Vibrational spectra and conformational isomerism of calixarene building blocks: 2-benzylphenol †

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The conformations and vibrational spectra of 2-benzylphenol have been analysed within the framework of scaled quantum mechanics. It is shown that the solid-state conformation of the 2-benzylphenol molecule corresponds to one of four potential energy minima predicted by non-empirical quantum chemical calculations for the isolated molecule. In the molten state and in diluted CCl_4 solutions of the title compound this conformer coexists with another two spectroscopically detected conformations. The presence of several conformers gives rise to the observation of the corresponding number of $\nu_s CH_2$ and $\nu_{as} CH_2$ bands in the IR spectra, thus providing experimental evidence of the conformational sensitivity of the νCH_2 frequencies. It is shown that νCH_2 wavenumbers of different kinds of molecules, containing diphenylmethane fragments, are determined by the dihedral angles between the planes of the aromatic rings and the plane of the connecting methylene bridges, except for the case of short intramolecular contacts with the participation of the methylene protons.

Introduction

Calixarenes are macrocyclic compounds consisting of phenol rings that are connected via the *ortho* positions by methylene groups. The chemistry and complexation properties of calixarenes are presently an important domain in supramolecular chemistry.[4,5] Several studies have been devoted to the investigation of the acyclic polyphenols, which are intermediates in the calixarene synthesis process and can be also used for complexation (*e.g.*[6]). Designing multidentate ligands for selective binding requires choosing approaches to quantitatively assess the influence of connecting structure on selectivity of binding, complex stability, etc. In particular, the magnitude of ligand conformational changes associated with complexation is a good indicator of the binding site organization.[7] Hence, the easy and fast quantitative evaluation of the conformation of calixarenes and acyclic polyphenols would be highly desirable.

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 related molecules is rather complex, and this is the reason why vibrational spectroscopy is not widely applied. Recently[1-3] we have tried to overcome these limitations using the scaled quantum mechanical (SQM) method[8] on the basis of density functional theory (DFT)[9] calculations, which produce surprisingly accurate vibrational frequencies. We were able to elucidate conformational properties and establish a reliable interpretation of the spectra of comparatively simple calixarene building blocks: diphenylmethane[1] (**1**) and bis(2-hydroxyphenyl)methane[2] (**2**). Conformational sensitivity of the stretching frequencies of CH_2 groups has been found, the frequencies depending not only on the mutual orientation of the phenolic residues.[2]

In the present work, we use the same approach to study normal modes and conformational behaviour of 2-benzylphenol

1   **2**

3
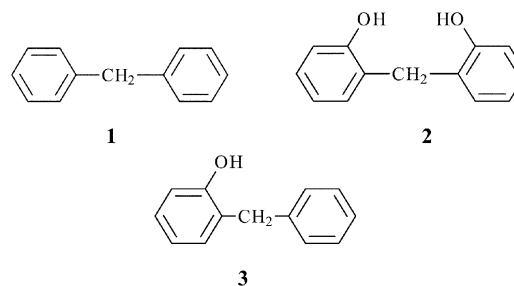
(**3**) in order to extend a set of structures with a variety of mutual orientations of aromatic rings connected by $-CH_2-$ bridges. It is hoped to establish on this basis a better understanding of various factors influencing νCH_2 vibrations and relate their frequencies quantitatively to dihedral angles determining conformations of molecular fragments of this type. The relationships could be used for the simple and fast quantitative evaluation of the conformations of calixarenes or polyphenols through the determination of νCH_2 wavenumbers in the IR or Raman spectra. It is worth mentioning that **3** is an efficient and selective extractant for caesium,[10] so its structure can also be of interest to chemists studying nuclear waste processing.
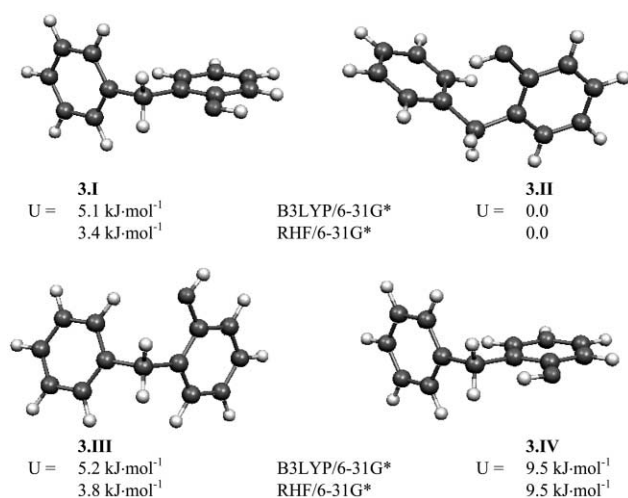
Computations

