NMR Shieldings in Benzoyl and 2-Hydroxybenzoyl Compounds. Experimental versus GIAO Calculated Data

Heike Lampert,[†] **Werner Mikenda,***[,†] **Alfred Karpfen,**[‡] **and Hanspeter Kählig**[†]

Institute of Organic Chemistry, and Institute of Theoretical Chemistry and Radiation Chemistry, University of Vienna, Währingerstrasse 38, A-1090 Vienna, Austria

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GIAO-calculated NMR chemical shifts (^{1}H, ^{13}C, and ^{17}O) as obtained at various computational levels are reported for the three parent compounds phenol, benzaldehyde, and salicylaldehyde, and for 13 different benzoyl and the 13 corresponding 2-hydroxybenzoyl compounds. The data are compared with experimental solution data, focusing on the agreement with spectral patterns and spectral trends. The influence of different optimized geometries (HF, MP2, B3LYP, BLYP), basis sets (6-31G(d,p) up to 6-311++G(2df,2dp)), and levels of theory (HF, B3LYP, BLYP) was investigated systematically by exhaustive calculations on the three parent compounds. With regard to the results obtained from this foregoing study, the GIAO calculations for the compounds of the two series were performed at two levels of theory, HF/6-311++G(d,p) and BLYP/6-311++G(d,p) for both the B3LYP/6-31G(d,p) and the HF/6-31G(d,p) optimized geometries. It turned out that, with the exception of the nuclei of the hydrogen-bonded OH groups, B3LYP and HF optimized geometries yield rather similar results. For aromatic carbons and protons, because of systematic shortcomings, the GIAO-HF calculations are distinctly worse than the GIAO-BLYP calculations. In the latter case, interchanges with respect to the experimental spectral patterns are obtained only in few instances and concern nuclei with rather small chemical shift differences (within 4 ppm for carbons, within 0.5 ppm for hydrogens). For the nuclei of the C═O and O−H groups, the experimentally observed spectral trends are reproduced in similar quality at both the HF and the BLYP levels of theory.

Introduction

Quantum chemical calculations of NMR chemical shifts have become a very active area of research within the past decade. Among the various approaches to overcome the so-called gauge-origin problem[1−7] the gauge-including atomic orbital method (GIAO) seems to be the most straightforward formulation and has become the most widely used approach in recent years. Following some earlier pioneering work[8−10] GIAO has been successfully implemented at various levels of theory.[11−17] The more recent implementations also account for electron correlation effects, which, at least for molecules containing multiple bonds, seems to be essential to obtain reliable nuclear shielding data.[18] Along with the development of high-level quantum chemical NMR calculations, the measurement and evaluation of high-quality gas-phase NMR spectra has also been distinctly improved during the years, including sophisticated methods for rotational−vibrational corrections in order to account for finite temperature effects.[19,20]

In contrast to the remarkable progress in the calculation of accurate absolute shielding constants of small molecules, the practical implications of ab initio NMR calculations are not so evident. In particular, when dealing with larger molecules, there are some obvious, but pertinent points that have to be considered. First, one must put up with standard condensed phase spectra from (more or less concentrated) solutions or from powders, that are inherently perturbed by intermolecular interactions. Second, zero temperature calculations do not account for coalescence phenomena that are usually associated with finite temperature measurements. Last but not least, for the calculations one must find a reasonable tradeoff between affordable cost and necessary accuracy. From these points it is evident that an agreement between experimental and calculated absolute chemical shift values can hardly be expected and, hence, one must be prepared for inherent (possibly systematic) differences. On the other hand, for practical purposes, such as the assistance with assignments or the prediction of spectra, an absolute agreement between calculated and experimental chemical shifts is of secondary importance only. It is much more essential, that details of spectral patterns, i.e., the chemical shift sequences, are correctly predicted, that similar compounds can safely be distinguished, or that systematic trends within a family of similar compounds are correctly reproduced.

These latter issues are the major focus of the present paper (for some recent papers that also address to these practical aspects, see e.g. refs 22−28). Here we report experimental and GIAO calculated ^{1}H, ^{13}C, and ^{17}O NMR data of two series of aromatic compounds, benzoyl compounds and 2-hydroxybenzoyl compounds, that have been obtained in the course of spectroscopic and theoretical studies on intramolecular hydrogen bonding.[29,30] With respect to the reproduction of NMR spectra, the two compound families exhibit some challenging questions, such as assignments of aromatic nuclei with small chemical shift differences, or systematic shifts caused by hydrogen bonding.

The paper is divided into two parts. The first part deals with the two smallest members of the two compound families, benzaldehyde and salicylaldehyde, and, additionally, with phenol, as a major parent compound. Chemical shifts as obtained at 18 computational levels—GIAO-(HF, B3LYP, BLYP)/(6-31G(d,p) up to 6-311G++(2df,2dp))//(HF, MP2, B3LYP, BLYP)/6-31G(d,p)—are inspected with respect to methodological effects, to select the most appropriate calculational procedures for the compounds of the two entire series. The second part deals with chemical shifts of the two compound series and concentrates on two computational levels: HF/6-

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[†] Institute of Organic Chemistry.

[‡] Institute of Theoretical Chemistry.

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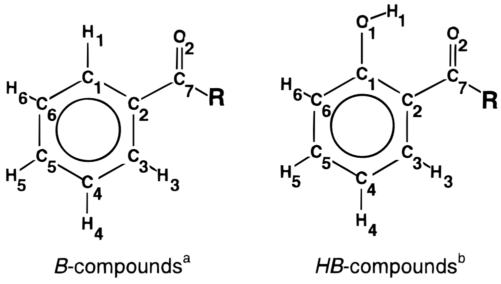
SCHEME 1: Atom Numberings, Compounds, and Compound Numberings



[a] for benzaldehyde: R has to be replaced by H_7

[b] for phenol: C_7 has to be replaced by H_2

n	-R
1	-Cl
2	$-N(CH_2-CH_2)_2=CH_2$
3	$-N(CH_3)_2$
4	-OH
5	-SH
6	$-OCH_3$
7	$-SCH_3$
8	-H
9	$-C_6H_5$
10	$-CH_3$
11	$-NH-NH_2$
12	$-NH_2$
13	$-NH-CH_3$

311++(d,p)//B3LYP/6-31G(d,p) and BLYP/6-311++(d,p)//B3LYP/6-31G(d,p). The data are analyzed mainly with respect to the agreement between calculated and experimental spectral patterns and with respect to trends within the two compound series. Only those nuclei are considered that are common to all compounds within a given series. Additionally, a short comparison is given between results obtained with B3LYP- and HF-optimized geometries.

Experimental and Computational Section

The compounds included in this study are shown in Scheme 1, along with the subsequently used compound and atom numberings. Short cut notations "*Bn*" and "*HBn*" (n = compound number) will be used to designate benzoyl and 2-hydroxybenzoyl compounds, respectively.

