

Photoelectron Spectra of *N*-substituted 1,4-Dihydro-4,4-dimethylpyridines

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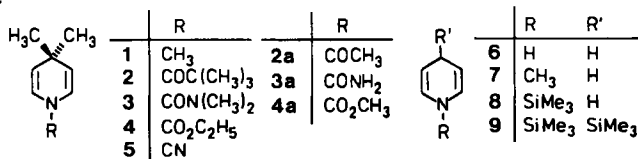
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Photoelektronenspektren von *N*-substituierten 1,4-Dihydro-4,4-dimethylpyridinen

Die He(I)-Photoelektronenspektren der *N*-substituierten 1,4-Dihydro-4,4-dimethylpyridine 1–5 wurden untersucht. Die Zuordnung der Banden basiert auf MNDO-Rechnungen. Der Vergleich der ersten Banden von 1 und 5 legt nahe, daß der CN-Substituent neben einem starken +I- einen schwachen –M-Effekt ausübt.

Recently Hünig et al. determined the redox potentials of the 1,4-dihydro-4,4-dimethylpyridine derivatives 1–5 and uncovered the exceptional redox behaviour of 4 and 5¹. Since the dihydropyridine moiety is very important in biological redox reactions^{2,3} the understanding of electronic effects associated with strong electron-withdrawing substituents is of interest. To contribute to this understanding we have investigated the *N*-substituted 1,4-dihydro-4,4-dimethylpyridines 1–5 in the gas phase by means of He(I) photoelectron (PE) spectroscopy.



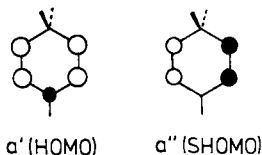
So far, only the PE data of 1,4-dihydropyridine (6) and its *N*-methyl congener (7)³, 1,4-dihydro-1-(trimethylsilyl)pyridine (8), and 1,4-dihydro-1,4-bis(trimethylsilyl)pyridine (9)⁴ have been reported. Based on a simple structure representation model⁵ the first two bands in the PE spectrum of 6 were assigned to ²B₁ and ²A₂ states, respectively (assuming C_{2v} symmetry)³. The assignment was confirmed by the subsequently performed MO calculations^{6,7}. The substitution of NH hydrogen by methyl group was found to influence the highest occupied orbitals of the dihydropyridine ring by a hyperconjugative effect³, while the trimethylsilyl substituents in 8 and 9 exhibited combined inductive and hyperconjugative action⁴.

Results and Discussion

The PE spectra of 1, 2, and 5 are shown in Fig. 1 as representative examples. All spectra exhibit one band between 7 and 8.2 eV clearly separated from bands between 9 and 10 eV. In Table 1 the first vertical ionization energies *I*_v of 1–5 are collected. To interpret the

spectra we make use of *Koopmans'* theorem⁸⁾ by assuming that the calculated negative values of the orbital energies $-\epsilon_i$ derived for the ground state can be set equal to the recorded vertical ionization energies. The orbital energies were derived by MNDO⁹⁾ calculations on 1–5. Since the geometries of these molecules were unknown we optimized all geometrical parameters with respect to the heat of formation. The calculated orbital energies are compared with the recorded ionization energies in Table 1. In the case of 2–4 the calculations were performed on the more simple models 2a, 3a, and 4a, respectively.

The PE spectrum of 1 exhibits two low lying bands with maxima at 7.15 and 9.31 eV. Comparison with the previously measured spectra of 6–9 and the results of semiempirical MNDO calculations indicate that these bands should correspond to ejection of electrons from 16a' and 9a'' orbitals (see below), the former being symmetric, the latter antisymmetric with respect to the symmetry plane passing through centres 1 and 4. Replacing the methyl group at the N atom by an electron withdrawing group leads us to expect a shift of both bands towards higher ionization energy. This expectation is based on arguments from first order perturbation theory¹⁰⁾, reasoning that a' is stabilized by interaction with a vacant π^* orbital of a substituent attached to the nitrogen center *and* the inductive effect exerted by the COX group. For reasons of symmetry, a'' (nodal plane through centres 1 and 4) is stabilized *only* by the inductive effect of a substituent at the nitrogen atom. We anticipate, therefore, a stronger shift of the first peak (a') in the PE spectra of 2–4 compared with the second one (a'').



To check this prediction we turned our attention to the N-COX (X = C(CH₃)₃, N(CH₃)₂, and OC₂H₅) substituted dihydropyridines 2–4.

As is seen from Figure 1, 2 shows two peaks in the low energy region of the PE spectrum. From the ratio of the relative intensities of the first and second peaks, the second peak is regarded to be composed of two bands with the maxima at 9.25 and 9.68 eV, respectively. In this region we expect two π bands of the dihydropyridine moiety and one n band mainly related to the oxygen center of the COC(CH₃)₃ group. The bands at 7.71 and 9.68 eV can be attributed to the π bands corresponding to the first two π bands in 1, on the basis of the MNDO calculations. The remaining band with the maximum at 9.25 eV, we assign to the ionization event from the oxygen lone pair (n_O).

