Estimation of the Energy of Hydrogen Bonds Formed in Crystals. II. Phenols

By Ariyuki AIHARA

(Received July 20, 1959)

The OH···O bonding is the most familiar of the hydrogen bonds and has already been widely explored; the phenomena in ice (or water), alcohols and acids have been studied in special detail. Nevertheless, data on hydrogen bonds in phenols are not so ample in literatures as those of alcohols and acids, at least so far as the crystalline state is concerned. In this connection the author has chosen, as the first of the series of investigation on the strength of hydrogen bond formed in crystals, a number of phenols of various kinds, and examined them following the procedure proposed in a previous paper[1]. The materials here examined include those the molecules of which have bulky substituents close to hydroxyl groups, preventing the formation of hydrogen bonds, such as *o*-hydroxydiphenyl or 2,4,6-tri-*tert*-butylphenol, and also 1- and 2-naphthols, which may be classified as phenols in a wider sense.

Experimental

The apparatus used for the measurement of sublimation pressures is the same as was used before[1].

Most of the materials dealt with in this paper are commercial products and purified by fractional sublimation before use. Four of them, i. e. 4-*tert*-butylphenol, 2-*tert*-butyl-4-methylphenol, 2-methyl-4-*tert*-butylphenol and 2,4,6-tri-*tert*-butylphenol were kindly sent by Professor M. Davies, Univ. Wales; these were purified in the same way as the others except 2-methyl-4-*tert*-butylphenol, which was fractionally distilled and measured in liquid state.

Results and Discussion

Sublimation Pressures. — Results of the measurements of sublimation pressures of thirteen phenols are shown in Tables I—XIII, respectively, together with vapor pressure equations obtained by the method of least squares.

TABLE I. SUBLIMATION PRESSURE OF *p*-HYDROXYDIPHENYL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^3$
327.6	3.88	337.7	1.10
329.1	4.54	339.4	1.33
329.8	4.94	342.6	1.84
331.2	5.67	345.6	2.46
335.1	8.48	347.6	3.02

$\log P(\text{mmHg}) = 12.056 - 5067.8/T$: m. p. 166°C

TABLE II. SUBLIMATION PRESSURE OF *o*-HYDROXYDIPHENYL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
292.0	0.819	302.4	2.71
294.4	1.12	304.4	3.33
296.0	1.31	306.6	4.26
297.3	1.55	308.3	5.13
299.7	2.01	310.6	6.50
300.4	2.13	313.8	8.73

$\log P(\text{mmHg}) = 11.754 - 4331.0/T$: m. p. 59.0°C

1) A. Aihara, This Bulletin, **32**, 1242 (1959).

TABLE III. SUBLIMATION PRESSURE OF *p*-BENZYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
313.8	2.75	323.8	8.48
315.4	3.29	326.1	10.9
317.1	4.07	328.3	14.2
318.5	4.71	330.7	18.1
320.0	5.65	332.1	21.1
321.8	6.76	335.0	29.8

$\log P\,(\text{mmHg}) = 12.600 - 5072.2/T$: m. p. 85.1°C

TABLE IV. SUBLIMATION PRESSURE OF *p*-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
281.0	4.57	289.7	13.6
281.5	5.04	293.5	21.3
282.3	5.38	295.5	27.5
283.8	6.72	299.0	40.5
285.1	7.78	301.2	52.4
287.8	10.8	303.6	67.9

$\log P(\text{mmHg}) = 12.332 - 4402.1/T$: m. p. 100.2°C

TABLE V. SUBLIMATION PRESSURE OF 2-*tert*-BUTYL-4-METHYLPHENOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
274.3	0.931	283.6	2.89
276.5	1.22	286.1	3.85
279.0	1.64	288.0	4.63
279.6	1.75	292.0	7.28
281.0	2.13	293.4	8.46

$\log P(\text{mmHg}) = 11.685 - 4035.9/T$: m. p. 53.4°C

TABLE VI. VAPOR PRESSURE OF 2-METHYL-4-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
275.3	0.692	286.9	2.59
277.4	0.895	288.9	3.33
279.5	1.15	292.6	4.78
282.9	1.69	294.5	5.74
285.6	2.32	297.2	8.33

