INFRARED SPECTRA OF CHALCONE HOMOLOGS CONTAINING A PYRROLE NUCLEUS

S. V. Tsukerman, V. P. Izvekov, Yu. S. Rozum, and V. F. Lavrushin

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 6, pp. 1011–1017, 1968

UDC 547.745: 543.422.4: 541.634

The IR-spectra of 29 chalcone homologs containing a pyrrole nucleus were recorded in the solid phase, and in some cases in carbon tetrachloride solutions of varying concentrations. All the compounds studied formed intermolecular hydrogen bonds; and, when the carbonyl group was located close to the pyrrole ring (propenones-1), intramolecular hydrogen bonds were also formed. According to the distribution of substituents about the aliphatic double bond, all the ketones studied were trans-isomers; and, according to the relative distribution of carbonyl and vinyl groups, they had an s-cis-conformation. In the propenone-1 series there was a satisfactory correlation between $\nu_{C=O}$ and Hammett's σ-parameters. The corresponding frequencies were investigated.

In previous papers we reported the electronic absorption spectra of pyrrole chalcone homologs in neutral solvents [1] as well as in strongly acid and alkaline media [2]. In this paper we investigated the infrared spectra of chalcones. There is a paucity of information in the literature on the vibration spectra of α, β-unsaturated ketones derived from pyrrole. Only a few papers [3, 4] include fragmentary data on the characteristic vibratory frequencies of some unsaturated ketones of the pyrrole series.

We recorded, in the solid phase (KBr pellet) and in some cases in CCl_4 solution, the IR-spectra of 29 chalcone homologs containing the pyrrole nucleus. Tables 1 and 2 present the characteristic vibration frequencies of the various groups, and Fig. 1 some absorption curves.

All the spectrograms recorded in the solid phase exhibited the broad, intense absorption band of the N—H group that participates in hydrogen bond formation. This band has a maximum that lies within a rather narrow region, at 3275–3300 cm^{-1}. Only compound XXVIII exhibited a very diffuse band at 3038–3088 cm^{-1}. We could not detect, in the solid state, the absorption characteristic of the unbound N—H group of the pyrrole ring, reported at 3400–3440 cm^{-1} [5] or at 3450–3500 cm^{-1} [6]. It may be supposed that in crystal form the molecules of pyrrolic chalcone homologs are bound in polymeric associations. These associations are formed not only because of a hydrogen bond between the hydrogen of the imino group and the oxygen of the carbonyl group, but also because of a hydrogen bond of the type N—H···N between pyrrole nuclei. This conclusion is confirmed by the fact that, in compound XXI, which contains two pyrrole rings, no absorption bands corresponding to a free N—H group was observed (Table 1). Furthermore, it is known that pyrrole itself is in a state of polymeric association [7, 8]. A study of the integral intensity of the absorption band of the N—H bond of carbonyl compounds of the pyrrole series leads to believe that in these compounds two similar types of intermolecular association are possible [9]. The usually low frequency of the N—H group of compound XXVIII may also be probably explained by the formation of a hydrogen bond between the hydrogen of the imino group of the pyrrole ring and the nitrogen of the quinoline ring.

The comparatively low value of $\nu_{N—H}$ in all the compounds studied (a lowering of 150–250 cm^{-1}) points out to a rather strong hydrogen bond which is formed in the crystalline state. This is reflected in the melting points of pyrrolic chalcones which are much higher than those of analogous compounds of the aromatic and furan series. For instance, ketones I, II, and XXI melt at 141°, 134°, and 172°,C, respectively [10], while chalcone melts at 58° C [11], and the corresponding furan compounds melt at 89°, 37.5°, and 90° C [12]. It is characteristic that upon N-methylation of I and II, i.e., by transforming them to compounds III and IV, the melting points sharply decrease (III melts at 112° C, and IV at 88° C) [1].

