# The Electronic Structures of 4-Substituted 3,5-Dihydro-4*H*-pyrazoles and 5-Substituted 1,4-Dihydro-5*H*-tetrazoles

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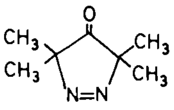
The He(I) photoelectron spectra of 4-oxo- (**1**), 4-methylimino- (**2**), 4-thioxo- (**3**), and 4-hydrazono-3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazole (**4**) as well as 5-oxo- (**7**), 5-imino- (**8**), and 5-thioxo-1,4-dimethyl-1,4-dihydro-5*H*-tetrazole (**9**) have been recorded. The assignment of the first PE bands is based on the comparison with the PE spectra of compounds of similar structures and the results of MO calculations (Hartree Fock ab initio method, MNDO and HAM/3). The investigations reveal for **1**–**4** that the first PE band is due to the ionization from the $n_-$ orbital localized at the azo group. For **7**–**9**, the first band is due to ionization from a $\pi$ MO of $b_1$ symmetry. While the energy of the first PE band of **1**–**4** varies only sligthly, that of **7**–**9** changes strongly. The UV/VIS spectra of **1**–**4** and **7**–**9** are interpreted on the basis of CNDO/S-CI calculations. The first band in the UV/VIS spectrum of **1**, **2**, and **4** is assigned to a $\pi^* \leftarrow n_-$ transition of the azo group; for **3**, the first band is due to a $\pi^* \leftarrow n_S$ transition localized at the CS group. The comparison between experiment and calculation suggests to assign the first UV band of **7**–**9** to a $\pi^* \leftarrow \pi$ transition.

**Die Elektronenstrukturen von 4-substituierten 3,5-Dihydro-4*H*-pyrazolen und 5-substituierten 1,4-Dihydro-5*H*-tetrazolen**

Die He(I)-Photoelektronenspektren von 4-Oxo- (**1**), 4-Methylimino- (**2**), 4-Thioxo- (**3**) und 4-Hydrazono-3,3,5,5-tetramethyl-3,5-dihydro-4*H*-pyrazol (**4**), sowie 5-Oxo- (**7**), 5-Imino- (**8**) und 5-Thioxo-1,4-dimethyl-1,4-dihydro-5*H*-tetrazol (**9**) wurden aufgenommen. Die Zuordnung der ersten PE-Banden basiert auf dem Vergleich mit den PE-Spektren von strukturell ähnlichen Verbindungen und den Resultaten von MO-Rechnungen (Hartree-Fock-ab-initio-Methode, MNDO und HAM/3). Die Untersuchungen an **1**–**4** ergeben, daß die erste Bande dem $n_-$-Orbital der Azogruppe zugeordnet werden kann. Im Gegensatz dazu wird die erste PE-Bande von **7**–**9** dem $\pi$-MO mit $b_1$-Symmetrie zugeordnet. Bei **1**–**4** beobachten wir nur eine leichte, bei **7**–**9** eine starke Variation der ersten Ionisierungsenergie. Die UV/VIS-Spektren von **1**–**4** und **7**–**9** wurden aufgrund von CNDO/S-CI-Rechnungen interpretiert. Die erste Bande im UV/VIS-Spektrum von **1**, **2** und **4** wird einem $\pi^* \leftarrow n_-$-Übergang der Azogruppe zugeordnet, bei **3** einem $\pi^* \leftarrow n_S$-Übergang der CS-Gruppe. Der Vergleich zwischen Experiment und Rechnung spricht dafür, die erste Bande im UV-Spektrum von **7**–**9** einem $\pi^* \leftarrow \pi$-Übergang zuzuschreiben.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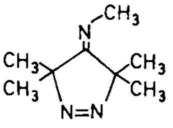
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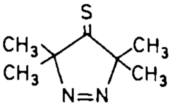
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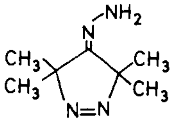
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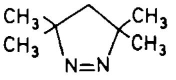
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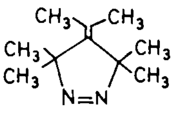
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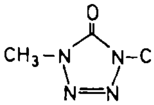
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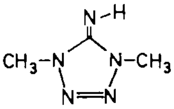
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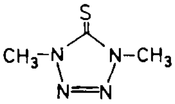
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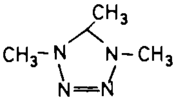
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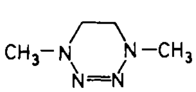
**11**