$\log P(\text{mmHg}) = 11.199 - 3952.3/T$:
b. p. 125°C (15 mmHg)

TABLE VII. SUBLIMATION PRESSURE OF THYMOL

T°K	P (mmHg) $\times 10^3$	T°K	P (mmHg) $\times 10^3$
273.9	1.12	282.2	2.92
275.1	1.26	286.6	4.86
276.8	1.56	290.7	7.45
278.5	1.92	294.7	11.31

$\log P(\text{mmHg}) = 11.361 - 3921.0/T$: m. p. 49.5°C

TABLE VIII. SUBLIMATION PRESSURE OF 2,4,6-tri-*tert*-BUTYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
291.7	3.07	301.6	9.55
293.4	3.63	304.5	12.9
295.2	4.52	306.2	15.6
297.4	5.83	309.7	22.9
299.7	7.63	312.9	30.9

$\log P(\text{mmHg}) = 11.507 - 4383.1/T$: m. p. 131.2°C

TABLE IX. SUBLIMATION PRESSURE OF *p*-FORMYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^3$
312.0	3.51	322.9	1.10
313.5	3.95	325.1	1.39
315.1	4.89	327.4	1.74
316.8	5.68	331.2	2.55
318.7	7.08	333.0	3.15
320.8	8.95	335.9	4.32

$\log P(\text{mmHg}) = 11.795 - 4762.3/T$: m. p. 118.5°C

TABLE X. SUBLIMATION PRESSURE OF *p*-ACETYLPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
320.5	4.07	337.5	23.8
323.0	5.38	339.9	32.1
326.0	7.33	342.3	40.8
328.3	9.47	345.0	53.0
332.2	14.0	347.4	65.5
335.7	20.5	348.9	72.5

$\log P(\text{mmHg}) = 12.216 - 5003.5/T$: m. p. 109.8°C

TABLE XI. SUBLIMATION PRESSURE OF *p*-METHOXYPHENOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
278.8	3.55	288.7	12.8
279.6	3.95	292.1	19.8
282.1	5.33	293.9	25.4
283.4	6.48	295.7	30.9
285.4	8.38	297.9	40.4
286.9	10.2	300.1	52.9

$\log P(\text{mmHg}) = 13.132 - 4624.5/T$: m. p. 56.4°C

TABLE XII. SUBLIMATION PRERSURE OF 1-NAPHTHOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
298.2	5.37	309.3	21.0
299.6	6.49	311.3	26.6
300.2	7.00	312.0	28.3
301.3	8.05	314.3	36.1
302.4	9.25	315.1	38.9
303.3	10.3	317.6	51.5
304.8	12.4	319.6	62.7
305.3	13.1	321.8	76.7
306.9	15.9	323.4	89.0
307.9	18.1		

$\log P(\text{mmHg}) = 13.074 - 4873.0/T$,
(below 312.6°K):
$\log P(\text{mmHg}) = 11.526 - 4389.1/T$,
(above 312.6°K):
m. p. 97.0°C: t. p. 39.4°C

TABLE XIII. SUBLIMATION PRESSURE OF 2-NAPHTHOL

T°K	P (mmHg) $\times 10^4$	T°K	P (mmHg) $\times 10^4$
298.8	1.82	307.1	5.29
300.0	2.11	309.4	7.04
301.9	2.73	312.0	9.57
302.4	2.94	314.9	13.1
302.8	3.06	316.4	15.3
303.6	3.36	320.0	22.5
304.7	3.89	324.0	33.6
305.3	4.16	327.8	50.0
306.5	4.90	331.8	71.4

$\log P(\text{mmHg}) = 13.356 - 5108.6/T$, (below 312.3°K):

$\log P(\text{mmHg}) = 11.660 - 4578.9/T$, (above 312.3°K):

m. p. 123°C: t. p. 39.1°C

The linear relation between $\log P$ and $1/T$ has been found quite satisfactory for all the measurements except those of 1- and 2-naphthols, both of which have shown transitional changes of $\log P \sim 1/T$ curves at about 39°C. To confirm this change, careful measurements of sublimation pressures were made repeatedly, and from the intersections of two lines representing $\log P \sim 1/T$ relations for both phases, 39.4 and 39.1°C have been obtained as transition points of 1-naphthol and 2-naphthol, respectively (Fig. 1). As it is not proper to conclude the existence of a transition by the measurement of sublimation pressures alone, especially when the heat of transition is small, a thermal analysis of these substances is now in progress and the results will be published later.

