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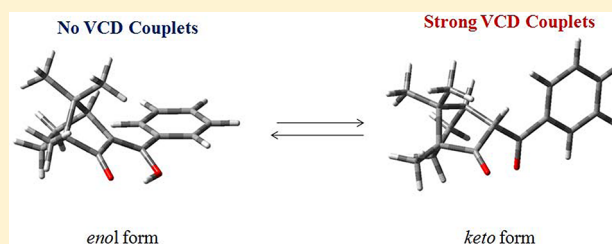
Exciton Coupling Analysis and Enolization Monitoring by Vibrational Circular Dichroism Spectra of Camphor Diketones

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S Supporting Information

ABSTRACT: The keto–enol tautomerization of (1R,3R,4R)-(+)-3-benzoylcamphor in solution was traced by the infrared (IR) and vibrational circular dichroism (VCD) spectra, reflecting the Boltzmann populations of the isomers. To investigate the exciton coupling of the carbonyl vibrations in the region 1800–1600 cm^{-1} , VCD spectra of a series of camphor derived β -diketones were analyzed with the support of density functional theory (DFT) calculations. The results confirm the importance of the exciton chirality for VCD and manifest that the VCD spectroscopy is a convenient technique to investigate the keto–enol tautomerization equilibria in chiral diketones.



■ INTRODUCTIONS

Chelating β -diketones and related ligands are popular functional building blocks extensively investigated in coordination chemistry for decades.^{1–3} Their complexes can be used in different areas based on their particular magnetic, electrochemical, or photophysical properties. For chiral species, they can be applied as NMR shift reagents and excellent catalysts for enantioselective reactions. Important structural aspects of the β -diketones associated complexes can be conveniently monitored by vibrational spectroscopy;^{4–6} related chiral species provide significant vibrational circular dichroic signal.^{7–12}

Vibrational circular dichroism (VCD) is the absorption difference between left and right circularly polarized light, usually in a chiral molecule caused by a vibrational transition with the electronic ground state. In the past decade, combining with density functional theory (DFT) calculations, VCD has been verified as an efficient tool for configurational and conformational analysis of chiral molecules.^{13–18} In particular, VCD can be utilized for nonempirically evaluating the chirality of molecules without the need of crystallization. For molecules with moderate complexity the determination of the absolute configuration is then quite straightforward.

Recently, Taniguchi and Monde¹⁹ suggested using the exciton chirality traditionally known in electronic circular dichroism (ECD) in the UV–visible region more extensively also for VCD in the infrared (IR) region. For a chiral molecule containing two IR chromophores, the absolute configuration can be then often determined without the aid of expensive theoretical simulations. Moreover, the VCD intensities can be strengthened and the amount of the sample for the detection can be lowered by the exciton coupling effect.

In this study we present VCD spectra of a group of camphor derived β -diketones and put specific focus on the analysis of the exciton coupling phenomenon. These compounds were chosen

because the camphor residue provides rich VCD and their rich structural information has been revealed.^{20–22} In the past, investigation of many IR and VCD spectra has also been performed on camphor and its derivatives both experimental and theoretically.^{12,23–28}

First, we present a conformational search and absolute configuration determination of (1R,3R,4R)-(+)-3-benzoylcamphor **1**. Then the exciton chirality method is explored to evaluate its absolute configuration. Finally, a broader analysis of the influence on VCD couplet by incorporating different functional group (compounds **2–7** in Chart 1) was performed.

■ MATERIALS AND METHODS

General Information. All reagents were obtained by commercial resources. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MATSSQ 710 mass spectrometer in the range 120–1000 amu. ¹H and ¹³C NMR spectra were obtained on a Bruker DRX 500 NMR spectrometer with CDCl₃ as solvents (except for compound **2** with DMSO-*d*₆). Chemical shifts are referenced to TMS. Spin–spin coupling constants are given in Hertz. Compounds **1** and **5** were obtained from both (*R*)-camphor and (*S*)-camphor; the other molecules were derived only from (*R*)-camphor. All the compounds were recrystallized from *n*-pentane or methanol and dried in vacuo for spectroscopic studies.