All restricted Hartree–Fock (RHF) and DFT calculations were done using the Gaussian 98 suite of programs.[11] We used Becke's three-parameter exchange functional[12] in combination with the Lee–Yang–Parr correlation functional[13] (B3LYP) and standard double-zeta (6-31G*, 6-31G**, 6-31+G**, 6-31++G**) basis sets. The 6-31G* set was used for RHF computations. All stationary points were characterized as minima by analysis of the Hessian matrices. The calculated force fields were transformed to internal coordinates, and the scaling procedure was applied with the use of the program described in ref. 14.

† Part IV. For Parts I–III see refs. 1–3.

Results and discussion

Geometry

According to our computations, the molecule **3** can exist in four stable conformations as shown in Fig. 1, the geometry of the

	3.I		**3.II**
U =	5.1 kJ·mol⁻¹	B3LYP/6-31G*	U = 0.0
	3.4 kJ·mol⁻¹	RHF/6-31G*	0.0

	3.III		**3.IV**
U =	5.2 kJ·mol⁻¹	B3LYP/6-31G*	U = 9.5 kJ·mol⁻¹
	3.8 kJ·mol⁻¹	RHF/6-31G*	9.5 kJ·mol⁻¹

Fig. 1 Calculated stable conformations of the molecule **3** and their conformational energies relative to those of the most stable conformation **3.II** (-577.8335 au at B3LYP/6-31G*; -574.1406 au at RHF/6-31G*). Selected torsion angles (B3LYP/6-31G*): **3.I** C1A–C2A–C7–C2B = 180.0°, C1B–C2B–C7–C2A = 89.9°; **3.II** C1A–C2A–C7–C2B = 59.9°, C1B–C2B–C7–C2A = $-132.1°$; **3.III** C1A–C2A–C7–C2B = 94.5°, C1B–C2B–C7–C2A = $-73.6°$; **3.IV** C1A–C2A–C7–C2B = 180.0°, C1B–C2B–C7–C2A = 89.8°. The symmetry of all conformers is C_1.

conformer **3.I** being very similar to the conformation found by a single-crystal X-ray study.[10] All the calculated structural parameters of the conformer **3.I** are in good agreement with the X-ray data. At least part of the deviation between the computed geometry and the experimental values (Table 1) is, probably, caused by intermolecular hydrogen bonding and numerous edge-to-face interactions between arene rings in the crystalline compound **3**.[10] These interactions were assumed [10] to play a crucial role in the stabilization of the observed conformation in the crystal, the assumption being based on the fact that MM3 calculations did not predict the corresponding potential energy minimum for the isolated molecule **3**. Nevertheless, our present results prove this hypothesis to be wrong, because both RHF and DFT calculations with all basis sets used predict the minimum for the conformer **3.I**.

CH₂ frequencies

The conformational homogeneity of **3** in the solid state facilitates the assignments of the fundamentals. Table 2 gives these assignments based on the present SQM computations, individual scaling factors [1,8] being used to improve the general agreement between the calculated and experimental wavenumbers of the fundamentals. As in the cases of **1** [1] and **2** [2] the agreement for conformer **3.I** is quite good.

Strictly speaking, the computed wavenumbers of the isolated molecule **3** should be compared with those of the gas phase spectra. But the low vapour pressure of the title compound makes spectroscopic measurements for gaseous **3** hardly possible. So, the calculated wavenumbers in Table 2 are compared to the recorded IR values not only for crystals but also for diluted CCl₄ solutions, wherein strong intermolecular interactions are absent. Unfortunately, highly diluted CCl₄ solutions are not transparent in the region below ~2100 cm⁻¹ and for this region the IR spectra of the molten compound **3** are presented (Table 2, column 2).