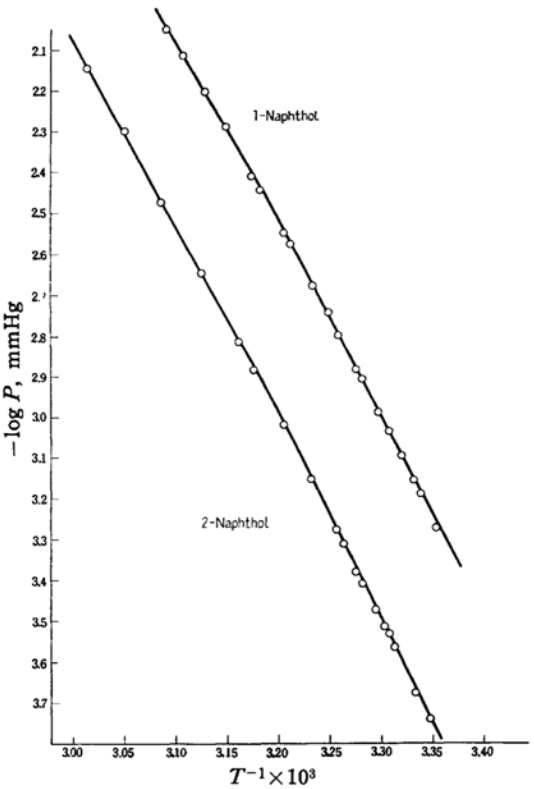


Fig. 1. Sublimation pressures of 1- and 2-naphthols.

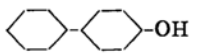
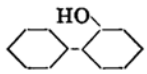
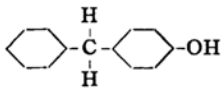
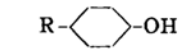
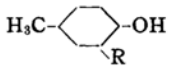
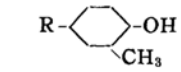
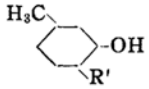
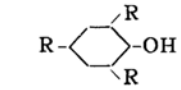
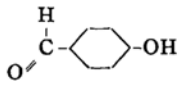
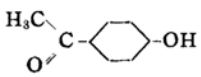
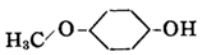
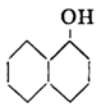
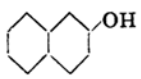
Balson[2] has also measured the sublimation pressure of thymol. However, his result, $\log P = 14.201 - 4766/T$, $\Delta H = 21.8$ kcal./mol., differs appreciably from the author's, the sublimation pressure being lower and the heat of sublimation being greater than the author's in the temperature range of the author's measurement. Considering the structure of this molecule Balson's value for the heat of sublimation of thymol seems to be too large.

Energy of Hydrogen Bond.—In Table XIV, the heats of sublimation of thirteen phenols, hypothetical lattice energies obtained assuming the additivity of lattice energies, and the energies of hydrogen bonds estimated by the procedure proposed before are shown by letters, ΔH, $\Delta H'$ and E, respectively. The changes of standard free energies at 298.2°K, $\Delta G^{298.2}$, and of entropies, ΔS, on sublimation are also shown in the table.

Let us first consider the case where the formation of OH···O bond seems rather difficult or almost impossible due to the presence of bulky substituted groups, such as phenyl and *tert*-butyl, in the vicinity of OH groups. Four compounds, i. e. *o*-hydroxydiphenyl, 2-*tert*-butyl-4-methylphenol, thymol and 2, 4, 6-tri-*tert*-butylphenol may fall in this category. As can be seen in Table XIV, the estimated values of hydrogen bonds for *o*-hydroxydiphenyl and 2-*tert*-butyl-4-methylphenol are negligibly small, being in fair agreement with the experimental results of infrared and ultraviolet absorption by Mecke[3], Coggeshall[4] and Josien[5]. According to Coggeshall[4], a phenol with one ortho position occupied by a *tert*-butyl and the other unoccupied, such as 2-*tert*-butyl-4-methylphenol, is partially hindered in forming a hydrogen bond. This means that one might expect, at least, a small

