UDC 543.422 + 547.741/748

INFRARED SPECTRA OF PYRROLES AND DIPYRRYLMETHANES

A. F. Mironov, L. D. Miroshnichenko, R. P. Evstigneeva, N. A. Preobrazhenskii

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 74-80, 1965

The IR spectra of 18 substituted pyrroles and 6 substituted dipyrrylmethanes are investigated. It is shown that the position of the valence vibrations frequency of the free NH group, $\nu_{\text{free NH}}$ depends on the number of substituents in the ring. The frequency is influenced by the electronegativity of a substituent, the effect of an α- being much more marked than that of a β-substituent. The stability of the hydrogen bond increases with increase in substituent electronegativity. When two electronegative substituents occupy the α and β positions, they have a mutually weakening effect. The $\nu_{C=O}$ (acetyl) absorption bands in pyrrole-containing compounds are situated 40-60 cm^{-1} lower than in aromatic ketones and greatly depend on the position and nature of the substituent in the pyrrole ring.

In continuance of work on the ability of pyrrole and pyrrole-containing compounds to undergo hydrogen bonding [1], the IR spectra of a series of substituted pyrroles and dipyrrylmethanes were measured. Special attention was paid to the frequencies of the valence vibrations of the N—H and C=O bonds, which are known to be measurable with certainty and are quite sensitive to changes in molecular structure.

Interaction of N—H bond electrons with nuclear substituents (conjugated effect, inductive effect) may weaken this bond to a definite extent, and this is shown in a lowering of the frequency of the valence vibrations of the NH group ($\nu_{\text{free NH}}$) and an increase in the ability of the proton at the nitrogen atom to form an inter- and intra-molecular hydrogen bond. It was previously shown [2] that increase in the number of alkyl substituents results in a lowering of $\nu_{\text{free NH}}$. The results of the present determinations lead to the conclusion that the accumulation of any substituents in the ring entails a lowering of the frequency $\nu_{\text{free NH}}$. An example is transition from pyrroles with two substituents (I, $\nu_{\text{free NH}}$ 3489 cm^{-1}; II, $\nu_{\text{free NH}}$ 3479 cm^{-1}) to trisubstituted (III, $\nu_{\text{free NH}}$ 3468 cm^{-1}; IX, $\nu_{\text{free NH}}$ 3466 cm^{-1}; XV, $\nu_{\text{free NH}}$ 3460 cm^{-1}) and tetrasubstituted pyrroles (IV, $\nu_{\text{free NH}}$ 3445 cm^{-1}; VIII, $\nu_{\text{free NH}}$ 3434 cm^{-1}; X, $\nu_{\text{free NH}}$ 3448 cm^{-1}; XI, $\nu_{\text{free NH}}$ 3417 cm^{-1}). The much lower value of $\nu_{\text{free NH}}$ for the pyrrole II as compared with that for compound I is ascribed to the high electronegativity of the carbethoxy group.

Consideration of the IR spectra of pyrroles III, IX, and XV, shows that an α substituent has a much greater effect than a β substituent. When in the α position, the carbethoxy group, which has a much less powerful electron-acceptor action, gives rise to an even greater lowering of $\nu_{\text{free NH}}$ than the more electronegative acetyl group in the β position. In the case of tetrasubstituted pyrroles, apart from a general tendency to a lowering of $\nu_{\text{free NH}}$, it is interesting to note the effect of various substituents in the α position. The frequency $\nu_{\text{free NH}}$ is most markedly affected by the carboxyl group (XI, $\nu_{\text{free NH}}$ 3417 cm^{-1}), after which comes the formyl group (VIII, $\nu_{\text{free NH}}$ 3434 cm^{-1}; XIV, $\nu_{\text{free NH}}$ 3436 cm^{-1}) and lastly, the ester group (IV, $\nu_{\text{free NH}}$ 3445 cm^{-1}; V, $\nu_{\text{free NH}}$ 3445 cm^{-1}; X, $\nu_{\text{free NH}}$ 3448 cm^{-1}). Thus, α substituents can be placed in the following order in respect to the magnitude of their effect on $\nu_{\text{free NH}}$: $\text{COOH} > \text{CHO} > \text{COOR}$ (where R = C_2H_5, $CH_2C_6H_5$).

