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CHEMISTRY OF DIPYRIDYLS

Use of Infra-Red Spectra for Determining Structures of Substituted Dipyrryls

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It is shown that it is possible to determine the position of substituents in dipyridyls in determining the frequencies of out-of-plane vibrations of C–H bonds in the 950–650 cm^{-1} region of their IR spectra.

Among the problems connected with the chemistry of dipyridyls is a need to demonstrate the position of substituents in molecules of their derivatives. Although chemical methods have already been developed for determining the structures of compounds of this type [1, 2], in the course of research work it was necessary to find a rapid and unequivocal method of determining the structures of molecules of substituted dipyridyls.

Hence the aim of the present work is to investigate the IR spectra of a number of derivatives of dipyridyls (α, α'-, α, β'-, β, β - and γ, γ' - isomers). To solve the problem, use was made of a method of determining the structures of benzene derivatives, for which it is known that the frequencies of the in-phase out-of-plane deformation vibrations of the C–H bonds in the aromatic ring depend on the number and relative positions of substituents, but only very slightly on their natures [3-6].

The possibility of using IR spectra for determining the position of substituents in dipyridyl molecules was discovered by comparing absorption bands of derivatives of benzene, pyridine, and dipyridyls in the 950–650 cm^{-1} region. The characteristic nature of bands of this type was shown for a series of some simple pyridine derivatives [7-10]; practically no work has been done on the effect of substituent for its more complex derivatives. Consequently, it is impossible to draw any general conclusion regarding the applicability of these rules to dipyridyl derivatives from some literature data.

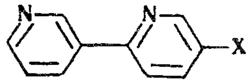
However, turning attention to the IR spectra of compounds whose structures have already been demonstrated: α, α'-, α, β'-, β, β'- and γ, γ' isomers, mono derivatives of α, β'-dipyridyl (fig. plots 1, 4-8, 11, 12), consideration of the bands in the 950–650 cm^{-1} region leads to a conclusion that the out-of-plane vibrations of C–H bonds of the aromatic rings of dipyrridyls retain their characteristic nature here, too. Hence our data make it possible to correlate frequencies of out-of-plane vibrations of dipyridyls and their derivatives with the spectra of the corresponding pyridine and benzene derivatives.

Since the pyridine molecule in dipyridyls has, as comparec with that of benzene, only four C–H bonds, the frequencies in the 950–650 cm^{-1} region can be compared with the bands of the corresponding disubstituted benzenes, or monosubstituted pyridines. The data in the table indicate the correctness of such an assignment.

