ELECTRONIC AND VIBRATIONAL SPECTRA OF CHALCONE ANALOGS DERIVED FROM 4- AND 5-NITROPYRROLES

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The electronic absorption spectra of ten chalcone analogs derived from 4- and 5-nitropyrroles have been measured in solution in ethanol, dioxane, concentrated sulfuric acid, and 20% ethanolic caustic potash and interpreted. The IR spectra of these compounds and also of 4- and 5-nitro-2-acetylpyrroles and 5-nitropyrrole-2-aldehyde have been measured in the 3700–500 cm^{-1} region, an assignment of frequencies has been carried out, and considerations have been put forward on the connection between the characteristic features of the absorption and the chemical structure.

In a preceding paper, we described the synthesis of chalcone analogs containing a 4- or 5-nitropyrrol-2-yl radical [1]. It appeared of interest to study their electronic and IR spectra. Literature information on spectral investigations of nitropyrroles is fairly limited in spite of the fact that some of them possesss biological activity [2, 3]. Among them we may mention investigations [4, 5] in which the UV spectra of the nitropyrroles were studied in connection with the phenomenon of tautomerism, and some others [6, 7]. The IR spectra of the nitropyrroles have been studied even less [7].

We have measured the absorption spectra in the UV and visible regions in solutions in ethanol, dioxane, concentrated sulfuric acid, and 20% ethanolic caustic potash of the isomeric 1-(5(4)-nitropyrrol-2-yl)-3-R-propenones with the carbonyl group in various positions in the conjugated chain, where R = phenyl (I–III), 4-anisyl (IV–VI), 4-nitrophenyl (VII–IX) and pyrrol-2-yl (X) (Table 1, Fig. 1). The IR spectra of these compounds and also of 5-nitropyrrole-2-aldehyde (XI) and of 4- and 5-nitro-2-acetylpyrroles (XII, XIII) were recorded in the solid phase (potassium bromide tablets) and, for the ketones I and III, also in carbon tetrachloride solution (Table 2, Fig. 2).

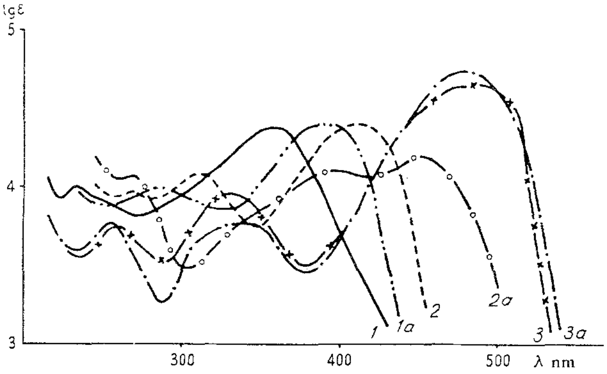


Fig. 1. Absorption curves of the ketones II and III, respectively, in: 1, 1a) ethanol, 2, 2a) 20% ethanolic caustic potash; 3, 3a) 95% sulfuric acid.

In neutral solvents, in the UV the compounds investigated generally have two well-defined strong absorption bands at 230–285 and 320–420 nm. In strong acid and alkaline media another band of longer wavelength is found, which is due to the absorption of the corresponding conjugated cation or anion. In view of its high intensity and its relation to the solvents, the long-wave absorption must be ascribed to π → π* electronic transitions in the main chromophore—the main chain of conjugation. In the shortwave region appears the quasi-autonomy of the individual chromophores—the aromatic and heterocyclic systems, and also the nitro group, which, as is well known, absorbs at about 270 nm [8]. The latter evidently appears best when two nitro groups are present at the ends of the molecule as, for example, in compounds VIII and IX.

