

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

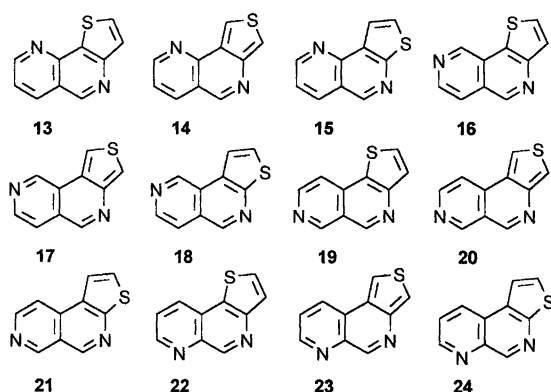
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The He(I) photoelectron spectra of twelve isomeric thienonaphthyridines (**13–24**) are reported and analysed. Analogous positional effects of the heteroatoms as in isomers **1–12**, reported in Part I, are observed. These effects can be used to characterize 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**.

Experimental

Materials. The following isomeric thienonaphthyridines are investigated in this paper: thieno[3,2-*h*][1,6]naph-

thyridine (**13**), thieno[3,4-*h*][1,6]naphthyridine (**14**), thieno[2,3-*h*][1,6]naphthyridine (**15**), thieno[3,2-*c*][2,6]naphthyridine (**16**), thieno[3,4-*c*][2,6]naphthyridine (**17**), thieno[2,3-*c*][2,6]naphthyridine (**18**), thieno[3,2-*c*][2,7]naphthyridine (**19**), thieno[3,4-*c*][2,7]naphthyridine (**20**), thieno[2,3-*c*][2,7]naphthyridine (**21**), thieno[2,3-*f*][1,7]naphthyridine (**22**), thieno[3,4-*f*][1,7]naphthyridine (**23**), and thieno[3,2-*f*][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^{4,5} calculations making use of Koopmans' theorem.⁶ 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_N orbitals are termed n_{I} and n_{II} .

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

[†] For Part VII see Ref. 1.

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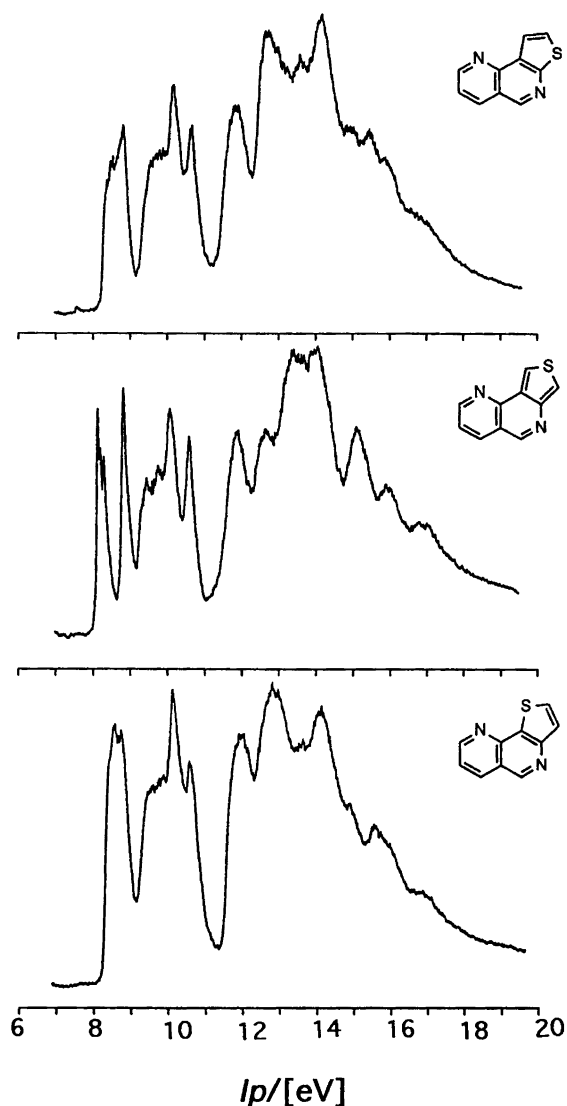


Fig. 1. PE spectra of thieno[1,5]naphthyridines **13–15**.

