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MICROWAVE SPECTRUM OF CATECHOL (1,2-DIHYDROXYBENZENE)

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ABSTRACT

The microwave spectra of the normal species and three deuterated species of catechol have been observed in the frequency ranges 8—18.6 and 26.5—40 GHz. The inertial defect and the r_s coordinates of the hydrogen obtained from the assigned spectra indicate that the conformation of the molecule is planar with intramolecular hydrogen bonding. A measure of the strength of the hydrogen bond is proposed from the difference of inertial defects in OH and OD species; the strength estimated for catechol almost equals that in 2-chlorophenol.

INTRODUCTION

Catechol is a biologically interesting molecule. It is not only a part of catecholamine but also an important material for metabolism of aromatic compounds in microbes. It was considered that the hydrogen bonding by two hydroxyl groups in catechol had a specific function in these mechanisms. The inter- and intramolecular hydrogen bonding of this molecule were studied by IR fifty years ago [1]. Recently, Tylli and Konschin [2] studied the Raman spectrum extensively and Konschin [3] carried out ab initio calculations for catechol. The strength of hydrogen bonding of catechol was evaluated from the ν_{OH} shift from that of phenol in the series of *ortho*-substituted phenols [4]. The crystal structure of catechol was studied by Brown [5], and later by Wunderlich and Mootz [6]. They reported the structural parameters of the *cis* conformation (I in Fig. 1) having an intramolecular hydrogen bond. This time, we have observed the microwave spectrum of catechol in the gas phase and discuss the strength of the intramolecular hydrogen bond from the data obtained for inertial defect.

EXPERIMENTAL

The microwave spectrum was measured with a conventional spectrometer using 100 kHz square-wave Stark modulation. The measured frequency regions were 11—18.6 and 26.5—40.3 GHz using a synthesizer (HP-8672A)

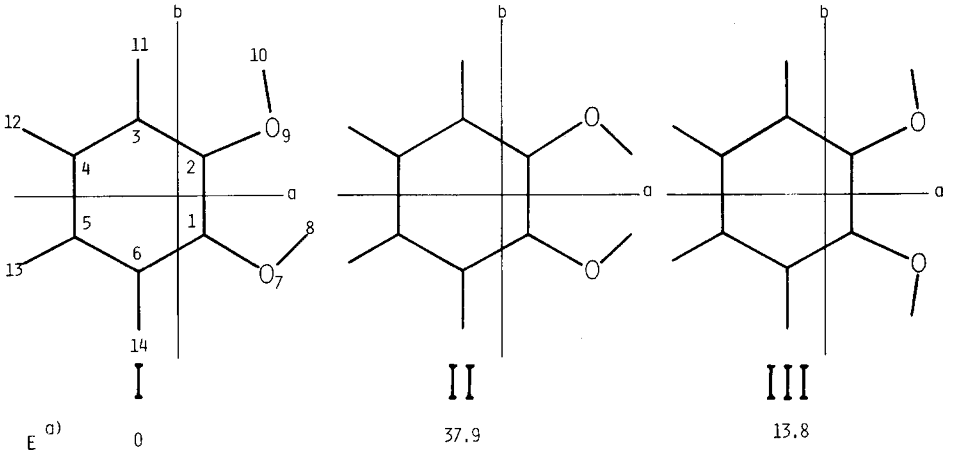

Fig. 1. Three geometrical isomers of planar catechol. Calculated total energy, E_{calc} (kJ mol^{-1}), by ab initio MO(STO-3G): I, 0; II, 37.9; III, 13.8 [3].

and a YIG tuned GaAs oscillator (Watkins-Johnson 5610-302FD), respectively. Measurement was made at about 25°C with sublimate pressure under flow conditions. The accuracy of the frequency measurement was better than 0.1 MHz.

The sample was obtained commercially (Tokyo Kasei) and used without further purification. The deuterated species were prepared by shaking a mixture of catechol and D_2O at room temperature under dark conditions for several days.

For the dried sample, the mass spectrum revealed the three parent peaks (m/z = 110, 111, 112) corresponding to C_6H_4—$(OH)_2$, —OHOD, —$(OD)_2$ species. Only the microwave spectrum of —$(OD)_2$ species was observed when the waveguide was well flashed by D_2O before introducing the sample gas. When introducing H_2O, instead of D_2O into the waveguide under the same condition, new lines appeared which were distinguished from those of $(OH)_2$ and $(OD)_2$ species. These were assigned to OH ··· OD and OD ··· OH species.*

ANALYSIS OF SPECTRA

Many spectral lines appeared in the observed regions. The complexity of the spectrum resulted from many low-lying vibrationally excited states. Six low frequency modes below 300 cm^{-1} were expected from the investigation

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*Four isotopic species with intramolecular hydrogen bonds are represented by OH ··· OH, OD ··· OD, OH ··· OD, and OD ··· OH, respectively. The dotted line denotes the intramolecular hydrogen bond, e.g. OD ··· OH means that a hydrogen bond forms between (O)D and O(H).

of vibrational spectra of catechol [2]. Three planar conformers were predicted to exist from the ab initio calculation by Konschin [3] as shown in Fig. 1. Of the three forms, II is in the energetically higher state and its spectral lines are unlikely to be observed. The *a*- and *b*-type transitions are expected for I, but only the *a*-type for III.

