Gas-phase Ultraviolet Photoelectron Spectroscopic Study of the 3,7-Diphenyl- and 3,7-Bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocines

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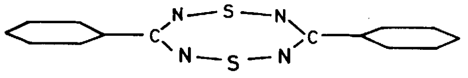
The He^{I} and He^{II} photoelectron spectra of 3,7-diphenyl- and 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocines are reported. Experimental results are in qualitative agreement with previously reported STO-3G and STO-3G + 5D calculations. An analysis of the spectral features confirms the predicted difference in the nature of the HOMO for the two compounds.

The discovery of the solid-state properties of polythiazyl or polysulphur nitride $(SN)_x$[1] has provided a strong impetus to the recent experimental and theoretical studies reported on sulphur–nitrogen compounds.[2–7] New structures, often displaying unusual chemical and physical behaviour, have been obtained from the many attempts to prepare polymers including CNSN and SCH units. For instance, in trying to synthesize the $(CNSN)_x$ polymer, Ernest *et al.* obtained 3,7-diphenyl- (1) (DTZ) and 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine (2) (DIATZ).[6]

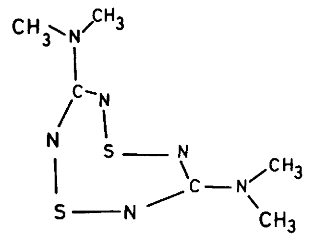
Our interest in these two systems lies in the different conformations adopted in the solid state by the $S_2N_4C_2$ dithiatetrazocine heterocycle when the endocyclic carbons are either substituted by phenyl (DTZ) or dimethylamino (DIATZ) groups. *X*-Ray diffraction measurements made on both compounds indicate that, in the case of DTZ, the dithiatetrazocine ring is planar while in DIATZ it is folded at an angle of 101° around the line joining the two endocyclic sulphur atoms. Moreover, the short transannular S-S distance, 2.428 Å, in DIATZ (3.786 Å in DTZ) suggests the existence of strong S–S bonding interactions in DIATZ which eventually should reflect in identifiable differences in the electronic structure of the two molecules. Minimal basis set, STO-3G and STO-3G + 5D, results and *X*-ray photoelectron spectra of these two molecules were recently published to contribute to the description of their electronic structure.[8] In the inner part of the valence region, experimental and theoretical data were found to be in satisfactory agreement, while, due to the lower photoionization cross-sections prevailing in the upper part of the valence spectrum, it was impossible to ascertain the theoretical predictions of the nature of the highest occupied levels.

Suitable experimental information on the nature and energy of the highest occupied states can be obtained by ultraviolet photoelectron spectroscopy (UPS). From motives similar to ours, Gleiter *et al.* have recently published the He^{I} photoelectron spectra of both DTZ and DIATZ.[9] To interpret their measurements, they also carried out model calculations (MNDO, STO-3G, STO-3G + 5D, 4-31G) which, when comparable, were similar to our previously published data.

While we could agree on their interpretation of the He^{I} photoelectron spectrum of DIATZ, we were unable to obtain a reasonable match between our calculated results and their published He^{I} spectrum of DTZ. For instance, the high-energy tail of the UPS spectrum of DTZ departs significantly and unexpectedly from what is observed in the same spectral region for both the 3,7-bis(dimethylamino)- and 3,7-bis-(t-butyl)-1,5-dithia-2,4,6,8-tetrazocine. Also, from the calculations one anticipates the presence of a well resolved line in the upper part of the UPS spectrum of DTZ which is not observed in their spectrum.



(1)



(2)

Figure 1. Schematic molecular structures of 3,7-diphenyl- (1) and 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocines (2)

In an attempt to elucidate these problems we have performed He^{I} and He^{II} UPS measurements on both DTZ and DIATZ. We also carried out additional 4-31G model calculations on analogous but simpler molecules to detect the most severe deficiencies of the STO-3G method which, due to computational limitations, has to be our main theoretical basis for interpretation.

