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# Vibrational and Electronic Circular Dichroism of Δ-TRISPHAT [Tris(tetrachlorobenzenediolato)-phosphate(V)] Anion

DELPHINE BAS,[1] THOMAS BÜRGI,[2]* JÉRÔME LACOUR,[1]* JÉRÔME VACHON,[1] AND JACQUES WEBER[1]

[1]*Départements de Chimie Organique et de Chimie Physique, Université de Genève, Genève, Switzerland*
[2]*Institut de Chimie, Université de Neuchâtel, Neuchâtel, Switzerland*

*ABSTRACT* Herein is reported an experimental and theoretical study of the circular dichroism properties of TRISPHAT (**1**) anion. ECD analysis of the [tetramethylammonium][Δ-**1**] salt confirms the absolute configuration assignment obtained through X-ray crystallographic analysis of the parent cinchonidium salt. The structure, infrared, and vibrational circular dichroism (VCD) spectra derived from density functional theory (DFT) calculations are compared with experimental data.

*KEY WORDS:* Δ-TRISPHAT anion; X-ray crystallography; CD properties; DFT; VCD

Chemical reactions and processes often involve cationic racemic or prochiral reagents, intermediates, or products. To afford nonracemic or enantiopure adducts, and to benefit from new possible applications, stereoselective ion pairing of these cations with enantiopure anions can be considered.[1–4] Recently, the chemistry of hexacoordinated phosphate anions has been rejuvenated for exactly this purpose, as chiral tris(tetrachlorobenzenediolato)-phosphate(V) anion **1**, known as TRISPHAT (Fig. 1),[5] has been shown to be a valuable NMR chiral solvating,[6–25] resolving,[26–32] asymmetry-inducing,[33–39] and solubilizing[40–44] reagent for organic, organometallic, metallo-organic, and polymeric substances.

TRISPHAT anion is best obtained in enantiomerically pure form by recrystallization of a cinchonidinium salt. In the original report,[5] an absolute Δ (delta) configuration for the anion was established by X-ray structural analysis. Both a determination of the absolute structure (Flack parameter) and the relationship of the anion to the *Cinchona* alkaloid cation were used for the assignment. There is thus little doubt about the absolute Δ configuration for anion **1** in crystalline [cinchonidinium][TRISPHAT] salts. However, as the parent tris(benzenediolato)phosphate anion is configurationally labile in solution when associated with an acidic ammonium cation,[45,46] there was a faint possibility that an acid-induced epimerization occurs upon dissolution of the crystalline [cinchonidinium][Δ-TRISPHAT] salt, resulting—possibly—in the formation of the diastereomeric [cinchonidinium][Λ-TRISPHAT] entity.

Herein we report that it is not the case, as the circular dichroism properties of a tetraalkyl ammonium salt derived from crystalline [cinchonidinium][Δ-TRISPHAT], namely, the [$Me_4N$][TRISPHAT] salt, confirm unambiguously the absolute Δ configuration of the anion in solution. After a primary assessment of the configuration by electronic circular dichroism (ECD), a theoretical study of the structural and vibrational properties of the TRISPHAT anion is reported. The structure, vibrational unpolarized absorption spectrum, and VCD spectrum of the TRISPHAT anion are obtained using density functional theory (DFT) calculations.

## MATERIALS AND METHODS

### *General Methods*

Column chromatography (basic alumina type 5016A, Fluka, Buchs, Switzerland) was performed in air and under pressure (0.1–0.3 bar). NMR spectra were recorded on a Bruker AMX-400 instrument at room temperature. $^1H$-NMR chemical shifts are given in ppm relative to $Me_4Si$, with the solvent resonance used as the internal standard. $^{31}P$-NMR chemical shifts are reported in ppm relative to $H_3PO_4$. $^{13}C$-NMR chemical shifts are given in ppm relative to $Me_4Si$, with the solvent resonance used as the internal standard ($CDCl_3$ δ 77.0 ppm, DMSO-$d_6$ δ 39.5 ppm). IR spectra of the neat solid sample were recorded with a