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 ϵ_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**,¹ $IP(\pi_7)$ of compounds with a 3,4-annulated thiophene ring is always lower than that of compounds with a 3,2- or 2,3-annulated thiophene ring. As the calculated enthalpies of formation (Table 2) indicate, the 3,4-annulated thienonaphthyridines are 12–14 kJ mol^{-1} less stable than those of 3,2- and 2,3-annulated thienonaphthyridines. This is in accordance with the well-known fact that annulation of a thiophene ring by its C^2-C^3 bond to

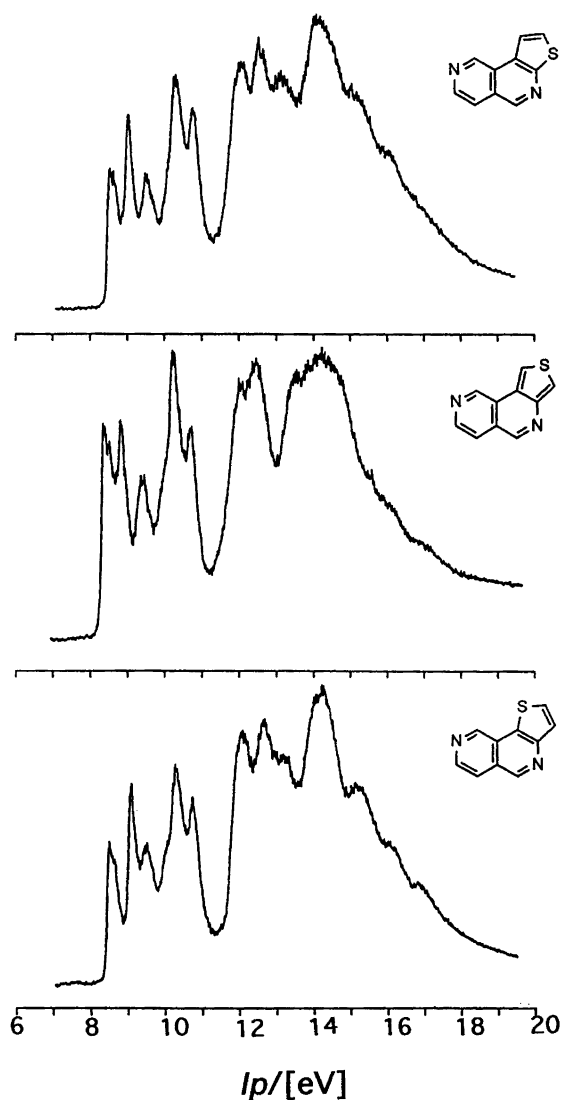


Fig. 2. PE spectra of thieno[2,6]naphthyridines **16–18**.

another aromatic system is more favorable than by its C^3-C^4 bond,^{7–9} and this is reflected in the energy of the HOMO. By the first ionization potential it is thus possible to determine the annulation mode of the thiophene ring in all 24 isomers. Even C^2-C^3 and C^3-C^2 annulation 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 π_6 ionization energies of **13–24** have a fairly constant value (8.9 ± 0.2 eV), independent of the mode of annulation. Also, the calculated π_6 orbital energies vary in a rather narrow range (-9.5 ± 0.2 eV).

