# Equilibrium Study of Biphenyl-2-ol by Infrared Spectroscopy

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Biphenyl-2-ol is composed of *cis*- and *trans*-isomers in CCl_4 solution. The percentage of *trans*-isomer is estimated by comparison of i.r. intensities for solutions in basic solvents; the proportion of *cis*-isomer is obtained by comparison with 2,6-diphenylphenol.

It is now well known [1] that in CCl_4 solution biphenyl-2-ol (1) is composed of *cis*- and *trans*-isomers, corresponding


trans   cis
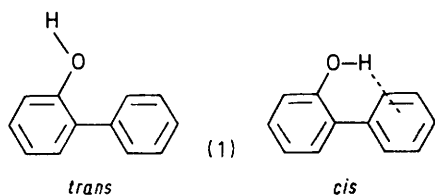
to an OH $\cdots$ π interaction and a free hydroxy-group, respectively. However, the proportion of the two

isomers has not been reported. In general, the measured *cis* : *trans* integrated intensity ratio for the OH stretching vibration does not give the relative percentage of the two isomers. In this paper, estimations of the percentage of *cis*- and *trans*-isomers were carried out by two different i.r. spectroscopic methods. Estimation of the *trans*-percentage was based on the effect of basic solvents which produced only the *trans*-form of biphenylols (1)— (4). The *cis*-percentage was estimated by application of

[1] M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, 1961, **34**, 1395.

the Hammett equation to 4-substituted 2,6-diphenyl-phenols in which only the cis-form is possible.
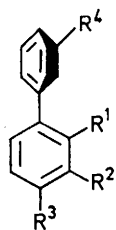
(1) R^1 = OH, R^2 = R^3 = R^4 = H
(2) R^2 = OH, R^1 = R^3 = R^4 = H
(3) R^3 = OH, R^1 = R^2 = R^4 = H
(4) R^2 = R^4 = OH, R^1 = R^3 = H
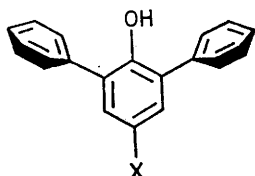
(5) X = NO_2
(6) X = CN
(7) X = H
(8) X = OCH_3
(9) X = NH_2

RESULTS AND DISCUSSION

Application of Solvent Effects to the Equilibrium Study.—The integrated intensities of the hydroxy-group frequency of the biphenylols (1)—(4) were measured for CCl_4 solutions and for basic solvents as proton acceptors (Table 1). In the basic solvents, the

TABLE 1

Integrated intensities and intensity ratios of biphenylols in CCl_4 and basic solvents

Integrated intensity 10^{-4} A/l mol^{-1} cm^{-2}

Com-	CCl_4		Solvents			
pounds	trans	cis	$CH_3C{\equiv}N$	THF	$C_4H_4O_2$ [a]	CH_3COCH_3
(1)	0.18	1.25	6.83	7.16	7.22	7.57
(2)	1.37		7.90	8.77	8.32	8.90
(3)	1.12		7.24	7.52	7.79	7.71
(4)	2.29		14.58	14.98	15.84	15.74

Integrated intensity ratio

Com-pound	Solvents				
pair	$CH_3C{\equiv}N$	THF	$C_4H_4O_2$ [a]	CH_3COCH_3	Average
A(1)/A(2)	0.86	0.82	0.87	0.85	0.85
A(1)/A(3)	0.94	0.95	0.93	0.98	0.95
A(1)/A(4)	0.47	0.48	0.46	0.48	0.47

[a] Dioxan.

hydroxy-group of the biphenylols is considered to fully interact with the lone pair electrons of the solvent. Therefore, as reported by Ōki *et al.*,[1] biphenyl-2-ol is forced into the *trans*-form,[2,*] because the OH$\cdots\pi$ interaction of the *cis*-form is not significant.

On the basis of the trend reported by Cole *et al.*,[3] it was found from Table 1 that the integrated intensity ratios for each compound remained constant regardless of the change of solvent. The constancy of integrated

* This compound exhibits only a single broad band attributed to intermolecular hydrogen bonding.

