INVESTIGATIONS OF CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING

XXI.* ELECTRONIC ABSORPTION AND FLUORESCENCE SPECTRA OF SOME CONDENSED THIOPHENE-CONTAINING SYSTEMS

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UDC 547.737:543.422.6'426

The electronic absorption and fluorescence spectra of a number of condensed heteroaromatic compounds containing a thiophene ring were studied. In connection with the fact that the theoretical treatment of the closeness of the electronic structure of thiophene and benzene molecules is based, in particular, on the similarity between the electronic absorption spectra of thiophene-containing systems and their polycyclic aromatic analogs, the spectra of the investigated compounds were compared with the corresponding polycyclic aromatic hydrocarbons. It was demonstrated that the differences introduced by the thiophene ring depend on the length of the chain of condensed benzene rings in the molecules of the thiophene-containing systems. The results can be used to analyze mixtures of such compounds.

Continuing our investigation of the chemical and physical properties of condensed heteroaromatic systems containing a thiophene ring, we have studied the electronic absorption spectra and, since many of the compounds fluoresce, the fluorescence spectra of solutions of 14 condensed thiophene-containing compounds (see Table 1), most of which we have obtained for the first time [2-4]. The quantum fluorescence yields were measured in some cases.

We note that the absorption spectra are known only for thiophene (I) [5], benzo[b]thiophene (II) [6], dibenzothiophene (III) [6], and benzo[b]naphtho[2,3-d]thiophene (IV) [7], while the fluorescence spectra are known for dibenzothiophene (III) [8] (in the crystalline state).

In contrast to thiophene (I), all of the investigated compounds, except for benzothienylanthraquinone (XV), fluoresce. The absorption and fluorescence spectra of solutions in dioxane and toluene of almost all of the compounds coincide. Exceptions to this are compounds bearing COOH and C=O functional groups (X-XII, XV), for which the spectra of solutions in cyclohexane were also measured.

The fluorescence intensity of solutions of the investigated compounds in dioxane exceeds the fluorescence intensity of solutions in toluene. In order to avoid the specific effect of the nature of the solvents, the fluorescence of toluene solutions was investigated.

Almost all of the compounds that we studied differ with respect to their spectra. A characteristic peculiarity of them is the presence of a vibrational structure in both the fluorescence spectra and in almost all of the absorption spectra. This facilitates identification of such compounds, and the results can be used to analyze mixtures of them.

The electronic spectra of polycyclic heteroaromatic compounds with a thiophene ring differ substantially from the spectra of thiophene (I) itself (Fig. 1). Commencing with benzo[b]thiophene (II), a vibrational

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*See [1] for communication XX.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 925-932, July, 1972. Original article submitted June 29, 1971.

TABLE 1. Electronic Absorption Spectra and Fluorescence Spectra of Some Condensed Heteroaromatic Compounds Containing a Thiophene Ring

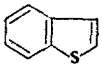
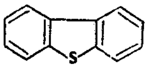
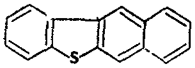
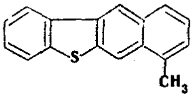
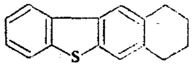
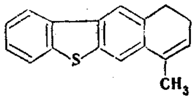
Comp. No.	Compound	Absorption, λ, nm*		Fluorescence, λ, nm
I	 †	H 235		—
II		D 250 260 265 280 290 298		Very weak
III		D 235 237 256 263 275 278 288 315 327	T 280 290 315 329	T 337 345
IV		D 230 245 265 278 283 295 303 315 330 356 373	T 304 317 332 356 373	T 382 397 420 shoulder D 380 390 415
V		D 232 248 265 278 285 318 332 357 375	T 319 334 358 375	T 382 397
VI		D 238 242 260 268 286 290 296 317 332	T 287 297 320 355	T 342 355 380 shoulder
VII		D 230 248 277 288 305 315 345	T 276 289 305 317 347	T 358 368

TABLE 1 (continued)

