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structural formulas I-VI

Figure 1: structural formulas I-VI

Abstract

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ON THE PROBLEM OF THE MICROSTRUCTURE OF THIOPHENE

AND THE GENETICS OF SPECTRA

(Presented by Academician M. I. Kabachnik on 29 VI 1964)

The genetics of the spectra of 3-nitro-5-acetyl-2-aminothiophene ($HATNH_2$) ($I, B^1 = CH_3CO$), 3,5-dinitro-2-aminothiophene ($DHTNH_2$) ($I, B^1 = NO_2$), and their N-substituted derivatives (II, III) has been established by comparison with the spectra of the corresponding benzene derivatives: 2-nitro-4-acetyl-aniline ($HAFNH_2$) ($IV, B^1 = CH_3CO$), 2,4-dinitro-aniline ($IV, B^1 = NO_2$), and their N-substituted derivatives (V, VI). Applying, for the analysis of structural effects, the principle of decomposition of the molecular structure into polar chromophoric systems (^{1,2}), we attempted to assign individual $\lambda_{\max}$ values to definite auxochromophoric systems (^{2}):
B^1KA^1, B^2KA^1, B^2K, KA^1 ($B^1 = NO_2,\ CH_3CO$; $B^2 = NO_2$; K is the benzene or thiophene nucleus *a*; $\Phi = n$-C_6H_4 nucleus *b*; $A^1 = NH_2,\ NMe_2$; in III and VI $A^1 = NH$, $A^2 = H,\ OCH_3,\ NH_2,\ NHCOCH_3,\ NMe_2$).

In the spectrum of 2,4-dinitroaniline (No. 4)*, Fig. 1, bands of two chromophoric systems (^{2}) were found: the para-system B^1KA^1 (n-$NO_2\ NH_2$), the 2_a-band** ($\lambda_{\max}$335 mμ), and the ortho-system B^2KA^1 (o-$O_2N\ NH_2$) (three absorption bands (^{3}), No. 2, Table 1). In the spectrum of 2-nitro-4-acetyl-aniline (No. 3) we find four absorption bands of the same systems. The intense band $\lambda_{\max}$300 mμ belongs to the 2_a-band of the para-system B^1KA^1 (n-$CH_3CO\ NH_2$) (band 2_a^1, corresponding to x^1 (^{4}), is overlapped). All three absorption bands of the ortho-system B^2KA^1 (o-$O_2N\ NH_2$) appear: the 1_a-band of the whole conjugated system B^2KA^1, $\lambda_{\max}$395 mμ; the 2_a-band of the B^2K system (ΦNO_2), $\lambda_{\max}$265 mμ; and the 2_a-band of the KA^1 system (ΦNH_2), $\lambda_{\max}$227 mμ, in agreement with (^{3}). Replacement of the strong electron-acceptor NO_2 by the weaker CH_3CO group does not affect the character of the spectral curve: in No. 3 the types of characteristic chromophoric components contained in molecule No. 4 are retained (see

Table 1).

The spectra of 3-nitro-5-acetyl-4-aminothiophene (HATNH_2, No. 5) and 3,5-dinitro-2-aminothiophene (DHTNH_2, No. 6) (5) proved to be very close to the spectra of their benzene analogues, Nos. 3, 4, Fig. 1, both in the character of the spectral curves and in the number of bands. This allows us, in the spectra (I), the intense

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* The numbers of the compounds in Figs. 1–3 correspond to the numbers in Table 1.

** In benzene derivatives we regard the 1_a-band as a shifted benzene 1-band, $\lambda_{\max}$254; the 2_a-band as a shifted benzene 2-band, $\lambda_{\max}$203.5. The prefixes *a* and *b*, added to the designation of the band type, indicate belonging to nucleus *a* or *b*.

Table 1

Absorption spectra in 95% ethanol, $C \cdot 10^{-4}$*

Abbreviations shown in the table:
NA = CH_3CO-substituted nitrophenyl derivative; NAT = CH_3CO-substituted nitrothienyl derivative; DN = O_2N-substituted nitrophenyl derivative; DNT = O_2N-substituted nitrothienyl derivative; Φ = C_6H_4 or C_6H_5.