2) E. W. Balson, *Trans. Faraday Soc*. **43**, 54 (1947).
3) R. Mecke and G. Rossmy, *Z. Elektrochem.*, **59**, 866 (1955).
4) N. D. Coggeshall and A. S. Glessner, Jr., *J. Am. Chem. Soc.*, **71**, 3150 (1949); N. D. Coggeshall and E. L. Saier, ibid., **73**, 5414 (1951).
5) M. L. Josien, N. L. Fuson and C. J. Lee, *Phys. Rev.*, **83**, 486 (1951).

TABLE XIV. VALUES OF THERMODYNAMIC FUNCTIONS AND ENERGIES OF HYDROGEN BOND

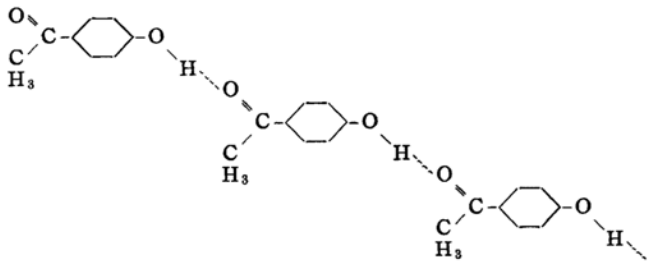
Compounds	ΔH kcal./mol.	$\Delta H'$ kcal./mol.	E kcal./mol.	$\Delta G^{298.2°}$ kcal./mol.	ΔS cal./deg. mol.
	23.19±0.12	20.0	3.2	10.67±0.23	42.0±0.4
	19.82±0.12	20.0	−0.2	7.70±0.24	40.6±0.4
	23.21±0.15	22.0	1.2	9.94±0.29	44.5±0.5
	20.14±0.08	16.5	3.6	7.24±0.16	43.3±0.3
	18.47±0.10	18.5	0.0	6.46±0.21	40.3±0.4
	18.09*±0.19	18.5	—	6.74*±0.38	38.1*±0.7
	17.94±0.09	16.5	1.4	6.37±0.18	38.8±0.3
	20.06±0.12	27.5	−7.4	8.29±0.24	39.5±0.4
	21.79±0.18	14.5	7.3	9.63±0.35	40.8±0.6
	22.90±0.16	16.5	6.4	10.16±0.31	42.7±0.5
	21.16±0.10	15.0	6.2	7.17±0.20	46.9±0.3
	22.30±0.17 (20.08±0.32)	17.5	4.8	8.39±0.33 (8.28±0.62)	46.6±0.6 (39.6±1.0)
	23.38±0.12 (20.95±0.18)	17.5	5.9	9.09±0.24 (8.97±0.35)	47.9±0.4 (40.2±0.6)

R=C(CH$_3$)$_3$, R'=CH(CH$_3$)$_2$

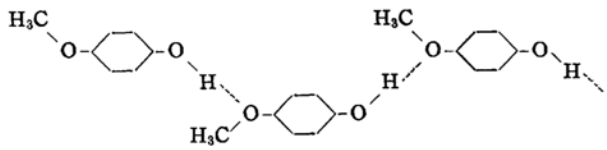
* For liquid state.

value of hydrogen bond energy for this compound instead of zero as shown in Table XIV. This discrepancy must be partly due to the difference in the states of the compound when it was examined, the one being solid and the other in solution, and partly due to the uncertainty of the method of estimation of hydrogen bond energy in this work. Thymol is a phenol with one ortho position occupied by an isopropyl group which is less powerful than *tert*-butyl in hindering the access of OH group of other molecules. Therefore, the energy of hydrogen bond in this compound, 1.4 kcal./mol., would be reasonable. A large negative value was obtained for 2, 4, 6-tri-*tert*-butylphenol. There will be no objection against believing that the OH group of this molecule is quite free from any intermolecular hydrogen bond, being protected by *tert*-butyl groups on both ortho positions, as was confirmed by Coggeshall[4] and Davies[6], by means of