Both our present calculations (the last three columns of Table 2) and previously published results [1,2] indicate, that $v\text{CH}_2$ vibrations are conformationally sensitive. Besides, they are not especially 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 state of compound **3**. According to the experiment (the first two columns of Table 2) the number of the $v\text{CH}_2$ bands in the spectra of the molten compound **3** increases threefold compared to the spectra of the crystalline sample. The same is true for the spectra in CCl₄ solution (Fig. 2). So, the number of the spectroscopically
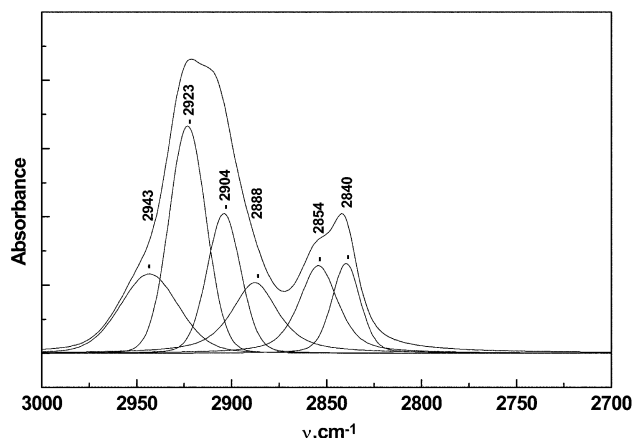

Fig. 2 CH₂ stretching region of IR spectrum of 2-benzylphenol in CCl₄ solution (C ~10^{-4} M). Curve fitting results are included.

detected conformers of molecule **3** in the solution or liquid state is equal to three. Most probably, these are conformers **3.I**, **3.II** and **3.III** (Fig. 1) with the lowest computed potential energies. The presence of conformer **3.II** with the intramolecular OH ⋯ π hydrogen bond in CCl₄ solution is evidenced by the presence of the corresponding $v\text{OH} \cdots \pi$ IR band [15,16] (Table 2). According to the quantitative measurements [15,16] the concentration of **3.II** conformer in diluted CCl₄ solutions is equal to ~33 % while the enthalpy difference between **3.II** and other conformers is about zero. Our computations (Fig. 1) overestimate the energy difference between the solid-state conformer **3.I** and the OH ⋯ π conformer **3.II**. Nevertheless, the calculated energies of conformers **3.I** and **3.III** practically coincide while the energy of the fourth stable conformation **3.IV** is, obviously, too high to allow its experimental detection. So, on the whole the quantum chemical predictions are in line with the spectroscopic observations.

It should be mentioned that the concentration dependencies of the three pairs of $v\text{CH}_2$ bands in the spectra of the CCl₄ solutions are quite distinct from each other which facilitates the assignment of the bands to conformers **3.I**, **3.II** and **3.III**, *i.e.* in the course of dilution (C ~ 10^{-3}–10^{-4} M) the bands at ~2900 and ~2840 cm⁻¹ grow, relative to the bands at ~2945 and ~2890 cm⁻¹ while the intensities of the bands at 2923 and 2854 cm⁻¹ decrease relative to the latter pair of bands. According to DFT computations (Table 2) the bands at ~2945 and ~2890 cm⁻¹ should be assigned to conformer **3.III**. The assignment of the bands at ~2900 and ~2840 cm⁻¹ to conformer **3.I** and the bands at 2923 and 2854 cm⁻¹ to conformer **3.II** (Table 2) seems to be less reliable. The problem is that the off-diagonal element of the Hessian matrix for $v\text{CH}_2$ vibrations usually cannot be calculated precisely at the B3LYP/6-31G* level of theory.[2] In a similar situation with the molecule **2**, B3LYP calculations using a 6-31++G** basis set allowed us to obtain better accuracy.[2] The use of larger, triple-zeta, basis sets would imply a reoptimisation [17] of the whole set of the scaling factors.[1,8] Therefore in the present work we have chosen the 6-31++G** basis, because the previously used scaling factors [1,8] are quite suitable for this set.[17]

