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Hartree−Fock and Density Functional Theory ab Initio Calculation of Optical Rotation Using GIAOs: Basis Set Dependence

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Ab initio Hartree−Fock (HF) and density functional theory (DFT) calculations of the electric dipole−magnetic dipole polarizability $\beta_{\alpha\beta}$ are reported for the chiral molecules methyloxirane (**1**) and *trans*-dimethylthiirane (**2**) in the static limit. Values of $\beta = {}^1/_3 Tr[\beta_{\alpha\beta}]$ obtained thence are used to predict the specific optical rotations $[\alpha]_D$ of **1** and **2**. Gauge-including atomic orbitals (GIAOs) are used to ensure origin independence of β and $[\alpha]_D$. β and $[\alpha]_D$ values converge slowly to the complete basis set limit. Basis sets including diffuse functions are required to achieve reliable results. HF and DFT values of $\beta_{\alpha\beta}$ differ generally by 10−30%. Calculated $[\alpha]_D$ values for **1** and **2** obtained using large basis sets agree well with experimental values in sign and magnitude. The deviations can be attributed in part to the neglect of the frequency dependence of β and of solvent effects.

Introduction

We report ab initio calculations of the optical rotation of the chiral molecules methyloxirane **1** and *trans*-dimethylthiirane **2** (Figure 1) using the Hartree−Fock (HF) and density functional theory (DFT) methodologies. Gauge-including atomic orbitals (GIAOs),[1,2] also referred to as London orbitals, are used to guarantee origin-independence. Our principal focus is the basis set dependence of calculated rotations.

The optical rotation ϕ in radians/cm at a frequency ν of an isotropic solution containing N chiral molecules/cm^3 is given by[3−5]

$$\phi = \frac{16\pi^3 N\nu^2}{c^2}\gamma_s\beta \qquad (1)$$

$\beta = {}^1/_3 Tr[\beta_{\alpha\beta}]$ where $\beta_{\alpha\beta}$ is the electric dipole−magnetic dipole polarizability, also referred to as $-(c/w)G'_{\alpha\beta}$ ($w = 2\pi\nu$).[6] $\beta_{\alpha\beta}$ is given by

$$\beta_{\alpha\beta} = \frac{c}{3\pi h}\mathrm{Im}\left[\sum_{k\neq 0}\frac{\langle 0|(\mu^e_{el})_\alpha|k\rangle\langle k|(\mu^e_{mag})_\beta|0\rangle}{\nu_{k0}^2 - \nu^2}\right] \qquad (2)$$

where 0 and k label ground and excited electronic states, and μ^e_{el} and μ^e_{mag} are the electronic electric and magnetic dipole operators. $\beta_{\alpha\beta}$ is origin-dependent; however, the isotropic polarizability β is origin independent. γ_s is the solvent effect, often approximated using the Lorentz factor:[4,7] $\gamma_s = (\epsilon + 2)/3 = (n^2 + 2)/3$. Experimental optical rotations are usually reported in terms of specific rotation $[\alpha] = \alpha/c$, where α is the rotation in degrees/dm and c is the concentration in g/cm^3. Specific rotations are most commonly measured using sodium D line (589.3 nm) radiation.

The calculation of $\beta_{\alpha\beta}$ using ab initio methods was first carried out by Amos.[8] The implementation was restricted to the zero-frequency (static) limit, when

$$\beta_{\alpha\beta} = \frac{hc}{3\pi}\mathrm{Im}\left[\left\langle\frac{\partial\Psi_0}{\partial E_\alpha}\middle|\frac{\partial\Psi_0}{\partial H_\beta}\right\rangle\right] \qquad (3)$$

$\partial\Psi_0/\partial E_\alpha$ and $\partial\Psi_0/\partial H_\beta$ are the derivatives of the ground-state electronic wave function with respect to E_α and H_β for the perturbations, $-(\mu^e_{el})_\alpha E_\alpha$ and $-(\mu^e_{mag})_\beta H_\beta$, respectively. $\partial\Psi_0/\partial E_\alpha$ and $\partial\Psi_0/\partial H_\beta$ were calculated at the HF level using analytical derivative methods and field-independent atomic orbitals (FIAOs). Subsequently, Helgaker et al.[9] used linear response methods at the HF level to calculate $\beta_{\alpha\beta}$ using either FIAOs or GIAOs without restriction to the static limit.

The algorithms of Amos and of Helgaker et al., implemented within the CADPAC[10] and DALTON[11] programs, respectively, have recently been used to predict the optical rotations of a range of chiral molecules.[12−19] These results have generated considerable optimism regarding the potential utility of ab initio prediction of optical rotation in determining the stereochemistry of chiral molecules. To date, however, several issues have not been fully addressed, including (1) origin-dependence, (2) basis set dependence, (3) electron correlation, (4) solvent effects, and (5) zero-point vibrational effects. The large majority of the results published so far have been obtained using FIAOs. However, it has not been noted that in this case optical rotations are origin-dependent and therefore cannot be meaningfully compared to experimental values. In addition, almost all of the results reported to date were obtained using small basis sets, predominantly 6-31G*[20] and DZP.[21−23] It is well-known that accurate calculation of the electric dipole−electric dipole polarizability $\alpha_{\alpha\beta}$ requires much larger basis sets, including diffuse functions.[24] Similar requirements are to be anticipated for $\beta_{\alpha\beta}$. Consistent with this expectation, considerable variation in predicted rotations has been reported for some molecules

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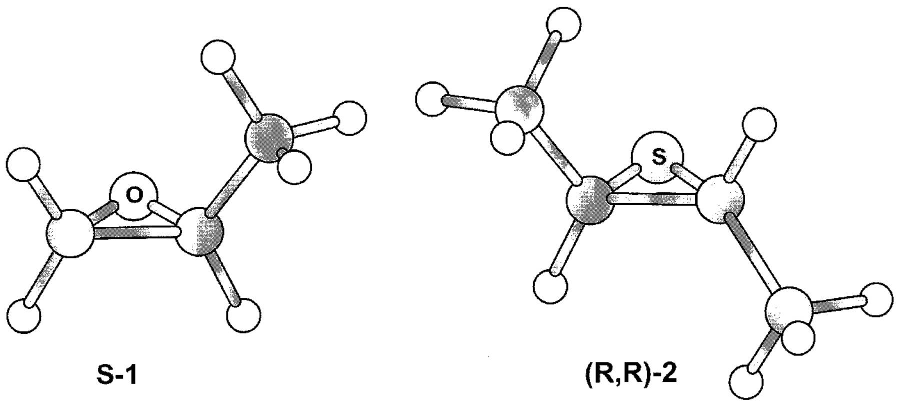

Figure 1. S-**1** and R,R-**2**. The Cartesian coordinates of the ring atoms (listed clockwise and in Ångstroms) are O, −0.780430, −0.751840, −0.233802; C, 0.202730, 0.003655, 0.490667; C, −0.989969, 0.656217, −0.057774 for S-**1** and S, 0.0, 0.0, 1.245253; C, 0.0, 0.738331, −0.453194; C, 0.0, −0.738331, −0.453194 for R,R-**2**.