NMR spectra were measured with a Bruker WA 400 WB spectrometer. ^1H and ^{13}C spectra, relative to tetramethylsilane (TMS), were obtained from $CDCl_3$ solutions. ^{17}O spectra, relative to H_2O, were obtained from CH_3CN solutions ($c \approx 50$ mg/mL) at 313 K. Although NMR spectra of the majority of the compounds are available in spectral libraries, all spectra were remeasured in order to ensure uniform experimental conditions. Moreover, the assignments of the aromatic nuclei, which are straightforward from standard NMR spectra only for the protons of the benzoyl compounds, were unambiguously determined for all compounds by proton detected heteronuclear shift correlation measurements (HMQC) or by one-dimensional INADEQUATE experiments. In some instances, erroneous or controversial literature assignments have been detected and corrected.

The quantum chemical calculations performed in this work were done with the Gaussian94 program.[31] Calculations of nuclear shieldings were performed at various computational levels, including three different levels of theory (HF, B3LYP, and BLYP), four different basis sets (6-31G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), and 6-311++G(2df,2pd), and four different optimized geometries (HF/6-31G(d,p), MP2/6-31G(d,p), B3LYP/6-31G(d,p), and BLYP/6-31G(d,p)). The calculated isotropic shielding constants, σ_i, were transformed to chemical shifts relative to CH_4 (for ^1H and ^{13}C) and H_2O (for ^{17}O) by $\delta_i = \sigma_{ref} - \sigma_i$, where both, σ_{ref} and σ_i, were taken from calculations at the same computational level (the absolute isotropic shielding constants of the reference nuclei are summarized in Table 1). Consequently, all the subsequently quoted experimental ^1H and ^{13}C chemical shifts were also rescaled to the CH_4 reference by considering the respective chemical shifts relative to the common tetramethylsilane (TMS) reference (CH_4: $\delta_H = 0.23$ ppm and $\delta_C = -2.3$ ppm relative to TMS).

Results and Discussion

Before going into details, two general points should be noted, that have already briefly be mentioned in the Introduction. First, inspecting the overall agreement between experimental and theoretical spectra, there are two alternative views to assess the quality of the calculations. One may either consider the absolute agreement (e.g. as measured by RMS errors), or consider the agreement between spectral patterns and trends (e.g. as measured by correlation coefficients). The second point of view, which seems to be certainly more important for practical applications of NMR calculations, will be our main concern. Second, due to the NMR time scale, which is much longer than the rotational correlation time of the $-OH$ and the $-COR$ substituents, the two ortho protons and carbons, as well as the two meta protons and carbons of phenol, benzaldehyde, and of all benzoyl compounds coalesce at normal temperature. For the subsequent considerations about spectral patterns, mean values of the corresponding calculated chemical shifts are, therefore, used.

A. Parent Compounds. The chemical shifts of phenol, benzaldehyde, and salicylaldehyde as obtained at 18 computational levels are summarized in Table 1, along with the corresponding experimental solution data. The data shall provide a sound basis for the inspection of methodological effects and, hence, for the choice of the most appropriate computational levels for the subsequent calculations of the *B*- and the *HB*-compounds.

Basis Set Convergence. To inspect the basis set convergence, GIAO-HF and GIAO-BLYP calculations were performed with four different basis sets, using the HF/6-31G(d,p) optimized geometries in all instances. The results are visualized in Figure 1 by plots of average differences between experimental and calculated chemical shifts, $\Delta\delta = \delta^{exp} - \delta^{calc}$, versus the four basis sets. For the carbons and the oxygens, $\Delta\delta$ significantly decreases when going from 6-31G(d,p) to 6-311++G(d,p), i.e., by adding diffuse functions, but there is almost no further change with the two still larger basis sets, 6-311++G(2d,2p) and 6-311++G(2df,2pd). This finding is very similar to that of a most recent GIAO-DFT study.[15] For the protons, the basis set convergence is not so clear, but in fact, all the changes are rather small and seem to be almost negligible on the whole. The only exceptions are the OH protons, for which $\Delta\delta$ smoothly decreases when moving from 6-31G(d,p) to 6-311++G(2df,2pd). Concerning the spectral patterns, the successive enlargement of the basis set does not change anything (except for the OH and CHO protons of salicylaldehyde, which become interchanged at the HF/6-311++G(2df,2pd) level). We, therefore, conclude that for the majority of the nuclei, a reasonable and sufficient basis set convergence is achieved with the 6-311++G(d,p) basis.

GIAO-HF versus GIAO-DFT. Because of the above findings about the basis set convergence, the following considerations will be restricted to the 6-311++G(d,p) basis set. Based on several optimized geometries (see below), GIAO calculations were performed at HF, B3LYP and BLYP levels of theory.

TABLE 1: Calculated Isotropic Shielding Constants of Reference Nuclei, $^1H(CH_4)$, $^{13}C(CH_4)$, and $^{17}O(H_2O)$, and Calculated and Experimental Chemical Shifts [ppm] (Relative to CH_4 for ^1H and ^{13}C; Relative to H_2O for ^{17}O) of Phenol, Benzaldehyde, and Salicylaldehyde