6) M. Davies and R. J. Meakins, *J. Chem. Phys.*, **26**, 1584 (1957).



or



infrared technique and dielectric method in microwave region, respectively. Therefore, the large difference between ΔH and $\Delta H'$ for 2,4,6-tri-*tert*-butylphenol must be ascribed to the failure of the assumption, for this compound, of the additivity of lattice energy. This is understandable when the fact is taken into consideration that three *tert*-butyl groups of this molecule are bulky enough to screen a phenyl nucleus, to which they are attached, from the others, thereby causing the decrease of the effect of dispersive force due to the phenyl group to a greater extent. It is likely, therefore, that the *tert*-butyl groups are mainly responsible for dispersive attraction in this case, as was found with a system of SF_6 and CF_4, where the intermolecular attraction was discussed as due to halogen atoms of the molecules exclusively[7,8].

The heat of vaporization of 2-methyl-4-*tert*-butylphenol, 18.1 kcal./mol., is almost the same as the heat of sublimation of 2-*tert*-butyl-4-methylphenol, 18.5 kcal/mol.; this means that the OH···O bond in the crystal of the former should be stronger than that of the latter, as predicted from their molecular structures.

The hydrogen bond energies for *p*-hydroxydiphenyl and *p*-*tert*-butylphenol, 3.2 and 3.6 kcal./mol., respectively, are almost of the same order of magnitude, but somewhat smaller than the value obtained for phenol by Nitta and Seki, 4.5 kcal./mol.[9] This is probably due to a steric effect of large substituents in para positions rather than to any change of proton donating (or accepting) power of the OH groups. This effect is much more enhanced in the case of *p*-benzylphenol, obtained energy being 1.2 kcal./mol.

Comparatively large values of the energies of hydrogen bonds were obtained for *p*-formylphenol, *p*-acetylphenol and *p*-methoxyphenol, i.e. 7.3, 6.4 and 6.2 kcal./mol., respectively. It is interesting to note that these molecules have a possibility of making head-to-tail associations by hydrogen bonds.

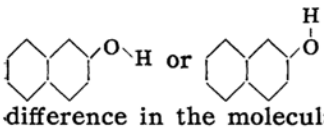
Then, the proton-donating power of OH and, at the same time, the proton-accepting power of O atoms of O=C and O–CH_3 groups must be increased appreciably, resulting in the increase of the strength of hydrogen bonds formed. As the crystal structures of these substances have not been analyzed as yet, a definite conclusion can not be drawn with regard to the mode of association of these molecules. Still, it will be quite safe to say that the OH···O bonds formed by these molecules are much stronger than those by other molecules mentioned above. The values for OH···O bonds obtained here can be compared with the energies of association of carboxylic acids in gaseous state, ~7 kcal./mol. (monomer), obtained by Taylor[10] and Nash[11]. Incidentally the pK_a values[12] of *p*-formylphenol, *p*-acetylphenol and *p*-methoxyphenol, which can be taken as the measure of proton-donating power of these molecules, 7.66, 7.95, 10.20, respectively, (in water at 25°C), support the correctness of the order of strength of

7) G. Thomaes, *J. chim. phys.*, **49**, 323 (1952).
8) J. S. Rowlinson, *J. Chem. Phys.*, **20**, 337 (1952).
9) I. Nitta and S. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **69**, 143 (1948); S. Seki, H. Chihara and K. Suzuki, "Hydrogen Bond", Iwanami-Shoten, Publishers, Tokyo (1956), p. 41.
10) M. D. Taylor, *J. Am. Chem. Soc.*, **73**, 315 (1951); M. D. Taylor and J. Bruton, ibid., **74**, 4151 (1952).
11) E. W. Johnson and L. K. Nash, ibid., **72**, 547 (1950); R. E. Lundin, F. E. Harris and L. K. Nash, ibid., **74**, 743, 4654 (1952).
12) E. A. Braud and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York (1955), p. 589, 598.

hydrogen bonds for these phenols as revealed here; the pK_a value of phenol is 9.95[12].

