Structural Chemistry of Polycyclic Heteroaromatic Compounds. Part 4.[†] Electronic Structures of Angular Dithienopyridines

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The HeI photoelectron spectra of nine isomeric [*b*,*d*]-annellated dithienopyridines (**5–13**) are reported and discussed including those of some closely related compounds such as phenanthridine (**2**), dithieno[3,4-*a*:3',4'-*c*]benzene (**4**) and its tetrahydro derivative **3**. The ionization potentials are assigned to molecular orbitals using the results of MNDO, AM1 and PM3 calculations. The ability of PE spectroscopy as an analytical method in the analysis of the isomers **5–13** is investigated. From the spectra as well as from the theoretical results, the isomers can be divided into two groups, depending on the mode of annellation. The crystal and molecular structures of one member of each group (isomers **9** and **12**) are determined by X-ray diffraction. The mode of annellation is also reflected in the bond lengths of the pyridine and thiophene rings.

Thiophene and pyridine are prototypes of π electron-rich and π electron-deficient aromatic compounds.[1] Their direct combination by annellation may lead to unusual electronic, structural and chemical properties and there is a considerable current interest in effects that arise from the fusion of such heterocycles.[2] We have investigated the electronic structures of nine dithienopyridines (**5–13**) by photoelectron (PE) spectroscopy and semiempirical quantum chemical calculations. By X-ray structure analysis compounds **9** and **12** have been studied. Compounds **1–4** can be considered as parent structures of the dithienopyridines and have, therefore, been included in this study. In addition, the tricyclic heterocycles **5–13** which recently were synthesized,[3] offer the opportunity to test the capacity of PE spectroscopy as an analytical tool to differentiate these types of isomer. For polycyclic aromatic hydrocarbons PE spectroscopy has also proved to be an excellent tool to distinguish isomers.[4]

Results and Discussion

Electronic Structures.—In the thiophene ring the sulfur atom formally replaces a carbon–carbon double bond of benzene. This is a minor perturbation of the π electron system and the aromatic systems of both molecules are therefore closely related to each other. This is expressed in the sulfur/double bond (SD) model.[5] Even more obvious is the relationship between the electronic structures of benzene and pyridine or of polycyclic aromatic molecules and their aza-analogues. In the same way the electronic structures of the dithienopyridines **5–13** should be related to those of benzo[1,2-*c*:3,4-*c*]dithiophene (**4**), phenanthridine (**2**) and phenanthrene (**1**). 1,3,6,8-Tetrahydrobenzo[1,2-*c*:3,4-*c*]dithiophene (**3**) has been included in this study because it has two sulfur atoms in a non-aromatic five-membered ring fused to a benzene unit.

The PE spectra of compounds **1–13** have been measured, the spectra of **3** and **5–13** are depicted in Figs. 1 and 2, respectively. Ionization potentials and calculated orbital energies are collected in Tables 1–5.

The spectra were analysed with the aid of semiempirical SCF MO calculations making use of Koopmans' theorem.[6] The MOs are also classified by their symmetry properties and the π orbitals of the same symmetry are numbered with increasing energy. Some of the ionization bands show resolved vibrational fine structure indicating transitions to different vibrational states of the respective radical cations.

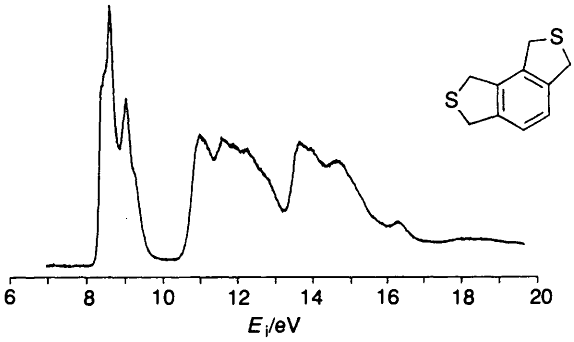

Fig. 1 PE spectrum of compound **3**

Table 1 Orbital energies $-\varepsilon_i^{SCF}$/eV, vertical ionization potentials E_i(v)/eV, and vibrational structure ν/cm^{-1} of phenanthrene (**1**)/C_{2v}

MNDO	AM1	PM3		E_i(v)/ν
8.48	8.61	8.74	$\pi_7/4b_1$	7.89/1400, 2200
8.70	8.87	8.98	$\pi_6/3a_2$	8.29/1500
9.66	9.98	10.04	$\pi_5/2a_2$	9.27/1200
10.17	10.58	10.59	$\pi_4/3b_1$	9.87/1300
11.07	11.60	11.56	$\pi_3/2b_1$	10.54
11.96	11.46	11.88	σ/b_2	11.02
12.21	11.77	12.36	σ/a_1	11.50
12.37	13.12	12.97	$\pi_2/1a_2$	12.06
12.83	12.42	12.98	σ/a_1	12.27
12.97	12.49	12.92	σ/b_2	12.4
13.54	14.59	14.29	$\pi_1/1b_1$	13.1
13.83	13.39	13.65	σ/b_2	13.9

The PE spectra of phenanthrene (**1**)[7] and phenanthridine (**2**)[8] have been studied previously. The observed E_i data (Tables 1 and 2) correspond to those in the literature to within the usual error limits. Because of the greater electronegativity of nitrogen compared with carbon, the π MOs of **2** are stabilized up to

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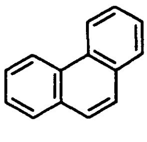
[†] For Part 3, see ref. 26.