It is noteworthy, that the ionization energy of the oxygen lone pair of 9.25 eV is similar to that reported for *tert*-butyl methyl ketone¹¹⁾.

By using similar arguments we assign the first band and the maximum of the third band in the PE spectrum of 3 to the ionization from the MO's mainly localized on the dihydropyridine ring. The second band is most probably associated with the antisymmetric π -orbital of the CON(CH₃)₂ group¹²⁾. The exact position of the band corresponding to the ionization out of the oxygen lone pair is, however, hard to assess due to the strong overlapping character of the second and third band. As in the case of the n_O lone pair orbital in 2, the ionization energy of the π MO related to the CON(CH₃)₂ group is only marginally influenced when compared with that reported for *N,N*-dimethylacetamide^{12,13)}.

Finally the first two bands in the PE spectrum of 4 appearing at 7.86 and 9.75 eV are assigned to the a'- and a''-like orbitals of the dihydropyridine ring. The ionizations from

the n_O and the antisymmetric π MO of the ethoxycarbonyl group are expected to occur at significantly higher energy; for instance, in $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ they appear at 10.39 and 10.99 eV, respectively¹².

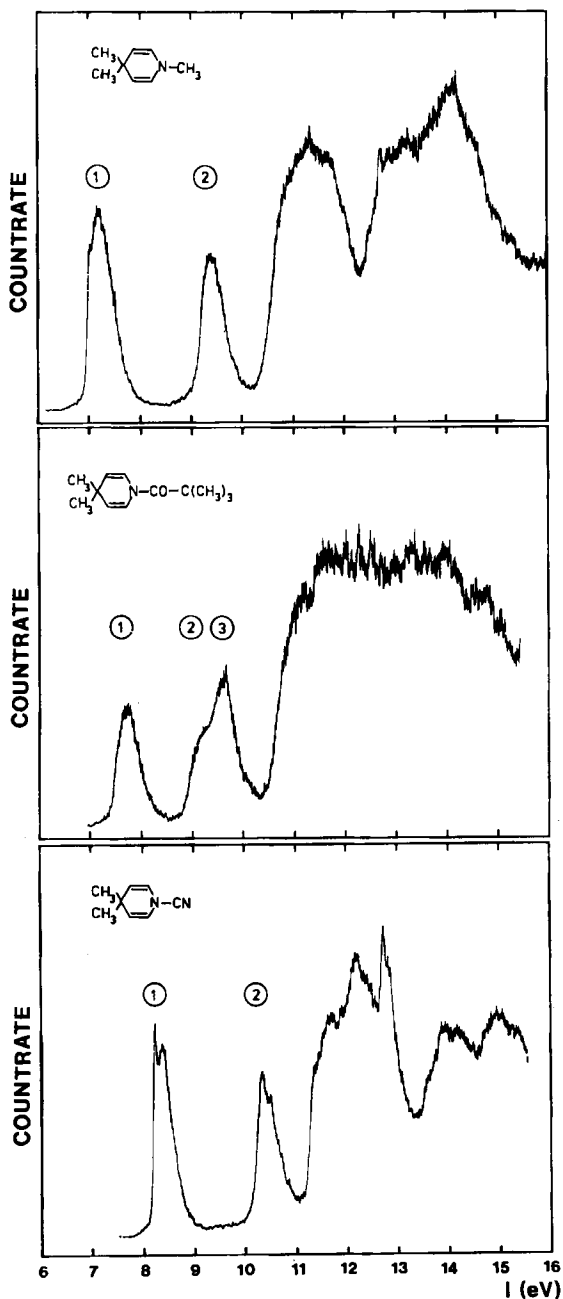


Fig. 1. PE spectra of 1, 2 and 5

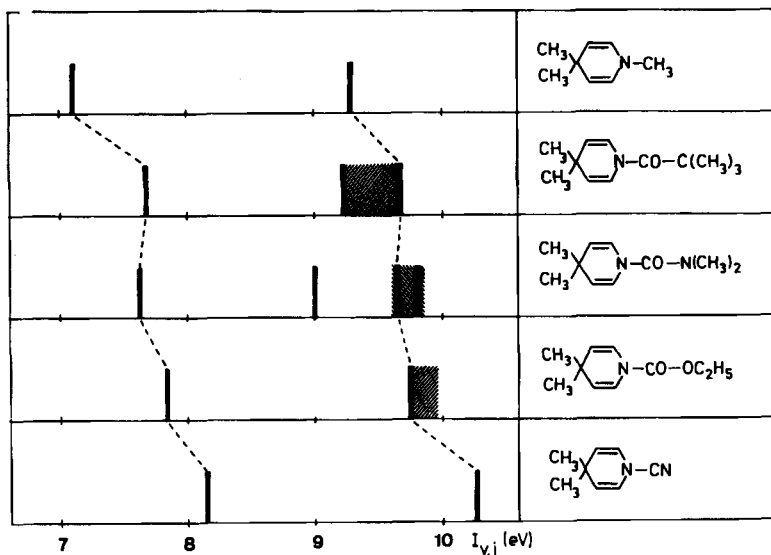


Fig. 2. Correlation between the first bands of the PE spectra of 1–5

Comparison of the measured ionization energies for N-COX substituted dihydropyridines 2–4 with that of 1 (Fig. 2) shows that substitution of the *N*-methyl group by strongly electron withdrawing –COX functional groups exerts a significant stabilization effect on both highest occupied orbitals related to the dihydropyridine ring. It is remarkable, however, that in all three compounds the stabilization of the highest occupied molecular orbital (HOMO) exceeds the stabilization of the second highest occupied molecular orbital (SHOMO) by ca. 0.2 eV. This trend is well reproduced in the MNDO calculated orbital energies for 2a, 3a and 4a, respectively. An analysis of the MNDO calculated wave functions for 2a–4a indicates that part of the stabilization energy is attained through the interaction of the highest occupied π^* orbital of the dihydropyridine moiety and the vacant π^* orbital of the appropriate symmetry of the –COX group. The stabilizing inductive electron withdrawing effect of –COX seems to be, however, more important, thus, rotation of the –COX functional group out of the ring-plane reduces the extent of stabilization only marginally, as revealed from the MNDO calculations on 4a. The MNDO calculated orbital energies of the two highest occupied MO's of nonplanar 4a in which the methoxycarbonyl group lies in the plane perpendicular to the ring-plane are 8.70 and 10.38 eV compared to 8.84 and 10.45 eV in planar conformation (Table 1).

