

ROTATIONAL ISOMERISM, VIBRATIONAL AND NMR SPECTRA OF 3-SUBSTITUTED ANISOLES*

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It has been inferred from vibrational spectra of 3-substituted anisoles that their molecules assume two distinguishable conformations in liquid state and in solutions. One of the conformations is being frozen out on transition to the solid crystalline state at the temperature of liquid nitrogen. On the basis of this finding the vibrational spectra of defined conformations of 3-substituted anisoles have been interpreted. Rotational isomerism is not manifested in NMR spectra of anisole derivatives. Couplings between protons of methoxy group and those of benzene ring are negligibly small, the signal of methoxy group protons is isolated, and the spectra of aromatic protons can be described by an ABCD four-spin model.

Infrared and Raman spectra of 4-halogenomethoxybenzenes¹ (4-substituted anisoles) are relatively simple, and they do not change essentially with a change of state of matter. Obviously, rotational isomerism is of no importance in this class of compounds. In contrast to this, the spectra of 3-halogeno derivatives are relatively complex in the liquid state (and in solutions), and they show considerable changes on cooling down from the liquid to the crystalline state at liquid nitrogen temperature. The different behaviour of 4- and 3-substituted anisoles can be explained by hindered rotation of the methoxy group; the resulting rotational isomers are, because of symmetry, resolved only in 3-substituted derivatives.

Steric arrangement of the methoxy group in the molecules of anisole and its derivatives have been studied by infrared^{2,3} and electron⁴⁻⁷ spectra, dipole moments⁸⁻¹⁰, dielectric relaxation¹¹, Kerr constants^{10,12,13} etc. Results of various authors differ from one another and do not solve the problem satisfactorily. We suppose that the spectra of *m*-derivatives of anisole will permit us to solve this problem with certainty and in favour of the structures having the methoxy group slightly turned out of the plane of the benzene ring.

EXPERIMENTAL

The preparation and purification of anisole derivatives were described in detail in ref.^{14,15}. The physical properties of the studied compounds are given in Table I.

A sample of 3-ClC₆H₄OCD₃ was prepared from potassium 3-chlorophenolate and CD₃I in absolute ethyl alcohol. The sample purified by chromatography exhibited less than 1% of impuri-

* The conformation of the molecule of anisole was studied in diploma and doctorate work of one of us.

ties in NMR and mass spectra. A sample of 3- $\text{IC}_6\text{H}_4\text{OCD}_3$ was obtained 98% pure (according to NMR and mass spectra) from 3-iodophenol, potash and CD_3I in dry acetone.

Infrared spectra were measured on Perkin-Elmer model 621 and 225 spectrophotometers. Spectra of cooled samples were obtained using a commercial cell with AgCl windows; the temperatures of the samples were monitored throughout the measurements by a calibrated thermocouple.

Raman spectra were recorded on a modified DFS-12 spectrometer equipped with a He/Ne laser excitation source (6358 Å).

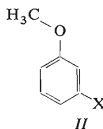
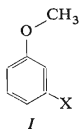
Proton NMR spectra were obtained on Tesla BS-487 spectrometer operating at 80 MHz; approximately 0.5 mol solutions were degassed and studied in an inert atmosphere using hexamethyldisiloxane as an internal reference. Spectra were measured at 25°C.

RESULTS AND DISCUSSION

In the anisole molecule the internal rotation is associated with the motion of the methoxy group around the $\text{C}_{\text{ar}}-\text{O}$ bond; neglecting the internal rotation around the $\text{O}-\text{C}_{\text{me}}$ bond, the conformation is determined by the torsion angle between the plane passing through atoms C_{ar} , O and C_{me} and the plane of the benzene ring.

The structures of the preferred conformations of anisole and its derivatives are determined by interactions of the methoxy group with the benzene ring. It follows from experiments that the most populated conformations are those with torsion angles close to 0° and 180°. In the case of anisole and its 4-derivatives, all stable conformations are indistinguishable;* it is immaterial in such a case whether the methoxy group is strictly coplanar (then there are two indistinguishable conformers) or whether it is twisted out of the plane (four indistinguishable conformers).