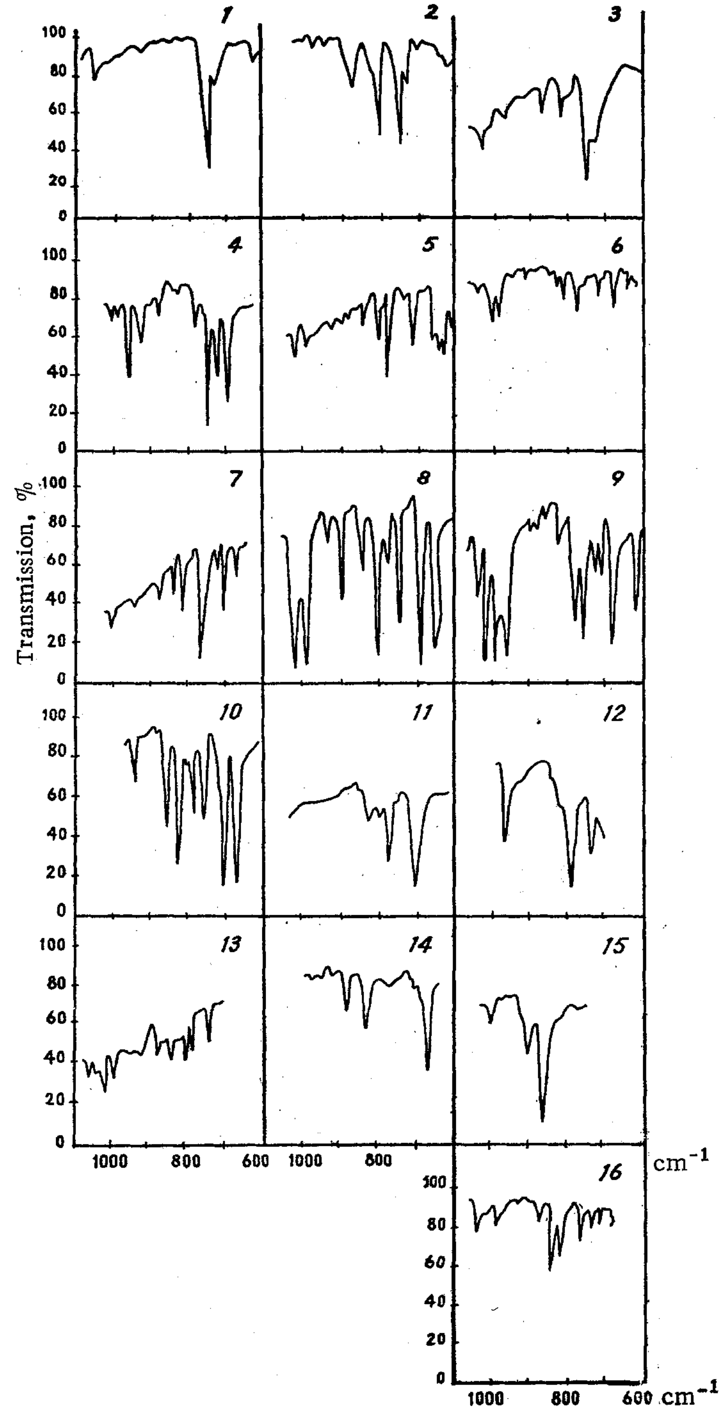
For example, the spectrum of α, α'-dipyridyl shows a band at 764 cm^{-1}, corresponding to a 1, 2-substituted benzene ring; the spectrum of γ, γ' -dipyridyl (fig. plot 12) has an intense band at 816 cm^{-1} (1, 4-substitution); α, β'-dipyridyl has an absorption band at 747 cm^{-1}, corresponding to 1, 2-substitution of the α ring, as well as bands at 717 and 772 cm^{-1}, corresponding to 1, 3-substitution of the β ring (fig. plot 4); the spectrum of β, β'-dipyridyl has bands at 791 and 707 cm^{-1}, corresponding to 1, 3-substitution (fig. plot 11).

A review of the spectra of the substituted dipyridyls gives convincing evidence of the possibility of applying these rules to a wider circle of compounds. Thus the spectra of the nitrile and monocarboxylic acid of α, α'-dipyridyl (fig. plots 2, 3) show bands corresponding to a substituted α-pyridine ring 753, 765 cm^{-1}; on the other hand, the occurrence of bands at 816, 801 cm^{-1} and 865, 862 cm^{-1} indicates 1, 2, 4-type substitution in the respective molecules of these compounds.

Regarding the compounds investigated, most detailed consideration has been given to the possibility of correlation for α, β'-dipyridyl derivatives. Plots 5-10 in the figure show that introduction of the substituents $-SO_3H$, $-COOH$, $-OH$, $-CN$ conditions appearance in the spectra of bands corresponding to a β-substituted pyridine ring 800–750 and 717–700 cm^{-1}. Further, new bands, corresponding to 1, 2, 4- type substitution also arise, which fully confirms the formula previously put forward for these compounds]:

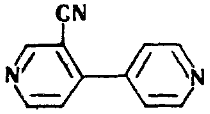


X = SO_3H, COOH, OH, CN.