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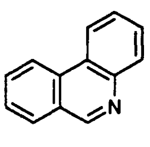

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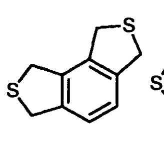

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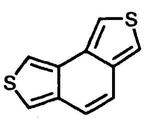

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0.98 eV relative to **1**. Except for the n_N orbital, for which the energy values calculated by MNDO and AM1 are too low, the three semiempirical methods find the same orbital sequence. Larger differences between observed E_i(v) and calculated data ($-\varepsilon$) are noted for n_N (MNDO, 1.59; AM1, 1.35; PM3, 0.98 eV), $\pi_3/3a''$ (AM1, 1.28 eV) and $\pi_2/2a''$ (AM1, 1.55; PM3, 1.38 eV).

Tetrahydrodithienobenzene (**3**) can formally be dissected into a benzene ring and two 2,5-dihydrothiophene molecules. Its PE spectrum may therefore be compared with those of 1,2,3,4-tetramethylbenzene and 2,5-dihydrothiophene or a simple dialkyl sulfide, such as dimethyl sulfide. The ionizations of the two highest occupied π MOs (π_2 and π_3) of the benzene derivative are found at 8.29 and 8.57 eV;[9] for 2,5-dihydrothiophene and the latter sulfide the ionizations of the sulfur lone-pairs are observed at 8.55 ($n_S\pi$) and 11.22 eV ($n_S\sigma$)[10] and at 8.72 ($n_S\pi$) and 11.30 eV ($n_S\sigma$),[11] respectively. For **3** ionizations quite close to the given values are to be expected, and in fact the first six ionization potentials can be associated with the aforementioned orbitals taking into consideration that there are two sulfur atoms in **3** and that both n_S orbitals form a symmetric ($n_S{}^+$) and an antisymmetric ($n_S{}^-$) linear combination. The split of the two $n_S\pi$ orbitals amounts to 0.07 eV and is

Table 2 Orbital energies $-\varepsilon_i^{SCF}$/eV, vertical ionization potentials E_i(v)/eV, and vibrational structure ν/cm^{-1} of phenanthridine (**2**)/C_s

MNDO	AM1	PM3		E_i(v)/ν
8.80	8.98	9.12	$\pi_7/7a''$	8.30
8.96	9.13	9.20	$\pi_6/6a''$	8.37
10.79	10.55	10.18	n_N/a'	9.20
9.91	10.21	10.26	$\pi_5/5a''$	9.59
10.38	10.80	10.79	$\pi_4/4a''$	10.13
11.99	12.48	12.14	$\pi_3/3a''$	11.20
12.45	11.99	12.42	σ/a'	11.5
12.62	13.33	13.16	$\pi_2/2a''$	11.9
12.81	12.34	12.67	σ/a'	12.6
14.21	15.10	14.64	$\pi_1/1a''$	14.1

Table 3 Orbital energies $-\varepsilon_i^{SCF}$/eV, vertical ionization potentials E_i(v)/eV, and vibrational structure ν/cm^{-1} of benzo[1,2-*c*:3,4-*c*]-dithiophene (**4**)/C_{2v}

MNDO	AM1	PM3		E_i(v)/ν
8.55	8.24	8.68	$\pi_7/4b_1$	7.66/1400
8.85	8.42	8.89	$\pi_6/3a_2$	7.84
9.86	9.73	10.07	$\pi_5/2a_2$	9.15/700
10.49	10.39	10.64	$\pi_4/3b_1$	9.85/1500
11.29	11.49	11.67	$\pi_3/2b_1$	10.72
12.40	11.94	12.76	σ/b_2	11.36
12.39	11.67	12.11	$n_S{}^+/a_1$	11.54
12.71	11.77	12.20	$n_S{}^-/b_2$	11.9
12.98	13.58	13.49	$\pi_2/1a_2$	12.43
13.98	14.88	14.74	$\pi_1/1b_1$	13.2
13.20	12.68	13.44	σ/a_1	13.5

Table 4 Vertical ionization potentials E_i(v)/eV of dithienopyridines **5**–**13**

Compound	$\pi_7/7a''$	$\pi_6/6a''$	n_N/a'	$\pi_5/5a''$	$\pi_4/4a''$	$\pi_3/3a''$	$n_S{}^+/a'$	$n_S{}^-/a'$	$\pi_2/2a''$	σ/a'	$\pi_1/1a''$
5	8.18	8.58	9.45sh	9.65	10.22	11.5sh	11.89	12.02	12.74	13.0	13.7
6	8.25	8.54	9.44	9.58	10.21	11.3sh	11.75	12.03	12.75	13.1	13.7
7	7.80	8.56	9.37	9.48	10.15	11.56	11.63	12.22	13.1	12.6	13.9
8	8.09	8.62	9.40sh	9.62	10.12	11.45	12.20	11.90	12.6	13.4	14.4
9	8.22	8.59	9.35sh	9.54	10.20	11.47	12.14	11.9	12.7	13.0	14.3
10	7.86	8.62	9.45sh	9.51	10.12	11.6sh	11.90	12.02	12.6	13.1	14.1
11	7.93	8.52	9.35sh	9.55	10.12	11.7sh	11.88	11.96	12.8	14.0	14.8
12	7.92	8.56	9.37	9.52	10.17	11.73	11.87	12.20	12.7	13.4	14.2
13	8.04	8.19	9.20sh	9.48	10.17	11.2sh	11.75	12.00	12.62	13.3	13.6

