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J. Pajak; Z. Galewski; M. Rospenk; L. Sobczyk

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Liquid crystalline properties of and intramolecular hydrogen bonding in 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes

J. PAJĄK, Z. GALEWSKI*, M. ROSPENK and L. SOBCZYK

Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie, 50-383 Wrocław, Poland

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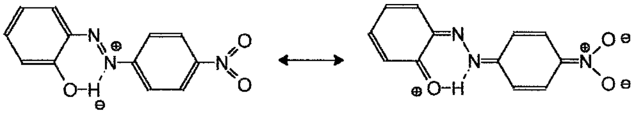
A homologous series of 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes with chain lengths from 1 to 12 carbon atoms was synthesized and the temperatures of melting, freezing and transition from nematic to isotropic phase were determined. The main thermodynamic characteristics for those transitions were estimated. The liquid crystalline properties were compared with those of homologous series without OH groups and show a marked extension of the nematic phase for the OH substituted compounds. The spectroscopic manifestations of the hydrogen-bonded OH… N chelate ring are discussed, based on a comparison of experimental and Density Functional Theory (DFT) calculated frequencies and IR intensities. The evolution of the IR absorption in the range 1540–1660 cm^{-1}, ascribed to the OH bending vibrations, is presented on going from the dilute CCl_4 solution through the isotropic and nematic phases to the solid state.

1. Introduction

Azobenzene derivatives belong to the oldest class of liquid crystalline compounds and have been extensively studied [1–4]. Commercial applications have been limited because they are associated with chemical and photochemical instability. However, azobenzenes are undergoing revived interest for use in new applications such as materials for controlled photoalignment of surfaces [5]. A full overview of the literature devoted to 4-, 4′-derivatives of azobenzenes was given in [6, 7].

A new group of mesogenic substances can be formed by introducing additional substituents and particularly the OH group, mainly in the 4′-position [8, 9]. This type of compound shows strong intermolecular interactions, which induce new mesophase types. The insertion of the OH group in the 2′-position was more seldom investigated [10–12]. This was however done, e.g. in [10] in which the properties of 4-nitro-4′-alkoxy-2′-hydroxyazobenzenes were described. In this case, the study seemed to be interesting not only from the point of view of the liquid crystalline properties, but also because of the properties of the hydrogen-bonded chelate ring itself. This system and its relevance to analogous Schiff's bases needs further explanation; possibly the study of a wide range of structures would help [13, 14]. The so-called resonance assisted hydrogen bond in such molecules is in itself of great interest [15, 16]. The Schiff's bases and the 2′-hydroxy derivatives of azobenzenes could become interesting and promising materials in molecular electronics [17–20].

In the paper devoted to 4-nitro derivatives of azobenzenes [10], a strong influence of the additional OH group on the transition temperatures and enhancement of the range of the liquid crystalline phases was put in evidence. However it seems that in this case, the main factor affecting the properties was the strong conjugation of the NO_2 group with the chelate ring expressed below by means of the mesomeric structures:



This leads to the enhancement of the dipole moments and intermolecular interactions. As a consequence one also observes a considerable increase in the freezing and clearing temperatures.

In the present paper we describe an investigation of the homologous series of 2′-hydroxy-4′-alkoxyazobenzenes with a methyl group in the 4-position. In this case there are no additional intramolecular interactions, and we wanted to see how the presence of the chelate ring itself affected the creation and the existence ranges of the mesophases. An aim of the present work was also the study of the chelate ring from a purely structural point of view. We describe the synthesis of the series with $n = 1$–12, and the determination of the phase

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*Author for correspondence; e-mail: zg@wchuwr.chem.uni.wroc.pl

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transition temperatures and the thermodynamic characteristics of the transitions; we compare the properties with those of the series without the OH group [21] and the series containing NO_2 and OH groups. Finally we present the main characteristics of the chelate ring in relation to that in analogous Schiff's bases.

