

Harmonic and Anharmonic Features of IR and NIR Absorption and VCD Spectra of Chiral 4-X-[2.2]Paracyclophanes

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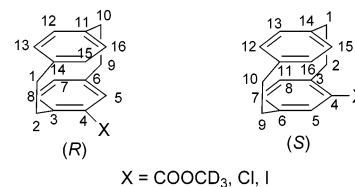
The vibrational absorption spectra and vibrational circular dichroism (VCD) spectra of both enantiomers of 4-X-[2.2]paracyclophanes (X = COOCD₃, Cl, I) have been recorded for a few regions in the range of 900–12000 cm⁻¹. The analysis of the VCD spectra for the two IR regions, 900–1600 cm⁻¹ and 2800–3200 cm⁻¹, is conducted by comparing with DFT calculations of the corresponding spectra; the latter region reveals common motifs of vibrational modes for the three molecules for aliphatic CH stretching fundamentals, whereas in the mid-IR region, one is able to identify specific signatures arising from the substituent groups X. In the CH stretching region between 2900 and 2800 cm⁻¹, we identify and interpret a group of three IR VCD bands due to HCH bending overtone transitions in Fermi resonance with CH stretching fundamental transitions. The analysis of the NIR region between ~8000 and ~9000 cm⁻¹ for X = COOCD₃ reveals important features of the aromatic CH stretching overtones that are of value since the aromatic CH stretching fundamentals are almost silent. The intensifying of such overtones is attributed to electrical anharmonicity terms, which are evaluated here by ab initio methods and compared with literature data.

1. Introduction

Since the first time of their synthesis,¹ [2.2]paracyclophanes (PC) have been considered interesting molecular systems and have been challenging various physical and chemical techniques in defining diverse aspects tied to their peculiar structure. Several characteristics that are mainly related to the planar chirality of the cyclophane moiety have been investigated,² and recently, there has been a renewed interest to use derivatives of PC in asymmetric catalysis³ or to employ them in material science.⁵ Herein, we are merely interested in chiroptical and spectroscopic aspects of some of these still exotic molecules, namely, 4-X-[2.2]paracyclophanes **1** (X = COOCD₃), **2** (X = Cl), and **3** (X = I) (Chart 1 below); yet, we have found results that allow an understanding of the general properties of the moieties of these molecules, namely, the aromatic rings, the polarizable halogen atoms, and the behavior of the methoxycarbonyl group and of bridging aliphatic CH₂ groups.

We have been doing so by use of absorption infrared (IR) and near infrared (NIR) spectroscopy, as well as by vibrational circular dichroism (VCD) spectroscopy both in the IR and NIR ranges. We were inspired by precedent research on 4-X-[2.2]-paracyclophanes by some of us^{6,7} who were able to relate the observed specific rotation values to the polarizability values of the substituent group⁶ and were also able to interpret the observed circular dichroism spectra in the UV range (CD) in terms of the exciton model⁸ supplemented with due accounting for the influence of the X group on tilting the transition moments

CHART 1



of the electronic transitions.⁷ Prior to this work, VCD spectroscopy in the 1000–1800 cm⁻¹ range had already been used on some chiral disubstituted [2.2]paracyclophanes,⁴ with the scope of making a safe assignment of the absolute configuration (AC), when charge-transfer effects were verified to obscure the simple interpretation of the UV-CD spectrum provided in ref 7. The scopes of the present work are somewhat different from those of ref 7 since here the AC is known from the beginning; we are going to focus on finer details of the VCD spectra, which will though be of help in understanding the characteristics of the different moieties of the molecules under investigation.

2. Materials and Methods

Synthesis and Polarimetric Measurements. The synthesis of both enantiomers of the 4-halogenated [2.2]paracyclophanes, **2** and **3**, was reported previously,⁶ and the measurements of the specific optical rotation were described therein. Both enantiomers of **1** were obtained by reacting optically pure (*R*)- and (*S*)-4-carboxy[2.2]paracyclophane⁶ with SOCl₂ followed by the DMAP-catalyzed solvolysis of the resulting acyl chloride in CD₃OH. The measurement of the specific rotation for **1** has given the following results: [α]_D²³ = +148.0 (*c* = 0.5, CHCl₃) for (*S*)-4-methoxycarbonyl-*d*₃-[2.2]paracyclophane, and [α]_D²³ = -149.7 (*c* = 0.5, CHCl₃) for (*R*)-4-methoxycarbonyl-*d*₃-[2.2]-

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71 paracyclophane. As discussed later, these values give further
72 credit to the interpretation put forward in ref 6.

73 **IR and IR-VCD Spectra Measurements.** IR absorption
74 spectra, IR spectra for short, and IR-VCD spectra were recorded
75 with a JASCO FVS4000 FTIR spectropolarimeter equipped with
76 two detectors, a MCT one and an InSb one. The first one has
77 been used to investigate the mid-IR region, 900–1600 cm^{-1}
78 and the second one for the CH stretching region, 2700–3200
79 cm^{-1} ; for the former region, 4000 scans were needed for each
80 spectra (~ 40 min), and for the latter 10000 were needed (~ 1.2
81 h). The spectra of both the enantiomers of **2** and **3** were recorded
82 for CCl_4 solutions (ca. 0.08–0.1 M, cell path length 500 μm),
83 whereas the spectra of the enantiomers of **1** were recorded for
84 CDCl_3 solutions (0.5 M, cell path length 100 μm) in BaF_2 cells.
85 The IR spectra reported below were obtained by subtracting
86 out the IR spectra of the solvent. The VCD spectra of the
87 enantiomers of each molecule were verified to be mirror images
88 of each other. However, to avoid confusion and for better
89 comparison with calculations, we will report in the following
90 just the average VCD spectra of the two (*R*) and (*S*) enantiomers,
91 namely, the VCD data for $(1/2)[(R) - (S)]$.

92 **NIR and NIR-VCD Spectra Measurements.** NIR absorption
93 spectra, NIR spectra for short, in the range of 1300–800 nm
94 and NIR-VCD spectra in the region of 1250–1050 nm have
95 been recorded with a homemade dispersive apparatus equipped
96 with an InGaAs detector described previously;^{9,10} in the range
97 of 1800–1600 nm, we used a Jasco 470 Plus. Spectra for the
98 first overtone of the CH stretchings ($\Delta\nu = 2$) (1800–1600 nm),
99 for the second overtone of the CH stretchings ($\Delta\nu = 3$) (1250–
100 1050 nm), and for the third overtone of the CH stretchings ($\Delta\nu$
101 = 4) (1000–800 nm) have been recorded for 0.5 M CDCl_3
102 solutions of **1** in 0.5, 2, and 2 cm quartz cuvettes, respectively.
103 The NIR-VCD spectra in the $\Delta\nu = 3$ region were registered
104 for the same solutions in the same cuvettes as those for the
105 NIR absorption experiments, averaging over four spectra of four
106 scans each. In Figure 5, the spectra of both enantiomers are
107 reported. Cautions in collecting NIR-VCD data for the interested
108 reader may be found in refs 9 and 10.