TABLE 1: Basis Set Labels and Composition

label	contracted set[a]	ref
6-31G	[4s3p/3s2p/2s]	20, 31, 32
6-31G*	[4s3p1d/3s2p1d/2s] (6d)	20, 31−33
6-31G**	[4s3p1d/3s2p1d/2s1p] (6d)	20, 31−33
6-31+G*	[5s4p1d/4s3p1d/2s] (6d)	20, 31, 32, 34−36
6-31+G**	[5s4p1d/4s3p1d/2s1p] (6d)	20, 31, 32, 34−36
6-311G	[6s5p/4s3p/3s]	35, 37
6-311G*	[6s5p1d/4s3p1d/3s] (5d)	35, 37
6-311G**	[6s5p1d/4s3p1d/3s1p] (5d)	35, 37
6-311G(2d)	[6s5p2d/4s3p2d/3s] (5d)	35, 37
6-311G(2d,p)	[6s5p2d/4s3p2d/3s1p] (5d)	35, 37
6-311G(2d,2p)	[6s5p2d/4s3p2d/3s2p] (5d)	35, 37, 38
6-311+G	[7s6p/5s4p/3s]	34−37
6-311+G*	[7s6p1d/5s4p1d/3s] (5d)	34−37
6-311+G**	[7s6p1d/5s4p1d/3s1p] (5d)	34−37
6-311+G(2d)	[7s6p2d/5s4p2d/3s] (5d)	34−37
6-311+G(2d,p)	[7s6p2d/5s4p2d/3s1p] (5d)	34−37
6-311+G(2d,2p)	[7s6p2d/5s4p2d/3s2p] (5d)	34−37
6-311++G	[7s6p/5s4p/4s]	34−37
6-311++G*	[7s6p1d/5s4p1d/4s] (5d)	34−37
6-311++G**	[7s6p1d/5s4p1d/4s1p] (5d)	34−37
6-311++G(2d)	[7s6p2d/5s4p2d/4s] (5d)	34−37
6-311++G(2d,p)	[7s6p2d/5s4p2d/4s1p] (5d)	34−37
6-311++G(2d,2p)	[7s6p2d/5s4p2d/4s2p] (5d)	34−38
6-311++G(2df,2pd)	[7s6p2d1f/5s4p2d1f/4s2p1d] (5d,7f)	34−38
6-311++G(3d2f,3p2d)	[7s6p3d2f/5s4p3d2f/4s3p2d] (5d,7f)	34−38
cc-pVDZ	[4s3p1d/3s2p1d/2s1p] (5d)	39
cc-pVTZ	[5s4p2d1f/4s3p2d1f/3s2p1d] (5d,7f)	39
cc-pVQZ	[6s5p3d2f1g/5s4p3d2f1g/4s3p2d1f] (5d,7f,9g)	39
aug-cc-pVDZ	[5s4p2d/4s3p2d/3s2p] (5d)	40
aug-cc-pVTZ	[6s5p3d2f/5s4p3d2f/4s3p2d] (5d,7f)	40
aug-cc-pVQZ	[7s6p4d3f2g/6s5p4d3f2g/5s4p3d2f] (5d,7f,9g)	40
d-aug-cc-pVDZ	[6s5p3d/5s4p3d/4s3p] (5d)	41
t-aug-cc-pVDZ	[7s6p4d/6s5p4d/5s4p] (5d)	41
DZP	[6s4p1d/4s2p1d/2s1p] (6d)	21−23
TZ2P	[9s6p2d/5s4p2d/3s2p] (6d)	2
VD3P	[/8s6p3d/6s3p] (6d)	42
vd9s5p1d/4s1p	[/9s5p1d/4s1p][b] (5d)	43
13s8p3d2f/10s3p2d	[/13s8p3d2f/10s3p2d][b] (5d)	38, 43

[a] Of the form [1/2/3] where the first term refers to the contracted set on sulfur, the second refers to the contracted set on carbon and oxygen and the third refers to the contracted set on hydrogen. The number(s) in parentheses refer(s) to the number of functions used for each type of polarization function. [b] Uncontracted basis set.

using different basis sets. To date, all calculations have used the HF method and the significance of electron correlation has not been investigated. Solvent effects have been included exclusively using the classical Lorentz approximation; modern methods have not been exploited. Lastly, the importance of zero-point vibrational effects[25] has not been addressed.

We have implemented the calculation of $\beta_{\alpha\beta}$ using HF and DFT methodologies. In this paper, we report calculations for two small molecules, **1** and **2**, in the static limit for a wide range of basis sets. Calculations using FIAOs and GIAOs document the origin-dependence and -independence respectively of resulting rotations. The accuracies of various types of basis set, relative to the complete basis set limit, are established. Lastly, comparison of HF and DFT calculations permits the significance of correlation to be assessed. In forthcoming papers[26] we will extend these calculations to include the frequency dependence of $\beta_{\alpha\beta}$ and to incorporate solvent effects using self-consistent reaction field methodologies.