Molecules of 3-substituted anisoles can be found in stable distinguishable conformations. In one of these (*cis* conformation, I) the methoxy group is closer to the substituent than it is in the other conformation (*trans* conformation, II).



According to the dipole moment analysis, the two forms differ considerably in their dipole moments μ (estimates of μ values^{14,15}, for the *cis* form of 3-halogeno derivatives range from 0.0 to 0.4 D; those for the *trans* form vary between 2.0 and 2.6 D) and therefore there is a basis for their vibrational spectra to be distinguishable. In NMR spectra the rotational isomerism is not reflected, since the coupling between methoxy protons and ring protons in positions 2 or 6 is smaller than the experimental linewidth.

* This is valid only if the other substituent does not bring about rotational isomerism, as similarly *e.g.* the halogen atom does not.

TABLE I

Physical Properties of Studied Anisole Derivatives

Anisole derivative	B.p. ^a	n_D^{20}	d^{20}
3-Fluoro	—	1.4890	—
3-Chloro	78	1.5353	1.17
3-Bromo	94	1.5644	1.49
3-Iodo	111	1.6138	1.765
3,4-Dimethyl	101 ^b	1.5175	—
3,4-Dichloro	124 ^b	1.5582	1.33
3-Methyl-4-chloro	113 ^b	1.5349	1.14
3,5-Dimethyl	95 ^b	1.5119	—

^a Boiling point in °C at reduced pressure of 10 Torr. ^b At pressure of 20 Torr.

TABLE II

Splitting of Vibrational Frequencies^a of Anisole 3-Halogeno Derivatives 3-X-C₆H₄OCH₃

Assignment	Form	X = F	X = Cl	X = Br	X = I	X = I, [OCD ₃] ^b
CC-stretching	<i>trans</i>	— ^c	— ^c	1 586	1 590	1 589
	<i>cis</i>	— ^c	— ^c	1 581	1 585	1 585
CC-stretching	<i>trans</i>	— ^c	— ^c	1 577	1 571	1 572
	<i>cis</i>	— ^c	— ^c	1 573	1 568	1 568
CC-stretching	<i>trans</i>	1 313	1 307	1 303	1 301	1 302
	<i>cis</i>	1 307	1 298	1 295	— ^d	— ^d
X-sensitive	<i>trans</i>	1 265, 1 268	1 231	1 229	1 230	1 233, 1 238
	<i>cis</i>	1 278	1 250	1 246	1 245	1 255
β-CH bending	<i>trans</i>	1 166	1 166	1 166	1 168	1 169
	<i>cis</i>	1 159	1 155	1 156	1 160	1 161
O—C(H ₃ /D ₃)stretching	<i>trans</i>	1 039	1 042	1 039	1 036	— ^c
	<i>cis</i>	1 046	1 046	1 045	1 039	— ^c
X-sensitive	<i>trans</i>	941	847	827	815	793
	<i>cis</i>	920	862	839	824	798
ν-CH bending	<i>trans</i>	758	762	761	761	772
	<i>cis</i>	766	766	766	766	762

^a From infrared spectra of samples dissolved in Nujol; ^b 3-I-C₆H₄OCD₃; ^c no splitting found; ^d obscured by other absorption.

TABLE III
Wavenumbers of Groups OCH₃ and OCD₃ Vibrations from Infrared Spectra of Liquid Samples of 3-Halogeno Derivatives, Anisole-[OCD₃], 3-Cl- and 3-I-anisole-[OCD₃] [cm⁻¹]