GIAO[a]	HF/b1	HF/b2	HF/b3	HF/b4	B3LYP/b2	BLYP/b1	BLYP/b2	BLYP/b3	BLYP/b4	HF/b2	B3LYP/b2	BLYP/b2	HF/b2	B3LYP/b2	BLYP/b2	HF/b2	B3LY/b2	BLYP/b2	
Geom[b]	HF/b1	HF/b1	HF/b1	HF/b1	HF/b1	HF/b1	HF/b1	HF/b1	HF/b1	MP2/b1	MP2/b1	MP2/b1	B3LYP/b1	B3LYP/b1	B3LYP/b1	BLYP/b1	BLYP/b1	BLYP/b1	exp[c]
References																			
H	31.83	31.96	31.76	31.69	31.99	31.82	32.06	31.81	31.73	31.90	31.93	32.00	31.67	31.70	31.77	31.43	31.47	31.54	
C	203.1	197.7	196.9	196.8	192.2	195.3	190.2	189.8	189.5	197.3	191.7	198.7	196.0	190.2	188.1	194.6	188.6	186.4	
O	347.1	333.4	334.4	335.5	332.5	338.8	331.7	333.5	334.6	324.2	322.7	321.7	322.1	320.5	319.4	316.4	314.5	313.2	
Phenol																			
C1	154.0	165.1	165.4	165.7	169.9	150.3	169.8	169.9	169.9	168.3	173.5	173.5	167.2	171.9	171.7	169.1	173.7	173.5	157.0
C2	109.6	117.7	117.4	117.5	123.0	109.1	122.6	122.8	122.7	120.3	125.2	124.7	119.3	124.1	123.6	120.8	125.3	124.6	118.0
C3	131.0	140.4	140.0	140.4	141.1	124.8	140.0	139.9	139.9	142.3	143.0	141.8	141.2	141.6	140.4	142.3	142.4	141.0	132.4
C4	116.9	126.0	125.2	125.3	131.0	115.3	130.4	130.1	129.9	128.8	133.5	132.8	127.4	132.0	131.3	129.0	133.2	132.3	123.7
C5	132.2	141.8	141.3	141.8	142.4	125.6	141.2	141.0	141.0	143.7	144.2	142.9	142.6	142.9	141.5	143.8	143.7	142.2	132.4
C6	113.4	122.6	121.7	121.8	126.6	110.7	125.7	125.2	125.1	125.8	129.3	128.2	124.1	127.6	126.4	125.7	128.7	127.4	118.0
H1	2.75	3.02	3.24	3.35	3.16	2.79	3.22	3.37	3.48	3.66	3.74	3.77	3.52	3.58	3.62	3.64	3.68	3.70	4.27
H2	6.12	6.25	6.39	6.32	6.41	6.06	6.40	6.54	6.50	6.44	6.57	6.55	6.25	6.39	6.37	6.27	6.38	6.35	6.47
H3	7.07	7.11	7.23	7.16	7.13	6.90	7.11	7.22	7.20	7.29	7.28	7.25	7.10	7.10	7.06	7.10	7.06	7.02	6.91
H4	6.57	6.60	6.72	6.66	6.80	6.59	6.79	6.92	6.89	6.78	6.95	6.93	6.60	6.77	6.75	6.62	6.75	6.72	6.58
H5	7.18	7.22	7.32	7.26	7.25	7.02	7.22	7.31	7.29	7.39	7.39	7.36	7.20	7.21	7.17	7.20	7.17	7.13	6.91
H6	6.71	6.84	6.89	6.80	6.92	6.52	6.88	6.95	6.90	7.07	7.12	7.06	6.87	6.92	6.86	6.89	6.91	6.85	6.47
O1	81.8	84.0	86.1	86.1	116.8	118.0	127.1	129.2	129.1	85.2	118.5	128.9	83.0	116.1	126.4	83.7	117.0	127.3	75.4
Benzaldehyde																			
C1	129.5	138.9	138.4	138.8	139.3	123.2	138.0	137.7	137.8	142.1	142.1	140.8	140.9	140.8	139.3	142.5	141.8	140.3	131.8
C2	133.4	143.2	143.1	142.8	150.0	133.1	149.8	149.8	149.5	144.9	151.5	151.2	143.8	150.1	149.8	145.3	151.3	150.8	138.7
C3	133.4	142.9	142.4	142.8	145.5	129.8	145.0	144.9	144.9	145.3	147.7	147.1	144.5	146.7	146.1	145.9	147.7	146.9	131.8
C4	125.4	134.9	134.3	134.5	140.6	125.3	140.6	140.3	140.3	137.0	142.7	142.6	135.5	141.2	141.1	136.6	142.0	141.8	131.2
C5	134.1	144.0	143.6	144.0	146.1	129.0	145.3	145.1	145.0	146.8	148.5	147.6	145.7	147.2	146.2	147.2	148.2	147.1	136.5
C6	126.3	135.7	135.2	135.4	141.0	125.4	140.8	140.5	140.5	137.9	143.2	142.9	136.3	141.5	141.2	137.4	142.4	141.9	131.2
C7	182.0	193.1	193.2	193.7	199.2	179.6	198.5	199.1	199.3	205.2	208.7	207.2	199.8	204.0	202.7	203.3	206.3	204.7	194.3
H1	8.28	8.37	8.45	8.37	8.24	7.89	8.16	8.24	8.20	8.71	8.51	8.42	8.47	8.28	8.19	8.48	8.26	8.16	7.62
H3	7.52	7.61	7.75	7.69	7.64	7.31	7.60	7.73	7.71	7.79	7.78	7.73	7.60	7.59	7.53	7.59	7.55	7.49	7.62
H4	7.23	7.27	7.39	7.32	7.52	7.34	7.54	7.65	7.62	7.41	7.64	7.66	7.24	7.47	7.48	7.23	7.44	7.44	7.27
H5	7.41	7.49	7.62	7.55	7.56	7.32	7.55	7.68	7.64	7.70	7.73	7.70	7.50	7.53	7.51	7.50	7.50	7.46	7.37
H6	7.27	7.28	7.40	7.33	7.50	7.33	7.51	7.61	7.57	7.44	7.63	7.63	7.26	7.46	7.46	7.25	7.42	7.41	7.27
H7	9.13	9.22	9.32	9.27	10.07	9.96	10.35	10.50	10.48	9.63	10.35	10.59	9.35	10.11	10.36	9.38	10.07	10.31	9.77
O2	591.0	610.7	606.2	605.8	624.1	581.8	617.4	617.2	617.1	639.0	654.4	646.6	623.4	637.9	630.2	633.2	647.3	638.7	564.0
Salicylaldehyde																			
C1	162.4	172.8	173.1	173.5	175.2	156.3	174.5	174.6	174.7	177.6	180.2	179.4	178.5	180.0	178.9	182.1	183.0	181.7	163.8
C2	114.8	122.7	122.6	122.2	132.6	119.1	133.3	133.5	133.1	125.2	134.9	135.6	123.4	133.1	133.8	125.1	134.7	135.2	122.9
C3	137.5	146.6	146.3	146.9	146.1	130.3	144.8	144.8	144.9	148.9	147.9	146.5	148.0	146.5	146.0	149.3	147.1	145.4	136.0
C4	113.2	122.0	121.1	121.2	130.1	115.6	130.4	130.0	129.9	124.4	132.4	132.7	122.0	130.4	130.7	122.9	131.3	131.5	122.1
C5	140.6	150.4	150.2	150.7	148.7	131.0	147.0	146.8	146.9	153.3	151.0	149.2	153.0	150.1	148.2	154.9	151.3	149.1	139.2
C6	113.9	122.9	121.9	122.0	129.9	115.0	129.8	129.4	129.2	125.7	132.6	132.5	123.4	130.5	130.5	124.7	131.6	131.5	119.8
C7	189.2	200.4	200.5	201.1	204.1	183.3	202.3	202.8	203.1	212.7	213.2	210.2	209.0	209.4	206.4	213.3	211.9	208.4	198.8
H1	8.76	8.86	9.19	9.31	9.33	9.54	9.58	9.91	10.03	11.00	11.30	11.48	11.87	12.06	12.2	12.87	12.91	13.00	10.77
H3	7.39	7.47	7.60	7.56	7.33	6.95	7.25	7.38	7.38	7.68	7.50	7.40	7.47	7.28	7.2	7.46	7.23	7.12	7.30
H4	6.54	6.53	6.67	6.61	6.84	6.65	6.85	7.00	6.97	6.68	6.97	6.98	6.46	6.77	6.8	6.44	6.73	6.73	6.77
H5	7.45	7.49	7.63	7.57	7.41	7.12	7.35	7.47	7.44	7.73	7.59	7.51	7.54	7.39	7.3	7.55	7.36	7.28	7.27
H6	6.72	6.81	6.87	6.79	6.94	6.57	6.90	6.98	6.93	7.04	7.16	7.10	6.82	6.95	6.9	6.84	6.95	6.89	6.74
H7	9.12	9.20	9.27	9.23	9.93	9.72	10.14	10.24	10.23	9.61	10.16	10.32	9.37	9.92	10.1	9.41	9.87	10.00	9.64
O1	87.3	94.4	97.1	97.4	128.5	123.5	139.5	142.2	142.3	96.5	131.3	142.4	99.9	134.6	145.5	103.9	138.8	151.0	79.2
O2	523.4	549.9	547.0	547.0	564.2	513.0	556.4	557.5	558.2	556.8	571.6	562.0	533.8	549.6	540.8	531.9	547.9	539.4	505.3

[a] GIAO calculation (b1 = 6-31G(d,p), b2 = 6-311++G(d,p), b3 = 6-311++G(2d,2p), b4 = 6-311++G(2df,2pd)). [b] Geometry optimization. [c] Solution values (see text).