Similarly, on analyzing the effect of β substituents, on the one hand, for pyrroles XVI ($\nu_{\text{free NH}}$ 3438 cm^{-1}), IV ($\nu_{\text{free NH}}$ 3445 cm^{-1}), and XVII ($\nu_{\text{free NH}}$ 3456 cm^{-1}), and on the other, for pyrroles VIII ($\nu_{\text{free NH}}$ 3434 cm^{-1}) and XIV ($\nu_{\text{free NH}}$ 3436 cm^{-1}), we also note that, despite some weakening, the effect of the electronegativity of the substituents on the value of $\nu_{\text{free NH}}$ follows the order $CHO > COCH_3 > COOC_2H_5 > CH_2CH_2COOCH_3$.

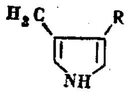
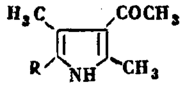
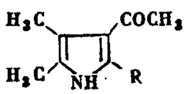
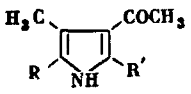
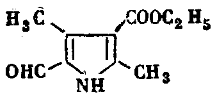
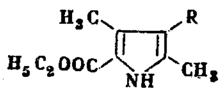
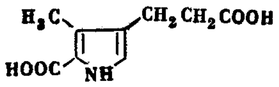
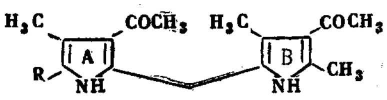
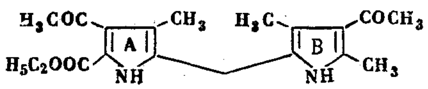
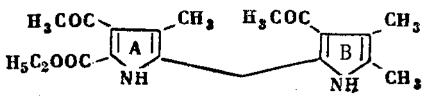
This agrees with results showing that the extent of conjugation of the group $C=O$ with the ring decreases for the above substituents in exactly the same order [3].

With unsymmetrical dipyrrylmethanes there must be two $\nu_{\text{free NH}}$ bands, corresponding to the two pyrrole components. Five diacetyl-substituted dipyrrylmethanes have been studied (the IR spectrum of XXI was not determined because of its low solubility in chloroform), but only in the case of the dipyrrylmethane XXII was it possible to discover both bands. The 3408 cm^{-1} frequency was ascribed to $\nu_{\text{free NH}}$ of ring A, with a formyl group, and the 3425 cm^{-1} frequency to ring B. Evidently for four other dipyrrylmethanes the bands were so close together that they could not be distinguished. The nature of the effect of substituents on $\nu_{\text{free NH}}$ is similar to that for the pyrroles previously discussed. Here it should be mentioned that the frequencies $\nu_{\text{free NH}}$ for the corresponding methanes are lower by 7-9 cm^{-1} than in the pyrroles.

The position of the second NH peak, corresponding to the valence vibrations of the NH group that participates in hydrogen bonding $\nu_{\text{assoc NH}}$, exhibits a less clear dependence on the nature of the substituent than does $\nu_{\text{free NH}}$. This is because the value of $\nu_{\text{assoc NH}}$ is determined, on the one hand, by the electron-attracting effect of the ring substituent, which weakens the N—H bond, and on the other, by the stability of the hydrogen bond, which also depends on

TABLE

Frequencies of valence vibration of the groups N—H and C = O and the pyrrol ring*