Table 1 Results obtained from the B3LYP/6-31G* geometry optimisation (bond lengths/Å; angles/°; total energy E/au) for the conformer **3.I** (Fig. 1)
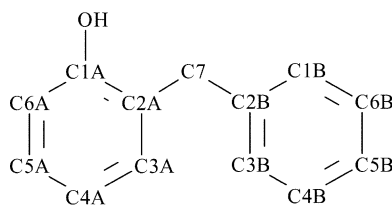
	Ring A		Ring B	
	Calculated	Experiment[a]	Calculated	Experiment[a]
O1–C1	1.373	1.390		
C1–C2	1.407	1.400	1.401	1.386
C2–C3	1.397	1.399	1.396	1.393
C3–C4	1.398	1.394	1.396	1.384
C4–C5	1.393	1.388	1.396	1.380
C5–C6	1.395	1.390	1.396	1.376
C6–C1	1.396	1.390	1.401	1.387
C2–C7	1.524	1.322	1.514	1.510
O–C1–C2	116.7	116.8		
O–C1–C6	122.1	121.4		
C1–C2–C7	118.4	119.2	120.8	121.5
C3–C2–C7	123.9	123.5	120.8	120.5
C1–O–H	108.9	111		

	Calculated	Experiment[a]
C2A–C7–C2B	115.7	115.3
C3A–C2A–C7–C2B	0.0	11.1
C3B–C2B–C7–C2A	90.0	79.9
E	−577.8315	—

[a] Ref. 10.

The B3LYP/6-31++G** calculated wavenumbers of νCH_2 vibrations are listed in Table 2 in parentheses. The quantitative agreement of these computations with the IR experiment is still rather poor. Nevertheless, the predicted relative order of magnitude of the νCH_2 wavenumbers for conformers **3.I** and **3.II** is now in accord with the aforementioned concentration dependence of the relative intensities of the bands at 2923, 2854 cm⁻¹ and 2908, 2840 cm⁻¹. This qualitative agreement also holds for the B3LYP/6-311G**, /6-311+G** and /6-311++G** computations.

The proposed variant of the assignments is in line with our observations on the dependence of the νCH_2 wavenumbers on the mutual orientation of the aromatic rings of the bisphenylmethanes.[2] According to these findings[2] the $\nu_{as}CH_2$ and $\nu_s CH_2$ wavenumbers are determined by the dihedral angles between the planes of the aromatic rings and the C2A–C7–C2B plane. So, similar conformations of molecules **1**, **2** and **3** should give rise to similar wavenumbers. In Table 3 the $\nu_{as}CH_2$ and $\nu_s CH_2$ frequencies of all the conformers of the bisphenylmethanes **1**,**2** and **3** are presented in ascending order of the calculated wavenumbers. It is easily seen that the above mentioned dihedral angles are increasing in approximately the same order. Several exceptions will be discussed later. The calculated νCH_2 wavenumbers of conformer **3.I.** are close to the corresponding wavenumbers of **2.V**. This is to be expected because the dihedral angles for both conformers practically coincide. The same reason, obviously, determines the very close proximity of the calculated wavenumbers for conformers **3.II**, **2.II** and **1**, and also **3.III.** and **2.I**. (Table 3).

The available experimental νCH_2 wavenumbers are compared in Table 4. Again, the wavenumbers of the conformer **3.II** almost coincide with the corresponding values for the similar conformation of molecule **1**. The observed wavenumbers of the conformers **3.III** and **2.I** with the larger dihedral angles are also

close to each other and are much higher than in the case of the conformers **3.II** and **1**. So, the νCH_2 frequencies are determined by the orientation of the aromatic rings relative to the connecting methylene bridge, irrespective of the sort of the molecule. Experimental data on the νCH_2 wavenumbers and the conformation of calix[4]arene (Table 4) provide further evidence in support of this statement: the close similarity of the dihedral angles ϕ_A and ϕ_B for bis(2-hydroxyphenyl)methane **2** and the macrocyclic calixarene molecule results in almost coincident wavenumbers. Unfortunately, their is no possibility of comparing the experimental νCH_2 wavenumbers for conformer **3.I** because similar conformations were observed neither for molecules **1** and **2** nor for calix[4]arene.