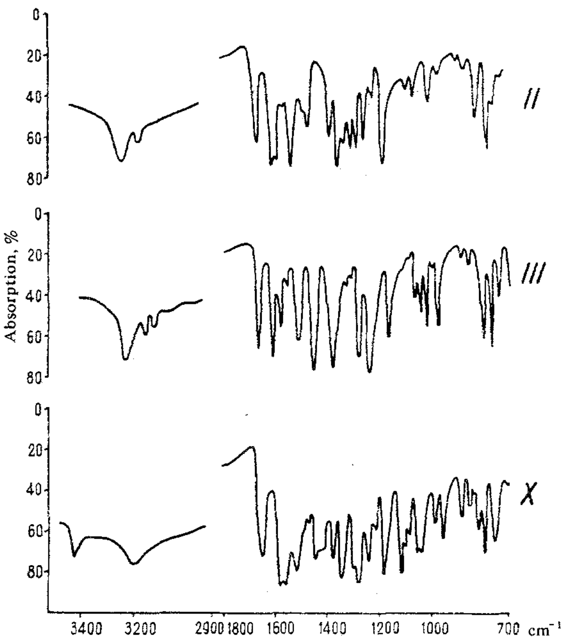
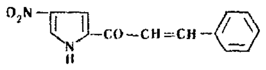
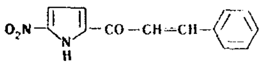
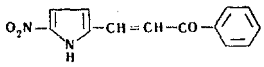
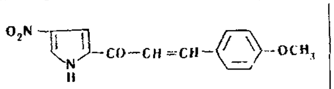
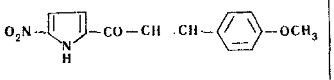
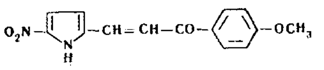
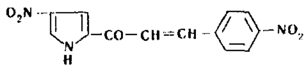
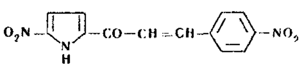
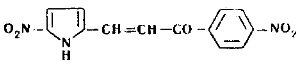
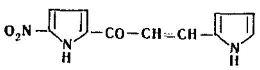


Fig. 2. IR spectra of the ketones II, III, and X.

In solutions in ethanol and dioxane, I–X may form hydrogen bonds with the solvent in which the hydrogen of the imino group (ethanol, dioxane) and of the carbonyl group (ethanol) take part. The formation of intermolecular polymeric associates of I–X at the concentrations at which the spectrophotometric measurements were carried out (10^{-5} M) must be excluded. The spectral curves in ethanol and dioxane are almost identical, but in the majority of cases the absorption maxima of the ethanolic solutions are shifted somewhat (2–6 nm) in the red direction. Thus, the difference in the types of hydrogen bonds in this case levels out.

Table 1

Spectral Characteristics of the Chalcone Analogs I–X in the UV and Visible Regions

Compound	Formula	λ_{max}, nm/ε						
		ethanol		dioxane	conc H_2SO_4		20% ethanolic solution of KOH	
I		230/12480 325/27860	340*	255/10340 323/28080	255/10960; 335/10650; 463/57410	415**	313/19400 393/20800	380*
II		232/9738 360/24140		354/31450	255/6300; 337/6130; 480/54000		270/9150; 312/13000 410/25100	
III		288/9488 390/26100	391*	285/9018 386/28500	260/5882; 330/9100 493/44810	473**	268/11600; 398/13000 450/15300	460*
IV		245/15000 355/27280	357*	243/15050 350/28330	265/11800; 345/11280 480/76340	462**	333/25200 395/24800	380*
V		247/9333 377/27330		245/10550 372/35080	270/7506; 350/7949 505/55200		272/14900 410/25100	
VI		323/13700 392/30100	392*	320/13000 386/30100	365/12150 495/43100	500**	270/18000; 405/13400 453/19000	455*
VII		322/23270	353*	323/22230	327/11520 424/38460	403**	—	—
VIII		245/11790 277/13320 333/12020		242/12390 275/11090 333/14610	317/5420; 345/5580; 443/36670		—	—
IX		270/16200 396/28160	417*	273/15910 392/25150	311/12280 490/46790	470**	—	—
X		260/6200 330/10850 421/30900	388*	268/3893 328/9408 424/24650	255/5715; 347/6767; 523/60150	477**	391/17300 457/23800	—

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*λ_{max} of the ketones without a nitro group in the pyrrole nucleus.

