Vibrational spectra and conformational isomerism of calixarene building blocks. II. Bis(2-hydroxyphenyl)methane† ‡

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The conformations and vibrational spectra of bis(2-hydroxyphenyl)methane have been analysed within the framework of density functional theory. The calculated force fields (B3LYP/6-31G*) of seven possible energy minima were transformed to internal coordinates, and a set of ten different scaling factors was applied. The scaled quantum mechanical (SQM) method reproduces the experimental IR and Raman spectra with high accuracy. The dependence of the CH_2 stretching vibrations on the conformation and the possibility of its use as a probe for larger systems, *e.g.*, calixarenes or polyphenols, are discussed.

Introduction

Calixarenes are macrocyclic compounds consisting of phenol rings that are connected *via* the *ortho* positions by methylene groups. They and their derivatives are increasingly being employed in the complexation of cations, anions and neutral molecules.[2,3] It is widely recognised that the complexing properties of ligands built on calixarenes may differ dramatically from those of their acyclic counterparts. Hence, it would be highly desirable to create approaches to quantitatively assess the influence of connecting structure on selectivity of binding, complex stability, *etc.* The possibility of easy and fast quantitative evaluation of the spatial structure of calixarene-based ligands is to become the first step in elaborating such an approach.

The single-crystal X-ray technique is unsuited to solutions, amorphous or powder samples. The 3D structure evaluation of conformationally flexible molecules on the basis of NMR spectroscopy is a very tedious task. Vibrational spectroscopy is known to be a versatile tool in the conformational analysis of both liquid and solid compounds or their solutions. However, an interpretation of IR and Raman spectra of the calixarenes and their derivatives is rather complex, and this is the reason why vibrational spectroscopy is not widely applied. Therefore, we have started systematic studies of vibrational spectra and conformational isomerism of comparatively simple calixarene building blocks to establish reliable interpretation of their spectra.[1]

For this purpose, we used DFT (density functional theory)[4] calculations, which produce surprisingly accurate vibrational frequencies. Nevertheless, these calculations show systematic errors mainly due to limited basis sets, harmonic approximation and remaining deficiencies in describing electron correlation. Transferable scaling factors are able to compensate for most of these systematic errors.[5] In a previous study[1] we were able to reproduce the complete experimental range of the IR and Raman spectra of diphenylmethane (**1**) using the scaled quantum mechanical (SQM) method. In the present work, we use the same approach to study normal modes and conformational behaviour of the title compound. This represents a more realistic model for calixarenes than diphenylmethane.

Experimental

Bis(2-hydroxyphenyl)methane (**2**) was obtained commercially from Aldrich with a purity of 99%. The purity was controlled by IR and ^{1}H NMR spectroscopy. The solvent, CCl_4, was stored, prior to use, on molecular sieves, 3 or 4 Å, to remove traces of water. All solution preparations were carried out in a glove box with exclusion of moisture. IR spectra of the compound as melted film between KBr plates were recorded on a Vector 22 FTIR spectrometer (Bruker) in the 400–4000 cm^{-1} range at a resolution of 1 cm^{-1}. Solid samples were prepared as KBr pellets. Spectra of CCl_4 solutions were recorded in 2 cm cells. The concentrations were about 10^{-4} M.

Computations

All DFT calculations were done using the Gaussian 98 suite of programs.[6] We used Becke‘s three-parameter exchange functional[7] in combination with the Lee–Yang–Parr correlation functional[8] (B3LYP) and a standard double-zeta basis (6-31G*). All stationary points were characterized as minima by analysis of the Hessian matrices.

Results and discussion

Geometry

According to our computations, the molecule **2** is able to exist in seven stable conformations depicted in Fig. 1, the geometry of the most stable of them (**2.I**) being very similar to the conformation found by a single-crystal X-ray study.[9] All the calculated structural parameters of the conformer **2.I** are in

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† For previous communication see ref. 1.