TABLE 2: Origin Dependence of β for S-1[a]

	FIAOs				GIAOs			
origin[b]	β_{xx}	β_{yy}	β_{zz}	β	β_{xx}	β_{yy}	β_{zz}	β
6-31G*:								
COM	1.9758	1.3412	−3.2329	−0.0280	1.8020	1.3892	−3.1168	−0.0248
O	0.0866	0.7608	−0.8380	−0.0031	0.1156	0.8823	−0.9236	−0.0248
H	−2.0241	8.2562	−6.3371	0.0350	−1.8225	7.8604	−5.9636	−0.0248
6-311++G(2d,2p):								
COM	0.8493	0.6943	−1.5148	−0.0096	0.8468	0.7041	−1.4956	−0.0184
O	−0.6412	0.6667	−0.0019	−0.0079	−0.5803	0.6769	−0.0413	−0.0184
H	−1.7160	4.8178	−3.0917	−0.0034	−1.6509	4.7135	−3.0073	−0.0184
aug-cc-pVDZ:								
COM	0.7319	0.5685	−1.2359	−0.0215	0.7287	0.5715	−1.2410	−0.0197
O	−0.5848	0.5921	0.0468	−0.0180	−0.5972	0.6008	0.0556	−0.0197
H	−1.6156	4.2519	−2.5563	−0.0267	−1.6462	4.2620	−2.5566	−0.0197

[a] Values of β are in atomic units. [b] COM is center-of-mass and H refers to the methyl hydrogen above the ring in Figure 1.

TABLE 3: Basis Set Dependence of Hartree−Fock and B3LYP Values of $\beta_{\alpha\alpha}$, β, and $[\alpha]_D$ for S-1[a]

		Hartree−Fock					B3LYP				
basis set	bfns[b]	β_{xx}	β_{yy}	β_{zz}	β	$[\alpha]_D$	β_{xx}	β_{yy}	β_{zz}	β	$[\alpha]_D$
6-31G	48	2.3636	1.2736	−3.4843	−0.0509	−33.92	2.7028	1.2383	−3.7539	−0.0624	−41.55
6-31G*	72	1.8020	1.3892	−3.1168	−0.0248	−16.49	2.1786	1.3398	−3.4091	−0.0364	−24.26
6-31G**	90	1.7607	1.3665	−3.0441	−0.0277	−18.45	2.1555	1.3278	−3.3622	−0.0404	−26.87
6-31+G*	88	1.2091	0.9776	−2.1358	−0.0170	−11.30	1.1751	0.8775	−2.0507	−0.0006	−0.42
6-31+G**	106	1.1580	0.9478	−2.0473	−0.0195	−12.97	1.1471	0.8606	−1.9960	−0.0039	−2.59
6-311G	70	2.0297	1.2376	−2.9955	−0.0906	−60.32	2.3149	1.2392	−3.1661	−0.1293	−86.13
6-311G*	90	1.5563	1.2505	−2.6215	−0.0617	−41.09	1.9069	1.2522	−2.8726	−0.0955	−63.59
6-311G**	108	1.4727	1.1922	−2.4676	−0.0658	−43.81	1.8470	1.2173	−2.7560	−0.1028	−68.43
6-311G(2d)	110	1.2807	1.0399	−2.1580	−0.0542	−36.09	1.5981	1.0804	−2.4258	−0.0842	−56.10
6-311G(2d,p)	128	1.2630	1.0594	−2.1536	−0.0562	−37.45	1.6036	1.1133	−2.4497	−0.0891	−59.30
6-311G(2d,2p)	146	1.1693	0.9765	−1.9942	−0.0506	−33.66	1.5065	1.0399	−2.3022	−0.0814	−54.19
6-311+G	86	1.7347	0.8430	−2.4301	−0.0492	−32.74	1.7599	0.8118	−2.4012	−0.0568	−37.85
6-311+G*	106	1.1394	0.9335	−2.0349	−0.0126	−8.42	1.1899	0.9035	−2.0453	−0.0160	−10.67
6-311+G**	124	1.0566	0.8704	−1.8922	−0.0116	−7.72	1.1311	0.8572	−1.9444	−0.0146	−9.74
6-311+G(2d)	126	0.9277	0.7464	−1.6747	0.0002	0.14	0.9516	0.7297	−1.7078	0.0088	5.88
6-311+G(2d,p)	144	0.9044	0.7585	−1.6768	0.0046	3.07	0.9538	0.7528	−1.7468	0.0134	8.90
6-311+G(2d,2p)	162	0.8235	0.6794	−1.5095	0.0022	1.46	0.8699	0.6842	−1.5896	0.0118	7.86
6-311++G	92	1.7051	0.8518	−2.3588	−0.0660	−43.96	1.7840	0.8730	−2.4021	−0.0849	−56.56
6-311++G*	112	1.1189	0.9585	−1.9852	−0.0307	−20.46	1.2203	0.9769	−2.0650	−0.0441	−29.36
6-311++G**	130	1.0485	0.8903	−1.8501	−0.0296	−19.68	1.1766	0.9238	−1.9695	−0.0436	−29.05
6-311++G(2d)	132	0.9337	0.7767	−1.6501	−0.0201	−13.38	1.0137	0.8057	−1.7411	−0.0261	−17.36
6-311++G(2d,p)	150	0.9207	0.7840	−1.6499	−0.0183	−12.17	1.0269	0.8232	−1.7742	−0.0253	−16.85
6-311++G(2d,2p)	168	0.8468	0.7041	−1.4956	−0.0184	−12.27	0.9534	0.7516	−1.6281	−0.0257	−17.09
6-311++G(2df,2pd)	226	0.8223	0.7165	−1.4841	−0.0182	−12.15	0.9323	0.7625	−1.6108	−0.0280	−18.64
6-311++G(3d2f,3p2d)	322	0.7098	0.5963	−1.2696	−0.0122	−8.12	0.8064	0.6349	−1.3795	−0.0206	−13.72
cc-pVDZ	86	1.4425	1.2997	−2.6061	−0.0454	−30.21	1.8615	1.3557	−2.9922	−0.0750	−49.94
cc-pVTZ	204	1.0320	0.9818	−1.9437	−0.0234	−15.56	1.3312	1.0717	−2.2835	−0.0398	−26.50
cc-pVQZ	400	0.8406	0.7813	−1.5779	−0.0147	−9.78	1.0670	0.8731	−1.8649	−0.0251	−16.69
aug-cc-pVDZ	146	0.7287	0.5715	−1.2410	−0.0197	−13.14	0.8005	0.6407	−1.3495	−0.0306	−20.37
aug-cc-pVTZ	322	0.7017	0.5937	−1.2594	−0.0120	−8.00	0.7911	0.6165	−1.3485	−0.0197	−13.12
aug-cc-pVQZ	596	0.6948	0.5989	−1.2600	−0.0112	−7.46	0.7816	0.6221	−1.3482	−0.0185	−12.33
d-aug-cc-pVDZ	206	0.7303	0.5944	−1.2738	−0.0170	−11.31	0.8306	0.6212	−1.3753	−0.0255	−16.99
t-aug-cc-pVDZ	266	0.7284	0.5917	−1.2808	−0.0131	−8.72	0.8353	0.6179	−1.3988	−0.0181	−12.08
DZP	94	0.9626	0.9817	−2.0275	0.0277	18.48	1.1520	0.8953	−2.0798	0.0108	7.21
TZ2P	170	0.8070	0.7588	−1.5772	0.0038	2.53	0.9370	0.7116	−1.6220	−0.0089	−5.90
VD3P	266	0.7354	0.6361	−1.3316	−0.0133	−8.87	0.8531	0.7012	−1.4735	−0.0269	−17.94
vd9s5p1d/4s1p	158	1.1951	1.3311	−2.4937	−0.0108	−7.21	1.4667	1.4148	−2.7999	−0.0272	−18.09
13s8p3d2f/10s3p2d	438	0.7173	0.6259	−1.3046	−0.0129	−8.57	0.8297	0.6845	−1.4354	−0.0263	−17.50

