

Absolute Configurations, Predominant Conformations, and Tautomeric Structures of Enantiomeric *tert*-Butylphenylphosphinothioic Acid

Feng Wang and Prasad L. Polavarapu*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, and

Józef Drabowicz, Marian Mikołajczyk, and Piotr Łyzwa

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, 93-236 Łódź, Sienkiewicza 112, Poland

Prasad.L.Polavarapu@vanderbilt.edu.

Received July 23, 2001

Vibrational absorption and circular dichroism spectra of dextrorotatory, levorotatory, and racemic mixture of *tert*-butylphenylphosphinothioic acid have been measured in CCl₄ solutions in the 2000–900 cm⁻¹ region. The conformations for both tautomeric structures of (*S*)-*tert*-butylphenylphosphinothioic acid are investigated using the B3LYP functional with the 6-31G* basis set. For the most stable conformation, the absorption and VCD spectra are predicted ab initio using the B3LYP functional with 6-31G*, 6-311G(2d, 2p), 6-31+G, and 6-311G(3df, 3pd) basis sets. A different functional, B3PW91, was also used with the 6-31G* basis set. The predicted spectra are compared to the experimental spectra. The comparison indicates that (–)-*tert*-butylphenylphosphinothioic acid is of the (*S*)-configuration and exists in only one tautomeric structure and one conformation in CCl₄ solution.

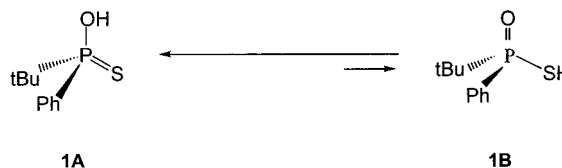
Introduction

Chiral organophosphorus compounds, especially phosphines, are extensively used in asymmetric and stereoselective synthesis,^{1–3} and synthesis and characterization of phosphines have attracted much attention in recent years. In a rich family of enantiomerically pure organophosphorus derivatives, the enantiomeric *tert*-butylphenylphosphinothioic acids have recently been used as versatile chiral solvating agents for the NMR determination of the enantiomeric excesses of a large number of chiral organic and heteroorganic compounds.^{4–6} *tert*-Butylphenylphosphinoselenoic acid has also been noted to behave similarly.⁷

tert-Butylphenylphosphinothioic acid can be prepared from *tert*-butylphenylphosphine oxide.⁸ (–)-*tert*-Butylphenylphosphine oxide was assigned the (*S*)-configuration by chemical correlation,^{8–10} and this assignment was

confirmed using vibrational circular dichroism (VCD).¹¹ (+)-*tert*-Butylphenylphosphinothioic acid was assigned the (*R*)-configuration by chemical correlation,⁸ and this assignment has not yet been confirmed by spectroscopic methods. (*R*)-(+)- and (*S*)-(–)-enantiomers of *tert*-butylphenylphosphinothioic acid have been studied using electronic CD spectra of their complexes with tetraacetatomolybdenum.¹² The possible tautomeric structures or conformations in each of the tautomeric structures of *tert*-butylphenylphosphinothioic acid, however, were not analyzed or determined in the literature.

Some theoretical studies on simple phosphine oxides, P(OH)₃, OPH(OH)₂, and phosphorothioate anions have been reported.¹³ *tert*-Butylphenylphosphinothioic acid **1**, like secondary phosphine oxides, phosphites, and phosphorothioate anions,¹⁴ can exist in an equilibrium between different tautomeric structures **1A** and **1B**. However, the stability of the different tautomeric forms of **1** has not been studied before, and the equilibrium constant is unknown.



The determination of absolute configuration by chemical methods is based on the assumption of the steric course of a given reaction. VCD is an independent

* Corresponding author. Fax: (615) 322-4936.

(1) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *9*, 1375.(2) (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994. (b) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, 2000. (c) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000.(3) Drabowicz, J.; Łyzwa, P.; Omelańczuk, J.; Pietrusiewicz, K. M.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2757.(4) Drabowicz, J.; Dudziński, B.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1992**, *3*, 1231.(5) Omelańczuk, J.; Mikołajczyk, M. *Tetrahedron: Asymmetry* **1996**, *7*, 2687.(6) Drabowicz, J.; Dudziński, B.; Mikołajczyk, M.; Colonna, S.; Gaggero, N. *Tetrahedron: Asymmetry* **1997**, *8*, 2267.