‡ Electronic supplementary information (ESI) available: Table 1S. Results obtained from geometry optimisation for conformer **2.I**. See http://www.rsc.org/suppdata/p2/b1/b108745b/

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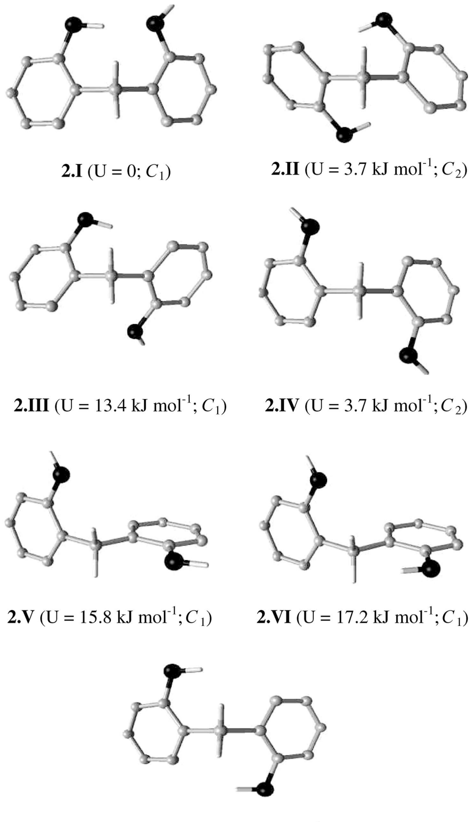


2.I (U = 0; C_1) **2.II** (U = 3.7 kJ mol^{-1}; C_2)

2.III (U = 13.4 kJ mol^{-1}; C_1) **2.IV** (U = 3.7 kJ mol^{-1}; C_2)

2.V (U = 15.8 kJ mol^{-1}; C_1) **2.VI** (U = 17.2 kJ mol^{-1}; C_1)

2.VII (U = 29.1 kJ mol^{-1}; C_2)

Fig. 1 Calculated stable conformations of the molecule **2**, their conformational energies relative to those of the most stable conformation **2.I** (−653.0536 a.u.), and their symmetry (in parentheses). Selected torsion angles (°) are the following: **2.II** C1A–C6A–C7–C6B = 55.8, C1B–C6B–C7–C6A = 55.8; **2.III** C1A–C6A–C7–C6B = −62.0, C1B–C6B–C7–C6A = −67.2; **2.IV** C1A–C6A–C7–C6B = 92.4, C1B–C6B–C7–C6A = 92.4; **2.V** C1A–C6A–C7–C6B = −64.4, C1B–C6B–C7–C6A = 162.2; **2.VI** C1A–C6A–C7–C6B = −83.3, C1B–C6B–C7–C6A = 176.6; **2.VII** C1A–C6A–C7–C6B = 96.8, C1B–C6B–C7–C6A = 96.8 (for numbering scheme see Table 3).

reasonable agreement with the X-ray data. At least part of the deviation between the computed geometry and the experimental values (Table 1S in supplementary data) is, probably, caused by rather strong intermolecular interactions in the crystalline compound **2**.[9]

O–H-frequencies

The conformational homogeneity of **2** in the solid state facilitates the assignments of the fundamentals. Table 1 gives these assignments based on the present computations. As in the case of diphenylmethane **1**,[1] uncorrected frequencies of **2** (Table 1, column A) are systematically higher than the corresponding experimental values. Hence, in a first step, individual scaling factors[1,5] (Table 2) were used to improve the results (Table 1, column B). At this stage, the calculated wavenumbers of the fundamentals almost coincided with the experiment. Only for the vibrations of the OH groups, the agreement was much worse. This discrepancy is due, apparently, to intermolecular hydrogen bonding in crystalline compound **2**.[9]

The computed wavenumbers of the OH vibrations should be compared with gas phase spectra. But the low vapour pressure of the title compound makes any reliable spectroscopic measurements for gaseous **2** hardly possible. So, the calculated frequencies of OH stretchings in Table 1 are compared to the recorded IR values for highly diluted CCl_4 solutions, wherein intermolecular hydrogen bonding is entirely absent. The OH stretching region in the CCl_4 solutions shows two distinct maxima, 3602 and 3472 cm^{-1}, and a weak shoulder at 3538 cm^{-1}. The bands at 3472 and 3602 cm^{-1} are assigned to the intramolecular OH ··· O hydrogen bond, and the free OH, respectively.[10] Also the presence of OH ··· π interactions can be recognised in the spectra at 3538 cm^{-1}.[10] According to our computations (Fig. 1, Table 1), the weak shoulder at 3538 cm^{-1} is mainly due to OH ··· π interactions present in conformer **2.II**. The very low intensity of the shoulder at 3538 cm^{-1} indicates that only trace amounts of the OH ··· π conformers are present in the diluted CCl_4 solutions.