Assignment of OCH ₃ /OCD ₃ vibrations ^a	Group OCH ₃		Group OCD ₃	
	<i>m</i> -Hal-C ₆ H ₄ OCH ₃ ^b	C ₆ H ₅ OCD ₃ ^c	<i>m</i> -Cl-C ₆ H ₄ OCD ₃	<i>m</i> -I-C ₆ H ₄ OCD ₃
Symmetrical stretching	3 004 ± 2	2 250 (1.33) ^d	2 256 (1.33)	2 253 (1.33)
Antisymmetrical stretching	2 961 ± 2	2 215 (1.34)	2 222 (1.33)	2 217 (1.34)
Symmetrical stretching + 2δ(OCX ₃) ^e	2 939 ± 3	2 128	2 127	2 126
Symmetrical stretching + 2δ(OCX ₃) ^e	2 835.5 ± 0.5	2 069 (1.37)	2 071 (1.37)	2 070 (1.37)
Symmetrical bending	1 464.5 ± 1.5	1 112 (1.32)	1 110 (1.32)	1 107 (1.32)
Antisymmetrical bending	1 456 ± 1	— ^f	— ^f	1 091 ^g
Symmetrical bending	1 441 ± 3	1 062 (1.36)	1 060 ^h (1.36)	1 058 (1.36)
Rocking	1 183 ± 1	955 (1.25) ⁱ	965 (1.23) ⁱ	959 (1.2) ⁱ
Rocking	1 158.5 ± 2.5 ^j	894 (1.29)	895 (1.29)	892 (1.30)
Stretching O—C(H ₃ /D ₃) ^k	1 037.5 ± 3.5	1 004 (1.03)	1 009 (1.03)	999 (1.03)

^a See ref. 1; ^b average values from wavenumbers of 3-F-, Cl-, Br- and I-anisole; ^c wavenumbers from ref. 19; ^d in parentheses isotopic shifts calculated from wavenumbers of corresponding OCH₃/OCD₃ pairs; ^e Fermi resonance splitting¹; ^f obscured by other absorption; ^g taken from spectrum of the crystalline sample; ^h inflexion, wavenumber therefore uncertain; ⁱ this strong band covers absorption of a CH out-of-plane bending vibration; ^j in *m*-derivatives obscured by medium/weak band of a CH in-plane bending vibration; ^k splitted by the effects of internal rotation under certain conditions.

Cooling the samples of 3-halogeno derivatives by liquid nitrogen to a temperature close to -180°C and crystallisation of the samples result in a significant simplification of their vibrational spectra (see the changes in the spectra of 3-iodoanisole in Fig. 1). The simplification is associated with the freezing out of one of the forms present in liquid samples at laboratory temperature. Analysis of the spectra of 3-halogeno derivatives of anisole in solutions established that it is form *I* that freezes out; the assignment of the bands in the spectra to the more polar (*II*) and to the less polar (*I*) forms was made on the basis of the experience that polar forms are more populated in polar solvents (nitromethane) than in non-polar solvents (tetrachloromethane, paraffine oil). Table II gives data about the frequencies of the bands which are different in the infrared spectra of forms *I* and *II*; the data were obtained in Nujol solutions in which the doublets were best resolved due to a small bandwidth.

In order to verify the above interpretation of rotational isomerism in 3-substituted anisoles we studied the effect of low temperature and of the state of matter on the spectra of some other derivatives. In accord with the assumptions the spectra of 4-halogeno derivatives of anisole are essentially independent of the temperature and the transitions from a liquid state to a cooled crystal brings about only a narrowing of the bands. Introduction of a second substituent to position 3 on the ring results again in distinguishable isomers, with all of the studied 3,4-disubstituted anisoles (Table I) exhibiting similar effects to those observed for 3-substituted derivatives. Compounds with symmetrically placed substituents in both *m*-positions support this view; the spectrum of 3,5-dimethylanisole again does not depend on temperature or state because the symmetrically placed substituents make the stable conformations

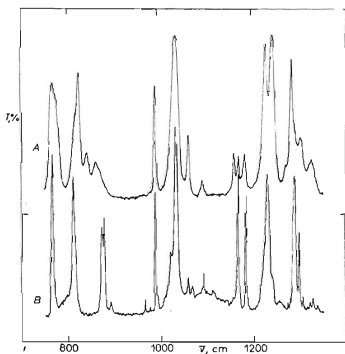


Fig. 1
Infrared Spectrum of 3-Iodoanisole
A Liquid sample, *B* polycrystalline sample
at -180°C .

indistinguishable. All the experiments give evidence for hindered internal rotation of the methoxy group in anisole and its derivatives, so in this respect the molecule of anisole is different from that of diphenylether in which both phenyl groups rotate almost freely^{16,17}.