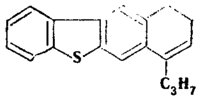
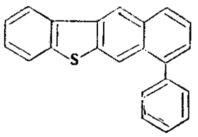
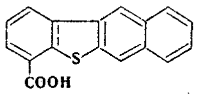
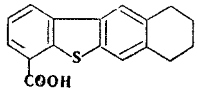
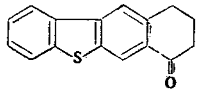
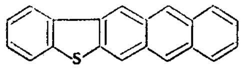
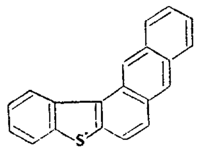
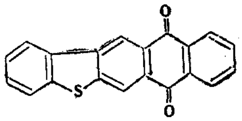
I	II	III		V	
VIII		D 248 278 286 305 317 348	T 290 308 318 348	T 355 367	
IX		D 238 255 268 280 286 shoulder 318 332 360 375	T 332 337 360 380	T 386 405	
X		C 233 248 258 275 284 310 320 333 345 365 384	T 284 292 330 357 396	T 427 450 shoulder	
XI		C 228 234 236 240 248 254 260 262 283 294 315 345 355	T 283 294 317 356	T 354	
XII		C 229 248 254 278 282 300 312 352 368	T 275 285 303 315 353 368	T 407 430	
XIII		D 250 295 345 365 389 415 440	T 348 367 388 415 442	D 442 470 502 550	T 445 473 505 545
XIV		D 223 250 258 275 285 297 340 358 368 375 385 400 405 440	T 358 367 375 385 400 405 shoulder 440	D 407 430 460	T 414 430 456

TABLE 1 (continued)

I	II	III		V
		C	T	
XV		223 230 250 255 258 265 295 305 325 388 405	310 403	Very weak

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[*] Solvents: hexane (H), dioxane (D), toluene (T), and cyclohexane (C).
[†] See [5].

structure, which is also observed in the fluorescence spectra, appears in these spectra, as already indicated. As usual, the absorption and fluorescence regions are shifted to the long-wave side as the number of condensed benzene rings in molecules of these compounds (II-IV, XIII) increases. However, replacement of the hydrogen atom by a phenyl group (IX) leads only to an insignificant bathochromic shift in the spectra. This is associated with the development of steric hindrance, because of which the phenyl group is oriented almost perpendicular to the plane of the condensed molecule. The introduction of an alkyl substituent into benzo[b]naphtho[2,3-d]thiophene (V) causes a small change in both the absorption spectra and fluorescence spectra. Replacement of one of the benzene rings in benzo[b]naphtho[2,3-d]thiophene (IV) by a cyclohexane ring (VI) induces a short-wave shift in the spectra, since the number of aromatic rings in the condensed system decreases in this case. However, when a benzene ring is replaced by a cyclohexene ring (VII, VIII), this shift is smaller. The presence of COOH and C = O functional groups in X-XII also induces a long-wave shift of the absorption and fluorescence region relative to benzo[b]naphtho[2,3-d]thiophene (IV), as was also observed for the corresponding aromatic analogs.

The optical characteristics of the isomeric anthrabenzothiophenes (XIII and XIV) differ. The absorption and fluorescence regions of anthra[2,1-b]benzo[d]thiophene (XIV) are shifted to the short-wave side as compared with anthra[2,3-d]benzo[d]thiophene (XIII).[*] The quantum yield of XIV is about 30% lower than that of XIII. They also differ with respect to the form of the absorption and fluorescence spectra (ratio of the band intensities). It is known [5,9] that this sort of difference in spectral properties is observed for "linear" and "angular" polycyclic aromatic hydrocarbons. A comparison of the spectra that we obtained for XIII and XIV with their molecular models confirms the previously drawn conclusion [2,3] regarding the structures of these isomeric anthrabenzothiophenes ("linear" structure XIII and "angular" structure XIV).

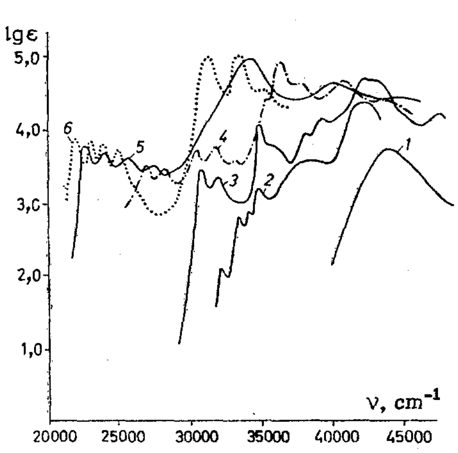

Fig. 1. Absorption spectra of solutions: 1) I; 2) II; 3) III; 4) IV; 5) XIII in dioxane; 6) XVII in benzene.