(7) Drabowicz, J.; Omelańczuk, J.; Mikołajczyk, M. Unpublished results.

(8) Michalski, J.; Skrzypczyński, Z. *J. Organomet. Chem.* **1975**, *97*, C31–C32.(9) Skrzypczyński, Z.; Michalski, J. *J. Org. Chem.* **1988**, *53*, 4549.(10) (a) Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 326.(b) Haynes, R. K.; Freeman, R. N.; Mitchell, C. R.; Vonwiller, S. C. *J. Org. Chem.* **1994**, *59*, 2919.(11) Wang, F.; Polavarapu, P. L.; Drabowicz, J.; Mikołajczyk, M. *J. Org. Chem.* **2000**, *65*, 7561–7565.(12) Omelańczuk, J.; Sznatzke, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 786.(13) (a) Chesnut, D. B. *Heteroat. Chem.* **2000**, *11*, 73. (b) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1987**, *109*, 6449.

spectroscopic method without dependency on such an assumption to determine the absolute configuration and predominant conformations in the solution phase. Recent developments in the application of density functional theory^{15–17} and improvements in VCD instrumentation make it possible to use VCD for a confident determination of the absolute configurations and/or conformations in solution phases.^{18–19} Successful determinations of both the absolute configurations and the predominant conformations of 1,2,2,2-tetrafluoroethylmethyl ether,^{18a} desflurane,^{18b} epichlorohydrin,^{18c} 3-butyn-2-ol,^{18d} Troger's base,^{19a} phenyloxirane,^{19b} *tert*-butyl *n*-butyl sulfoxide,^{19c} and *tert*-butylphenylphosphine oxide¹¹ in the solution phase are some recent examples that reflect the reliability of VCD method. In addition, the combination of ab initio and experimental methods can be used to study chemical reactions and elucidate their equilibria.²⁰

The equilibrium between tautomeric structures of *tert*-butylphenylphosphine oxide and its dominant conformation has been determined earlier using theoretical and experimental VCD spectra. Such information is not available for *tert*-butylphenylphosphinothioic acid. Therefore, we have measured the VCD of (–), (+), and (±)-*tert*-butylphenylphosphinothioic acid and undertaken the state-of-the-art ab initio theoretical VCD investigations using density functional method and different basis sets. These results are used to elucidate the absolute configuration, predominant conformation, and tautomeric structures of chiral *tert*-butylphenylphosphinothioic acid.

Results and Discussion

The geometries were optimized at the B3LYP/6-31G* level using the standard dihedral angles of 0, 60, 120, 180, 240, or 300° for the *Ct*–*P*–*C*₁–*C*₂ segment (where *Ct* is the central carbon atom of *tert*-butyl group, see Figure 1) for the two tautomeric structures of (*S*)-*tert*-

