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Calculations of optical rotation: Influence of molecular structure

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Abstract: The *ab initio* Hartree–Fock (HF) method and the Density Functional Theory (DFT) were used to calculate the optical rotation of 26 chiral compounds. The effects of the theory and basis sets used for the calculation, the influence of the solvent on the geometry and the values of the calculated optical rotation are all discussed. The polarizable continuum model, included in the calculation, did not improve the accuracy effectively, but was superior to γ_s . The optical rotation of five- and six-membered cyclic compounds was calculated and 17 pyrrolidine or piperidine derivatives, which were calculated by the HF and DFT methods, gave acceptable predictions. The nitrogen atom dramatically affected the calculation results and it is necessary in the molecular structure in order to obtain an accurate computation result. Namely, when the nitrogen atom was substituted by an oxygen atom in the ring, the calculation result deteriorated.

Keywords: *ab initio*; chiral molecules; molecular structure; optical rotation; solvent effect.

INTRODUCTION

Optical rotation (OR) at the sodium D line ($[\alpha]_D$) is one of the most common experimental data that characterizes an optically active compound, and it can be correlated with the absolute configuration by reliable algorithms.¹ In recent years, there has been increasing interest in the calculation of the optical rotation at the sodium D line. Polavarapu² identified a “renaissance” in optical rotation. The first *ab initio* calculation of optical rotation was reported by Polavarapu and co-workers³ in 1997 and subsequently more attention was paid to this calculation. In the beginning, most calculations were concentrated on small and rigid molecules for accuracy. Polavarapu and co-workers⁴ calculated the optical rotation of small molecules: H₂O₂ and H₂S₂. With the development of computers and algorithms,

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more calculations were directed to large and flexible molecules or natural product molecules, even to the determination of the absolute configuration of molecules.⁵ Moreover, the absolute configuration of more complex molecules can be determined combined with other calculations.⁶ Although great progress was made in these years with the development of quantum chemical models, accurate computation results remained unreliable. Hence, researchers still focus on improvement of the calculation accuracy,⁷ and many calculation methods have demonstrated an encouraging agreement between the observed and predicted optical rotation.

The determination of the absolute configuration of chiral molecules is a challenging task. Optical rotation can be used to determine the absolute configuration of the molecules.⁸ If calculation methods are easy and the results are sufficiently accurate, they will be helpful for the assignment of absolute configuration. Great effort should still be made in this field. Density functional theory (DFT) is widely used for the calculation of OR, and nowadays it has become a major trend. Several authors have reported the performance of DFT in the determination of the sodium D-line specific rotation $[\alpha]_D$ of a number of rigid chiral molecules. In addition, the coupled cluster theory was reported by Ruud *et al.*⁹ Stephens *et al.*¹⁰ reported that the *ab initio* calculation of the OR (and of electronic circular dichroism, ECD) provided reliable results only when the TDDFT method with extended basis sets (*i.e.*, including both polarization and diffuse functions) was used. Although this kind of method has been applied by many researchers and its availability has been approved, strong computational capability is compulsory when a large and complicated molecule is studied. The Hartree–Fock (HF) theory should be considered in the calculation of OR.

The specific rotation of a chiral molecule at a frequency ν is given by:^{11–13}

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

where N is the number of chiral molecules cm^{-3} in an isotropic solution and $\beta = 1/3\text{Tr}[\beta_{\alpha\beta}]$, where $\beta_{\alpha\beta}$ is the electric dipole – magnetic dipole polarizability. $\beta_{\alpha\beta}$ is given by:

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

where 0 and k label the ground and excited electronic states, μ_{el}^e and μ_{mag}^e are the electronic electric and magnetic dipole operators, respectively and γ_s is the solvent effect. However, the inclusion of γ_s in the calculated ORs values leads to deterioration from the experiment data. The solvent correction is neglected ($\gamma_s = 1$) in the first calculation. Then next calculation is approximated by using the Lo-

rentz expression: $\gamma_s = (n^2+2)/3$.^{12,14} Optical rotations are usually measured using D line (589.3 nm) radiation.