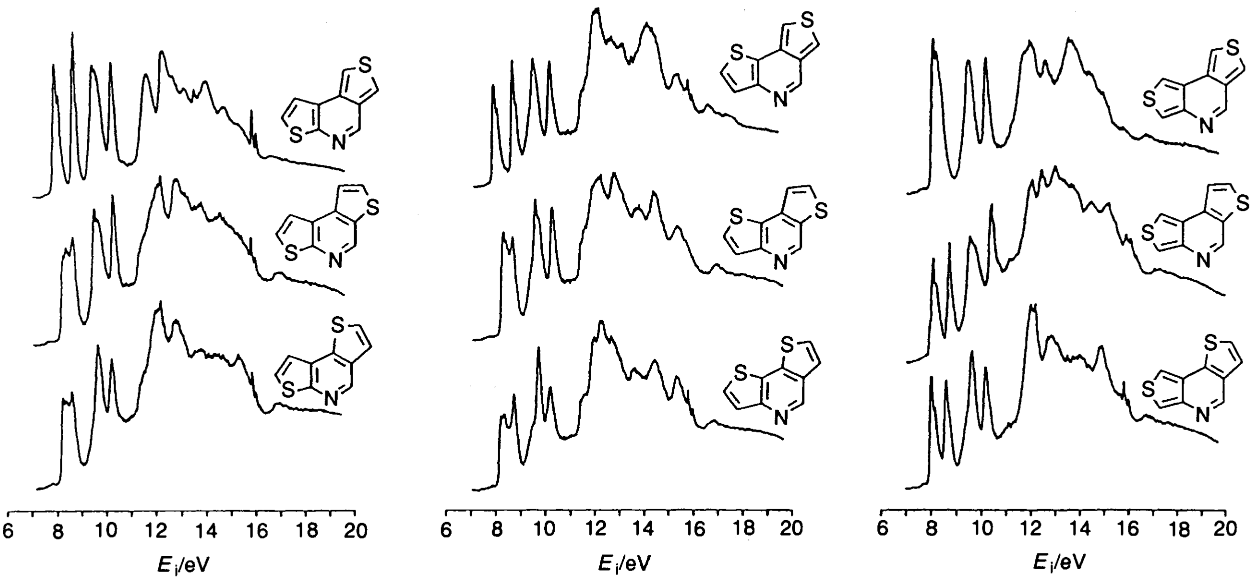


Fig. 2 PE spectra of compounds **5**–**13**

Table 5 Orbital energies $-\varepsilon_i^{SCF}$/eV of dithienopyridines **5–13** (PM3 results)

Compound	$\pi_7/7a''$	$\pi_6/6a''$	n_N/a'	$\pi_5/5a''$	$\pi_4/4a''$	$\pi_3/3a''$	n_S^+/a'	n_S^-/a'	$\pi_2/2a''$	σ/a'	$\pi_1/1a''$
5	9.11	9.17	10.44	10.30	10.98	12.37	12.28	12.46	13.57	13.53	15.27
6	9.06	9.18	10.46	10.53	10.75	12.20	12.28	12.42	13.60	13.46	15.26
7	8.94	9.18	10.35	10.24	10.38	12.34	12.13	12.59	13.66	13.59	15.11
8	9.02	9.33	10.44	10.15	11.15	12.30	12.55	12.26	13.53	13.34	15.28
9	9.04	9.22	10.47	10.37	10.96	12.34	12.41	12.33	13.56	13.40	15.26
10	8.93	9.23	10.30	10.15	10.95	12.29	12.30	12.53	13.63	13.49	15.12
11	9.02	9.20	10.28	10.11	10.98	12.30	12.44	12.38	13.63	13.47	15.12
12	9.03	9.14	10.32	10.12	10.85	12.33	12.28	12.50	13.66	13.43	15.10
13	9.05	9.12	10.28	10.29	10.83	12.34	12.28	12.55	13.68	13.58	15.04

Table 6 Enthalpies of formation $\Delta_f H$/kJ mol^{-1} of dithienopyridines **5–13**

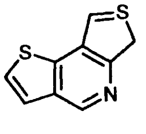
Compound	MNDO	AM1	PM3
5	241.41	296.45	313.53
6	242.57	297.46	312.24
7	277.83	315.87	336.27
8	243.25	303.49	313.05
9	243.91	304.67	313.32
10	279.02	322.61	337.15
11	280.65	323.68	337.16
12	281.66	324.55	335.77
13	290.71	333.06	339.40

caused by through-bond interactions,[12] while the two $n_S\sigma$ orbitals were found to be degenerated.