Methods and Results

As pointed out in previous work,[8] constraints in our computational facilities have restricted us to minimal basis set

Table 1. Theoretical *ab initio* (STO-3G and STO-3G + 5D) molecular orbitals energies and experimental ionization potentials of 3,7-diphenyl-1,5-dithia-2,4,6,8-tetrazocine (DTZ) (eV)

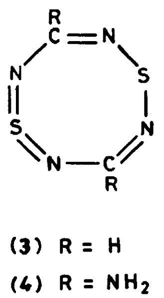
	Calculated MO energy[a]			
Assignment	STO-3G	STO-3G + 5D	4.31G[c]	Ionization potentials
$\pi\ 4b_{1u}$	6.18	5.71	9.54	8.00 (A)
$\pi\ 2a_{1u}$	6.36	7.30	10.36	
$\pi\ 3b_{2g}$	7.50	7.62	11.51	9.15 (B)
$\pi\ 2b_{3g}$	7.56	7.63	11.86	
$\pi\ 1a_{1u}$	7.56	7.64		
$\sigma\ 8b_{1g}$	8.27	8.59		
$\sigma\ 10b_{3u}$	8.70	*9.03*[b]		9.85 (C)
$\pi\ 3b_{1u}$	8.82	*8.60*[b]		
$\sigma\ 9b_{2u}$	8.98	9.47		10.50 (D)
$\sigma\ 11a_{1g}$	11.10	11.04		

[a] Absolute values. [b] Notice the inversion. [c] Calculations performed on the planar 1,5-dithia-2,4,6,8-tetrazocine.

Table 2. Theoretical *ab initio* (STO-3G and STO-3G + 5D) molecular orbitals energies and experimental ionization potentials of 3,7-bis-(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine (DIATZ) (eV)

	Calculated MO energy[a]			
Assignment	STO-3G	STO-3G + 5D	4-31G[c]	Ionization potentials
$8a_2$	6.16	5.80	10.09	8.55 (A)
$12a_1$	6.62	6.67		
$9b_2$	6.85	*7.21*[b]		9.25 (B)
$7a_2$	7.12	*7.33*[b]		
$10b_1$	7.27	*7.13*[b]		
$11a_1$	8.00	7.89		
$9b_1$	9.91	*10.12*[b]		10.80 (C)
$8b_2$	10.07	*9.65*[b]		
$10a_1$	11.28	11.08		11.15 (D)
$8b_1$	12.65	12.51		

[a] Absolute values. [b] Notice the inversion. [c] Calculations performed on the folded 3,7-diamino-1,5-dithia-2,4,6,8-tetrazocine.



(3) R = H

(4) R = NH_2

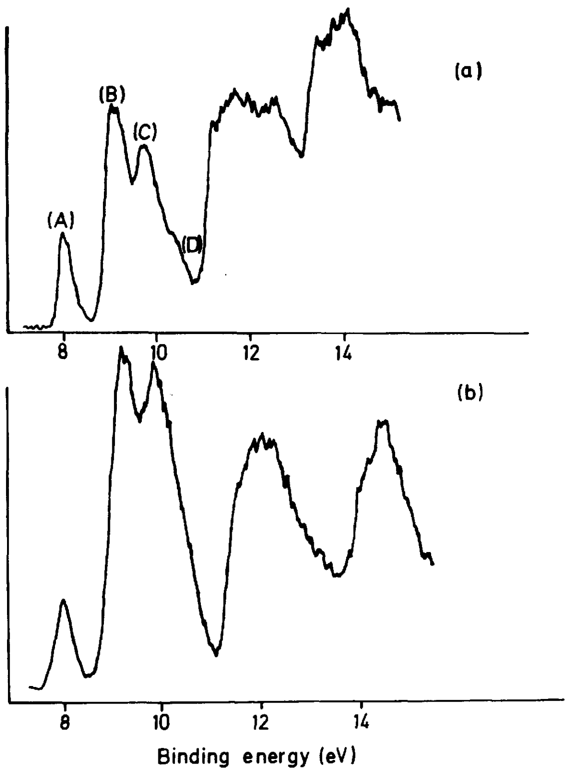


Figure 2. He^{I} (a) and He^{II} (b) spectra of 3,7-diphenyl-1,5-dithia-2,4,6,8-tetrazocine (DTZ)

