The Electronic Structure of 2-Azapentalenes. Photoelectron Spectroscopic Investigations

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The He(I) photoelectron spectra of eight 2-azapentalenes, substituted in 1,3-position by electron releasing groups (dimethylamino, ethoxy, and *tert*-butyl) revealed that the first four ionization energies (6.4−9.3 eV) are due to ionziation from π MO's. This assignment is based on the comparison with the PE data of 1,3-bis(dimethylamino)pentalene (**10**) and the results of MNDO calculations. The comparison between experiment and calculations suggests that the first two bands are due to ionizations from π MO's mainly localized in the pentalene moiety.

Die Elektronenstruktur von 2-Azapentalenen. Photoelektronenspektroskopische Untersuchungen

Die He(I)-Photoelektronen-Spektren von acht in 1,3-Position durch elektronenabgebende Gruppen (Dimethylamino-, Ethoxy- und *tert*-Butylgruppe) substituierten 2-Azapentalenen ergaben, daß die ersten vier Ionisierungsenergien (6.4−9.3 eV) durch Ionisierungen aus π-MO's herrühren. Diese Zuordnung basiert auf dem Vergleich mit den PE-Daten von 1,3-Bis(dimethylamino)pentalen (**10**) und mit den Resultaten von MNDO-Rechnungen. Der Vergleich zwischen Experiment und Rechnung legt nahe, daß die ersten beiden PE-Banden von π-MO's stammen, die hauptsächlich im Pentalen-Teil lokalisiert sind.

The close similarity between 2-azapentalene and the pentalene moiety has aroused considerable interest followed by numerous investigations of its chemical and physical properties[1]. Although, in full analogy to the carbocyclic congener, 2-azapentalene (**1**) has so far escaped all efforts of isolation, its several derivatives, however, appear to be stable compounds[2−4]. Comparison of their reactivity with the reactivity of related pentalenes has shown that both classes of compounds behave identically in the protonation reactions, while strikingl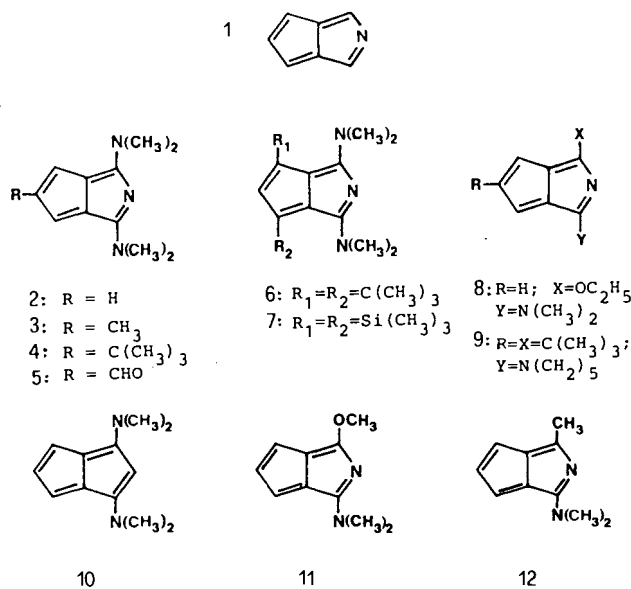y different behaviour was observed in the [2 + 2] cycloadditions[5]. The latter finding was rationalized in terms of the altered localization properties of the more electronegative nitrogen at position 2 of the highest occupied molecular orbital (HOMO). To provide a deeper insight into the electronic structure of the 2-azapentalenes we undertook a photoelectron (PE) spectroscopy study of the 2-azapentalene derivatives as well as the 1,3-bis(dimethylamino)pentalene (**10**).

Photoelectron Spectra

The PE spectra of **3**, **8**, and **10** are displayed in Figure 1 as representative examples. The vertical ionization energies ($I_{v,j}$'s) estimated from the measured PE band maxima for **2−9** are collected in Table 1. In Figure 2 we have correlated the first bands of **2−10** adopting the assignment given in Table 1.

The PE spectra of **2** to **10** are very similar in so far as they exhibit two Gaussian shape bands at the low energy region followed by a sharp band between 8 and 9 eV. At higher energies one or two Gaussian type bands follow (see Figure 2).