The PE spectrum of benzo[1,2-*c*:3,4-*c*]dithiophene (**4**) has already been published,[5b,13] and the E_i values compare well with ours. The two n_S orbitals (n_S^+ and n_S^-), which correspond to $n_S\sigma$ of compound **3**, differ in energy by 0.34 eV. The two $n_S\pi$ are now included into the aromatic π electron system and **4** has the same number of occupied π MOs as **1** and **2**. Furthermore, also the structures and energies of the π MOs of these molecules are rather similar. This is confirmed by the similarity of their PE spectra below *ca.* 11 eV. The π ionizations of **1**, **2** and **4** differ only by 0.3–0.7 eV. Substitution of two C=C double bonds in **1** by sulfur atoms leading to compound **4** causes destabilization of the π MOs of up to 0.5 eV.

The PE spectra of **5–13** are actually rather similar to each other, although they are clearly discernible. As a characteristic pattern, there are four usually sharp ionization bands in the low-energy region (< 11 eV). Only in the case of compound **13** are the first two E_i values so close together that they form a single band. In most spectra the third ionization band ($E_i \approx$ 9.4–9.6 eV) is either broader or has a shoulder on the low-energy side indicating overlap of two bands of similar energy. Since there are no fundamental differences between the results of the different semiempirical quantum chemical methods only the PM3 results are given for **5–13** in Table 6.*

Comparison with the spectrum of phenanthridine (**3**, Fig. 1) suggests that the n_N ionizations of **5–13** form a broad band of low intensity which is located close to that of the π_5 ionization. Therefore, we assign n_N and π_5 to the broad band at ≈9.5 eV. Because of the overlap of the first two ionizations in compound **13** it is difficult to determine the E_i(v) value of the second band precisely. Above 11 eV strong overlap of several bands usually occurs so that correct identification of E_i(v) values and assignments become difficult.



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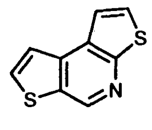

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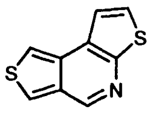

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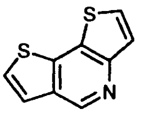

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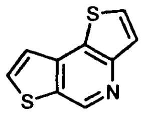

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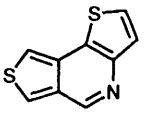

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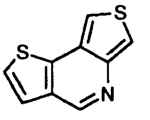

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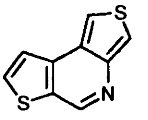

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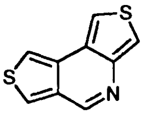

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In **5–13**, as in **1**, **2** and **4**, there are seven occupied π MOs and the heteroaromatic compounds have one lone-pair orbital per heteroatom (n_N or n_S). Also here we have a symmetric (n_S^+) and an antisymmetric (n_S^-) linear combination of the $n_S\sigma$ orbitals. The shapes of the π MOs of **5–13** are similar and the energy sequence of π and n orbitals is also largely the same.

According to the SD-model[5] the E_i of π electrons below *ca.* 11 eV of **5–13** should correspond to those of the parent molecules **1** and **2**. Relative to phenanthrene (**1**) most π MOs of **5–13** are stabilized; exceptions are the HOMOs of isomers with C^3–C^4 annellated thiophene rings (**7**, **10–13**) which remain nearly constant at 7.80–8.04 eV. For the MOs π_4–π_7 of the other isomers the energy differences amount to 0.2–0.4 eV (mean value 0.28 eV). While—relative to phenanthridine (**2**)—most π ionizations of **5–13** show little variation, the first E_i is lowered by up to 0.50 eV (mean value 0.27 eV) indicating sizeable destabilization of the HOMO.

The n_N orbital of **5–13** is stabilized relative to that of **2** by ≈0.2 eV and has a rather constant value close to 9.40 eV, independent of the mode of annellation. The only exception is compound **13** with an n_N ionization of 9.20 eV which is the same as in **2**. Comparison of the benzodithiophene **4** with the dithienopyridine of the same mode of annellation (**13**) indicates that the replacement of a CH group by an N atom induces stabilization of the π MOs by 0.36 eV and of the n_S orbitals by 0.1–0.2 eV.

In Fig. 3 a correlation diagram of the lower ionization potentials of **5–13** is shown. The spectra (Fig. 2) and Fig. 3 reveal a split of the first two bands as the most significant difference and it would be of great importance if this could be

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* Full lists of orbital energies (MNDO, AM1, PM3), vertical ionization energies and vibrational structure for compounds 3 and 5–13 have been deposited as supplementary data at the British Library, Sup. No. 57022 (11 pp.). For details of the British Library deposition scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