2. Experimental

2.1. *Synthesis*

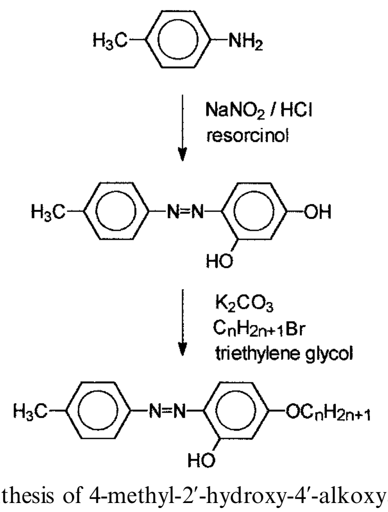
The main features of the synthesis are presented in the scheme below. 4-Toluidine was used as the commercially available starting material from E. Merck Ltd.

2.1.1. *4-Methyl-2′,4′-dihydroxyazobenzene*

This was synthesized by a method similar to that of Ho and Fung [10] with some modifications. A mixture of sodium nitrite (28 g, 0.4 mol) in water (100 g) was added slowly to a cold (~ 5°C) mixture of 4-methylaniline (42.8 g, 0.4 mol) and hydrochloric acid (0.8 mol) in water. The mixture was stirred in an ice bath. After 30 min the diazonium salt solution was added slowly to a cold mixture of resorcinol (44 g, 0.4 mol) and sodium hydroxide (0.8 mol, 32 g) in water (200 ml). Hydrochloric acid was then added after 15 min to give a pH to 7. The crude purple precipitate was isolated by filtration and purified by repeated recrystallization from methanol, affording the desired 4-methyl-2′-4′-dihydroxyazobenzene, 21 g (23%), m.p. 172°C (with sublimation, and formation of a glass on cooling), as a light purple solid. ^{1}H NMR ($CDCl_3$) δ: 2.41 (3H, s, CH_3), 3.40 (1H, s, OH), 6.40 (1H, d, Ph−H), 6.61 (1H, d-d, Ph−H), 7.36 (2H, d, Ph−H), 7.73 (3H, m, Ph−H), 13.20 (1H, s, O−H).

2.1.2. *4-Methyl-2′-hydroxy-4′-ethoxyazobenzene*

A mixture of 4-methyl-2′,4′-dihydroxybenzene (3 g), bromoethane (2.2 g) and anhydrous K_2CO_3 (2 g) in triethyleneglycol (30 ml) was heated under reflux for 4 h. After cooling to room temperature, the solution was shaken with diethyl ether (2 × 70 ml) and the ether extract washed with water (2 × 20 ml). After evaporating the solvent, the crude product was recrystallized from methanol using decolourizing carbon, and finally submitted to flash column chromatography (Fluka silica gel 60 mesh, $CHCl_3$ as eluent). The resulting product was still a mixture of two compounds (4-methyl-2′-hydroxy-4′-ethoxyazobenzene and 4-methyl-4′-hydroxy-2′-ethoxyazobenzene). This was dissolved in a mixture of methanol and sodium hydroxide. To this solution water was then added slowly. The precipitate was removed and hydrochloric acid added to the filtrate. The precipitate was filtered off and several times recrystallized from methanol (12% yield). ^{1}H NMR ($CDCl_3$) δ: 1.45 (3H, t, CH_3), 2.41 (3H, s, CH_3), 4.14 (2H, m, Ph−OCH_2), 6.60 (1H, d-d, Ph−H), 6.72 (1H, d, Ph−H), 7.28 (2H, d, Ph−H), 7.66 (2H, d, Ph−H), 7.70 (1H, d, Ph−H), 13.79 (1H, s, O−H).



Scheme. Synthesis of 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes.

2.2. *Characterization*

The composition and purity of the final products and intermediates were monitored by thin layer chromatography (TLC), by ^{1}H NMR spectroscopy (Bruker AMX 300 MHz) and by HP 5890II gas chromatography with a mass selective detector HP5974A. Microanalyses were carried out using a Perkin Elmer 2400 CHN Elemental Analyser (table 1). Transition temperatures were measured using a Linkam THMS 600 hot stage and a TMS 93 control unit in conjunction with an Olympus BX60P polarizing microscope and were confirmed by DSC (Perkin Elmer DSC7, 5 K min^{-1}). The thermo-optical analysis (TOA) set-up has been described elsewhere [22]. The IR spectra of CCl_4 solutions were recorded using a Nicolet FTIR Nexus spectrophotometer. The studies of temperature effects on the IR spectra were

Table 1. Elemental analysis of 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes.