[a] Values of β are in atomic units; values of $[\alpha]_D$ assume $\gamma_s = 1$ (see text) and are in deg[dm·(gm/cc)]$^{-1}$. [b] Number of basis functions.

Methods

The methodology employed in calculating $\beta_{\alpha\beta}$ in the static limit (eq 3) is a direct extension of that previously used in calculating electric field derivatives,[27] nuclear magnetic shielding tensors,[28] and atomic axial tensors[29] at both the Hartree−Fock and DFT levels of theory. All calculations were performed using direct, analytical derivative methods implemented within a development version of Gaussian.[30] The basis sets used are listed in Table 1. The functionals used in DFT calculations are B3LYP,[44−46] PBE1PBE,[47,48] B3PW91,[44,49] and B3P86.[44,50]

Results

HF values of the diagonal elements of $\beta_{\alpha\beta}$, $\beta_{\alpha\alpha}$, and of β for S-**1**, calculated at the B3LYP/TZ2P geometry for three different origins and using both FIAOs and GIAOs at the 6-31G* basis set level are given in Table 2. The three origins used are the center of mass, the oxygen nucleus and a methyl hydrogen nucleus. Both FIAOs and GIAOs lead to origin-dependent $\beta_{\alpha\alpha}$ components. FIAOs lead to origin-dependent β. The variation in β with change of origin is large; the sign of β changes sign in moving the origin from the center-of-mass to the methyl hydrogen. GIAOs yield origin-independent β. Results obtained using the much larger 6-311++G(2d,2p) and aug-cc-pVDZ basis sets are also given in Table 2. The origin-dependence of FIAO-based β values diminishes with increasing basis set size. Since origin-dependent predictions are not physically meaningful, all subsequent calculations use GIAOs.

Values of the diagonal elements $\beta_{\alpha\alpha}$ and of β for S-**1**

TABLE 4: Basis Set Dependence of Hartree−Fock and B3LYP Values of $\beta_{\alpha\alpha}$, β, and $[\alpha]_D$ for R,R-2[a]

		Hartree−Fock					B3LYP				
basis set	bfns[b]	β_{xx}	β_{yy}	β_{zz}	β	$[\alpha]_D$	β_{xx}	β_{yy}	β_{zz}	β	$[\alpha]_D$
6-31G	65	−2.7434	−0.8216	2.4217	0.3811	167.16	−3.2721	−0.6082	2.8583	0.3407	149.42
6-31G*	95	−2.6478	−0.5408	2.3789	0.2699	118.39	−3.2232	−0.4851	3.0283	0.2267	99.42
6-31G**	119	−2.6155	−0.6235	2.4062	0.2776	121.76	−3.1771	−0.5752	3.0413	0.2370	103.96
6-31+G**	139	−2.0788	−1.8245	2.7419	0.3871	169.81	−2.8627	−1.8381	3.2434	0.4858	213.10
6-311G	97	−3.3323	−0.8892	2.3691	0.6175	270.83	−4.1265	−0.5040	2.7891	0.6138	269.23
6-311G*	122	−3.2805	−0.6790	2.5171	0.4808	210.90	−4.1203	−0.4504	3.1525	0.4727	207.35
6-311G**	146	−3.1920	−0.8310	2.5812	0.4806	210.81	−4.0089	−0.6191	3.1982	0.4766	209.06
6-311G(2d)	147	−3.1290	−0.8283	2.8023	0.3850	168.88	−3.8926	−0.6096	3.4421	0.3534	155.00
6-311G(2d,p)	171	−3.0824	−0.9142	2.8038	0.3976	174.41	−3.8483	−0.7257	3.4443	0.3766	165.19
6-311G(2d,2p)	195	−2.9830	−0.9035	2.7797	0.3689	161.82	−3.7243	−0.7410	3.4306	0.3449	151.30
6-311+G	117	−2.1370	−1.9166	2.4319	0.5405	237.10	−2.6994	−1.7482	2.7184	0.5764	252.81
6-311+G*	142	−2.0388	−1.8495	2.6093	0.4263	187.00	−2.6934	−1.8134	3.0921	0.4716	206.84
6-311+G**	166	−2.0086	−1.9804	2.6768	0.4374	191.87	−2.6746	−1.9332	3.1534	0.4848	212.64
6-311+G(2d)	167	−2.0414	−1.9183	2.8716	0.3627	159.09	−2.6654	−1.8782	3.3764	0.3891	170.67
6-311+G(2d,p)	191	−2.0272	−1.9413	2.8548	0.3712	162.83	−2.6752	−1.9063	3.3677	0.4046	177.47
6-311+G(2d,2p)	215	−1.9879	−1.9344	2.7935	0.3762	165.03	−2.6396	−1.9025	3.3018	0.4134	181.34
6-311++G	125	−2.3040	−1.4225	2.4066	0.4400	192.98	−2.8419	−1.1439	2.6258	0.4533	198.85
6-311++G*	150	−2.1737	−1.4136	2.4806	0.3689	161.80	−2.8098	−1.2585	2.9089	0.3865	169.52
6-311++G**	174	−2.1442	−1.5554	2.5720	0.3759	164.87	−2.7956	−1.3856	2.9917	0.3965	173.93
6-311++G(2d)	175	−2.1576	−1.5447	2.7259	0.3254	142.75	−2.7647	−1.3930	3.1834	0.3248	142.45
6-311++G(2d,p)	199	−2.1397	−1.5759	2.7242	0.3304	144.94	−2.7759	−1.4205	3.1869	0.3365	147.60
6-311++G(2d,2p)	223	−2.0864	−1.5925	2.6917	0.3291	144.33	−2.7255	−1.4577	3.1533	0.3433	150.58
6-311++G(2df,2pd)	298	−2.1069	−1.5942	2.7020	0.3330	146.08	−2.7478	−1.4603	3.1511	0.3523	154.55
6-311++G(3d2f,3p2d)	422	−2.0667	−1.4469	2.6235	0.2967	130.15	−2.6565	−1.3802	3.1053	0.3105	136.18
cc-pVDZ	114	−2.7955	−1.1638	2.7149	0.4148	181.94	−3.5133	−0.9497	3.2522	0.4036	177.04
cc-pVTZ	266	−2.8917	−0.8438	2.5953	0.3801	166.70	−3.6394	−0.5972	3.0788	0.3859	169.28
cc-pVQZ	519	−2.6151	−0.9623	2.5850	0.3308	145.10	−3.3717	−0.7089	3.0477	0.3443	151.02
aug-cc-pVDZ	191	−2.0982	−1.4828	2.5980	0.3277	143.73	−2.6198	−1.4843	3.0477	0.3521	154.46
aug-cc-pVTZ	418	−1.9936	−1.4397	2.5667	0.2888	126.70	−2.5108	−1.3901	3.0239	0.2923	128.23
aug-cc-pVQZ	772	−1.9890	−1.4334	2.5714	0.2837	124.43	−2.5098	−1.3744	3.0343	0.2833	124.27
d-aug-cc-pVDZ	268	−2.0217	−1.4248	2.5856	0.2870	125.88	−2.5298	−1.3633	3.0319	0.2871	125.93
t-aug-cc-pVDZ	345	−2.0290	−1.4246	2.5891	0.2881	126.39	−2.5496	−1.3521	3.0563	0.2818	123.60
DZP	128	−1.8725	−2.2566	2.5182	0.5370	235.53	−2.2248	−2.8855	3.1966	0.6379	279.81
TZ2P	227	−1.8634	−2.2725	2.8431	0.4309	189.02	−2.2322	−2.7761	3.4634	0.5150	225.88