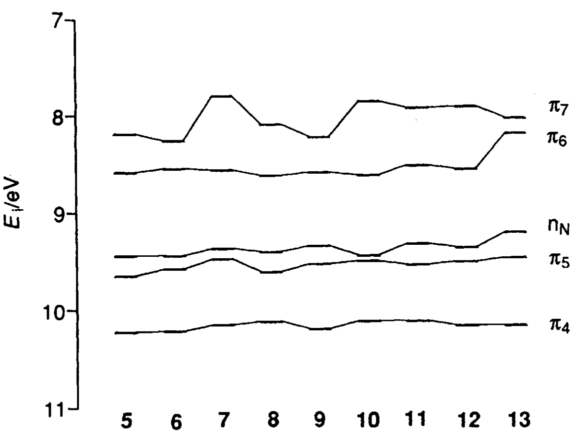

Fig. 3 Correlation diagram for ionization potentials of compounds **5–13**

used to distinguish the isomers. The E_i values differ by 0.15–0.76 eV with a mean value of 0.50 eV. The corresponding data of phenanthrene (**1**) and phenanthridine (**2**) are 0.40 and 0.07 eV, respectively. A closer inspection of the first two bands indicates that—with the exception of **13**—the E_i values of π_6 lie in rather a narrow range (8.57 ± 0.05 eV) while the first E_i values (π_7 = HOMO) vary to a larger degree (8.03 ± 0.23 eV). As has already been mentioned, low E_i values (*i.e.*, high-lying HOMOs) are found when thiophene rings are fused with the central pyridine molecule by their C^3–C^4 bond (isomers **7**, **10–13**). On the other hand, higher $E_i(1)$ values (*i.e.*, lower HOMOs) are observed for isomers with C^2–C^3 bond fusion of the thiophene (**5**, **6**, **8**, **9**).

In **13** the second E_i is found outside the above given range by 0.4 eV. The largest energy difference (0.76 eV) of the first two ionizations is observed for isomers **7** and **10** which structurally differ only in the annellation of one thiophene ring. Small splits (< 0.3 eV) are found for **6** and **13**. The latter compound is the third isomer to **7** and **10** having identical *d*-annellated thiophene rings.

Since the π electron energy contributes to the total energy of a molecule, the variation of the position of the π_7 MOs of **5–13** might be reflected in the relative stability of the isomers. That this is actually the case is revealed by the calculated enthalpies of formation (Table 6). The three methods used in this study lead to the same conclusion although the absolute values differ considerably. Only the PM3 results are mentioned in the following. The results fall into two groups: isomers **5**, **6**, **8** and **9** have values between 312.24 and 313.53 kJ mol^{-1} while for **7**, **10–13** values from 335.77 to 339.40 kJ mol^{-1} are obtained. This is the same grouping as detected for the $E_i(1)$ values (see above).

Correlation analysis indicates a rough linear correlation of $E_i(1)$ and $\Delta_f H$ values ($r = 0.86$, when compound **13** is omitted $r = 0.94$). As a result it can be stated that the four isomers in which all thiophene rings are fused by their C^2–C^3 bond to the pyridine nucleus have higher $E_i(1)$ values and are more stable than the other isomers where at least one thiophene ring shares its C^3–C^4 bond with pyridine. These findings are consistent with the expectation that the 'electron-rich' sulfur atoms should be as close as possible to the π electron-deficient pyridine ring. In accordance with this, isomer **13** is the least stable since both thiophene rings are fused by their C^3–C^4 bond. The unexpected or unusual behaviour of this isomer concerning the first two ionization potentials (see Fig. 3) is probably due to its more symmetrical, radialene-like structure with an aromatic perimeter of 10 π electrons.

Comparison of the $E_i(1)$ and $\Delta_f H$ results of isomer **6** with those of **5** and **7** or with **9** and **12** reveals that the rotation of the thiophene rings has a stronger effect in the *d* than in the *b* position of pyridine. There even seems to be a correlation with the reactivity in electrophilic substitution. Thiophene rings of the same mode of annellation are more reactive in the *b* than in the *d* position and a C^2–C^3 fused thiophene ring is more reactive than a C^3–C^4 fused ring.[2]

Favourable π electron delocalization is usually visualized by means of appropriate resonance structures. In the compounds studied here, this would mean structures with a positively charged sulfur and a negatively charged nitrogen atom. Since such formulae are possible for members of both groups of isomers having two or four bonds between S and N, the observed differences cannot be explained by this method.

Significant differences in the spectra are also perceptible in the region above 11 eV. But since here band overlap usually prevents the correct determination of E_i values and assignments, this part is of lower diagnostic value.

The quantum chemical calculations in most cases are consistent in the sequence of the π MOs of **5–13**. Only for **11–13** does the AM1 method exchange $\pi_7/7a''$ and $\pi_6/6a''$. For the n_N orbitals energy values that are generally too low are calculated. While PM3 always places $\pi_3/3a''$ between the two n_S orbitals, the AM1 method always finds $\pi_3/3a''$ below the n_S MOs. Deviations from Koopmans' theorem,[6] $E_i(i) = -\varepsilon_i$, of greater than 1 eV, are observed for all three methods. These are for MNDO n_N (1.6–1.8 eV), for AM1 n_N (1.1–1.4 eV) and $\pi_1/1a''$ (1.2–1.9 eV) and for PM3 $\pi_1/1a''$ (1.1–1.6 eV). However, the deviations for $\pi_1/1a''$ might indicate wrong assignments of the PE spectra, since the analysis of this region is rather difficult.

