Structural Chemistry of Polycyclic Heteroaromatic Compounds. Part VIII.† Photoelectron Spectra and Electronic Structures of Thienonaphthyridines. Part II.

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The Het(I) photoelectron spectra of twelve isomeric thienonaphthyridines (13–24) are reported and analysed. Analogous positional effects of the heteroatoms as in isomers I–12, reported in Part I, are observed. These effects can be used to characterize and to distinguish between the isomers. The investigation of a large ensemble of isomers permits some general conclusions to be drawn regarding the electronic structure, which cannot be obtained from consideration of single compounds.

This is the second of two papers dealing with the photoelectron (PE) spectra of isomeric thienonaphthyridines. In comparison with the compounds investigated in Part I,1 the two annelands of the central pyridine ring have exchanged their positions. In order not to confuse the discussion, the compounds in this paper are numbered consecutively to those of Part I.

![Scheme 1. Molecular formulae of thienonaphthyridines 13-24.](image)

**Experimental**

**Materials.** The following isomeric thienonaphthyridines are investigated in this paper: thieno[3,2-α][1,6]naphthrydine (13), thieno[3,4-α][1,6]naphthyridine (14), thieno[2,3-α][1,6]naphthyridine (15), thieno[3,4-β][2,6]-naphthyridine (16), thieno[3,4-α][2,6]naphthyridine (17), thieno[2,3-α][2,6]naphthyridine (18), thieno[3,2-β][2,7]-naphthyridine (19), thieno[3,4-α][2,7]naphthyridine (20), thieno[2,3-β][2,7]naphthyridine (21), thieno[2,3-β][1,7]-naphthyridine (22), thieno[3,4-β][1,7]naphthyridine (23), and thieno[3,2-β][1,7]naphthyridine (24). Their syntheses have already been described in the literature.2,3 In these papers compounds 13–24 were regarded as thieno-b-annelated 2,5-, 2,6-, 2,7- and 2,8-naphthyridines for convenient comparison with the c-fused systems, 1–12.

**Spectra and calculations.** For details see Part I.1

**Results and discussion**

The PE spectra of compounds 13–24 are depicted in Figs. 1–4. IPs are summarized in Table 1 and the calculated orbital energies are given in Table 2.

The spectra were analysed in the same way as described in Part I1 with the aid of semiempirical PM3 calculations making use of Koopmans' theorem.9 The MOs are classified according to their symmetry properties regarding the C_s symmetry of the molecules. The seven doubly occupied π MOs are numbered with increasing energy, and the two n_on orbitals are termed n_1 and n_2.

In some of these isomers analysis of the spectra is also hampered by strong overlap of ionization bands. In particular, in compounds 13, 15 and 19, the first two to three
bands, in compounds 13–15 the third and the fourth bands and in compounds 19–24 the fourth and the fifth bands are very close to each other. Here again, the safe determination of the corresponding IP values relies largely on the comparison with the spectra of other isomers. The accuracy of the assignments of measured ionization potentials $IP_i$ to calculated orbital energies $\epsilon_i$ is confirmed by a linear regression with a correlation coefficient $r = 0.996$ (Fig. 5).

The ionization potentials are discussed with reference to the correlation diagram depicted in Fig. 6. As in isomers 1–12, $IP(\pi_\pi)$ of compounds with a 3,4-annelated thiophene ring is always lower than that of compounds with a 3,2- or 2,3-annelated thiophene ring. As the calculated enthalpies of formation (Table 2) indicate, the 3,4-annelated thienonaphthyridines are 12–14 kJ mol$^{-1}$ less stable than those of 3,2- and 2,3-annelated thienonaphthyridines. This is in accordance with the well-known fact that annelation of a thiophene ring by its C$^2$–C$^3$ bond to another aromatic system is more favorable than by its C$^1$–C$^2$ bond,$^{7,8}$ and this is reflected in the energy of the HOMO. By the first ionization potential it is thus possible to determine the annelation mode of the thiophene ring in all 24 isomers. Even C$^2$–C$^3$ and C$^3$–C$^4$ annelation of the thiophene ring seems to be distinguishable, although the difference in the IPs is rather small for isomers 16/18 and 22/24. In the latter aspect, isomers 13–24 show more systematic behavior than 1–12 for which no such distinction is possible. This is probably caused by the closer vicinity of the heteroatoms S and N of the thiophene and the central pyridine ring in the former group of compounds.

The $\pi_\pi$ ionization energies of 13–24 have a fairly constant value (8.9 ± 0.2 eV), independent of the mode of annelation. Also, the calculated $\pi_\pi$ orbital energies vary in a rather narrow range (−9.5 ± 0.2 eV).