The replacement of the *N*-methyl group by a cyano group leads, as could be expected on the basis of the high electron withdrawing power of this group, to the strongest stabilization of the highest occupied orbitals among the studied dihydropyridines. Thus, passing from 1 to 5 causes an increase in the first two ionization energies of 1.02 and 0.95 eV, respectively. The stabilization of the latter orbital corresponds exactly to the inductive stabilization of the e_{1g} orbital on going from benzene to cyanobenzene¹⁴.

In contrast to the COX substituted dihydropyridines 2–4 the magnitude of stabilization of the HOMO of 5 is nearly identical to that of the SHOMO. This observation can be interpreted by assuming that the above mentioned stabilization of a' by interaction with

the empty π^* orbital of the substituent is essentially canceled by the destabilizing interaction between the a' (HOMO) of the dihydropyridine moiety and the occupied π -orbital of the CN group. Because of the large energy gap between the interacting orbitals the inductive effect is by far more effective¹⁰.

Table 1. Measured ionization energies $I_{v,j}$ of 1–5 and calculated orbital energies ϵ_j

| Compound | Band | $I_{v,j}$ eV | Assignment | $-\epsilon_j$ (MNDO) eV |
|----------|------|-----------------|------------------|----------------------------|
| 1 | 1 | 7.15 | π | 8.09 |
| | 2 | 9.31 | π | 9.94 |
| 2 | 1 | 7.71 | π | 8.63 ^{a)} |
| | 2 | 9.25 | π_{O} | 11.32 |
| | 3 | 9.68 | π | 10.26 |
| 3 | 1 | 7.66 | π | 8.75 ^{b)} |
| | 2 | 9.02 | π (COX) | 11.80 |
| | 3 | 9.66 | π | 10.36 |
| 4 | 1 | 7.86 | π | 8.84 ^{c)} |
| | 2 | 9.75 | π | 10.45 |
| 5 | 1 | 8.17 | π | 8.84 |
| | 2 | 10.26 | π | 10.58 |

^{a)} Calculations were performed on 2a. — ^{b)} Calculations were performed on 3a. — ^{c)} Calculations performed on 4a.

Although our results indicate that the effect of the CN group can best be described by assuming two competing effects, a stabilizing inductive and a destabilizing conjugative effect, the latter one must be much smaller than the first one. These findings are qualitatively in line with recent findings^{1,15} and their theoretical interpretations¹⁶.

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Experimental Part

The preparations of 1–5 have been described¹¹. The He(I) spectra were recorded on a Perkin-Elmer PS-18 spectrometer. The spectra have been calibrated with Ar and Xe.

CAS Registry Numbers

1: 59547-47-6 / 2: 84567-24-8 / 2a: 67402-84-0 / 3: 84567-23-7 / 3a: 101376-29-8 / 4: 37778-34-0 / 4a: 101376-30-1 / 5: 84567-25-9

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