The hydrogen bond formed in the crystal of 2-naphthol is stronger than that in 1-naphthol, while the latter seems to be of the same order of strength as the bond in phenol[9]. A similar result was obtained by Nagakura[13] when he studied the proton-donating power of phenols and naphthols by the measurement of near ultraviolet absorption of these substances in appropriate solvents to which some proton-acceptors, such as methylacetate or dioxane were added; his values of the energies of OH···O bonds for phenol, 1-naphthol, and 2-naphthol are 5.3, 5.7 and 6.1 kcal./mol., respectively. These results are rather strange, as Nagakura pointed out, if the fact is considered that the extent of electron migration into the naphthyl ring from oxygen atom is almost of the same order as that into a benzene ring in the case of phenol, and therefore, that the pK_a values[12] and the dipole moments[14-16] of these three compounds are identical; pK_a=9.95, 9.85, 9.93 in water at 25°C, μ=1.5, 1.4, 1.5 D, respectively.

The author is inclined to presume that the main factor differentiating 1-naphthol from 2- with regard to the power of forming hydrogen bond is steric hindrance due to a hydrogen atom at 8-position in case of 1-naphthol. Thus, the OH group must be obliged to take only such a direction as to be opposite to the 8-position of the naphthyl nucleus. On the other hand, the OH group in 2-naphthol is quite free from such hindrance as mentioned above, and can take either of the directions,



, with a slight difference in the molecular structure.

In this connection a comment will be made of the transitions found with 1- and 2-naphthol. The fact of interest is that the transition points of these substances, 39.4 and 39.1°C, respectively, are very close to the melting point of phenol, 40.8°C, and that the heats of transition, 2.2 and 2.4 kcal./mol., respectively, are almost of the same order as the heat of fusion of phenol, 2.7 kcal./mol.[17] This would mean that the transitions and melting of the above substances might occur under the same mechanisms. It is most likely that intramolecular rotation about C–O bond[18] takes place at the melting point of phenol thereby leading to a less ordered state of liquid. As the O–H groups are bound to each other through chains of hydrogen bonds, a rotating part of the molecule will be mostly phenyl nucleus. That the change of entropy on melting at 40.8°C, 8.6 cal./deg. mol.[17], is almost the same as that of benzene at 5.5°C[17], and smaller than that of thiophenol, 10.5 cal./deg. mol. at −14.9 °C[17], may support the above argument. In the case of 1- and 2-naphthol, the onset of intramolecular rotations would lead to a transition in the crystalline states, but not to melting, because the effect of dispersive forces due to naphthyl rings is strong, as was found in the present experiment. Detaits will be published later.

Summary

The energies of hydrogen bonds formed in the crystalline state of twelve phenols have been estimated by a procedure proposed in a previous paper. The values of energy range from zero to 7 kcal./mol. depending upon the difference of molecular structures: the phenols with bulky substituents in the vicinity of OH groups are non- or weakly-hydrogen-bonded, while those with carbonyl or methoxy groups at para positions are strongly bonded presumably by head-to-tail association. The other phenols fall between the two extremes. Incidentally it is interesting that the highest values of OH···O bond are rather close to the energies of association of carboxylic acids in the gaseous state.

With 1- and 2-naphthols, a parallel relation between the transitions of the above substances and the melting of phenol has been pointed out.

The author is grateful to Professor M. Davies for sending some of the samples

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16) R. J. W. Le Fèvre, "Dipole Moment", Methuen & Co., Ltd., London (1953), p. 133.

17) The Chemical Society of Japan, "A Handbook of Chemistry (Kagaku Binran)", Maruzen Co., Ltd., Tokyo (1958), p. 709, 710.

18) A potential barrier hindering the rotation of OH group in phenol is known to amount to 3.2 kcal./mol. [T. Nishikawa, *J. Jap. Chem.* (*Kagaku-no-Ryōiki*), **13**, 385 (1959)]; in 2,4,6-tri-*tert*-butylphenol it is 2.2 kcal./mol. [R. J. Meakins, *Trans. Faraday Soc.*, **52**, 320 (1956)].

dealt with in this work. The cost of the work was partly defrayed by the financial support of the Ministry of Education to which the author's thanks are due.

Department of Chemistry
Faculty of Liberal Arts & Science
Shinshu University
Agata-machi, Matsumoto