calculations, STO-3G and STO-3G + 5D, for (**1**) and (**2**). These results are summarized in Tables 1 and 2. A detailed description is available in ref. 8 and can be usefully supplemented by the recent analysis of Gleiter *et al.*[9] As in ref. 8, Koopmans' theorem[10] is assumed to hold in our interpretation and consequently the observed ionization potentials can be directly correlated with the calculated STO-3G and STO-3G + 5D one-electron energies. However, recent theoretical studies have stressed the importance of both basis set extension and electron correlation effects in the assignment of UPS spectra of sulphur nitrides closely related to DTZ and DIATZ. In order to take at least partial account of these facts, we have made additional 4-31G calculations on the planar 1,5-dithia-2,4,6,8-tetrazocine (**3**) and the folded 3,7-diamino-1,5-dithia-2,4,6,8-tetrazocine (**4**) which are simpler systems. The geometrical parameters of the experimental geometries of (**1**) and (**2**) have been used to design the model structure of (**3**) and (**4**), respectively. For the comparable MOs of (**1**) with (**3**) and (**2**) with (**4**), significant inversions between 4-31G and STO-3G results have been detected. They will be indicated at the appropriate places in the text in connection with the assignment of UPS lines.

Molecules (**1**) and (**2**) exhibit complex spectra and require all possible approaches for their electronic structure to be fully understood. This is especially important in view of the somewhat restricted theoretical basis available. Therefore we have used both the He^{I} (21.21 eV) and the He^{II} (40.82 eV) excitation energies for identifying the photoelectron transitions. With S, N, and C as basic atomic entities, molecules (**1**) and (**2**) are thus well suited to yield information due to the distinct behaviour of the differential cross-section of certain transitions subjected to different excitations energies. Indeed, it is well established that cross-section for ionization of predominantly $3s$ and/or $3p$ levels is drastically lower for He^{II} excitation compared with ionization from $2s$ and/or $2p$ orbitals. Both the He^{I} and He^{II} spectra of DTZ and DIATZ molecules have been recorded, they are respectively displayed in Figures 2 and 3. These were measured at 383 (DIATZ) and 403 K (DTZ) on a Perkin-Elmer PS-18 spectrometer. The experiment has been repeated twice and the spectra were reproducible. Calibration was achieved by using Xe $5p_{3/2}$ (12.13 eV) and Xe $5p_{1/2}$ (13.43 eV), and Ar$3p_{3/2}$ (15.76 eV) and Ar $3p_{1/2}$ (15.94 eV). While our He^{I} spectrum of DIATZ is fully comparable with that published by Gleiter *et al.*, their He^{I} measurements on DTZ are in qualitative disagreement with ours. In order to detect some of the possible causes for the discrepancy, we have first checked the stoicheiometry of our DTZ sample by inspecting the intensity of the *X*-ray photoelectron signals on samples originating from the same batch used in the UPS measurements. The intensity of each core