Experiments described here show that the methoxy group is placed close to the benzene ring plane; otherwise, if it were in the perpendicular plane ($\tau = 90^\circ$ or 270°) introduction of a substituent into the 3 position could not result in distinguishable rotational isomers. Analysis of structural effects in the anisole molecule allows us to assume that the methoxyl group is slightly twisted out of the benzene ring plane. If the structure of the molecule were determined by oxygen atom conjugation with the phenyl nucleus only the planar conformations with torsion angles $\tau = 0^\circ$ or 180° would be the most stable ones, as they most probably are in the related phenol. In anisole, however, the steric effect is also of importance; the bulky methoxy group could get very close to the hydrogen atoms in the 2 or 6 position of the phenyl group¹⁸. Superposition of the two effects determines which conformations have minimum potential energy. In view of the fact that the contributions of conjugation and of steric effect to the potential energy show an opposite dependence on the torsion angle τ

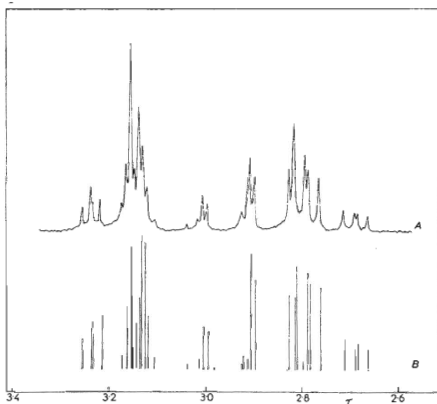


FIG. 2

NMR Spectrum of 3-Iodoanisole OCD_3

A Spectrum of 0.5 mol solution, B calculated spectrum.

TABLE IV

Wavenumbers of 3-X-C₆H₄O Frame Vibrations from Infrared Spectra of Liquid Samples of Anisole 3-Halogeno Derivatives and its Deuterio Derivatives 3-X-C₆H₄OCY₃ [cm⁻¹]

Assignment ^a	X = F	X = Cl		X = Br	X = I	
	Y = H	Y = H	Y = D	Y = H	Y = H	Y = D
CH stretching	—	—	—	—	—	3 086
CH stretching	3 088	3 086	3 082	3 080	3 076	3 075
CH stretching	3 070	3 073	3 066	3 067	—	—
CH stretching	—	—	—	—	3 062	3 057
CC stretching	1 615	1 597	1 594	1 589	1 585	1 584
CC stretching	1 592	1 580	1 577	1 573	1 568	1 566
CC stretching ^b	1 491	1 484	1 480	1 478	1 474	1 474
						1 470
CC stretching ^c	1 453	1 432	1 435	1 429	1 424	1 425
		1 423	1 428	1 421	1 415	1 417
CC stretching	1 315	1 309	1 307	1 306	1 304	1 304
β-CH bending ^d	1 282	1 284	1 289	1 285	1 285	1 288
X-sensitive ^b	1 278	1 249	1 258	1 246	1 244	1 255
	1 268, 1 264	1 232	1 239	1 231	1 230	1 230
β-CH bending ^b	1 166	1 167	1 167	1 168	1 171	1 169
	1 159	1 156	1 156	1 158	1 161	1 161
β-CH bending	1 135	1 091	1 093	1 090	1 091	1 095
β-CH bending	1 072	1 072	1 066	1 065	1 062	1 062
Ring mode	998	994	991	992	991	989
X-sensitive ^b	941	861	834	837	825	797
	918	846	824	826	819	793
X-sensitive	728	— ^e	— ^e	666	653	651
X-sensitive	468	455 ^{Ra f}	— ^g	452 ^{Ra}	451 ^{Ra}	—
X-sensitive	456	444	444	442	437	434
X-sensitive	516	405	— ^g	305 ^{Ra}	257 ^{Ra}	250 ^{Ra}
X-sensitive	365	310 ^{Ra}	— ^g	283 ^{Ra}	222 ^{Ra}	—
γ-CH bending	962	964	— ^e	965	966	966
γ-CH bending	849	— ^e	859	857	861	858
γ-CH bending	834	840	840	— ^e	842	840
γ-CH bending ^b	769	771	771	771	771	772
	764	768	766	766	768	766
Γ CC	681	683	680	681	683	679
Γ CC	575	563	543	564	564	538
X-sensitive	554	551	532	555	554	530
Γ CC	—	—	—	—	—	—
X-sensitive	225 ^h	195 ^{Ra}	— ^g	176 ^{Ra}	158 ^{Ra}	147 ^{Ra}