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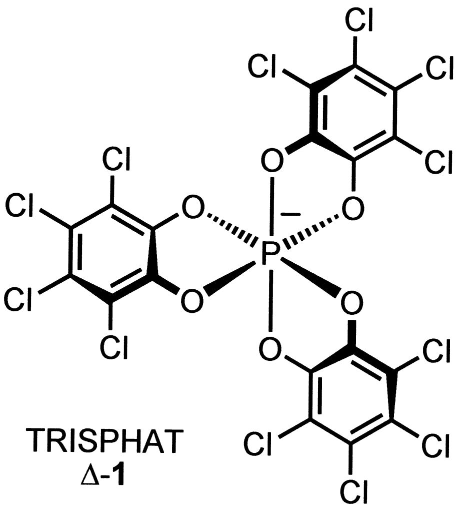
*Correspondence to: Thomas Bürgi and Jérôme Lacour. E-mail: thomas.buergi@unine.ch; jerome.lacour@chiorg.unige.ch



TRISPHAT
Δ-**1**

**Fig. 1.** Hexacoordinated phosphorus anion **1** (TRISPHAT).

PerkinElmer 1650 FT-IR spectrometer using the Golden Gate diamond ATR sampling system. Melting points (mp) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Electrospray mass spectra (ES-MS) were obtained on an Applied Biosystems API 150EX of the Department of Mass Spectroscopy of the University of Geneva. UV spectra were recorded on a CARY-1E spectrometer in a 1.0-cm quartz cell; $\lambda_{max}$ are given in nm, and the molar adsorption coefficient $\varepsilon$ in $cm^{-1}$ $dm^3$ $mol^{-1}$. CD spectra were recorded on a JASCO J-715 polarimeter in a 1.0-cm quartz cell; λ are given in nm, and molar CD absorptions ($\Delta\varepsilon$) in $cm^{-1}$ $dm^3$ $mol^{-1}$. Optical rotations were measured on a PerkinElmer 241 or JASCO P-1030 polarimeter in a thermostated (20°C) 10.0-cm long microcell with high-pressure sodium lamps and are reported as follows $[\alpha]_{\lambda}^{20}$ ($c$ in g/100 ml, solvent).

DFT closed-shell calculations were performed using the Gaussian 98 suite of programs.[47] Complete optimization of all internal coordinates of the molecule was performed at the BP86,[48,49] B3LYP,[50,51] and B3PW91[51,52] level of theory using the 6-31G** basis set. The vibrational frequencies were calculated for the minimized structure. Absorption and VCD spectra were constructed from calculated normal modes, dipole strengths, and rotational strengths assuming a Lorentzian band shape of 4 $cm^{-1}$ half-width at half-maximum.

IR and VCD spectra were recorded on a Bruker PMA 50 accessory coupled to a Tensor 27 Fourier transform infrared spectrometer. A photoelastic modulator (Hinds PEM 90) set at l/4 retardation was used to modulate the handedness of the circular-polarized light. Demodulation was performed by a lock-in amplifier (SR830 DSP). An optical low-pass filter (<1800 $cm^{-1}$) placed before the photoelastic modulator was used to enhance the signal/noise ratio. A thermostated transmission cell (18°C) equipped with KBr windows and a 1-mm Teflon spacer was used. All solutions of the $[Me_4N]$[TRISPHAT] salt in $CD_2Cl_2$ or $CH_2Cl_2$ were prepared at a concentration of 3.5 mg in 600 μl of solvent. A spectrum of the neat solvent ($CD_2Cl_2$ or $CH_2Cl_2$) recorded in VCD mode was subtracted from the VCD spectrum of the dissolved molecules. The spectra are presented without smoothing or further data processing. More information about the experimental procedure can be found elsewhere.[53,54]