The light-induced extrusion of molecular nitrogen from five-membered cyclic azo compounds having exocyclic double bonds represents a convenient route to methylenecyclopropanes[1a)] and hetero analogues thereof[1b)] as well as to trimethylenemethane derivatives[1c)]. For example, although the pyrazolinone **1**, which had been designed as a precursor of tetramethylcyclopropanone[2a)], is surprisingly reluctant, it can be photolyzed to yield as primary products tetramethylcyclopropanone and acetone azine besides molecular nitrogen and carbon monoxide, respectively. The imine **2** exhibits an activation barrier towards nitrogen extrusion from the excited state. Thus, only at elevated temperatures high yields of the tetramethylcyclopropanimine are obtained. While **1** and **2** yield least motion products on photolysis, photo-extrusion of molecular nitrogen from the thione **3** affords tetramethylmethylenethiirane[2b)]. The irradiation of the tetrazolone **7** at low temperature yields 1,2-dimethyldiaziridinone[3)], while the tetrazolethione **9** looses

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molecular nitrogen and the sulfur atom and gives dimethylcarbodiimide. To understand the photochemistry of such azo compounds, a knowledge of their electronic structure is essential. To contribute to this question, we have investigated the He(I) photoelectron (PE) spectra and the electronic absorption spectra of **1**−**4**[2], as well as **7**−**9**[3]. Since the PE spectra of **1**−**4** differ considerably from those of **7**−**9** we will discuss both groups separately.

## Results and Discussion

The PE spectra of **1**, **3**, **7**, and **9** are shown in Figure 1. The recorded vertical ionization energies of **1**−**4** and **7**−**9** are listed in Tab. 1. To interpret PE spectra, we proceed in two ways. We compare the shape and positions of the bands to those of related molecules (e.g. **5** and **6**[4] for **1**−**4**, and **10**[5] and **11**[6] for **7**−**9**) whose PE bands have been assigned, and we compare the recorded ionization energies with calculated ones. For the calculations, we used the Hartree Fock (HF) ab initio method employing a 6−31 G basis[7], as well as the MNDO[8] and the HAM/3[9] procedures.

In the case of the HF/SCF and MNDO results we relate the calculated orbital energies ($-\varepsilon_j$) to the vertical ionization energies ($I_{v,j}$) assuming an approximate cancelling of correlation and relaxation effects (Koopmans' theorem[10]). The HAM/3 calculations were carried out because this method considers in part correlation effects. As structural data were missing, the calculations were based on geometrical parameters derived through the MNDO method. We minimized all geometrical parameters with respect to the total energy, maintaining $C_{2v}$ (**1**, **3**, **7**, **9**) or $C_s$ symmetry (**2**, **4**, **8**). The results of the calculations are shown in Table 1.

Table 1. Comparison between the recorded vertical ionization energies, $I_{v,j}$, of **1**−**4** and **5**−**9** and the calculated orbital energies, $\varepsilon_j$ (all values in eV)