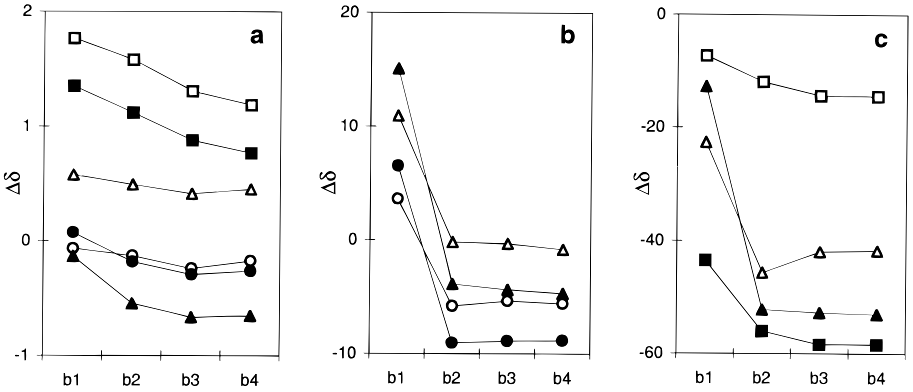


Figure 1. Average differences between experimental and GIAO calculated chemical shifts, $\Delta\delta = \delta^{exp} - \delta^{calc}$ [ppm], of phenol, benzaldehyde, and salicylaldehyde as obtained with different basis sets (all calculations with HF/6-31G(d,p) optimized geometries): (a) protons, (b) carbons, (c) oxygens (circles = aromatic CH, triangles = aldehyde CHO, squares = hydroxylic OH nuclei; open symbols = HF, filled symbols = BLYP).

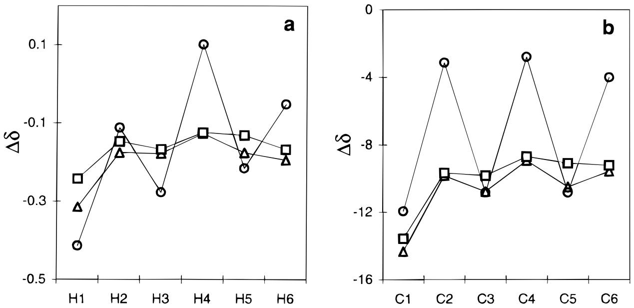


Figure 2. 2. Differences between experimental and GIAO calculated chemical shifts, $\Delta\delta = \delta^{exp} - \delta^{calc}$ [ppm], of aromatic protons and carbons of phenol, benzaldehyde, and salicylaldehyde as obtained at different levels (all calculations with the 6-311++G(d,p) basis set and with B3LYP/6-31G(d,p) optimized geometries): (a) aromatic protons, (b) aromatic carbons (circles = HF, triangles = B3LYP, squares = BLYP).

Whereas the two DFT variants yield highly similar results throughout, there are significant differences between GIAO-HF and GIAO-DFT calculated chemical shifts. Concerning the spectral patterns of aromatic protons and carbons, inspection of Table 1 reveals the following features: (i) the patterns of ^{1}H and ^{13}C spectra of phenol are correctly reproduced at all computational levels; (ii) with benzaldehyde, the aromatic carbons C1/C3, C2 and C5 (the experimental range of chemical shifts is about 7 ppm) are interchanged with all GIAO-HF calculations, while the GIAO-DFT calculations yield correct sequences in all instances; (iii) with salicylaldehyde, the sequence of the carbon resonances is correctly reproduced at all computational levels, whereas the two pairs of overlapping protons, H3/H5 and H4/H6, with experimental chemical shift differences of only about 0.03 ppm, are interchanged throughout. While the latter point (iii) seems to be not too severe, the second point (ii) indicates an intrinsic problem. Actually, closer inspection shows that, concerning aromatic carbons and protons, GIAO-HF calculations suffer from systematic shortcomings. As shown in Figure 2 for calculations with B3LYP/6-31G(d,p) optimized geometries, with all three parent compounds and for both, carbons and protons, the GIAO-HF calculations yield something like a systematic "shift alternation", which is superimposed on the "correct" spectral patterns. The effect is most prominent for carbons (C1,C3,C5 are downfield shifted by about 5−10 ppm with respect to C2,C4,C6), but it is also evident for protons (H1,H3,H5 are downfield shifted by about 0.2−0.5 ppm with respect to H2,H4,H6).

Influence of Optimized Geometries. GIAO calculations were performed with four different optimized geometries: HF, MP2, B3LYP, and BLYP, using the 6-31G(d,p) basis in all instances. As shown in Figure 3 for GIAO-BLYP calculations, the influence of the geometries is by far not obvious. With the exception of the OH protons and oxygens, for which larger OH bond distances correspond to larger chemical shifts, no systematic dependencies could be found. On the other hand, concerning the spectral patterns, there are almost no differences between calculations based on differently calculated, optimized geometries. Not unexpectedly, again the only exceptions are the OH and CHO protons of salicylaldehyde, for which δ_H(OH) < δ_H(CHO) is obtained with the HF optimized geometry, but δ_H(OH) > δ_H(CHO) with the MP2 and the DFT optimized geometries, which is obviously due to the underestimation of hydrogen bond interactions and the respective overestimation of O···O and H···O hydrogen bond distances at the HF level.

B. Benzoyl- and 2-Hydroxybenzoyl compounds. Since we are mainly interested in comparisons between the compounds of the two series, only the atoms common to all compounds of either of the two series are considered (i.e., the nuclei of the R-substituent groups are omitted). The chemical shifts calculated at HF/6-311++G(d,p) and BLYP/6-311++G(d,p) levels of theory, using the B3LYP/6-31G(d,p) optimized geometries, are compiled in Tables 2 and 3, along with the corresponding experimental solution data. Table 4 summarizes correlation coefficients and standard deviations of linear regressions between experimental and calculated chemical shifts of different nuclei. For results obtained at other computational levels, we note (i) that the computationally more demanding GIAO−B3LYP calculations (in some few instances they exceeded the limits of our facilities) yield results that are qualitatively and quantitatively largely similar to GIAO-BLYP calculated results and (ii) that, with respect to spectral patterns and trends, results obtained with the computationally less expendable HF optimized geometries are very similar to those obtained with the B3LYP optimized geometries (Table 4 also covers the respective data obtained with HF optimized geometries).

Aromatic Carbons. Experimental versus calculated shifts of the aromatic carbons are shown in Figure 4 (average values of C1/C3 and of C4/C6 are used in case of the *Bn* compounds). For both series, the GIAO-BLYP calculated data are qualitatively superior than the GIAO-HF calculated data (see also Table 4), although the latter are closer to the absolute experimental values. Basically, this is just the same finding we obtained with the parent compounds; the worse GIAO-HF description of the spectral patterns mainly results from the above-discussed shift alternation associated with GIAO-HF calculations.