	Calculated			Found		
n	%C	%H	%N	%C	%H	%N
1	69.41	5.82	11.56	69.26	6.11	11.20
2	70.29	6.29	10.93	70.44	6.44	11.04
3	71.09	6.71	10.36	71.24	6.91	10.40
4	71.81	7.09	9.85	71.67	6.93	9.85
5	72.46	7.43	9.39	72.58	7.53	9.14
6	73.05	7.74	8.97	72.94	7.75	9.08
7	73.59	8.03	8.58	73.75	8.30	8.57
8	74.08	8.29	8.23	74.15	8.39	8.07
9	74.54	8.53	7.90	74.43	8.25	7.95
10	74.96	8.75	7.60	75.23	8.98	7.64
11	75.35	8.96	7.32	75.27	9.28	7.01
12	75.72	9.15	7.06	75.71	9.36	6.94

performed using a Nicolet 360 FTIR Avatar E.S.R. instrument. In this case the sample was placed between KRS-5 plates. The fused substances were introduced into the cell by using capillary action. Then the cell was placed in the compartment of a Grasby Specac cryostat. An automatic temperature controller (Grasby specac) was used.

Typical DSC and TOA runs are shown in figure 1 using 4-methyl-2′-hydroxy-4′-heptyloxyazobenzene as an example. This reflects the complementarity of those techniques in characterizing liquid crystalline compounds.

3. Results and discussion

The results obtained with respect to the transition temperatures and enthalpies are collected in table 2 and presented in figure 2. The comparisons with the properties of the homologous series without an OH group are shown in figures 3 and 4. These comparisons prove that introduction of the OH group does not change the melting points greatly for short alkoxy chains, while a marked decrease in the temperature takes place for $n \geqslant 7$ (over 10°C), i.e. for derivatives most interesting from the point of view of their liquid crystalline properties. On the other hand, as can be seen in figure 3, a considerable increase in the nematic–isotropic transition temperature takes place. The extension of the existence range of the nematic phase is thus similar to that found for the homologous series with the nitro group [10, 23], but in the latter case, a considerable increase in recrystallization temperature is observed.

Because the introduction of the OH group advantageously changes the existence range of the nematic phase and improves the thermal stability of the compounds [11, 23], we decided to look more carefully at the chelate ring with the OH … N bridge. Thus in the NMR spectrum, one observes a very broad signal close to 14 ppm indicating a medium-strong hydrogen bonding. Also the position and intensity of the IR band at 2650 cm^{-1} ascribed to the ν(OH) stretching vibrations confirm rather strong hydrogen bonding. The unusually low intensity of this band proves that there is a substantial contribution from the π-electron system in

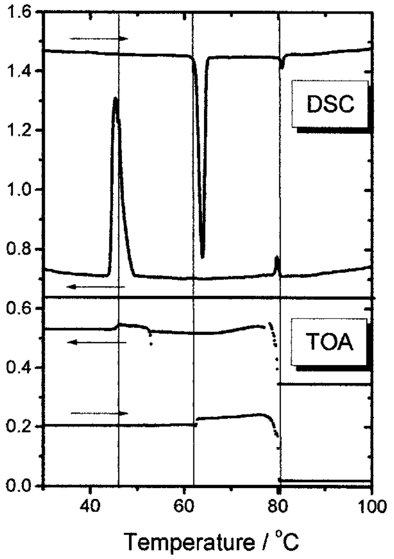


Figure 1. DSC and TOA scans for 4-methyl-2′-hydroxy-4′-heptyloxyazobenzene.

Table 2. Temperatures (°C) and enthalpies (square parenthesis, in kJ mol^{-1}) of phase transitions for 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes.

n	Melting	Recrystallisation	N–I
1	94.6	48.7	(51.2)
	[20.4]	[14.7]	[0.014]
2	130.6	104.1	(98)[a]
	[35.6]	[32.4]	
3	97.1	58.0	(70.1)
	[33.1]	[29.2]	[0.78]
4	84.4	61.9	86.7
	[29.6]	[23.6]	[0.77]
5	66.7	42.8	75.6
	[27.7]	[24.3]	[0.83]
6	87.1	78.2	(85.1)
	[38.5]	[36.0]	[0.9]
7	62.8	46.1	80.0
	[28.7]	[26.0]	[1.0]
8	68.9	58.2	85.7
	[29.9]	[29.0]	[1.12]
9	66.5	55.9	82.1
	[31.9]	[29.8]	[0.83]
10	68.6	58.9	84.9
	[31.9]	[28.8]	[1.1]
11	66.4	53.8	77.4
	[38.4]	[38.4]	[1.0]
12	62.2	48.7	77.2
	[24.1]	[25.0]	[1.7]

[a] Data obtained in the scan at 100°C min^{-1}.