109 **Density Functional Theory (DFT) Calculations.** As first
110 described by Stephens¹¹ and amply used in the VCD literature,^{12–17}
111 the VCD spectra in the IR can be easily assigned when they
112 are accompanied by DFT calculations. For this reason, by use
113 of the GAUSSIAN03 suite of programs¹⁷ for **1–3** (*R*), we ran
114 DFT calculations with B3LYP functionals and with both
115 6-31G** and TZVP bases; for the iodine atom in compound **3**,
116 we adopted the 3-21G** basis set. By comparing experimental
117 and calculated IR and VCD spectra, we propose that TZVP is
118 a better choice for all three molecular species. Moreover, for **1**,
119 we have studied two conformers, namely, the one in which the
120 C=O in the substituent X = COOCD_3 is closer to (conformer
121 A) or farther from (conformer B) the aliphatic moiety nearby,
122 bridging the two aromatic rings. The two conformers are
123 depicted in Figure 1 and are separated by an ~ 0.95 kcal/mol
124 energy difference in the B3LYP/TZVP choice, yielding a
125 population ratio of 84 versus 16% for A versus B at room
126 temperature (taking into account the Gibbs free energy and the
127 zero point energy, the population of conformer A decreases to
128 82% and the one of B increases to 18%). Conformation A should
129 then account for almost all of the observed spectroscopic features
130 derived in the present work. For all three molecules, we have
131 not been able to find the two possible skew conformations of
132 the two phenyl rings, as done by Grimme and Bahlmann¹⁹ for
133 4-F-[2.2]paracyclophane; we think that, here, bulky substituent
134 X groups favor the conformation where the nearest methylenic

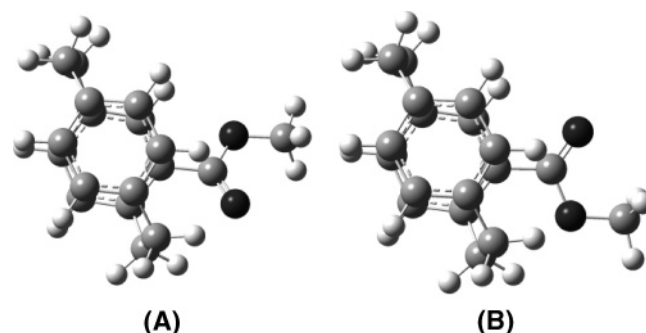


Figure 1. Calculated conformations of minimum energy for (*R*)-4-methoxycarbonyl- d_3 -[2.2]paracyclophane (**1**). The conformation on the left is the absolute minimum, and on the right is a secondary minimum (population ratio 84/16 on the basis of B3LYP/TZVP calculations).

hydrogen is away from the phenyl plane. The calculations allow
one to come up with harmonic frequencies and dipole and
rotational strengths, which, in turn, can be used to generate a
calculated IR and VCD spectrum for each molecule by assigning
a Lorentzian band shape to each fundamental vibrational
transition. We have done so by using a routine in the JASCO
FVS4000 software with $\gamma = 8 \text{ cm}^{-1}$ (γ is the half-width at half-
maximum) (for the mid-IR region) and $\gamma = 16 \text{ cm}^{-1}$ (for the
CH stretching region); in the latter case, a frequency scaling
has been adopted in order to facilitate the comparison of
calculated and experimental spectra. However, quantum mech-
anical calculations have been found to be useful also for
interpreting some important aspects of the NIR and NIR-VCD
spectra.^{9,17} Further and new use has been made here of these
calculations, which has allowed us to better understand NIR
data.

3. Results and Discussion

Each investigated spectral region brings useful information
on which we comment below.

The Mid-IR Region (1600–900 cm^{-1}). In Figure 2, the
experimental IR (left) and VCD spectra (right) of the three (*R*)-
4-X-[2.2]paracyclophanes **1–3** (continuous lines) and, super-
imposed, the corresponding calculated spectra (dotted lines) are
reported. As observed in several cases of rigid molecules or in
molecules with limited conformational flexibility,^{11,17} the agree-
ment of calculated and experimental IR and VCD spectra is
quite good. At first sight, one may grasp interesting differences
and analogies among the three molecules. Three groups of bands
are worth comment.

i. Region between 1000 and 1100 cm^{-1} . Two intense IR bands
with corresponding positive VCD bands are observed and also
calculated for **2** and **3** at ~ 1050 and $\sim 1010 \text{ cm}^{-1}$, respectively.
From the analysis of DFT calculations, we may state that these
bands are due to normal mode (NM) 44, involving the following
linear combination of CC stretchings of the ring containing the
X atom: $(\text{C}_6\text{C}_5 + \text{C}_6\text{C}_7 - \text{C}_3\text{C}_4 - \text{C}_3\text{C}_8)$, mixed with in-plane
CH bending vibrations of the same ring (see the electronic
Supporting Information, ESI). For compound **1**, a very intense
IR band at $\sim 1100 \text{ cm}^{-1}$, which corresponds to a couple of
positive VCD features, is observed. The intense absorption band
corresponds to NMs 56 and 57; the first NM is similar to the
one described above for compounds **2** and **3** and bears high
rotational strength, the second one involves the COOCD_3
moiety, and its frequency is nearly the same in the two
conformers. The second VCD band observed at $\sim 1105 \text{ cm}^{-1}$
is due to NM 58 of conformer B (see ESI Tables).