A correlation of calculated orbital energies and measured vertical ionization potentials for π and n orbitals of compounds **1–13** according to Koopmans' theorem[6] leads to a linear regression $E_i(i) = a(-\varepsilon_i) + b[\mathrm{eV}]$ with correlation coefficients $r = 0.959$ (MNDO), 0.957 (PM3) and 0.927 (AM1). As has already been mentioned, larger deviations between measured and calculated values occur only for the n_N orbitals. On the average, the ε_i values are too small by 0.95 (MNDO), 0.72 (AM1) and 0.18 eV (PM3). If these values are used to correct the ε_i values, the correlation coefficients become even better: $r = 0.992$ (MNDO), 0.988 (PM3) and 0.979 (AM1).[14] In order to identify the isomers **5–13** by their PE spectra, one would use the regression equations to calculate theoretical spectra, and then compare these with the observed E_i values. Unfortunately, in spite of the excellent correlations this is possible in an unambiguous manner in only a few cases. This may be due to failure of the Koopmans' theorem,[6] which actually is an approximation,[12] or—more likely—is a consequence of the inability of the semiempirical methods to recognize the differences in the electronic structures of the isomers with sufficient precision. Also for geometrical structure parameters we found that neither method could reproduce the experimentally observed variations.[14]

As mentioned above, the most significant differences in the PE spectra of **5–13** are observed in the relative position of the first two ionization bands and the question has been raised whether this could be used to identify the isomers. Since the calculated orbital energies reflect the observed ΔE_i values only to a limited degree, they are of little help. Making use of the SD model[5] and taking phenanthridine (**2**) as the reference molecule for **5–13**, large effects on the energies of π MOs are expected when the particular MO has large coefficients at the bond which is replaced by sulfur. However, in this way only a few of the data can be explained so that this idea was abandoned.

X-Ray Structure Analyses.—As outlined in the preceding section, the nine dithienopyridines (**5–13**) can be divided into two groups, depending on the mode of annellation. One member of each group was investigated by X-ray analysis.

Dithieno[3,2-b:3′,2′-d]*pyridine* (**9**).—**9** Crystallizes in the

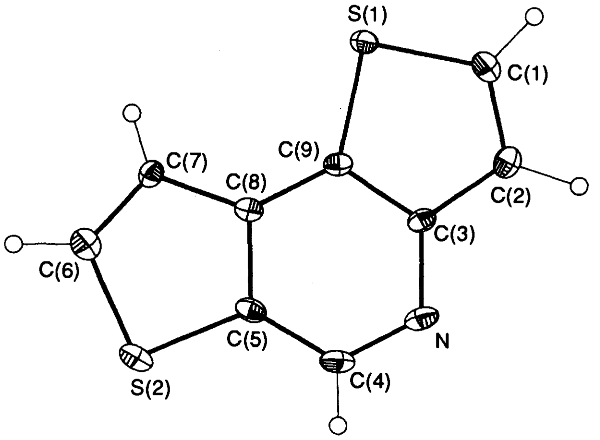

Fig. 4 Molecular structure of compound **9** with thermal ellipsoids for non-hydrogen atoms (50% probability)

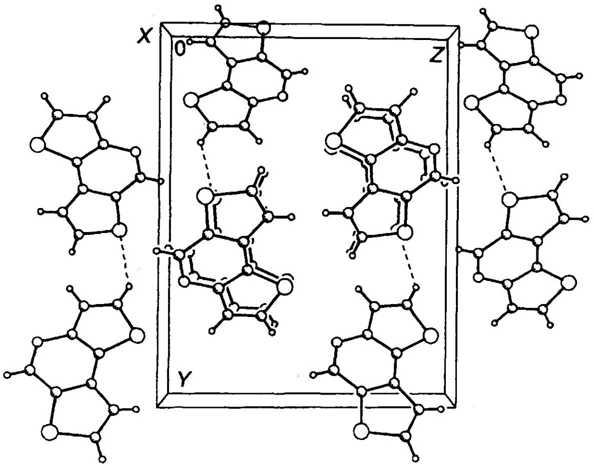

Fig. 5 View of **9** showing the crystal packing along the x axis

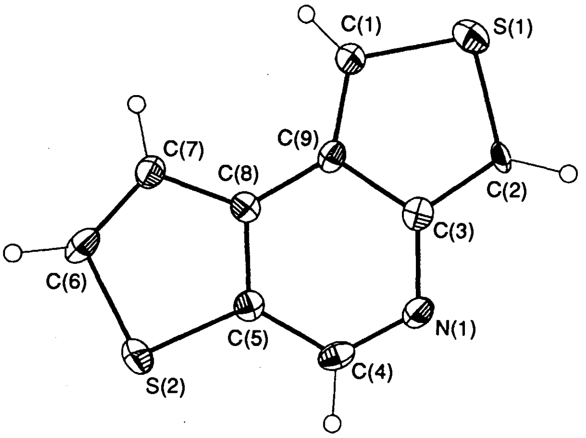

Fig. 6 Molecular structure of compound **12** (only molecule 1 is presented) with thermal ellipsoids for non-hydrogen atoms (50% probability)