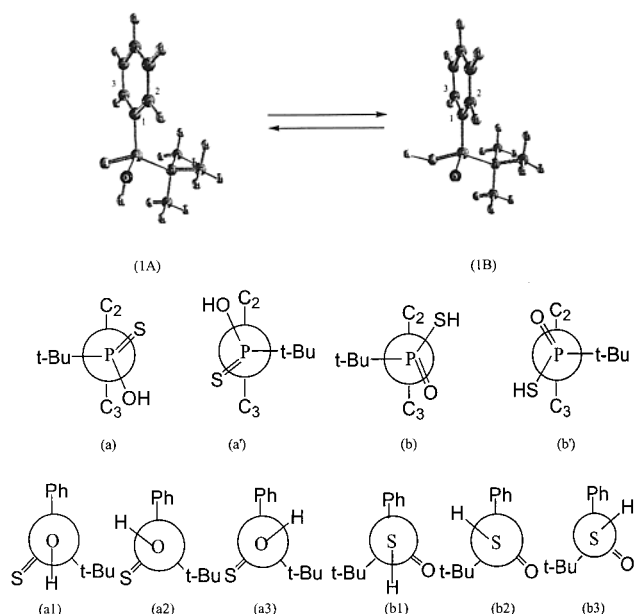


Figure 1. Tautomeric structures and different conformations of (*S*)-*tert*-butylphenylphosphinothioic acid. Compounds **1A** and **1B** are different tautomeric structures; **a** and **a'** are conformations around the *C*₂–*C*₁–*P*–*C*_t dihedral segment for **1A**; **b** and **b'** are conformations around the *C*₂–*C*₁–*P*–*C*_t dihedral segment for **1B**; **a1**–**a3** are conformations around the *C*_t–*P*–*O*–*H* dihedral segment for **1A**; and **b1**–**b3** are conformations around the *C*_t–*P*–*S*–*H* dihedral segment for **1B**.

butylphenylphosphinothioic acid. These starting geometries converged to two conformations for each of the two tautomeric forms, differing in the dihedral angles for the *C*_t–*P*–*C*₁–*C*₂ segment (**a** and **a'** for tautomeric structure **1A**; **b** and **b'** for tautomeric structure **1B**), as summarized in Table 1 and shown in Figure 1. Because of the symmetry of the benzene ring, the two different conformations based on the dihedral angle *C*₂–*C*₁–*P*–*C*_t for each tautomeric structure have the same energies and they cannot be distinguished. Keeping the *C*_t–*P*–*C*₁–*C*₂ segment in the gauche plus (labeled as **a** and **b**) conformation, we studied the stability of the resulting three conformations based on the difference in the dihedral angles *H*–*O*–*P*–*Ph* and *H*–*S*–*P*–*Ph* of forms **1A** and **1B** (**a1**–**a3** and **b1**–**b3** in Figure 1). Only one stable conformation **a2** is obtained for tautomeric structure **a**; **a1** and **a3** conformations converged to **a2** (possibly due to the interaction between the hydroxyl hydrogen atom and the benzene ring and sulfur). For tautomeric structure **1B**, three stable conformations are obtained. The converged *C*₂–*C*₁–*P*–*C*_t, *C*₂–*C*₁–*P*–*O*, *C*₂–*C*₁–*P*–*S*, *Ph*–*POH*, and *PhPSH* dihedral angles, optimized electronic energies, Gibbs energies, and relative populations are listed in Table 1. Tautomeric form **1A** has a much lower energy than tautomeric form **1B**. On the basis of the relative populations, we predicted the equilibrium constant to be 1.9×10^{-4} for the equilibrium between two tautomeric structures of (*S*)-*tert*-butylphenylphosphinothioic acid. Thus, for isolated (*S*)-*tert*-butylphenylphosphinothioic acid, the predominant tautomeric structure is **1A** and the conformation is **a2**.

The converged tautomeric forms were found to have potential energy minima (i.e., all vibrational frequencies are real) at the B3LYP/6-31G* level. The absorption and VCD intensities were calculated for conformations **a2** and

(14) (a) Stawiński, J. *Handbook of Organophosphorus Chemistry*; Engel, R., Ed.; Marcel Dekker: New York, 1992; p 377. (b) Baraniak, J.; Frey, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 4059. (c) Frey, P. A.; Reimschüssel, W.; Paneth, P. *J. Am. Chem. Soc.* **1986**, *108*, 1720. (d) Kabachnik, M. I.; Mastyukova, T. A.; Matrosov, E. I.; Fisher, B. *Zh. Strukt. Khim.* **1965**, *6*, 691.

(15) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Cheeseman, J. R.; Frisch, M. J.; Devlin, F. J.; Stephens, P. J. *J. Chem. Phys. Lett.* **1996**, *252*, 211.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(18) (a) Polavarapu, P. L.; Zhao, C.; Ramig, K. *Tetrahedron: Asymmetry* **1999**, *10*, 1099. (b) Polavarapu, P. L.; Zhao, C.; Chollis, A. L.; Vernice, G. *J. Phys. Chem. B* **1999**, *103*, 6127. (c) Wang, F.; Polavarapu, P. L. *J. Phys. Chem. A* **2000**, *104*, 6189. (d) Wang, F.; Polavarapu, P. L. *J. Phys. Chem. A* **2000**, *104*, 1822.