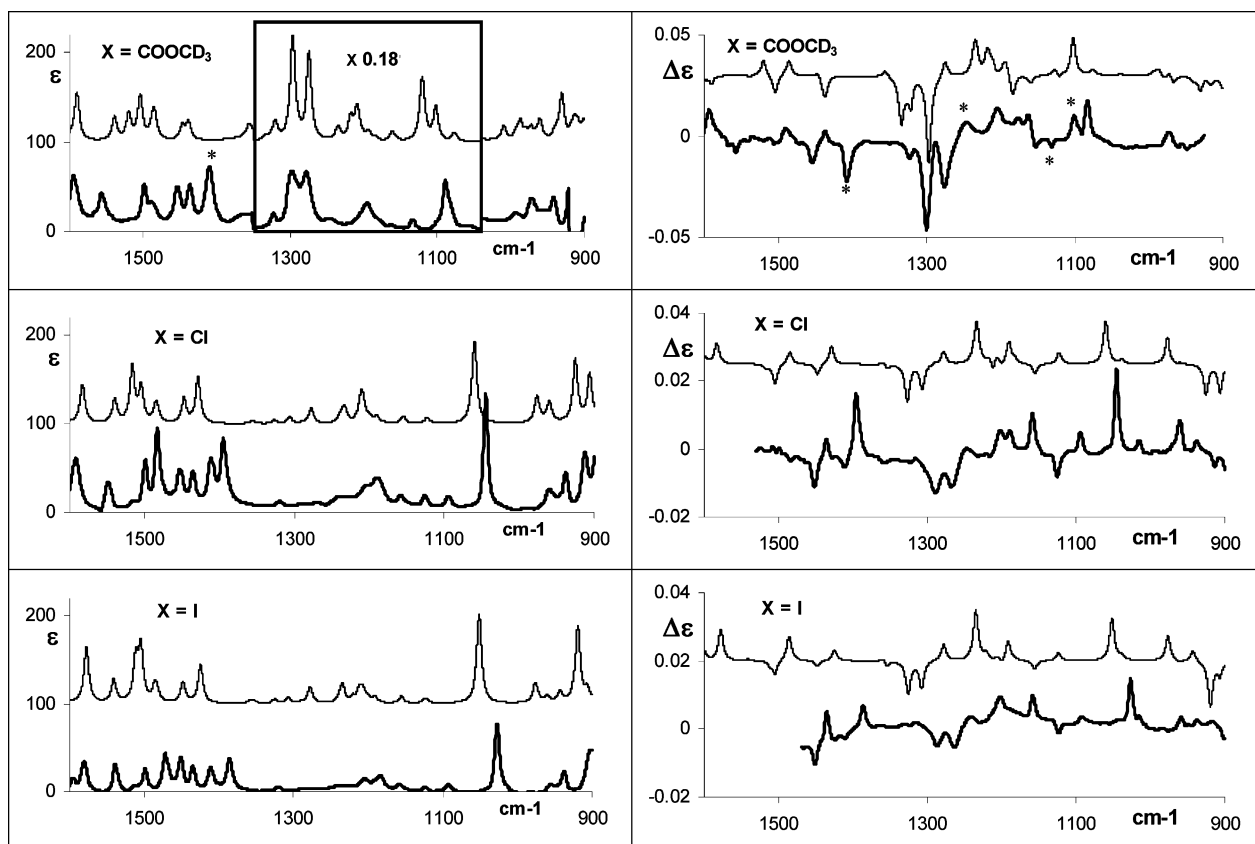


Figure 2. Experimental (bold character) and calculated (light character) IR absorption (left) and VCD (right) spectra in the mid-IR region for (*R*)-4-methoxycarbonyl-*d*₃-[2.2]paracyclophane (**1**) (Top), for (*R*)-4-chloro-[2.2]paracyclophane (**2**) (Center), and for (*R*)-4-iodo-[2.2]paracyclophane (**3**) (Bottom). On the experimental IR and VCD spectra of **1**, we denote with an asterisk the bands due to the less populated conformer B. In all graphs, ϵ and $\Delta\epsilon$ are in $10^3 \text{ cm}^2 \text{ mol}^{-1}$ units. The inset in the top left panel has the y axis (coinciding with the inset height) reduced by a factor 0.18 so that the full scale is 1100.

181 *ii. VCD Doublet between 1250 and 1300 cm^{-1} .* For the three
 182 X-substituted PC, one observes a negative VCD doublet, which
 183 is much more intense for **1** than for **2** and **3**. In all cases, the
 184 DFT calculations allow one to assign these bands to NMs
 185 containing important contributions from CH_2 wagging and
 186 twisting modes of the aliphatic moiety bridging the two aromatic
 187 rings on the side of the stereogenic group X. For **1**, the COOCD_3
 188 group causes the enhancement of the intensity of the doublet
 189 both in absorption and CD. This effect can be traced back to
 190 the influence of the oxygen atom, as observed in other
 191 substituted cyclophanes⁴ and in other cases^{15,17} (see also the
 192 comments iv to the data in this section). The negative VCD
 193 doublet can be ascribed to the prevalence of conformer A over
 194 conformer B; indeed, for conformer A, calculations provide a
 195 negative doublet due to the CO- and CC stretching vibrations
 196 of the two bonds adjacent to the carbonyl, while, for the same
 197 NMs, a (-,+ doublet (in order of increasing frequencies) is
 198 calculated for conformer B.

199 *iii. VCD Band at 1400 cm^{-1} .* This VCD band is in cor-
 200 respondence with a couple of moderately intense IR bands and
 201 is negative for **1** and positive for **2** and **3**. On the basis of
 202 calculated NMs (see ESI material), we assign it to the CH_2
 203 modes on the bridging aliphatic moiety opposite to the stereo-
 204 genic group X plus in-plane bending modes of nearby CH bonds
 205 on the aromatic ring containing X (see ESI). Intense negative
 206 VCD is associated with conformer B.

207 *iv. IR Intensities (Dipole Strengths).* The IR spectra of **1**
 208 in the range of 1050–1350 cm^{-1} are much more intense than those
 209 of **2** and **3**. This is due to the influence of the oxygen atoms, as

210 it was observed previously.^{4,15,17} The calculations presented in
 211 Figure 2 reproduce this fact very well.

212 *v. IR and VCD Bands of the Less Populated Conformer.* As
 213 reported above, conformer A has a population of $\sim 84\%$ versus
 214 conformer B, which is populated at $\sim 16\%$. This has a nice
 215 counterpart in the finding that almost all of the experimental
 216 IR and VCD bands are attributed to calculated IR and VCD
 217 bands for conformer A (see ESI material, Table and Figure 1).
 218 However, as may be seen from the ESI material, there are some
 219 isolated and intense VCD and IR bands of conformer B which
 220 “survive” the statistical average and show up in the experimental
 221 spectra. We have been able to identify four of them in the VCD
 222 spectrum at 1407 (-), 1246 (+), 1131 (-), and 1100 (+) cm^{-1}
 223 and one in the IR spectrum at 1437 cm^{-1} ; in Figure 2, they are
 224 marked with an asterisk, and they suggest a higher population
 225 for B than that computed by our *in vacuo* calculation. In any
 226 case, bands associated with the less-populated conformers have
 227 been observed in many instances; we cite a very analogous
 228 situation, namely, the study of (*3R*)-(+)-methylcyclohexanone.²⁰

229 As a general comment, we may say that there is an overall
 230 similarity in the mid-IR absorption and VCD spectra of **2** and
 231 **3** as opposed to those of **1**. Only in part can these differences
 232 be ascribed to the presence of additional normal modes of the
 233 COOCD_3 moiety; the X substituent, in fact, determines also
 234 dipole and rotational strengths of other normal modes, for
 235 example, in-plane bending of phenyl rings and deformation
 236 modes of aliphatic bridges, thus differentiating the spectroscopic
 237 behavior of 4-X-[2.2]paracyclophanes. Some analogy may be
 238 found with the previous study of ref 6, where a linear correlation