[a] Values of β are in atomic units; values of $[\alpha]_D$ assume $\gamma_s = 1$ (see text) and are in deg[dm·(gm/cc)]$^{-1}$. [b] Number of basis functions.

calculated using 38 basis sets at both HF and DFT levels of theory are given in Table 3. Values of the diagonal elements of $\beta_{\alpha\beta}$ and of β, plotted against the number of basis functions, are displayed in Figure 2. Corresponding values of $[\alpha]_D$, obtained with $\gamma_s = 1$, are also given in Table 3. The number of basis functions varies from 48 (6-31G) to 596 (aug-cc-pVQZ). The absolute values of β_{xx}, β_{yy}, and β_{zz} calculated using $\lesssim$200 basis functions vary greatly. Overall, $\beta_{\alpha\alpha}$ absolute values decrease with increasing basis set size; however, scatter is substantial. Calculations using $\gtrsim$200 basis functions give much more stable results, indicating proximity to the complete basis set limit. Values obtained using the largest basis set, aug-cc-pVQZ, should be very close to this limit.

The signs of β_{xx} and β_{yy} are the same (+ for S-**1**); β_{zz} is of opposite sign. The magnitudes of $(\beta_{xx} + \beta_{yy})$ and β_{zz} are similar. Consequently, β values are much less than individual $\beta_{\alpha\alpha}$ values and basis set errors are amplified in β. As a result, values of β calculated using $\lesssim$200 basis functions show no discernible trend and vary not only in magnitude but also in sign. For $\gtrsim$200 basis functions, in contrast, values vary relatively little in magnitude and are uniformly negative in sign.

$\beta_{\alpha\alpha}$ values obtained using Dunning's correlation consistent basis sets cc-pVXZ, X = D, T, and Q, and their augmented counterparts exhibit regular variation with increasing substrate size and with increasing augmentation with diffuse functions. When diffuse functions are absent, dependence on X is considerable. However, with one set of diffuse functions, dependence on X is much smaller. In the case of X = D, further changes are small with double- and triple-augmentation.

$\beta_{\alpha\alpha}$ values obtained with basis sets derived from the 6-31G and 6-311G basis sets by addition of polarization functions and/or diffuse functions also exhibit fairly regular variation. Overall, increasing basis set size leads to greater accuracy, relative to the aug-cc-pVQZ values. As with the cc-pVXZ basis sets, substantial changes occur with the addition of diffuse functions.

The very large "conventional" basis sets VD3P and uncontracted 13s8p3d2f/10s3p2d give results in good agreement with aug-cc-pVQZ, indicating that with substrates of these sizes, additional diffuse functions are unnecessary. Even a modest reduction in size, however, leads to inaccurate results. For example, TZ2P, a moderately large basis set, yields a positive value of β. Small basis sets, such as 6-31G**, DZP, and cc-pVDZ, give $\beta_{\alpha\alpha}$ and β values which are both very different from each other and also very different from the aug-cc-pVQZ values. DZP gives a positive β in contrast to 6-31G** and cc-pVDZ.

Comparison of HF and B3LYP values of $\beta_{\alpha\alpha}$ for **1** shows that the differences are mostly in the range 10−30%. Due to the varying signs of β_{xx}, β_{yy}, and β_{zz}, HF and B3LYP values of β differ by much larger percentages, and in one case (TZ2P) in sign.