| Compound | Band | $I_{v,j}$ | Assignment | I(HAM/3) | $-\varepsilon_j$(MNDO) | $-\varepsilon_j$(6−31G) |
|---|---|---|---|---|---|---|
| **1** | 1 | 8.6 | $5b_2(n_-)$ | 8.98 | 10.82 | 10.26 |
| | 2 | 10.1 | $4b_2(n_O)$ | 10.51 | 10.10 | 12.90 |
| | 3 | 11.5 | $3b_1(\pi_{NN})$ | 12.13 | 12.81 | 12.95 |
| | 4 | 12.1 | $7a_1(n_+)$ | 12.97 | 13.96 | 15.10 |
| | 5 | 12.6 | $2b_1(\pi_{CO})$ | 13.56 | 14.59 | 19.83 |
| **2** | 1 | 8.3 | $14a'(n_-)$ | 8.39 | 11.60 | 9.77 |
| | 2 | $9.5_5$ | $13a'(n_N)$ | 9.40 | 10.66 | 10.97 |
| | 3 | 10.1 | $5a''(\pi_{CN})$ | 10.16 | 11.49 | 11.51 |
| | 4 | 11.6 | $4a''(\pi_{NN})$ | 12.29 | 13.10 | 13.22 |
| | 5 | 11.8 | $12a'(n_+)$ | 12.30 | 13.48 | 14.41 |
| **3** | 1 | 8.40 | $5b_2(n_-)$ | | 11.57 | 11.36 |
| | 2 | 9.31 | $4b_2(n_S)$ | | 9.76 | 9.13 |
| | 3 | 10.38 | $3b_1(\pi_{CS})$ | | 11.32 | 11.19 |
| | 4 | 11.7 | $2b_1(\pi_{NN})$ | | 13.29 | 13.54 |
| | 5 | 11.9 | $7a_1(n_+)$ | | 13.31 | 14.18 |
| **4** | 1 | 8.7 | $14a'(n_-)$ | 8.26 | 10.86 | 10.01 |
| | 2 | 8.9 | $5a''(n_N)$ | 7.85 | 9.55 | 9.00 |
| | 3 | 10.01 | $13a'(\pi_{CNN})$ | 9.89 | 11.99 | 12.30 |
| | 4 | 11.6 | $4a''(\pi_{NN})$ | 11.74 | 12.58 | 12.79 |
| | 5 | 12.0 | $12a'(n_+)$ | 11.99 | 13.40 | 14.45 |
| **7** | 1 | 9.36 | $4b_1(\pi)$ | 8.77 | 10.11 | 9.93 |
| | 2 | 10.21 | $7b_2(n_O)$ | 9.71 | 11.61 | 11.64 |
| | 3 | 11.05 | $2a_2(\pi)$ | 11.11 | 11.92 | 12.56 |
| | 4 | 12.10 | $6b_2(n_-)$ | 11.42 | 13.87 | 14.21 |
| | 5 | 12.9 | $3b_1(\pi_{CO})$ | 12.70 | 14.20 | 15.00 |
| | 6 | 14.2 | $9a_1(n_+)$ | 12.42 | 13.94 | 15.18 |
| **8** | 1 | 8.21 | $6a''(\pi)$ | 7.83 | 9.39 | 8.77 |
| | 2 | 10.1 | $16a'(n_N)$ | 9.53 | 11.61 | 11.16 |
| | 3 | 10.76 | $5a''(\pi)$ | 10.81 | 11.76 | 12.30 |
| | 4 | 11.6 | $15a'(n_-)$ | 10.98 | 13.37 | 13.19 |
| | 5 | 12.0 | $4a''(\pi_{CN})$ | 11.45 | 12.89 | 13.40 |
| | 6 | 12.6 | $4a'(n_+)$ | 12.15 | 13.89 | 14.97 |
| **9** | 1 | 8.44 | $4b_1(\pi)$ | | 9.16 | 8.79 |
| | 2 | 8.57 | $7b_2(n_S)$ | | 9.37 | 9.40 |
| | 3 | 11.1 | $2a_2(\pi)$ | | 12.09 | 12.57 |
| | 4 | 11.8 | $3b_1(\pi_{CS})$ | | 12.56 | 13.17 |
| | | | $6b_2(n_-)$ | | 13.63 | 13.32 |
| | 5 | 12.7 | $9a_1(n_+)$ | | 14.41 | 14.79 |

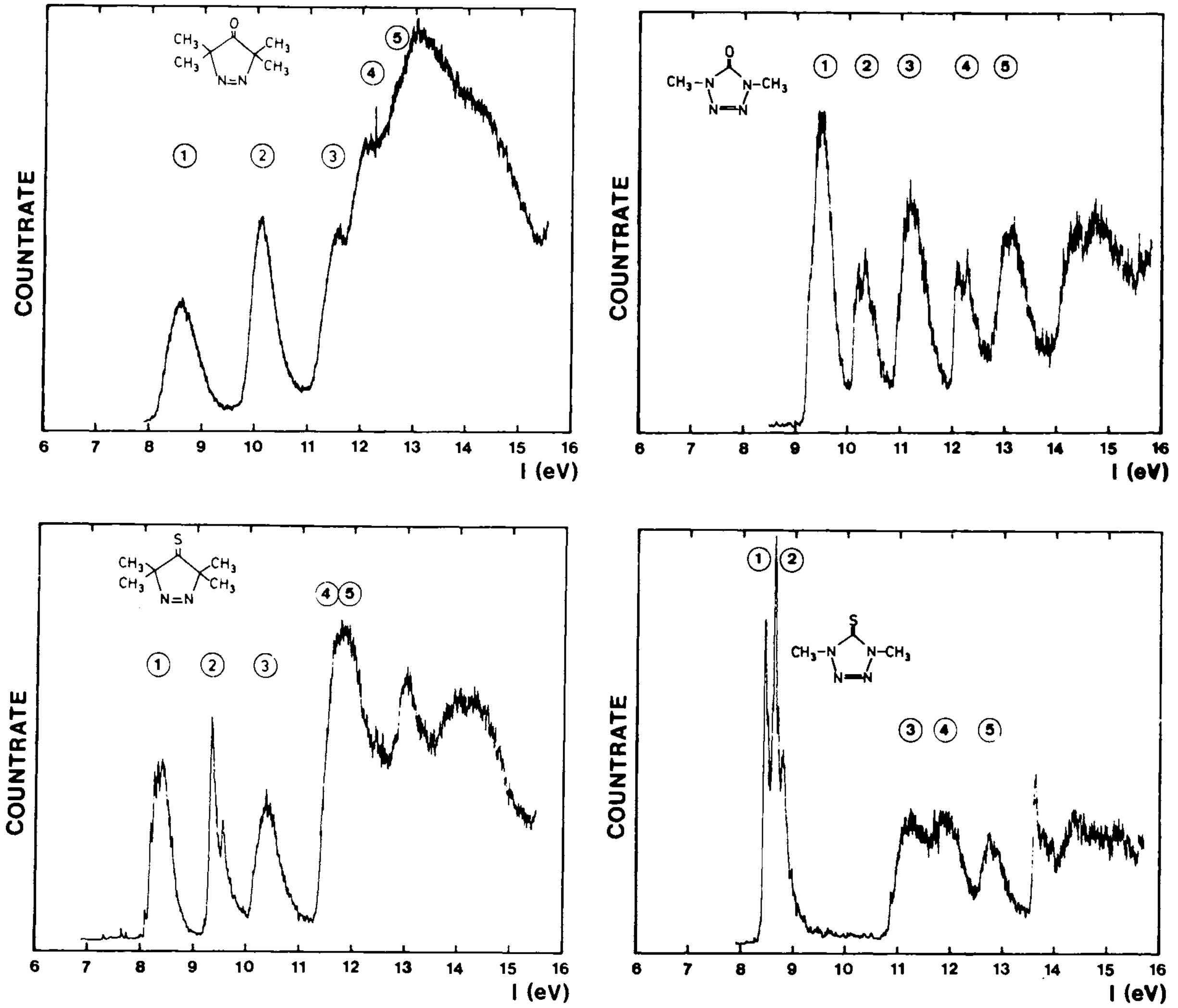
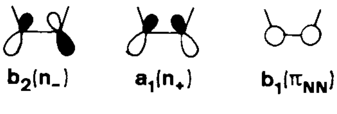