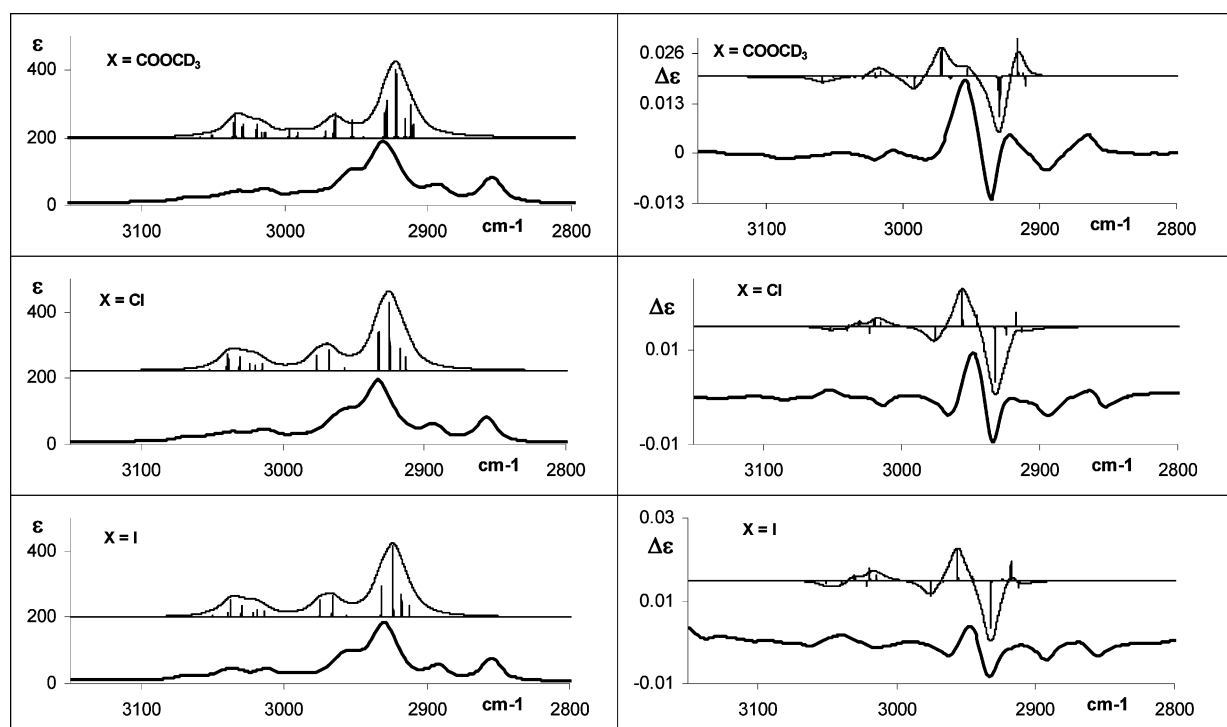


Figure 3. Experimental (bold character) and calculated (light character) IR absorption (left) and VCD (right) spectra in the fundamental CH stretching region for (*R*)-4-methoxycarbonyl-*d*₃-[2.2]paracyclophane (**1**) (Top), for (*R*)-4-chloro-[2.2]paracyclophane (**2**) (Center), and for (*R*)-4-iodo-[2.2]paracyclophane (**3**) (Bottom). Underneath of the calculated IR and VCD bands of **1**, at the calculated wavenumbers, we report bars that are proportional to calculated dipole and rotational strengths, respectively. In all graphs, ϵ and $\Delta\epsilon$ are in $10^3 \text{ cm}^2 \text{ mol}^{-1}$ units.

239 of the specific rotation value $[\alpha]$ with the polarizability value
 240 P_X of the X group was proposed; therein, two distinct correlation
 241 straight lines were found between $[\alpha]$ and P_X , one for X = Cl,
 242 Br, and I substituents and the other for all other substituent
 243 groups X. (Parenthetically, we observe that in ref 6, the case of
 244 X = COOCD₃ was not reported in the correlation plot; however,
 245 if we consider the relationship $P_X = -0.017[\alpha] + 1.58$ being
 246 valid, from a mean experimental value of $[\alpha]_D^{23} = -149$, a P_X
 247 value of 4.11 \AA^3 can be deduced for the (*R*) enantiomer. This
 248 value is in accord with those ($P_X = 4.17 \text{ \AA}^3$) calculated for the
 249 COOCH₃ group from the mean polarizability values given in
 250 ref 21 for formaldehyde, dimethyl ether, and CH₄ and C₂H₆,
 251 on the basis of a hypothesis of the polarizability additivity.)

252 Coming back to absorption and VCD spectra, we find much
 253 larger dipole and rotational strengths in IR and VCD spectra
 254 between 1050 and 1300 cm^{-1} for **1** as opposed to **2** and **3**; also,
 255 differences in intensities can be noticed between compounds **2**
 256 and **3**. Whether this is related to some characteristic invariant
 257 of atomic polar tensors, in response to a different substituent
 258 group X, remains to be investigated but is beyond the scope of
 259 the present study.

260 **The CH Stretching Region ($2800\text{--}3200 \text{ cm}^{-1}$).** The ex-
 261 perimental IR and VCD spectra of **1**, **2**, and **3** are quite similar
 262 (Figure 3, continuous lines) and comprise three groups of bands,
 263 two groups in the aliphatic region (below 3000 cm^{-1}) and one
 264 group in the aromatic region. The DFT harmonic calculations
 265 allow one to get a clue for the assignment of the observed bands
 266 between 3200 and 2900 cm^{-1} as well as to acceptably simulate
 267 the observed IR and VCD features in the same range (see Figure
 268 3, dotted lines). Furthermore, we give here a quantitatively
 269 acceptable interpretation of the features in the range of 2800--
 270 2900 cm^{-1} in terms of anharmonic parameters previously
 271 derived to interpret the Fermi resonance (FR) phenomenon in
 272 CH₂ moieties.^{22,23} Let us analyze the spectra in detail.

The Aliphatic Region. a. Bands between 2900 and 3000 273
 274 cm^{-1} . There is a very intense IR band centered at $\sim 2930 \text{ cm}^{-1}$ 274
 275 with one broad shoulder at $2950\text{--}2960 \text{ cm}^{-1}$. In correspondence 275
 276 with it, a couple of evident VCD bands can be observed at 276
 277 ~ 2930 and 2950 cm^{-1} having opposite signs ($-$, $+$) for the (*R*) 277
 278 enantiomer, with rotational strengths that are more intense for 278
 279 **1** than for **2** and **3**. Other VCD features in the same region are 279
 280 observed at ~ 2920 ($+$) and $\sim 2980 \text{ cm}^{-1}$ ($-$, very weak) for **1** 280
 281 and at $\sim 2965 \text{ cm}^{-1}$ ($-$) for **2** and **3**. The calculations allow 281
 282 assignment of the major IR feature at $\sim 2930 \text{ cm}^{-1}$ to the four 282
 283 CH₂-symmetric stretching vibrations and the IR shoulder at 283
 284 $\sim 2950 \text{ cm}^{-1}$ to the four CH₂-antisymmetric stretchings. Cor- 284
 285 respondingly, referring to the (*R*) enantiomer, the pair of major 285
 286 VCD bands with ($-$) and ($+$) signs are attributed to superim- 286
 287 posed VCD CH₂-symmetric and CH₂-antisymmetric vibrational 287
 288 transitions, respectively, bearing mostly (but not exclusively) 288
 289 ($-$) and ($+$) signs. The other observed VCD features at 289
 290 frequencies just above and below the major VCD bands are 290
 291 due to lower intensity components bearing different signs 291
 292 embedded in the major VCD features (see Figure 3 and ESI). 292

b. Bands between 2800 and 2900 cm^{-1} . Looking at the 293
 294 experimental spectra of Figure 3, two IR bands at ~ 2850 and 294
 295 $\sim 2890 \text{ cm}^{-1}$, with constant intensity ratio and a triplet of VCD 295
 296 features of alternating sign ($-$, $+$, $-$) in correspondence with 296
 297 them, can be observed for **1**, **2**, and **3** (for **1**, just the $+$ and $-$ 297
 298 bands are observed). In the DFT calculations (Figure 3, dotted 298
 299 lines), there is no trace of these features, and we attribute them 299
 300 to strong FR anharmonic phenomena, such that the CH₂ bending 300
 301 overtone and combination transitions “acquire” dipole strengths 301
 302 or rotational strengths from nearby CH₂-symmetric stretching 302
 303 fundamentals. 303

To get a first, qualitatively and quantitatively acceptable 304
 305 interpretation of the FR phenomenon, we adopt the approach 305
 306 of ref 22, where the case of CD₃CH₂CH₂CD₃ was examined. 306

