Chiroptical Effects

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Large Solvation Effect in the Optical Rotatory Dispersion of Norbornenone**

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Abstract: *The anomalously large chiroptical response of (1R,4R)-norbornenone has been probed under complementary vapor-phase and solution-phase conditions to assess the putative roles of environmental perturbations. Measurements of the specific rotation for isolated (gas-phase) molecules could not be reproduced quantitatively by comprehensive quantum-chemical calculations based on density-functional or coupled-cluster levels of linear-response theory, which suggests that higher-order treatments may be needed to accurately predict such intrinsic behavior. A substantial, yet unexpected, dependence of the dispersive optical activity on the nature (phase) of the surrounding medium has been uncovered, with the venerable Lorentz local-field correction reproducing solvent-mediated trends in rotatory dispersion surprisingly well, whereas more modern polarizable continuum models for implicit solvation performed less satisfactorily.*

Among the many physical properties that distinguish chiral molecules, perhaps none has had as profound and sustained an impact on the realm of chemistry as the characteristic interactions that take place with polarized light.[1] Of special note is the dispersive (non-resonant) phenomenon of circular birefringence (CB),[2] the manifestation of which was first reported over two centuries ago,[1a] and which still is used routinely (in the more familiar guise of specific optical rotation) to gauge the enantiomeric purity of products emerging from asymmetric syntheses.[3] Reduced to most basic terms, this effect stems from the differential retardation that the right-circular and left-circular components of an electromagnetic wave experience as they propagate through a chiral medium. The resulting direction and magnitude of linear-polarization rotation reflect the intrinsic handedness of the sample, thereby affording a facile means for discriminating relative stereochemistry. Correlation of an observed chiroptical response with an individual enantiomer has historically relied on supplementary physicochemical information or empirical structure–property models;[3] however, the advent of robust quantum-chemical methods for predicting optical activity from first principles has led to a veritable renaissance in our ability to assign absolute stereochemical configuration solely on the basis of spectroscopic measurements.[4] As part of an ongoing effort to establish experimental benchmarks for assessing such chiroptical calculations, the present work has examined the optical rotatory dispersion (ORD or wavelength-resolved CB) of (1*R*,4*R*)-norbornenone (**1**), where proximate olefin and ketone functional groups synergistically engender rotatory powers that are nearly 100 times larger than those of comparably sized organic molecules. In particular, the specific optical rotation, $[\alpha]_{\lambda}^{T}$, has been probed under ambient conditions (25 °C) at discrete wavelengths (λ) spanning the visible and ultraviolet regions, with complementary vapor-phase and solution-phase studies revealing the strong, yet hitherto unexpected, influence of a solvated environment.

The unusual chiroptical behavior of β,γ-unsaturated ketones has long been a subject of intense speculation and inquiry.[5] The large rotatory powers exhibited by these species have historically been attributed to the inherent dissymmetry that arises from a twisted arrangement of interacting C=C and C=O chromophores,[6] an observation that facilitated generalization of the octant structure–property rules to this class of molecules.[7] Norbornenone or bicyclo[2.2.1]hept-5-en-2-one is an archetypal member of this family in which the olefin and ketone moieties are embedded in a rigid skeleton of minimal complexity. Mislow and Berger[8] first reported the specific rotation of **1** to be $+1140\,\mathrm{deg\,dm^{-1}\,(g/mL)^{-1}}$ in isooctane at the sodium *D*-line wavelength (589.3 nm), with the correction applied for enantiomeric excess (ca. 48 % *ee*) being gauged by derivatization. These pioneering efforts served to motivate early theoretical[9] and experimental[10] endeavors, the latter including extensive studies of dispersive and absorptive chiroptical phenomena in the solution phase. Plettner et al.[11] have compiled $[\alpha]_D$ values from several asymmetric syntheses of norbornenone and have assigned the (1*R*,4*R*) absolute configuration to the positive sign of this quantity through crystallographic analyses of a chemical precursor. The small spread among such solution-phase parameters at 589.3 nm (e.g., $+1236\,\mathrm{deg\,dm^{-1}\,(g/mL)^{-1}}$ in chloroform[12] and

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$+1146\ \mathrm{deg\,dm^{-1}\,(g/mL)^{-1}}$ in hexane[13]) has been taken as evidence for negligible solvent effects;[14] however, the present work will show that a pronounced medium or phase dependence exists between isolated (vapor-phase) and solvated (solution-phase) conditions.