No.	Compound	Para system of nucleus a (B^1KA^1), 2_a-band, λ	Para system of nucleus a (B^1KA^1), 2_a-band, ε	Para system of nucleus a, 2_a^1-band (*), λ	Para system of nucleus a, 2_a^1-band (*), ε	Ortho system of nucleus a (B^2KA^1), 1_a-band B^2KA^1, λ	Ortho system of nucleus a, 1_a-band B^2KA^1, ε	Ortho system of nucleus a, 2_a-band B^2K, λ	Ortho system of nucleus a, 2_a-band B^2K, ε	Ortho system of nucleus a, 2_a-band A^1K, λ	Ortho system of nucleus a, 2_a-band A^1K, ε	System of nucleus b, A^1 A^2, NH A^2, 2_b-band A^1 A^2, λ	System of nucleus b, A^1 A^2, NH A^2, 2_b-band A^1 A^2, ε	m.p., °C (analyses see (12))
1	n-CH_3CO NH_2 (4)	317	20 100	233	6750									
2	o-O_2N H_2 (3)			overlap		403	5 300	276	4 900	231	16 600			
3	NA NH_2	310	19 880	overlap		395	5 295	265	15 000	227	9 000			153 – 154°
4	DN NH_2 (2)	335	13 900	overlap		~ 375	~ 7000	257	9 160	225	9 900			

No.	Compound	Para system of nucleus a (B^1KA^1), 2_a-band, λ	Para system of nucleus a (B^1KA^1), 2_a-band, ε	Para system of nucleus a, 2^1_a-band (*), λ	Para system of nucleus a, 2^1_a-band (*), ε	Ortho system of nucleus a (B^2KA^1), 1_a-band B^2KA^2, λ	Ortho system of nucleus a, 1_a-band B^2KA^2, ε	Ortho system of nucleus a, 2_a-band, B^2K, λ	Ortho system of nucleus a, 2_a-band, B^2K, ε	Ortho system of nucleus a, 2_a-band A^1K, λ	Ortho system of nucleus a, 2_a-band A^1K, ε	System of nucleus b, A^1 A^2, NH A^2, 2_b-band A^1 A^2, λ	System of nucleus b, A^1 A^2, NH A^2, 2_b-band A^1 A^2, ε	m.p., °C (analyses see (12))
5	NAT NH_2 (5)	322	14 480	overlap		375	11 690	262	8 280	245	10 019			227–228°
6	DNT NH_2 (5)	~ 323	~ 14000	overlap		~ 375	~ 11500	~ 270	~ 8000	~ 243	~ 10000			
7	DN NMe_2 (2)	367	• 16 300	220	13 000									
8	NAT NMe_2	342	17 480	255	4 710	~ 375	~ 7500					230	12 090	150–151°
9	NA NH	310	18 750	overlap		407	5 750	270	12 700	overlap				109.5–110.5°
10	NAT NH (5)	342	1 748	overlap		~ 395	~ 11190	265	7 220	overlap		232	11 890	
11	DN NH (2)	352	18 000	overlap		~ 385	~ 11600	overlap		232	14 200	257	11 200	
12	DNT NH (5)	400	16 570	overlap		~ 420	~ 14000	overlap		~ 225	~ 10680	247	12 730	
13	NAT NH OCH_3	342	15 230	overlap		~ 385	~ 12480	~ 265	~ 7190	overlap		232	12 870	163.5–164.5°
14	DNT NH OCH_3	407	17 200	overlap		overlap		overlap		230	16 280	250	12 140	163.6–163.9° (decomp.)
15	NA NH $NHCOCH_3$	315	19 650	overlap		407	6 310	overlap		overlap		250	18 900	206.5–207.5°