307 Here, FR is originated within each one of the four CH₂ units
 308 by an anharmonic interaction between the HCH bending
 309 coordinate (δ) and the two CH stretching coordinates (d_1 and
 310 d_2). As done in ref 22, we write this interaction Hamiltonian as

$$V_{\text{anh}} = f_{\delta\delta\delta}[(d_{\text{II}} + d_{2\text{I}})\delta_1^2 + (d_{\text{III}} + d_{2\text{II}})\delta_{\text{II}}^2] + f_{\delta\delta\delta}[(d_{\text{III}} + d_{2\text{III}})\delta_{\text{III}}^2 + (d_{\text{IV}} + d_{2\text{IV}})\delta_{\text{IV}}^2] = V_{\text{anh}}(1,2) + V_{\text{anh}}(9,10) \quad (1)$$

311 Here, I, II, III, and IV denote the CH₂ units originated from
 312 carbon atoms 1, 2, 9, and 10, respectively. As discussed in the
 313 Appendix, the anharmonic interaction force constant $f_{\delta\delta\delta}$ is an
 314 “effective” measure of the anharmonic interaction between
 315 bendings and stretchings; in general, one should “divide” it into
 316 several contributions, part of them being of kinetic nature, tied
 317 to the curvilinear nature of internal coordinates. For now, we
 318 settle for the heuristic value derived in ref 22 relative to
 319 hexadeuterated *n*-butane. Albeit the merely phenomenological
 320 value of this approach, we notice that it was used in the past
 321 for several molecules containing CH₂ units, and the values of
 322 the anharmonic constant $f_{\delta\delta\delta}$ were successfully transferred to
 323 several molecules containing methylenes.²³ From the ESI
 324 material, we may learn that, as expected, the CH stretching
 325 normal modes involve contributions from either the (1,2) or from
 326 the (9,10) moiety but are not mixtures of (1,2) and (9,10) units.
 327 As such, we assume, for the (1,2) moiety, a symmetric bending
 328 normal mode Q_{bs} and an antisymmetric bending normal mode
 329 Q_{ba} , while there are four stretching normal modes Q_{S} , Q_{aS} , Q_{sA} ,
 330 and Q_{aA} , which are symmetric or antisymmetric within the CH₂
 331 units (S or A) or between the two CH₂ units (s or a). In this
 332 simplified scheme, they are tied to the internal coordinates by
 333 the relations

$$Q_{\text{bs}} = \frac{1}{\sqrt{2}}L_{\delta}^{-1}\delta_1 + \frac{1}{\sqrt{2}}L_{\delta}^{-1}\delta_{\text{II}} \\ Q_{\text{ba}} = \frac{1}{\sqrt{2}}L_{\delta}^{-1}\delta_1 - \frac{1}{\sqrt{2}}L_{\delta}^{-1}\delta_{\text{II}}$$

334 and

$$Q_{\text{S}} = \frac{1}{2}L_{\text{str}}^{-1}d_{\text{II}} + \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{I}} + \frac{1}{2}L_{\text{str}}^{-1}d_{\text{III}} + \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{II}} \\ Q_{\text{aS}} = \frac{1}{2}L_{\text{str}}^{-1}d_{\text{II}} + \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{I}} - \frac{1}{2}L_{\text{str}}^{-1}d_{\text{III}} - \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{II}} \\ Q_{\text{sA}} = \frac{1}{2}L_{\text{str}}^{-1}d_{\text{II}} - \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{I}} + \frac{1}{2}L_{\text{str}}^{-1}d_{\text{III}} - \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{II}} \\ Q_{\text{aA}} = \frac{1}{2}L_{\text{str}}^{-1}d_{\text{II}} - \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{I}} - \frac{1}{2}L_{\text{str}}^{-1}d_{\text{III}} + \frac{1}{2}L_{\text{str}}^{-1}d_{2\text{II}}$$

335 These assumptions are quite simplifying, but they are not too
 336 far from what can be found by the precise normal-mode analysis
 337 obtained by use of Gaussian03 (see ESI). The inverse of the
 338 above relations may be substituted into eq 1, obtaining

$$V_{\text{anh}}(1,2) = f_{\delta\delta\delta}L_{\text{str}}L_{\delta}^2(Q_{\text{S}}Q_{\text{bs}}^2 + Q_{\text{S}}Q_{\text{ba}}^2 + 2Q_{\text{aS}}Q_{\text{bs}}Q_{\text{ba}}) \quad (2)$$

339 Analogous results can be found for $V_{\text{anh}}(9,10)$. From eq 2, for
 340 the moiety (1,2) and analogously for moiety (9,10), two
 341 interaction matrices, given in the Appendix, can be obtained.
 342 The first one is a (3 × 3) and describes the interaction of the
 343 CH stretching fundamental associated with normal mode Q_{S}