The rotational constants shown in Table 1 were obtained by least-squares fitting of the observed frequencies of the *b*-type *Q*- and *R*-branch transitions to the Hamiltonian including centrifugal distortion effects. A search for the lines of the *a*-type *R*-branch transition, of which the frequencies were predicted from the observed *b*-type lines, was not successful. The observed transitions and their frequencies are available as Sup. Pub. No. SUP 26329 (4 pages) from B.L.L.D., Boston Spa, Wetherby, Gt. Britain.

DISCUSSION

The *b*-type transitions were observed and therefore the assigned spectra are of conformer I. The small inertial defect of the four isotopic species indicates that catechol has a planar equilibrium structure. Its negative value arises from large amplitude OH tortion as discussed below. The r_s coordinates of the two hydroxyl hydrogen were calculated and are shown in Table 2. The coordinates of the optimized structure obtained by the ab initio MO method for conformer I coincide well with the observed r_s-structure. In the present measurements *a*-type transitions were not observed. The *a*- and *b*-components of the dipole moment, calculated from summation of the moment of phenol [7] were 0.23 D and 2.11 D, respectively. Therefore the *a*-type transition should be very weak.

Assuming a rigid planar structure, information on eight structure parameters was obtained from the four isotopic species. Assuming the benzene moiety to be a regular hexagon and taking fixed bond lengths for C—C and

TABLE 1

Rotational and centrifugal distortion constants of catechol

Constant	OH · · · OH[a]	OD · · · OD	OD · · · OH	OH · · · OD
A (MHz)	3387.619(10)[b]	3268.044(8)	3377.002(13)	3282.312(8)
B (MHz)	2246.178(7)	2165.851(6)	2190.418(8)	2218.039(7)
C (MHz)	1350.967(6)	1303.026(5)	1328.998(7)	1324.026(6)
τ_{aaaa} (kHz)	−5.3(5)	−3.0(3)	−4.9(5)	−3.5(3)
τ_{bbbb} (kHz)	−0.4(1)	−0.3(1)	−0.5(1)	−0.5(1)
τ_{aabb} (kHz)	1.3(5)	1.1(4)	0.4(6)	0.6(5)
τ_{abab} (kHz)	−0.6(2)	−0.6(2)	−0.3(2)	−0.4(2)
$\Delta(\mu A^2)$[c]	−0.092(3)	−0.132(3)	−0.105(3)	−0.121(3)
N[d]	55	54	41	47

[a] Dotted line indicates intramolecular hydrogen bond. [b] Figures in parentheses are the uncertainty as one standard deviation. [c] $\Delta = I_c - I_a - I_b$. [d] Number of assigned transitions.

TABLE 2

r_s Coordinates of hydroxyl hydrogen in catechol

	H_8[a]		H_{10}[a]	
	This work	Ref. 3[b]	This work	Ref. 3[b]
$\|a\|$ (Å)	2.3892(3)	2.38167	1.6376(4)	1.58851
$\|b\|$ (Å)	0.7113(11)	−0.70594	2.2317(3)	2.27700

[a]For numbering of hydrogen atoms, see Fig. 1.
[b]Coordinates calculated from the ab initio optimizing structure.

TABLE 3

Structural parameters of catechol

Parameter[a,b]	r_0 Structure	Ab initio MO[c]	Crystal[d]
C_1C_2 (ring)[c]	1.3970[e]	1.3895[f]	1.384[f]
C_1O_7	1.323	1.3948	1.369
C_2O_9	1.406	1.4006	1.373
O_7H_8	0.9896[e]	0.9896	0.80
O_9H_{10}	0.9871[e]	0.9871	0.81
C—H (ring)	1.0840[e]	1.0817[f]	0.99[f]
$C_2C_1O_7$	118.95	120.84	121.0
$C_3C_2O_9$	122.35	124.98	123.3
$C_1O_7H_8$	108.28	104.01	106
$C_2O_9H_{10}$	109.57	106.01	111
CCC (ring)	120.00[e]	120.00[f]	120.0[f]

[a]Bond lengths in Å, angles in degrees. [b]For numbering of atoms, see Fig. 1. [c]Ref. 3. [d]Ref. 6. [e]Fixed. [f]Mean value.