No.	Compound	Para system of nucleus a (B^1KA^1), 2_a-band, λ	Para system of nucleus a (B^1KA^1), 2_a-band, ε	Para system of nucleus a, 2^1_a-band (*), λ	Para system of nucleus a, 2^1_a-band (*), ε	Ortho system of nucleus a (B^2KA^1), 1_a-band B^2KA^1, λ	Ortho system of nucleus a, 1_a-band B^2KA^1, ε	Ortho system of nucleus a, 2_a-band B^2K, λ	Ortho system of nucleus a, 2_a-band B^2K, ε	Ortho system of nucleus a, 2_a-band A^1K, λ	Ortho system of nucleus a, 2_a-band A^1K, ε	System of nucleus b, A^1A^2NH A^2, 2_b-band A^1A^2, λ	System of nucleus b, A^1A^2NH A^2, 2_b-band A^1A^2, ε	m.p., °C (analyses, see (12))
16	NATNH NHCOCH$_3$	352	17 520	overlap		overlap		overlap		overlap		245	21 810	242 – 243° (decomp.)
17	NA NH NH$_2$	312	17 580	overlap		412	6 170	overlap		overlap		247	16 220	162.5 – 163.5°
18	NATNH NH$_2$	365	13 670	overlap		overlap		overlap		overlap		247	18 170	209 – 210° (decomp.)
19	NATNH NMe$_2$	375	14 080	overlap		overlap		overlap		overlap		262	22 230	191 – 191.5° (decomp.)
20	DN NH NMe$_2$ (2)	365	12 340	overlap		overlap		overlap		overlap		260	21 000	
21	DNTNH NHCOCH$_3$	402	18 020	overlap		overlap		overlap		overlap		247	20 190	254 – 254.5° (expl.)

* The melting point is given only for undescribed compounds. Values marked with ∞ were determined approximately from the curve (inflection).

bands λ_{max} 322–323 mμ as the 2_a-bands* of the "para-systems" B^1KA^1 (5-CH_3CO-2-NH_2-thiophene (No. 5) and 5-NO_2-2-NH_2-thiophene (No. 6)), analogous to the 2_a-bands of the benzene para-systems $B^1KA^1_B$ (IV). As in the case of benzene derivatives (IV), the 2^1_a-bands of these systems in (I) are overlapped. The ortho-systems in (I) B^2KA^1 (3-NO_2-2NH_2-thiophene) appear in Nos. 5 and

Fig. 1

Figure 2: Fig. 1

6 as three bands of three quasi-autonomous systems: the 1-band of the entire conjugated system B^2KA^1, λ_{max} 375 mμ; the 2_a-band of the partial system B^2K (3-NO_2-thiophene), λ_{max} 262-270 mμ, and the 2_a-band of the partial system KA^1 (2-NH_2-thiophene), λ_{max} 245-242 mμ (Fig. 1, Table 1). In the amines of the thiophene series, as in the amines of the benzene series, replacement of the NO_2 group by CH_3CO does not change the general character of the spectrum.

Fig. 1

The similarity in the general character of the spectra of derivatives with benzene and thiophene nuclei in the presence of identical chromophoric components is a consequence of a certain analogy in their electronic structures. However, this analogy applies only to the structure of para-systems of the type B^1KA^1, having the structure $B^1{-}C{=}C{-}C{=}C{-}NR_2$ (IV, V and I, II). In the microstructure of thiophene there is no such equalization of the lengths and orders of the bonds, no such symmetry and equivalence of angles, as in benzene. Geometrical data**, obtained by the electron-diffraction method ([8]) and by the molecular-orbital method ([6]), clearly indicate the possibility that a butadiene quasi-autonomous chromophoric system is manifested in the microstructure and in the spectrum of thiophene derivatives (I, II).

We see confirmation of this conclusion in the differences found by us in the spectra of $HATNH_2$ No. 5 and $DHTNH_2$ No. 6 (I, II) for the 1_a-bands of the ortho-system B^2KA^1 ($O_2N{-}C{=}C{-}NH_2$). In contrast to (IV, V) $HAFNH_2$ No. 3 and $DHFNH_2$ No. 4, ε_{max} of the 1_a-band in the thiophene derivatives is approximately twice as large as in the benzene derivatives (Table 1, Fig. 1). Whether we regard the 1_a-band of the B^2KA^1 system as the band of an electronic transition polarized along the C=C bond toward the NO_2 group ([9]), or as a charge-transfer band from the NH_2 orbital to the NO_2-group orbital ([10]), the increase in ε_{max} is a consequence of the shift of the bond order of $C_2 \dots C_3$ in (I, II) toward that of a double bond, with enhancement of its polarization under the influence of the S atom. The internuclear distances in the thiophene molecule are $C_2 \dots C_3$ 1.35 Å; $C_3 \dots C_4$ 1.44 Å; $S \dots C_2$ 1.74 Å.