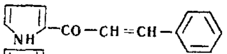
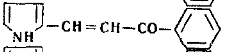
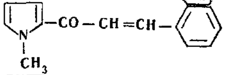
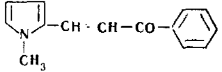
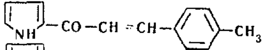
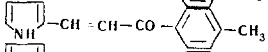
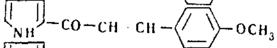
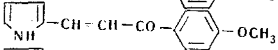
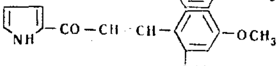
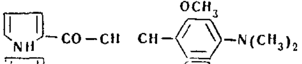
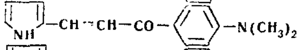
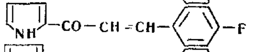
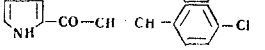
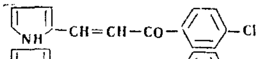
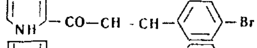
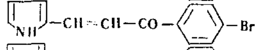
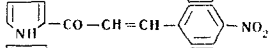
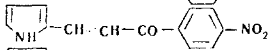
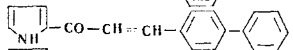
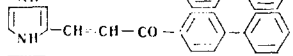
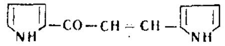
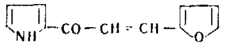
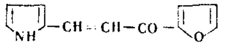
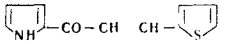
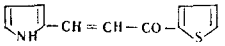
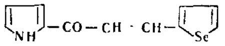
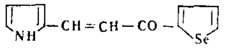
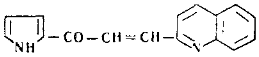
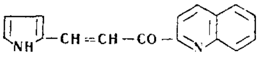
It may also be observed that, in the isomeric ketones (I and II, V, and VI, and so forth), the $\nu_{N—H}$ is, as a rule, smaller in that isomer in which the carbonyl group is located next to the pyrrole cycle (propenone-1). This may explain the increased mobility of the imino group hydrogen under the influence of the electron-acceptor properties of carbonyl and, consequently, the formation of a stronger hydrogen bond.

In addition to the absorption band of the bound N—H group, the IR-spectrograms of pyrrolic chalcones solutions in CCl_4 exhibit a band in the 3450–3480 cm^{-1} region. This band is characteristic of a free N—H group that does not participate in hydrogen bond formation (Table 2). Furthermore, the $\nu_{N—H}$ of the bound group is found at somewhat higher frequencies (up to 20–30 cm^{-1} higher) than the analogous absorption in the solid phase. In dilute solutions of I, II, V, VI, at concentrations from $1 \cdot 10^{-2}$ to $1 \cdot 10^{-3}$ M (see Table 2) the relation between the absorption intensities of the bound and the free N—H groups is altered: there is an increase in the relative absorption intensity of the free N—H group, and this is characteristic of an intermolecular hydrogen bond. The data presented in Table 2 on the absorption intensities of free and bond N—H groups warrant the hypothesis that, at the concentrations studied, there is fundamentally an equilibrium between the nonassociated molecules and their linear dimers.

It is worth noticing that the relation between the absorption intensities (% transmission) of the free and the bound N—H groups in ketones I and V are higher at the same concentrations than those of the isomeric ketones II and VI. Furthermore, the $\nu_{N—H}$ of I and V are located at lower frequencies than the $\nu_{N—H}$ of II and VI (14–27 cm^{-1} lower for the free group and 32–49

Table 1

Characteristic Frequencies of the Pyrrolic Homologs of Chalcone, cm^{-1}

Compound	Structural formula	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{pyrrole\ ring}$	$\nu_{trans-H-C=C-H}$	β_{N-H}	β_{C-H}	γ_{C-H}
I		3232	1650	1590	1546 1408	980	1140 1115	1057 1043	940 890 837 772 742
II		3253	1652	1586	1547 1418	980	1136 —	1031 1022	930 884 852 830 780 740
III		—	1650	1593	1537 1412	992	— —	1072 1052	878 776 750
IV		—	1650	1590	1570 1415	970	— —	1063 1038 1020	845 775 745
V		3252	1645	1586	1542 1406	985	1134 1113	1060 1040	940 816 730
VI		3280	1651	1610	1545 1418	980	1135	1032 1020	884 815 736
VII		3257	1644	1573	1515 1406	973	1135 1115	1063 1045 1030	947 885 828 770 755
VIII		3230	1655	1610	1550 1415	983	1137	1030	883 830 743
IX		3252	1634	1603	1548 1405	990	1130 1118	1060 1030	945 885 855 830 766
X		3238	1632	1608	1534 1407	987	1138 1110	1055	942 890 847 817 787 752
XI		3240	1645	1605	1530 1420	980	1133	1030	950 882 815 755
XII		3249	1654	1583	1554 1414	986	1140 1115	1062	948 892 833 778 753
XIII		3268	1648	1590	1545 1410	986	1138 1112	1058 1040	942 821 780 755
XIV		3312	1652	1585	1550 1416	983	1132	1035 1015	880 821 750
XV		3275	1658	1605	1558 1420	990	1142 1120	1062 1043	945 820 775 756
XVI		3312	1667	1598	1559 1423	985	1140	1078 1048	881 822 750
XVII		3250	1645	1590	1548 1418	985	1140 1115	1070 1045	945 887 845 774 756
XVIII		3290	1645	1603	1522 1428	987	1137 1110	1040 1010	850 830 760 740
XIX		3253	1651	1588	1548 1410	980	1142 1113	1060	945 888 832 772 750
XX		3290	1652	1578	1545 1413	980	1135	1035	885 835 820 775 738
XXI		3270	1638	1570	1540 1405	970	1135 1120	1065 1034	948 880 760 735
XXII		3232	1650	1590	1558 1403	970	1140 1110	1056 1030	943 884 855 785 755 734
XXIII		3215	1640	1575	1550 1415	983	1137	1070 1055	938 881 855 830 755 740
XXIV		3248	1640	1580	1542 1405	970	1140 1112	1060 1038	940 885 865 825 745
XXV		3232	1644	1572	1550 1412	983	1138	1065 1038	883 838 720
XXVI		3250	1640	1582	1550 1405	958	1140 1110	1057 1040	940 830 743
XXVII		3330 3260	1640	1562	1545 1415	980	1128	1082 1035	963 882 847 817 746 730
XXVIII		3088 3038	1651	1595	1550 1408	976	1115 1138	1060	940 880 832 762 750 728
XXIX		3282	1654	1590	1558 1430	978	1140 1120	1078	952 885 835 820 771 740