C—H bonds, the structural parameters shown in Table 3 were obtained by the least-squares method. In this procedure, parameters for two OH bonds were found to correlate with each other and the lengths for OH bonds were fixed to the values of the optimized structure from the MO calculation. It was found that C_1O_7 was very much shorter than C_2O_9, where O_7 bonded to H_8 which intramolecularly hydrogen bonded with O_9. These parameters also depended on the fixed parameters and correlated with each other. However the difference in the length of the two C—O bonds was definitive from the statistical inspection using the SALS system [8].

The inertial defect for a planar molecule has been formulated by Oka and Morino [9]. The negative contribution to the inertial defect arises from mainly out-of-plane vibration of the molecule. The negative small defect for phenol was observed and explained by the OH torsional vibration, despite of its equilibrium planar structure. The difference between the inertial defects of OH and OD species reflects the difference in torsional amplitude of hydrogen and deuterium. (Larsen [10] indicated that the major part of this

TABLE 4

Inertial defects (uÅ^2) of phenol derivatives

	Species	Δ^a	$\Delta\Delta^b$	Ref.
Phenol	OH	−0.0299(19)		7
	OD	−0.04817(8)	0.0183	
4-Fluorophenol	OH	−0.0728(2)		10
	OD	−0.0945(6)	0.0217	
4-Chlorophenol	OH	−0.0761(4)		10
	OD	−0.0963(2)	0.0202	
Catechol	OH · · · OH	−0.092(3)		This work
	OH · · · OD	−0.121(3)	0.029^c	
	OD · · · OD	−0.132(3)	0.027^d	
	OD · · · OH	−0.105(3)	0.013^e	
	OD · · · OD	−0.132(3)	0.011^f	
2-Chlorophenol	OH	0.014(2)		11
	OD	0.006(2)	0.008	
2-Nitrophenol	OH	−0.356(8)		12
	OD	−0.355(7)	−0.001	
Salicylaldehyde	OH	−0.091		13
	OD	−0.091	0.000	

[a] $\Delta = I_c - I_a - I_b$. [b] $\Delta\Delta = \Delta(\mathrm{OH}) - \Delta(\mathrm{OD})$. [c] $\Delta(\mathrm{OH}\cdots\mathrm{OH}) - \Delta(\mathrm{OH}\cdots\mathrm{OD})$. [d] $\Delta(\mathrm{OD}\cdots\mathrm{OH}) - \Delta(\mathrm{OD}\cdots\mathrm{OD})$. [e] $\Delta(\mathrm{OH}\cdots\mathrm{OH}) - \Delta(\mathrm{OD}\cdots\mathrm{OH})$. [f] $\Delta(\mathrm{OH}\cdots\mathrm{OD}) - \Delta(\mathrm{OD}\cdots\mathrm{OD})$.

difference was caused by the torsional mode.) The difference, $\Delta\Delta$, was calculated to be 0.0183 uÅ^2 for phenol as shown in Table 4. Although the inertial defects for various phenol derivatives were of quite different values from one another, the differences fell in the small range 0 to about 0.03 uÅ^2. The difference for molecules with no intramolecular hydrogen bond, 4-fluoro- and 4-chlorophenol, is about 0.02 uÅ^2. For 2-nitrophenol and salicylaldehyde, on the other hand, both OH and OD species have the same inertial defect. These molecules are known to have strong intramolecular hydrogen bonding between hydroxyl hydrogen and oxygen. A small contribution is expected to the inertial defect from the OH torsion in these molecules because the motion of the H atom is more frozen than in the former group of molecules. The smaller magnitude of $\Delta\Delta$ seems to reflect the smaller amplitude of OH torsion and the stronger hydrogen bonding.

Because the values of the difference are generally rather small, any comparison must be made after careful consideration of the error attached to the inertial defect. Catechol has two hydroxyl hydrogen atoms; one is involved in the intramolecular hydrogen bond and the other is not. The differences of inertial defect for isotopic species of catechol were calculated for the two kinds of hydroxyl hydrogens as shown in Table 4. Two distinct values of the difference were obtained for bonded OH and non-bonded OH, i.e. 0.012 uÅ^2 and 0.028 uÅ^2 (mean values), respectively. The value 0.012 uÅ^2 is nearly the same as for 2-chlorophenol. Assuming that the difference of inertial defect reflects the strength of the hydrogen bond, the strength for catechol is nearly equal to that for 2-chlorophenol.

The strength of the hydrogen bond has been discussed from the viewpoint of OH stretching frequency shifts [12, 13] and the torsional frequency shifts [4]. The intermediate strength of the hydrogen bond for 2-chlorophenol was reported by IR [14], CNDO [15], and microwave spectroscopic [11] studies. It is concluded that the strength for catechol, as in 2-chlorophenol, is intermediate.

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