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A RAMAN SPECTROSCOPIC STUDY OF THE LOW-FREQUENCY VIBRATIONS OF *o*-DIMETHOXYBENZENE AND ITS METHYL DEUTERATED ANALOGUES

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ABSTRACT

The low-frequency (100—400 cm^{-1}) Raman spectra of liquid (at 300 K) and solid (at 130 K) veratrole (*o*-dimethoxybenzene), and its methyl deuterated analogues, have been measured. The methyl and methoxyl torsional transitions have been identified, and the corresponding rotational barriers have been determined. The interpretation of the spectra points to a conformationally mixed situation for solid veratrole, in which both planar and non-planar conformers may co-exist.

INTRODUCTION

Considerable experimental [1—19] and theoretical [15—23] effort has been exercised on the problem of the conformational preference of methoxyl groups in *ortho*-dimethoxybenzene (veratrole) and its derivatives. The theoretical investigations span a range from early π-electron [20, 21] and ZDO calculations [22] to more recent STO-3G ab initio [17] and INDO MO FPT calculations; the latter combined with magnetic resonance spin—spin coupling results [18].

Indirect experimental information about the conformation of veratrole has accumulated from measurements of dielectric [2, 4] and spin—lattice [11] relaxation times, from studies of the temperature and solvent dependence of the dipole moment [1—3], and from UV- [7, 19], NMR- [5, 6, 8, 12, 13, 18, 19] and PE-spectroscopic [14—17] investigations. A discussion of early results obtained with the above-mentioned methods may be found in refs. 17 and 22. Both theory and experiment have generally led to controversial conclusions regarding the planarity or non-planarity of the methoxyl groups in veratrole. Recently, arguments for co-planarity of the OCH_3 groups with respect to the ring have been presented for veratrole in solution [11, 18], as well as for solid state veratrole and for a majority of solid veratrole derivatives [23]. These arguments cannot, however, be easily reconciled with the measurement of the explicit temperature dependence of the dipole moment, as reported by Mizushima et al. [1] for veratrole in

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solution, and by Roberti and co-workers [3] for liquid veratrole and veratrole in different solvents. Non-planar methoxyl conformations have been suggested, mainly on the basis of STO-3G calculations combined with PE-spectroscopic measurements [16, 17]. The STO-3G calculations were, however, done either with a standard geometry or a partially optimized geometry, transferred from an anisole structure, a fact which somewhat weakens the arguments presented.

Previously, it was suggested [24] that the torsion of the methyl group in a methoxyl substituent acts as a sensitive conformational probe. If several torsional transitions are observed and identified by selective deuteration, the existence of differently orientated methoxyl groups is indicated. To obtain further experimental information about the conformational behaviour of the OCH_3 groups in veratrole, it was decided to study the low-frequency Raman spectra of liquid (300 K) and solid (130 K) veratrole, and its methyl deuterated analogues.

EXPERIMENTAL

Veratrole-d_0 (Fluka AG, purum) was purified by repeated distillation at reduced pressure. Veratrole-d_3 was prepared by methylation of guaiacol (Fluka AG, purum) with dimethyl-sulphate-d_6 (Merck AG, degree of deuteration 99%). Veratrole-d_6 was prepared by methylation of catechol (Fluka AG, puriss.) with $(CD_3)_2SO_4$ in 25% NaOH solution, and separated from the other main product, guaiacol-d_3, by column chromatography as described elsewhere [25]. The deuterated samples were further purified by distillation at reduced pressure. The Raman spectra of veratrole-d_0, veratrole-d_3 and veratrole-d_6 were measured as reported previously [26]. The samples were forced to crystallize rapidly by filling liquid nitrogen into the low-temperature cell. No glass formation was observed.

