

STUDY OF HYDROGEN BONDING IN 2,4- AND 3,5-XYLENOL

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Intermolecular hydrogen bonding exhibited by xylenols in different solvents was studied by infrared spectroscopy in the 700–1600 cm^{-1} region by Neuilly (1954) and by n.m.r. spectroscopy by Yamaguchi (1961), who noted that xylenols with one or more methyl group in the ortho position with respect to the OH group show weaker intermolecular hydrogen bonding than other xylenols. The difference in properties of xylenols was also commented on by Sears and Kitchen (1949), Buckingham (1960), Schaefer and Schneider (1960) and Bono (1956). The infrared absorption spectra of xylenols in different solutions in the fundamental OH frequency region were not apparently reported by any previous worker and an investigation was undertaken to record and compare the positions of OH stretching vibrational bands of xylenols in different environments in order to find out any evidence of difference in the hydrogen bonding behaviour of these compounds. In the present note preliminary results obtained in the case of 2, 4- and 3, 5-xyleneol have been reported.

The spectra were measured with a Perkin Elmer Model 21 Spectrophotometer with rock salt optics and calibration of spectra was made by recording the 3741 cm^{-1} absorption band of atmospheric water vapour. The xylenols and the solvents used were carefully purified and dehydrated. The accuracy of measurement in the position of the bands is $\pm 5 \text{ cm}^{-1}$.

The wave numbers of the OH vibrational bands due to 2, 4- and 3, 5-xyleneol in the pure state and in different solvents are given in Table I. The infrared spectra of dilute solutions of 3, 5- and 2, 4-xyleneol in CCl_4 show the free OH vibrational bands at 3622 and 3623 cm^{-1} respectively. In solution in benzene the band maximum shifts by about 57 cm^{-1} in the case of 3, 5-xyleneol and about 45 cm^{-1} in the case of 2, 4-xyleneol towards lower frequencies. This seems to indicate that in these cases some weak but definite intermolecular association takes place between molecules of xylenols and benzene, which is a π -electron donor, through the OH group and the π -electron.

In solutions in dioxane, ether and nitrobenzene, 3, 5-xyleneol shows intermolecular hydrogen bonding of different strengths with proton acceptor groups in the solvents through the OH group, as is evident from the shift of the OH band

from 3622 cm^{-1} in CCl_4 solution to 3340, 3345 and 3495 cm^{-1} respectively. Similar intermolecular hydrogen bonding is also exhibited by 2, 4-xylenol in which case the OH band shifts from 3623 cm^{-1} in CCl_4 solution to 3370, 3370 and 3518 cm^{-1} in solutions in dioxane, ether and nitrobenzene, respectively. The shifts in the OH vibrational band of 3, 5-xylenol in different solvents with respect to its

TABLE I
Position of OH vibrational band in cm^{-1}

Substance	Solution in						Pure
	carbon tetra chloride	chloroform	dioxane	ether	nitro benzene	benzene	
2, 4-Xylenol	3623	3613	3370	3370	3518	3578	3418
3, 5-Xylenol	3622	3611	3340	3345	3495	3565	3330*

*solid

position in the CCl_4 solution are thus larger than those observed in the case of 2, 4-xylenol. This may be due to the fact that in the latter molecule the CH_3 group which is in 2-position sterically hinders the OH group and affects the hydrogen bonding situation as suggested by Yamaguchi (1961) from n.m.r. studies. The corresponding shifts of the OH band in the cases of crystals of 3, 5-xylenol and the liquid film of 2, 4-xylenol indicate formation of intermolecular hydrogen bond in these states of aggregation also. The comparatively large shift in the case of 3, 5-xylenol in the solid state probably indicates presence of polymeric groups of intermolecularly associated molecules formed through OH...O bonds.

Further detailed study with these and other xylenols is in progress.

The authors are grateful to Professor S. C. Sirkar, D.Sc., F.N.I. for helpful discussions and to Professor G. S. Kastha, D.Sc., for kindly providing laboratory facilities. One of the authors (S.B.B.) acknowledges financial support by the C.S.I.R. (India) as a Pool Officer.

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