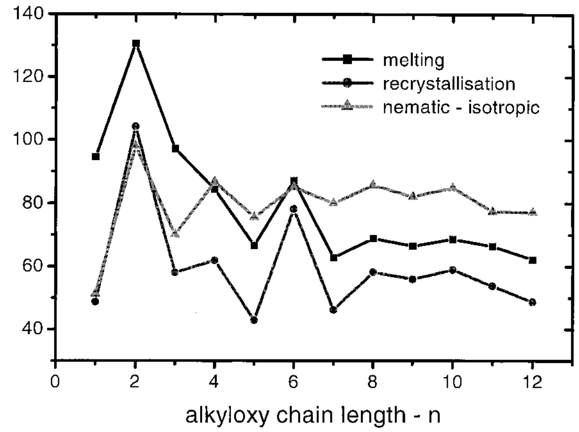


Figure 2. Diagram of melting, freezing and nematic–isotropic temperatures for 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes.

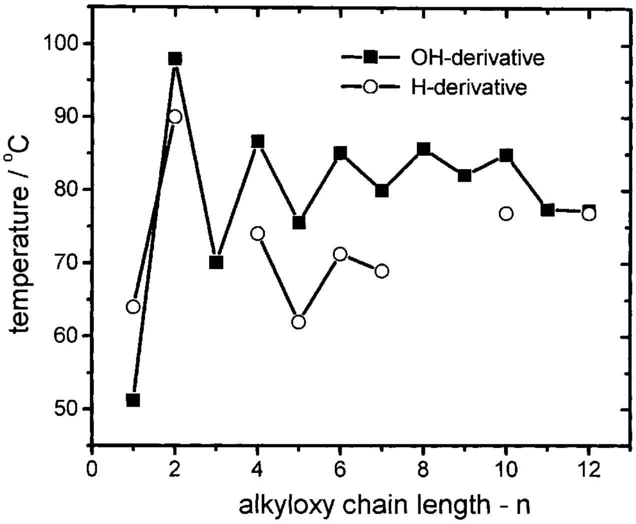


Figure 3. Comparison of nematic–isotropic transition temperatures for 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes and 4-methyl-4′-alkoxyazobenzenes.

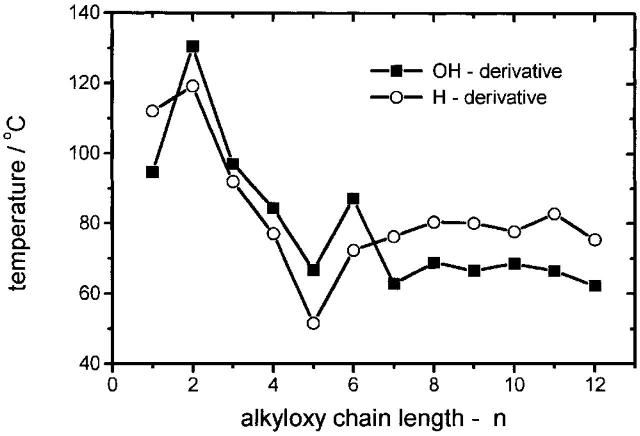


Figure 4. Comparison of melting transition temperatures for 4-methyl-2′-hydroxy-4′-alkoxyazobenzenes and 4-methyl-4′-alkoxyazobenzenes.

stabilizing the system and coupling the motion of the proton with the electrons, similarly to the case for Schiff's bases [24].

It seemed interesting to look at the evolution of the IR spectra caused by the phase transitions. The most suitable range of the spectrum appeared to be that connected with the deformation vibrations of the OH group.