Although the quantum mechanical origin of the optical rotation angle was described by Rosenfeld in 1928, Amos first realized the calculation of $\beta_{\alpha\beta}$ using *ab initio* methods in 1982. In this paper, our focus was on *ab initio* optical rotation studies of molecules with similar structures (pyrrolidine or piperidine derivatives), whereby attempts were made to find some relations between calculation methods and molecular structure. The accuracy of various types of methods and basis sets are discussed for five- or six-membered nitrogen-containing compounds. The application of the HF and DFT methodologies in the calculation of optical rotation is discussed and acceptable prediction was currently proved for 17 pyrrolidine or piperidine derivatives. Finally, the inclusion of polarizable continuum model (PCM) in the calculations is discussed and compared to inclusion of the solvent effect γ_s .

COMPUTATIONAL DETAILS

The OR was calculated by the HF and DFT methods utilizing two exchange-correlation functional, B3-LYP¹⁵⁻¹⁷ (hybrid three-parameter Becke–Lee–Yang–Parr functional) and B3PW91^{15,18,19} (hybrid three-parameter Becke–Perdew–Wang91 functional). Three basis sets were used in both the HF and DFT methods: 6-31G(d), 6-311+G(d) and 6-311++G(3df, 2pd). Another three basis sets were only used in the HF method: cc-pVDZ, cc-pVDZ, aug-cc-pVDZ. In order to characterize the accuracy of these methods in calculations of this kind of molecules, it is necessary to choose sufficient samples. Both rigid and flexible molecules were studied. Considering confirmation of the configuration of flexible molecules is difficult and is easily affected by the environment, 26 molecules were selected, all of which were heterocyclic compounds. Their structures are detailed in Fig. 1 and the values of their experimental optical rotation are listed in Table I.

All molecules were optimized at the B3LYP/6-31G(d) level, which is reported to be good enough for the optimization of molecular structure.⁴² The calculation was focused on discussing whether specific structures of the molecules influence the calculation results. The specific rotations were calculated for the sodium D-line wavelength (589.3 nm). In order to improve the accuracy, PCM and the solvent effect γ_s were considered in some calculations.⁴³ Calculations in this investigation have been carried out following the protocol as below: if great difference existed between computation and experimental values, priority was given to regulation of the input conformation.

All calculations were performed using the Gaussian 03 program.⁴⁴

RESULTS AND DISCUSSION

First, the calculation results for the 26 compounds are investigated and the calculation errors discussed, and the solvent effect is analyzed. Second, an attempt is made to discuss the relationship between the OR calculation result and molecular structure.

Calculation values with the DFT and HF methods

Values of $[\alpha]_D$ which neglect the solvent effect γ_s ($\gamma_s = 1$) were obtained by using HF and DFT and different basis sets are listed in Table SI of the Supplementary material to this paper. Absolute differences between calculated and experimental $[\alpha]_D$ values are also given. The largest deviations were obtained for molecules **7**, **8**, **10**, **11**, **19** and **20**. However these results do not mean that DFT or HF method is unsuitable for these molecules, because there may be many factors which could influence the calculation.