CALCULATIONS

To the authors' knowledge, no accurate structure determinations exist for veratrole. A plausible reference geometry (Fig. 1) was therefore constructed using structural elements from catechol [27], anisic acid [10], and 2,3-dimethoxybenzoic acid [9]. The reduced moments of inertia, I_r, for the different tops were calculated as described by Larsen and Nicolaisen [28], and in ref. 25. I_r for the OCH_3 top in planar *cis-trans*-veratrole (Fig. 1, using the terminology introduced by Curran [29]), is 19.2 amu Å^2, whereas the value for planar *trans-trans*-veratrole is 19.6 amu Å^2. A test calculation using Pitzer's and Gwinn's formula for I_r [30], gave negligible differences compared to the aforementioned values. The torsional barriers were obtained by solving the Mathieu equation numerically with a computer program [26] modified to search linearly for that torsional s-parameter which gives agreement with the experimentally determined Δb-values. The initial s-values were taken from the tabulations of b for large s-values by Fateley et al. [31].

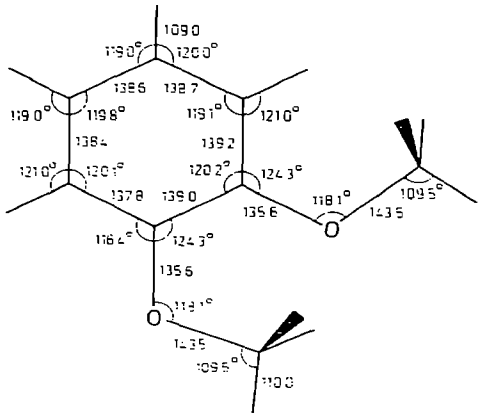

Fig. 1. Reference geometry of solid state veratrole used in the barrier calculations. Bond lengths in pm.

RESULTS AND DISCUSSION

The low-frequency Raman spectra of liquid veratrole-d_0, veratrole-d_3 and veratrole-d_6 are shown in Fig. 2. The corresponding solid-state spectra are collected in Fig. 3. The Raman spectrum of liquid veratrole has been recorded previously [1, 32—36], and the present results essentially confirm the earlier findings. The low-frequency spectrum of the liquid shows several broad

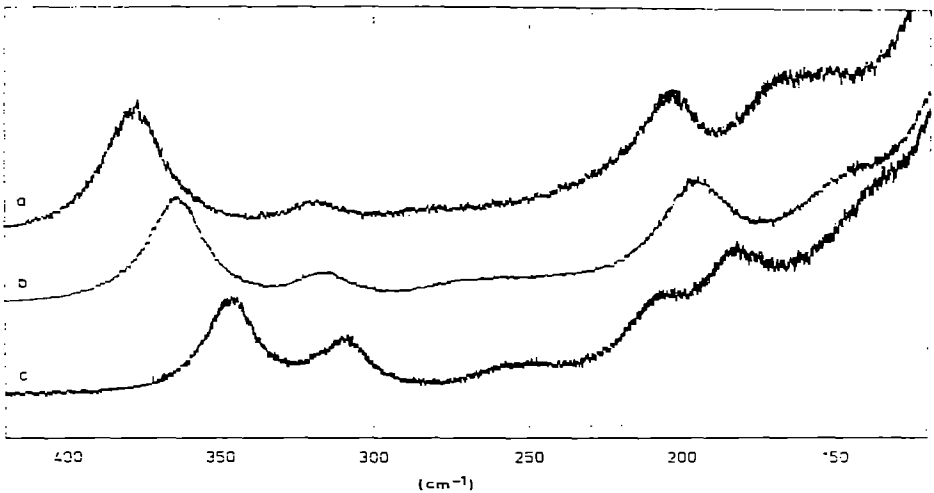

Fig. 2. Comparison of parts of the liquid phase low-frequency Raman spectra of veratrole and its methyl deuterated analogues at 300 K: (a) veratrole-d_0, slit 2.5 cm^{-1}, 2 × 10^3 counts · s^{-1}; (b) veratrole-d_3, slit 2.5 cm^{-1}, 5 × 10^3 counts · s^{-1}; (c) veratrole-d_6, slit 2.5 cm^{-1}, 2 × 10^3 counts · s^{-1}.