In more detail, for the benzoyl series we obtain incorrect chemical shift sequences for all 13 compounds at the HF level

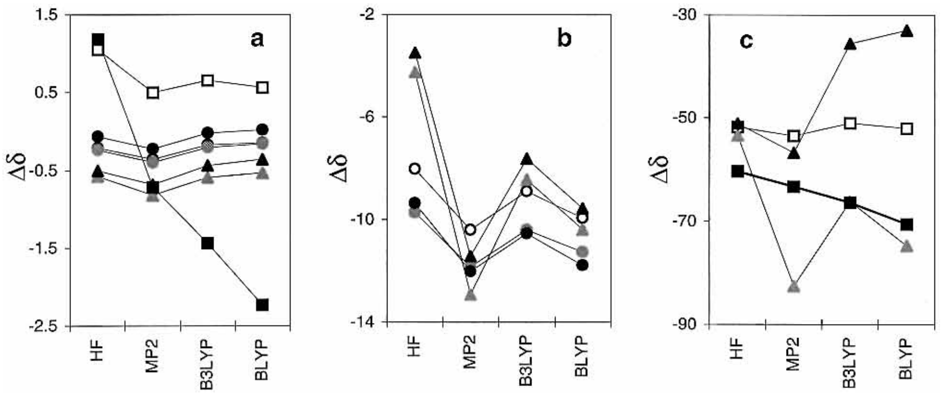


Figure 3. 3. Average differences between experimental and GIAO calculated chemical shifts, $\Delta\delta = \delta^{\text{exp}} - \delta^{\text{calc}}$ [ppm], of phenol, benzaldehyde, and salicylaldehyde as obtained from BLYP/6-311++G(d,p) calculations based on different optimized geometries (all geometry optimizations with 6-31G(d,p) basis): (a) protons, (b) carbons, (c) oxygens (circles = aromatic CH, triangles = aldehyde CHO, squares = hydroxylic OH nuclei; open symbols = phenol, gray symbols = benzaldehyde, filled symbols = salicylaldehyde).

TABLE 2: Experimental and Calculated Chemical Shifts [ppm] (Relative to CH_4 for ^1H and ^{13}C, and Relative to H_2O for ^{17}O) of Benzoyl Compounds[a,b]

n[c]		C1	C2	C3	C4	C5	C6	C7	H1	H3	H4	H5	H6	O2
1	exp	133.7	135.5	133.7	131.2	137.6	131.2	170.7	7.88	7.88	7.28	7.45	7.28	483.6
	HF	*145.4*	*138.2*	*146.4*	134.9	148.0	135.2	179.0	8.42	8.28	7.19	7.59	7.20	546.4
	BLYP	143.9	145.7	146.6	141.0	147.1	140.8	188.3	8.16	8.30	7.42	7.52	7.39	525.2
2	exp	128.9	136.7	128.9	130.5	131.5	130.5	172.4	7.11	7.11	7.11	7.11	7.11	338.8
	HF	*143.7*	145.6	*138.5*	*134.7*	141.1	*137.5*	186.1	7.85	7.27	7.10	7.31	7.25	413.1
	BLYP	*143.9*	150.6	*138.3*	*138.1*	141.3	*141.0*	181.7	7.77	7.28	7.20	7.30	7.38	429.8
3	exp	129.2	138.6	129.2	130.5	131.6	130.5	173.8	7.12	7.12	7.12	7.12	7.12	348.0
	HF	*143.7*	145.2	*139.2*	*134.7*	*141.3*	*137.4*	186.1	7.89	7.24	7.12	7.32	7.25	412.1
	BLYP	*143.9*	150.3	*138.9*	*138.1*	141.4	*141.0*	181.7	7.82	7.23	7.22	7.31	7.38	429.7
4	exp	132.5	131.6	132.5	130.8	136.1	130.8	174.9	7.91	7.91	7.25	7.39	7.25	250.5
	HF	145.9	135.2	143.4	134.7	146.1	135.4	177.6	8.51	8.18	7.14	7.51	7.19	378.6
	BLYP	144.1	141.3	142.3	140.1	145.2	140.5	178.0	8.32	8.12	7.35	7.47	7.39	392.2
5	exp	131.0	138.8	131.0	130.1	136.2	130.1	192.5	7.66	7.66	7.21	7.35	7.21	529.2
	HF	*141.9*	*141.8*	*142.1*	135.1	*146.2*	135.7	201.8	8.40	7.83	7.16	7.50	7.20	572.1
	BLYP	139.6	148.4	141.8	140.5	145.6	140.6	203.4	8.08	7.75	7.34	7.44	7.37	559.5
6	exp	131.8	132.4	131.8	130.6	135.1	130.6	169.3	7.80	7.80	7.19	7.31	7.19	337.3
	HF	*145.2*	*137.2*	*142.8*	134.7	145.3	135.4	178.5	8.53	8.17	7.11	7.46	7.18	381.3
	BLYP	143.3	143.4	141.4	139.8	144.4	140.3	179.4	8.35	8.10	7.31	7.42	7.38	392.9
7	exp	129.3	139.3	129.3	130.8	135.5	130.8	194.6	7.73	7.73	7.20	7.31	7.20	488.9
	HF	142.3	*142.1*	141.4	135.0	*145.7*	135.5	204.3	8.52	8.02	7.12	7.45	7.18	537.1
	BLYP	*140.1*	148.8	*139.8*	*140.1*	145.0	*140.5*	203.5	8.25	8.01	7.31	7.39	7.36	510.1
8	exp	131.9	138.6	131.9	131.2	136.7	131.2	194.3	7.62	7.62	7.27	7.37	7.27	564.0
	HF	140.9	*143.8*	144.5	135.5	*145.7*	136.3	199.8	8.47	7.60	7.24	7.50	7.26	623.4
	BLYP	139.3	149.8	146.1	141.1	146.2	141.2	202.7	8.19	7.53	7.48	7.51	7.46	630
9	exp	132.2	139.8	132.2	130.5	134.6	130.5	198.9	7.57	7.57	7.24	7.34	7.24	552.0
	HF	144.9	145.4	142.5	134.2	143.8	136.8	205.9	8.48	7.64	7.17	7.50	7.37	600.0
	BLYP	144.3	151.2	143.1	138.6	144.0	141.2	208.1	8.23	7.66	7.34	7.49	7.53	618.5
10	exp	130.5	139.3	130.5	130.8	135.3	130.8	200.3	7.70	7.70	7.20	7.30	7.20	548.6
	HF	*142.5*	*143.7*	*140.4*	*134.9*	*144.5*	*136.2*	206.2	8.63	7.74	7.13	7.42	7.24	609.3
	BLYP	*140.8*	149.0	*141.0*	*140.0*	144.8	*140.9*	208.7	8.37	7.78	7.34	7.41	7.42	620.8
11	exp	129.1	134.9	129.1	131.0	134.1	131.0	171.0	7.51	7.51	7.18	7.27	7.18	308.7
	HF	143.7	*140.6*	137.0	135.5	*143.7*	137.1	183.1	8.40	7.46	7.13	7.42	7.28	378.6
	BLYP	*142.3*	146.6	*135.9*	*139.6*	143.4	*141.2*	181.0	8.23	7.43	7.27	7.39	7.43	391.0
12	exp	129.6	135.7	129.6	130.9	134.3	130.9	171.9	7.58	7.58	7.20	7.29	7.20	329.0
	HF	*144.1*	*141.6*	*137.0*	*135.2*	*143.5*	*137.0*	180.8	8.46	7.49	7.12	7.40	7.27	387.1
	BLYP	142.7	146.9	136.6	139.4	143.3	141.0	178.0	8.27	7.50	7.27	7.38	7.43	406.3
13	exp	129.1	136.8	129.1	130.6	133.4	130.6	170.6	7.52	7.52	7.10	7.19	7.10	314.3
	HF	143.9	143.5	135.9	135.4	142.7	137.3	179.5	8.41	7.35	7.10	7.36	7.26	367.1
	BLYP	*142.7*	149.1	*135.2*	*139.2*	142.5	*141.0*	176.2	8.24	7.35	7.24	7.33	7.41	382.9