**λ_{max} of the ketones in a 30% solution of sulfuric acid in glacial acetic acid.

Table 2

Characteristic Frequencies of Compounds I–XIII (IR Spectra)

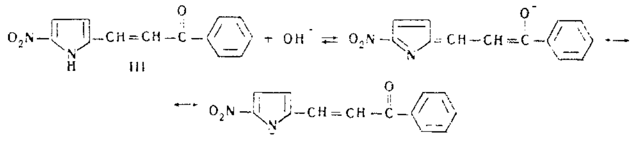
Compound	ν_{NH}	ν_{CH}	$\nu_{C=O}$	$\nu_{C=C}$	ν for the pyrrole ring			$\gamma_{CH=CH}$	ν_{NO_2}		β_{N-H}	β_{C-H}
									ν_{as}	ν_s		
I	3300—3220	3138	1667	1609	1565	1460	1397	981	1505	1352	1150	1050
II	3200	3150; 3138	1665	1600	1550	1455	1375	987	1525	1340	1170	1052
III	3215	3130; 3110	1665	1610	1582	1460	1380	978	1515	1280	1167	1052
IV	3170	3130	1640	1580	1565	1470	1413	984	1512	1360	1152	1055
V	3200	3142	1663	1590	1575	1460	1372	995	1520	1345	1170	1050
VI	3210	3124; 3108	1670	1615	1585	1465	1400	980	1515	1285	1185	1047
VII	3200	3136; 3118	1670	1603	1565	1470	1410	980	1512	1350	1155	1050
VIII	3210	3134; 3122	1675	1612	1566	1480	1374	992	1522	1348; 1322	1176	1060
IX	3265	3141; 3115	1668	1590	—	1466	1378	985	1532	1360; 1330	1164	1040
X	3410; 3180—3160	—	1640	1563	1555	1470	1360	980	1505	1335	1173	1050
XI	3190—3145	—	1690	—	1560	1476	1372	—	1530	1350; 1285	1156	1058
XII	3230	3130	1657	—	1557	—	1392	—	1495	1322	1175	1078
XIII	3240	3134; 3112	1685	—	1560	1478	1382	—	1520	1305	1205	1058

We have previously [9, 10] studied the electronic spectra of otherwise analogous ketones containing no nitro groups in the pyrrole ring. The comparison of the spectra made shows that the introduction of a nitro group into position 5 of a pyrrole nucleus adjacent to the carbonyl group for ketones in the molecule of which there is a donor radical (II, V, X) causes a considerable bathochromic effect (20–33 nm). Conversely, the introduction of a nitro group in position 4 (I, IV, VII) always leads to a blue shift of the absorption maximum of the long-wave band (by 2–31 nm). Where the pyrrole chalcone contains an electron-accepting radical (4-nitrophenyl, VII–IX), then, regardless of the position of the carbonyl in the conjugated chain, on the introduction of a nitro group (in position 4 or 5) a blue-shift is observed (by 20–31 nm). The latter fact is in agreement with the rule found previously in a study of the spectra of furan chalcones [11] and thiophene chalcones [12] that the introduction of a second nitro group into the distal end of a chalcone molecule either has no effect on λ_{max} or, more frequently, causes a hypsochromic shift. It is true that this blue shift is particularly large for the pyrrole ketones. It is interesting that a nitro group in the pyrrole nucleus remote from the carbonyl group has no appreciable influence on the UV spectrum (III, VI).

In addition to this, if we consider how the replacement of one of the phenyls in chalcone (λ_{max} in ethanol 312 nm) by a 4- or 5-nitropyrrol-2-yl group affects the long-wave absorption, it can be seen that the red shift increases sharply in the sequence I > II > III. It is natural that a nitro group in position 4 of the pyrrolyl group has a smaller influence on the spectrum, since this position in five-membered heterocycles is equivalent to a meta position of compounds of the benzene series, where the conjugation effect is absent.