Figure 1. He(I) PE spectra of **1**, **3** (left), **7**, **9** (right)

### PE Spectra of the 3,5-Dihydro-4*H*-pyrazoles 1–4

The first PE bands of **1**, **2**, and **4** are broad and devoid of fine structure, while the two bands of lowest energy in the PE spectrum of **3** do show vibrational fine structure ($\tilde{\nu}$ ① $\approx 1200\ \mathrm{cm}^{-1}$, $\tilde{\nu}$ ② $\approx 1800\ \mathrm{cm}^{-1}$). Most of the PE studies on various azo compounds substituted by alkyl, aryl, or acyl groups[4,11–22] agree in so far as the first three bands are due to an ionization from $n_-$, $\pi_{NN}$, and $n_+$ (in descending order). The designation $n_-$ and $n_+$ refers to the anti-bonding and bonding linear combination of the lone-pair orbitals at the nitrogen atoms of the azo group (see schematic drawing). It is known that the energy difference between the bands of $n_-$ and $n_+$ depends on the substituents X of the azo group as well as on the X–N–N bond angle. Previous PE studies[4,11–12] support the expectation to find the ionization energy of the $n_-$ combination between 8 and 9 eV, while the band which is due to the $n_+$ combination is anticipated between 11 and 12 eV. The $\pi_{NN}$ band is expected between 10.5 and 11.5 eV[4]. Furthermore, in our examples, we expect at energies smaller than 11 eV the ionization from the lone pair at the carbonyl oxygen (**1**) and at the sulfur of the thiocarbonyl group (**3**), from the lone-pair(s) of the imine (**2**), and hydrazone (**4**) moiety as well as from the CC double bond in **6**. We start our empirical assignment for **1**–**4** by comparing the first band of **5**[4] to that of **1**–**3** (see Figure 2).



All four bands are found at similar energies. They also exhibit a similar Gaussian shape. Therefore, we attribute the first band of **1**–**3** to the ionization from $n_-$. The comparison of the intensity of the first peak of **4** to that of its second peak indicates that two transitions produce the first peak as in the case of **6** (see Figure 2).

We assign the second band of **1** (10.1 eV) to the ionization from the lone pair of the carbonyl oxygen. This assignment is supported by the similarity to the first band in the PE spectrum of acetone (9.7 eV)[23]. The third and fourth band of **1** result from the ionization from the π MO and the $n_+$ combination of the azo group, respectively. This assignment