In our previous publication[2] we mentioned that the CH_2 stretching vibrations of the bisphenylmethanes do not depend only on the mutual orientation of the aromatic rings. This conclusion was drawn on the basis of the comparison of the calculated νCH_2 wavenumbers of the similar conformers **2.I** and **2.VII**, and also of **2.V** and **2.VI** (Table 3). We assumed that the νCH_2 frequencies of the conformers **2.VI** and **2.VII** are lowered by (O)H · · · H(C) short intramolecular contacts which are absent in the similar conformations **2.V** and **2.I** respectively. Our present results for the conformers **3.I.** and **3.IV** (Table 3) conform to this assumption. Indeed, the orientation of the aromatic rings in conformation **3.IV** is exactly the same as in conformation **3.I**, but the (O)H · · · H(C) short intramolecular contacts (2.18 A), present in the former conformer, are absent in the latter. As a result, the νCH_2 wavenumbers for conformer **3.IV** are much lower than for **3.I**.

Conclusions

The solid-state conformation of the molecule **3** corresponds to one of four potential energy minima predicted by non-
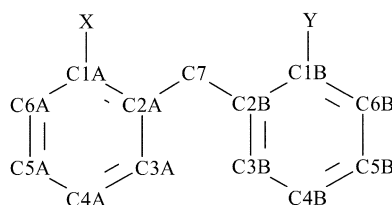
Table 2 IR spectra of 2-benzylphenol (**3**)