^a Under consideration of C_s point symmetry group there are 21 A' and 9 A'' vibrations; ^b frequencies splitted due to rotational isomerism; ^c splitted for unknown reasons; ^d β CH denotes in-plane, γ CH out-of-plane bending vibrations; ^e obscured by other absorption; ^f upper index Ra denotes frequencies taken from the Raman spectrum; ^g not investigated; ^h wavenumber from ref. ².

TABLE V

Wavenumbers of 3-I-C₆H₄OCH₃ and 3-I-C₆H₄OCD₃ Vibrations from Infrared and Raman Spectra of Liquid and Crystalline Samples (below 1 600 cm⁻¹) [cm⁻¹]

Assignment ^a	3-I-C ₆ H ₄ OCH ₃			3-I-C ₆ H ₄ OCD ₃		
	liquid		crystal	liquid		crystal
	Ra ^b	IR ^c	IR ^c	Ra ^b	IR ^c	IR ^c
CC-stretching	1 585 S	1 585 S	1 587 S	1 584 S	1 584 S	1 587 S
CC-stretching	1 570 S	1 568 S	1 572 S	1 566 S	1 566 S	1 570 S
		1 538	1 546		1 557 i	1 556 i
		1 520	1 525		1 520	1 525
CC-stretching (<i>cis</i>)				1 471 m, p	1 474 S	— ^d
CC-stretching (<i>trans</i>)		1 474 S	1 475 S		1 470 S	1 470 S
Bending OCH ₃	1 460	1 463 i	1 464 m	— ^e	— ^e	— ^e
Bending OCH ₃		1 457 i	1 450 m	— ^e	— ^e	— ^e
Bending OCH ₃	1 441	1 440 m	1 442	— ^e	— ^e	— ^e
CC-stretching		1 424 m	1 430 m		1 425 i	1 433 m
		1 415 m	1 423 m	1 417	1 417 m	1 424 m
			1 338			1 337
		1 326	1 328		1 325	1 327
			1 322			1 322
CC-stretching		1 304	1 307		1 304	1 304
		1 294 i	1 299 m		— ^f	1 299 m
β-CH bending	1 286 p	1 285 S	1 288 S	1 288 m, p	1 288 S	1 291 S
			1 278			1 276
			1 274	1 269		1 271
X-sensitive (<i>cis</i>)	1 244 S, p	1 244 S	— ^d	1 255 m, p	1 255 S	— ^d
						1 246 m
X-sensitive (<i>trans</i>)	1 230 p	1 230 S	1 231 S	1 234	1 233 S	1 239 m
			1 225i			1 231 m
						1 221
Rocking OCH ₃	1 182 p	1 183 m	1 185 S	— ^e	— ^e	— ^e
β-CH bending (<i>trans</i>)		1 171 m	1 169 S	1 170	1 169	1 171 S
β-CH bending (<i>cis</i>)	1 165 p	1 161 m	— ^d	1 163	1 161	— ^d
Rocking OCH ₃		— ^f	1 156	— ^e	— ^e	— ^e
Bending OCD ₃	— ^e	— ^e	— ^e	1 107 S, p	1 107 S	1 108 S
β-CH bending		1 091	1 093	1 094	1 095i	1 096
Bending OCD ₃	— ^e	— ^e	— ^e			1 091
						1 076
			1 068			1 066
Bending OCD ₃	— ^e	— ^e	— ^e		1 058	1 061
β-CH bending	1 062 S, p	1 062 m	1 059	1 059 S, p	1 062i	1 054
O—C(H ₃ /D ₃) stretching	1 033 p	1 035 S	1 033 S	996	999 S	999 S
			1 022			1 032
Ring mode	989 S, p	991 S	990 S	989 S, p	989 m	991 m
		978	977	976 p	976i	976