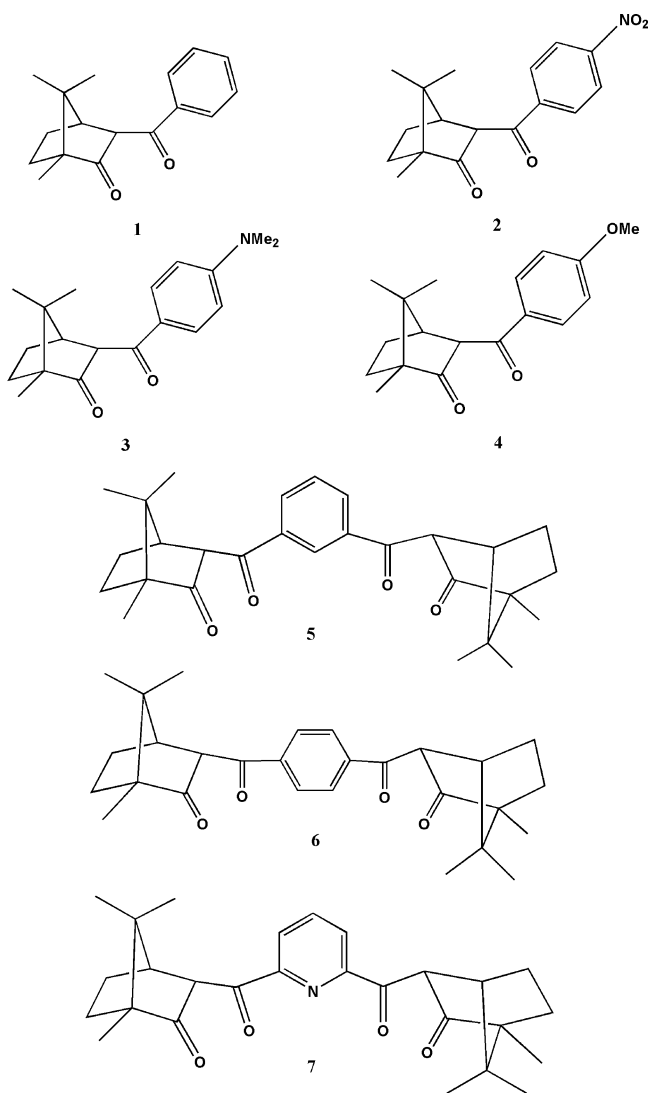
IR and VCD Spectra Measurements. IR and VCD spectra were recorded on a VERTEX 80v Fourier transform infrared spectrometer equipped with a PMA 50 VCD/IRRAS module (Bruker, Germany) in the region 1800–800 cm^{-1} using

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Chart 1. Structures of Camphor Derived β -Diketones

standard procedures.^{28,29} The photoelastic modulator (PEM) was set to 1500 cm^{-1} , the spectral resolution was 4 cm^{-1} , and the zero filling factor was 4. A demountable cuvette A145 with KBr or CaF_2 with 0.12 mm Teflon spacer was used. All solution samples were dissolved in deuterated chloroform (CDCl_3) (except for compound 2 with deuterated DMSO and methanol). The measurements were performed after a thermal equilibrium time of 30–40 min. All VCD measurements were collected for 4 h composed of 12 blocks in 20 min. Baseline correction was performed with the spectra of deuterated solvent using the same measurement setup as for VCD.

Computation Details. DFT simulations were carried out with Gaussian 09.³⁰ For free ligand, molecular structures of both enol and keto forms were generated from crystal structures.^{21,22} The conformational search of (1R,3R,4R)-

(+)-3-benzoylcamphor was done with the AM1 method. Structures of all the tautomers were optimized at the B3LYP level with the 6-311++G(d,p) basis set. The effect of the solvent was modeled by the CPCM dielectric model for chloroform. The calculations of IR and VCD spectra were also carried out under B3LYP level with the 6-311++G(d,p) basis set.

Synthesis of Diketones. All these organic molecules were prepared by camphor and related esters under a common procedure.²⁰ The synthetic procedures and related structural characterizations are listed in the Supporting Information.