The presence of a C = O functional group in the benzothienylanthraquinone (XV) molecules induces a short-wave shift in the absorption spectra as compared with anthra[2,3-b]benzo[d]thiophene (XIII) and almost complete quenching of the fluorescence. This is apparently associated with rupture of the chain of conjugated double bonds in the polycyclic system and the quenching action of this group.

The quantum fluorescence yield increases as the number of condensed benzene rings in the molecule increases. The quantum yields for anthra[2,3-b]benzo[d]thiophene (XIII), benzo[b]naphtho[2,3-d]thiophene (IV, and dibenzothiophene (III) are, respectively,

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[*] The presence of a long-wave band at 440 nm in the absorption spectrum of XIV (see Table 1 and Fig. 4) is apparently due to contamination by XIII. Gas-liquid-chromatographic analysis demonstrated slight XIII contamination in XIV.

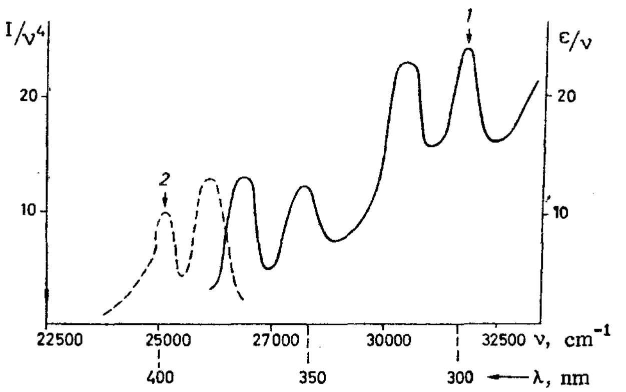


Fig. 2. Absorption (1) and fluorescence (2) spectra of a solution of IV in toluene.

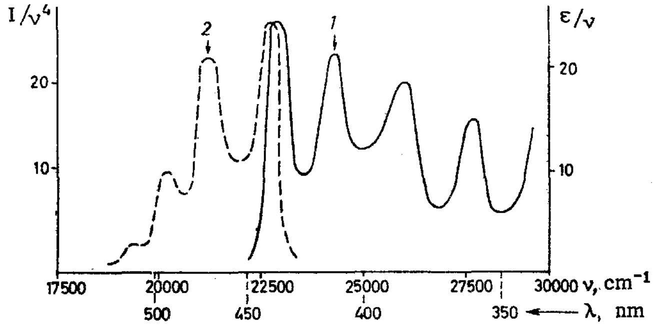


Fig. 3. Absorption (1) and fluorescence (2) spectra of XIII in toluene.

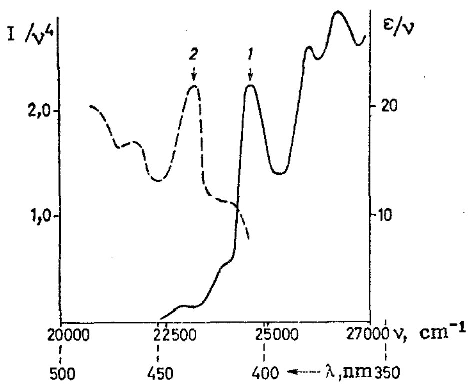


Fig. 4. Absorption (1) and fluorescence (2) spectra of XIV in toluene.

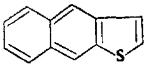
0.20, 0.02, and about 0.001. Benzo[b]thiophene (II) fluoresces very weakly. The quantum fluorescence yield of a benzene solution of anthracene in the presence of air oxygen is 0.10 [10]. We note that the quantum fluorescence yields decrease for polycyclic aromatic hydrocarbons as the number of condensed benzene rings increases, commencing with tetracene [9].

Mirror symmetry between the fluorescence spectra and the long-wave group of bands in the absorption spectra (Figs. 2-4) is observed for most of the compounds we investigated. Consequently, the nuclear configurations of these molecules do not change on transition from the ground to the excited state.