To interpret the recorded spectra we rely on the validity of Koopmans' theorem[7] assuming that the negative value of the orbital energy ($-\varepsilon_j$) calculated for the ground state can be directly correlated with the vertical ionization energy ($I_{v,j}$). The orbital energies were derived by MNDO calculations[8] on **2** and **5** as well as **11** and **12**, which were used as models for the more complex compounds **8** and **9**, respectively. For all four molecules a geometry optimization
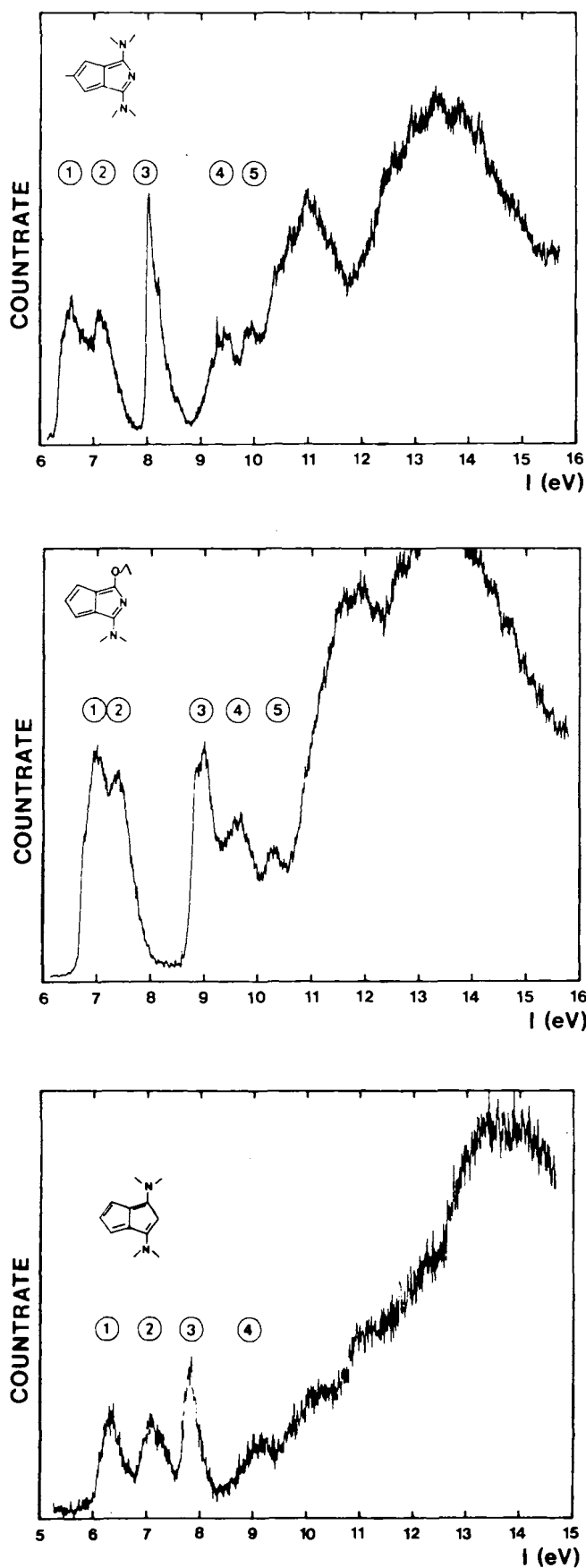
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2: R = H
3: R = CH₃
4: R = C(CH₃)₃
5: R = CHO

6: R₁=R₂=C(CH₃)₃
7: R₁=R₂=Si(CH₃)₃

8: R=H; X=OC₂H₅
Y=N(CH₃)₂
9: R=X=C(CH₃)₃;
Y=N(CH₂)₅

10 11 12

Table 1. Comparison between measured vertical ionization energies ($I_{v,j}$) and calculated orbital energies, ε_j, according to MNDO for **2 — 10**. All values in eV

Com-pound	Bands	$I_{v,j}$	Assign-ment	$-\varepsilon_j$ (MNDO)
2	①	6.65	π	7.67
	②	7.02	π	8.11
	③	7.95	$\pi - (n,n)$	9.58
	④	9.3	π	11.21
	⑤	10.2	$\sigma(N)$	10.82
3	①	6.5	π	
	②	7.05	π	
	③	8.98	$\pi - (n,n)$	
	④	9.4	π	
	⑤	9.95	$\sigma(N)$	
4	①	6.4	π	
	②	7.0	π	
	③	7.9	$\pi - (n,n)$	
	④	9.3	π	
	⑤	9.9 (sh)	$\sigma(N)$	
5	①	7.2	π	8.10
	②	7.6	π	8.49
	③	8.4	π	9.89
	④	10.0	π	11.73
6	①	6.6	π	
	②	6.8	π	
	③	7.9	$\pi - (n,n)$	
	④	9.2 (sh)	π	
7	①	6.7	π	
	②	7.1	π	
	③	8.0	$\pi - (n,n)$	
	④	9.2 (sh)	π	
8	①	7.0	π	7.98 [a]
	②	7.5	π	8.53
	③	9.0	$\pi - (n,n)$	10.11
	④	9.7	$\pi + (n,n)$	11.55
	⑤	10.3	σ_{N2}	11.05
9	①	6.8	π	8.50 [b]
	②	7.3	π	9.28
	③	9.1	$\pi - n_N$	10.61
	④			11.07
	⑤			11.76
10	①	6.1	π	7.45
	②	6.8	π	8.20
	③	7.55	π	8.86
	④	8.9	π	10.97
	⑤	9.6	π	11.30