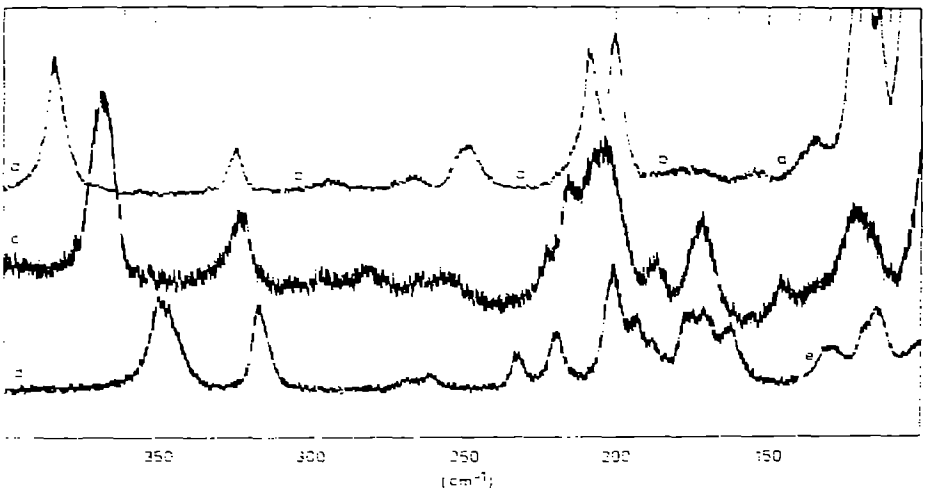

Fig. 3. Comparison of parts of the solid phase low-frequency Raman spectra of veratrole and its methyl deuterated analogues at 130 K: (a) and (b) veratrole-d_0, slit widths 2.5 cm^{-1} and 3.2 cm^{-1}, 2 × 10^3 counts·s^{-1}; (c) veratrole-d_3, slit 2.7 cm^{-1}, 1 × 10^3 counts·s^{-1}; (d) and (e) veratrole-d_6, slit 2.7 cm^{-1} and sensitivity 1 × 10^3 counts·s^{-1} and 2 × 10^3 counts·s^{-1}, respectively.

bands (half-widths ~20 cm^{-1}). These bands are systematically shifted to lower wavenumbers with increasing degree of deuteration (Fig. 2), as expected for X-sensitive modes. The assignments proposed for the liquid phase Raman bands are given in Table 1. The analysis of the vibronic spectrum of veratrole by Urba et al. [37] locates vibrational modes at about 200, 270 and 375 cm^{-1}, which correspond to the modes 17b and 9a and the COC bending mode (Table 1).

TABLE 1

Assignment of low-frequency liquid phase (300 K) Raman bands for veratrole and its deuterated analogues (transitions in cm^{-1})

Mode[a]	Veratrole-d_0	Veratrole-d_3	Veratrole-d_6
17a out-of-plane out-of-phase	167	151	143
17b out-of-plane in-phase	205	197	185
			210
9a in-plane out-of-phase	281	270	256
18a in-plane in-phase	319	316	310
COC bending	377	364	346

[a]Mode numbering according to Wilson [40]; assignment according to Varsányi [41].

The solid-phase Raman bands are much narrower than those of the liquid. Therefore splittings and additional bands are observed in the solid-state spectra (Fig. 3). The strongly asymmetric 205 cm^{-1} band of the liquid is split into a doublet with maxima at 200 and 209 cm^{-1}, and the broad wing on the high-frequency side of the band reveals two additional bands at 249 and 267 cm^{-1}. These bands merge into one band in the spectrum of veratrole-d_3 and are absent in the spectrum of solid veratrole-d_6. These bands are assigned here to the CH_3 torsions. For veratrole-d_3 the CH_3 torsion appears at 255 cm^{-1} and two CD_3 torsions, at 188 and 173 cm^{-1}, are observed. The spectrum of solid veratrole-d_6 shows three partly overlapping bands at 163, 172 and 177 cm^{-1}, which are assigned to CD_3 torsions.

The methoxyl torsion generally appears close to the lattice region in accordance with earlier observations of similar systems [25, 26, 38]. For solid veratrole-d_0 the OCH_3 torsion at 136 cm^{-1} is well separated from the lattice bands, as is the OCD_3 torsion at 130 cm^{-1} for veratrole-d_6 (Fig. 3). Assigning the corresponding torsional band in the spectrum of veratrole-d_3 is more difficult, since the first lattice band has shifted to a higher frequency compared to veratrole-d_0 and veratrole-d_6. Consequently the OCH_3 torsion is seen only as a shoulder at 135 cm^{-1}, whereas the OCD_3 torsion is probably hidden under the lattice band.