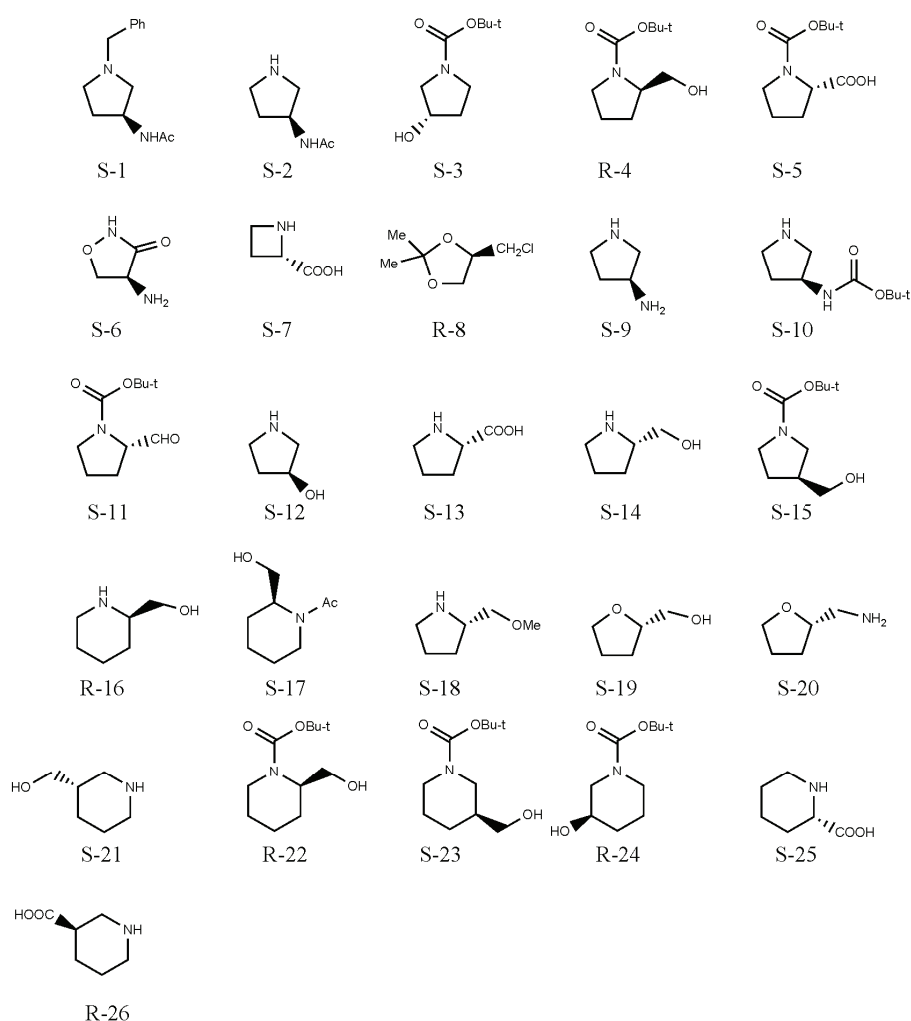


Fig. 1. Molecules **1–26**. The absolute configurations are those for which *ab initio* optical rotation calculations were performed (see Table SI in the Supplementary material to this paper).

TABLE I. Experimental specific rotations of compounds **1–26**

Compound	Configuration	<i>t</i> °C	<i>c</i> g (100 mL) ⁻¹	Solvent	$[\alpha]_D$ ° dm ⁻¹ g ⁻¹ cm ³	Ref.
1	<i>S</i>	20	1.00	Chloroform	-19	20
2	<i>S</i>	20	1	Methanol	-46.5	21
3	<i>S</i>	27	1.02	Chloroform	22.75	22
4	<i>R</i>	20	3.0	Chloroform	44	23
5	<i>S</i>	24	1.40	Chloroform	-72.7	24
6	<i>S</i>	22	–	Water	-115	25
7	<i>S</i>	20	3.6	Water	-118	26
8	<i>R</i>	25	5.03	Benzene	35.9	27
9	<i>S</i>	20	–	Neat	-20	21
10	<i>S</i>	20	1	Ethanol	-21	21
11	<i>S</i>	23	1.1	Chloroform	-90.1	28
12	<i>S</i>	20	3.5	Ethanol	-6.5	21
13	<i>S</i>	25	0.83	Chloroform	-40.1	29
14	<i>S</i>	–	1.3	Chloroform	11.69	30
15	<i>S</i>	24	0.9	Chloroform	-6.5	31
16	<i>R</i>	20	2.38	Ethanol	-13.5	32
17	<i>S</i>	25	4.00	Chloroform	20.5	33
18	<i>S</i>	20	2.00	Benzene	3	34
19	<i>S</i>	20	–	Neat	2.3	21
20	<i>S</i>	20	5.05	Chloroform	12.15	35
21	<i>S</i>	21	18	–	-3.8	36
22	<i>R</i>	20	2	Chloroform	31.2	37
23	<i>S</i>	20	1	Chloroform	11.2	38
24	<i>R</i>	20	1.11	Chloroform	-10.8	39
25	<i>S</i>	22	1.0	Water	-25.9	40
26	<i>R</i>	23	–	–	-3.4	41