### *Synthesis*

**[Tetramethylammonium][Δ-TRISPHAT] salt.** To a solution of [cinchonidinium][Δ-TRISPHAT] (300 mg, 0.282 mmol, 1 equiv) in acetone (4 ml) was added a solution of tetramethylammonium bromide (86.9 mg, 0.564 mmol, 2 equiv) in methanol (2 ml). A white precipitate appeared immediately. After stirring for 5 min, the mixture was concentrated in vacuo. The white solid obtained was purified by chromatography on basic alumina using dichloromethane as eluent ($R_f$ = 0.40) to afford $[Me_4N]$[**1**] as a white solid (225 mg, 95%); mp 220°C (decomp); $[\alpha]_D^{20} = -409.5$ ($c$ = 0.10, EtOH); MS(ES) (+) 916.5 ($([Me_4N]^+)_2[TRISPHAT]^-$), 74.7 ($[Me_4N]^+$); (–) 768.5 ($[TRISPHAT]^-$). IR: $\nu_{max}/cm^{-1}$ = 2924 (w), 1595 (w), 1443 (s), 1388 (m), 1301 (m), 1235 (m), 988 (s), 816 (s), 718 (m), 666 (s). $^1$H NMR ($CDCl^3$/10% DMSO-$d_6$, 400 MHz): δ 3.23 (s, 12H, $CH_3$). $^{13}$C NMR ($CDCl_3$/10% DMSO-$d_6$, 100 MHz): δ 141.2 (d, $^2J$(C,P) = 6.6 Hz, 6C), 122.4 (6C), 113.3 (d, $^3J$(C,P) = 19.8 Hz, 6C), 55.7 (t, $^2J$(C,N) = 3.7 Hz, $4CH_3$). $^{31}$P NMR ($CDCl_3$/10% DMSO-$d_6$, 162 MHz): δ −81.2. UV ($c$ = $1.10^{-5}$ $mol \cdot l^{-1}$, ethanol): $\varepsilon$ ($\lambda_{max}$) = $1.43 \times 10^4$ (300 nm), $1.70 \times 10^5$ (217 nm). CD ($c$ = $1.10^{-5}$ $mol \cdot l^{-1}$, ethanol): $\Delta\varepsilon$ ($\lambda_{max}$) = −53.0 (245 nm), −213.5 (222 nm), 171.2 (213 nm).

## RESULTS AND DISCUSSION

To confirm in solution the absolute Δ configuration of the TRISPHAT anion derived from the crystalline cinchonidinium salt, the electronic circular dichroism (ECD) spectrum was recorded in ethanol and its analysis ($6.01 \times 10^{-6}$ M, 20°C) revealed a negative Cotton effect at higher wavelength ($\Delta\varepsilon_{244} = -93$) together with a strong exciton coupling in the $\pi-\pi^*$ region ($\Delta\varepsilon_{220} = -336$, $\Delta\varepsilon_{211} = +220$). Positive and negative bands were thus obtained for the exciton couplet at lower and higher wavelengths, respectively. In accordance with the results of Mason and co-workers for $D_3$-symmetric structures,[55] and for the tris(benzenediolato)arsenate **2** and tris-biphenyl-2,2′-diylphosphate(V) **3** anions in particular (Fig. 2),[56,57] this seemed to confirm the absolute Δ (delta) configuration for the TRISPHAT anion in solution.

However, due to the presence of the cinchonidinium moiety as counter ion, it was debatable whether the CD bands were only due to the $D_3$-symmetric anion. This prompted us to prepare a TRISPHAT salt for which no or little direct or induced circular dichroism could be expected from the cationic part of the salt, namely, the tetramethylammonium derivative, $[Me_4N]$[**1**].

Previously, it was observed that anion **1** confers to its salts a poor affinity for polar chromatographic phases as they elute rapidly over alumina or silica gel.[58] For the preparation of the desired $[Me_4N]$[**1**] salt, solutions made

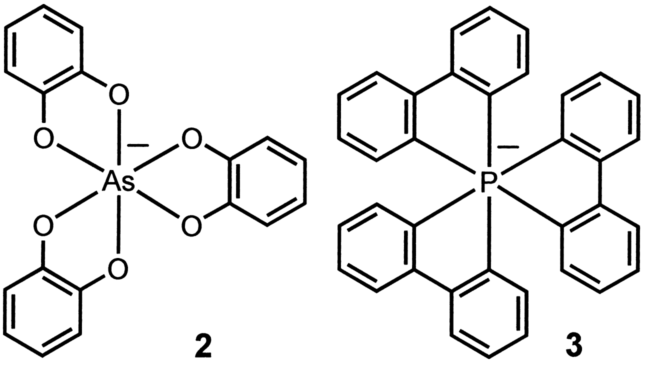


**Fig. 2.** Tris(benzenediolato)arsenate **2** and tris-biphenyl-2,2′-diylphosphate(V) **3** anions.

of tetramethylammonium bromide (2.0 equiv, MeOH) and of crystalline [cinchonidinium][Δ-**1**] (1.0 equiv, acetone) were prepared and mixed together. Preparative column chromatography ($Al_2O_3$, $CH_2Cl_2$) afforded [$Me_4N$][**1**] as the only eluted compounds in good chemical yield (95%, $R_f = 0.40$). The success of the ion metathesis was proven by the spectral characterization of the salt (NMR, MS, IR, UV). The presence of a specific optical rotation showed clearly that the anion was optically active in the isolated sample. The ECD spectrum was then measured, and it matched our expectations as the positive and negative bands were again obtained for the exciton couplet in the $\pi-\pi^*$ region at lower and higher wavelengths, respectively ($\Delta\varepsilon_{222} = -214$, $\Delta\varepsilon_{213} = +171$); this result is in complete agreement with Mason's theory.[56] In Figure 3 are reported the UV and CD spectra of [$Me_4N$][**1**].