The $\pi_\pi$ ionization of 13–24, which in most compounds is overlapped by the $n_\pi$ ionization, is found between 9.9
and 10.2 eV. In 13–18 π₃ is stabilized relative to the other isomers and this coincides with large coefficients in π₃ of phenanthrene in the corresponding positions of the nitrogen atom in the peripheral ring.

The IP of electrons from π₃ of 13–24 show a variation of 10.6–10.9 eV; however, the effects as a function of the topology are the opposite of those of π₃: π₄ is stabilized in isomers 19–24. This is an indication of large coefficients in the corresponding phenanthrene MO⁹ in the positions of the nitrogen atom, which is actually the case.

The variation of π₃ with the position of the N atom in the left-hand ring is similar to that of isomers 1–12.¹ The π₃ ionizations of 13–24 are found to be between 11.6 and 12.5 eV. Relatively low values (11.6–11.8 eV) are observed for the last three isomers (22–24), while 13–15 and 19–21 have higher and relatively constant values (11.95 ± 0.06 eV). These data reflect the coefficient size of π₃ of phenanthrene in the respective positions of the N

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**Fig. 3.** PE spectra of thieno[2,7]naphthyridines 19–21.

**Fig. 4.** PE spectra of thieno[1,7]naphthyridines 22–24.

**Fig. 5.** Correlation diagram for ionization potentials IP, and orbital energies εₚₙ₃ of π, nₓ, and nᵧ orbitals of thieno-naphthyridines 13–24.
atom in the peripheral pyridine ring of these molecules. In 16–18 the ionizations originating from $n_3$ lead to very high IP values (12.46–12.66 eV).

The $n_3$ ionizations vary from 11.88 to 12.21 eV and do not reveal any systematic correlation with the annelation mode of the thiophene ring. Comparing the IP($n_3$) values of thienonaphthyridines with those of naphthothiophenes, thieno-quinolines and -isoquinolines, a constant shift of 0.5 eV per nitrogen atom to higher energies is found.

As in compounds 1–12, there is a clear variation of the split $\Delta N$ of the two $n_3$ ionizations, which is essentially independent of the annelation of the thiophene ring. The smallest split (about 0.3 eV) is found for 13–15. Isomers 16–18 and 22–24 have a separation of these IP values of about 0.6 eV, while in 19–21 the corresponding value is about 0.8 eV. If we neglect the thiophene unit, the nitrogen atoms of 4–6 and 13–15 are in identical positions and the same $\Delta N$ of 0.3 eV is observed. The same holds for 7–9 and 22–24 with $\Delta N$ equal to 0.6–0.7 eV. The observed $\Delta N$ values indeed coincide within ±0.1 eV with those observed for the corresponding naphthyridines. To explain the relatively large $\Delta N$ values of 16–18 (0.6 eV) and of 19–21 (0.8 eV), similar arguments can be used as for 1–3 (1.1 eV) and 10–12 (0.8 eV). The naphthyridine fragments have $C_{2v}$ or $C_{2v}$ symmetry and...
in \( n_t \) and \( n_{13} \) the coefficients of \( n_1 \) and \( n_2 \) are of equal size. In addition, effective through-bond interaction is possible because both \( n_1 \) and \( n_2 \) overlap with the same \( \sigma \) bonds.

To sum up the results for all 24 isomeric thienonaphthyridines, the following conclusions are possible. The annelation mode of the thiophene ring is clearly reflected in the energy of the first IP, \( C^2-C^3 \) annelation leads to a higher first IP than \( C^3-C^4 \) annelation. Even \( C^2-C^3 \) and \( C^2-C^2 \) annelation can be distinguished in the second group of isomers (13–24). The two nitrogen atoms cause topological effects in the energies of \( \pi \) ionizations and in the energy separation of the two \( n_N \) ionizations. The variation of \( \pi \) ionizations can be rationalized by first-order perturbations of the respective \( \pi \) MOs of phenanthrene, which are stabilized proportionally to the size of the coefficients in the positions of the N atoms. The main contribution to the split \( \Delta n_N \) of the orbitals (\( n_1 \) and \( n_{13} \)) is caused by through-bond effects, which are most effective when the N atoms in the naphthyridine fragment are symmetry-related.

With regard to first-order perturbation theory, it can be stated that the investigation of photodneutral spectra of several isomeric thienonaphthyridines provides an experimental analysis of the electron distribution in individual MOs. By comparing the ionization potentials related to the \( \pi \) MOs in such a series of compounds we can experimentally classify the orbitals and determine the electron distribution. This is an excellent possibility to test and examine the results of quantum chemical calculations, which can be useful to estimate reactivity and selectively of such compounds in various chemical reactions.

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References


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