Ultraviolet Photoelectron Spectra of Some Methyl Esters of Dithiocarbazic Acids and of $[Ni\{N(CH_3)_2-N=C(-S)SCH_3\}_2]$ † and Comparison with Quantum-mechanical Calculations

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Ultraviolet photoelectron spectra of $NH_2-NH-C(=S)SCH_3$, $NH_2-NCH_3-C(=S)SCH_3$, $N(CH_3)_2-NH-C(=S)SCH_3$, $NHC_6H_5-NH-C(=S)SCH_3$, $N(C_6H_5)_2-NH-C(=S)SCH_3$, and $[Ni\{N(CH_3)_2-N=C(-S)SCH_3\}_2]$ have been recorded, and the ionisation energies related to the results of quantum-mechanical calculations. Assignments are made on the grounds of this comparison and by correlation with the parent molecules.

METHYL esters of dithiocarbazic acids of general formula $NR^1R^2-NR^3-C(=S)SCH_3$ and their co-ordination compounds are currently being studied at our C.N.R. laboratory.

The ultraviolet photoelectron spectra (u.v.p.e.) of $NH_2-NH-C(=S)SCH_3$, $NH_2-NCH_3-C(=S)SCH_3$, $N(CH_3)_2-NH-C(=S)SCH_3$, $NHC_6H_5-NH-C(=S)SCH_3$, $N(C_6H_5)_2-NH-C(=S)SCH_3$, and $[Ni\{N(CH_3)_2-N=C(-S)SCH_3\}_2]$ have been studied in order to obtain the energies of the molecular orbitals (m.o.s) involving sulphur in molecules already studied through electronic, i.r.,[1,2] n.m.r.,[3-5] ESCA,[6,7] and *X*-ray[8-10] measurements.

The compound $[Ni\{N(CH_3)_2N=C(-S)SCH_3\}_2]$ is prepared by treating $N(CH_3)_2-NH-C(=S)SCH_3$ with $NiCl_2 \cdot 6H_2O$ in ethanol. Its chromophore seems to be NiN_2S_2;[2,10] its i.r. spectrum has ν(CN) at 1 550 cm^{-1},[2] and the *X*-ray structure determination[10] indicates a bond length of C–N 1.27 Å amounting to an almost pure C–N double bond.

Extensive u.v.p.e. investigations on related sulphur- and nitrogen-containing compounds have already been performed by our group,[11-15] giving information on the role of the orbitals of these atoms in the valence m.o.s. CNDO/2[16] calculations have been performed on the previously mentioned esters and the ionisation energies obtained experimentally have been compared with those derived from the SCF procedure. The assignments are made on the basis both of comparison with already assigned u.v.p.e. spectra of related compounds and of the analysis of the m.o.s computed with the above method; we have also taken into account the results of *ab initio* calculations performed by one of us (A. A. B.) together with C. Battistoni and A. Lapiccirella.[17]

EXPERIMENTAL

The esters $NH_2-NH-C(=S)SCH_3$, $NH_2-NCH_3-C(=S)SCH_3$, $N(CH_3)_2-NH-C(=S)SCH_3$, $NHC_6H_5-NH-C(=S)SCH_3$,[18-20] and $N(C_6H_5)_2-NH-C(=S)SCH_3$ and $[Ni\{N(CH_3)_2-N=C(-S)SCH_3\}_2]$[2] were prepared as described previously.

U.v.p.e. spectra were recorded on a Perkin-Elmer PS 18 spectrometer using He(I) radiation (21.22 eV ‡) and CH_3I, Xe, and Ar as the calibrant gases. For the solid samples, spectra were run at temperatures close to the respective melting points.

TABLE 1

Ionisation energies (eV) of methyl esters of dithiocarbazic acids and of $[Ni\{N(CH_3)_2-N=C(-S)SCH_3\}_2]$

$NH_2-NH-C(=S)SCH_3$	$NH_2-NCH_3-C(=S)SCH_3$	$N(CH_3)_2-NH-C(=S)SCH_3$	$NHC_6H_5-NH-C(=S)SCH_3$	$N(C_6H_5)_2-NH-C(=S)SCH_3$	$[Ni\{N(CH_3)_2N=C(-S)SCH_3\}_2]$
					7.33
					7.77
			8.47	7.47	8.33
8.81	8.39	8.37	8.85	8.46	8.63
9.21	9.06	9.09	9.31	9.19	9.27
10.93	10.91	9.51	9.63	10.09	9.63
					10.47
11.73	11.33	11.37	10.85	10.67	11.35
12.53	11.88	12.09	11.77		11.79
13.31	12.94	12.87	12.58	12.13	12.94
		13.44			13.58
14.05	14.32	14.12	14.32	14.11	
				(14.70) *	15.52

* Shoulder.