The π_5 ionization of **13–24**, which in most compounds is overlapped by the n_1 ionization, is found between 9.9

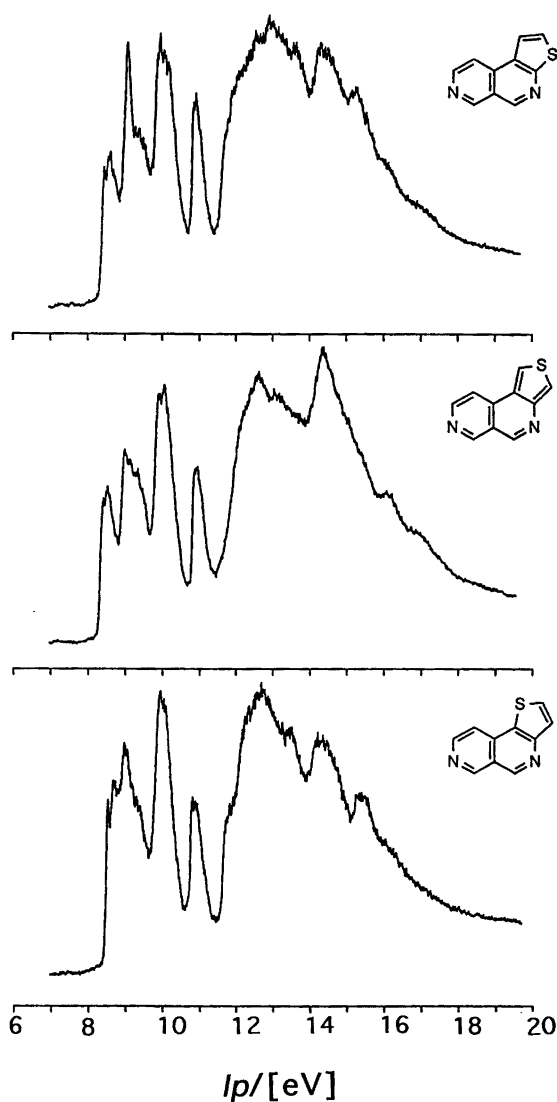


Fig. 3. PE spectra of thieno[2,7]naphthyridines **19–21**.

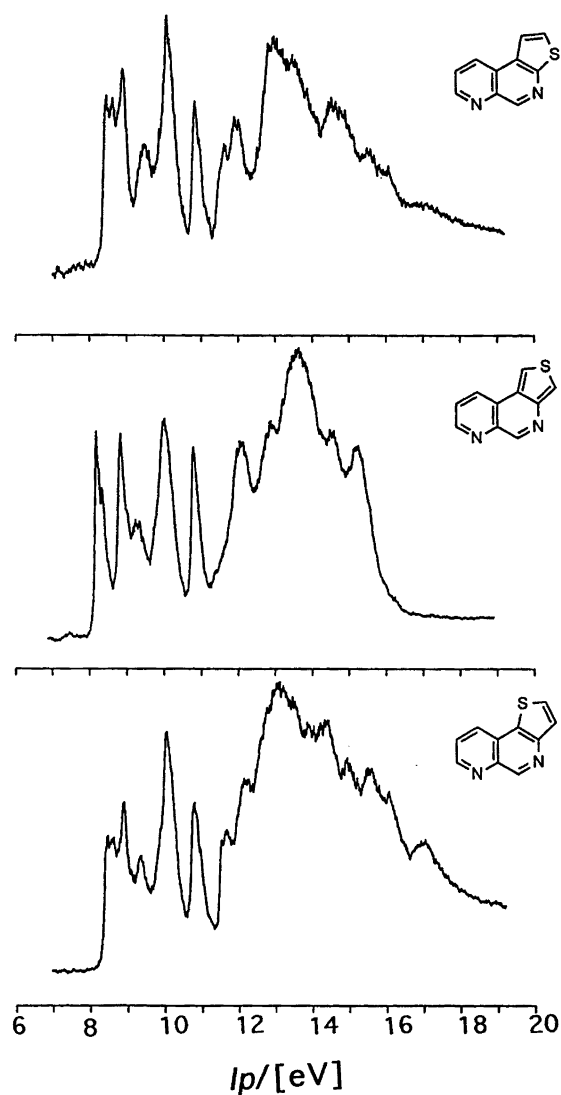


Fig. 4. PE spectra of thieno[1,7]naphthyridines **22–24**.

and 10.2 eV. In **13–18** π_5 is stabilized relative to the other isomers and this coincides with large coefficients in π_5 of phenanthrene⁹ in the corresponding positions of the nitrogen atom in the peripheral ring.

