Tetrahedron Letters No. 14, pp. 1-7, 1959. Pergamon Press Ltd. Printed in
Great Britain.

HYDROGEN BONDING IN β-ARYL ETHANOLS

P. von R. Schleyer, Claude Wintner, Daniel S. Trifan* and Robert Bacskai*
Frick Laboratory, Princeton University, Princeton, N.J.

(Received 10 August 1959)

THE great potential of spectroscopic investigations of hydrogen bonding applied to the solution of configurational and conformational problems in organic chemistry is becoming more widely recognized. As part of a program of research in this field,[1] we have had occasion to examine a large number of nuclear and side-chain substituted β-phenyl ethanols.[2] Very recently, Mateos and Cram[3] have reported spectral observations of a number of diasteriomeric polysubstituted β-phenyl ethanols in the OH region of the infrared. Conclusions concerning the preferred conformations and the steric environments of the hydroxyl group were advanced. It is noteworthy that our interpretations differ from those of the California workers in almost all significant respects. We wish to record a portion of our results and to discuss the reasons for the differences in interpretation.

---

* Plastic Laboratory, Princeton University, Princeton, N.J.

[1] D. S. Trifan, L. Weinmann and L. P. Kuhn, J. Amer. Chem. Soc. 79, 6566 (1957); P. von R. Schleyer, D. S. Trifan and R. Bacskai, Ibid. 80, 6691 (1958).

[2] D. S. Trifan, R. Bacskai, P. von R. Schleyer and C. Wintner, Abstracts, 135th National Meeting of the Amer. Chem. Soc., Boston, Mass., April, 1959, p. 98-O; C. Wintner, A. B. Thesis, Princeton University, (1959).

[3] J. L. Mateos and D. J. Cram, J. Amer. Chem. Soc. 81, 2756 (1959).

Since 1936 evidence has been accumulating in the literature[4] that π -electron systems, such as aromatic rings, can function as weak proton acceptor groups in hydrogen bonding. β-Phenyl ethanol itself has been found by several investigators to be intramolecularly hydrogen bonded. Very dilute solutions of this compound in an inert solvent display two concentration independent peaks in the OH stretching region (2.75μ)[1,5] and first overtone region (1.4μ).[6] In their paper, Mateos and Cram did not consider the factor of OH ... π hydrogen bonding.

Our results with β-aryl ethanol, $ArCH_2CH_2OH$, are summarized in Table 1. Listed are the positions of the free peaks, the π -intramolecularly bonded peaks and the ratio of their apparent extinction coefficients. The differences in the two positions, $\Delta\nu$, is taken as a measure of the enthalpy of the hydrogen bond. In addition, the relative proton donor abilities of the various alcohols were determined by ascertaining the position of the intermolecular peak with n-butyl ether as the standard reference proton acceptor.

The effect of nuclear substitution can easily be predicted on theoretical grounds: two effects, working in opposing directions, should be present. For example, a p-nitro group would by its electrical character withdraw electrons from the ring, making it less able to interact with the hydroxyl proton. At the same time, the hydrogen bonding acidity of the side-chain OH group should be enhanced. Electron releasing substituents would

---

[4] For literature citations see ref. 1; also, refs. 5,6.

[5] D. Barnard, K. R. Hargrave and G. M. C. Higgins, J. Chem. Soc. 2845 (1956); A. W. Baker and A. T. Shulgin, J. Amer. Chem. Soc. **80**, 5358 (1958); H. Kwart and R. T. Keen, Ibid. **81**, 943 (1959).

[6] I. M. Goldman and R. O. Crisler, J. Org. Chem. **23**, 751 (1958).

TABLE 1[a]. β-Aryl ethanols, $ArCH_2CH_2OH$ (values in cm^{-1})

Aryl group	ν Free	ν Bonded	ε f/ε b[b]	Δν	Δν to Bu_2O[c]
p-Dimethylamino-phenyl	3631	3595	0.94	36	--
p-Aminophenyl	3633	3598	1.08	35	141
o-Aminophenyl	3632	3600	1.61	32	--
p-Methoxyphenyl	3633	3602	1.26	31	156
Mesityl	3632	3601_5	1.79	30_5	161
2-Naphthyl	3632	3602_5	1.34	29_5	158
1-Naphthyl	3632	3604	1.32	28	159
Phenyl	3631	3604	1.25	27	160
m-Methoxyphenyl	3631	3605	1.17	26	157
p-Chlorophenyl	3632	3612	1.36	20	171
m-Chlorophenyl	3632	3614	1.17	18	172
4-Pyridyl	3632	3619	1.32	13	--
o-Nitrophenyl	3631	3620	1.40	11	181
p-Nitrophenyl	3632	3621_5	1.44	10_5	182
2-Pyridyl[d]	3632	3623	--	9	--
Cyclohexyl	3635	none	--	--	147
1-Cyclohexenyl	3632	3579	1.75	53	149

[a] Perkin-Elmer Model 21 Spectrophotometer, LiF prism. Solutions about 0.005 M in CCl_4. Machine calibrated several times daily against water vapor; the values are corrected averages of several runs and should be accurate to ±1 or 2 cm^{-1}.

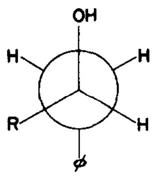
[b] Ratio of the apparent extinction coefficients. Since there is considerable overlap of peaks, these are not very accurate, but can be used for approximate comparisons. These are not measures of the relative fractions of bonded and free molecules because of differences in extinction coefficients.

[c] Probable error: ± 3 cm^{-1}. Solutions about 1 M in Bu_2O.