HF and DFT methods are compared in the calculation results listed in Table II. For molecules **2**, **4**, **5**, **13**, **15**, **16** and **24–26** the HF method gave accurate calculations and the range of derivations were **2**: 4.05–6.41; **4**: 0.6–2.65; **5**: 1.87–11.64; **13**: 7.42–17.9; **15**: 1.28–20.71; **16**: 4.79–35.89; **24**: 0.6–12.6; **25**: 5.3–15.03 and **26**: 2.1–5.45. Conversely, for molecules **3**, **6**, **9**, **14**, **18** and **21–23** the DFT method had a better performance and the range of derivations were **3**: 0.92–42.93, **6**: 7.5–64.3; **9**: 1.97–83.88, **14**: 0.17–16.32, **18**: 2.66–15.97, **21**: 6.59–25.07, **22**: 0.75–24.65, **23**: 1.68–11.36. However, it should be registered that both the HF and DFT method could give acceptable computational results for molecules **2–6**, **9**, **13–16**, **18** and **21–26**.

Analysis of factors influencing the calculated data

Through the calculations of the OR of 26 molecules, it could be seen that the HF or DFT method were suitable for the molecules as follows: 1) which are all pyrrolidine derivatives or piperidine derivatives; 2) the chiral centers have short

chains, such as $-\text{CH}_2\text{OH}$, $-\text{NHAc}$, $-\text{OH}$ or $-\text{COOH}$; 3) weak electron-attracting-group, $-\text{H}$ or $-\text{COOC}(\text{CH}_3)_3$, was linked to the nitrogen. However, bad calculation results were obtained for molecules **12**, **15** and **21**, which also belonged to this kind of molecule; hence, some other limits may exist. The differences between calculated and experimental $[\alpha]_{\text{D}}$ values can be attributed to many factors, such as: 1) error in the configuration; 2) solvent effect; 3) error in experimental $[\alpha]_{\text{D}}$ values, *etc.* Especially for the configuration, the computed optical rotation angles are very sensitive to geometry. For molecule **15**, initially neither the HF nor the DFT method could predict the sign correctly. Even for calculations with the big basis set, the correct sign was not given. This may result from errors in configuration. Hence, the input configuration was modified and then the calculation results gave the correct sign. Hence, properly optimized geometries are essential for the calculation of reliable rotation angles. Recently, Mazzeo *et al.*⁴⁵ thought that a higher level of theory may be required after geometry optimization by the commonly used DFT/B3LYP/6-31G(d). Thus, the importance of the optimized geometry can be seen.

TABLE II. Comparison of the $[\alpha]_{\text{D}}$ ($\text{dm}^{-1} \text{g}^{-1} \text{cm}^3$) obtained using the HF and DFT methods