CH_2-frequencies

According to our calculations, there is no distinct dependency of the aromatic ring vibrations on the conformation of the molecule **2** (compare columns B and C of Table 1), while OH and CH_2 vibrations are definitely conformationally sensitive. Again, direct comparison of the predicted OH modes is reasonable only for highly diluted CCl_4 solutions, which are not transparent in the region below ~2100 cm^{-1}, where OH bendings and torsions could be observed. On the other hand, CH_2 vibrations are much less liable to intermolecular interactions and could therefore be used as a probe for conformational changes not only in solution, but also in the solid and molten compound **2**. Unfortunately, the spectral region of the δCH_2, tCH_2 and wCH_2 modes is too overcrowded to allow any definite conclusion to be drawn. So, only the νCH_2 vibrations will be discussed below. As was mentioned before, the conformers **2.II** and **2.III** are practically absent in dilute CCl_4 solution. So, most probably, the less stable conformers **2.IV**–**VII** are absent too, and the experimental spectra are due, almost solely, to the conformer **2.I**. Hence, experimental $\nu_{as}CH_2$ and ν_sCH_2 wavenumbers should be compared directly with the corresponding values computed for **2.I**.

The difference between the experimental ν_sCH_2 and $\nu_{as}CH_2$ wavenumbers is nearly twice as large as that between the calculated values (Table 1) and, even after additional optimisation of the scaling factors, quantitative agreement cannot be achieved. The latter fact suggests erroneous off-diagonal elements of the Hessian matrix. We therefore conducted additional B3LYP calculations of the complete matrix of energy second derivatives using a double-zeta basis augmented with polarisation and diffuse orbitals on both heavy and hydrogen atoms (6-31++G**). The higher flexibility of this basis set lowers the coupling force constant connecting the methylene C–H bonds (0.0387 instead of 0.0459 aJ Å^{-2}) for conformer **2.I**, which is indeed pointing to an overestimation of the coupling constant calculated with the smaller 6-31G* basis. Probably, further enlargement of the basis set would allow us to obtain even better accuracy, but at a much higher computational cost. Besides, the use of basis sets different from 6-31G* would imply a reoptimisation of the whole set of scaling factors.[1,5] We therefore decided just to eliminate this specific coupling constant (see footnote *g* to Table 1). It should be noted that a similar situation applied in the case of the molecule **1**:[1] the computations fitted the experiment better with the coupling force constant taken as zero.

The $\nu_{as}CH_2$ and ν_sCH_2 frequencies of all the conformers are presented in Table 3 in ascending order of wavenumbers. With the exception of the conformers **2.V**–**VII** the dihedrals between the planes of the aromatic rings and the C6A–C7–C6B plane are increasing in the same order. If this correlation holds for any C_{ar}–CH_2–C_{ar} moiety, then $\nu_{as}CH_2$ and ν_sCH_2 wavenumbers of conformer **2.II** should be comparable to the corresponding wavenumbers of the molecule **1**, because in both cases the dihedrals are equal to ~56° (see Table 3 and ref. 1).

The predicted CH_2 frequencies for **2.II**, namely 2890 and 2856 cm^{-1}, do practically coincide with the experimental (2909 and 2844 cm^{-1}) and the computed (2906 and 2846 cm^{-1}) values of the molecule **1**.[1] The latter frequencies were calculated under the abovementioned approximation that the C–H/C–H coupling force constant for the methylene bridge is absent.