Experiment			Computation			
$\nu(\mathrm{cm^{-1}})$, I^a				$\nu(\mathrm{cm^{-1}})$		
Solid	Liquid	Assignment[b]	I_{IR}/km mol^{-1}	3.I.[c]	3.II.[d]	3.III.[e]
	3610 vs (CCl$_4$)	νOH$_{\mathrm{free}}$	41.0	3597		3600
~3541 vw sh	3559 s (CCl$_4$)	νOH $\cdots$ π			3547	
3316 vs	~3422 s, br	νOH $\cdots$ O$_{\mathrm{inter}}$				
3087 vw	3082 w (CCl$_4$)	νCH$_{\mathrm{ar}}$	11.9	3077	3077	3072
		νCH$_{\mathrm{ar}}$	22.4	3069	3073	3069
3063 m	3061 m (CCl$_4$)	νCH$_{\mathrm{ar}}$	25.1	3065	3067	3063
		νCH$_{\mathrm{ar}}$	44.2	3058	3063	3056
3043 w		νCH$_{\mathrm{ar}}$	7.3	3051	3055	3052
		νCH$_{\mathrm{ar}}$	11.1	3049	3051	3042
3038 sh		νCH$_{\mathrm{ar}}$	2.8	3039	3047	3041
		νCH$_{\mathrm{ar}}$	7.4	3037	3037	3033
3026 m	3027 s (CCl$_4$)	νCH$_{\mathrm{ar}}$	21.8	3023	3035	3024
3004 w	3002 vw (CCl$_4$)					
	2950 vw, br	ν_{as}CH$_2$				2930 (2926)^f
2917 w						
2901 s	2918 m	ν_{as}CH$_2$	10.7	2890 (2890)^f		
2886 w						
	2904 sh	ν_{as}CH$_2$			2892 (2888)^f	
	2883 vw	ν_{s}CH$_2$				2886 (2881)^f
2841 m-s	2857 vw	ν_{s}CH$_2$	15.8	2865 (2863)^f		
	2842 w	ν_{s}CH$_2$			2855 (2850)^f	
1624 vw	1609 sh	Ring	10.5	1612	1617	1614
1607 s	1600 w sh	Ring	17.9	1608	1606	1607
1590 vs	1592 s	Ring	18.1	1595	1587	1598
1572 w sh	1584 w sh	Ring	0.8	1589	1584	1589
1561 sh						
1502 vs	1504 s	Ring	23.6	1509	1503	1517
1496 vs	1494 vs	Ring	8.9	1507	1499	1505
1454 vs, br	1453 vs	Ring	33.3	1464	1473	1467
		Ring	5.1	1463	1463	1462
1434 w	1434 w, br	δCH$_2$	28.6	1443	1441	1452
1420 w						
1350 vs, br	1357 sh	wCH$_2$	19.6	1346	1346	1341
1332 s	1328 s	Ring	32.3	1334	1328	1330
		Ring, δArOH	0.3	1324	1324	1324
1300 w		Ring	0.0	1310	1314	1319
1274 s		Ring	59.4	1281	1276	1300
1247 w	1257 s, br	νAr-O	34.3	1251	1256	1254
1218 vs, br	1232 w	νPh–CH$_2$	3.3	1197	1202	1194
1204 vs	1212 s	tCH$_2$	99.2	1185	1184	1185
		Ring	0.1	1178	1180	1178
		Ring	2.2	1166	1177	1168
1169 s	1167 s	Ring	10.2	1161	1160	1160
		Ring	0.0	1158	1159	1158
1153 vw	1153 w	δArOH	1.4	1151	1151	1146
1109 vw						
1090 s	1093 vs	Ring, δArOH	38.1	1083	1096	1093
1074 m	1074 m	Ring	6.2	1082	1083	1074
1040 m-s	1040 m-s	Ring	7.7	1043	1036	1043
1031 m	1030 m	Ring	2.3	1030	1029	1031
1003 w	1003 w	Ring	0.6	996	995	995
984 vw	984 vw	Ring	0.2	974	981	976
978 w						
966 vw	969 w	Ring	0.1	951	956	952
950 w-m		Ring	0.0	948	952	947
920 w-m	935 m	Ring	0.3	934	935	925
915 w-m		Ring	3.9	914	922	915
886 vw	888 w, br	Ring, rCH$_2$	0.2	900	899	905
858 sh	862 sh	Ring	0.0	846	863	850
852 s	851 s	Ring, ν_{as}CAr$_2$	13.6	844	851	846
815 m-s	817 w, br	Ring	1.0	828	847	836
792 m-s	791 m	Ring, ν_{s}CAr$_2$	4.0	810	805	809
766 s-m	782 m-s	Ring	12.5	789	771	776
732 m-s	754 vs	Ring	47.4	750	755	749
716 w	730 s	Ring	17.9	731	731	737
		Ring	3.8	703	713	715
699 m	698 s	Ring	20.8	699	697	699
672 w, br	667 vw, br					
615 m	623 w	Ring	0.0	628	628	627
615 m	613 m	δCAr$_2$, Ring	1.5	618	622	613
578 m-w	579 w	Ring	2.5	578	587	581
560 vw						
546 m-w	537 m	Ring	0.8	541	539	539

Table 2 (*Contd.*)

Experiment			Computation			
$v(cm^{-1})$, I^a				$v(cm^{-1})$		
Solid	Liquid	Assignment[b]	I_{IR}/km mol^{-1}	3.I.[c]	3.II.[d]	3.III.[e]
532 m-s	531 sh	Ring	9.2	538	529	530
478 w	474 w	Ring	3.5	467	480	473
450 m	452 w-m	Ring	6.1	447	451	454
444 sh	438 vw	Ring	0.2	439	428	425

[a] w, weak; m, medium; s, strong; v, very; sh, shoulder; br, broad. [b] v, stretch; δ, bend; w, wagging; t, twisting; r, rocking; s, symmetrical; as, antisymmetrical. "Ring" is used for the vibrations of the phenyl rings. "Inter" stands for intermolecular H-bonding. [c] SQM scaled wavenumbers of conformer **3.I** (Fig. 1). [d] SQM scaled wavenumbers of conformer **3.II** (Fig. 1). [e] SQM scaled wavenumbers of conformer **3.III** (Fig. 1). [f] 6–31++G** computations (see text).