[a] All calculations with the 6-311++G(d,p) basis set using the B3LYP/6-31G(d,p) optimized geometries. [b] Italics denote interchanges between experiment and theory. [c] Compound number (see Scheme 1).

of theory, while there are errors for only 5 compounds at the BLYP level of theory. Moreover, the largest errors (i.e., the differences between experimental and calculated chemical shift differences) amount to more than 8 ppm at the HF level, as opposed to only 3 ppm at the BLYP level. The shift alternation associated with the GIAO-HF calculations is also present with the 2-hydroxybenzoyl compounds, although the effects are less evident at a first glance, because the total range of chemical shifts is much larger and the carbons are well separated (with the exception of C4 and C6). Nevertheless, the spectral patterns are again distinctly better reproduced at the BLYP than at the HF level. Comparison with experiment shows that the two nearby carbons C4 and C6 (δ^{exp}(C4) > δ^{exp}(C6) for all compounds) are interchanged in all 13 instances at the HF level and in 11 out of 13 instances at the BLYP level. At the HF level, we find five additional interchanges, whereas at the BLYP

TABLE 3: Experimental and Calculated Chemical Shifts [ppm] (Relative to CH_4 for ^1H and ^{13}C, and Relative to H_2O for ^{17}O) of 2-Hydroxybenzoyl Compounds[a,b]

n[c]		C1	C2	C3	C4	C5	C6	C7	H1	H3	H4	H5	H6	O1	O2
1	exp	163.9	119.5	136.2	122.6	140.6	120.4	175.9	9.40	7.59	6.74	7.09	7.01	86.7	457.2
	HF	178.9	118.1	149.2	*122.1*	154.9	*123.5*	190.6	10.39	8.08	6.44	7.59	6.80	103.7	492.6
	BLYP	177.8	129.1	146.6	131.3	149.4	130.2	192.9	10.26	7.92	6.76	7.34	6.91	152.6	479.9
2	exp	161.0	119.9	130.4	120.7	134.5	120.1	172.9	9.42	6.99	6.58	7.05	6.73	76.0	318.9
	HF	177.2	119.4	143.7	*121.0*	148.6	*125.4*	191.6	11.30	7.29	6.36	7.37	6.85	96.4	359.3
	BLYP	177.8	127.4	139.4	*127.5*	144.2	*131.0*	185.1	11.24	7.11	6.57	7.16	6.92	142.1	375.8
3	exp	161.4	119.4	130.8	120.5	134.8	120.1	174.1	9.71	7.06	6.59	7.07	6.74	77.6	319.8
	HF	178.0	118.5	144.3	*120.6*	148.9	*125.3*	191.4	11.80	7.30	6.36	7.39	6.85	98.9	352.7
	BLYP	178.3	126.5	140.0	*127.2*	144.3	*131.0*	184.8	11.69	7.13	6.58	7.17	6.92	145.1	371.3
4	exp	164.5	113.6	133.3	121.9	139.3	120.2	177.2	10.12	7.70	6.71	7.30	6.78	84.1	240.3
	HF	179.2	112.8	146.5	*121.8*	153.1	*123.5*	185.1	11.19	8.04	6.39	7.53	6.78	102.7	344.6
	BLYP	178.9	121.9	142.3	*129.9*	148.0	*130.1*	183.4	11.18	7.81	6.67	7.30	6.88	150.7	359.1
5	exp	162.1	122.0	132.6	121.8	139.0	120.6	198.3	10.45	7.46	6.67	7.25	6.74	82.9	458.7
	HF	177.0	*121.4*	145.6	*122.0*	153.0	*124.2*	214.7	11.41	7.65	6.39	7.50	6.78	101.3	501.5
	BLYP	176.1	131.5	142.0	*130.2*	147.7	*130.9*	209.9	11.24	7.39	6.65	7.25	6.86	147.6	498.1
6	exp	163.8	114.6	132.1	121.4	137.9	119.8	172.8	10.52	7.59	6.63	7.21	6.74	82.7	318.9
	HF	178.7	114.8	146.1	*121.8*	152.1	*123.6*	185.8	11.36	8.03	6.37	7.48	6.76	100.9	347.2
	BLYP	178.4	124.1	141.5	*129.6*	147.1	*130.1*	184.3	11.37	7.79	6.64	7.26	6.86	147.6	360.6
7	exp	161.5	122.3	131.0	121.5	138.0	120.4	199.9	10.80	7.62	6.65	7.21	6.73	79.9	444.6
	HF	176.7	*121.9*	144.9	*121.9*	152.3	*124.1*	219.1	11.79	7.81	6.36	7.46	6.77	99.9	488.5
	BLYP	175.8	132.0	140.1	*129.8*	146.8	*130.9*	212.3	11.67	7.60	6.62	7.22	6.86	145.0	476.8
8	exp	163.8	122.9	136.0	122.1	139.2	119.8	198.8	10.77	7.30	6.77	7.27	6.74	79.2	505.3
	HF	178.5	*123.4*	148.0	*122.0*	153.0	*123.4*	209.0	11.87	*7.47*	6.46	7.54	6.82	99.9	533.8
	BLYP	178.9	133.8	146.0	130.7	148.2	130.5	206.4	12.21	*7.17*	6.77	7.32	6.89	145.5	540.8
9	exp	165.4	121.3	135.8	120.8	138.5	120.6	203.8	11.83	7.26	6.63	7.36	6.84	82.2	486.7
	HF	181.0	*121.5*	148.6	*120.3*	152.4	*124.4*	216.2	13.25	*7.84*	6.34	*7.54*	6.92	105.9	509.1
	BLYP	180.7	*131.4*	145.3	*128.9*	147.4	*131.8*	213.3	13.33	*7.68*	6.65	*7.31*	7.01	151.1	520.3
10	exp	164.6	121.9	133.0	121.2	138.7	120.6	206.8	12.02	7.48	6.65	7.22	6.72	84.1	487.5
	HF	179.2	*122.2*	144.8	*121.1*	152.1	*124.5*	218.4	13.01	7.65	6.35	7.46	6.81	104.2	523.3
	BLYP	179.2	131.9	141.7	*129.2*	147.7	*131.6*	215.5	13.10	7.48	6.63	7.25	6.89	151.2	533.0
11	exp	163.4	115.2	127.2	121.3	136.9	121.0	172.9	11.50	7.08	6.62	7.18	6.77	83.3	276.0
	HF	178.4	115.3	139.7	*122.1*	150.5	*125.7*	188.3	12.59	7.23	6.35	7.43	6.86	102.9	324.3
	BLYP	178.2	124.4	134.7	*128.9*	145.9	*131.7*	184.2	12.54	7.04	6.56	7.21	6.91	149.7	340.8
12	exp	164.4	115.5	128.7	121.1	137.3	121.0	174.9	11.89	7.14	6.63	7.20	6.77	86.0	288.2
	HF	179.1	115.9	140.4	*121.6*	150.6	*125.7*	187.8	12.98	7.23	6.33	7.42	6.85	105.2	331.0
	BLYP	179.1	124.6	136.4	*128.5*	146.1	*131.8*	183.0	12.85	7.07	6.55	7.21	6.89	153.0	352.5
13	exp	163.4	116.6	127.8	121.0	136.3	120.6	172.9	11.84	7.15	6.57	7.11	6.71	84.8	281.7
	HF	178.6	117.0	139.4	*121.6*	149.6	*126.0*	187.0	13.12	*7.13*	6.31	*7.38*	6.83	103.8	326.5
	BLYP	178.6	125.8	134.9	*128.2*	145.1	*131.8*	182.0	13.00	*6.96*	6.51	*7.16*	6.87	150.6	346.9