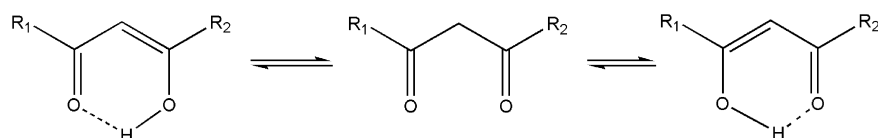
■ ABSOLUTE CONFIGURATION OF (1R,3R,4R)-(+)-3-BENZOYL CAMPHOR

It is well-known that the compound containing a carbonyl group ($\text{C}=\text{O}$) normally has a rapid chemical equilibrium between a keto form and an enol form, assigned as keto–enol tautomerization. Keto–enol tautomerism in β -diketones (Chart 2) has been extensively explored in solution by IR and NMR spectroscopy and in the solid state by X-ray single crystal diffraction.^{2,31–34}

Generally, there are two stereoisomers of the keto form and two possible architectures for the enol form of β -diketone. The keto and enol form conformations of (1R,3R,4R)-(+)-3-benzoylcamphor have been confirmed and characterized.^{20–22} Normally, it is not necessary to consider conformation influence of the methyl groups in the analysis of their vibrational spectra for camphor and its derivatives.^{25,26} In this work, we considered three possible structures of (1R,3R,4R)-(+)-3-benzoylcamphor as Enol1, Enol2, and Keto forms (Figure 1).

The calculated energies are listed in Table 1, and the correlated structures are exhibited in Figure 1. The populations of the keto and enol form conformations in equilibrium are similar with that of (1R,3R,4R)-(+)-3-trifluoroacetyl camphor,²⁵ where the population of the enol form conformations is much higher than that of keto form conformations, and the population of the exo form conformation is higher than that of the endo form conformation. The keto form significantly contributes to IR and VCD and cannot be ignored as that in (1R,3R,4R)-(+)-3-trifluoroacetyl camphor.

The comparison of the experimental IR and VCD spectra of (1R,3R,4R)-(+)-3-benzoylcamphor with simulated results are shown in Figure 2, and the main measured IR spectral features and comparison with simulations are listed in Table 2. According to the exciton chirality method in VCD proposed by Taniguchi and Monde,¹⁹ the interaction of the two carbonyl group of a keto form conformer would generate a large VCD couplet and manifest the absolute configuration of the molecule. In Figure 2, the simulated $\text{C}=\text{O}$ stretching vibrational mode in both exo and endo form conformations exhibits a strong and sharp VCD exciton coupling effect, which contributes to the conformationally averaged VCD spectrum as a positive exciton couplet with first positive Cotton effect at lower wavenumber 1706 cm^{-1} and second negative Cotton