[a] Calculations performed on **11**. — [b] Calculations performed on **12**.

was performed with the imposed restrictions of planarity for the azapentalene moiety and equality of the N—C and C—H bond distances in the substituents. In all cases the optimized structures exhibit a pronounced bond alternation within the ring in accordance with the X-ray data for **4**[9]. The calculated orbital energies are compared with the recorded ionization energies in Table 1.

The sequence of the highest occupied MO's of **2** as well as their relations to the highest occupied MO's of pentalene (**13**) is shown qualitatively in Figure 3. At the left of this Figure the three highest occupied MO's of **13** (D_{2h}) are depicted. As a result of the replacement of the CH unit of the 2-position of **13** by nitrogen those MO's will be lowered that show a sizeable AO coefficient at this position ($2b_{3u}$, $1b_{2g}$). In addition a new MO, $9a_1$, belonging to the lone pair at the nitrogen atom, emerges (second column from left). In

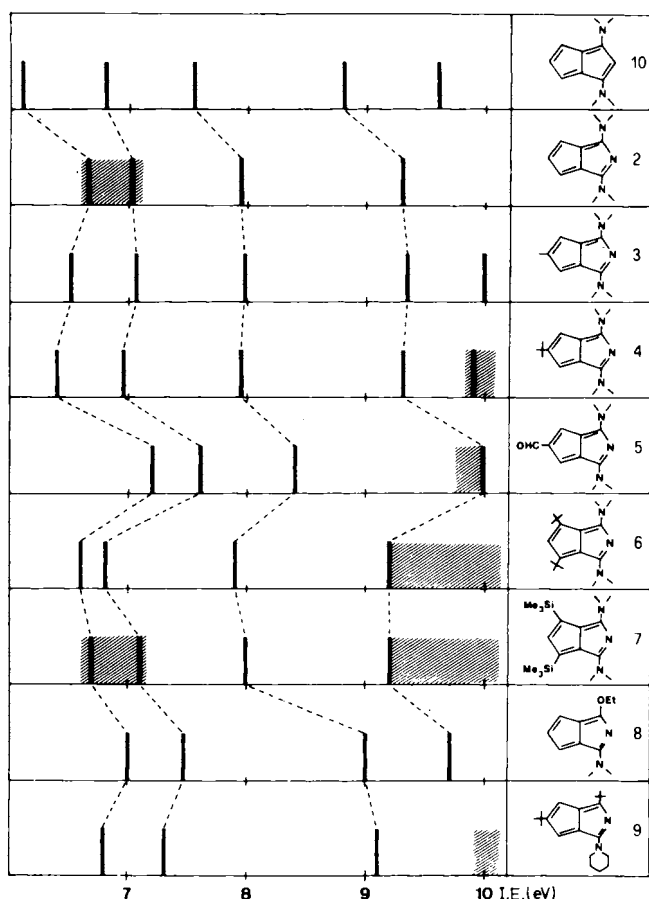Figure 1. He(I$_\alpha$) photoelectron spectra of **3**, **8**, and **10**

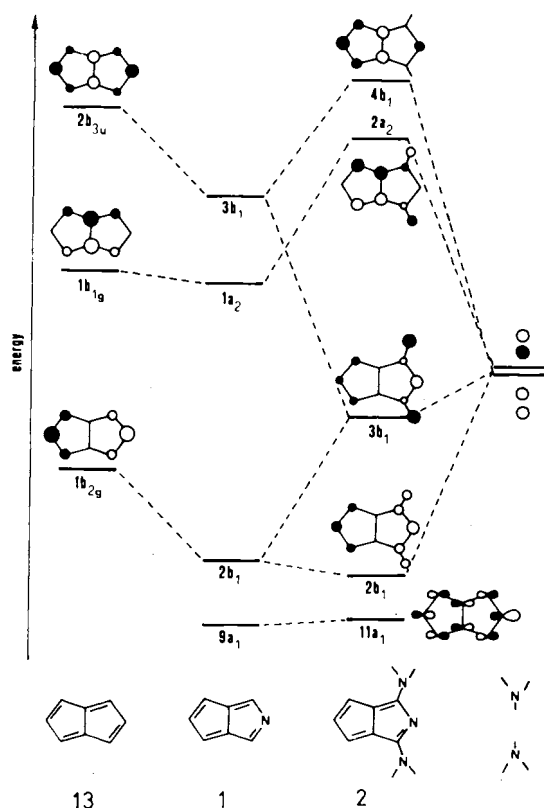Figure 2. Comparison between the first PE bands of 2 – 10