Values of the diagonal elements of $\beta_{\alpha\beta}$, $\beta_{\alpha\alpha}$ and of β for R,R-**2** calculated at the B3LYP/TZ2P geometry using 34 basis sets at both HF and DFT levels of theory are given in Table 4. Values of the diagonal elements $\beta_{\alpha\alpha}$ and of β, plotted against the number of basis functions, are displayed in Figure 3. Corresponding values of $[\alpha]_D$, with $\gamma_s = 1$, are also given in Table 4. In this case, the number of basis functions varies from 65 (6-31G) to 772 (aug-cc-pVQZ). These results parallel those for **1**. The principal difference is that there is much less

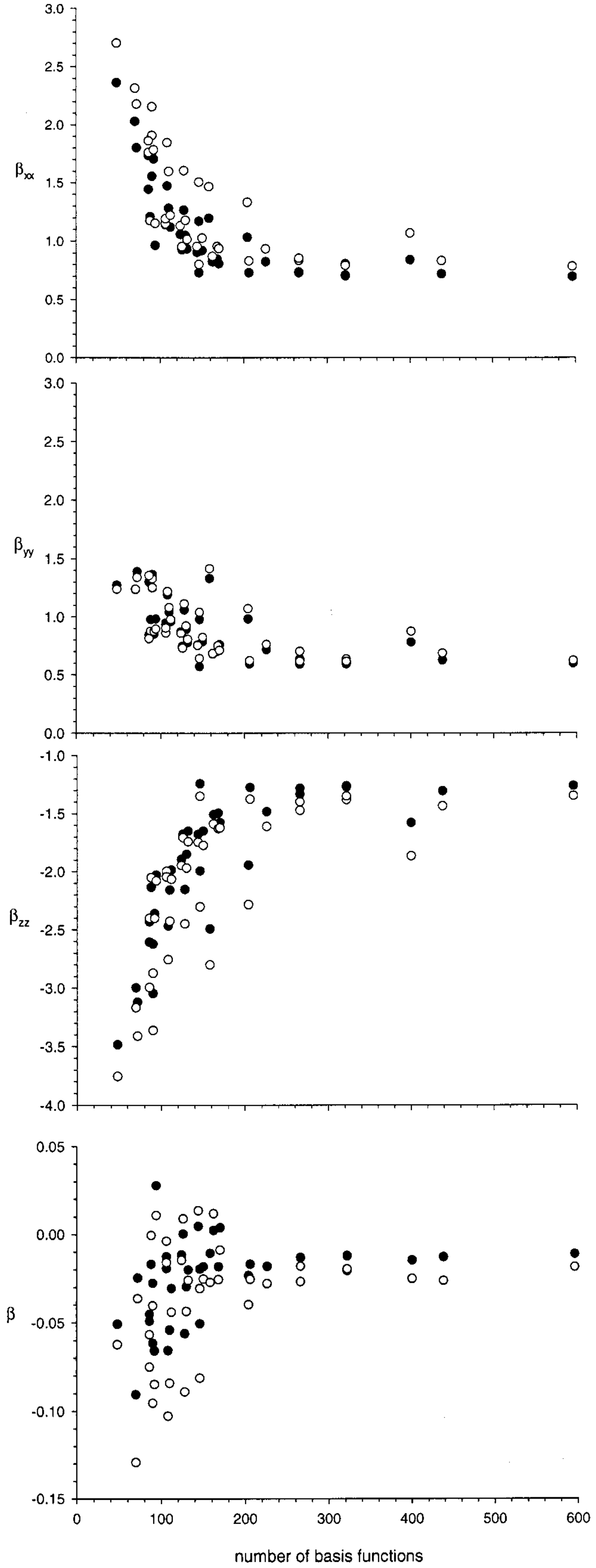

Figure 2. Dependence of calculated $\beta_{\alpha\alpha}$ and β (in au) on the number of basis functions for S-**1** at the Hartree−Fock (●) and B3LYP (○) levels of theory.

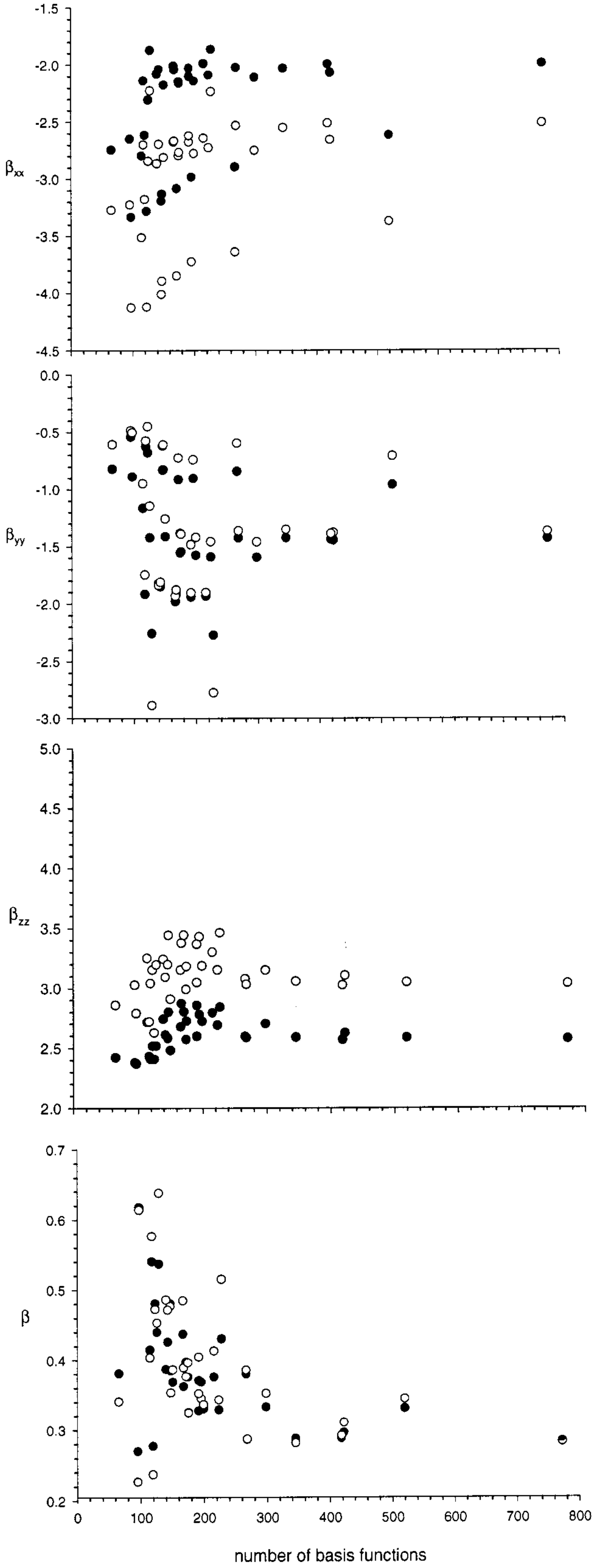

Figure 3. Dependence of calculated $\beta_{\alpha\alpha}$ and β (in au) on the number of basis functions for R,R-**2** at the Hartree−Fock (●) and B3LYP (○) levels of theory.

cancellation of β_{xx}, β_{yy}, and β_{zz} values, so that β values of **2** are much larger than β values of **1**. Absolute values of β_{xx}, β_{yy}, β_{zz}, and β calculated using $\lesssim$250 basis functions vary greatly. Calculations using $\gtrsim$250 basis functions give much more stable results, indicating proximity to the complete basis set limit. Values obtained using the largest basis set, aug-cc-pVQZ, should be very close to this limit. Again, accurate results require the inclusion of diffuse functions in the basis set.