As can be seen from a comparison of the derivatives with $n = 8$ (figure 5), the insertion of the OH group leads to the appearance of several bands which proves that there are no free OH deformation vibrations, in agreement with the commonly accepted picture of hydrogen bond dynamics [25]. Our detailed studies over a broad range of temperature and changing values of n allowed us to conclude that the band most sensitive to the

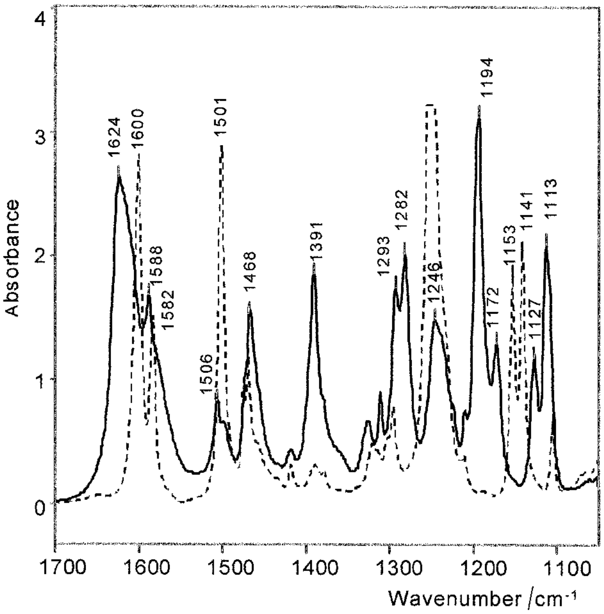


Figure 5. Infrared spectra in the finger print region for 4-methyl-2′-hydroxy-4′-octyloxyazobenzenes (solid line) and 4-methyl-4′-octyloxyazobenzene (dashed line); at 298 K, $d = 0.6$ mm, $c = 0.1$M, in CCl_4.

change in aggregation is that at 1624 cm^{-1}, a band which should be assigned to δ(OH) vibrations coupled with ring vibrations. The evolution of the absorption around 1600 cm^{-1} is shown in figure 6. The most intense band at 1624 cm^{-1} is that for the CCl_4 solution; its intensity decreases successively on going to the isotropic

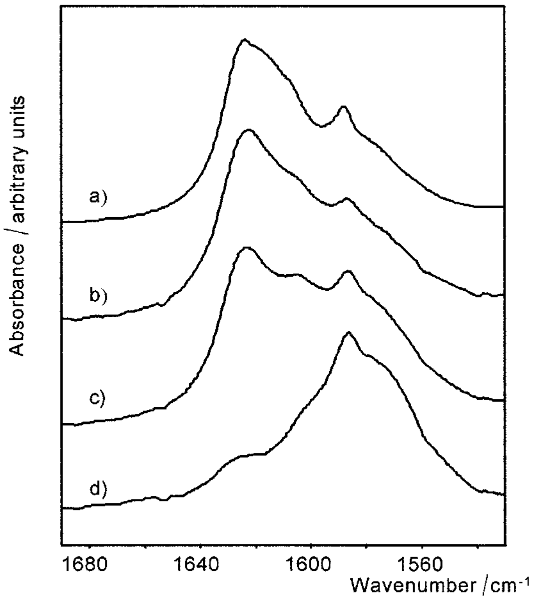


Figure 6. Evolution of the absorption in the region around 1600 cm^{-1} for 4-methyl-2′-hydroxy-4′-octyloxyazobenzene: (*a*) CCl_4 solution, (*b*) isotropic phase at 90°C, (*c*) nematic phase at 70°C, (*d*) solid state at room temperature.

phase, nematic phase and solid state. One can conclude that the drop in intensity (may even be a complete disappearance of that band) is caused by strong intermolecular interactions with participation of OH groups. This can be realized only when the chelate rings are oriented parallel as shown in figure 7, so that bifurcated hydrogen bonds are formed. In the solid state all the molecules are most probably engaged in such interactions so that we observe vanishing of the absorption at 1624 cm^{-1} below the recrystallization temperature. This reflects a complete change in the dynamics of the chelate ring with respect to the OH deformation mode mixed with the ring vibrations. For the CCl_4 solution and the isotropic phase, the spectra are identical and show the intense band at 1624 cm^{-1}. However for the nematic phase we notice a slight but meaningful drop in the absorption in this region which could indicate only some contribution from dimers of the kind shown in figure 7.