Figure 3. Qualitative correlation between the highest occupied MO's of pentalene (13) with that of 2-azapentalene (1) (left) and qualitative interaction diagram between the highest occupied MO's of 1 with two dimethylamino groups to yield the MO's of 2 (right)

contrast to Figure 3 it is predicted by the MNDO method to be 0.3 eV above $2b_1(\pi)$. The consequence of the substitution of two H atoms by two dimethylamino groups at positions 1 and 3 of 1 is shown in the third column from the left of Figure 3. The two highest occupied π MO's of 1 will be destabilized by interacting with the a_2 and b_1 linear combinations of the $2p_\pi$ orbitals at the dimethylamino groups. The third MO of 2 is essentially a nonbonding π MO $(3b_1)$ mainly localized at the two substituents and the ring nitrogen. Its bonding counterpart is predicted by the MNDO method to be 0.4 eV below the highest occupied σ level $(11a_1)$. This predicted order is opposite to that shown in Figure 3 (see below).

Since the semiempirical methods very often predict σ MO's at too low orbital energies[8,10] we investigated the PE spectrum of 10 (see Figure 1). A comparison between the first four PE bands of 2 and 10 (top of Figure 2) reveals that bands ①, ③, and ④ of 10 are shifted towards higher energy by 0.4 to 0.6 eV, while band ② is shifted by only 0.2 eV. This result is anticipated on the basis of Figure 3 if we assume that the first four PE bands of 2 are due to the ionization from π orbitals: The corresponding wave functions of the first, third, and fourth π MO from top (Figure 3) show large coefficients at center 2, while the second MO from top $(2a_2)$ has a node passing through the vertices. If band ③ would be due to the ionization from $11a_1$ it should have no counterpart in the PE spectrum of 10. This is, how-

ever, not the case. The comparison between the first PE bands of 2 and 10 suggests that the ionization energy for the lone pair at position 2 of 2 should be assigned to energies higher than 9.3 eV.

The assignment of the first two bands in the PE spectrum of 2 to the ionization from π MO's is corroborated by the characteristic "π-type shapes"[6], which strongly resemble the shapes of the first two PE bands of 1,3,5-tri-*tert*-butyl-pentalene[11,12]. The narrow band envelope of the third PE band, which does not have its counterpart in the PE spectrum of 1,3,5-tri-*tert*-butylpentalene, might be understood in terms of the localization properties of the corresponding MO in 2 (see $3b_1$ of Figure 3). An equally valid rational rests on the assumption that nitrogen atoms within dimethyl-amino groups in 2 adopt a nearly planar geometry[13]. Due to the lack of the gas phase structural data for 1,3-bis(di-methylamino)-2-azapentalenes such an assumption is sheer speculation. It should be stressed, however, that X-ray data, which are available for 4[1,9], indicate that the sum of bond angles around the N atoms within both $N(CH_3)_2$ groups is as large as 360°, which is compatible with a planar trigonal geometry.

The above proposed assignment of the lowest ionization energies for 2 is further substantiated by considering the changes in the PE spectra upon successive introduction of substituents at the 5- (3, 4, and 5) and 4- and 6- (6 and 7) ring positions. Thus, the replacement of 5-H in 2 by a CH_3

(3) or $C(CH_3)_3$ (4) group mostly influences the first ionization band. It moves towards the lower ionization energy side by 0.15 and 0.30 eV, respectively (see Figure 2). The shifting of the second band appears to be less significant, and it is experimentally detected only in going from 2 to 4. The HOMO of 2 has a large amplitude at C-5, whilst the next MO has a node at this position. These orbitals are therefore destabilized to different extents by introducing an alkyl group at the C-5 ring position. The effect on the higher ionization events is negligible as expected on the basis of the composition of the corresponding MO's. The fifth ionization event in the PE spectra of 3 and 4 does not have, as already mentioned, a discernible representative in the PE spectrum of 2. According to Figure 3 this band corresponds, very likely, to the lone pair on the ring nitrogen.