	General formula	Compound	R	R′
1.		I	CH_2CH_2COOH	
		II	$COOCH_2CH_3$	
2.		III	H	
		IV	$COOC_2H_5$	
		V	$COOCH_2C_6H_5$	
		VI	COOH	
		VII	COONa	
		VIII	CHO	
3.		IX	H	
		X	$COOC_2H_5$	
		XI	COOH	
4.		XII	CH_2Cl	$COOC_2H_5$
		XIII	$COOC_2H_5$	CH_2Cl
5.		XIV		
6.		XV	H	
		XVI	CHO	
		XVII	$CH_2CH_2COOCH_3$	
7.		XVIII		
8.		XIX	H	
		XX	$COOC_2H_5$	
		XXI	COOH	
		XXII	CHO	
9.		XXIII		
10.		XXIV		

*The IR spectra were obtained with a UR-10 double-beam spectrophotometer. In the solid state all substances except I and XVII were measured in the form of tablets

TABLE (CONTINUED)

	ν_{N-H}					$\nu_{C=O}$				Ring vibration	
	As solid		In solution		$\Delta\nu$	COOR COOH	CHO	$COCH_3$		I	II
	I	II	$\nu_{\text{free NH}}$	$\nu_{\text{assoc NH}}$				I	II		
1.	3418	—	3489	3350	139	1712				1554	1505
	3295	—	3479	3338	141	1682				1564	1525
2.	3240	—	3468	3315	153			1619		1590	1520
	3310	—	3445	3305	140	1683		1650		1555	1515
	3190	—	3445	3280	165	1684		1630		1561	1509
	3276	—	3435	3275	160	1666		1648		1555	1513
	3375	3240	—	—	—	1570		1615		—	1508
	3250	—	3434	3257	177		1662	1625		1557	1523
3.	3235	—	3466	3310	156			1626		1565	1517
	3312	—	3448	3312	136	1708		1668		1583	1503
	3275	3150	3417	3255	162	1683		1591		1565	1510
4.	3240	3140	3442	—	—	1707		1664		1575	1507
	3270	—	—	—	—	1667		1645		1558	—
5.	3230	3120	3436	3257	179	1690	1630			1562	1513
6.	3290	3150	3460	3330	130	1667				1579	1527
	3305	—	3438	3290	148	1680	1665			1579	1530
	3300	—	3456	3320	136	1737				1577	1508
						1663					
7.	3390	—	3458	3360	98	1723 1667				1580	1522
8.	3210–3180	3100	3459	3340	119			1633	1615	1563	1520
	3320	3150	3438	3360	78	1709		1639	1609–1598	1565	1512
	3373	3142	—	—	—	1707		1642	1614	1562	1517
	3313	3158	3425	3365	60		1672	1642	1596	1564	1517
			3408	3270	128						
9.	3324	3250	3445	3320	125	1690		1648	1662	1574	1500
10.	3325	3270	3449	3325	124	1714		1640	1658	1574	1496

with KBr. The spectra of the pyrroles I and XVII were measured in vaseline. Measurements in solution were made with chloroform, the concentrations of the substances being 1-2%.

steric factors. The value of the shift $\Delta\nu = \nu_{\text{free NH}} - \nu_{\text{assoc NH}}$ can conveniently be used to characterize the effect of substituents on the hydrogen bond, for it is known that this shift is a direct function of the hydrogen bond strength [4]. From the table given it is evident that the formyl group has the greatest effect ($\Delta\nu$ for pyrroles VIII and XIV is 177 and 179 cm^{-1}). The other groups follow the formyl group in the order: $CHO > COOH > COOC_2H_5$.

Note that according to the literature [5], the carboxyl group comes after the carbethoxy group in respect to the strength of the inductive effect. In the present case, as mentioned above, from the effects on $\Delta\nu$ and $\nu_{\text{free NH}}$ it comes before. Obviously, factors other than the inductive effect are operative here.