The assignments of the respective torsional modes, together with the corresponding calculated barrier values, are collected in Table 2, where the methoxyl torsional barriers were calculated with the reduced moment of inertia for the *cis-trans* conformer. To check possible conformational deviations, the OCH_3 torsional frequency for veratrole was also calculated, using the *trans-trans* I_r value and the barrier 5265 cm^{-1} (Table 2). The result, 134.5 cm^{-1}, falls well within the observed transition band width. A comparison with previously reported methoxyl torsional frequency and barrier values for β-phase guaiacol [25], suggests that at least one of the methoxyl groups in veratrole adopts a predominantly planar heavy-atom orientation with respect to the ring. From the OCH_3 torsional data alone it is, however, impossible to distinguish between the two possible planar veratrole conformers.

The methyl torsional frequencies for veratrole-d_0 and veratrole-d_3 given

TABLE 2

Assignment of the torsional transitions (cm^{-1}), and calculated barrier values, V(cm^{-1}), in veratrole and its methyl deuterated analogues

Assignment	Veratrole-d_0		Veratrole-d_3		Veratrole-d_6	
	Transition	V	Transition	V	Transition	V
Methyl torsion	249	1481	173 (τCD_3)	1390	163	1240
	267	1692	188 (τCD_3)	1633	172	1375
			255 (τCH_3)	1550	177	1453
Methoxyl torsion	136	5265	135 (τOCH_3)	5213	130	5800

in Table 2 are remarkably close to the corresponding frequencies observed for the α- and β-phase guaiacols [25], where the occurrence of two phases was presumed to originate from the co-existence of planar and non-planar conformers in the system. If the present assignment is correct, the two observed methyl transition frequencies for veratrole-d_0 (Table 2), show that the respective methyl groups experience slightly different torsional potentials. A straightforward, if conformationally biased, interpretation of this observation, allows either the existence of one unique conformer (*cis-trans* or out-of-plane-*trans*), or the co-existence of two or more different conformers. In the latter case contributions from *cis-trans*, *trans-trans* and out-of-plane-*trans* structures could produce the observed spectral features. For symmetry reasons the *trans-trans* veratrole conformer would give rise to only one CH_3 torsional band, whereas the *cis-trans* or out-of-plane-*trans* conformers would each give rise to two different methyl torsional transitions, one of which would remain unresolved, because it would merge with the CH_3 band for the *trans-trans* conformer. The intensity difference between the two methyl bands in Fig. 3a could, to a first approximation, indicate the relative amounts of different conformers present, also accounting for the polarizability changes introduced upon rotating a methyl group out of the plane.

For veratrole-d_3 two additional bands, one in the CH_3 and the other in the CD_3 region of the spectrum, should be observable, irrespective of whether one or more conformers are present. Fig. 3c shows that two CD_3 torsional transitions are observed at 188 and 173 cm^{-1}, whereas for the CH_3 torsion the situation is less clear-cut. The veratrole-d_0 bands at 249 and 267 cm^{-1} seem to have merged into one broad, weak band at about 255 cm^{-1}. The failure to locate two CH_3 torsional transitions in this region could be because the intensity of the second transition is too low for it to be observed with the present equipment. Difficulties in assigning the CH_3 torsions are also introduced if there is coupling between the methyl torsion and the X-sensitive doublet at 205 cm^{-1}, a possibility which cannot be excluded on the basis of the spectra in Fig. 3. The doublet band is further split with increasing deuteration (Fig. 3c, d); this type of coupling was found for anisole and guaiacol [25, 26].

For veratrole-d_6 it is seen (Fig. 3d, Table 2) that the spectral characteristics no longer support a discussion allowing only one predominant conformer, unless the three bands assigned as CD_3 torsions really consist of two CD_3 bands split via coupling to other low-frequency modes or lattice vibrations. The three observed CD_3 torsional transitions in veratrole-d_6 support the hypothesis that at least two different conformers co-exist for solid veratrole. The fact that the spectral pattern for the methyl torsional transitions is more resolved for veratrole-d_6 than for veratrole-d_0 can perhaps be traced to effects introduced upon deuteration. The deuterium-substituted internal rotor energy levels lie below those of the hydrogen-substituted internal rotor. Consequently, the corresponding methyl torsional transitions would be more easily distinguished in the deuterated case.