Chart 2. Keto–Enol Tautomerism in β -Diketones

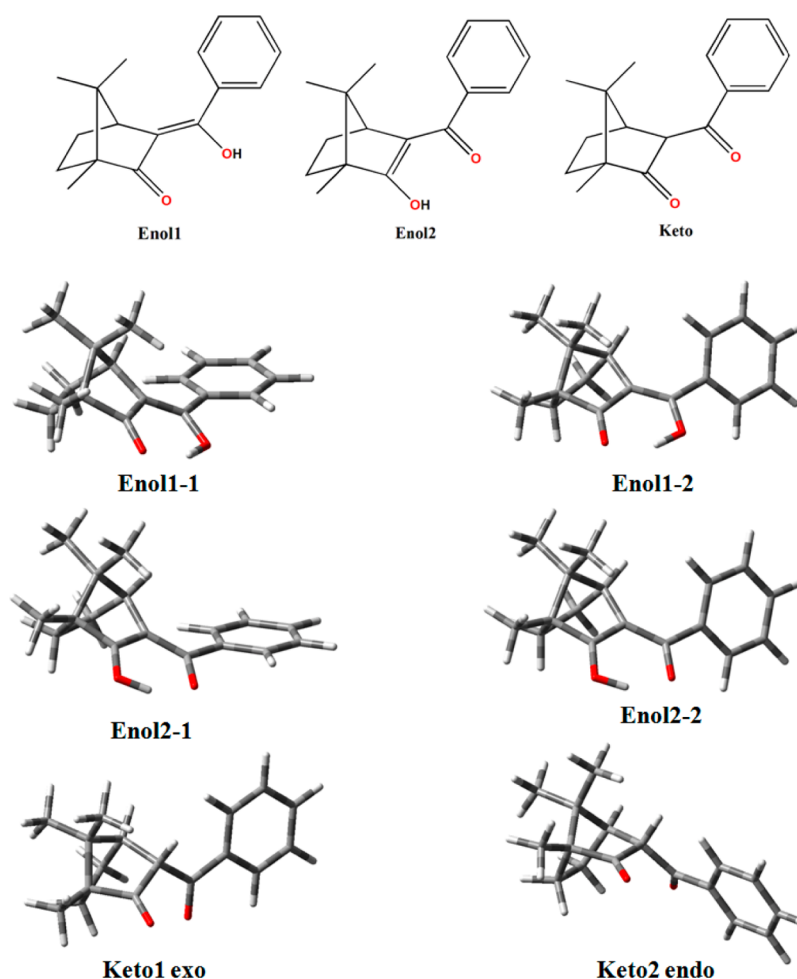


Figure 1. Three possible structures and their six lowest-energy conformers of (1R,3R,4R)-(+)-3-benzoylcamphor.

Table 1. Gibbs Free Energies, Energy Differences Relative to Enol1-1, and Boltzmann Population of the Six Conformers of (1R,3R,4R)-3-Benzoyl-(+)-camphor in Chloroform (B3LYP/6-311++G(d,p))

conformer	Gibbs free energy(hartree)	ΔG (kcal/mol)	population (%)
Enol1-1 (O---HO)	−810.241495	0	68.5
Enol1-2 (O---HO)	−810.240298	3.1	18.9
Enol2-1 (HO---O)	−810.234801	17.6	0
Enol2-2 (HO---O)	−810.234271	19.0	0
Keto-1 (exo)	−810.239746	4.6	10.4
Keto-2 (endo)	−810.238295	8.4	2.2

effect at higher wavenumber 1790 cm^{-1} . As expected, the experimental VCD spectrum also displays a positive exciton couplet with one positive Cotton effect at lower wavenumber 1672 cm^{-1} and the other negative Cotton effect at higher wavenumber 1748 cm^{-1} . This positive chirality means that the special arrangement between the two chromospheres ($\text{C}=\text{O}$) should be clockwise twist. Although the bands are shifted and there are some differences in the intensities, the conformationally averaged IR and VCD spectra are appreciably coincident with the experimental IR and VCD spectra.

Theoretically, VCD coupling is not restricted to carbonyl groups. In an enol form, the electric transition directions^{35,36} of $\text{C}=\text{O}$ stretching and $\text{C}=\text{C}$ stretching vibrational mode are almost parallel to the $\text{C}=\text{O}$ bond and $\text{C}=\text{C}$ bond, respectively. Moreover, the frequency differences between vibrational mode of $\text{C}=\text{O}$ stretching and $\text{C}=\text{C}$ stretching is relatively small; therefore, another VCD couplet would be expected to appear. In an early reported VCD spectra of the nearly full-occupied enolic form of (1R,3R,4R)-(+)-3-trifluoroacetyl camphor, a weak exciton couplet between $\text{C}=\text{O}$ stretching and $\text{C}=\text{C}$ stretching is observable in the both measured and simulated results.²⁴ Unfortunately, by comparison of the experimental VCD spectrum with the simulated VCD spectra of the four enolic forms conformers of (1R,3R,4R)-(+)-3-benzoylcamphor, no clear exciton coupling phenomenon has been probed. This is probably because of the intervention of the identical vibrational frequency of the $\text{C}-\text{C}$ bond stretches of the aromatic group.

■ COMPARATIVE ANALYSIS OF VCD COUPLET AND ENOLIZATION OF (1R,3R,4R)-(+)-3-BENZOYLCAMPHOR DERIVATIVES

To better understand factors influencing the VCD exciton features, we prepared a series of analogous diketones by modifications of the aromatic group of (1R,3R,4R)-(+)-3-benzoylcamphor (Figure 1). Figure 3 shows the IR and VCD