TABLE 5: Variation of $\beta_{\alpha\alpha}$, β, and $[\alpha]_D$ with Density Functional for S-1 and (R,R)-2[a]

functional	β_{xx}	β_{yy}	β_{zz}	β	$[\alpha]_D$
			S-**1**		
6-311++G(2d,2p):					
B3LYP	0.9534	0.7516	−1.6281	−0.0257	−17.09
PBE1PBE	0.9404	0.7298	−1.5884	−0.0273	−18.15
B3PW91	0.9776	0.7312	−1.6199	−0.0296	−19.73
B3P86	0.9831	0.7266	−1.6182	−0.0305	−20.30
aug-cc-pVDZ:					
B3LYP	0.8005	0.6407	−1.3495	−0.0306	−20.37
PBE1PBE	0.7938	0.6086	−1.3074	−0.0317	−21.09
B3PW91	0.8160	0.6077	−1.3244	−0.0331	−22.03
B3P86	0.8210	0.6035	−1.3232	−0.0338	−22.48
			(R,R)-**2**		
6-311++G(2d,2p):					
B3LYP	−2.7255	−1.4577	3.1533	0.3433	150.58
PBE1PBE	−2.5954	−1.6129	3.1939	0.3381	148.31
B3PW91	−2.6037	−1.6503	3.2619	0.3307	145.04
B3P86	−2.5919	−1.6559	3.2548	0.3310	145.20
aug-cc-pVDZ:					
B3LYP	−2.6198	−1.4843	3.0477	0.3521	154.46
PBE1PBE	−2.5200	−1.5714	3.0950	0.3321	145.67
B3PW91	−2.5184	−1.6121	3.1505	0.3267	143.29
B3P86	−2.5036	−1.6249	3.1323	0.3320	145.64

[a] Values of β are in atomic units; values of $[\alpha]_D$ assume $\gamma_s = 1$ (see text) and are in deg[dm·(gm/cc)]$^{-1}$.

The values of the diagonal elements of $\beta_{\alpha\beta}$, β, and $[\alpha]_D$ for **1** and **2** obtained at the 6-311++G(2d,2p) and aug-cc-pVDZ basis set levels using three alternative hybrid functionals (PBE1PBE, B3PW91 and B3P86) are compared to B3LYP values in Table 5. Variation in $\beta_{\alpha\alpha}$, β and $[\alpha]_D$ between the four functionals is small.

Values of β and $[\alpha]_D$ for **1** and **2** obtained at the 6-311++G(2d,2p) and aug-cc-pVDZ basis set levels for three alternative choices of geometry are presented in Table 6. The variations in β and $[\alpha]_D$ are somewhat larger than those obtained on variation of the density functional and than the differences in 6-311++G(2d,2p) and aug-cc-pVDZ values at the same geometry.

Experimental values of $[\alpha]_D$ for 1 have been reported for a range of solvents.[51] In the nonpolar, low dielectric constant solvents CCl_4 and CS_2 $[\alpha]_D$ for S-**1** is −18.7° and −19.4° respectively. The $[\alpha]_D$ of neat liquid R,R-**2** is 129°.[52] Large basis set HF and B3LYP calculations are quite successful in predicting the signs and magnitudes of the $[\alpha]_D$ values of **1** and **2**. We emphasize, however, that the calculations here include neither the frequency dependence of β nor solvent effects. Further comparison to experiment requires these important contributions to be included.

Discussion

The electric dipole−magnetic dipole polarizability $\beta_{\alpha\beta}$ is an intrinsically origin-dependent tensor. Its origin-dependence is given by

$$(\beta_{\alpha\beta})^{O'} = (\beta_{\alpha\beta})^{O} - \frac{e}{6\pi hm}\mathrm{Im}\left\{\sum_{k\neq 0}\frac{\langle 0|(\mu_{\mathrm{el}})_\alpha|k\rangle[\Delta \times \langle k|\mathbf{P}|0\rangle]_\beta}{\nu_{k0}^2 - \nu^2}\right\} \tag{4}$$

where O' is displaced from O by Δ and $\mathbf{P} = \sum_i \mathbf{p_i}$. Introducing the hypervirial relationship between matrix elements of $\mathbf{r_i}$ and $\mathbf{p_i}$,[53]

$$\langle 0|\mathbf{P}|k\rangle = \frac{im}{e\hbar}(E_0 - E_k)\langle 0|(\mu_{\mathrm{el}})|k\rangle \tag{5}$$

eq 4 becomes

$$(\beta_{\alpha\beta})^{O'} = (\beta_{\alpha\beta})^{O} - \frac{1}{3h}\left\{\sum_{k\neq 0}\frac{\nu_{k0}\langle 0|(\mu_{\mathrm{el}})_\alpha|k\rangle[\Delta \times \langle k|(\mu_{\mathrm{el}})|0\rangle]_\beta}{\nu_{k0}^2 - \nu^2}\right\} \tag{6}$$

whence

$$(\beta)^{O'} = \frac{1}{3}Tr[(\beta_{\alpha\beta})^{O'}] = (\beta)^{O} \tag{7}$$

i.e., β is origin-independent, an indispensable result for an observable property. Approximate calculations do not automatically satisfy eq 5 and yield origin-independent values of β. In particular, calculations using FIAOs only provide origin-independent values of β in the complete basis set limit; in contrast the use of GIAOs guarantees origin-independent results for any basis set size. Meaningful comparison of predicted β and $[\alpha]$ values to experiment requires origin-independent predictions. In practice, therefore, the use of GIAOs is mandated. In this regard, the calculation of β parallels the calculation of paramagnetic susceptibilities,[2] nuclear paramagnetic shielding tensors,[2] and atomic axial tensors.[29,54]