[2] T. Kinugasa, unpublished data.
[3] A. R. H. Cole, L. H. Little, and A. J. Michell, *Spectrochim. Acta*, 1965, **21**, 1169.
[4] L. J. Bellamy, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 1961, 4762.
[5] O. Nillius and H. Kriegsmann, *Spectrochim. Acta*, 1970, **26A**, 121.

intensity ratios for other compounds having a hydroxy-group was tested using data reported in the literature [4,5]

$$[A(1)/A(n)] = K \text{ (constant)}, \quad n = 2—4 \quad (1)$$

(Table 2), thus establishing the utility of the method. From this, a calculated integrated intensity due to the *trans*-only form of biphenyl-2-ol in CCl_4, $A'(1)_t$, can be

TABLE 2

Integrated intensities and intensity ratios of silanols [a]

Integrated intensity $(10^{-4}$ A/l mol^{-1} $cm^{-2})$

	Solvent			
Compounds	$CHCl_3$	CCl_4	C_6H_{12} [b]	CS_2
$Ph_2MeSiOH$ (I)	1.72	1.28	1.09	1.51
$PhMe_2SiOH$ (II)	1.59	1.17	1.03	1.30
Me_3SiOH (III)	1.37	1.00	0.97	1.07
Et_3SiOH (IV)	1.31	0.98	0.83	1.03
Pr^n_3SiOH (V)	1.28	0.96	0.81	0.99
Bu^n_3SiOH (VI)	1.11	0.93	0.79	0.97

Integrated intensity ratios

	Solvent			
Compound	$CHCl_3$	CCl_4	C_6H_{12} [b]	CS_2
A(I)/A(II)	1.08	1.09	1.06	1.16
A(I)/A(III)	1.26	1.28	1.24	1.41
A(I)/A(IV)	1.31	1.31	1.31	1.47
A(I)/A(V)	1.34	1.33	1.35	1.53
A(I)/A(VI)	1.55	1.38	1.38	1.56

[a] Data are taken from ref. 5. [b] Cyclohexane.

estimated by the interpolation of the K value in equation (1) into (2), assuming the constancy of the integrated intensity ratios with the change from basic solvent to CCl_4. Thus, equation (3) affords the average percentage of *trans*-isomer.

$$[A(n)]_{CCl_4}K = A'(1)_t \quad (2)$$

$$\% \text{ trans} = 100 [A(1)_t/A'(1)_t] = ca. \text{ 16—17\%} \quad (3)$$

Application of Hammett Treatment to the Equilibrium Study.—Since 2,6-diphenylphenol (7) possesses the *cis*-only form in CCl_4,[6] an estimate of the integrated intensity due to the hydroxy-group of the *cis*-only form of biphenyl-2-ol can be obtained from the measured intensity for 2,6-diphenylphenol by applying a correction for the polar effect of an *ortho*-phenyl substituent. Therefore, the $\sigma_0(ortho)$ value for the phenyl substituent was estimated by the use of the Hammett equation.

The values for the OH stretching frequencies of 3- and 4-substituted phenols [7] were satisfactorily correlated by the Yukawa–Tsuno equation [8] (4) where (X) is the sub-

$$\nu OH_{(X)} - \nu OH_{(H)} = -13.97\sigma - 10.62 (\sigma^- - \sigma) + 0.02 \quad (4)$$
$$(s \text{ 0.81 } cm^{-1}, r \text{ 0.993})$$

stituent and the σ constants are taken from ref. 9. It is

[6] M. Ōki, H. Hosoya, and H. Iwamura, *Bull. Chem. Soc. Japan*, 1961, **34**, 1391.
[7] L. L. Ingraham, J. Corse, G. F. Bailey, and F. Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.
[8] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.
[9] J. A. Gordon and R. A. Ford, ' The Chemist's Companion. A Handbook of Practical Data, Techniques, and References,' Wiley, New York, 1972, pp. 152—153.