The IP of electrons from π_4 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 π_5 : π_4 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 π_3 with the position of the N atom in the left-hand ring is similar to that of isomers **1–12**.¹ The π_3 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 π_3 of phenanthrene⁹ in the respective positions of the N

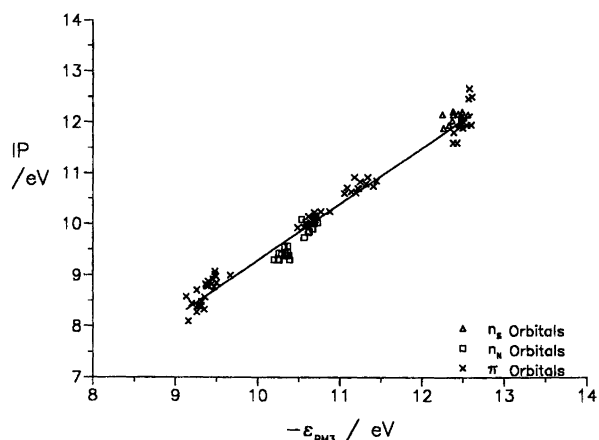


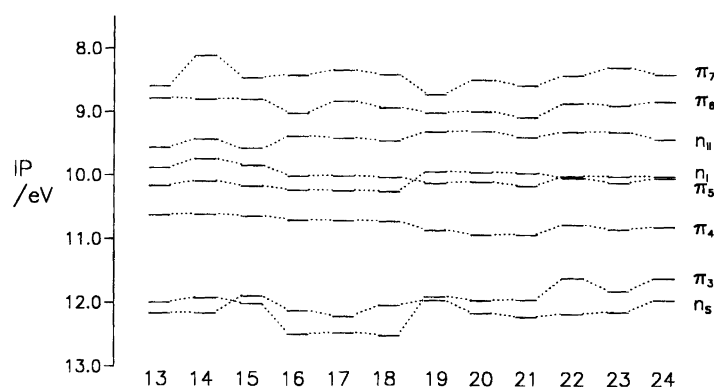
Fig. 5. Correlation diagram for ionization potentials IP_v and orbital energies $-\epsilon_{PM3}$ of π , n_N and n_S orbitals of thienonaphthyridines **13–24**.

Table 1. Vertical potentials IP_V (eV) and vibrational fine structure (cm^{-1}) of thienonaphthyridines **13–24**.

Compound	$\pi_7/7a''$	$\pi_6/6a''$	n_{II}/a'	n_I/a'	$\pi_5/5a''$	$\pi_4/4a''$	$\pi_3/3a''$	n_S/a'	σ/a'
13	8.58	8.77	9.55	9.85	10.15	10.61	11.98	12.15	12.92
14	8.10/600	8.79	9.42	9.73	10.08	10.60	11.91	12.15	12.68
15	8.45	8.79	9.56	9.83	10.16	10.63	12.00	11.88	12.71
16	8.41/1100	9.01	9.37	10.00	10.24	10.69	12.66	12.11	12.80
17	8.33/1050	8.82	9.40	10.00	10.23	10.70	12.46	12.20	12.62
18	8.40/900	8.92	9.44	10.02	10.24	10.71	12.50	12.03	12.63
19	8.71	9.00	9.30	10.11	9.93	10.85	11.89	11.95	12.79
20	8.48	8.98	9.29	10.09	9.94	10.92	11.95	12.15	12.64
21	8.57	9.07	9.38	10.15	9.95	10.92	11.94	12.21	12.71
22	8.41	8.85	9.30	9.90	10.03	10.74	11.60	12.16	12.95
23	8.28	8.88	9.30	10.00	10.10	10.83	11.80	12.13	12.93
24	8.39	8.82	9.41	10.00	10.03	10.79	11.60	11.94	12.96

Table 2. Calculated enthalpies of formation ΔH_f ($kJ\ mol^{-1}$) and orbital energies $-\varepsilon_{PM3}$ (eV) of thienonaphthyridines **13–24**.