(19) (a) Aamouche, A.; Devlin, F. J.; Stephens, P. J. *J. Am. Chem. Soc.* **2000**, *122*, 2346. (b) Ashvar, C. S.; Devlin, F. J.; Stephens, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 2836. (c) Drabowicz, J.; Dudziński, B.; Mikołajczyk, M.; Wang, F.; Dehlavi, A.; Goring, J.; Park, M.; Rizzo, C. J.; Polavarapu, P. L.; Biscarini, P.; Wiczorek, M. W.; Majzner, W. R. *J. Org. Chem.* **2001**, *66*, 1122.

(20) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; John Wiley & Sons: 1986.

Table 1. Conformations and Energies of (*S*)-*tert*-Butylphenylphosphinothioic Acid

taut. struct.	starting geometry ^a				converged geometry ^a				label ^b	energy ^c			
	C ₂ C ₁ Pc _t	C ₂ C ₁ PO	C ₂ C ₁ P S	D	C ₂ C ₁ Pc _t	C ₂ C ₁ PO	C ₂ C ₁ PS	D		electronic	Gibbs	ΔE ^d	pop. ^e (%)
A	0	-120	120	180	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	100
	60	-60	180	180	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	
	120	0	-120	180	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	
	180	60	-60	180	-85.6	20.3	144.1	102.2	a2'	-1204.917683	-1204.726322	0	
	-120	120	0	180	-85.6	20.3	144.1	102.2	a2'	-1204.917683	-1204.726322	0	
	-60	180	60	180	-85.6	20.3	144.1	102.2	a2'	-1204.917683	-1204.726322	0	
	95	-160	-36	180	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	
	95	-160	-36	-60	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	
	95	-160	-36	60	94.7	-159.5	-35.8	102.2	a2	-1204.917683	-1204.726322	0	
	90	-160	-20	180	74.1	-160.2	-36.0	168.4	b1	-1204.905865			
90	-160	-20	60	74.1	-160.2	-36.0	51.1	b2	-1204.902132				
90	-160	-20	-60	74.1	-160.2	-36.0	-84.3	b3	-1204.906337	-1204.718249	5.07		
-90	20	160	-60	-105.8	19.9	144.1	-84.3	b3'	-1204.906337	-1204.718249	5.07		

^a Dihedral angles are given in degrees; D stands for PhPOH for the tautomeric form **1A** and PhPSH for the tautomeric form **1B**. ^b See Figure 1 for the labels. ^c In Hartrees. ^d Relative energy difference given in kcal/mol. ^e Percent population based on Gibbs energies.