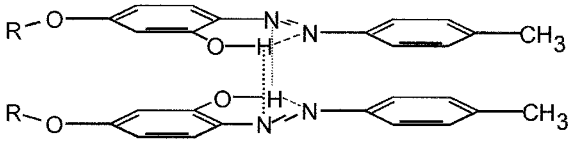
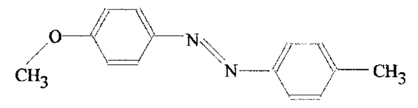


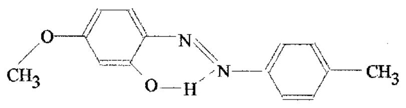
Figure 7. Possible configuration of dimers.

For a better insight into the problem of the dynamics of the hydrogen-bonded chelate ring, DFT calculations were undertaken with respect to the vibration frequencies and IR intensities. For simplicity the first members of the series were chosen for the calculations which were performed on a B3LYP/6-31G** level by using the Gaussian programme [26]. The scaling factor equal to 0.9612 was assumed.

In table 3 there are compared the calculated and experimental frequencies in the finger-print region. Only

Table 3. Calculated and experimental frequencies in the finger print region for modes with IR intensities above 10 km mol^{-1}. Those with intensities above 100 km mol^{-1} are underlined. The underlined experimental values refer to very strong bands.





Assignment	calc.	exp.	Assignment	calc.	exp.
ring def.	1601	$\underline{1600}$	δ(OH)+ ring def.	$\underline{1617}$	$\underline{1624}$
ring def.	1596		δ(OH)+ ring def.	$\underline{1571}$	1588
		$\underline{1582}$	δ(OH)+ ring def.	1560	
ν(NN)+ δ(CH)	1565		δ(OH)+ δ(CH)	1502	1505
ν(NN)+ δ(CH)	1498	$\underline{1501}$	δ(OH)+ δ(CH)+ δ(CH_3)	1487	1498
δ(CH)	1488	1472	δ(OH)+ δ(CH)+ δ(CH_3)	1472	1468
δ(OCH_3)	1459		δ(OCH_3)	1456	
δ(CH_3)	1429		δ(CH_3)	1451	
δ(CNN)+ ring def.	1313		δ(CH_3)+ δ(OH)	1436	
		1296	δ(CH)+ ν(NN)+ δ(OH)	1413	1418
ring def.	1302		δ(OH)+ ring def.+ δ(CH_3)	$\underline{1398}$	$\underline{1391}$
ν(CO)+ δ(CH)	$\underline{1254}$	$\underline{1252}$	ν(NN)+ δ(CH)	1385	
δ(CH_3)	1162	$\underline{1153}$	δ(OH)+ ring def.	1325	1326
δ(CH)	1136	1141	δ(CH)+ ring def.+ δ(OH)	$\underline{1305}$	1311
δ(CH)	1120		δ(CH)+ ring def.+ δ(OH)	1290	$\underline{1293}$
		1105	δ(CH)+ δ(OH)	1278	1282
δ(CH)	1091		δ(CH)+ δ(OH)	$\underline{1246}$	$\underline{1246}$
ν(CO)+ ring def.	1030	1028	δ(CH)+ δ(OH)	1214	1210
γ(CH)	829	$\underline{839}$	δ(CH)	1197	$\underline{1194}$
γ(CH)	543	548	δ(CH)+ ring def.	1189	
δ(COC)	484				1172
			δ(CH)+ ring def.	1185	
			δ(CH)	1096	1127
			δ(CH)	1095	$\underline{1113}$
			δ(CH)	1023	1024
			δ(CH)	949	
			γ(OH)	863	855?
			γ(CH)	809	828
			γ(CH)	523	527
			δ(COC)	491	

the modes with theoretical IR intensities exceeding 10 km mol^{-1} are considered. A few meaningful conclusions can be drawn from the data in table 3. Firstly, there are no doubts that the most intense band at 1624 cm^{-1} should be assigned to the OH bending vibration with a minor contribution from coordinates of ring carbon atoms. Secondly, the IR spectrum of the OH substituted compound is much richer than that of the unsubstituted compound. The calculations show that this is due to the appearance of new modes related to the OH deformation vibrations. However all of them are mixed with motions of other atoms and particularly of phenyl rings. The contribution of those atoms is the greater the lower the frequencies are. Probably this is a reason why we observe considerable changes caused by aggregation only at the highest frequency, i.e. at 1624 cm^{-1}.

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