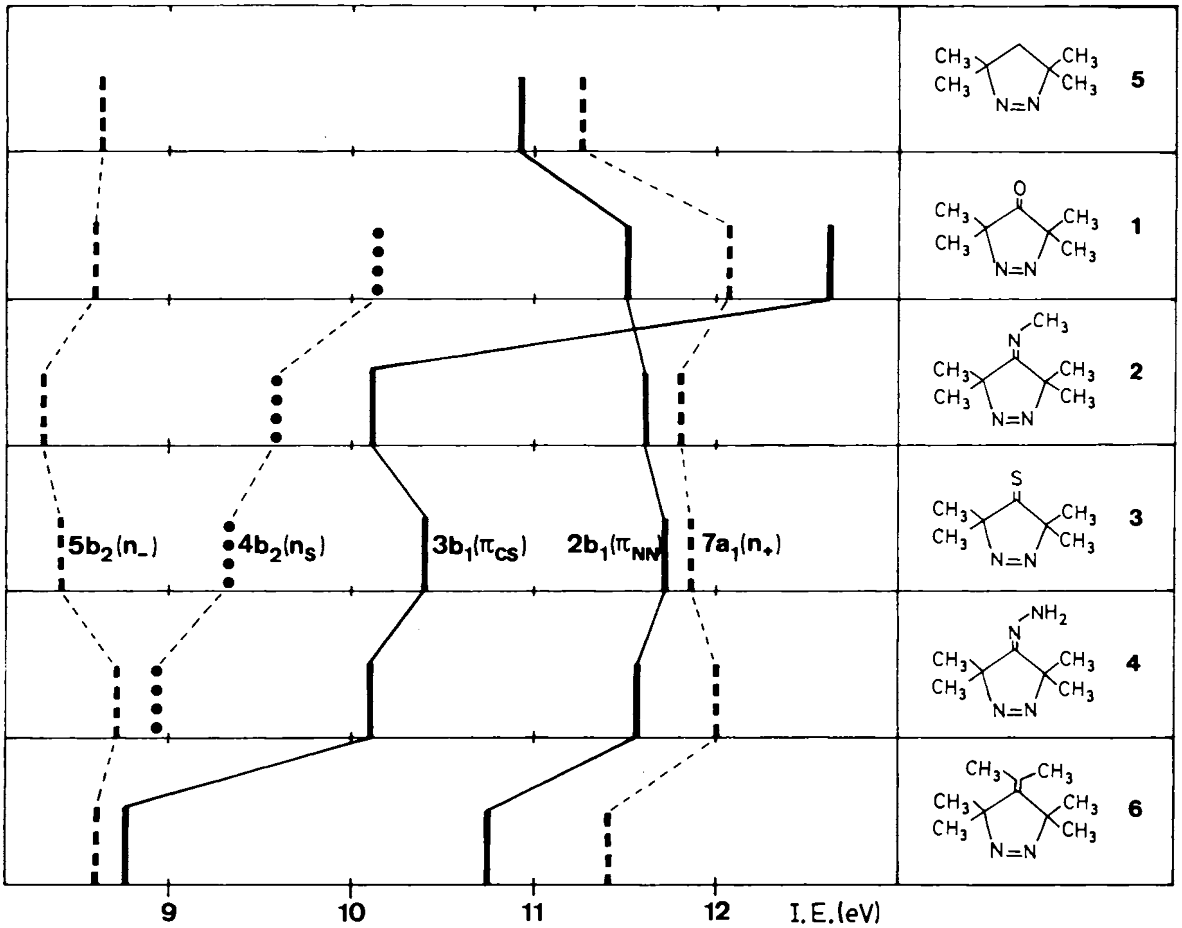


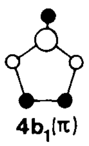
Figure 2. Correlation between the first PE bands of **1** – **6**

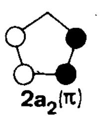
rests on a comparison between the PE bands of **1** and **5** (see Figure 2). Bands 3 and 4 of **1** are shifted towards higher energies as compared to the corresponding bands of **5**. This shift is anticipated in view of the inductive effect of the carbonyl group. That the first band of both **1** and **5** occurs at the same energy can be ascribed to two opposing effects: the inductive effect of the carbonyl group which stabilizes the $n_-$ orbital, and the interaction between the $n_-$ combination of the azo group and the 2p lone pair at the oxygen atom which leads to a destabilization of $n_-$. Both effects seem to cancel each other. We assign the fifth band of **1** (12.6 eV) to the ionic state arising from the π MO of the carbonyl group. Here again we rely on the similarity to the corresponding value from acetone (12.6 eV)[23].