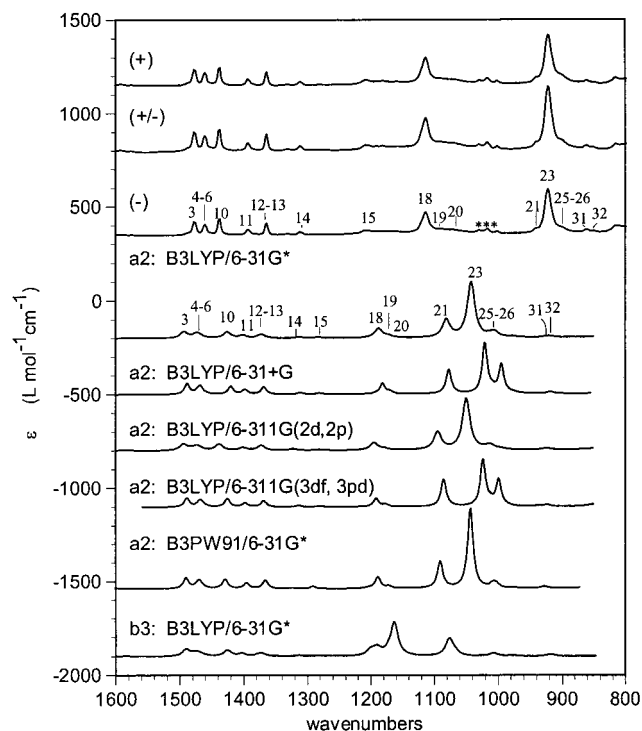


Figure 2. Comparison of the experimental absorption spectra of enantiomeric *tert*-butylphenylphosphinothioic acid at ~0.34 M in CCl₄ solution (top three traces) with the predicted absorption spectra (bottom six traces) of different stable conformations of the (*S*)-configuration (structure and conformation labels in Figure 1) obtained with different basis sets. The predicted bands in the 1500–900 cm⁻¹ region are numbered in the theoretical spectra as 1–36 in the decreasing order of frequency. The corresponding experimental bands are identified in the experimental spectra by these numbers. The bands in the experimental spectra marked by asterisks are considered to be due to impurities.

b3 at the B3LYP/6-31G* level. The predicted absorption and VCD spectra were simulated with 5 cm⁻¹ half widths and Lorentzian band shapes. The theoretical spectra for the predominant conformation **a2** can be compared to the experimental spectra in Figures 2 and 3.

The experimental absorption spectra obtained for 0.34 M CCl₄ solution are shown in Figure 2, where the absorption spectrum of the solvent has been subtracted. The absorption bands in the predicted spectrum (B3LYP/6-31G*) for conformation **a2** show a one-to-one correspondence with the absorption bands in experimental

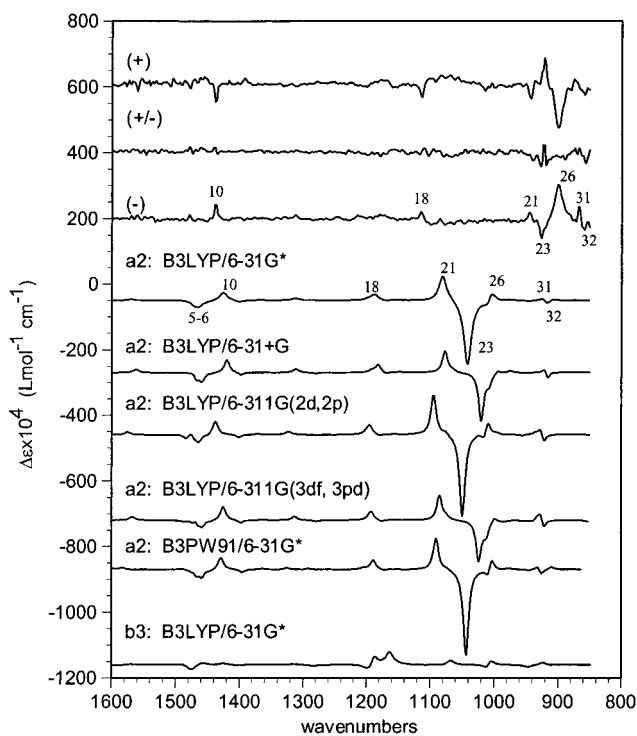


Figure 3. Comparison of the experimental VCD spectra of enantiomeric *tert*-butylphenylphosphinothioic acid at ~0.34 M in CCl₄ solution (top three traces) with the predicted VCD spectra (bottom six traces) of different stable conformations of the (*S*)-configuration (structure and conformation labels in Figure 1) obtained with different basis sets. The predicted bands in the 1500–900 cm⁻¹ region are numbered in the predicted spectra as 1–36 in the decreasing order of frequency. The corresponding experimental bands are identified in the experimental spectra by these numbers.

spectrum. The notable differences are the following. (a) The predicted frequencies of the bands for conformation **a2** in the range from 1220 to 800 cm⁻¹ are much larger than the frequencies of the corresponding bands in the experimental spectra. (b) The bands at 1083 (peak 21) and 1045 cm⁻¹ (peak 23) in the predicted spectrum for conformation **a2** are separated by a much larger gap than the corresponding bands around 920 cm⁻¹ in the experimental spectra. (c) There are no bands corresponding to the weak bands observed around 1020 cm⁻¹ in the experimental spectra. Except for these differences, the experimental spectra in CCl₄ and solution are considered to be in agreement with the predicted absorption spec-

trum for conformation **a2**. In addition, since the predicted absorption spectrum for conformer **b3** does not correspond well to the experimental absorption spectrum, it is concluded that the tautomeric structure **1B** does not have a dominant population in CCl₄ solution.