Compd.	HF	$[\alpha]_{\text{D}}$	DFT	$[\alpha]_{\text{D}}$
1	6-311++G(3df,2pd)	20.49	B3PW91/6-311++G(3df,2pd)	17.38
2	6-311+G(d)	4.05	B3PW91/6-311++G(3df,2pd)	65.83
3	6-311++G(3df,2pd)	5.41	B3LYP/6-31G(d)	0.92
4	6-31G(d)	0.60	B3PW91/6-31G(d)	5.90
5	6-31G(d)	1.87	B3LYP/6-31G(d)	37.18
6	6-311++G(3df,2pd)	54.20	B3PW91/6-311++G(3df,2pd)	7.50
7	6-31G(d)	128.31	B3PW91/6-31G(d)	79.05
8	6-311++G(3df,2pd)	123.88	B3LYP/6-311++G(3df,2pd)	142.24
9	6-311++G(3df,2pd)	26.02	B3LYP/6-311+G(d)	1.97
10	6-31G(d)	55.28	B3LYP/6-31G(d)	67.36
11	6-31G(d)	113.16	B3PW91/6-31G(d)	118.42
12	6-31G(d)	17.50	B3PW91/6-31G(d)	38.73
13	6-311++G(3df,2pd)	7.42	B3PW91/6-31G(d)	55.15
14	6-31G(d)	2.59	B3LYP/6-31G(d)	0.17
15	6-31G(d)	9.73	B3PW91/6-31G(d)	26.62
16	6-31G(d)	4.79	B3LYP/6-31G(d)	4.95
17	6-311+G(d)	30.71	B3LYP/6-311+G(d)	34.5
18	6-31G(d)	15.47	B3PW91/6-311++G(3df,2pd)	2.66
19	6-311+G(d)	44.64	B3LYP/6-311+G(d)	52.52
20	6-31G(d)	49.70	B3PW91/6-31G(d)	74.13
21	6-31G(d)	15.63	B3LYP/6-31G(d)	14.19
22	6-31G(d)	14.06	B3LYP/6-31G(d)	0.75
23	6-311++G(3df,2pd)	4.54	B3LYP/6-311+G(d)	1.68
24	6-311+G(d)	0.60	B3PW91/6-311+G(d)	8.25
25	6-31G(d)	6.10	B3PW91/6-31G(d)	43.36
26	6-311++G(3df,2pd)	2.10	B3LYP/6-31G(d)	3.06

The studied molecules have a stable ring structure, short chains with low flexibility and an atomic electron that does not drift dramatically. The nitrogen atom may be very important for the obtained calculation results, and when the nitrogen atom was substituted by an oxygen atom in the ring, the calculation result deteriorated. For molecules **8**, **19** and **20**, the derivation was about 50 to 120 degrees from the experiment value.

Consideration of the solvent effect in the calculations

Then both solvent effects γ_s and PCM were considered in a further HF calculation, the results of which are given in Table III. The effects of the addition of PCM and γ_s in the calculations of molecules **2**, **3**, **15** and **16** were compared. Comparison of the experimental $[\alpha]_D$ values with the calculated values for the 17 molecules is shown in Figs. 2 and 3. Comparison of solvent effect with γ_s and PCM included in the calculation is shown in Fig. 3. Inclusion of the solvent effect factor γ_s in the calculation led to a deterioration of the results for most of the molecules. PCM was also considered for some molecules (**2**, **3**, **15** and **16**) to improve the computation effect. However, the results differed from one another (Figs. 4 and 5). For molecules **2** and **16**, the calculations were especially improved on addition of PCM in the geometry optimization with the relative deviation decreasing from 8.7 to 1.5 % and from 34.5 to 7.8 %, respectively. However, the calculations of **3** and **15** deteriorated a little with PCM in the geometry optimization. It is clear that the calculations will be changed when PCM is introduced in the geometry optimization, but the variation is not large. Although it has been reported that PCM does not effectively contribute to the calculation.