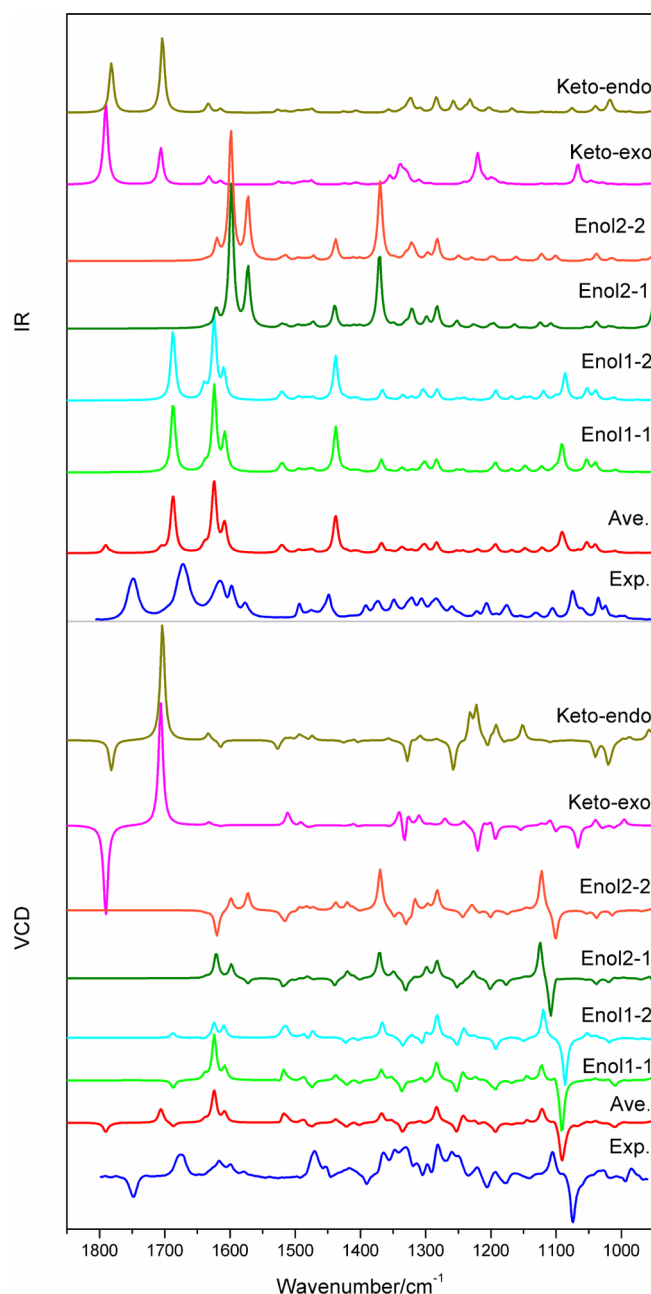


Figure 2. Experimental and calculated IR (upper) and VCD (lower) spectra of six lowest-energy conformers (cf. Table 1) of (1R,3R,4R)-(+)-3-benzoylcamphor.

Table 2. Comparison of the Main Experimental IR Spectral Features for (1R,3R,4R)-3-Benzoyl-(+)-camphor to the Calculated Transitions (Figure 2)

exp (cm ⁻¹)	av of calc (cm ⁻¹)	band assignment
1748	1790	C=O stretching of camphor cyclic
1672	1706	C=O stretching of benzoyl group
1615	1639	C=C stretching of enol form
1598	1624	C—C stretching of benzene ring
1577	1608	C—C stretching of benzene ring
1494	1438	O—H in-plane bending
1470	1518	C—H deformation
1106	1122	C—H deformation
1075	1091	C—H deformation

spectra of these compounds, and Table 3 presents the comparison on measured values of $\Delta\epsilon_1$ (lower wavenumber), $\Delta\epsilon_2$ (higher wavenumber), anisotropy ratio g factor (also called dissymmetry factor, defined as $g = \Delta\epsilon/\epsilon$),^{29,35} and the amplitude of the couplet A (defined as $\Delta\epsilon_1 - \Delta\epsilon_2$) of the two carbonyl groups in each compound.