Compound	ΔH_f	$\pi_7/7a''$	$\pi_6/6a''$	n_{II}/a'	n_I/a'	$\pi_5/5a''$	$\pi_4/4a''$	$\pi_3/3a''$	n_S/a'	σ/a'
13	320.1	9.13	9.47	10.33	10.63	10.62	11.20	12.48	12.25	13.66
14	331.2	9.16	9.38	10.26	10.57	10.70	11.06	12.46	12.38	13.56
15	318.1	9.20	9.40	10.37	10.62	10.69	11.14	12.51	12.26	13.54
16	320.5	9.32	9.48	10.35	10.68	10.77	11.23	12.58	12.48	13.32
17	332.0	9.35	9.37	10.29	10.65	10.69	11.22	12.57	12.49	13.26
18	318.2	9.31	9.46	10.37	10.73	10.88	11.09	12.61	12.37	13.32
19	318.7	9.26	9.67	10.39	10.69	10.49	11.45	12.50	12.45	13.38
20	330.7	9.32	9.49	10.26	10.54	10.57	11.18	12.60	12.56	13.35
21	316.7	9.36	9.48	10.38	10.71	10.63	11.34	12.55	12.38	13.35
22	321.2	9.27	9.50	10.25	10.67	10.59	11.41	12.38	12.44	13.76
23	333.1	9.26	9.40	10.20	10.65	10.68	11.25	12.39	12.48	13.67
24	319.1	9.29	9.44	10.34	10.69	10.65	11.32	12.43	12.33	13.60

Fig. 6. Correlation diagram for ionization potentials of thienonaphthyridines **13–24**.

atom in the peripheral pyridine ring of these molecules. In **16–18** the ionizations originating from π_3 lead to very high IP values (12.46–12.66 eV).

The n_S 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 $IP(n_S)$ values of thienonaphthyridines with those of naphthothiophenes,⁹ thieno-quinolines and -isoquinolines,⁹ a constant shift of 0.5 eV per nitrogen atom to higher energies is found.

As in compounds **1–12**,¹ there is a clear variation of the split Δn_N of the two n_N 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 Δn_N of 0.3 eV is observed. The same holds for **7–9** and **22–24** with Δn_N equal to 0.6–0.7 eV. The observed Δn_N values indeed coincide within ± 0.1 eV with those observed for the corresponding naphthyridines.¹⁰ To explain the relatively large Δn_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)¹ and **10–12** (0.8 eV).¹ The naphthyridine fragments have C_{2h} or C_{2v} symmetry and

in n_I and n_{II} 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 σ 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. C²-C³ annelation leads to a higher first IP than C³-C⁴ annelation. Even C²-C³ and C³-C² annelation can be distinguished in the second group of isomers (**13-24**). The two nitrogen atoms cause topological effects in the energies of π ionizations and in the energy separation of the two n_N ionizations. The variation of π ionizations can be rationalized by first-order perturbations of the respective π MOs of phenanthrene,⁹ which are stabilized proportionally to the size of the coefficients in the positions of the N atoms. The main contribution to the split Δn_N of the orbitals (n_I and n_{II}) 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 photoelectron spectra of several isomeric thienonaphthyridines provides an experimental analysis of the electron distribution in individual MOs. By comparing the ionization potentials related to the π 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 calcula-

tions, which can be useful to estimate reactivity and selectivity of such compounds in various chemical reactions.

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