The experimental VCD spectra obtained for 0.34 M CCl₄ solution are shown in Figure 3, where the VCD spectrum of the solvent has been subtracted. The significant VCD bands in the predicted spectrum (B3LYP/6-31G*) for the conformation **a2** of (*S*)-*tert*-butylphenylphosphinothioic acid are a negative–positive couplet with a positive maximum at 1428 cm⁻¹ (peak 10) and a negative maximum at 1474 cm⁻¹ (peaks 5 and 6), a positive band at 1189 cm⁻¹ (peak 18), and a positive–negative–positive triplet at 1083 (peak 21), 1045 (peak 23), and 1006 cm⁻¹ (peak 26). The same features are seen in the experimental VCD spectrum for the (–)-*tert*-butylphenylphosphinothioic acid except for the following: (a) the relative intensities for the bands of the triplet are different in the experimental VCD spectrum and (b) there is no negative band in the experimental VCD spectrum corresponding to the predicted negative band at 1474 cm⁻¹. These differences may come from the remaining inaccuracy of the predicted relative intensities and frequencies in calculation. The intensities of the bands in the B3LYP/6-31G*-predicted VCD spectrum of conformation **b3** are very small compared to those predicted for conformation **a2**; also, the VCD sign pattern predicted for **b3** does not match the experimentally observed sign pattern. Thus, as concluded earlier, the population of tautomeric structure **1B** is not expected to be significant in CCl₄ solution.

The discussion presented above for predicted spectra pertains to those obtained at the B3LYP/6-31G* level. To investigate the influence of basis set on the observed differences between experimental and predicted spectra, calculations were also undertaken with larger basis sets, namely, 6-311G(2d, 2p), 6-31+G, and 6-311G(3df, 3pd), using the same functional. The geometry of conformation **a2** was optimized with each of these basis sets, and vibrational absorption and VCD spectra were obtained at the optimized geometries. These calculations were also repeated with a different functional, namely, B3PW91, using the 6-31G* basis set. All of these results are presented, along with B3LYP/6-31G* results, in Figures 2 and 3. As can be seen in Figures 2 and 3, the overall spectral patterns did not change significantly in these calculations. The frequencies of bands 23, 25, and 26 are predicted to be slightly lower, by 6-31+G and 6-311G(3df, 3pd) basis sets, approaching closer to the experimental frequencies. But the relative absorption intensity for band 26 is predicted to be larger than that observed, and the relative VCD intensity for band 26 is predicted to be much smaller than that observed. To summarize these observations, the quality of predicted spectra did not improve upon going from 6-31G* to the 6-31+G, 6-311G(2d, 2p), or 6-311G(3df, 3pd) basis set. Similarly, there is not a significant change in the predictions when the functional is changed from B3LYP/6-31G* to B3PW91/6-31G*. Finally, it is somewhat unusual that the difference between observed and calculated frequencies is rather large in the 1200–900 cm⁻¹ region for this molecule. This discrepancy may be attributed to the presence of heavy atoms in this molecule.

Conclusion

The comparison of experimental and ab initio predicted absorptions and VCD spectra indicates the following. (a) (–)-*tert*-Butylphenylphosphinothioic acid is of the (*S*)-configuration; the (–)-(*S*)-configuration is in agreement with the chemical correlation reported in ref 8. (b) Only one tautomeric structure and one conformation are predominant for (–)-*tert*-butylphenylphosphinothioic acid in CCl₄ solution. (c) P-Chiral phosphines can be studied using a combination of experimental and ab initio VCD investigations because such molecules do show significant VCD signals, but the accuracy of the calculated frequencies needs to be improved when there are heavy atoms in the molecule.