RESULTS AND DISCUSSION

The most representative u.v.p.e. spectra are presented in Figure 1 and the measured ionisation energies (i.e.s) are reported in Table 1.

In the spectra of the unsubstituted and *N*-alkyl-substituted esters we expect ionisations from the following orbitals, in the i.e. region below *ca.* 11 eV: (*i*) the in-plane lone pair of the thionic sulphur atom; (*ii*) the π lone pair of both thionic and thiolic sulphur atoms; (*iii*) the π orbitals localised on the N^2 atom; and (*iv*) the lone pair of the terminal N atom.

The spectrum of the unsubstituted ester shows two bands at low i.e. (8.81 and 9.21 eV). This part of the

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† Bis[*S*-methyl 3,3-dimethyldithiocarbazato(1–)]nickel(II).

‡ Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

spectrum is similar to the corresponding region of the spectrum of methyl *NN*-dimethyldithiocarbamate,[21] suggesting a similar composition of the orbitals involved in the ionisation processes. Guimon *et al.*[21] assign the first band (with a shoulder to low energy) to the ionisations of both *n* and π electrons of the thionic sulphur atom, and the second band to a π molecular orbital localised mainly on the thiolic sulphur, with a contribution from nitrogen. This assignment was supported by CNDO-type calculations, which, however, exaggerate the distance between the second and third ionisation.

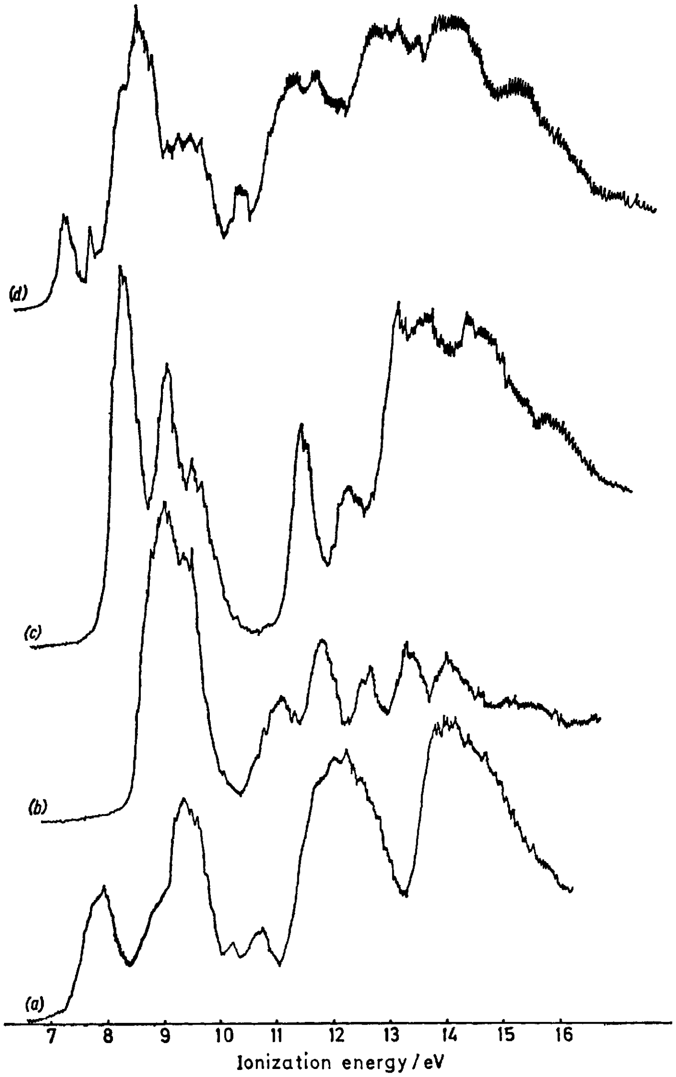

FIGURE 1 Gas-phase He(I) photoelectron spectra of: (*a*) $N(C_6H_5)_2$–NH–C(=S)SCH_3, (*b*) NH_2–NH–C(=S)SCH_3, (*c*) $N(CH_3)_2$–NH–C(=S)SCH_3, and (*d*) [Ni{$N(CH_3)_2$–N=C(–S)-SCH_3}$_2$]