The chief advocates of the case for non-planar *o*-dimethoxybenzene structures have been Houk and co-workers [16, 17], who found the orthogonal-*trans* conformer to be the most stable species in the gas phase on the basis of STO-3G calculations combined with interpretations of the molecular PE-spectra. Preliminary STO-3G investigations using superimposed, fully optimized anisole structures with additional, extensive optimization of the substituent geometry parameters [39], give the *trans-trans* conformation of veratrole as the global energy minimum. The orthogonal-*trans* and the orthogonal-orthogonal (opposite sides of the ring) conformations lie about 3 and 7 kJ mol^{-1}, respectively, above the minimum. But, the planar *cis-trans* conformer lies only about 14 kJ mol^{-1} above the energy minimum, whereas ref. 17 sets this value at about 42 kJ mol^{-1} for standard geometries. Firstly, the present calculations indicate that optimization of pertinent structural features must be attempted when exploring conformational preferences; secondly, although calculated minimal-basis conformational energy differences must be regarded as largely qualitative, they usually indicate upper limit values. Consequently, the energy differences of the various conformers, as reported above, all show an order of magnitude which can easily be overcome by solvation or packing forces in condensed media. Hence the observation by Schaefer and Laatikainen [18] and Makriyannis and Fesik [11] that veratrole in solution exists predominantly in a planar conformation. Caillet [23] also concludes that the preferred conformation of a majority of dimethoxy-substituted compounds in the crystal phase is a planar one. The present data for the simplest *o*-dimethoxybenzene, veratrole, are not necessarily in conflict with Caillet's results. Rather, the low-frequency Raman spectra of veratrole can be interpreted in favour of a conformationally mixed situation, where both planar and non-planar conformers co-exist in the crystal. As Caillet [23] points out, different conformers can retain their structural preference if suitable spacings persist in the structure upon crystallization.

According to ref. 3, the dipole moment of liquid veratrole increases almost linearly with temperature in the range 20—160°C, whereas for veratrole dissolved in different hydrocarbons, a levelling effect is observed. These observations imply that different Boltzmann-weighted conformers may also co-exist in liquid veratrole, and that solvent—solute interactions may selectively stabilize certain veratrole conformers in solution. A selective stabilization may also occur in the solid state, due to the rapid crystallization of the samples, which possibly "freeze" into different conformations.

CONCLUSIONS

The low-frequency Raman spectra of veratrole and its methyl deuterated analogues have been measured, and the various methyl torsional transitions have been identified. The torsional barriers for the methoxyl and methyl torsions have been estimated and compared with previously reported results

for similar molecular systems. The interpretation of the spectral features indicate that the veratrole spectra cannot be easily assigned to only one predominant conformer. The situation prevailing in solid state veratrole seems to favour the co-existence of at least two different conformers. Preliminary test calculations on the STO-3G level of accuracy show that the most stable gas phase conformer would be expected to be planar, but the energy differences between various local minima and the global hypersurface energy minimum are of an order of magnitude which makes interpretations based upon the existence of various conformers far from trivial, especially when liquid, solution or crystal systems are considered.