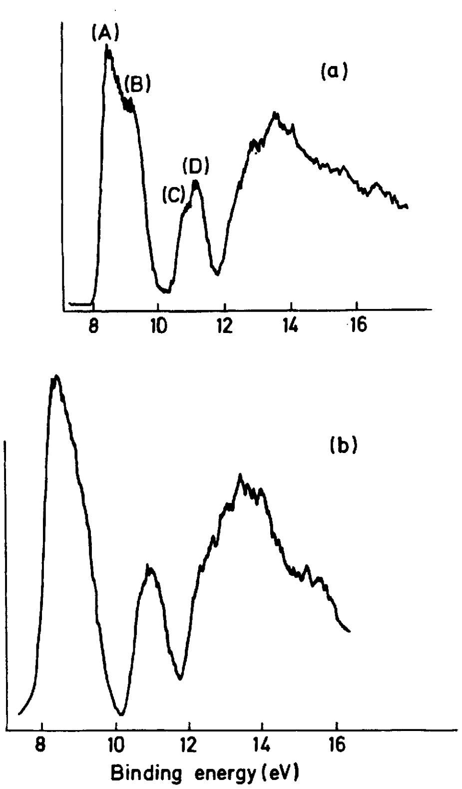


Figure 3. He^I (a) and He^{II} (b) spectra of 3,7-bis(dimethylamino)-1,5-dithia-2,4,6,8-tetrazocine (DIATZ)

level was calibrated from data on well defined reference compounds (thiophene, pyrrole, *etc.*). The resulting C:S and C:N atomic ratios match the assumed structure of DTZ. It is worth stressing that the core level features reported in our previous work were also in good agreement with both the DTZ and DIATZ elemental formulae. To assess the quality of the UPS measurements further, we have recorded both the He^I and He^{II} spectra of DTZ on a different experimental set up (Helectros 0018 spectrometer). The corresponding spectra are identical. From these experimental checks we believe that our recorded UPS spectra do indeed correspond to DTZ and DIATZ as further shown from the comparison with the theoretical predictions.

Discussion

As already mentioned, Koopmans' theorem[10] is assumed to hold, and accordingly the observed ionization potentials are directly correlated with the calculated (STO-3G; STO-3G + 5D) one-electron eigenvalues (see Figures 2 and 3 and Tables 1 and 2). A look at these tables shows a significant energy shift for the π $2a_{1u}$ state in DTZ and few inversions among closely lying levels in both DTZ and DIATZ when comparing the STO-3G and STO-3G + 5D results. In order further to assess the dependence of the ordering of the one-electron states upon basis-set extension in these critical regions, we will occasionally refer to the 4-31G results obtained on the planar $S_2N_4C_2H_2$ and folded $S_2N_4C_2(NH_2)_2$ model systems. In those cases, we have used the experimental geometrical parameters of DTZ and DIATZ to construct the model structures of $S_2N_4C_2H_2$ and $S_2N_4C_2(NH_2)_2$, respectively.

In DTZ, the HOMO is the π $4b_{1u}$ MO mainly having S $3p_z$ contributions and predicted at 6.18 eV on the energy scale by STO-3G. It is immediately followed at 6.36 eV by the π $2a_{1u}$ MO characterized by dominant N $2p_z$ character. Their proximity in energy suggests joint participation in peak (A) in Figure 2. However, STO-3G + 5D and 4-31 G energies, 7.30 and 10.36 eV respectively, of the π $2a_{1u}$ level are significantly lower than the corresponding STO-3G value, 6.36 eV, and indicate that this level should rather be assigned to peak (B). Assuming that the level separation remains within experimental resolution, this question is tentatively resolved by examining the shape variation of peak (A) upon changing from He^I to He^{II} excitation. Since S $3p_z$ and N $2p_z$ cross-sections vary in opposite directions, the undistorted shrinkage observed in peak (A) when going from He^I to He^{II} tends to indicate the existence of one level only which we assign to π $4b_{1u}$.

