x$	0.94	+0.11
	$2p_y$	0.95	
	$2p_z$	0.97	
$C'H_3CNCC'H_3$			
C	2s	1.11	
	$2p_x$	0.75	+0.42
	$2p_y$	0.96	
	$2p_z$	0.75	
N	2s	1.50	
	$2p_{\parallel NC'}$	1.14	–0.31
	$2p_y$	1.20	
	$2p_{\perp CNC'}$	1.46	
C'	2s	1.00	
	$2p_{\parallel NC'}$	0.96	+0.14
	$2p_y$	0.93	
	$2p_{\perp CNC'}$	0.96	

[a] The results in the X_α program are available on request.

of the molecule and therefore raises the corresponding energy levels. The same shift occurs in the carbodiimine series but to a lesser extent since the ethyl derivative deviates significantly.

In Table III are summarized the results of the population analysis for the methyl derivatives; we see that for both types of molecules the central atom holds a positive charge due to the strong π-bond between the central atom and the nitrogen atoms. This is confirmed by the population of the p_z atomic orbitals on the central atom and on the nitrogen atoms. A similar finding was reported by Grunwell and Danison [19].

The delocalization of electrons obtained in the Slater X_α-calculations is much more pronounced, which may be due to the lack of d-orbitals on sulfur.

Finally we conclude that the molecules reported here can easily coordinate to transition metals. Coordination via the sulfur atom is less favoured because of its positive charge. The nitrogen atoms almost always act as electron donors [1]. Although coordination through N–S π-bonds is not yet known in the literature, the calculations show that in principle the possibility exists. A current study of the corresponding complexes will give us more details.

Acknowledgments

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