Even with much lower concentration for measurement, the absorption of all derivatives in Figure 3 is still much stronger than that of 3-benzoylcamphor. As shown in Table 3, nearly all compounds share the feature vibrational mode of C=O stretching around 1746–1751 cm⁻¹ except for compound 5, which could be viewed as an effective standard for conformational analysis of keto and enol tautomers. Compound 2 has a very poor solubility in CDCl₃; its VCD and IR spectra were thus measured in deuterated DMSO and methanol (Figure S1, Supporting Information). The conformational analysis of compound 2 (as shown in Table S1 and Figure S2, Supporting Information) reveals that the Boltzmann population of the enol form conformation is a bit higher than that of compound 1, which is similar to that of (1R,3R,4R)-(+)-3-trifluoroacetyl camphor, coincident with the fact that the enolization prefers to the carbonyl group linked to an electron-withdrawing substituent.²⁵ As expected, no obvious VCD couplets was detected for C=O band stretches (Figure S1, Supporting Information). The conformational analysis of compound 3 (as shown in Table S2 and Figure S3, Supporting Information) shows that the Boltzmann population of the keto form has almost become the exclusive conformation. The electron-donating effect of dimethylamino group is distinctively efficient, which not only evidently enhances the IR absorptions but also presents much stronger exciton coupling effect (the value of A is almost 5 times higher than that of compound 1 as shown in Table 3). The conformational analysis of compound 4 (as shown in Table S3 and Figure S4, Supporting Information) reveals that the Boltzmann population of the keto form conformation is lower than that of compound 3, but much higher than that of compound 1. Consequently, the electron-donating methoxy group contributes to the enhancement of VCD intensity, as well as to the exciton coupling effect. The value of A is about 2 times higher than that of compound 1 as shown in Table 3.

The conformational arrangements of compounds 5–7, bis- β -diketones, are much more complicated compared to those of compounds 1–4. Both the IR and VCD spectra of bis-diketone 5 are quite similar to that of diketone 1, and the VCD couplet of carbonyl group is similar to that of compound 4. The IR and VCD spectral bands of the two carbonyl groups of compound 6 as the isomer of bis-diketone 5, shifted to lower wavenumber. Although there is a broad absorption band around 1733 cm⁻¹, no corresponding VCD signal has been probed. Such a shape is quite similar to that of β -diketone 3-trifluoroacetyl camphor,²⁵ suggesting that the exclusive conformation in compound 6 should be an enolic form. The higher structural symmetry and lower steric hindrance of para-substitute might be helpful to stabilize the enolic form structures. Compound 7 possesses the strongest VCD couplet among all compounds, which reveals the exciton coupling effect is the strongest in all compounds. The pyridine nitrogen atom is somewhat basic which would be helpful to stabilize the enolic form conformers (strong ¹H NMR signal δ 12.61, 12.58, Supporting Information). The double diketone skeleton might contain an enol form on one side and a keto form on the other side.