Ongoing developments in quantum chemistry have renewed interest in the dispersive optical activity of norbornenone, with predictions for the isolated (solvent-free) species revealing serious incongruities between computations performed at comparable levels of density-functional theory (DFT) and coupled cluster (CC) theory.[14b] Stephens et al.[15] exploited the B3LYP functional and an augmented double-ζ basis set to find $[\alpha]_D = -1215.8\ \mathrm{deg\,dm^{-1}\,(g/mL)^{-1}}$ for the (1*S*,4*S*) enantiomer, which was shown to be in reasonable accord with available (solution-phase) polarimetric data. In contrast, application of an origin-independent CC framework that included singles and doubles excitations (CCSD) led Crawford and co-workers[14b,16] to predict an $[\alpha]_D$ value of $-559.9\ \mathrm{deg\,dm^{-1}\,(g/mL)^{-1}}$, which represents less than half of the magnitude estimated by DFT calculations. Related efforts have explored the state-by-state decomposition of $[\alpha]_\lambda^T$,[17] with the conclusion that the lowest-lying electronic transition dominates the composite response affording a viable explanation for discrepancies between DFT and CC treatments (which yield different transition energies and rotatory strengths). Most recently, Autschbach[18] and co-workers have analyzed the rotatory power of norbornenone by expressing each element of the Rosenfeld (chiroptical) tensor in terms of contributions made by individual chemical bonds and lone-pair electrons, asserting that extensive delocalization of π-type orbitals plays a crucial role in determining non-resonant behavior. Prior to the present work, all ab initio calculations of intrinsic CB for **1** have been assessed against solution-phase results, thus ignoring the often unexpected influence[19] of solute–solvent coupling.

Requisite samples of **1** were synthesized by established methods (Supporting Information, Section S2) and isolated in 86.8 ± 2.1 % *ee*, where the error bar denotes an uncertainty of one standard deviation. Solution-phase specific rotation was probed at discrete wavelengths that were filtered from NaI and HgI emission lamps through the use of a commercial polarimeter (PerkinElmer 341; ± 0.002° accuracy) and a temperature-stabilized quartz cell (10.000 cm length at 25 °C). All solvents were of spectrophotometric grade (Sigma–Aldrich), and concentrations were kept low enough to discount solute–solute interactions. Studies of intrinsic chiroptical response at 355 nm and 633 nm exploited cavity ring-down polarimetry[20] (CRDP) to extract the pressure dependence of the rotatory power exhibited by isolated (vapor-phase) molecules entrained in a high-finesse resonator. The basic instrumentation and analysis procedures for these ultrasensitive polarimetric measurements have been described elsewhere.[21]

ORD calculations built upon the DFT linear-response formalism utilized the hybrid B3LYP correlation-exchange functional as implemented in the Gaussian09 package[22] (rev. C.01), whereas analogous CCSD treatments were executed under the Psi3.4 program[23] (Xander release of February 16, 2009) and a developmental version of Gaussian[24] (rev. H.27). The canonical aug-cc-pVDZ and aug-cc-pVTZ basis sets (abbreviated as apVDZ and apVTZ) were selected for the present study with core orbitals frozen during post-Hartree–Fock computations. The results obtained for isolated molecules reflect the geometry optimized at the B3LYP/apVTZ level of theory by applying very tight convergence criteria (Table S1). Density-functional predictions of optical activity made use of the dipole-length gauge (LG) in conjunction with gauge-including atomic orbitals to ensure translational invariance (Table S3). As canonical coupled-cluster methods cannot take advantage of this approach, specific rotations obtained from the modified velocity gauge (MVG) ansatz of Pedersen et al.[25] are reported as the most reliable CCSD estimates for chiroptical behavior (Table S4).

Table 1 contains a subset of specific rotations acquired for **1** under vapor-phase and solution-phase conditions, where the latter are reported for dilute cyclohexane and acetonitrile media that represent low and high extremes of solvent polarity (Table S2). Predictions of isolated-molecule response that emerge from density-functional and coupled-cluster analyses are also tabulated. The corresponding ORD profiles are shown in Figure 1, with the curve superimposed on each data set following from a Drude-like model[1a] that was designed to facilitate comparison of discrete wavelength points (Section S3 and Table S5). Even a cursory inspection reveals marked differences among these theoretical and experimental results. CRDP measurements of $[\alpha]_\lambda^T$ at 355 nm (633 nm) differ from computed DFT and CCSD values by +72.5 % (+53.0 %) and −41.1 % (−26.5 %), respectively, suggesting the latter to offer more reliable estimates for intrinsic optical activity. However, this assertion must be tempered by assumptions inherent to the present calculations, including use of a rigid geometry specified by the minimum-energy configuration of the ground electronic state (Table S1). Whereas conformational degrees of freedom can be dismissed owing to the inflexible nature of the bicyclic skeleton, norbornenone does undergo small-amplitude vibrational motion. Indeed, zero-point nuclear displacement has been found to be a potent mediator of dispersive chiroptical

Table 1: Dispersive optical activity of (1*R*,4*R*)-norbornenone.