REFERENCES

1 S. Mizushima, Y. Morino and H. Okazaki, Sci. Pap. Inst. Phys. Chem. Res. (Jpn.), 34 (1938) 1147.
2 D. M. Roberti and C. P. Smyth, J. Am. Chem. Soc., 82 (1960) 2106.
3 L. M. DiBello, H. M. McDevitt and D. M. Roberti, J. Phys. Chem., 72 (1968) 1405.
4 K. N. Abd-El-Nour, Z. Phys. Chem. (Leipzig), 263 (1982) 1050.
5 K. S. Dhami and J. B. Stothers, Can. J. Chem., 44 (1966) 2855.
6 R. W. Crecely, K. W. McCracken and J. H. Goldstein, Tetrahedron, 25 (1969) 877.
7 J. C. Dearden and W. F. Forbes, Can. J. Chem., 37 (1959) 1305.
8 P. Khare and R. C. Gupta, J. Mol. Struct., 70 (1981) 213.
9 R. F. Bryan and D. H. White, Acta Crystallogr., Sect. B, 38 (1982) 1012.
10 M. Colapietro and A. Domenicano, Acta Crystallogr., Sect. B, 34 (1978) 3277.
11 A. Makriyannis and S. Fesik, J. Am. Chem. Soc., 104 (1982) 6462.
12 J. J. Knittel and A. Makriyannis, J. Med. Chem., 24 (1981) 606.
13 A. Makriyannis and J. J. Knittel, Tetrahedron Lett., (1979) 2753.
14 L. N. Domelsmith, L. L. Munchausen and K. N. Houk, J. Am. Chem. Soc., 99 (1977) 4311.
15 L. N. Domelsmith and K. N. Houk, Int. J. Quantum Chem., Quantum Biol. Symp., 5 (1978) 257.
16 L. N. Domelsmith, T. A. Eaton, K. N. Houk, G. M. Anderson III, R. A. Glennon, A. T. Shulgin, N. Castagnoli, Jr. and P. A. Kollman, J. Med. Chem., 24 (1981) 1414.
17 G. M. Anderson III, P. A. Kollman, L. N. Domelsmith and K. N. Houk, J. Am. Chem. Soc., 101 (1979) 2344.
18 T. Schaefer and R. Laatikainen, Can. J. Chem., 61 (1983) 224.
19 P. Hencsei and J. Nagy, Acta Chim. (Budapest), 101 (1979) 359.
20 P. Hencsei, G. Pongor and J. Nagy, Acta Chim. (Budapest), 101 (1979) 367.
21 J. Nagy and P. Hencsei, Acta Chim. (Budapest), 71 (1972) 83.
22 H. Tylli, Fin. Kemists. Medd., 82 (1973) 16.
23 J. Caillet, Acta Crystallogr., Sect. B, 38 (1982) 1786.
24 H. Konschin, H. Tylli and C. Grundfelt-Forsius, J. Mol. Struct., 77 (1981) 51.
25 H. Tylli, H. Konschin and C. Grundfelt-Forsius, J. Mol. Struct., 77 (1981) 37.
26 H. Tylli and H. Konschin, J. Mol. Struct., 42 (1977) 7.
27 H. Wunderlich and D. Mootz, Acta Crystallogr., Sect. B, 27 (1971) 1684.
28 N. W. Larsen and F. M. Nicolaisen, J. Mol. Struct., 22 (1974) 29.
29 B. C. Curran, J. Am. Chem. Soc., 67 (1945) 1835.
30 K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., 10 (1942) 428.
31 W. G. Fateley, F. A. Miller and R. E. Witkowski, Far Infrared Spectra of Halogenated Phenols: The Calculation of the Barrier Height of the Hydroxy Group from the Observed Torsional Vibrations, Mellon Institute, Pittsburgh Tech. Rep. AFML-TR-66-408, January 1967, Section II.

32 K. W. F. Kohlrausch and A. Pongratz, Monatsh. Chem., 65 (1934) 6.
33 A. W. Reitz and Gr. Prinz Ypsilanti, Monatsh. Chem., 66 (1935) 299.
34 E. Herz, Monatsh. Chem., 76 (1946) 1.
35 K. W. F. Kohlrausch, Monatsh. Chem., 76 (1946) 231.
36 J. Lecomte, J. Phys. Radium, 9 (1938) 13.
37 V. A. Urba, V. N. Kietienė, V. V. Šalna and H. P. Jonaitis, Liet. Fiz. Rinkinys, 11 (1971) 295.
38 H. Tylli, H. Konschin and C. Grundfelt-Forsius, J. Mol. Struct., 55 (1979) 157.
39 H. Konschin, J. Mol. Struct., Theochem, 105 (1983) 213.
40 E. B. Wilson Jr., Phys. Rev., 45 (1934) 706.
41 G. Varsányi, Vibrational Spectra of Benzene Derivatives, Academic Press, New York, 1969.