Recently, vibrational circular dichroism (VCD) spectroscopy has become a valuable complementary or alternative method for absolute configuration determination of non racemic compounds.[59–61] A rather large variety of structurally different chemical substances have been analyzed. To our knowledge, experimental and theoretical studies on $D_3$-symmetric molecules, however, have been limited.[62] This prompted us to study the VCD spectrum of the ammonium TRISPHAT salt both experimentally and theoretically. Figure 4 shows the optimized structure of the isolated TRISPHAT anion. Figures 5 and 6 compare experimental and calculated infrared and VCD spectra, respectively.

Inspection of the spectra in Figures 5 and 6 (experimental and calculated IR and VCD spectra) undoubtedly shows that the calculations were made on the same enantiomer of the TRISPHAT anion as the experiment, namely, on the enantiomer with Δ (delta) configuration. This shows that VCD is well-suited for the determination of the absolute configuration of $D_3$ symmetric molecules of the TRISPHAT type. Most diagnostic are the spectral features of bands 9 and 10 at about 1600 $cm^{-1}$, band 5 at 1390 $cm^{-1}$, and bands 1–3 between 1200 and 1250 $cm^{-1}$. Despite the qualitatively good agreement between calculated and experimental spectra, quantitative discrepancies concerning relative intensities remain. For example, the VCD intensity of bands 2, 3, and 4 is too weak in the calculations. Calculations using the B3PW91 density functional gave very similar results as the ones shown for B3LYP, whereas the use of BP86 resulted in somewhat worse agreement concerning the relative band intensities and positions. Inclusion of the counter ion in the calculation (compare spectra (a) and (b) in Figs. 5 and 6) had a minor effect on position and intensity of bands associated with the TRISPHAT ion. However, some induced VCD activity was calculated for vibrations of the [$Me_4N$] ion (see the spectral region around 1500 $cm^{-1}$). Note that for the optimization including the counter ion $C_3$ symmetry was assumed for the overall complex. In the subsequent normal-mode analysis, no imaginary frequencies were obtained, showing that the located structure is a true minimum on the potential energy surface.

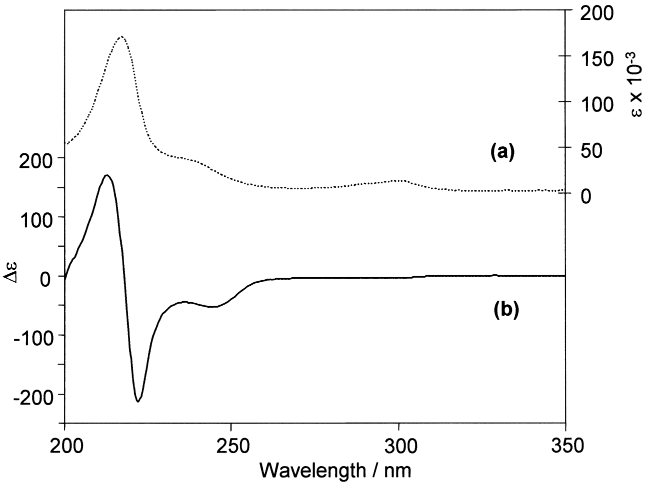


**Fig. 3.** UV (a) and ECD (b) spectra of [$Me_4N$][**1**] salt derived from crystalline [cinchonidinium][Δ-**1**] salt (EtOH, $1.0 \times 10^{-5}$ M, 20°C).

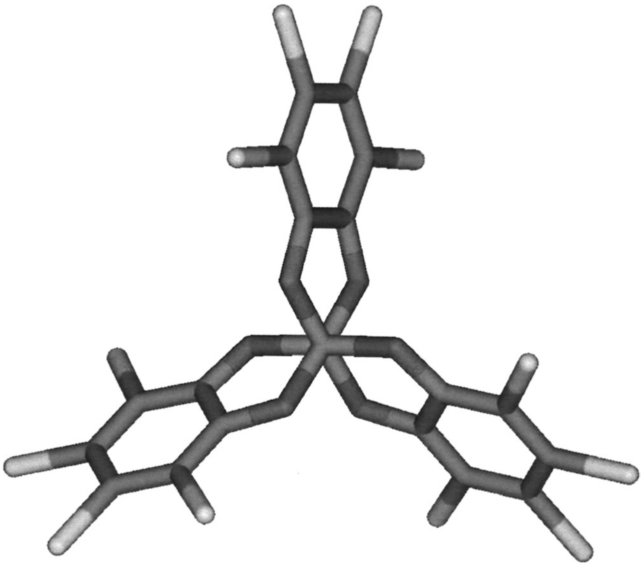


**Fig. 4.** Top view of the optimized structure of the Δ (delta) enantiomer of $D_3$-symmetric TRISPHAT anion **1** (B3LYP/6-31G**).