reported [1] that the free hydroxy stretching frequencies for 2-phenyl-4(or-5)-substituted phenols also show a good Yukana–Tsuno correlation [equation (5)]. Equ-

$$vOH_{(X)} - vOH_{(H)} =$$
$$-13.62\sigma - 15.45\ (\sigma^- - \sigma) + 0.356 \quad (5)$$
$$(s\ 1.40\ cm^{-1},\ r\ 0.996)$$

ation (5) has ρ and r values sufficiently close to those of equation (4) to suggest that the o-phenyl substituent has an effectively constant effect. This justifies the interpolation of vOH (free) for biphenyl-2-ol into equation (4) in order to estimate the σ_0 value for the o-phenyl substituent.

$$3\ 607.4 - 3\ 610.1 =$$
$$-13.97\sigma - 10.62\ (\sigma^- - \sigma) + 0.02 \quad (6)$$

On the assumption that the $(\sigma^- - \sigma)$ term is small, the σ_0 value for an o-phenyl substituent can be estimated by use of equation (6) (σ_0 $ca.$ 0.2). Furthermore, a Yukawa–Tsuno equation when applied to the integrated intensities (Table 3) for 4-substituted 2,6-diphenyl-

TABLE 3

Integrated intensities of 4-substituted 2,6-diphenylphenols

	(5)	(6)	(7)	(8)	(9)
$10^{-4}\ A/$ mol^{-1} cm^{-2}	2.28	2.08	1.60	1.46	1.30

phenols gives equation (7) whence the integrated inten-

$$A_{(X)} - A_{(H)} = 0.47\sigma + 0.667\ (\sigma^- - \sigma) + 0.002 \quad (7)$$
$$(s\ 0.015A \times 10^{-4}\ mol^{-1}\ cm^{-2},\ r\ 1.000)$$

sity, A', for one o-phenyl group is given by equation (8).

$$A' = 0.47 \times 0.2 = 0.094 \quad (8)$$

From this, it is possible to obtain the percentage of the

[10] C. Häussermann and H. Teichmann, $Ber.$, 1894, **27**, 2108.
[11] S. Ueji, N. Ueda, and T. Kinugasa, $J.C.S.$ $Perkin$ II, 1976, 178.

cis-isomer of biphenyl-2-ol according to equation (9).

$$\%\ cis = A(1) \times 100/A(7) - A' = ca.\ 83\% \quad (9)$$

Thus, the percentage of cis-isomer was estimated from the Hammett treatment to be $ca.$ 80—85%.

We conclude that the results of two different methods lead to satisfactory agreement, $i.e.$, the $trans$-isomer is present in $ca.$ 16—17% with the cis-isomer in $ca.$ 80—85% for biphenyl-2-ol in CCl$_4$.

EXPERIMENTAL

Compounds (1)—(3) were commercial samples, recrystallized before use. Compound (4) was prepared by a literature method.[10] Compounds (5) and (7)—(9) were prepared earlier.[11]

4-Hydroxy-3,5-diphenylbenzonitrile (6).—Diazotization of 4-amino-2,6-diphenylphenol (3 g) [12] in glacial acetic acid (40 ml) at 0 to $-5°$ afforded 4-diazo-2,6-diphenylcyclohexa-2,5-dienone (2.4 g), m.p. 130° (decomp.) (from acetone). To a solution of the diazo-ketone (2 g) in acetic acid (40 ml) and concentrated hydrochloric acid (1.8 ml) was added potassium iodide (2.6 g) at room temperature. Work-up in the usual way gave a viscous oil which was purified by chromatography on silica gel to give 4-iodo-2,6-diphenylphenol (1.8 g). The iodo-compound (1 g) was treated with copper(I) cyanide–pyridine [with copper(II) sulphate and p-cyanotoluene as catalyst] under reflux for 9 h. The usual work-up afforded the $nitrile$ (6) (0.5 g), m.p. 159.5—160.5° (from methanol) (Found: C, 84.05; H, 4.9; N, 5.25. C$_{19}$H$_{13}$ON requires C, 84.1; H, 4.85; N, 5.15%).

I.r. spectra were measured in the 3 μm region with a JASCO 402G grating spectrometer at a spectral slit width of 2 cm^{-1} at 29°. Other experimental conditions for recording spectra were as reported previously.[11]

[12] E. Charles, S. Jones, and J. Kenner, $J.$ $Chem.$ $Soc.$, 1931, 1842.