(anharmonic frequency $\omega_{\text{S}} - 2\chi_{\text{str}}$) and the first overtones of 344
 normal modes Q_{bs} and Q_{ba} (anharmonic frequencies $2\omega_{\text{bs}} - 6\chi_{\text{b}}$ 345
 and $2\omega_{\text{ba}} - 6\chi_{\text{b}}$); the second one is a (2 × 2) and describes the 346
 interaction of CH stretching fundamental associated with normal 347
 mode Q_{aS} (anharmonic frequency $\omega_{\text{aS}} - 2\chi_{\text{str}}$) with the 348
 combination of normal modes Q_{bs} and Q_{ba} (anharmonic 349
 frequency $\omega_{\text{bs}} + \omega_{\text{ba}} - 4\chi_{\text{b}}$). Here, χ_{b} is an effective anharmonic 350
 correction, whose value is commented below. The diagonal- 351
 ization of these four matrices provides four new frequencies 352
 associated with locally symmetric CH stretchings, plus six 353
 frequencies associated with bending overtones and combina- 354
 tions; further, it provides normalized eigenvectors, whose first 355
 coefficients square may be used to weight the CH stretching 356
 fundamental dipole and rotational strengths, as done in refs 22 357
 and 23. The matrices are presented in the Appendix. From DFT 358
 calculations on molecule 2, we have obtained for moiety (1,2) 359
 the values $\omega_{\text{S}} = 3062.2 \text{ cm}^{-1}$, $\omega_{\text{aS}} = 3045.7 \text{ cm}^{-1}$, $\omega_{\text{bs}} = 1504.4$ 360
 cm^{-1} , and $\omega_{\text{ba}} = 1485.4 \text{ cm}^{-1}$; for moiety (9,10), the values ω_{S} 361
 $= 3053.8 \text{ cm}^{-1}$, $\omega_{\text{aS}} = 3041.2 \text{ cm}^{-1}$, $\omega_{\text{bs}} = 1504.9 \text{ cm}^{-1}$, and 362
 $\omega_{\text{ba}} = 1483.3 \text{ cm}^{-1}$ were obtained in the same way (see ESI). 363
 As anharmonicity constants, we assumed $\chi_{\text{str}} = 60.6 \text{ cm}^{-1}$ and 364
 $\chi_{\text{b}} = 25$, or 20, or 15 cm^{-1} , and $f_{\delta\delta\delta} = 0.201 \text{ mdyn}\cdot\text{rad}^{-2}$. We 365
 obtained the results of Figure 4, which we consider quite 366
 satisfactory, especially for the case of $\chi_{\text{b}} = 15 \text{ cm}^{-1}$ (in Figure 367
 4, to each transition, we associated a Lorentzian band, centered 368
 at the calculated frequency, with the (signed) area equal to the 369
 calculated dipole (rotational) strength and with $\gamma = 8 \text{ cm}^{-1}$). 370
 Before commenting on the results, let us discuss how the values 371
 for anharmonicity constants were derived. χ_{str} has been obtained 372
 from experimental IR and NIR CH stretching frequencies fitted 373
 to a Birge–Sponer plot²⁴ (reported in Figure 3 of ESI, on the 374
 basis of the frequencies of experimental NIR absorption bands 375
 of Figure 2, ESI). $\chi_{\text{b}} = 25 \text{ cm}^{-1}$ was obtained by assuming 376
 that the difference between bending harmonic frequencies ω_{bs} 377
 and ω_{ba} calculated with Gaussian03 and of the frequencies for 378
 the observed VCD and absorption features at 1443 and 1425 379
 cm^{-1} (assigned to the fundamental Q_{ba} and Q_{bs} normal modes, 380
 respectively) was equal to $2\chi_{\text{b}}$. $\chi_{\text{b}} = 15 \text{ cm}^{-1}$ was instead 381
 proposed in ref 26 in a study of overtone spectra of *n*-paraffins, 382
 and $\chi_{\text{b}} = 20 \text{ cm}^{-1}$ was an intermediate tentative value. Finally, 383
 $f_{\delta\delta\delta} = 0.201 \text{ mdyn}\cdot\text{rad}^{-2}$ was derived in ref 22 and used in refs 384
 23 and 26. The aromatic region, not effected by FR, is also 385
 reported in Figure 4; it was obtained from the Gaussian03 results 386
 by subtracting $\chi_{\text{str}} = 65.4 \text{ cm}^{-1}$, as evaluated from the Birge– 387
 Sponer plot presented in the ESI. In Figure 4, we compare the 388
 FR results with those obtained with no FR interaction taking 389
 place. In this Figure, we did not adopt an arbitrary frequency 390
 shift (see Figure 3); instead, having inserted the contribution 391
 of stretching anharmonicity χ_{str} , we obtained a satisfactory 392
 prediction of experimental absorption and VCD spectra with 393
 respect to frequencies. On the basis of the complete results of 394
 Figure 4, we propose that the three (–,+,–) VCD features 395
 observed below 2900 cm^{-1} acquired their rotational strength 396
 from the CH₂-symmetric stretching fundamental; the latter 397
 modes gave rise to the intense and unresolved VCD negative 398
 feature at 2940 cm^{-1} . The higher frequency region, not involved 399
 in FR, is well reproduced by this frequency anharmonic 400
 correction treatment. As a general conclusion, we observe that 401
 this is an instance where anharmonicity does not obscure the 402
 usability of the VCD data; indeed, the VCD spectra are similar 403
 for **1**, **2**, and **3**, and thus, we surmise that the same phenomenon 404
 is taking place in the same way for the three molecules. As a 405
 final comment and as noticed at the beginning of this paragraph, 406
 we remark that the anharmonic interactions of eq 1 may not be 407

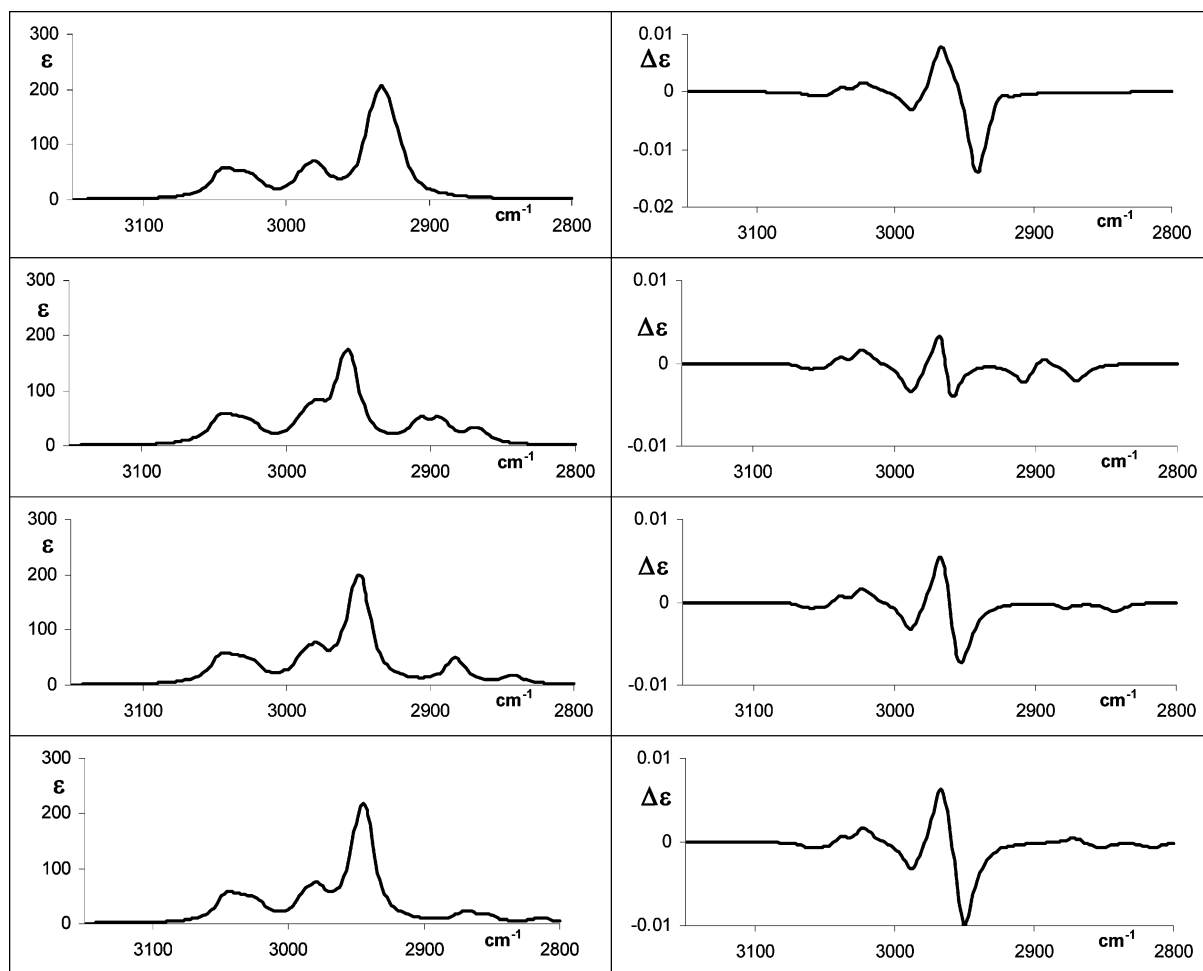


Figure 4. Calculated absorption and CD spectra for molecule **2**. From top to bottom: without Fermi resonance (top row), with Fermi Resonance, and $\chi_b = 15, 20,$ and 25 (second, third, and fourth row, respectively) (see text).