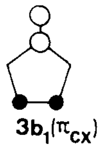
Comparing the PE bands of **1** and **2**, we assign the second band of **2** to the ionization from the lone pair at the imine nitrogen atom and the fourth and fifth band to ionizations from the π MO and $n_+$ MO of the azo group, respectively. The position of the PE bands of *N*-ethylidenemethylamine (9.49 and 10.66 eV[13]) suggests that the second and third bands of **2** originate from the lone pair at the imine nitrogen atom and the $\pi_{CN}$ MO. Comparing the PE bands of **3** to those of **5** we assign the second band to the ionization from the 3p lone pair at the sulfur atom and the third band to the $\pi_{CS}$ orbital. This assignment is confirmed by the resemblance to the PE bands of thioketones[24] which show ionization energies between 8.0 and 8.6 eV for the 3p lone pair and 9.6 – 10.5 eV for the CS π bond. Further support of our assignment of the second band of **3** is provided by the shape of this band. The steep onset and the narrow half width are typical of ionization events from sulfur 3p orbitals[24]. The comparison between the PE bands of **2** – **4** leads to the assignment given in Figure 2. The results of the MO calculations on **1** yield the same sequence for the MOs as shown in Figure 2. For **2** and **4**, however, the calculations predict that the lone pair at the imine nitrogen is the HOMO. This prediction is at variance with our assignment.

### PE Spectra of the 1,4-Dihydro-5*H*-tetrazoles 7 – 9

In contrast to the PE spectra of **1** – **4**, those of **7** – **9** show a very intense first band exhibiting pronounced fine structure in the case of **8** and **9** (see Figure 1). Furthermore, we observe an energy difference of 1.2 eV between the position of the first band of **7** (9.4 eV) and that of **8** (8.2 eV). These experimental facts suggest that, in contrast to **1** – **6**, the first band of **7** – **9** is not due to the ionization starting from $n_-$. The results of the calculation carried out for **7** – **9** (Table 1) imply that the first band of **7** – **9** is due to the ionization from $4b_1(\pi)$ (see below) and that the bands corresponding to $6b_2(n_-)$ can be expected to occur at energies around 12 eV.







This result is surprising in view of the orbital sequence of **1**–**6** where $n_-$ is found at a value around 8.5 eV. In cyclic tetrazenes like **10** and **11**, however, also rather high values for the $n_-$ band (10.2 and 10.7 eV, respectively)[4,5] have been reported. Model calculations on **7** and open-chain tetrazenes using the MNDO[8] and the HF-(6-31G)[7] procedure suggest that the orbital energy of $n_-$ in tetrazenes depends mainly on three factors i) the interaction with $b_2(2p)$ of the carbonyl group, ii) the inductive effect of the carbonyl group and iii) the NNN angle. In Figure 3, we have correlated the first PE bands of **10** and **11** with those of **7**. The comparison between the first PE bands of **10** to those of **11** yields a constant shift towards higher energy. We interpret this in terms of a smaller inductive effect of the bridge in **10** compared to that of **11**. The comparison between **10** and **7** reveals a further stabilization of the π MOs (full line).

The above-mentioned interaction between the 2p orbital at the oxygen atom of the carbonyl group of **7** and the tetrazene moiety is shown schematically in Figure 4. Because of this interaction, the PE band of the $6b_2(n_-)$ linear combination is found at rather high energy. The replacement of the oxygen atom in **7** by the imino group (**8**) yields a strong lowering of the π bands belonging to the irreducible representation $b_1$ while $a_2(\pi)$ and $b_2(n_x)$ change only slightly. This behaviour is anticipated on the basis of perturbation theoretical arguments if we consider the smaller electronegativity of the NH group compared to oxygen. The correlation of Figure 3 suggests two ionization events for the first peak of **9**. The low ionization energy of the 3p orbital on sulfur is in line with our findings on **3**.

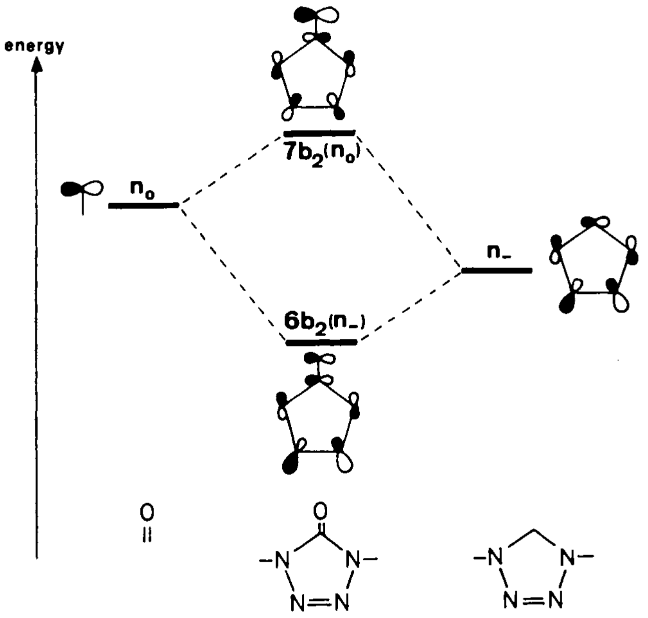


Figure 4. Qualitative interaction diagram of the 2p lone-pair of a carbonyl group and $n_-$ of **11** to yield $7b_2$ and $6b_2$ of **7**