TABLE III. Hartree–Fock method with the solvent effect included in the calculations

Compd.	γ_s	$[\alpha]_D / \text{dm}^{-1} \text{g}^{-1} \text{cm}^3$	PCM	$[\alpha]_D / \text{dm}^{-1} \text{g}^{-1} \text{cm}^3$
2	6-311++G(3df,2pd)	4.7	6-31G(d)	0.69
3	6-311++G(3df,2pd)	1.2	6-311++G(3df,2pd)	11.28
4	6-311++G(3df,2pd)	12.8		
5	6-31G(d)	28.9		
6	6-311++G(3df,2pd)	33.93		
9	–	–		
13	6-311++G(3df,2pd)	24.7		
14	6-31G(d)	7.8		
15	6-31G(d)	10.9	6-31G(d)	9.75
16	6-31G(d)	2.3	6-31G(d)	1.05
18	6-31G(d)	23.19		
21	–	–		
22	6-31G(d)	7.8		
23	6-311++G(3df,2pd)	2.1		
24	6-311++G(3df,2pd)	0.8		
25	6-31G(d)	16.77		
26	–	–		

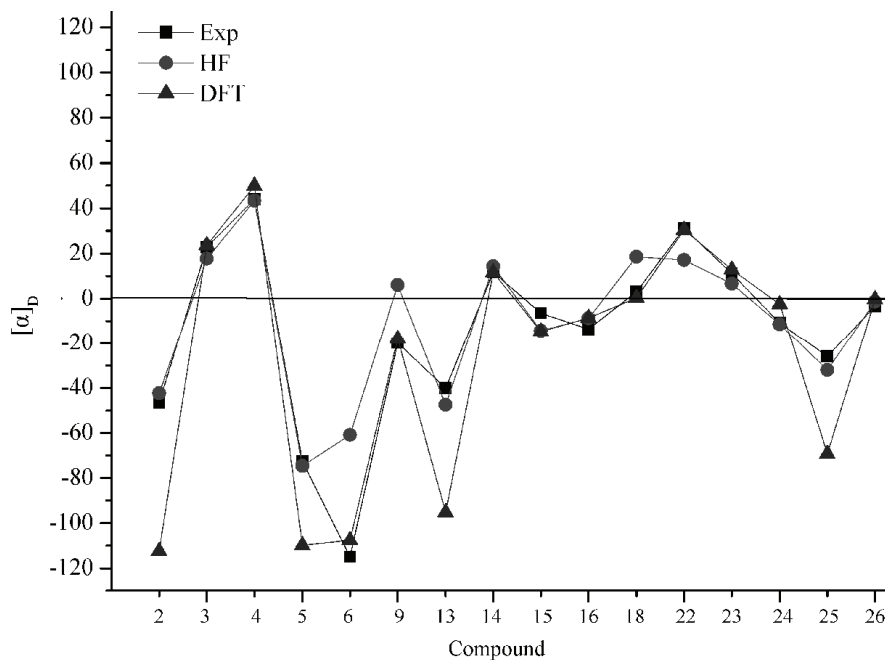


Fig. 2. Comparison of the $[\alpha]_D$ ($\text{dm}^{-1} \text{g}^{-1} \text{cm}^3$) of 17 molecules calculated by HF or DFT method with the experimental $[\alpha]_D$ values.