Table 3 B3LYP/6-31G* predicted conformational sensitivity of the CH$_2$ stretching vibrations of the molecules **1**, **2** and **3**

Conformer	3.IV	2.VI[a]	2.VII[a]	2.II[a]	3.II.	1[b]	3.I.	2.V[a]	2.III[a]	2.I[a]	3.III.	2.IV[a]
$v_{as}CH_2$[c]	2845	2865	2872	2890	2892	2894	2890	2907	2912	2922	2930	2943
v_sCH_2[c]	2820	2804	2853	2856	2855	2857	2865	2870	2862	2886	2886	2901
$\phi_A/°$[d]	0	18	82	56	49	56	0	4	62	81	74	87
$\phi_B/°$[e]	90	64	82	56	60	56	90	83	67	80	85	87

[a] From ref. 2. [b] From ref. 1. [c] SQM scaled wavenumbers/cm^{-1}. [d] Dihedral angle between the ring A plane and the C2A–C7–C2B plane (**1**: X = Y = H; **2**: X = Y = OH; **3**: X = OH, Y = H). [e] Dihedral angle between the ring B plane and the C2A–C7–C2B plane (**1**: X = Y = H; **2**: X = Y = OH; **3**: X = OH, Y = H).

Table 4 Observed conformational sensitivity of the CH$_2$ stretching vibrations of the bisphenylmethanes **1**, **2**, **3** and calix[4]arene. X-ray data are marked in bold

	Conformer				
	3.II (in CCl$_4$)	1[a] (melt)	2.I[b] (solid)	Calix[4]arene (solid)	3.III (in CCl$_4$)
$v_{as}CH_2$, cm^{-1}	2904	2909	2926	2935	2943
v_sCH_2, cm^{-1}	2840	2844	2873/2856	2867	2888
$\phi_A/°$[a]	49	56	**74**[c]	**77/76**[d]	74
$\phi_B/°$[b]	60	56	**83**[c]	**84/85**[d]	85

[a] From ref. 1 [b] From ref. 2 [c] Dihedral angle between the ring A plane and the C2A–C7–C2B plane (**1**: X = Y = H; **2**: X = Y = OH; **3**: X = OH, Y = H). [d] X-ray data.[18] [e] X-ray data.[19] [f] Dihedral angle between the ring B plane and the C2A–C7–C2B plane (**1**: X = Y = H; **2**: X = Y = OH; **3**: X = OH, Y = H).

empirical quantum chemical calculations for the isolated molecule. In the molten state and in diluted CCl$_4$ solutions of **3** this conformer coexists with another two spectroscopically detected conformations. The presence of several conformers causes the presence of the corresponding number of v_sCH_2 and $v_{as}CH_2$ bands in the IR spectra, thus providing experimental evidence of the conformational sensitivity of the vCH$_2$ frequencies. A comparison of the latter for diphenylmethane **1**, bis(2-hydroxyphenyl)methane **2**, 2-benzylphenol **3** and calix[4]arene demonstrate that their wavenumbers are determined by the dihedrals between the planes of the aromatic rings and the plane of the connecting methylene bridges. Irrespective of the sort of the molecule, the larger dihedrals result in higher vCH$_2$ wavenumbers, except for the case of short intramolecular contacts with the participation of the methylene protons. So, it is possible to relate the vCH$_2$ frequencies quantitatively to the dihedrals on the basis of the joint statistical treatment of the experimental data on the vCH$_2$ wavenumbers and on the conformational characteristics of calixarenes, polyphenols,

diphenylmethanes, and other related compounds. These studies are in progress. Hopefully, they will result in convenient spectroscopic conformational markers suitable for any molecules containing diphenylmethane fragments.

Experimental

2-Benzylphenol (**3**) 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, over molecular sieves, Ø 3 or 4 Å, to remove traces of water. All preparations of solutions were carried out in a glove box with exclusion of moisture. IR spectra of the compound as a molten film between KBr plates were recorded on a FTIR spectrometer (Vector 22, Bruker) in the 400–4000 cm^{-1} range at a resolution of 1 cm^{-1}. Solid samples were prepared both as polycrystalline films formed from the molten compound and as KBr pellets. Spectra of CCl$_4$ solutions were recorded in 2 and 5 cm cells. The concentrations were ~10^{-3}–10^{-4} M.

Acknowledgements

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