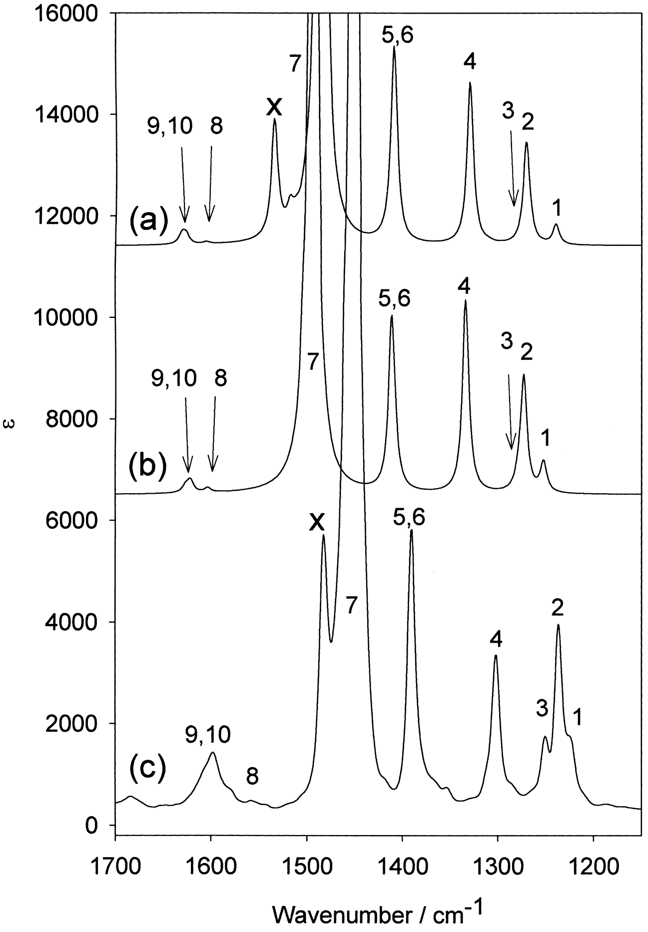


**Fig. 5.** Calculated ((a) with counter ion; (b) without counter ion) and experimental (c) infrared spectra of [$Me_4N$][TRISPHAT] salt in $CD_2Cl_2$ ($C$ = 3.5 mg in 600 μl, $T$ = 18°C, path length 1 mm). Calculations were made at the B3LYP/6-31G** level of theory. The numbers designate a selection of corresponding bands in the experimental and calculated infrared and VCD spectra. The calculated spectra were obtained by convolution of the IR intensity with a Lorentzian of 4-$cm^{-1}$ line-width (half-width at half-maximum). The calculated spectra were scaled (by a factor of 5) and shifted for comparison with the experimental spectra. The band marked with an “X” is associated with [$Me_4N^+$].