The π $2a_{1u}$, π $3b_{2g}$, π $2b_{3g}$, and π $1a_{1u}$ MOs should thus contribute to peak (B). The atomic orbital contributions to the first two, π $2a_{1u}$ and π $3b_{2g}$, come mainly from the N $2p_z$ functions on the ring and the C $2p_z$ functions on the phenyl groups (see Figure 2 of ref. 8). In the case of π $2b_{3g}$ and π $1a_{1u}$ the atomic orbital contributions arise from the phenyl C $2p_z$ functions only. All these orbitals exhibit nodes on the sulphur atoms and thus have zero contributions from the S $3p_z$ functions. This is in agreement with the experimental observations of higher peak (B):peak (A) intensity ratio in the He^{II} spectrum largely influenced by the N $2p_z$ higher cross-sections.

We assign σ $8b_{1g}$, π $3b_{1u}$, and σ $10b_{3u}$ orbitals to peak (C) and σ $9b_{2u}$ to the shoulder (D) in Figure 2, located at *ca.* 10.50 eV. The decay of structure (D), compared with peak (C), when using the He^{II} incident radiation is interpreted as the result of strong contributions from sulphur atomic functions in the latter orbital.

The remaining valence levels of DTZ are considerably less interesting. Their onset in the UPS spectrum is visible at *ca.* 11.0 eV as also predicted by our calculations.[8]

The UPS spectrum of the DIATZ molecule (Figure 3) can be understood by making a similar comparison with theoretical results. Experimentally the HOMO is observed at 8.55 eV [(peak (A)]. The corresponding STO-3G, STO-3G + 5D, and 4-31 G [for $S_2N_4C_2(NH_2)_2$ in this case], energy eigenvalues of the HOMO, denoted $8a_2$ in Table 2, are respectively equal to 6.16, 5.80, and 10.09 eV. The experimental energy shift between the first ionization potential of DTZ and DIATZ is 0.55 eV. STO-3G and STO-3G + 5D calculations predict much smaller energy differences, namely 0.01 and 0.09 eV. However, assuming there is a direct relation between the HOMOs of DTZ and DIATZ, on one side, and of $S_2N_4C_2H_2$ and $S_2N_4C_2(NH_2)_2$, on the other, we can obtain a 4-31G estimate of the energy shift by subtracting the first ionization potentials of $S_2N_4C_2H_3$ and $S_2N_4C_2(CH_2)_2$. The 4-31G value, 0.55 eV, turns out fortuitously to be the exact experimental value.

The six highest occupied levels correspond to peaks (A) and (B). Unfortunately their sequence cannot easily be determined only from the experimental information due to insufficient resolution. Using the theoretical values listed in Table 2 we tentatively assign the first peak (A) to the $8a_2$ and $9b_2$ orbitals whose linear combinations are predominantly formed from π-atomic functions centred on the ring nitrogens.* Similarly, $12a_1$, $7a_2$, $10b_1$, and $11a_1$ should contribute to peak (B) observed at 9.25 eV. The lowering of the intensity of this line compared with line (A) when probed with He^{II} incident radiation can be related to the important contributions of the S $3p_x$ AOs in the $11a_1$ and $12a_1$ MOs which describe the bonding between the sulphur atoms.

As predicted by the three basis sets both the $9b_1$ and $8b_2$ MOs are higher in energy than the $10a_1$ orbital. Accordingly the first

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* We use the π terminology somewhat inaccurately, to refer to atomic orbitals perpendicular to the plane of each moiety of DIATZ.

two levels are assumed to form peak (C) observed at 10.80 eV while the latter should contribute to the line (D) at 11.5 eV. In agreement with the theoretical data, the onset of the remaining lines is lower on the energy scale for DIATZ (12.0 eV) than for DTZ (11.0 eV).

Conclusions.—The present UPS analysis has provided a more detailed picture of the electronic structure of DTZ and DIATZ. The combination of both He^I and He^{II} measurements has made possible an experimentally based confirmation of the different nature of the highest occupied molecular orbitals of DTZ and DIATZ. Finally, the overall consistency of the theoretical and experimental results presented in this work allows one to conclude that our UPS spectra do indeed correspond to the DTZ and DIATZ molecular species.

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