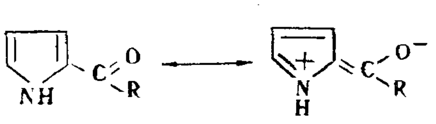
If there are two electronegative groups in the α and β positions, respectively, then their effect on the value of $\Delta\nu$ is a mutually weakening one, as follows on comparing pyrroles IX ($\Delta\nu$ 156 cm^{-1}) and X ($\Delta\nu$ 136 cm^{-1}), and also pyrroles III ($\Delta\nu$ 153 cm^{-1}) and IV ($\Delta\nu$ 140 cm^{-1}).

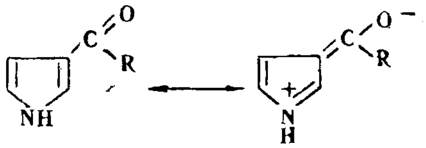
Pyrrole V departs from the general rule; its $\Delta\nu$ (165 cm^{-1}) differs markedly from the $\Delta\nu$ (140 cm^{-1}) of its analog IV. This may be ascribed to the participation in the intermolecular interaction of the benzene ring of the ester group [6].

In the dipyrrylmethane series there is, in general, a lowering of the hydrogen bond frequency as compared with pyrroles with similar substituents, this being shown by the smaller value of the quantity $\Delta\nu$. Obviously, this is due to added steric hindrances. Here the substituents fall in the same order in respect to their effect on the strength of the hydrogen bond.

For all the compounds studied in the solid state one (for dipyrryl methanes, two) peak was found, corresponding to the NH group. It approximately coincides in position with the $\nu_{\text{assoc NH}}$ peak in solution. Exceptions are partially substituted pyrroles and the methane XIX, for which $\nu_{\text{assoc NH}}$ in the solid state is some tens of cm^{-1} lower than in solution, as well as the pyrrole V ($\nu_{\text{assoc NH}}$ 3190 cm^{-1}); the anomalously low position of $\nu_{\text{assoc NH}}$ in chloroform has already been mentioned.

In the valence vibrations region of the carbonyl group, special interest attaches to bands corresponding to absorption by acetyl-substituted compounds. The $\nu_{C=O}$ frequencies for ketones conjugated with an aromatic system [7] usually lie in the range 1690-1670 cm^{-1}; in the present case a sharp lowering of $\nu_{C=O}$, indicating definite structural peculiarities for the compounds under investigation, is observed. Thus, an unusually low value of $\nu_{C=O}$ is found for acetylpyrroles with a free position (III, $\nu_{C=O}$ 1619 cm^{-1}; IX, $\nu_{C=O}$ 1626 cm^{-1}), and also a formyl (VIII, $\nu_{C=O}$ 1625 cm^{-1} or carboxyl group (XI, $\nu_{C=O}$ 1591 cm^{-1}) as a substituent. This lowering of the frequency of the valence vibrations of the carbonyl group is brought about by a significant alteration in electron densities, which leads to the C=O group partially losing its double-bond character. There are indications that the polar form thus formed (b) is stabilized by participation of the nitrogen atom [8].