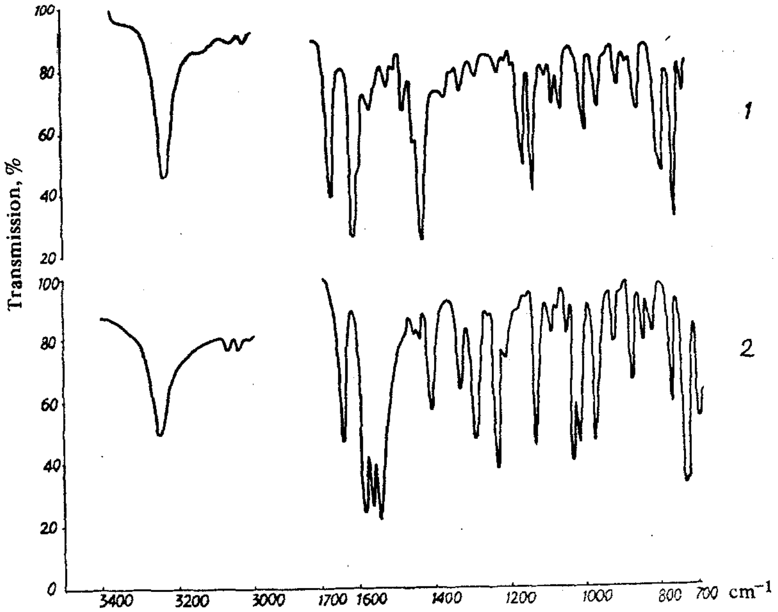


Fig. 1. IR-spectra of the compounds: 1) 1-(pyrryl-2)-3-phenylpropenone-1 (I); 2) 1-(pyrryl-2)-3-phenylpropenone-3 (II).

cm^{-1} lower for the bound N—H group). This would lead us to expect an inverse intensity ratio. This may be due to the formation, in compounds containing a carbonyl group next to the pyrrole cycle (I, V, and others, of an intramolecular hydrogen bond in addition to the intermolecular one. The intramolecular bond is, however, not very stable, and in propenones-1 there is an equilibrium between forms with intra- and with intermolecular hydrogen bonds. The intramolecular hydrogen bond is often energetically more advantageous than the intermolecular [13]. Yet the energy of the intramolecular bond depends, other conditions being equal, on the configuration of the cycle formed [14]. For the formation of an intramolecular hydrogen bond, the most favorable distribution of all the three participating atoms is that of a straight line [15]. In propenones-1 the angle between N—H···O, as may be seen from Stuart-Briegleb models, is too acute. Therefore, the intramolecular hydrogen bond is energetically less favorable than the intermolecular. According to Grigg's data [16], the esters of pyrrol 2-carboxylic acids may form both intra- and intermolecular hydrogen bonds, in which the $\nu_{N—H}$ of the free group of that bound by intramolecular hydrogen bonds are not much different from each other, and the latter frequently appears only as a shoulder on the fundamental absorption band or its asymmetric form. Furthermore, a recent investigation of 2-acyl pyrroles and of the methyl esters of pyrrole carboxylic acids [19], although it does not deny the possible formation in them of intramolecular hydrogen bonds, contains data that contradict such a view [16]. It should be noted that the absorption band of the carbonyl group of compounds II and VI (Table 2) is split up, while that of I and V does not exhibit such a clear splitting of the $\nu_{C=O}$. Evidently, in the first case the frequencies of the free and the bound intermolecular hydrogen bonds of the carbonyl groups are comparatively more apart than in compounds I and V, which possess both intra-and intermolecular hydrogen bonds, and the difference between the corresponding frequencies is less.