Table 1 Vibrational spectra of bis(2-hydroxyphenyl)methane

Experiment			Computations			
Solid	Liquid			ν/cm^{-1}		
ν/cm^{-1}, I[a]	ν/cm^{-1}, I[a]	Assignment[b]	I_{IR}	A[c]	B[d]	C[e]
	3602 vs (CCl$_4$)	νOH$_{free}$	58	3756	3600	
						3525
~3541 vw sh	3538 vvw (CCl$_4$)	νOH $\cdots$ π				
						3515
	3472 vs, br (CCl$_4$)	νOH $\cdots$ O$_{intra}$	466	3624	3475	
3398 sh						
3316 vs	~3322 vbr (CCl$_4$)[f]	νOH $\cdots$ O$_{inter}$				
~3247 sh						
3087 vvw		νCH$_{ar}$	14	3214	3076	3079
	3071 m (CCl$_4$)	νCH$_{ar}$	23	3214	3075	3079
3066 vw		νCH$_{ar}$	30	3204	3065	3071
	3047 sh (CCl$_4$)	νCH$_{ar}$	15	3199	3063	3071
		νCH$_{ar}$	11	3187	3054	3054
3035 w	3034 s (CCl$_4$)	νCH$_{ar}$	4	3185	3048	3054
		νCH$_{ar}$	19	3168	3030	3033
3019 vw	3016 w sh (CCl$_4$)	νCH$_{ar}$	9	3168	3030	3033
2926 w-m	2938 w br (CCl$_4$)	ν_{as}CH$_2$	6	3099	2922[g]	2890
2873 vw						
	2873 vw (CCl$_4$)	ν_sCH$_2$	21	3062	2886[g]	2856
2856 vw						
1613 w-m	1612 w	Ring	14	1675	1617	1616
		Ring	5	1667	1609	1610
1593 sh		Ring	18	1652	1596	1583
1586 s	1585 s	Ring	27	1640	1583	1580
1503 sh	1503 sh	Ring	35	1553	1508	1497
		Ring	64	1541	1498	1495
1490 vs	1488 vs	Ring	14	1512	1474	1472
		Ring	6	1504	1465	1472
1457 vvs	1454 vvs	δCH$_2$	48	1526	1459	1438
1415 w sh	1418 vw					
1397 s	1384 sh	δArOH$_{bond}$	59	1408	1341	1329
1377 sh	~1372?					1326
1358 sh	1364 m					
		tCH$_2$,ring	16	1367	1326	1317
1320 vw	1327 w-m	wCH$_2$	28	1358	1321	1335
		δArOH$_{free}$ring	10	1376	1319	
1283 vw	1304 w	Ring, wCH$_2$	20	1342	1300	1285
~1260 vw sh		νAr–O$_{bond}$	32	1311	1268	1264
						1249
1248 vs	1243 s	νAr–O$_{free}$	106	1286	1238	
		δArOH$_{bond}$, νArO$_{bond}$	46	1264	1215	1205
1225 sh	1229 s					1197
		νAr–C, δArOH$_{free}$	14	1232	1188	1179
1162 m	1168 m	Ring, tCH$_2$	38	1199	1164	1168
		Ring	2	1195	1162	1158
		Ring	7	1191	1160	1154
1152 m-w	1156 m-w	Ring	8	1185	1154	1146
1108 m	1102 m-s	δArOH$_{free}$	6	1204	1144	
1086 w	1084 sh	Ring, δArOH$_{free}$	29	1127	1095	1096
		Ring, δArOH$_{free}$	14	1105	1077	1092
1040 m-s	1041 m	Ring	38	1073	1040	1038
		Ring	37	1069	1036	1032
971 vw	~970?					
940 w-m	940 w	Ring	0	972	952	959
		Ring	0	969	949	959
		Ring	4	940	922	931
917 m	915 w-m	Ring	3	929	917	927
		rCH$_2$, ring	3	938	911	912
871 m	~870 sh	Ring	3	877	962	866
861 m-w	859 m-w	ν_{as}CAr$_2$, ring	6	869	850	861
		Ring	2	856	841	848
836 m-s	836 m	Ring	8	846	829	846
794 m-s	790 w	δCAr$_2$, ring	6	801	784	771
		Ring	3	782	756	758
753 vvs	752 vvs	Ring	38	765	752	756
		Ring	51	762	750	754
724 w-m	720 w	Ring	0	726	713	708
714 w	713 w	Ring	1	722	703	702
667 sh?	665 w					
652 w	658 vw					
615 m	617 m	Ring	8	628	616	629
	601 w					
		Ring	5	605	593	604

Table 1 Vibrational spectra of bis(2-hydroxyphenyl)methane (continued)

Experiment			Computations			
Solid	Liquid			ν/cm^{-1}		
ν/cm^{-1}, I^{a}	ν/cm^{-1}, I^{a}	Assignment^{b}	I_{IR}	A^{c}	B^{d}	C^{e}
591 m	593 vw					
562 w	564 w	Ring	136	572	560	557
546 vw	543 vw	torsAr–OH$_{bond}$, ring	4	594	554	442
		Ring	3	551	540	542
518 w-m	523 w-m	Ring	9	532	523	536
		Ring, torsAr–OH$_{bond}$	6	543	522	523
	504 vvw					
483 w	486 vw	Ring	0	489	476	471
449 w	448 w	Ring	4	457	447	459
		Ring	5	454	444	441
426?	421 vw	Ring	5	429	417	420

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder. [b] ν, stretch; δ, bend; w, wagging; t, twisting; r, rocking; s, symmetrical; as, asymmetrical. 'Ring' is used for vibrations of phenyl rings. 'Free' (or 'bond') designates an OH group, participating in intramolecular H-bonding as an acceptor (or donor, respectively) of the proton. 'Intra' and 'inter' stand for intra- and intermolecular H-bonds, respectively. [c] Unscaled wavenumbers of conformer 2.I (Fig. 1) [d] SQM scaled wavenumbers of conformer 2.I (Fig.1) [e] SQM scaled wavenumbers of conformer 2.II (Fig. 1) [f] For concentrations > 10^{-4} M [g] $\nu_{as}CH_2 = 2935$ cm^{-1} and $\nu_{s}CH_2 = 2874$ cm^{-1} provided that the coupling CH–CH force constant = 0 (see text).