408 the only anharmonic interaction of HCH bending modes and
 409 CH stretching modes. However, we think that what really
 410 matters is that the nondiagonal interaction terms Λ given in
 411 the Appendix be on the order of $20\text{--}30\text{ cm}^{-1}$ (see also refs 22
 412 and 23). The fact that they depend solely on $f_{\alpha\delta\delta}$, (as done here)
 413 or on other parameters is not crucial; we defer some further
 414 discussion to the Appendix.

415 We recognize that the recent works of Barone and co-workers
 416 should be considered if one wishes to evaluate anharmonic force
 417 constants by ab initio methods.²⁶ Indeed, calculations of cubic
 418 and semidiagonal quartic force constants have been recently
 419 implemented in Gaussian in the frame of second-order perturba-
 420 tion theory; this permits also evaluation of anharmonic-corrected
 421 frequencies (here, done by means of experimentally deduced
 422 χ_{str}) on which FR treatment must be conducted.

423 **The Aromatic Region.** The IR spectrum of **1**, **2**, and **3** is
 424 comprised of three weak bands at $\sim 3010, 3040,$ and 3070 cm^{-1} ;
 425 the corresponding VCD features are weak as well. For **1**, one
 426 observes a $(+,-,+)$ triplet, where the negative feature is the
 427 weakest, and the highest frequency positive feature is very
 428 broad; for **2**, one has a $(-,+,-,+)$ quadruplet, in which the
 429 last component is very broad, and the lowest frequency
 430 component is at $\sim 3000\text{ cm}^{-1}$. For **3**, one has a $(-,+,-)$ triplet,
 431 where the broadest feature is the middle, positive one. The
 432 calculations do not provide a one-to-one assignment of the three
 433 IR bands and of the three or four VCD bands; however, they
 434 are somewhat helpful. First of all, the calculated dipole and
 435 rotational strengths are all weak, as are the experimental data.
 436 A close analysis of the calculation outcome allows us to identify

437 a single absorption feature composed of three shoulders. It
 438 consists of seven transitions; the lowest frequency features are
 439 the three antisymmetric combinations of pairs of CH stretchings
 440 that are localized on each benzene ring on the same side with
 441 respect to the aliphatic moiety connecting the two aromatic rings.
 442 The highest frequency components of that feature are the
 443 corresponding three symmetric combinations and the localized
 444 CH stretching mode of C(5), which is the closest to the
 445 substituent group. The latter vibrational mode has a negative
 446 VCD in all three cases and has the highest frequency and does
 447 not correlate with experiment, except for **3**. The other calculated
 448 VCD features associated with the other modes can hardly be
 449 correlated with the VCD experimental features.

450 **The NIR Region.** Considering NIR data are important not
 451 only per se but also to obtain parameters useful for improving
 452 the interpretation of the IR absorption and IR-VCD spectra. In
 453 Figure 2 ESI, we show the CH stretching fundamental absorp-
 454 tion spectra for **1**, for the $\Delta\nu = 1$ region ($3200\text{--}3600\text{ nm}$), the
 455 CH stretching first overtone region $\Delta\nu = 2$ ($1600\text{--}1800\text{ nm}$),
 456 the CH stretching second overtone region $\Delta\nu = 3$ ($1100\text{--}1220$
 457 nm), and the CH stretching third overtone region ($800\text{--}1000$
 458 nm). As one may immediately appreciate, the aromatic region
 459 is of much weaker intensity than the aliphatic region at $\Delta\nu = 1$
 460 but is of comparable intensity at $\Delta\nu = 3$ and 4. This had
 461 been observed previously in other compounds.^{27,28} The rather
 462 evident difference between the $\Delta\nu = 1$ and the $\Delta\nu = 2$ and 3
 463 regions is not only due to the local mode regime taking over
 464 for $\Delta\nu \geq 3$ with respect to a normal mode one because of
 465 mechanical anharmonicity, but it is also due to high nonlin-

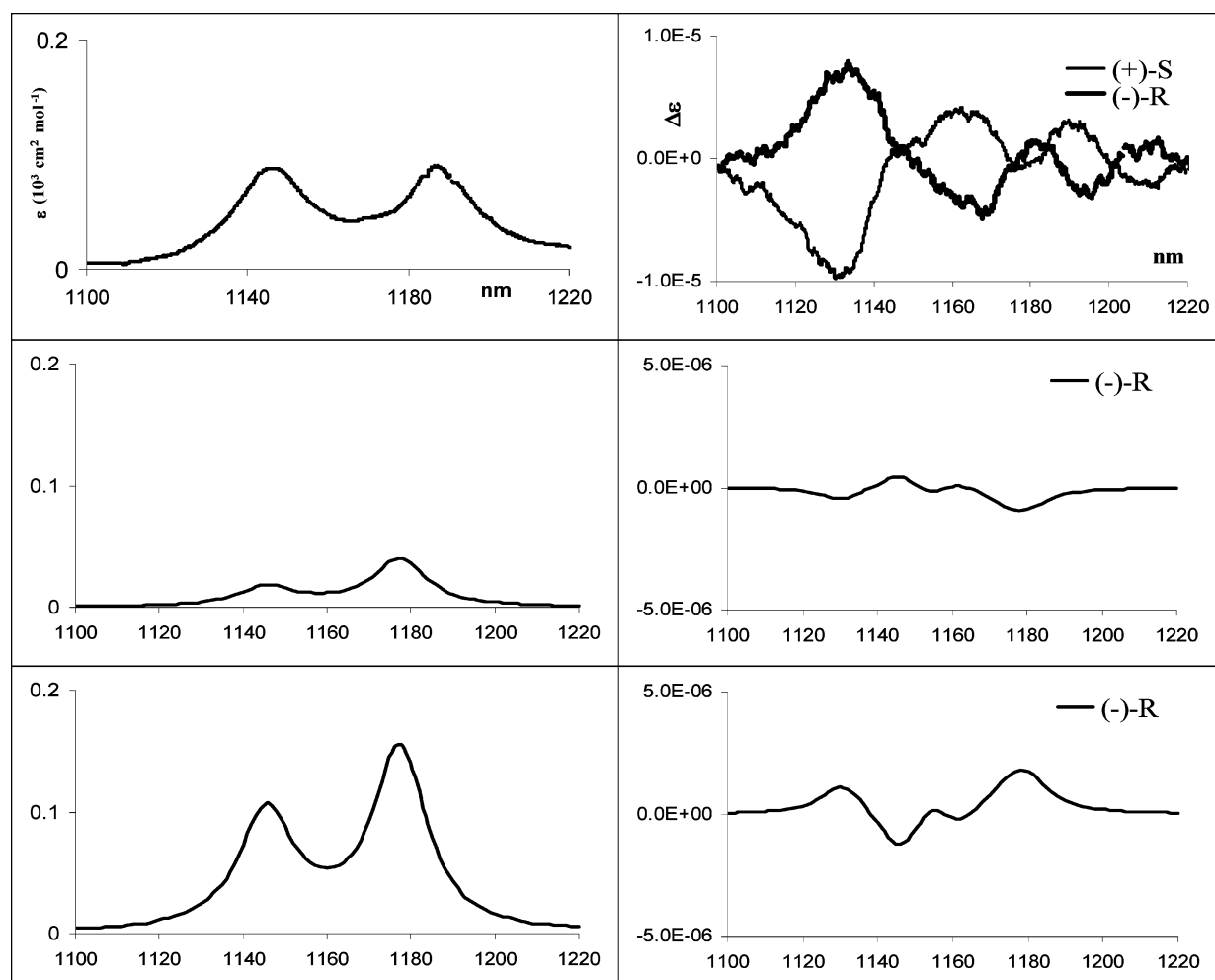


Figure 5. Comparison of experimental (top row, both enantiomers) and calculated (*R* configuration) NIR-VCD spectra at $\Delta v = 3$ for molecule **1**. Absorption and rotational strengths have been evaluated, as explained in the text in the hypothesis of the electric harmonic approximation (middle row) and with electrical anharmonicity (bottom row).