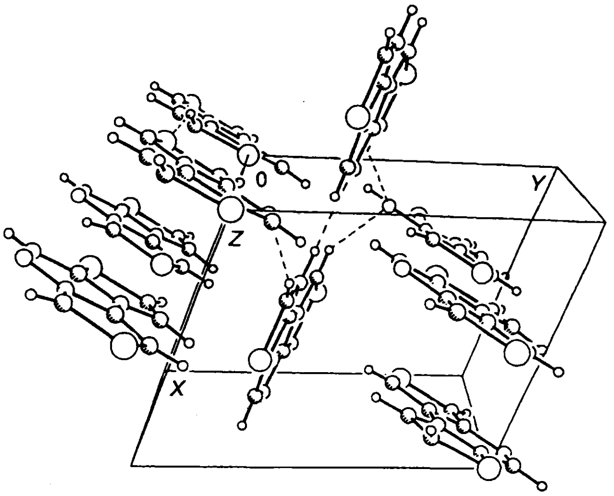

Fig. 7 View of **12** showing the crystal packing along the z axis

monoclinic space group $P2_1/n$ with four molecules in the unit cell and the molecular structure is shown in Fig. 4. The molecule is planar with a mean displacement from the plane of the C, N and S atoms of 2.6 pm. The C–C bonds of the central ring are of nearly equal length (140.5–141.1 pm), relative to pyridine[15] these bonds are increased by *ca.* 3 pm. The C–N bonds of **9** differ in length by 4.8 pm, the C^3–N bond is increased by 3.7 pm and the C^4–N bond is decreased by 1.1 pm relative to pyridine.[15] The two thiophene rings of **9** have essentially the same structure and the bond lengths show little variations relative to thiophene itself.[16] In **9** the CS bonds are longer by *ca.* 2 pm than in thiophene, the C–C bonds are either increased by *ca.* 1 pm (C^2–C^3, C^7–C^8) or compressed by *ca.* 2 pm (C^1–C^2, C^6–C^7).

The molecules form stacks along the x axis, which are stabilized in the xy plane by S • • • H contacts of 293.6 pm (Fig. 5).

Dithieno[3,4-b : 3′,2′-d]*pyridine* (**12**).—**12** Crystallizes in the triclinic space group $P1$. There are three independent molecules in the unit cell which is rather unusual. The molecular structure is depicted in Fig. 6.

The three independent molecules in the unit cell are essentially planar, mean displacements from the C, N, S planes being 0.95, 1.44 and 1.59 pm, respectively. The planes of molecules 1 and 3 are parallel to within 1.3° and their corresponding atoms are centred about the point [1.170(7), 1.329(13), 0.284(7)]. In addition, the plane of molecule 2 is approximately perpendicular to that of planes 1 and 3. These unusual features of the crystal structure suggest the presence of higher symmetry. However, detailed photographic studies have failed to reveal an alternative space group.

The pyridine rings are slightly more expanded than in **9**. The CN bonds have lengths between 130.0 and 139.0 pm (mean value 134.7 pm); on average they are 1.1 pm longer than in pyridine (133.6 pm).[15] However, because of the asymmetry of compound **12**, there is a short (average length 130.9 pm) and a long C–N bond (average length 138.5 pm). The difference of these bond lengths is even somewhat larger than in isomer **9**. The C–C bond lengths in the pyridine ring of **12** range from 137.6 to 145.1 pm. Also these values show that the pyridine ring in **12** is perturbed by the thiophene rings more than in **9**. This is a result of the different modes of fusion: while in **9** both thiophene rings are fused *via* C^2–C^3 bonds, in **12** a C^2–C^3 and a C^3–C^4 bond are used for annellation.

For the two thiophene rings different structures are found. The C^3–C^4-annellated ring has largely the same structure as its analogue in compound **9**, however the C^5–C^8 bond is 3.1 pm shorter and the C^6–C^7 bond is 3.7 pm longer than in **9** based on mean values for molecules 1 to 3 of **12**. On the other hand, the C^2–C^3-annellated thiophene ring has shortened C–S and lengthened C–C bonds close to the respective values in thiophene.[16]

In the crystal molecules form stacks along the x axis and layers between the stacks (Fig. 7). Within the stacks there are S • • • H contacts (287.8 pm) and within the layers and between layers and stacks there are N • • • H contacts (249–261 pm).

Conclusions

The different modes of fusion in the angular dithienopyridines **5**–**13** cause differences in their electronic structures and their stabilities which are reflected in their PE spectra and can be used for their analysis. The mode of annellation can be determined from the spectra and there is an excellent linear correlation of calculated orbital energies with the observed vertical ionization potentials. However, the individual isomers cannot be identified unambigously making use of this correlation.

The isomers can be divided in two groups, **5**, **6**, **8** and **9** with both sulfur atoms directly attached to the pyridine nucleus are more stable and have higher first ionization potentials than the other isomers (**7**, **10**–**13**) in which at least one sulfur atom is separated by a CH group from the central ring. Rotation of the *d*-annellated thiophene ring causes stronger variations of the first vertical ionization potential and the enthalpy of formation than rotation of the *b*-ring. In the first group of isomers, interactions between the electron-deficient pyridine ring and its electron-rich annellands are more effective than in the second group.