The change in the PE spectra in passing from 2 to 5 can be readily interpreted in terms of inductive perturbation by the CHO group[14,15]. The trend is well reproduced in the MNDO calculated orbital energies for 2 and 5. Slightly larger increase of the highest occupied π MO's of 2 and the vacant π^* orbital of the CHO moiety also takes place. MNDO calculations support this supposition.

The PE spectra of 6 and 7 appear to be considerably less resolved than those of the previously discussed 1,3-bis(dimethylamino)-2-azapentalenes. Hence, the influence of the $C(CH_3)_3$ and $Si(CH_3)_3$ groups occupying 4- and 6-ring positions on the highest occupied MO's of 2 could be estimated only for the first three PE bands. In the series 2, 6, and 7 we observe that the positions of the bands ① and ③ are almost insensitive to the replacement of hydrogen atoms in the 4,6-ring positions by either $C(CH_3)_3$ or $Si(CH_3)_3$ groups. The second band undergoes shifts towards lower binding energy (by ca. 0.2 eV) on going from 2 to 6, while on passing from 2 to 7 a shift of less than 0.1 eV towards higher binding energy is evident (Figure 2). Such a behaviour contradicts expectations based on the inductive and conjugative abilities of the two substituents[16,17]. The experimentally observed trends can be, however, satisfactorily rationalized by considering the effects of steric influence of the bulky *tert*-butyl- or even more of the trimethylsilyl group on the geometry of the dimethylamino fragments and their coplanarity with the azapentalene ring. Change in the degree of pyramidality at nitrogens as well as the twisting of the $N(CH_3)_2$ groups should affect the basis energy of the nitrogen lone pairs with concomitant change in the extent of interaction between nitrogen lone pairs and MO's related to the azapentalene ring (see Figure 3). Hence, the changes in the PE spectra caused by 2,6-substitution [by either $C(CH_3)_3$ or $Si(CH_3)_3$ groups] are, in fact, the result of a delicate balance of at least three factors: (a) change in geometry within the $N(CH_3)_2$ fragments, (b) differences in inductive power, and (c) differences in the mechanism of conjugative interaction between *tert*-butyl and trimethylsilyl groups.

The PE spectra of 8 and 9 are of considerable interest since they provide a direct insight into sensitivity of the highest occupied MO's of 2 upon replacement of one of the $N(CH_3)_2$ groups with substituents of entirely different electron withdrawing and conjugating abilities. On the basis of

localization properties of the three highest occupied MO's in 2 we expect that the change of substituents at C-1 and/ or C-3 will effect the first two MO's much less than the third one.

Comparison of the measured PE spectra of 8 and 9 with that of the related 1,3-bis(dimethylamino)-2-azapentalenes 2 and 4, respectively, shows that this is indeed the case (Figure 2, Table 1). For instance, the first three ionization bands of 8 are shifted to higher ionization energy relative to 2 by 0.35, 0.44, and 1.05 eV (Table 1). The significantly larger increase of $I_{v,j}$ for the third ionization event reveals that the third highest occupied MO in 2 is by far more influenced through the change in the conjugative type of interaction. A similar trend is also observed by comparison of the PE spectrum of 9 with that of its closest bis(dimethylamino) congener 4. Here the replacement of the dimethylamino groups by a $C(CH_3)_3$ moiety or a piperidinyl ring, respectively, leads to an increase of the first two $I_{v,j}$'s by ca. 0.3 eV (Table 1). The third band moves towards higher energy value by 1.05 eV relative to its position in 5. However, due to a pronounced difference between the structural features of 4 and 9, it is difficult to make more quantitative distinction between the contribution of either inductive or resonance effects to the stabilization observed.

Concluding Remarks

Our PE-spectroscopic investigations of nine 1,3-donor-substituted 2-azapentalenes reveal that the highest four occupied MO's are π in character. We estimate that the ionization energy of the nitrogen lone pair at the 2-position is higher than 9.3 eV. Our results furthermore reveal that the replacement of one dialkylamino group by an ethoxy or a *tert*-butyl group affects the two highest occupied MO's only to a minor extent. They also show that the substitution of the 5-position by an electron accepting group produces a strong stabilization. The results suggest that an electrophilic substitution on the 2-azapentalenes investigated should take place preferentially at position 5 and to a lesser extent at position 4. Attack on the ring nitrogen should not be preferred.

Experimental

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