All the ketones studied possess halochromic properties. The introduction of a nitro group into them lowers their basicity, on the one hand, and considerably increases their resistance to the aggressive action of mineral acids, on the other hand. Thus, while the ordinary pyrrole chalcones very rapidly resinify in concentrated sulfuric acid and the position of λ_{max} can be recorded only qualitatively in self-recording spectrophotometers, compounds I–X are completely stable for 2–3 hr. In a 30% solution of sulfuric acid in glacial acetic acid, in which the pyrrole ketones without nitro groups were studied [10], the halochromism is not shown because of the low basicity of I–X. A nitro group in a pyrrolyl radical deepens the halochromic coloration by 20–65 nm (I, II, III). The greatest bathochromic effect is observed when the nitro group is introduced into the heterocycle adjacent to the carbonyl group and it can be understood that it exerts a greater effect in position 5 than in position 4. In sulfuric acid the addition of a proton to the carbonyl group takes place [10], with the formation of the conjugate carbonium ion, the color of which depends on the electron displacements in the chain of conjugation in the direction towards the carbonium atom > C^+OH. It is natural that a nitro group in the pyrrole ring (II) promotes this shift of the electron density and leads to the maximum bathochromic effect.

The compounds investigated possesss not only basic properties but also a fairly well expressed acidic nature. The presence of a nitro group in a pyrrole ring enhances their acidic properties and, as a rule, they dissolve in alcoholic solutions of alkalis with the formation of colored anions. The presence of an isobestic point on the absorption curves of the ketone III measured in ethanolic solutions of caustic potash of various concentrations shows the existence of the acid-base equilibrium:



Of the two mesomeric structures*, the first—with a negative charge on the oxygen—must have the deeper color [10]. The nitro group increases the proportion of the structure with a minus on the nitrogen and leads to a hypsochromic shift by 10 nm in comparison with the ketone without a nitro group. The opposite phenomenon

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*A structure with a minus on the oxygen of the nitro group is also possible.

is observed for the anions of compounds I and II, in which the introduction of a nitro group causes a bathochromic effect of 13–30 nm. A comparison of the absorption maxima of the long-wave band of the anions of I, II, and III with IV, V, and VI, respectively, shows that, as has been reported previously [10], a methoxy group in the aromatic nucleus has no significant effect on the coloration.

A study of the IR spectra of compounds I–XIII (Table 2, Fig. 2) shows that in the crystalline state they are associated through a hydrogen bond between the imino group and the carbonyl. Thus, in all the spectrograms there is a broad absorption band of the NH group participating in the formation of a hydrogen bond with a maximum in the 3145–3265 cm^{-1} region. The absorption characteristic for a free imino group in pyrroles, located, according to the literature, at 3400–3440 cm^{-1} [13] or at 3450–3500 cm^{-1} [14] was found only in compound X, which contains two pyrrole rings in the molecule (3410 cm^{-1}). At high dilution (10^{-5}–10^{-6} M) in carbon tetrachloride, the absorption characteristic for a nonbound NH group is also found for ketones II and III at 3425–3430 cm^{-1}. It must be assumed that the hydrogen bond in the nitropyrrole chalcone analogs is stronger than in the analogous chalcones not containing a nitro group, since ν_{NH} in the latter case is located at higher frequencies—3232–3290 cm^{-1} [15]. At the same time, in the pairs of isomeric ketones II and III, V and VI, and VIII and IX, ν_{NH} is lower for that isomer in which the carbonyl group is adjacent to the nitropyrrole ring, since under these conditions the N—H bond is looser. The presence of a stronger hydrogen bond in I–XIII is also confirmed by the fact that the planar deformation vibrations of the N—H group (β_{NH}) are shifted into the high-frequency region—1150–1205 cm^{-1} as compared with 1136 ± 1 cm^{-1} according to literature data [15]. For the derivatives of 4-nitropyrrole, β_{NH} is somewhat lower than for the isomeric 5-nitro compounds.