Our CNDO/2 calculations, as shown in Table 2, suggest that in the present case the three highest occupied m.o.s (corresponding to the first two bands at 8.81 and 9.21 eV, with intensity ratio 2 : 1) are localised on the sulphur atoms, with a significant contribution from the π orbital of N^2 to the third highest m.o. At higher i.e.s the spectrum shows five bands of approximately equal intensity. According to CNDO/2 calculations the fourth and fifth orbitals are mainly of C–S σ type, while the first m.o. with significant N^3 lone-pair contribution is the sixth orbital, calculated at 16.48 eV. Assignments made along these lines seem to be unlikely, given that in hydrazine the nitrogen lone pairs give rise to two bands (n_+ and n_-) at 9.90 and 10.75 eV (baricentre 10.32 eV)[22] and in ammonia the nitrogen lone-pair band occurs at 10.16 eV;[23b] we therefore expect ionisation from an orbital mainly localised on the N^3 lone pair in the region 10—11 eV of the spectrum of $NH_2NHCSSCH_3$, which could be identified with the band at 10.93 eV. In order to clarify this point, we have examined the results of the previously quoted[17] *ab initio* calculations, which are in better agreement with the last hypothesis. In fact, although the computed energy values are exceedingly low compared to experimental data, the composition of the m.o.s as shown in Table 2 differs from CNDO/2 results in presenting the fourth orbital (corresponding to the third p.e. band, at 10.93 eV) as mainly localised on the N^3 lone pair; furthermore, in the third level (p.e. band at 9.21 eV) the contribution of the N^2 π orbital is more important than in CNDO/2 calculations.

TABLE 2

Comparison of experimental i.e.s (eV) of NH_2–NH–C(=S)-SCH_3 with results of quantum-mechanical calculations

	CNDO/2		*ab initio*	
Experimental	Calc.	Main localisation of m.o.s	Calc.	Main localisation of m.o.s
8.81	10.26	$\pi(C\equiv S)$	5.16	$\pi(C\equiv S)$
	10.52	$n(S)$	5.21	$n(S)$
9.21	12.70	$\pi(SCH_3) + \pi(N^2)$	8.09	$\pi(SCH_3) + \pi(N^2)$
10.93	13.76	$\sigma(C{=}S)$	10.04	$n(N^3)$
11.73	14.72	$\sigma(CSCH_3)$	10.28	$\sigma(C{=}S)$

Subsequent bands are to be related to ionisations from σ(CS) orbitals, a π orbital localised mainly on N^2, and σ(CH) orbitals.

The u.v.p.e. spectrum of NH_2–NCH_3–C(=S)SCH_3 is similar in general pattern, band shape, and i.e. values to the unsubstituted compound and is to be interpreted along the same lines. There is a slight shift of the bands to lower i.e.s, as expected due to the $+I$ effect of the substituent methyl group. Our assignment is parallel to that for the unsubstituted ester: the first band, at 8.39 eV, is probably due to the ionisations of the in- and out-of-plane lone pairs of the sulphur, the second band, at 9.06 eV, is due to ionisation from a π orbital mainly localised on the thiolic sulphur and on N^2, and the third band is due to ionisation from an orbital of predominant N^3 lone-pair character. Again, this assignment is only in agreement with CNDO/2 calculations for the first three ionisations, whereas the m.o. sequence is better reproduced by the results of *ab initio* computations (see Table 3).

The u.v.p.e. spectrum of $N(CH_3)_2$–NH–C(=S)SCH_3 is qualitatively different from the two previous cases in having three instead of two early i.e. bands (at 8.37, 9.09, and 9.51 eV) before the region of the highest ionisations,

TABLE 3

Comparison of experimental i.e.s (eV) of NH_2-$N(CH_3)$-C(=S)SCH_3 with results of quantum-mechanical calculations

	CNDO/2		ab initio	
Experimental	Calc.	Main localisation of m.o.s	Calc.	Main localisation of m.o.s
8.39	10.02	n(S)	4.85	n(S)
	10.22	π(C=S)	4.93	π(C=S)
9.06	12.12	$\pi(SCH_3) + \pi(N^2)$	7.43	$\pi(SCH_3) + \pi(N^2)$
10.91	13.14	σ(C=S)	8.90	$n(N^3) + \pi(SCH_3)$
11.33	15.38	$\sigma(CSCH_3)$	10.22	$n(N^3)$

beginning with a band at 11.37 eV. The assignment of the first two bands is completely analogous to that of the previous compounds, the further shift to lower i.e. being attributable to the presence of two electron-releasing methyl groups. A much larger shift (9.51 as compared to 10.93 eV in the unsubstituted ester) is observed for the third band; this supports the hypothesis that this band is due to ionisation of the N^3 lone pair. In fact, the presence of two methyl groups on N^3 strongly affects the position of this band, which is practically unshifted (10.91 *vs.* 10.93 eV) in NH_2-$N(CH_3)$-C(=S)SCH_3. The shift of the N^3 lone-pair band is consistent with the behaviour of the corresponding bands in the u.v.p.e. spectrum of *NN*-dimethylhydrazine with respect to unsubstituted hydrazine.[21] Again the CNDO/2 results fit the experimental data for the first three ionisations, whereas only *ab initio* results attribute the third band to an orbital localised on N^3; the shift of this band to lower i.e. is also reproduced by the *ab initio* calculations (see Table 4). A correlation between the experimental i.e.s of the above three compounds and the related molecule