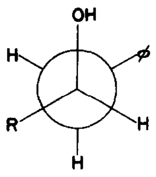
[d] Intramolecular bonding to N very strong; $\Delta\nu = 205$.

have the opposite effects. In the aromatic carbinols, $ArCH_2OH$, these effects very largely counterbalance each other.[2] The Bu_2O data of Table 1 reveal that the interposition of the additional methylene group in the side chain of the β-aryl ethanols has resulted in a marked reduction, but not a complete elimination, of the second effect. In consequence, the hydrogen bonding basicity of the aromatic ring is the more important factor and marked differences in both the free-bonded $\Delta\nu$ values and their intensity ratios are noted. The $\Delta\nu$ values correlate very well with the Hammett σ constants.

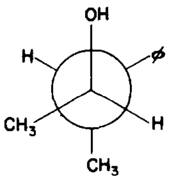
Conformational influences are illustrated by the results with side-chain alkyl substituents (Table 2). α-Substitution decreases the proton donor ability of the OH group, which is known to be in the order primary alcohols > secondary > tertiary.[7] Therefore, $\Delta\nu$ decreases. However, the relative intensity of the bonded peak increases. For steric reasons an increased percentage of molecules are present in the bonding skew conformation II and a decreased percentage in the staggered conformation I, in which intramolecular hydrogen



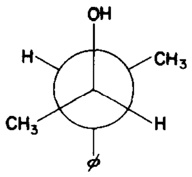
I



II



III



IV

---

[7] L. P. Kuhn, J. Amer. Chem. Soc. 74, 2492 (1952).

bonding is not possible. β-Phenyl ethanol itself must exist to an appreciable extent in the skew conformation (II, R=H). The energy of the intramolecular bond, estimated by our temperature studies to be about 1.4 kcal, overcomes the stereo-electric factors which usually favor the staggered arrangement.

β-Substitution increases both $\Delta\nu$ and the relative intensity of the bonded peak. The latter result is easily explained on conformational grounds similar to the above. Perhaps angle deformation[7] ("Thorpe - Ingold effect") contributes to the former.

The other polysubstituted compounds represent combinations of these effects. The diasteriomeric 3-phenyl-2-butanols, typical of the compounds examined by Mateos and Cram, are worthy of further comment. The $\Delta\nu$ values of the two isomers do not differ significantly, but the free/bonded intensity ratios are strikingly different. In the threo isomer the bonded band is much the stronger of the two, but the erythro compound displays a more intense free peak. Conformation III, with the phenyl and the OH in a skew relationship, is of major importance with the threo isomer, but the staggered rotomer, IV, must be more favorable for the erythro material.

Using a spectrometer equipped only with a low resolution NaCl prism, not capable of resolving the details of the intramolecular hydrogen bonding (discussed above), Mateos and Cram examined the intermolecular (OH...O type) dimerization of their alcohols. The threo isomer had a less intense dimer peak than the erythro, but both absorbed at about the same position. The intensity relationships of the so-called "free" peaks were in the reverse order with

TABLE 2. Effect of side chain substitution in β-phenyl ethanols (cm^{-1})

Substituents	ν Free	ν Bonded	$\varepsilon f/\varepsilon b$	Δν	Δν to Bu_2O
None	3631	3604	1.25	27	160
α-Methyl	3622_5	3602	0.81	20_5	146
α-_t_-Butyl	3631	3605	0.52	26	149
α,α-Dimethyl	3611	3594	0.94	17	133
β-Methyl	3636	3603	0.98	33	155
β-Ethyl	3635	3601	0.86	34	162
β,β-Dimethyl	3639	3601	0.86	38	161
α,β-Dimethyl-_threo_	3622	3595	0.45	27	145
α,β-Dimethyl-_erythro_	3629	3602	1.50	27	151
α,α,β-Trimethyl	3614	3591	0.89	23	127
α,α,β,β-Tetramethyl	3619	3593	0.70	26	136
trans-2-Phenylcyclohexanol-1	3621w	3598	0.23	23	147

the _threo_ isomer appearing to absorb at very much lower frequencies. Both the apparently lower Δν (dimer) and the smaller amount of dimerization of the _threo_ compounds were explained on the presumption of a more hindered average environment of the hydroxyl group.

A more convincing explanation of these results is as follows. The _threo_ isomer is much more highly _intramolecularly_ bonded. The "free" peak observed by Mateos and Cram for this compound is in reality predominantly the intramolecularly π-bonded peak. In actual fact the positions of the free peaks for the two diasteriomers are not very different, and the Δν -dimer values are quite comparable (dimer positions: _threo_, 3496; _erythro_, 3498). Steric effects, therefore, are not influencing appreciably the strength (Δν) of the intermolecular hydrogen bonds in these compounds. While more hindered alcohols in general do form a smaller percentage of dimer, it seems likely that the less intense dimer peak of the threo isomer is due principally to competitive intramolecular bonding..Similar reinterpretations are necessary for the other diasteriomeric pairs reported by Mateos and Cram. It is clear that the factor of OH...π hydrogen bonding must be taken into account in interpreting the NMR and other physical properties of these compounds. Such hydrogen bonding contributes importantly to the energy relationships of the possible conformations of molecules.

The points raised here will be elaborated and the effects of polyphenyl substitution and incorporation of these functional groups in cyclic systems will be described in forthcoming publications. We have noted similar effects in the spectra of alcohols possessing other proton accepting functional groups.

Acknowledgement - We are grateful to Mr. Lewis Robinson for redetermining the spectra of all of the compounds.