A doublet of bands of low and medium intensity is frequently observed in the 3110–3140 cm^{-1} region which, according to Lord and Miller [16], may be ascribed to the stretching vibrations of the C—H bonds (ν_{CH}) of the pyrrole ring. The absence of such vibrations in the case of compound X can be explained by their overlapping with the adjacent broad absorption band of an NH group participating in the formation of a hydrogen bond.

The characteristic frequency of the vibrations of a carbonyl group ($\nu_{C=O}$) of the compounds studied is found in the range from 1690 to 1640 cm^{-1}. This is considerably higher than for the corresponding substances not containing a nitro group and is a consequence of the electron-accepting nature of the latter, which leads to a decrease in the polarization of the carbonyl. The stretching vibrations of an aliphatic double bond ($\nu_{C=C}$) are located in the 1620–1590 cm^{-1} region, and their intensity is considerably higher than the intensity of $\nu_{C=O}$ (Fig. 2). Such a relationship of the intensities of $\nu_{C=O}$ and $\nu_{C=C}$ is characteristic for the s-cis arrangement of the corresponding bonds in α,β-unsaturated ketones [17]. However, the presence of absorption in the 995–978 cm^{-1} region (nonplanar deformation vibrations of the hydrogens of a vinylene group—$\gamma_{CH=CH}$) enables compounds I–X to be assigned, with respect to the arrangement of the substituents about the double bond, to the trans isomers.

The nitro groups in compounds I–XIII are comparatively readily detected by means of the antisymmetrical (ν_{as}) and symmetrical (ν_s) stretching vibrations of medium and high intensity at 1500–1532 cm^{-1} and 1285–1360 cm^{-1}, respectively. While the assignment of ν_{as} does not give rise to doubt, in contrast to this, ν_s is present in the region in which many other vibrations fall and it may be split [18], and therefore its assignment is not always sufficiently strict. In compounds VII–IX, which have two nitro groups—in the pyrrole and benzene nuclei—it is not possible to record the corresponding vibration bands separately and the absorptions of the two nitro groups are superposed. The somewhat low value of ν_{as} in the pyrrole ketones is probably connected with the strong electron-donating nature of the heterocycle, which also leads to a lowering of the frequency [19]. It is interesting that a nitro group in position 4 of the pyrrole ring of the compounds studied has ν_{as} in the range of frequencies somewhat lower than for the isomers in which the nitro group is in position 5 (I and II, IV and V, VII and VIII, XII and XIII). This is probably connected with the fact that in the first case it is not conjugated with the electron-accepting carbonyl and is under the influence only of the electron-donating pyrrole ring.

The introduction of a nitro group into the pyrrole nucleus is also reflected in the stretching vibrations of the heterocycle. In the preceding investigation [15] on the analogous chalcones not containing a nitro group, two types of skeletal vibrations of the pyrrole nucleus were found: 1547 ± 3 cm^{-1} and 1413 ± 3 cm^{-1}. In our compounds, the first type of vibrations lies in the 1550–1585 cm^{-1} region but appears as a very weak band, and only for I, IV, VII, and XII with a nitro group in position 4 do these vibrations attain a moderate intensity. This is confirmed by results [20] according to which the band close to 1565 cm^{-1} is strongest in 2, 3- and 2, 4-disubstituted pyrroles and is weakest in the 2, 5- isomers. The second type of skeletal vibrations of pyrrole mentioned is considerably shifted under the influence of a nitro group into the low-frequency region—1372–1413 cm^{-1}—with absorption of medium and high intensity, and this shift is greater for the 5-nitropyrrole derivatives than for the 4-nitro isomers. In the substances studied, especially for the 2, 5-disubstituted pyrroles, a third type of stretching vibrations of the heterocycle, which has recently been reported [21], is found at 1455–1480 cm^{-1}.