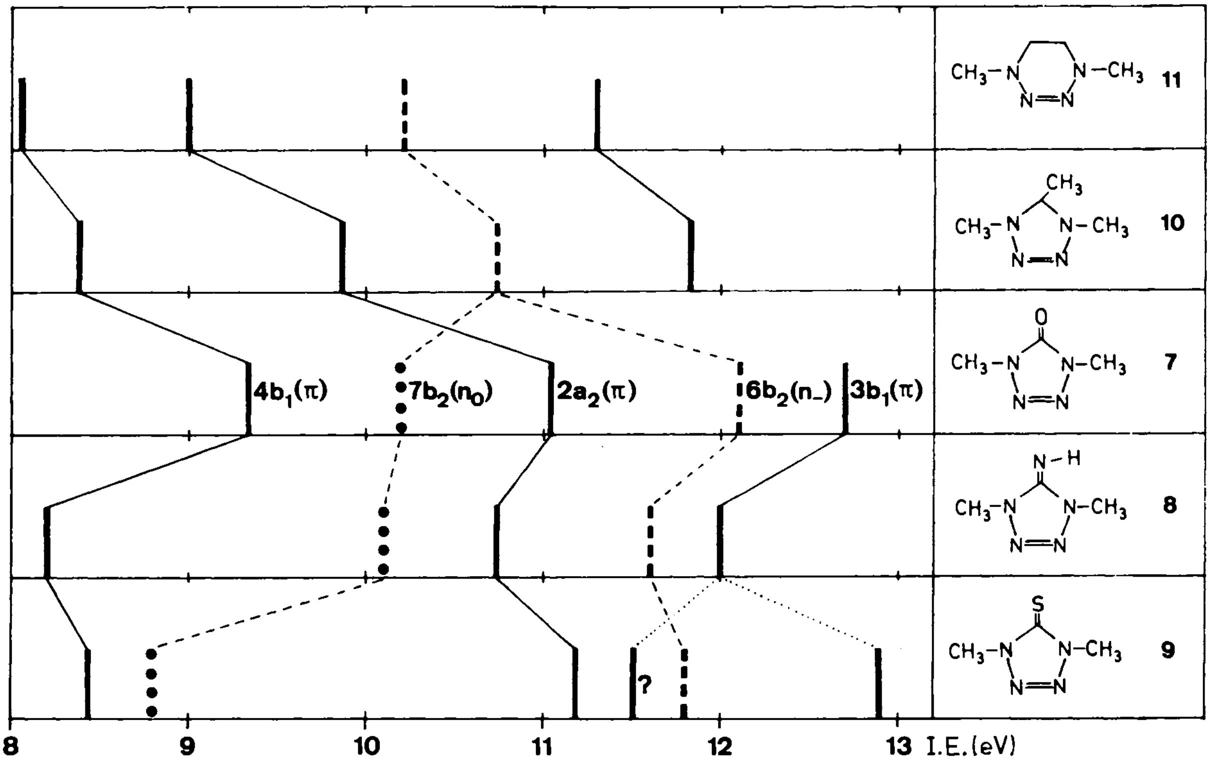


Figure 3. Correlation between the first PE bands of **7**–**11**

Table 2. Observed and calculated (CNDO/S-CI) transitions for **1**–**9**. If not otherwise noted, the experimental values refer to measurements in hexane