In all pyrrolic homologs of chalcones, the characteristic vibration frequency of the carbonyl group lies between 1632 and 1667 cm^{-1} (Table 1). This frequency is, in most cases, somewhat lower than the $\nu_{C=O}$ in chalcone and its furan [18] and thiophene [19] homologs. This is associated with the relatively high electron-donating capacity of the pyrrole cycle [1], which is capable of polarizing the carbonyl group. On this account, the $\nu_{C=O}$ of propenones-1 is always lower than that of propenones-3. The introduction of electron-donating substituents into aromatic nuclei I and II, as was to be expected, lowers $\nu_{C=O}$, while electron-accepting substituents raise $\nu_{C=O}$, Within the propenones-1 series, the correlation between ν C=O and the Hammett's σ-constants is quite well maintained (Fig. 2), according to the equation:

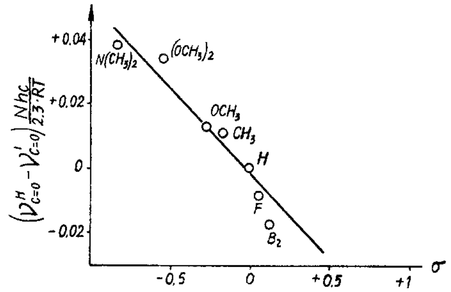


Fig. 2. Correlation between $\nu_{C=O}$ and Hammett's σ-constants. $\rho = 0.05$; s = 0.01.

$$(\nu^{H}_{C=O} - \nu^{i}_{C=O})\frac{Nhc}{2.3\cdot RT} = \rho\sigma,$$

where $\nu^{H}_{C=O}$ and $\nu^{i}_{C=O}$ are the valence vibrations of carbonyl in 1-(pyrryl-2)-3-phenylpropenone-1 (I) and in its substituted derivatives, respectively.

The vibration frequency of the aliphatic double bond lies between the limits 1570–1610 cm^{-1}. The intensity of the $\nu_{C=C}$ band is almost always higher than that of

Table 2

Valence Vibrations of the C=O and N—H Bonds of the Pyrrolic Homologs of Chalcone, Measured in CCl_4 Solution

Compound	Concentration, M	Vibration frequencies, cm^{-1}			
		N–H bond		C=O bond	
		free	combined	free	combined
I	$5.48\cdot10^{-2}$	3456 (67)*	3256 (30)	—	1652 (46)
	$2.74\cdot10^{-2}$	3456 (49)	3256 (13)	—	1652 (34)
	$1.37\cdot10^{-2}$	3456 (31)	3256 (5)	—	1652 (19)
II	$5.05\cdot10^{-2}$	3470 (31)	3305 (44)	1660 (19)	1646 (25)
	$2.52\cdot10^{-2}$	3470 (22)	3305 (20)	1660 (15)	1646 (17)
	$1.26\cdot10^{-2}$	3470 (12)	3305 (8)	1660 (5)	1646 (5)
III	$5\cdot10^{-3}$	—	—	1660	—
IV	$5\cdot10^{-3}$	—	—	1658	—
V	$1\cdot10^{-2}$	3451 (48)	3258 (28)	—	1658 (67)
	$5\cdot10^{-3}$	3451 (38)	3258 (20)	—	1658 (58)
	$1\cdot10^{-3}$	3451 (16)	—	—	1658 (22)
VI	$1\cdot10^{-2}$	3478 (38)	3290 (44)	1660 (16)	1648 (20)
	$5\cdot10^{-3}$	3478 (21)	3290 (22)	1660 (10)	1648 (8)
	$1\cdot10^{-3}$	3478 (14)	—	1660 (5)	—

---

*In parentheses, percent transmission.

$\nu_{C=O}$, and this is characteristic of the s-cis-distribution of the corresponding bonds [20]. As to the distribution of the substituents about the aliphatic double bond, all the compounds studied are trans isomers. This is quite evident from the average and high intensities of the absorption at 958–992 cm^{-1}, which is characteristic of the trans vinyl group [21].