Medium	Source	Specific rotation [deg dm^{-1} (g/mL)$^{-1}$] 355.0 nm	 589.3 nm	 633.0 nm
isolated vapor	expt	6310 ± 160	755[a]	617 ± 15
	DFT[d]	10 887	1159.2	944.1
	CCSD[e]	3716.3	549.5	453.3
CH_3CN solution	expt	8607[b]	950.46	776[b]
	LLF[f]	8098 ± 205	958[c]	782 ± 19
	PCM[d]	11 742	1276.8	1040.1
C_6H_{12} solution	expt	9159[b]	980.63	799[b]
	LLF[f]	8631 ± 219	1017[c]	830 ± 20
	PCM[d]	11 953	1310.7	1068.7

[a] Interpolated from vapor-phase data using a modeled ORD profile. [b] Extrapolated from solution-phase data using a modeled ORD profile. [c] Based on extrapolated vapor-phase results. [d] B3LYP/apVTZ level of theory. [e] CCSD/apVDZ (MVG) level of theory. [f] Lorentz local-field correction.

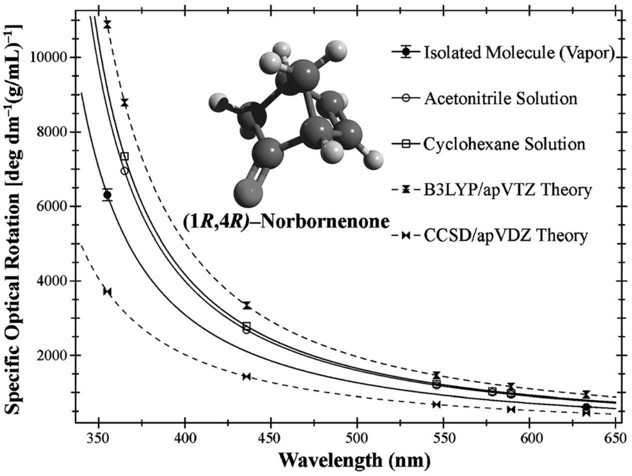

Figure 1. Specific rotations measured for (1*R*,4*R*)-norbornenone under vapor-phase and solution-phase conditions are depicted as a function of wavelength. Results obtained for the isolated molecule are compared to DFT and CCSD linear-response predictions.

properties,[2] especially for systems that possess weak rotatory powers (e.g., oxirane derivatives).[26] The sizable purely electronic response for **1** would tend to discount the importance of such effects, with vibrational corrections deduced for the (1*S*,4*S*) enantiomer[27] producing only a 4.4% increase in the computed magnitude of $[\alpha]_D$.

Assuming vibrational effects to be negligible, discrepancies between theory and experiment for the chiroptical properties of isolated norbornenone might reflect shortcomings inherent to the exploited quantum-chemical methods. An improvement of basis-set quality for DFT(B3LYP) analyses clearly shows the present calculations to be well converged, with the successive use of double-ζ (apVDZ), triple-ζ (apVTZ), and quadruple-ζ (apVQZ) forms leading to rotatory powers at 589.3 nm of 1179.5, 1159.2, and 1159.8 deg dm^{-1} (g/mL)$^{-1}$, respectively. For the more arduous CCSD treatment,[16] the triple-ζ (apVTZ) model predicts a *D*-line specific rotation that departs from its double-ζ (apVDZ) counterpart in Table 1 by −4.0 deg dm^{-1} (g/mL)$^{-1}$, representing a percentage deviation of only −0.73%. Whereas this result would suggest that saturation of the function space has been attained for the coupled-cluster ansatz, further tests that make use of larger or more flexible basis sets are beyond available computational resources.

The ubiquitous B3LYP functional has been suggested to overestimate rotatory powers owing to inherent delocalization errors, with Autschbach and co-workers advocating alternative forms that embody range-separated exchange.[18,28] Indeed, replacement of the B3LYP functional by its long-range corrected variant[29] markedly improves the agreement between predictions and measurements of $[\alpha]_\lambda^T$ for isolated (1*R*,4*R*)-norbornenone (Table S3), yielding specific rotation values of 6880 deg dm^{-1} (g/mL)$^{-1}$ and 738.2 deg dm^{-1} (g/mL)$^{-1}$ at 355 nm and 633 nm, which deviate from their respective experimental counterparts by only +9.04% and +19.6%. However, such enhanced performance might be serendipitous, as a systematic investigation of dispersive optical activity for 45 organic molecules and transition-metal complexes found neither range-separated nor conventional functionals to afford a clear advantage (on average) for chiroptical predictions.[28a]