| Observed | | | Calculated | | | |
|---|---|---|---|---|---|---|
| Compound | $\lambda_{max}$ [nm] | $\log\varepsilon$ | $\lambda_{max}$ [nm] | $\log\varepsilon$ | Leading configuration | |
| **1** | 357 | 2.22 | 347 | 2.82 | $2a_2(\pi^*_{NN})\leftarrow 5b_2(n_-)$ | (25%) |
| | | | | | $2a_2(\pi^*_{NN})\leftarrow 4b_2(n_O)$ | (74%) |
| **2** | 342 | 2.31 | 341 | 2.87 | $6a''(\pi^*_{NN})\leftarrow 14a'(n_-)$ | (81%) |
| | 273 | 1.93 | 301 | 2.75 | $7a''(\pi^*_{C=N})\leftarrow 13a'(\pi_{C=N})$ | (88%) |
| **3** | 600 | 0.02 | 607 | | | |
| | 554 | 1.02 | | 0.0 | $4b_1(\pi^*_{C=S})\leftarrow 4b_2(n_S)$ | (90%) |
| | 529 | 0.98 | | | | |
| | 341 | 2.36 | 356 | 2.84 | $2a_2(\pi^*_{NN})\leftarrow 5b_2(n_-)$ | (77%) |
| | 304 | 2.12 | 241 | 2.03 | $2a_2(\pi^*_{NN})\leftarrow 7a_1(n_+)$ | (69%) |
| | 235 | 3.95 | | | | |
| **4**[a] | 334.5 | 2.26 | 336 | 2.84 | $6a''(\pi^*_{NN})\leftarrow 14a'(n_-)$ | (90%) |
| | 215 | 3.81 | 284 | 2.80 | $7a''(\pi^*_{CN})\leftarrow 13a'(\pi_{CN})$ | (90%) |
| | | | 217 | 0.61 | $6a''(\pi^*_{NN})\leftarrow 12a'(n_+)$ | |
| **5** | 327 | 2.28 | 364 | 2.85 | $2a_2(\pi^*_{NN})\leftarrow 4b_2(n_-)$ | (98%) |
| **6** | 327 | 2.20 | 324 | 2.79 | $3a'_2(\pi^*_{NN})\leftarrow 7b_2(n_-)$ | (97%) |
| **7** | 230 | 3.54 | 256 | 0.00 | $5b_1(\pi^*)\leftarrow 7b_2(n_O)$ | (94%) |
| | | | 249 | 3.19 | $3a_2(\pi^*)\leftarrow 6b_2(\pi)$ | (61%) |
| **8** | 264 | 3.67 | 264 | 3.42 | $7a''(\pi^*)\leftarrow 6a''(\pi)$ | (79%) |
| **9** | 248 | 4.09 | 473 | 0.00 | $5b_1(\pi^*)\leftarrow 7b_2(n_S)$ | (92%) |
| | 209 | 3.78 | 319 | 1.39 | $3a_2(\pi^*)\leftarrow 7b_2(n_S)$ | (72%) |
| | | | 292 | 3.02 | $3a_2(\pi^*)\leftarrow 4b_1(\pi)$ | (71%) |
| | | | 271 | 4.02 | $5b_1(\pi^*)\leftarrow 4b_1(\pi)$ | (88%) |
| | | | 213 | 3.17 | $3a_2(\pi^*)\leftarrow 6b_2(\pi)$ | (94%) |

[a] Recorded in methanol.

The only uncertainty in our assignments concerns the area between 11 and 13 eV in the PE spectrum of **9**. The calculation suggests a destabilization of the $3b_1(\pi_{CX})$ level in proceeding from **8** to **9**. Therefore, we have tentatively assigned three ionic states between 11 and 12 eV. Of course, we cannot rule out that $3b_1(\pi)$ is the origin of the fifth band at 12.7 eV as indicated in Figure 3.

### Electronic Absorption Spectra of 1–9

In view of the photochemical experiments carried out on **1**–**9**[1–3], the nature of the first excited state of these molecules is of interest. In Table 2, we have compared the energies of the first bands of the electronic absorption spectra of **1**–**9** with the results of CNDO/S-CI calculations[25]. The comparison yields for **1**–**4** agreement between experiment and calculation with respect to both the energy and the intensity of the bands listed.

The comparison between the UV bands of **7**–**9** and the MO results is less satisfactory. For **2**, **4**, **5**, and **6** we notice that the first excited state can be described the $a_2(\pi)\leftarrow b_2(n_-)$ transition. Two configurations, e.g. $2a_2(\pi^*)\leftarrow 5b_2(n_-)$ and $2a_2(\pi^*)\leftarrow(n_O)$, contribute in the case of **1**. The calculations predict a predominance of the latter which involves the 2p lone pair at the oxygen atom. The first excited state of **3** is mainly localized at the CS group. The $2a_2(\pi^*)\leftarrow 5b_2(n_-)$ transition for **3** is predicted at similar values as for the other compounds. For **7** and **9**, two low-energy forbidden bands of the type $5b_1(\pi^*)\leftarrow 7b_2(n_x)$ are predicted which are not observed, however.

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## Experimental

The syntheses of **1**–**4**[2], **7**, **9**[3], and **8**[26] have been described in the literature. The He(I) photoelectron spectra of the analytically pure samples have been recorded with a Perkin-Elmer PS 18 instrument. Compounds **1**–**4** were used at room temperature. Compounds **7**–**9** were investigated at 45°C. The spectra were calibrated with Ar and Xe. The UV/VIS data shown in Table 2 were measured (**8**) or taken from the literature[2–4].

CAS Registry Numbers

**1**: 30467-62-0 / **2**: 72443-11-9 / **3**: 65927-08-4 / **4**: 16642-47-0 / **5**: 2721-31-5 / **6**: 55204-47-0 / **7**: 13576-20-0 / **8**: 6473-98-9 / **9**: 54986-14-0

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