So far as concerns the other absorption peaks lying below 1200 cm^{-1}, they mainly relate to the planar and nonplanar vibrations of the CH groups of the aromatic and pyrrole rings, and it is extremely difficult to identify them in many cases. In Table 2 we give only the well-defined absorption of medium and high intensity at 1058–1078 cm^{-1} which must probably be assigned to the planar deformation vibrations of the hydrogen of the nitropyrrolyl group (β_{CH}).

For 5-nitropyrrole-2-aldehyde (XI) and 2-acetyl-5-nitropyrrole (XIII), only two high-intensity peaks are observed in the 990–700 cm^{-1} region, at 810, 770 and 819, 750 cm^{-1}, respectively, which can be assigned to the nonplanar deformation vibrations of the two hydrogen atoms adjacent to one another in the 3, 4-positions of the pyrrole ring. For the purposes of identification, it is of interest to mention that in the case of 4-nitro-2-acetylpyrrole (XII) there are five maxima of medium and high intensity in this region.

EXPERIMENTAL

The measurement of the electronic absorption spectra was carried out on an SF-4 spectrophotometer with $2 \cdot 10^{-5}$ to $4 \cdot 10^{-5}$ M solutions. The IR spectra were recorded for the substances in the solid phase in the form of tablets with potassium bromide (2 mg of substance per 100 mg of KBr), and compounds I and III were also recorded in carbon tetrachloride solution at a concentration of $1 \cdot 10^{-5}$–$1 \cdot 10^{-6}$ M in a UR-10 instrument in the range from 3700 to 500 cm^{-1}.

The solvents were purified as described by Weissberger et al. [22].

REFERENCES

1. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], **2**, 387, 1966.
2. U. S. patent no. 2962503; RZhKh, 6L279, 1962.
3. F. M. Riccieri, F. Gualtieri, and B. Babudieri, Farmaco Ed. Sci., **20**, 707, 1965; C. A., **64**, 15820d, 1966.
4. S. S. Novikov, V. M. Belikov, Yu. P. Egorov, E. N. Safonova, and L. V. Semenov, Izv. AN SSSR. OKhN, 1438, 1959.
5. V. M. Belikov, S. G. Mairanovskii, E. N. Safonova, and S. S. Novikov, Izv. AN SSSR. OKhN, 1488, 1958.
6. P. Fournari, M. Person, G. Watella-Marion, and M. Delepine, C. r., **253**, 1059, 1961.
7. K. J. Morgan and D. P. Morrey, Tetrah., **22**, 57, 1966.
8. C. N. O. Rao, Chemical Applications of Infrared Spectroscopy [Russian translation], Mir, Moscow, pp. 46, 78, 1964.
9. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS, collection **1**, p. 9, 1967.
10. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], **4**, 823, 11968.
11. S. V. Tsukerman, A. I. Artemenko, and V. F. Lavrushin, ZhOKh, **33**, 3528, 1963; **34**, 487, 1964.
12. S. V. Tsukerman, V. M. Nikitchenko, and V. F. Lavrushin, ZhOKh, **33**, 1255, 2563, 1963.
13. R. M. Silverstein and G. S. Bassler, Spectrometric Identification of Organic Compounds, New York-London, 1964.
14. P. Mirone and V. Lorenzelli, Ann. Chim. (Rome), **48**, 72, 881, 1958.
15. S. V. Tsukerman, V. P. Izvekov, Yu. S. Rozum, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], **4**, 1011, 1968.
16. R. C. Lord and F. A. Miller, J. Chem. Phys., **10**, 328, 1942.
17. E. L. Eliel, Stereochemistry of Carbon Compounds [Russian translation], Moscow, p. 324, 1965.
18. A. V. Ioganseen and G. D. Litovchenko, ZhPS [Journal of Applied Spectroscopy], **2**, 258, 1965.
19. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 1963.
20. U. Eisnel and R. L. Erskine, J. Chem. Soc., 971, 1958.
21. R. A. Jones, Austr. J. Chem., **16**, 93, 1963.
22. A. Weissberger, E. Proskauer, J. Riddick, and E. Toops, Organic Solvents [Russian translation], IL, Moscow, 1958.

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