TABLE V
(Continued)

Assignment ^a	3-I-C ₆ H ₄ OCH ₃			3-I-C ₆ H ₄ OCD ₃		
	liquid		crystal	liquid		crystal
	Ra ^b	IR ^c	IR ^c	Ra ^b	IR ^c	IR ^c
γ -CH bending		966	967		966i	967
Rocking OCD ₃	— ^e	— ^e	— ^e	959	959 m	961 S
Rocking OCD ₃	— ^e	— ^e	— ^e	893	892	901
		872i	894		870i	888
γ -CH bending		861	879 m		858	879 m
			877 m			
γ -CH bending		842 m	875 m		840 m	874 S
X-sensitive (<i>cis</i>)	826 p	825 S	— ^d	796	797 S	— ^d
X-sensitive (<i>trans</i>)	809 p	819i	812 S		793i	791 S
γ -CH bending (<i>cis</i>)		771i	— ^d		772i	— ^d
γ -CH bending (<i>trans</i>)	771	768 S	768 S	756	766 S	768 S
			765			
Γ CC		683 S	684 S		679 S	684 S
X-sensitive	654 S, p	653	652	649 S, p	651	652
Γ CC	560	564 m	570 m	556	538	545
X-sensitive		554i	559	534	530	
						511
X-sensitive	451 S, p		455	438 S, p	434	435 m
		437 m	436 m			
X-sensitive	257 S, p	— ^g	— ^g	257 S, p	— ^g	— ^g
				239		
X-sensitive	222 S, p					
				170		
X-sensitive	158 S			150		
				134		

^a Some vibrations assigned to *cis* and *trans* forms; ^b strong Raman lines are denoted by S, strongly polarizes lines by p; ^c strong and medium infrared bands denoted by S and m; ^d bands of the *cis* form frozen out in crystal; ^e bands alternately present in one isotopic species only; ^f obscured by other absorption; ^g infrared spectra below 350 cm⁻¹ not investigated.

of the methoxyl group, the energetically most favoured conformations should have the methoxyl group twisted out of the benzene ring plane^{14,15}.

Realization of the fact that the molecules of 3-halogeno derivatives of anisole are subjected to rotational isomerism simplified analysis of their vibrational spectra. Vibrational frequencies of OCH₃ and OCD₃ are assembled in Table III except for deformation vibration of the angle COC and both torsional oscillations which could

not be determined with certainty. The assignments of bands used here is in accord with that employed in the analysis of the spectra of 4-halogeno derivatives of anisole¹. The frequencies¹⁹ in the spectra of $C_6H_5OCD_3$ also satisfy the present assignment although some of the frequencies were originally assigned¹⁹ to other vibrations. The frequencies and their isotopic shifts fit the data obtained from the analysis of vibrational spectra of dimethyl ether and its D_6 -derivative²⁰. Thirty vibrations localised in the aromatic part of the molecule were interpreted as $21A' + 9A''$ on the basis of local symmetry group C_s of the fragment



The assignment of these vibrations is in good agreement with the interpretation of the spectra of 1,3-disubstituted benzene derivatives^{21,22} and does not need any comment. Frequencies of the spectra of liquid samples of 3-fluoro-, 3-chloro-, 3-bromo-, and 3-iodoanisole and of OCD_3 derivatives of 3-chloro- and 3-iodoanisole are assembled in Table IV; infrared and Raman spectra of 3-iodoanisole and its OCD_3 derivative in liquid and crystalline (at 180°C) states are described in detail in Table V.