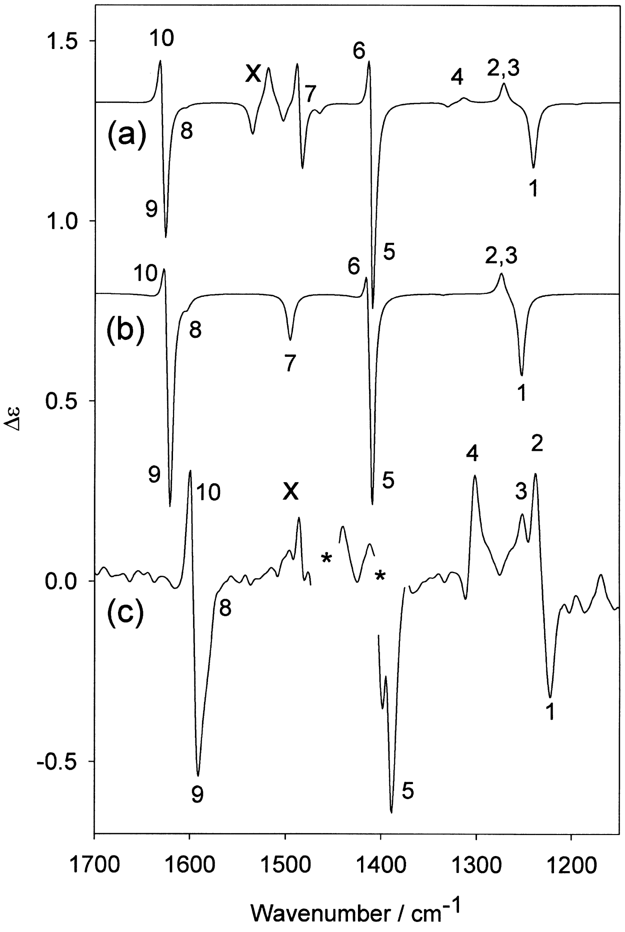


**Fig. 6.** Calculated ((a), with counter ion, (b) without counter ion) and experimental (c) VCD spectra of [$Me_4N$][TRISPHAT] salt in $CD_2Cl_2$ ($C$ = 3.5 mg in 600 μl, $T$ = 18°C, path length 1 mm). The spectral region around 1400 $cm^{-1}$ (band 5) was recorded in $CH_2Cl_2$ at the same concentration. Asterisks designate spectral regions of extra strong absorption due to solvent or the dissolved molecule (band 7 at about 1460 $cm^{-1}$). Calculations were made at the B3LYP/6-31G** level of theory. The calculated spectra were obtained by convolution of the VCD intensity with a Lorentzian of 4 $cm^{-1}$ line-width (half-width at half-maximum). The calculated spectra were scaled (by a factor of 5) and shifted for comparison with the experimental spectra. The numbers designate a selection of corresponding bands in the experimental and calculated infrared and VCD spectra. The band marked with an “X” is associated with [$Me_4N^+$].

Due to the symmetry properties of the TRISPHAT ion, vibrational modes associated with the benzene rings come in “triplets.” One can view such modes as symmetry-adapted linear combinations of modes located in the individual benzene rings. Depending on the nature of the localized modes, the three symmetry-adapted linear combinations belong to different representations within the $D_3$ point group, for example, E plus $A_1$ or E plus $A_2$. The strongest band in the infrared spectrum (band 7) belongs to the former possibility. It has C–O stretching character and is associated with a doubly degenerate vibration belonging to the E representation. The corresponding third vibration with similar character is a totally symmetric $A_1$ mode at slightly higher energy. The latter is silent in the IR (and VCD) spectrum because $A_1$ modes are not IR or VCD active within $D_3$. The other type of combination (E and $A_2$) is found, for example, for the feature at about 1600 $cm^{-1}$ (bands 9 and 10). Band 9 is a degenerate E mode, and band 10, the corresponding $A_2$ mode. In the infrared spectrum, the modes are not well resolved, whereas in the VCD spectrum the E and $A_2$ modes around 1600 $cm^{-1}$ are easily resolved as they have opposite sign. A similar situation is also found for bands 5 and 6. The energy difference between the E and corresponding $A_2$ modes are small. For bands 9 and 10 the calculated energy difference is about 5 $cm^{-1}$, whereas the VCD spectra reveal a spacing on the order of 8 $cm^{-1}$. The under-estimation of the energy difference may be largely due to the harmonic approximation inherent in the normal-mode analysis.

Of course the appearance of the VCD spectrum for close-lying bands with opposite sign depends strongly on the energy difference between the bands, the band widths, and, for the experimental VCD spectra, the resolution of the instrument. In the present case, the spectra were recorded with a resolution of 4 cm$^{-1}$ while the calculated spectra were generated by convolution with a Lorentzian of 4 cm$^{-1}$ line-width (half-width at half-maximum). Simulations with broader band widths led to cancellation of close bands with opposite sign. For example, band 10 vanishes in the simulated VCD spectrum when the band width in the simulation becomes too large.

The band marked with an "X" in the experimental infrared spectrum in Figure 5 is missing in the calculated spectrum of the TRISPHAT anion and is associated with C–H deformation vibrations of the [$Me_4N^+$] counterion. This band is also weakly observed in the VCD spectrum in Figure 6, although we note that in this spectral region the signal to noise ratio is relatively low due to solvent absorption. The appearance of this band indicates weak induced VCD activity in the nonchiral counter ion, similar to that predicted by the calculations (see Fig. 6c).

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