The pyrrole ring is of course most easily detected by the valence vibrations of the N—H group. According to R. A. Jones [4], the plane deformation vibrations of the N—H group in 2-substituted pyrroles lie at 1117 ±3 cm^{-1}, and those of pyrrole itself at 1146 cm^{-1} [22]. We found that, in this region, propenones-1 have two absorption bands of average and high intensities at 1130–1142 cm^{-1} (1136 ±1) and at 1110–1120 cm^{-1} (1114 ± 2), but that propenones-3 have only one band at a higher frequency. It is possible that propenones-1 may have two types of hydrogen bonds in which the N—H group participates, and to which is due the presence of a second absorption maximum. This does not exclude the existence of "breathing" vibrations in the pyrrole cycle, to which is conventionally ascribed the band at 1133 ± 3 cm^{-1} [4]. However, N-methylated III and IV do not exhibit absorption in this region.

Two strong bands at 1565 and 1500 cm^{-1} [23] are usually adduced to the skeletal vibrations of the pyrrole cycle. R. A. Jones [4] observed three absorption bands at 1550, 1470, and 1420 cm^{-1}. In the compounds studied by us, only two corresponding vibration type at 1530–1570 (1547±3) cm^{-1} and at 1405–1430 (1413 ± 3) cm^{-1} were well observed (Table 1). The first band was more intense and better developed in propenones-3, in which the carbonyl group is separated from the heterocycle by a vinyl group. On the other hand, the second vibration type (at 1405–1430 cm^{-1}) was more intense and oustanding in propenones-1.

The absorptions at 1000–1100 and below 960 cm^{-1} (Table 1) were considered as corresponding to the plane and out-of-plane deformation vibrations of the C—H group.

It may be noted that the total number of absorption bands and their intensities are appreciably greater in propenones-3 than in propenones-1, especially in the 1200–1400 cm^{-1} region (Fig. 1) This is evidently a result of the greater interlinking in the first case of the carbonyl group with the pyrrole cycle. It is interesting that furan [18] and thiophene [19] chalcone homologs exhibit an inverse picture.

EXPERIMENTAL

The IR-spectra of pyrrolic chalcone homologs were recorded in the solid phase in KBR pellets (1 mg of substance and 100 mg of KBr) in a UR-10 infrared spectrometer in the 600–3500 cm^{-1} region. The spectra of compounds I–VI were recorded in CCl_4 solution at concentrations from $1 \cdot 10^{-2}$ to $1 \cdot 10^{-3}$ M, with an IKS-14 apparatus.

REFERENCES

1. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, Azotsoderzhashchie geterotsikly, 1, 9, 1967.
2. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 823, 1968.
3. W. Herz and J. Brasch, J. Org. Chem., 23, 1513, 1958.
4. R. A. Jones, Austral. J. Chem., 16, 93, 1963.
5. R. M. Silverstein and G. S. Bassler, Spectrometric Identification of Organic Compounds, New York-London, 1964.
6. P. Mirone and V. Lorenzelli, Ann. Chim., 48, 72, 881, 1958.
7. P. Mirone and M. Vampiri, Atti Accad. naz. Lincei Rend. classe sci. fis. mat. e nat., 12, 405, 1952.
8. V. Lorenzelli and A. Alemagna, C.r. 257, 2977, 1963.
9. P. Mirone and V. Lorenzelli, Ann. Chim., 49, 59, 1959.
10. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 527, 1965.
11. R. J. W. Le Fevre, J. Chem. Soc., 1037, 1937.
12. V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, ZhOKh, 31, 3037, 1961.
13. H. H. Jaffe, J. Am. Chem. Soc., 79, 2373, 1957.
14. I. M. Ginzburg, DAN, 156, 1382, 1964; ZhOKh, 34, 1624, 2204, 1964.
15. J. Pimentel and O. McClelland, The Hydrogen Bond [Russian translation], IL, Moscow, 1964.
16. R. Grigg, J. Chem. Soc., 5149, 1965.
17. M. K. A, Khan and K. J. Morgan, J. Chem. Soc., 2579, 1964; Tetrahedron 21, 2197, 1965.
18. S. V. Tsukerman, A. I. Artemenko, V. F. Lavrushin, and Yu. S. Rozum, ZhOKh, 34, 2309, 1964.
19. S. V. Tsukerman, V. M. Nikitchenko, Yu. S. Rozum, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 452, 1967.
20. E. Iliel, Stereochemistry of Carbon Compounds [Russian translation], IL, Moscow, 324, 1965.
21. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], IL, Moscow, 69, 1963.
22. R. C. Lord and F. A. Miller, J. Chem. Phys., 10, 328, 1942.
23. U. Eisner and R. L. Erskine, J. Chem. Soc., 971, 1958.

8 September 1966

Gor'kii Khar'kov State University

Institute of Organic Chemistry
AS UkrSSR, Kiev