Table 2 Scaling factors for the force field of the molecule **2**

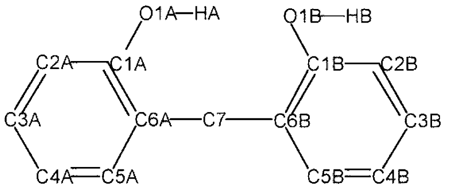
	Scaling factor	Value
Stretch	C–H (arom.)	0.915^{a}
Stretch	C–H (aliphat.)	0.889^{a}
Stretch	CC	0.922^{b}
Stretch	CO	0.922^{b}
Stretch	O–H	0.920^{b}
Bend	CCC	0.990^{b}
Bend	CCO	0.990^{b}
Bend	CCH	0.950^{b}
Bend	HCH	0.915^{b}
Bend	COH	0.876^{b}
Out of plane	Ar–C(bridging), Ar–H, Ar–O	0.976^{b}
Torsion	Conjugated	0.935^{b}
Torsion	Single bond	0.831^{b}

[a] Ref. 1. [b] Ref. 5.

Using the same assumption for the conformer **2.II** the SQM scaled wavenumbers are 2902 and 2844 cm^{-1}, respectively.

It is worth mentioning that in CCl_4 solution, experimental νCH_2 frequencies of bis(2-hydroxyphenyl)methane are higher than for the solid sample (Table 1). This is in line with our computations, which predict larger dihedrals and higher νCH_2 frequencies for the isolated molecule **2** compared to the solid-state structure (Table 1S in supplementary data). Based on this observation, one could expect even higher wavenumbers for the CH_2 stretchings in conformer **2.VII**, because of a further enlargement of the dihedrals relative to the crystal structure (Table 3). Nevertheless, the calculated νCH_2 frequencies of conformer **2.VII** are lower than in the case of conformer **2.I**. The latter deviation of the discussed wavenumbers from proportionality to the dihedrals proves that the CH_2 stretching vibrations do not depend only on the mutual orientation of the aromatic rings. Some tentative conclusions can be drawn that the νCH_2 frequencies of the conformer **2.VII** are influenced by the (O)H ··· H(C) short intramolecular contacts (1.88 Å) which are absent in the similar conformation **2.I**. The same reason is, probably, valid for another couple of similar conformations **2.V** and **2.VI**. The latter also has a short (O)H ··· H(C) contact, about 1.97 Å, and, respectively, much lower νCH_2 frequencies as compared to the conformer **2.V**.

Table 3 SQM predicted conformational sensitivity of the molecule **2** CH_2 stretching vibrations



Conformer	**2.VI**	**2.VII**	**2.II**	**2.V**	**2.III**	**2.I**	**2.IV**
$\nu_{as}CH_2{}^{a}$/cm^{-1}	2865	2872	2890	2907	2912	2922	2943
$\nu_{s}CH_2{}^{a}$/cm^{-1}	2804	2853	2856	2870	2862	2886	2901
φA^{b}/°	18	82	56	4	62	81	87
φB^{c}/°	64	82	56	83	67	80	87

[a] SQM scaled values. [b] Dihedral angle between the ring A plane and C6A–C7–C6B plane. [c] Dihedral angle between the ring B plane and C6A–C7–C6B plane.

Conclusions

The data obtained demonstrate that the SQM method, applied to DFT force fields, successfully reproduces the spectra of polyphenolic molecules. In the case of bis(2-hydroxyphenyl)methane, there are seven possible energy minima. Only two of them are detectable *via* IR experiments in dilute CCl_4 solutions. The global minimum conformation is abundant and stabilised by an intramolecular hydrogen bond. The second detectable conformer, which is present in trace amounts, has two intramolecular OH ··· π bonds (C_2-symmetry). The conformational dependence of C–H frequencies in methylene bridges could be used as a probe for larger systems, for example calixarenes or polyphenols. Further studies are in progress.

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