Experimental Section

General. NMR spectra were recorded at 200 MHz.

Racemic and Enantiomeric *tert*-Butylphenylphosphinothioic Acid 1. Racemic thio acid **1** was prepared²¹ by the addition of elemental sulfur to the sodium salt of racemic *tert*-butylphenylphosphine oxide in methanol. The formed crude sodium salts of the thio acid **1**, dissolved in a water–methanol mixture, were converted into the free acid **1** by acidification of a water–methanol solution with diluted hydrochloric acid. The formed thio acid **1** was extracted with chloroform. Evaporation of the chloroform gave the chemically pure thio acid **1**: ¹H NMR (CDCl₃) δ 1.163 (d, *J* = 10.4 Hz, 9H), 7.250–7.500 (m, 3H), 7.720–7.830 (m, 2H); ³¹P NMR (CDCl₃) δ 98.42 (s). Optically active enantiomers of the thio acid **1** were prepared via diastereomeric salts of the thio acid **1** with enantiomers of optically active α-methylbenzylamine. The particular diastereomers were formed in situ by the addition of elemental sulfur to racemic *tert*-butylphenylphosphine oxide in the presence of the optically active amine.²¹ The particular enantiomer of the thio acid **1** was liberated from the given diastereomeric salt with optically active amine by acidification with hydrochloric acid and had the following optical rotations: dextrorotatory enantiomer [α]₅₈₉ = +27.3 (*c* 1.75, MeOH), ee = 91.6%; levorotatory enantiomer [α]₅₈₉ = –28.3 (*c* 1.20, MeOH), ee = 95%. The spectral data (¹H and ³¹P NMR) were in full agreement with those reported above for the racemic thio acid **1**. Earlier, the racemic thio acid **1** was resolved into enantiomers via diastereomeric salts with enantiomers of α-methylbenzylamine.^{8–10}

Measurements. The VCD spectra¹⁸ were recorded with 3 h of data collection time at a 4 cm⁻¹ resolution. Spectra were measured in CCl₄ solvent at a concentration of ~0.34 M and at path lengths of 60 and 130 μm. Spectra for (–)-*tert*-butylphenylphosphinothioic acid have also been collected in CCl₄ solvent at different concentrations and in CHCl₃ at 0.38 M. The sample was held in a variable path length cell with BaF₂ windows. In the presented absorption spectra, the solvent absorption was subtracted out. In the presented VCD spectra, the raw VCD spectrum of the solvent was subtracted.

Calculations. The ab initio vibrational frequencies, absorption, and VCD intensities for (*S*)-*tert*-butylphenylphosphinothioic acid were calculated using the Gaussian 98 program¹⁷ on a Pentium II 300 MHz PC. The calculations used the density functional theory (DFT) with Becke-style B3LYP and B3PW91¹⁵ hybrid functionals and 6-31G*, 6-31+G, 6-311G(2d, 2p), and 6-311gG(3df, 3pd) basis sets.²⁰ The procedure for calculating the VCD intensities using DFT theory from Cheeseman et al.¹⁶ as implemented in the Gaussian 98 program.¹⁷ The theoretical absorption and VCD spectra were simulated with Lorentzian band shapes and 5 cm⁻¹ full width at half-height. Since the ab initio-predicted band positions are higher than the experimental values, the ab initio frequencies obtained with 6-31G* basis set were scaled with a factor of 0.9613, and those based on other basis sets are scaled with a factor of 0.975.

(21) Drabowicz, J.; Mikołajczyk, M. Unpublished results.

Acknowledgment. Grants from the NSF (CHE-0092922) and Vanderbilt University are gratefully acknowledged. Studies in Łódź were supported by the State Committee for Scientific Research (KBN) (Grant T09A 077 14 to J.D.).

Supporting Information Available: Cartesian coordinates for the two optimized tautomeric structures of (*S*)-*tert*-

butylphenylphosphinothioic acid; a table of calculated frequencies, absorption, and VCD intensities with five different basis sets; and a table containing the comparison of calculated and observed frequencies along with vibrational assignments in the 1500–850 cm^{-1} region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO0107406