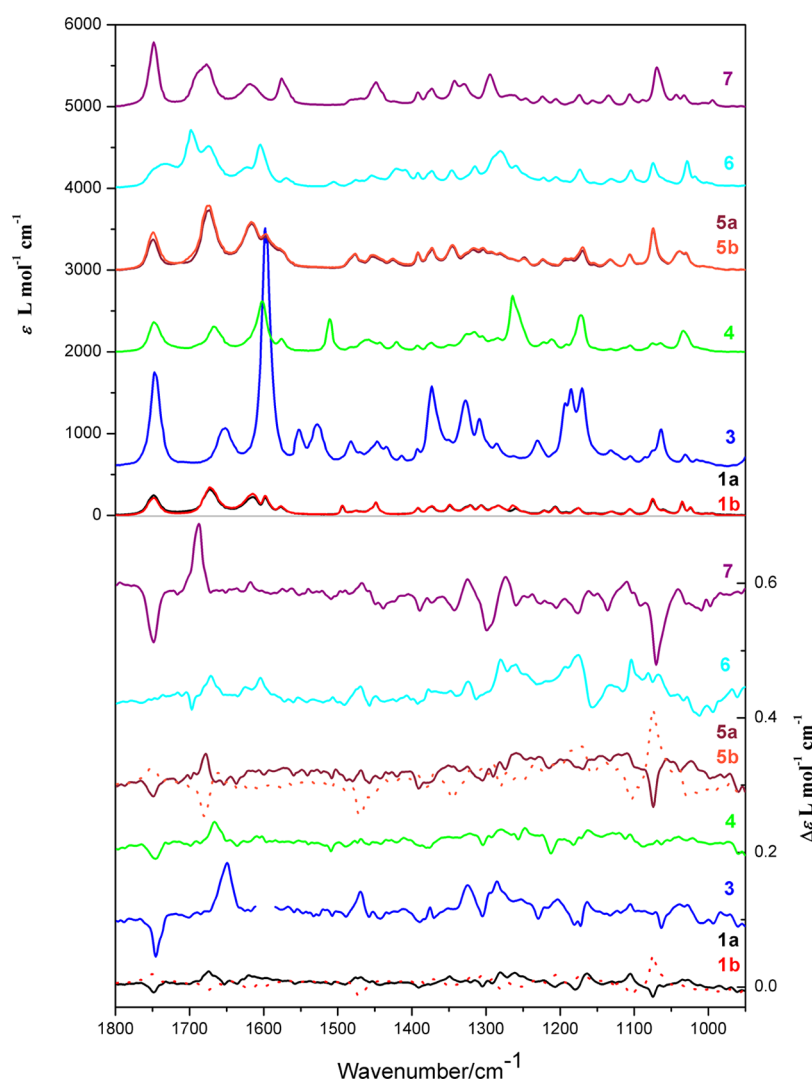


Figure 3. Comparison of IR (upper) and VCD (lower) spectra of various derivatives of (1R,3R,4R)-(+)-3-benzoylcamphor. Each spectrum was measured using CDCl₃ (*c* = 0.08 M) except for compound **1a** and its enantiomer **1b** (both 0.2 M).

Table 3. VCD Couplet by the Two Carbonyl Groups of Keto and Enol Tautomers in Camphor Derived Diketones (Figure 3)

	$\Delta\epsilon_1/\nu$ [(L mol ⁻¹ cm ⁻¹)/cm ⁻¹]	$g_1 = \Delta\epsilon_1/\epsilon_1$	$\Delta\epsilon_2/\nu$ [(L mol ⁻¹ cm ⁻¹)/cm ⁻¹]	$g_2 = \Delta\epsilon_2/\epsilon_2$	$A = \Delta\epsilon_1 - \Delta\epsilon_2$
1a (R)	0.018/1672	5.06×10^{-5}	-0.012/1748	5.66×10^{-5}	0.030
1b (S)	-0.011/1672	3.28×10^{-5}	0.013/1748	6.07×10^{-5}	-0.024
3 (R)	0.079/1650	1.66×10^{-4}	-0.061/1746	4.94×10^{-5}	0.140
4 (R)	0.034/1666	9.19×10^{-5}	-0.022/1747	7.40×10^{-5}	0.056
5a (R)	0.042/1678	5.23×10^{-5}	-0.021/1751	6.66×10^{-5}	0.063
5b (S)	-0.046/1678	6.64×10^{-5}	0.026/1751	4.26×10^{-5}	-0.072
6 (R)	0.026/1671	5.87×10^{-5}	-0.024/1698	2.82×10^{-5}	0.050
7 (R)	0.089/1688	2.18×10^{-4}	-0.086/1749	9.95×10^{-5}	0.175

The *g* factor is the VCD signal normalized by the corresponding absorption. The values of *g*₂ in these compounds show no sharp differences, whereas the values of *g*₁ in compound **3** and **7** are much higher than that in other compounds, which is consistent with that of the shifts of the amplitude of the couplet *A*.

These results manifest that by modifying the aromatic group of 3-benzoylcamphor, the VCD couplets could be strengthened especially with electron-donating group. Furthermore, derivatives with electron-withdrawing group would promote the chemical equilibrium from keto form to enol form, whereas the

electron-donating group would promote the chemical equilibrium from enol form to keto form, indicating that VCD spectroscopy is an evident probe for monitoring keto–enol tautomerism in β -diketones.

CONCLUSIONS

We measured and analyzed VCD and IR spectra of a series of camphor derived β -diketones. Under the support of DFT calculations, we can conclude that the exciton chirality method can be employed for a fast analysis of absolute configurations of those compounds. We verified the reliability of VCD exciton

coupling analysis for molecules with two IR chromophores even containing various conformers. The results also manifest that VCD spectroscopy is quite useful for monitoring the keto–enol tautomerization in β -diketone related compounds.

■ ASSOCIATED CONTENT

● Supporting Information

Synthetic procedures, NMR spectra, IR and VCD spectra of compound **2**, and conformational search for **2** and **3** with related tables (Gibbs free energies, energy differences, and Boltzmann populations) and conformer structures. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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