a b a b

For confirmation that the $\nu_{C=O}$ lowering effect considered is connected with the presence of a polar form, the sodium salt of 2,4-dimethyl-3-acetyl-5-pyrrole carboxylic acid (VII) was investigated. As expected, a low value of $\nu_{C\ O}$ (1615 cm^{-1}) was found, and this was even less than for the starting acid (VI, $\nu_{C=O}$ 1648 cm^{-1}). The acetylpyrroles X ($\nu_{C=O}$ 1668 cm^{-1}), XII ($\nu_{C=O}$ 1664 cm^{-1}), IV ($\nu_{C=O}$ 1650 cm^{-1}), and XIII ($\nu_{C=O}$ 1645 cm^{-1}), with a carbethoxy group substituent, have much higher values of $\nu_{C=O}$. The last four compounds serve as examples for drawing attention to the dependence of the frequency $\nu_{C=O}$ on the positions of the substituents with respect to one another in the ring. With acetyl and carbethoxy groups adjacent, as in pyrroles X and XII, the values of $\nu_{C=O}$ are higher than when they are separated by one carbon atom, as in pyrroles IV and XIII. The stated relationship is also confirmed for a series of dipyrrylmethanes. The vibration frequencies of acetyl groups of ring B of the methanes XIX-XXIV lie in the interval 1648-1633 cm^{-1} (see table, $\nu_{C=O,\,COCH_3}$, I). At the same time, the values of $\nu_{C=O}$ of the acetyl group of ring A ($\nu_{C=O,\,COCH_3}$, II) are greatly dependent on molecular structure. When the acetyl and carbethoxy groups are adjacent, as in the case of pyrroles X and XII, high values for $\nu_{C=O}$ are observed (XXIII, $\nu_{C=O}$ 1662 cm^{-1}; XXIV, $\nu_{C=O}$ 1658 cm^{-1}). Then if there are two electronegative groups opposite one another, as in pyrroles IV and XIII, a low value is found (XX, $\nu_{C=O}$ doublet 1609-1598 cm^{-1}). Similar values of $\nu_{C=O}$ (acetyl) are also found for the corresponding pyrroles, with the dipyrrylmethanes substituted in ring A by a carboxyl or formyl group (XXI, $\nu_{C=O}$ 1614 cm^{-1}; XXII, $\nu_{C=O}$ 1596 cm^{-1}), and also for those with a free α position (XIX, $\nu_{C=O}$ 1615 cm^{-1}). It may be mentioned that in general the values of $\nu_{C=O}$ (acetyl) for dipyrrylmethanes are lower than for the analogous pyrroles.

Compound V ($\nu_{C=O}$ 1630 cm^{-1}) with a carbobenzoxy group, has a much lower value for $\nu_{C=O}$ (acetyl) than pyrrole IV with a carbethoxy group, and this is in agreement with the assumptions made above regarding participation of the benzene ring in intermolecular interaction.

The C=O valence vibration frequencies of the formyl group are found to be less dependent on structure than $\nu_{C=O}$ (acetyl). However, they are 20-30 cm^{-1} lower than for ordinary aromatic aldehydes.

The C=O valence vibrations of the ester group are also lowered as compared with those for esters of aromatic carboxylic acids [9] (1720 cm^{-1}) and lie in the region 1714-1663 cm^{-1}. $\nu_{C=O}$ carboxyl group absorption bands lie even lower than for the corresponding aromatic esters.

For all the compounds studied two bands were found in the 1600-1500 cm^{-1} region. These are attributed to vibrations of the pyrrole ring. The first band lies in the range 1580-1560 cm^{-1}, and the second in the range 1530-1500 cm^{-1}.

REFERENCES

1. L. D. Miroshnichenko, R. P. Evstigneeva, N. A. Preobrazhenskii, ZhOKh, 33, 2885, 1963.
2. R. J. Abraham, E. Bullock, S. S. Mitra, Canad. J. Chem., 37, 11, 1959.
3. M. Scrocco, L. Caglioti, Atti accad. naz. Lincei Rend. cl. sci. fis. mat. e nat., 24, 316, 1958.
4. G. B. Sutherland, Trans. Farad. Soc., 38, 889, 1940.
5. M. J. S. Dewar, P. J. Grisdale, J. Am. Chem. Soc., 84, 3548, 1962.
6. N. Fuson, P. Pineau, M. J. Josein, Hydrogen Bonding, 169, 1957.
7. V. West, Applications of Spectroscopy in Chemistry [Russian Translation], IL, Moscow, 1959.
8. U. Eisner, R. L. Erskin, J. Chem. Soc., 971, 1958.
9. G. M. Barrow, J. Phys. Chem., 21, 2008, 1953.
10. J. F. Grove, H. A. Willis, J. Chem. Soc., 512, 1951.

25 November 1963

Lomonosov Institute of Fine Chemical Technology, Moscow