TABLE 4

Comparison of experimental i.e.s (eV) of $N(CH_3)_2$-NH-C(=S)SCH_3 with the results of quantum-mechanical calculations

	CNDO/2		ab initio	
Experimental	Calc.	Main localisation of m.o.s	Calc.	Main localisation of m.o.s
8.37	10.03	π(C=S)	4.88	π(C=S)
	10.26	n(S)	4.92	n(S)
9.09	12.27	$\pi(SCH_3) + \pi(N^2)$	7.62	$\pi(SCH_3) + \pi(N^2)$
9.51	13.01	σ(SCN)	8.77	$n(N^3)$
11.37	14.14	$n(N^3)$	9.40	$n(N^3)$

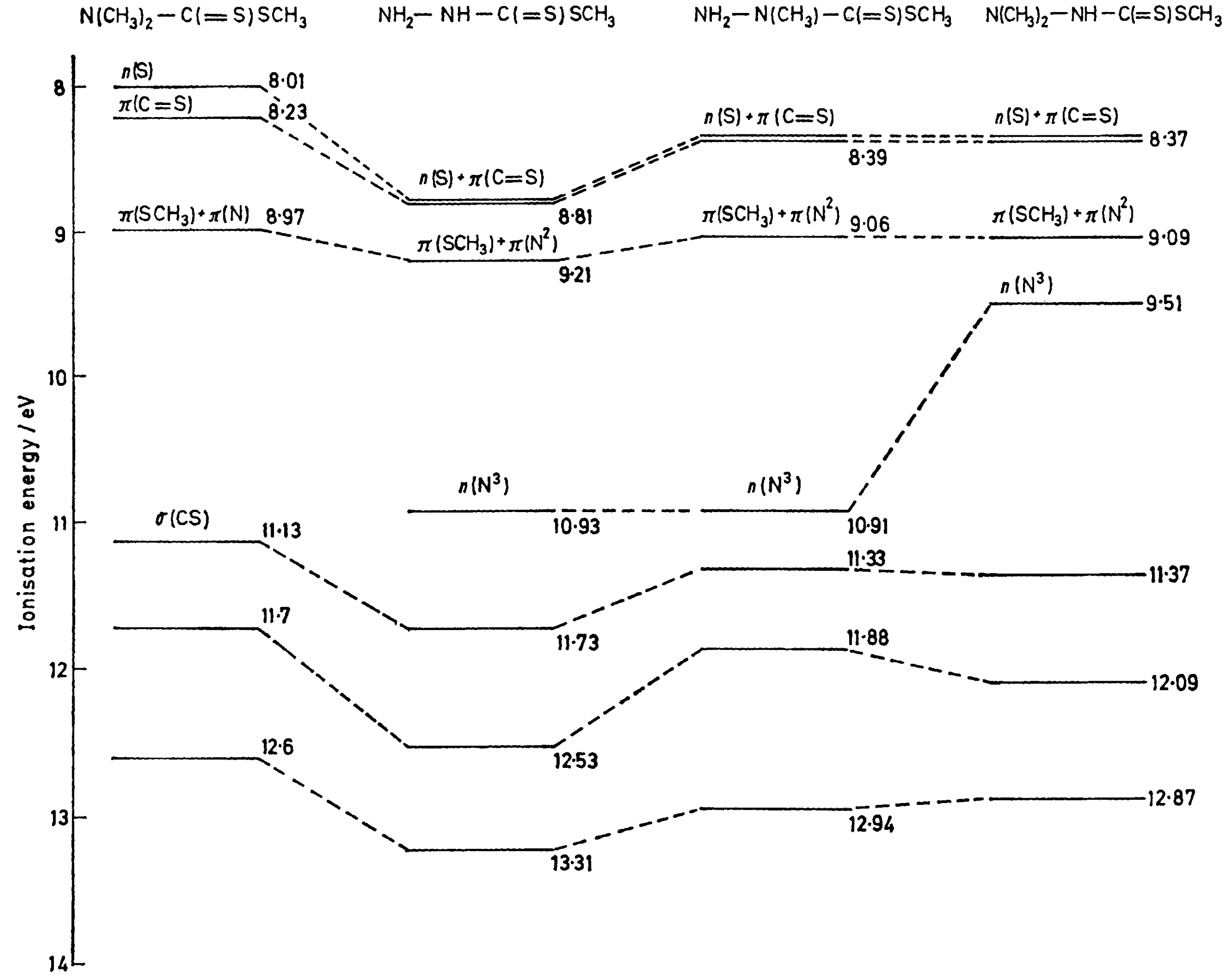

FIGURE 2 Correlation of experimental i.e.s between some studied compounds and the related molecule $N(CH_3)_2$–C(=S)SCH_3

$N(CH_3)_2$–C(=S)SCH_3 is shown in Figure 2. In the spectrum of the complex $[Ni\{N(CH_3)_2–N=C(–S)SCH_3\}_2]$ the appearance of extra bands with respect to the free ligand, arising from ionisations of nickel *d* electrons, differences due to the thiolic structure in the complex, and to the involvement of sulphur and nitrogen lone pairs in the co-ordinative bonding, are to be expected. In fact we observe two, or possibly three, bands, with no counterpart in the free ligand, at 7.33, 7.77, and 8.33 eV, in the spectrum of this compound which we assign to ionisation of *d* electrons, the last one probably being mixed with ligand ionisation; the observed intensities suggest the ordering of orbital energies $(xz,yz) > z^2$ or $(x^2 - y^2) > (x^2 - y^2)$ or z^2.

The ionisation energies of the *d* orbitals can be compared with those of other quadratic nickel(II) complexes, *e.g.* 6.95 and 7.13 eV in nickel(II) diethyldithiocarbamate,[12] 7.63, 7.73, and 8.31 eV in nickel(II) dithioacetylacetonate,[11,14] and 7.31, 7.78, and 8.14 eV in nickel(II) *NN'*-ethylenebis(thioacetylacetoneiminate).[15] The remaining part of the spectrum, although similar to that of the free ligand, shows some differences. Possible assignments are as follows. The intense band at 8.63 eV can be associated with the ionisation of π-type electrons mainly localised on the sulphur atoms while the bands at 9.27 and 9.63 eV may arise from ionisation of another π orbital localised on sulphur and N^2 atoms. The band at 10.47 eV is probably due to ionisation of the highest metal–ligand σ bond, the remaining metal–ligand σ ionisations giving rise to bands overlapping with the subsequent broad envelope.