IR spectra of dipyridyls and their derivatives: 1) α, α'-dipyridyl; 2) 5-nitryl-α,α'-dipyridyl; 3) α,α'-dipyridyl-5-carboxylic acid; 4) α,β'-dipyridyl; 5) α,β'-dipyridyl-5-carboxylic acid; 6) 5-hydroxy-α,β'-dipyridyl; 7) 5-cyano-α, β'-dipyridyl; 8) α,β'-dipyridyl-5-sulfonic acid; 9) Barium α,β'-dipyridyl-5-sulfonate; 10)potassium α,β'-dipyridyl-5-sulfonate; 11) β,β'-dipyridyl; 12) γ,γ'-dipyridyl; 13) γ,γ'-dipyridyl-3, 3', 5, 5'-tetrasulfonic acid; 14) barium γ,γ' -dipyridyl-3, 3', 5, 5'-tetrasulfonate; 15) anhydride of γ,γ'-dipyridyl-3, 3', 5, 5'-tetrasulfonic acid; 16) 3-cyano-γ,γ'-dipyridyl.

Of γ,γ'-dipyridyl derivatives, tetra-substituted ones and the mononitrile have been investigated. The spectrum of the latter (fig. plot 16) has a band at 809 cm^{-1}, — a 1, 4-substituted ring, and bands at 826 and 866 cm^{-1} are clearly visible, — 1, 2, 4-substitution. The formula of the mononitrile

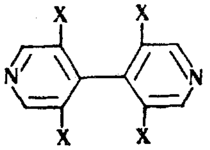


is in accordance with the above.

Characteristic Bands of Out-of-Plane Vibrations of C—H Bonds of Benzene and Dipyridyl Derivatives, cm^{-1}

Compound	Type of substitution					Plot no. in Fig.
	1,2	1,3	1,4	1,2,4	1,2,3,5	
Benzene derivative	760—740	800—770 710—690	833—810	825—805 885—870	850—840	
α, α'-dipyridyl	764					1
5-cyano-α, α'-dipyridyl	753			801, 865		2
5-COOH-α, α'-dipyridyl	765			816, 862		3
α, β'-dipyridyl	747	772, 717				4
5-COOH-α, β'-dipyridyl		782, 715		826, 871		5
5-OH-α, β'-dipyridyl		754, 709		809, 844		6
5-cyano-α, β'-dipyridyl		787, 708		831, 865		7
α, β'-dipyridyl-5-sulfonic acid		775, 702		824, 858		8
Ba α, β'-dipyridyl-5-sulfonate		766, 710 796		820, 857		9
K α, β'-dipyridyl-5-sulfonate		761, 715 787		823, 858		10
β, β'-dipyridyl		791, 707				11
γ, γ'-dipyridyl			816			12
γ, γ'-dipyridyl-3, 3', 5, 5'-tetrasulfonic acid					860	13
Ba γ, γ'-dipyridyl-3, 3', 5, 5'-tetrasulfonate					879	14
γ, γ'-dipyridyl-3, 3', 5, 5'-tetrasulfonic anhydride					868 828	15 16
3-Cyano-γ, γ'-dipyridyl			809		873	

The spectrum of γ, γ'-dipyridyl tetrasulfonic acid lacks bands, corresponding to 1, 4 substitution; instead, absorption at 825 and 860 cm^{-1} is observed. The positions of these bands are practically unchanged in the spectra of the Ba salt and anhydride of the acid. Bands at 879 and 868 cm^{-1} (slightly displaced in comparison with the bands for 1, 2, 3, 5-substituted benzene) indicate 1, 2, 3, 5-substitution, in complete agreement with the formula put forward for these compounds [2]:



Consideration of the region of plane deformation vibrations of C—H bonds (1000–1250 cm^{-1}) shows that these bands, as with benzene derivatives, are also characteristic. However, here the absorption is much weaker in intensity, and these bands often overlap bands of deformation and valence vibrations of functional groups, making their identification and use difficult.

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