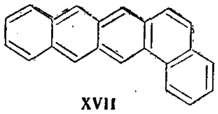
The theoretical treatment [11] of the closeness of the electronic structures of thiophene and benzene, upon which the idea of pd hybridization in the thiophene molecule was based, is based, in particular, on the closeness of several physical and chemical properties of thiophene compounds and their benzene analogs, including the electronic absorption spectra.

In [6, 12, 13] it was noted that the electronic absorption spectra of benzo[b]thiophene (II), dibenzothiophene (III), and benzo[b]naphtho[2,3-d]thiophene (IV) are close to the spectra of the corresponding isoelectronic, polycyclic, aromatic hydrocarbons but are shifted as compared with the latter to the short-wave region by 20-40 nm. However, this analogy reduces to rather general features. It should also be noted that different absorption spectra, for example, for dibenzothiophene (III) and naphthothiophene (XVI), are observed for condensed heteroaromatic compounds with the same number of rings but different positions of the thiophene ring in the chains. Of the compounds that we investigated, the absorption spectra of anthrabenzothiophene (XIII) and the isoelectronic isopentacene (XVII) [5] in the long-wave region are rather close.

Spectra in the long-wave region that are similar in form are also observed for tetracene [5], anthracene, and its substituted compounds [14]. However, they are considerably shifted to the shorter-wave side for anthracene and to the long-wave side for tetracene as compared with the spectra of XIII. This sort of correspondence in the spectra is not observed for the other compounds that we investigated, for example, dibenzothiophene (III) and the isoelectronic phenanthrene (or anthracene), benzo[b]naphtho[2,3-d]thiophene (IV), and 1,2-benzoanthracene.



XVI



XVII

On the basis of these results, it can be assumed that the best correspondence between the spectra of condensed heteroaromatic compounds containing a thiophene ring and their carbocyclic analogs should be observed for heteroaromatic compounds with a sufficiently extended chain of condensed benzene rings. In this case, the effect of the thiophene ring decreases, and the properties of the chain of condensed benzene rings that are peculiar to polycyclic aromatic hydrocarbons are manifested to a greater extent. This is also confirmed by the change in the absorption spectrum of benzothienylanthraquinone XV as compared with the spectrum of anthra[2,3-b]benzo[b]thiophene (XIII) and by the difference in the spectra of dibenzothiophene (III) and naphthothiophene (XVI). The absorption spectrum of XVI is considerably closer to the spectrum of anthracene than to that of III.

A gradual increase in the fluorescence quantum yields of solutions of aromatic hydrocarbons [15] is observed in the benzene–anthracene series. The quantum yields for the compounds investigated by us decrease very sharply on passing from XIII to IV and III. This decrease in the quantum yield is probably also associated with an increase in the quenching action of the thiophene ring as the length of the chain of condensed benzene rings in molecules of these compounds decreases.

Thus the presence of a thiophene ring in molecules of heteroaromatic polycyclic compounds leads to an appreciable change in the electronic absorption and fluorescence spectra as compared with their analogs – polycyclic aromatic hydrocarbons. These changes become sharper as the length of the chain of condensed benzene rings in the molecule decreases, since in this case the relative spacing of the $n\pi^*$ and $\pi\pi^*$ levels apparently changes [16].

EXPERIMENTAL

The absorption spectra were measured with a Unicam SP-700 spectrophotometer, and the fluorescence spectra were measured with an apparatus prepared in the laboratory and assembled from a mirror-diffraction monochromator with automatic recording. The fluorescence was excited by means of the radiation of a mercury lamp, from the luminous flux of which the lines at 365 and 313 nm were isolated. The apparatus was calibrated in relative energy units by means of a standard lamp. The fluorescence quantum yield was determined without removal of oxygen by the method in [17]. Dioxane, toluene, and, in individual cases, cyclohexane and heptane were used as the solvent. The solution concentrations were $\sim 10^{-3}$-10^{-5} M and $\sim 10^{-6}$ M. Reabsorption was taken into account in investigating the fluorescence spectra. The methods used to obtain the investigated compounds and their physical constants are presented in [1-4].

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