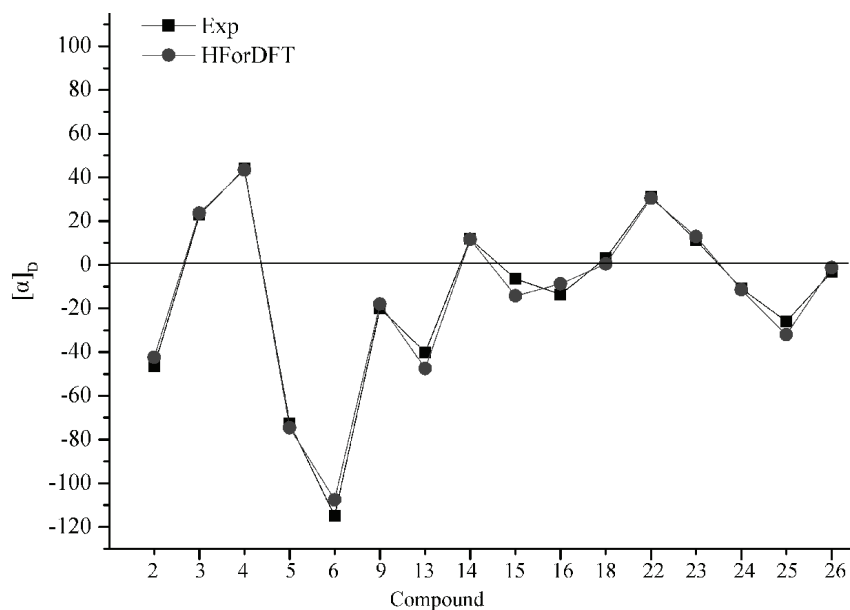


Fig. 3. Comparison of the $[\alpha]_D$ ($\text{dm}^{-1} \text{g}^{-1} \text{cm}^3$) calculated by the HF and DFT methods with the experimental $[\alpha]_D$ values.

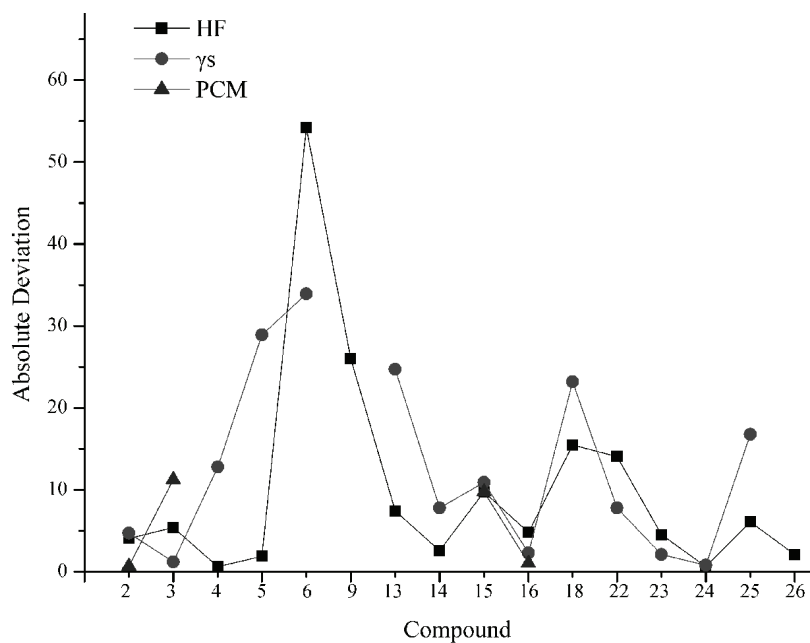


Fig. 4. Comparison of the $[\alpha]_D$ ($\text{dm}^{-1} \text{g}^{-1} \text{cm}^3$) calculated by the HF method including the solvent effect with the experimental $[\alpha]_D$ values.