A principal advantage of coupled-cluster methods is that they are convergent, which implies that one may extend the atomic-orbital basis set and include higher levels of dynamical electron correlation to approach the exact wavefunction systematically.[30] Although incorporation of triples excitations into the CC linear-response formalism is not feasible at present for a molecule having the size of norbornenone, studies performed on smaller surrogates have shown that CCSD estimates of $[\alpha]_\lambda$ recover the major fraction of the chiroptical response computed by triples-corrected schemes (e.g., CC3). For example, CC3 analysis of pyramidalized fluoroformaldehyde (Tables S6 and S7), which supports a low-lying $\pi^* \leftarrow n$ transition similar to that of **1**, show a 20.6% increase in rotatory power at 589 nm relative to their CCSD counterparts. In contrast, lower-order correlation schemes (e.g., CC2) yield differences in excess of 90%, and calculations at the Hartree–Fock level of theory incorrectly predict the sign of optical rotation. Extrapolation of these results to the dual-chromophore topology that characterizes norbornenone remains an active topic of investigation.

Table 1 includes rotatory powers measured for (1*R*,4*R*)-norbornenone in acetonitrile (35.69) and cyclohexane (2.02), where parentheses denote values of the static (zero-frequency) dielectric constant,[22] $\varepsilon \equiv \varepsilon(0)$. The change in rotatory power between these extremes of solvent polarity is remarkably small, with the difference of approximately 3.1% for sodium *D*-line excitation being consistent with the results of prior studies. In contrast, the solution-phase ORD profiles in Figure 1 show a uniform and sizable increase in magnitude over their vapor-phase analogue, yielding percentage deviations from the intrinsic response at 355 nm (633 nm) of +36.4% (+25.7%) and +45.2% (+29.5%) for acetonitrile and cyclohexane, respectively. Such behavior clearly indicates a strong dependence of chiroptical properties on the phase of the surrounding medium and concurs with that suggested by the Lorentz local-field (LLF) correction,[31] which relates specific rotation acquired under isolated (gas) and solvated (sol) conditions through $[\alpha]_{\lambda,\mathrm{sol}}^T = \gamma_s(\nu)[\alpha]_{\lambda,\mathrm{gas}}^T$, where $\gamma_s(\nu) = (\varepsilon(\nu)+2)/3$ embodies the frequency-dependent index of refraction, $n(\nu)^2 = \varepsilon(\nu)$. As highlighted by Table 1, application of this dielectric-polarization model to the $[\alpha]_{\lambda,\mathrm{gas}}^T$ parameters extracted for **1** yields "solvated" values at 355 nm (633 nm) that depart from their experimental counterparts by −5.9% (+0.86%) for acetonitrile and −5.8% (+3.9%) for cyclohexane.

The apparent success of the Lorentz local-field correction for norbornenone is to be contrasted with glaring deficiencies that have been reported in other studies of dispersive optical activity,[15,21b,32] including erroneous predictions for the sign of solvent shifts. This dichotomy might reflect the rigid structure and large rotatory powers of **1**, both of which would tend to mitigate the importance of secondary effects such as those ascribed to vibrational motion. As shown in Table 1, attempts to exploit a polarizable continuum model (PCM)[32,33] for solvation performed less satisfactorily, leading to specific-rotation estimates at 589.3 nm that deviate from polarimetric measurements in acetonitrile and cyclohexane by +34.3% and +33.7%, respectively. The PCM treatment, which entailed geometry re-optimization in the dielectric medium (causing insignificant shifts in CB), reproduces the direction of change in $[\alpha]^{25^{\circ}\mathrm{C}}_{\lambda,\mathrm{gas}}$; however, the attendant magnitude is grossly underestimated.

In summary, the optical rotatory dispersion of (1*R*,4*R*)-norbornenone has been probed under solvated and isolated conditions, where the latter vapor-phase results have revealed the pronounced effects that are incurred by solvation. Intrinsic values of specific rotation are not reproduced quantitatively by substantial density-functional and coupled-cluster calculations, suggesting that higher-level treatments are needed to describe such dispersive properties. A marked and unexpected dependence of chiroptical response on the nature (phase) of the surrounding medium has been uncovered, with the venerable Lorentz local-field correction reproducing solvent-mediated trends surprisingly well, whereas more modern polarizable continuum models perform less satisfactorily. These findings are the subject of ongoing experimental and theoretical efforts, as are the electronic and structural origins for the sizable rotatory powers displayed by norbornenone and related chiral species.

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