[a] All calculations with the 6-311++G(d,p) basis set using the B3LYP/6-31G(d,p) optimized geometries. [b] Italics denote interchanges between experiment and theory. [c] Compound number (see Scheme 1).

TABLE 4: Details of Linear Regressions between Experimental and Calculated Chemical Shifts of *Bn* and *HBn* Compounds (Number of Data Points in Parentheses): Correlation Coefficients, *r*, and Standard Deviations, *σ* [ppm]

		HF//HF[a]		HF//B3LYP[a]		BLYP//HF[a]		BLYP//B3LYP[a]	
nuclei	compounds	*r*	*σ*	*r*	*σ*	*r*	*σ*	*r*	*σ*
aromatic carbons	*B* (52)	0.763	2.1	0.672	2.4	0.927	1.2	0.945	1.1
	HB (78)	0.980	3.1	0.984	2.8	0.996	1.5	0.996	1.4
	all (130)	0.975	2.7	0.976	2.7	0.993	1.5	0.995	1.3
aromatic protons	*B* (39)	0.936	0.08	0.937	0.08	0.949	0.07	0.951	0.07
	HB (52)	0.940	0.11	0.952	0.10	0.923	0.12	0.945	0.11
	all (91)	0.949	0.11	0.956	0.10	0.950	0.13	0.958	0.10
carbonyl carbons	*B* (13)	0.876	6.1	0.972	3.0	0.867	6.3	0.966	3.4
	HB (13)	0.953	4.4	0.973	3.4	0.973	3.4	0.981	2.9
	all (26)	0.923	5.2	0.952	4.1	0.929	5.1	0.973	3.1
carbonyl oxygens	*B* (13)	0.985	20.5	0.984	21.3	0.978	24.9	0.970	28.6
	HB (13)	0.985	17.6	0.982	19.4	0.981	20.0	0.981	19.7
	all (26)	0.984	17.2	0.977	23.1	0.978	18.8	0.968	26.9
hydroxyl protons	*HB* (13)	0.654	0.76	0.921	0.39	0.698	0.72	0.918	0.40
hydroxyl oxygens	*HB* (13)	0.439	3.0	0.855	1.7	0.499	2.9	0.941	1.2

[a] NMR calculations with the 6-311++G(d,p) basis set, geometry optimization with the 6-31G(d,p) basis set.

level only one additional interchange, all of them involving the carbonyl substituted C2 carbon; the maximum errors are about 5 and 4 ppm, respectively.

Aromatic Protons. Experimental versus calculated shifts of the aromatic protons are shown in Figure 5, using average values of H1/H3 and of H4/H6 in case of the benzoyl compounds. For both series, the GIAO-HF calculated data and the GIAO-BLYP calculated data yield very similar results with respect to both spectral patterns and agreement with experiment (see also Table 4). The two most significant outlying points among the benzoyl compounds are due to the two tertiary amides, *B2* and *B3*; a poor description of the torsion angles could be a possible reason.

Closer inspection of the spectral patterns of the individual compounds shows, that for all *Bn* compounds the common sequence H4/H6 < H5 < H1/H3 is correctly reproduced at both

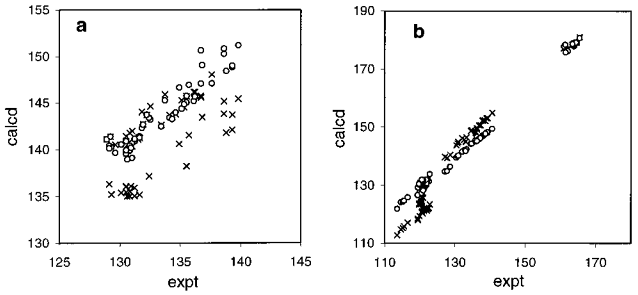


Figure 4. Experimental versus GIAO calculated chemical shifts [ppm] of aromatic carbons (relative to CH_4) of (a) benzoyl and (b) 2-hydroxybenzoyl compounds (crosses = HF, circles = BLYP).

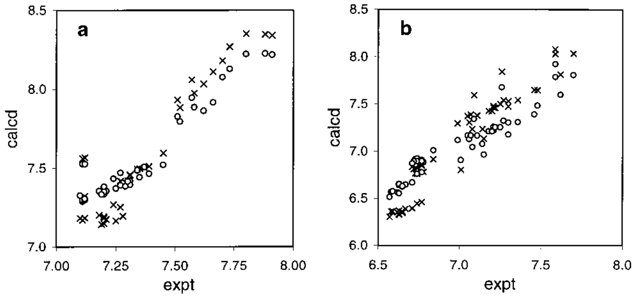


Figure 5. Experimental versus GIAO calculated chemical shifts [ppm] of aromatic protons (relative to CH_4) of (a) benzoyl and (b) 2-hydroxybenzoyl compounds (crosses = HF, circles = BLYP).

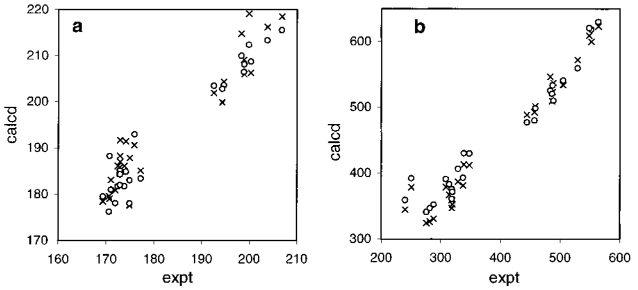


Figure 6. Experimental versus GIAO calculated chemical shifts [ppm] of (a) carbonyl carbons (relative to CH_4) and (b) carbonyl oxygens (relative to H_2O) of benzoyl and 2-hydroxybenzoyl compounds (crosses = HF, circles = BLYP).

levels of theory. For the *HBn* compounds, we find interchanges for three out of the 13 compounds (*HB8*, *HB9*, *HB13*) at both levels, with maximum errors below 0.5 ppm. In either case, the H3 atom is involved, which is more or less strongly affected by the R-substituents. Although both levels yield qualitatively similar results, the experimental patterns are slightly better reproduced by GIAO-BLYP than by GIAO-HF calculations.