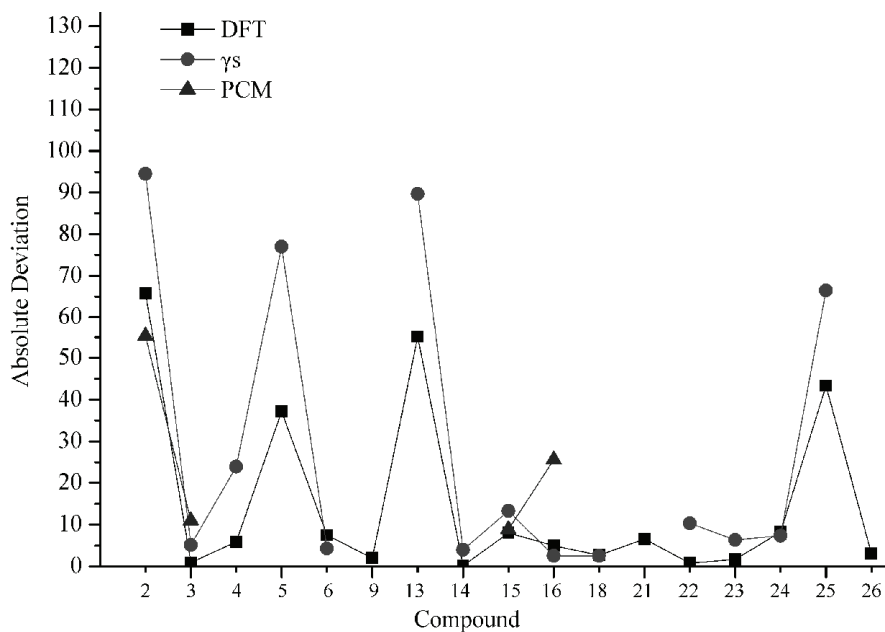


Fig. 5. Comparison of the $[\alpha]_D$ ($\text{dm}^{-1} \text{g}^{-1} \text{cm}^3$) calculated by the DFT method including the solvent effect with the experimental $[\alpha]_D$ values.

PCM is still a commonly used method to evaluate solvent effects in optical rotation calculations. In the present study, PCM worked well in some cases, such as for molecules **2**, **10** and **16**, but led to a deterioration of the results in other cases. Thus, PCM is not ineffective and there may exist some rules to use this model, such as molecular structure, solvent, the property calculated, *etc.*, which could produce desirable calculations. The addition of the factor γ_s to solve solvent effect may not be an effective way. It is clear that solvent effect γ_s changes the results dramatically, while inclusion of PCM in the calculation only produces a change of several degrees.

The chiral molecules in the present calculations were considered as being in the gaseous state, and the HF method gave admirable predictions. This may be because the experimental specific rotations were measured in a weak polar solvent that had little interaction with the molecules.

CONCLUSIONS

The accuracy of the HF and DFT methods was evaluated for the calculation of the optical rotation of 26 molecules. The HF method with six basis sets was employed for the calculations. In parallel, B3LYP and B3PW91 functionals with three basis sets have been performed. The result showed that for the 17 chiral molecules that have specific structures, the HF or DFT substantially gave acceptable predictions. Previous studies focused on the methods and the basis sets of the computation to improve accuracy, but the present study may prove that the structures of the molecules have a strong influence on the calculation values for an established method, or for a certain kind of molecules, some established method probably exists to give an accurate prediction. Our attention was no longer focused on the use of large basis sets or new methods to improve the accuracy of calculations for molecules that do not have similarity in their structure. For a large group of molecules, increasing the amount of computation to prove the accuracy have been widely discussed,⁴⁶ and in some cases, this is completely valid. However, for a certain kind of molecules, if an effective method can be found, it is still meaningful to decrease the amount of calculation and still obtain accurate calculation values.

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SUPPLEMENTARY MATERIAL

Comparison of $[\alpha]_D$ values obtained using HF and DFT methods with different basis sets are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

РАЧУНАЊЕ ОПТИЧКЕ РОТАЦИЈЕ: УТИЦАЈ МОЛЕКУЛСКЕ СТРУКТУРЕ

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Ab initio Хартри–Фокова (HF) метода и теорија функције густине (DFT) су примењене за израчунавање оптичке ротације 26 једињења. Разматрани су утицај нивоа теорије и избора базних функција, као и утицај растварача на геометрију и вредност оптичке ротације. Модел континуиране поларизабилности није повећао тачност рачунања, али је дао боље резултате него γ_s . Израчунате су оптичке ротације за једињења са пето- и шесточланим прстеновима за 17 пиролдинских и пиперидинских деривата. Предвиђања на основу HF и DFT метода дају задовољавајуће резултате. Атом азота драматично утиче на резултате израчунавања, и такав атом је неопходан у молекулској структури да би се добили довољно тачни резултати. Наиме, када је атом азота у прстену замењен кисеоником, резултати израчунавања су постајали слабији.

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