The molecular structures of the isomers **9** and **12**, which belong to different groups and differ only in the orientation of one thiophene ring, show clear differences especially in the bond lengths of the pyridine ring. While in **9** the C–C bonds in the six-membered ring show little variation, in **12** a clear tendency towards bond alternation is obvious. Annellation of a thiophene ring by its C^3–C^4 bond causes stronger perturbations of both the pyridine and the thiophene ring than fusion by its C^2–C^3 bond. Because of this, isomer **9** is more aromatic than **12**. Similar structural results are to be expected for the remaining members of each group.

Experimental

Phenanthrene (**1**) and phenanthridine (**2**) are commercially available. 1,3,6,8-Tetrahydrobenzo[1,2-*c*:3,4-*c*]dithiophene (**3**) was synthesized in two steps from 1,2,3,4-tetramethylbenzene[17] and dehydrogenated to the aromatic compound benzo[1,2-*c*:3,4-*c*]dithiophene (**4**).[18] The syntheses of the dithienopyridines **5**–**13** are described elsewhere.[3]

Photoelectron Spectroscopy.—The PE spectra were recorded at temperatures of *ca.* 60 °C (**3**, **4**), 100 °C (**2**) and 120 °C (**1**, **5**–**13**) in the region 6–20 eV using a Leybold–Heraeus UPG 200 spectrometer with HeI excitation (21.21 eV). The calibration of the energy scale was performed with an Ar-Xe mixture. The accuracy of the measurements was ± 0.02 eV for ionization potentials, for broad or overlapping signals it was only ± 0.1 eV.

MNDO[19] and PM3[20] calculations were performed with MOPAC 5.12[21] and AM1 calculations[22] with MOPAC 6.1.[23] All computations were carried out with full geometry optimization on an IBM 4381 R23 (VM/SP HPO Rel. 5, CMS Rel. 5.0 GCS Rel. 5).

Point groups were defined according to the rules described in ref. 24.

X-Ray Structure Analysis of **9**.*—*Crystal data.* $C_9H_5NS_2$, $M = 191.27$, $T = 104$ K. Monoclinic, $a = 443.5(1)$, $b = 1508.7(5)$, $c = 1190.6(4)$ pm, $\beta = 92.27(3)°$, $V = 796.0(5) \times 10^6$ pm^3 (by least-squares refinement on diffractometer angles for 50 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/n$ (No. 14), $Z = 4$, $D_x = 1.60$ g cm^{-3}. Pale yellow needles. Crystal dimensions: $0.50 \times 0.48 \times 0.21$ mm^3, μ(Mo-Kα) = 0.57 mm^{-1}.

Data collection and processing. Nicolet R 3m/V four-circle diffractometer, with Wyckoff-scan, $3 < 2\theta/\text{deg} < 60$, scan speed 1.0 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 1739 unique reflections measured giving 1659 with $F_o > 4\sigma(F_o)$.

Structure analysis and refinement. The co-ordinates of all non-hydrogen atoms were determined by direct methods and full-matrix refinement on F using the SHELXTL-PLUS program system[25] on a Micro Vax II computer. 129 parameters were refined. The positions of the hydrogen atoms were calculated on ideal geometry and refined as rigid groups (C–H distance 96 pm, H–C–H angle 109.5°). The isotropic temperature factors were given the 1.2 fold of the U_{ij} tensor of the corresponding C atom. The refinement converged to $R = 0.040$, $R_w = 0.052$, weighting scheme $w^{-1} = \sigma^2(F) + 17.1 \times 10^{-4}F^2$. Residual electron density max. 0.52, min. -0.38 e Å^{-3}.

X-Ray Structure Analysis of **12**.*—*Crystal data.* $C_9H_5NS_2$, $M = 191.27$, $T = 103$ K. Triclinic, $a = 728.9(1)$, $b = 922.2(1)$, $c = 979.2(1)$ pm, $\alpha = 100.67(1)$, $\beta = 102.16(1)$, $\gamma = 104.53(1)°$, $V = 602.8(3) \times 10^6$ pm^3 (by least-squares refinement on diffractometer angles for 49 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P1$ (No. 1), $Z = 3$, $D_x = 1.581$ g cm^{-3}. Pale yellow needles. Crystal dimensions: $0.11 \times 0.23 \times 0.43$ mm^3, μ(Mo-Kα) = 0.59 mm^{-1}.

Data collection and processing. Nicolet R 3m/V four-circle diffractometer, with Wyckoff-scan, $3 < 2\theta/\text{deg} < 50$, scan speed 0.8 deg min^{-1}, graphite-monochromated Mo-Kα radiation; 3923 unique reflections measured giving 3850 with $F_o > 4\sigma(F_o)$.

Structure analysis and refinement. 338 parameters were refined. The refinement converged to $R = 0.028$, $R_w = 0.033$, weighting scheme $w^{-1} = \sigma^2(F) + 4.0 \times 10^{-3}F^2$. Residual electron density max. 0.68, min. -0.52 e Å^{-3}.

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* Further details of the crystal structure investigations are available on request from the *Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH*, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-400101 (for **9**) and CSD-400102 (for **12**), the names of the authors and the journal citation. Tables of atomic coordinates, selected bond lengths and angles and equivalent isotropic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme, see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

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