The NMR spectra of the studied compounds are relatively complex (Fig. 2). The signal at $\tau = 6,26$ p.p.m., corresponds to protons of the OCH_3 group; other signals could be analysed only after some numerical calculations. Results of numerical analysis of a four-spin ABCD system as carried out on National Elliot 503 computer using the iterative procedure according to Špirko²³ are assembled in Table VI. Due to the difficulties in analysing the spectrum of the 3-fluoro derivative the NMR parameters for this compound were only estimated; the best results were obtained for the 3-chloro and 3-iodo derivative for which the NMR spectra of OCD_3 derivatives were also available.

Rotational isomerism and analysis of vibrational spectra of halogeno derivatives of anisole, including 3-halogeno derivatives, were studied by Owen and Hester². Although their view of the structural aspects of the problem is identical with ours (they assume distinguishable rotational isomers for 3-halogeno derivatives of anisole), their interpretation of the spectra differs significantly from our results and from the results of analysis of the spectra of 1,3-disubstituted derivatives of benzene carried out earlier^{21,22}. These authors² were mainly concerned with calculations of internal rotational barriers of the methoxyl group from the torsional frequencies; their values around $7 \text{ kcal} \cdot \text{mol}^{-1}$ are too high to be real.

A closing remark on the sensitivity of out-of-plane deformation vibrations of aromatic hydrogen atoms to the state of matter and the nature of the solvent. With increasing polarity of the solvent²⁴ and even more significantly with the transition

TABLE VI
Proton Chemical Shifts $H(i)$ and Coupling Constants J_{ij} of Anisole 3-Halogeno Derivatives
3- $\text{XC}_6\text{H}_4\text{OCH}_3$

NMR Parameters ^a	X = F	X = Cl ^b	X = Br	X = I ^b
$H(2)$	3.37	3.171	3.03	2.813
$H(4)$	3.37	3.128	2.99	2.767
$H(5)$	2.94	2.867	2.93	3.050
$H(6)$	3.47	3.288	3.32	3.198
J_{24}	2.3	1.83	2.0	1.54
J_{25}	0.2	0.34	-0.2	0.31
J_{26}	2.4	2.51	2.8	2.40
J_{45}	8.2	7.78	8.5	7.35
J_{46}	0.7	0.91	0.4	1.04
J_{56}	8.3	8.38	8.6	8.04
$\pm\Delta H$	0.006	0.0004	0.004	0.0006
$\pm\Delta J$	0.5	0.06	0.4	0.07

^a Parameters $H(i)$ (τ , p.p.m.) and J_{ij} (Hz); $\pm\Delta H$ and $\pm\Delta J$ are RMS errors in estimation of parameters $H(i)$ and J_{ij} ; ^b also spectra of $[\text{OCD}_3]$ derivatives were used.

from the liquid state to the cooled crystalline state the bands of these vibrations shift to higher wave number values. The effect is projected into the $2000-1600\text{ cm}^{-1}$ region where the shift of the second harmonics and combinational frequencies is even more apparent than it is in the fundamental frequency region. In that way the above mentioned region, often employed in the determination of substitution type²⁵, becomes actually the most sensitive region of the whole spectrum to changes of the state and solvent.

It cannot be excluded that the splitting of some bands observed in the spectra of 3-substituted phenols²⁶ which was not explained in the original work²⁶ is caused by rotational isomerism of their molecules. It is quite likely that 3-substituted phenols would exhibit similar distinguishability of the preferred conformations as it is in the case of 2-substituted phenols. In contradistinction to 3-substituted anisoles the rotational isomerism does not sometimes show up in the spectra of 2-substituted anisoles because the substituent in the 2 position does not let the methoxy group take the position in which the methoxy group would be too close to the substituent.

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