For **1** and **2**, HF and DFT values of $\beta_{\alpha\beta}$, calculated using GIAOs, exhibit very considerable basis set dependence. Fairly large basis sets, including diffuse functions on both heavy atoms and hydrogen atoms, are necessary to achieve results close to the complete basis set limit. Small basis sets such as 6-31G** and DZP yield inaccurate results. This behavior parallels that of the electric dipole−electric dipole polarizability tensor $\alpha_{\alpha\beta}$ and is, therefore, quite unsurprising. (Indeed, the alternative

TABLE 6: Geometry Dependence of β and $[\alpha]_D$ for S-1 and (R,R)-2[a]

	6-311++G(2d,2p)				aug-cc-pVDZ			
	HF		B3LYP		HF		B3LYP	
geometry[b]	β	$[\alpha]_D$	β	$[\alpha]_D$	β	$[\alpha]_D$	β	$[\alpha]_D$
				S-**1**				
HF/STO-3G	−0.0141	−9.41	−0.0261	−17.37	−0.0077	−5.14	−0.0199	−13.23
B3LYP/6-31G*	−0.0209	−13.92	−0.0276	−18.37	−0.0228	−15.17	−0.0338	−22.50
B3LYP/TZ2P	−0.0184	−12.27	−0.0257	−17.09	−0.0197	−13.14	−0.0306	−20.37
MP2/6-31G*	−0.0248	−16.52	−0.0301	−20.04	−0.0267	−17.76	−0.0362	−24.08
				(R,R)-**2**				
HF/STO-3G	0.3536	155.12	0.4025	176.53	0.3626	159.03	0.4235	185.76
B3LYP/6-31G*	0.3402	149.21	0.3563	156.26	0.3402	149.21	0.3673	161.10
B3LYP/TZ2P	0.3291	144.33	0.3433	150.58	0.3277	143.73	0.3521	154.46
MP2/6-31G*	0.3465	152.00	0.3716	163.01	0.3463	151.90	0.3819	167.51

[a] Values of β are in atomic units; values of $[\alpha]_D$ assume $\gamma_s = 1$ (see text) and are in deg[dm·(gm/cc)]$^{-1}$. [b] Geometry optimized at this level of theory.

outcome—rapid convergence of $\beta_{\alpha\beta}$ with increasing basis set size—would have been extremely surprising.) It is standard dogma in the literature that reliable calculations of $\alpha_{\alpha\beta}$ require basis sets including diffuse functions.[55] We have shown that the same is the case for $\beta_{\alpha\beta}$.

Our DFT calculations of $\beta_{\alpha\beta}$ are the first to include correlation. Using the hybrid B3LYP functional a substantial fraction of the correlation error of HF calculations should be removed.[28,29,56−58] B3LYP and HF values of $\beta_{\alpha\beta}$ generally differ by 10−30%. The percentage differences are larger for β when $\beta_{\alpha\alpha}$ values vary in sign and cancellation occurs. Other hybrid functionals, such as PBE1PBE, B3PW91, and B3P86 give similar results. We expect the DFT calculations to be more accurate than the HF calculations. Comparison to experiment does not clearly support this expectation, however, since the differences between HF and DFT rotations are comparable in magnitude to the errors in calculated rotations resulting from the neglect of the frequency dependence of β and of solvent effects. Thus: HF and B3LYP aug-cc-pVQZ values of $[\alpha]_D$ for **1** (Table 3) differ by 4.9°, while reported $[\alpha]_D$ values in 35 solvents vary from −30.6° to +4.3°,[51] a range of 34.9°. Precise definition of the accuracies of HF and DFT rotations requires the inclusion of the frequency dependence of β and of solvent effects.

Polavarapu et al. and Kondru et al. have reported HF calculations of β and $[\alpha]_D$ carried out using CADPAC with FIAOs and DALTON with either FIAOs or GIAOs.[12−19] β values obtained using CADPAC were for the static limit while those obtained using DALTON were calculated at the frequency of the sodium D line. The large majority of calculations were carried out using CADPAC. The basis sets used in these studies were 4-31G, 6-31G, 4-31G*, 6-31G*, 6-31G**, DZP, and 6-31G(ext); 6-31G* and DZP were used predominantly. The origin-dependence of the results obtained using FIAOs was not explicitly remarked upon, nor were the origins used specified. We have shown that the origin-dependence of β and $[\alpha]_D$ are substantial at small basis set levels and this must be the case for all FIAO calculations reported. It follows that these results cannot be meaningfully compared to experiment.

The basis sets used in the prior calculations were small, with the exception of 6-31G(ext), and none included diffuse functions. It follows that, even when GIAOs were used, good agreement with experiment is fortuitous. Results for **1** and **2** illustrate this conclusion. Polavarapu and Zhao[15] derived $[\alpha]_D = -23°$ (this includes the Lorentz factor) for S-**1** from a frequency-dependent 6-31G* calculation using GIAOs. As we have shown, the 6-31G* values of $\beta_{\alpha\alpha}$ are far from the complete basis set limit. However, fortuitous cancellation of error yields a β value of the correct sign and similar magnitude. GIAO calculations were not reported for **1** for other basis sets. In the case of **2**, Polavarapu and Zhao[15] derived $[\alpha]_D = 162°$ and 353° from frequency-dependent GIAO calculations using 6-31G* and DZP, respectively. Again, we have shown that the values of $\beta_{\alpha\alpha}$ are far from the complete basis set limit for both basis sets and that the closeness of the 6-31G* α_D to experiment is fortuitous.

Conclusion

We have presented calculations of the optical rotations of two simple chiral molecules using the HF and DFT methodologies. Our DFT calculations are the first to include correlation. We have carried out calculations over a very wide range of basis sets. Our results demonstrate the importance of the choice of basis set in calculating optical rotation. First, the use of GIAOs is required to obtain origin-independent results for finite basis sets. Secondly, it is important to include diffuse functions in the basis set. Of the basis sets utilized here, aug-cc-pVDZ and 6-311++G(2d,2p) appear to be the most cost-effective, i.e., the best compromise of accuracy and computational cost. In contrast, small basis sets such as 6-31G* and DZP do not yield reliable results. Our calculations here do not include the frequency dependence of β and solvent effects. In future publications[26] we will report HF and DFT calculations in which these important contributions are included. Our conclusions with regard to the choice of basis set will apply equally to such calculations.

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