The p.e. spectral patterns of NHC_6H_5–NH–C(=S)SCH_3 closely resemble those of the unsubstituted ester, with the addition of two bands in the region 9—10 eV and a strong increase in intensity of the bands in the regions around 11.8 and 14.0 eV. The spectrum can be viewed, therefore, as the result of the superposition and interaction of the spectra of unsubstituted dithiocarbazate and of the phenyl group (in the spectrum of benzene π and σ ionisations are reported [24] at 9.3, 11.4—12.1, and 13.8—14.7 eV). Specifically, the region 8—10 eV contains four bands, attributable to the *n* and π sulphur orbitals and to the products of the e_{1g} π orbitals of benzene, which are widely split in aniline derivatives.[23a]

It is more difficult to assign each of the four bands in this region. One possibility would be to assign the band at 8.85 eV as the practically unperturbed *n*(s) ionisation and that at 9.31 eV as the non-interacting split term of the phenyl π doublet, while the bands at 8.47 and 9.63 eV should contain the interacting π level from π (S, N) and the second π phenyl orbital derived from the benzene e_{1g} orbital. The rest of the spectrum is very similar to that of NH_2–NH–C(=S)SCH_3, apart from addition of the benzene bands resulting in increased intensity of the bands at 11.77 and 14.2 eV. The p.e. spectrum of $N(C_6H_5)_2$–NH–C(=S)SCH_3 is dominated by the phenyl ionisation bands, which are more intense than in the preceding case since they correspond to two phenyl groups per molecule. The interpretation here is more difficult than in the mono-phenyl derivative; the higher relative intensity of the band at 9.19 eV suggests its assignment as the unperturbed component of the benzene e_{1g} orbital in both phenyl substituents, masking the bands from the π and *n* sulphur–nitrogen system, while the band at 7.47 eV is likely to be the interaction product of the same benzene orbital with the rest of the molecule. The other benzenoid ionisations could be identified with the broad bands with peaks at 12.13 and 14.4 eV; the remaining bands, at 8.46, 10.09, and 10.67 eV, are probably due to ionisations from orbitals localised on the N–N–CS_2 skeleton.

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