Differences in the microstructure and valence angles in thiophene and benzene are also manifested in the different influence of replacement of NH_2 by the NMe_2 group. In the spectrum of $DHFNMe_2$, the bands of the *o*-system B^2KA^1 disappear completely, and only the 2_a-band of the *n*-system B^1KA^1 appears (No. 7, Table 1) ([2]). This was explained by the establishment of coplanarity of NMe_2 and the complete withdrawal of *o*-NO_2 from conjugation. In the spectrum of $HATNMe_2$ (No. 8), however, in addition to the 2_a-band at 342 mμ of the *n*-system B^1KA^1 5-$CH_3CO{-}C{=}C{-}C{=}C{-}NMe_2$-2, there is present the 1_a-band

* Taking into account that the electronic structure of thiophene is intermediate

Fig. 2

Figure 3: Fig. 2

between benzene and butadiene, but closer to that of benzene (^{6}), it may be assumed that the thiophene bands at 220–260 mμ and 200–220 mμ correspond to the benzene bands at 254 and 203.5 mμ (^{7}).

** Bond lengths in thiophene, butadiene, and cyclopentadiene: for C=C, 1.35, 1.37, 1.35 Å; for C—C, 1.44, 1.47, 1.46 Å.

of the o-system B^2KA^1 (3-$NO_2-C{=}C-NMe_2-2$), $\lambda_{\max}\sim 375$ mμ. This is a consequence of the incomplete removal of 3-NO_2 from coplanarity and conjugation with the thiophene nucleus, owing to the fact that the valence angle in thiophene between the bonds to the NO_2 and NMe_2 groups is $67°30'$ greater than in benzene ($60°$).

Fig. 2

The study of the effect of replacing NH_2 groups by $NH\Phi$ and $NH\Phi A^2$ showed that, upon phenylation of the NH_2 group in amines of the thiophene series (III) and the benzene series (VI), a complete analogy is observed in the spectral changes. We are dealing with compounds of the $BKQKA$ type, having two chromophoric systems, nucleus a and nucleus b, separated by the group $Q = NH$ (BKNHKA). A single conjugated system involving the p-electrons of NH with a single excitation vector along the π-system is absent. There are bands of the para- and ortho-chromophoric systems of nucleus a and a band of the system of nucleus b, $A^1\Phi A^2$ ($NH\Phi$, $NH\Phi A^2$) (Table 1, Figs. 2 and 3). The interaction of the chromophoric systems of nuclei a and b occurs as in inductively interacting systems (^{2,11}), with NH entering into conjugation with nucleus a and with nucleus b. Increased polarization of nucleus b under the influence of A^2 creates a charge δ^- on the n-C atom of nucleus b, which inductively increases the charge $\Delta+$ on NH and enhances the electronic displacements in the system of nucleus a, as in (^{2,11}).

In the spectra, in addition to the 2_a-band of nucleus a, the 2_b-band $A^1\Phi A^2$ appears clearly, with the largest $\varepsilon_{\max}$ in the case $A^2 = NHCOCH_3, NMe_2$ (Nos. 19, 21, Fig. 3). In contrast to No. 7, the spectra of compounds Nos. 9, 15, 17 contain a 1_a-band (Nos. 9, 17, Figs. 2, 3). This is a consequence of the lower energy of conjugation of 4-CH_3CO with NH through the benzene nucleus than in the case of the 4-NO_2NH-system.

In the spectra of the N-phenyl derivatives DNTH$_2$, Nos. 12, 14, 21 (Figs. 2, 3), a low-intensity band was found in the region 535 mμ, $\lambda_{\max}\sim 1920$. Its origin is unclear. It may be associated with intermolecular interaction or with tautomerism. The latter may be the cause of the fine structure of the long-wavelength bands $\sim$ 350—450 mμ of thiophene compounds Nos. 13, 14, 19, 21.

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