Carbonyl Groups. Experimental versus calculated shifts of the carbonyl carbons and carbonyl oxygens are shown in Figure 6. For the carbonyl carbons, the agreement between experimental and theoretical trends is distinctly better in the low-field than in the high-field range, in particular, for the GIAO-BLYP calculations. On the whole, the agreement seems to be less satisfying than for all other nuclei under consideration. At the BLYP level, the most significantly outlying points result from the chlorides, *B1* and *HB1*, and from the acids, *B4* and *HB4*. For carbonyl oxygens, the trends are well reproduced at both levels. The four significantly outlying points result from the acids, *B4* and *HB4*, for which the experimental values are seemingly much too low, due to intermolecular association effects at the necessarily highly concentrated solutions.

Hydroxyl Groups. Experimental versus calculated shifts of the hydroxyl protons and oxygens of the HB compounds are shown in Figure 7. For the protons, the agreement between experiment and theory is fairly good at both levels. The most significant discrepancies concern the tertiary amides *B2* and *HB2*, and *B3* and *HB3*, which again may be a problem with a correct description of the torsion angles. For the oxygens, the agreement between experiment and theory is distinctly better at the BLYP than at the HF level of theory. Here the most prominent outlying points are due to 2-hydroxybenzophenone, *HB9*. Moreover, Figure 8 shows that the calculated proton shifts comply reasonably well with the hydrogen bond distances *R*(OH) and *R*(H···O), which characterize the hydrogen bond strengths.[29]

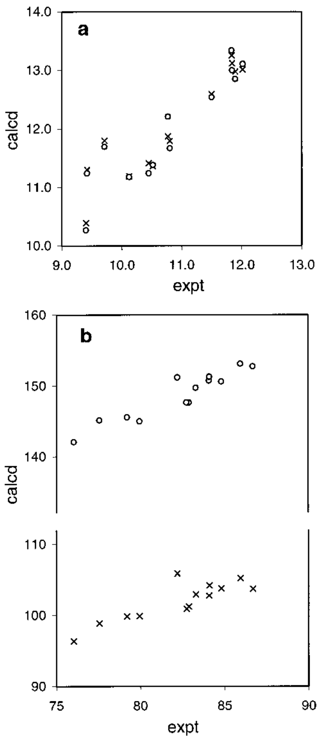


Figure 7. Experimental versus GIAO calculated chemical shifts [ppm] of (a) hydroxyl protons (relative to CH_4) and (b) hydroxyl oxygens (relative to H_2O) of 2-hydroxybenzoyl compounds (crosses = HF, circles = BLYP).

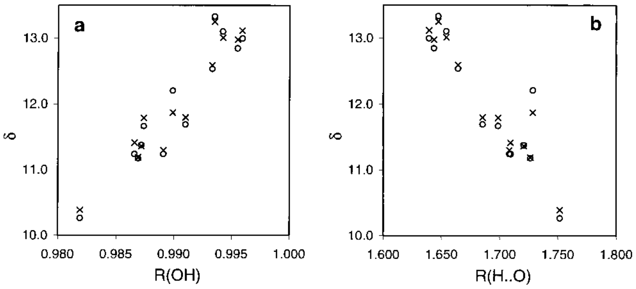


Figure 8. Calculated chemical shifts [ppm] of hydroxyl protons versus (a) *R*(OH) and (b) *R*(H···O) bond distances [Å] of 2-hydroxybenzoyl compounds (crosses = GIAO-HF, circles = GIAO-BLYP; bond distances from B3LYP/6-31G(d,p) geometry optimizations[29]).

B3LYP versus HF Optimized Geometries. Table 4 covers details of a statistical analysis of the chemical shift data obtained with both B3LYP/6-31G(d,p) and HF/6-31G(d,p) optimized geometries. Closer inspection of the table reveals that for aromatic carbons and protons, and for carbonyl oxygens the performance of the calculations is largely similar for both geometry optimizations, whereas for carbonyl carbons the HF geometries yield slightly worse results. For hydroxyl protons and oxygens, however, the results are distinctly worse for HF than for B3LYP geometries, which is not unexpected, since it is well-known that the geometries of (intramolecular) hydrogen bonds are poorly described at the HF level of theory.[29]

Summary

GIAO calculated NMR chemical shifts of phenol, benzaldehyde, and salicylaldehyde (^{1}H, ^{13}C, and ^{17}O) as obtained at various computational levels have been inspected with respect to methodological effects. Although the absolute chemical shift values significantly depend on the optimized geometries, on which the GIAO calculations are based, no systematic dependence on geometric data (such as bond distances) could be found (except for the ^{1}H and ^{17}O shifts of O−H groups). Concerning the basis sets used for the GIAO calculations, satisfactory convergence seems to be achieved with the 6-311++(d,p) basis. One important result seems to be the finding about an, obviously inherent, shortcoming of GIAO-HF calculations of the chemical shifts of aromatic carbons and, to a minor extent also, of aromatic protons: the "correct" spectral pattern seems to be superimposed by a remarkable chemical shift alternation, which measures about 5−10 ppm for the carbons and about 0.2−0.4 ppm for the protons. With GIAO-DFT (BLYP and B3LYP) calculations these shift alternations vanish almost completely.

GIAO calculated NMR chemical shifts of 13 benzoyl and of 13 corresponding 2-hydroxybenzoyl compounds as obtained at the HF/6-311++G(d,p)//B3LYP/6-31G(d,p) and at the BLYP/6-311++G(d,p)//B3LYP/6-31G(d,p) level of theory have been inspected with respect to the agreement between experiment and theory. Due to the above-mentioned systematic chemical shift alternation, the spectral patterns of the aromatic carbons and, to a minor extent, also of the protons are partially badly described at the HF level of theory. GIAO-BLYP (and GIAO-B3LYP) calculations yield much more satisfying results; interchanges with respect to experiment are confined to chemical shift differences of about 4 ppm for the carbons and of about 0.5 ppm for the protons. For the nuclei of the C═O and the O−H groups, the experimentally observed trends are similarly reproduced at both the HF and BLYP level of theory. For GIAO-HF calculations, linear regressions between experimental and theoretical chemical shifts yield correlation coefficients in the range from 0.855 to 0.977; for GIAO-BLYP calculations correlation coefficients in the range 0.918 to 0.973 are obtained.

The GIAO-HF and GIAO-BLYP calculated NMR chemical shifts of the two compound series as obtained with the B3LYP/6-31G(d,p) optimized geometries have been compared with the corresponding data obtained with the HF/6-31G(d,p) optimized geometries. With respect to spectral patterns and spectral trends both geometries yield rather similar results (with the exception of the protons and oxygens of the hydrogen bonded O−H groups). Thus it turns out that, unless intramolecularly hydrogen-bonded nuclei are considered, the computationally less demanding HF geometries seem to be quite suitable for GIAO calculations.

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