466 erities in the CH bond electrical dipole moment functions. The
 467 $\Delta v = 2$ region is of intermediate character and thus is hard
 468 to decipher. Due to local mode behavior at $\Delta v \geq 3$, one is able to
 469 deduce ω_0 and χ^{24} from a Birge–Sponer plot; this is done in
 470 Figure 3 ESI and gives $\omega_0 = 3045 \text{ cm}^{-1}$ and $\chi = 60.6 \text{ cm}^{-1}$
 471 for aliphatic CH stretchings and $\omega_0 = 3173 \text{ cm}^{-1}$ and $\chi = 65.4$
 472 cm^{-1} for aromatic CH stretchings. This is in accord with
 473 literature data²⁸ and, as we have seen above in Figure 4, allows
 474 one to acceptably reproduce the normal-mode observed frequen-
 475 cies at $\Delta v = 1$ by subtracting the empirical mechanical
 476 anharmonicity χ from the ab initio-calculated normal-mode
 477 frequencies.

478 While the mechanical anharmonicity can be easily evaluated
 479 as done above, the electrical anharmonicity needs to be dealt
 480 with in a different way; as it will be seen below, it has important
 481 effects on absorption and VCD spectra at $\Delta v = 3$. Indeed, in
 482 Figure 5, we compare experimental data at $\Delta v = 3$ of compound
 483 **1** with calculated spectra with and without electrical anhar-
 484 monicities in the assumption of local modes. In the top two panels
 485 of this figure, we report the experimental data (VCD data are
 486 for both enantiomers); in the center two panels are the results
 487 of a first set of calculations for the (*R*) enantiomer, performed
 488 in the same way as in ref 10. As done there, we transfer the
 489 results of CH stretching fundamental “local mode” transitions
 490 $\Delta v = 1$ (where local modes are obtained by considering the
 491 molecule with all H atoms but one substituted by deuterium)¹⁰

to $\Delta v = 3$, applying the hypothesis of electrical harmonicity. 492
 We have inserted here the correction factor 493

$$\frac{\langle 0|r-r_0|v\rangle}{\langle 0|r-r_0|1\rangle} \cong \frac{1}{v^2} \frac{v!}{(2K)^{v-1}}$$

(being $2K = \omega_0/2\chi$) for dipole strengths (2.64×10^{-4} for 494
 aliphatic CHs and 2.83×10^{-4} for aromatic CHs, for $v = 3$) 495
 and the correction factor 496

$$\frac{\langle 0|r-r_0|v\rangle\langle v|p|0\rangle}{\langle 0|r-r_0|1\rangle\langle 1|p|0\rangle} \cong \frac{1}{v} \frac{v!}{(2K)^{v-1}}$$

for rotational strengths (7.92×10^{-4} for aliphatic CHs and 8.49 497
 $\times 10^{-4}$ for aromatic CHs, for $v = 3$). The above factors have 498
 been evaluated using Morse wave functions and under the 499
 hypothesis that the electric dipole moment function depends 500
 linearly on $(r - r_0)$ and the magnetic dipole moment is 501
 proportional to p ; the transition moments for $(r - r_0)$ and p are 502
 given in ref 29 and here have been approximated under the 503
 hypothesis that $2K \gg v$. By comparing calculated and experi- 504
 mental results, we see that our model gives dipole and rotational 505
 strengths less intense than those observed. As is well-known 506
 from the literature, this fact is related to assuming zero electrical 507
 anharmonicity.³⁰ Furthermore, the aromatic feature at shorter 508
 wavelengths is underestimated with respect to the aliphatic one 509

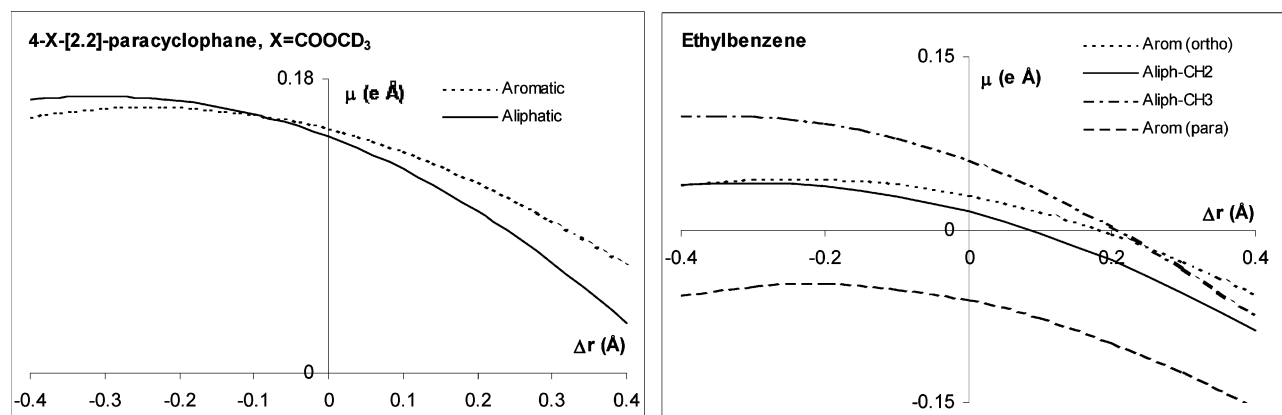


Figure 6. Calculated dependence of the molecular dipole moment function projected onto selected CH bonds on H-atom displacements along the bond itself for compound **1** (left) and ethylbenzene (right). For the latter molecule, distinction is made between one of the aromatic atoms next to the CH₂CH₃ group and the one farthest off; similar calculations have been repeated for an aliphatic methylene CH and for a methyl CH.

TABLE 1: Comparison of Calculated and Experimental Dipole Moment Derivatives with respect to CH Stretching Coordinates (See Text and Figure 6)^a

	4-X-[2.2]-paracyclophane (X = COOCD ₃)		ethylbenzene ^b			
	Arom	Aliph	Arom-o	Arom-p	Aliph-CH ₂	Aliph-CH ₃
	Calculated					
$(\partial\mu/\partial r)_0(e)$	-0.114	-0.168	-0.121	-0.127	-0.161	-0.227
$(\partial^2\mu/\partial r^2)_0(e/\text{Å})$	-0.501	-0.603	-0.496	-0.578	-0.567	-0.325
	Experimental					
$(\partial\mu/\partial r)_0(e)$				-0.063		-0.101
$(\partial^2\mu/\partial r^2)_0(e/\text{Å})$				-0.360		-0.400
	toluene ^c					
$(\partial\mu/\partial r)_0(e)$				-0.066		-0.067
$(\partial^2\mu/\partial r^2)_0(e/\text{Å})$				-0.366		-0.355

^a Arom-o: CH position is ortho to CH₂CH₃. Arom-p: CH position is para to CH₂CH₃. ^b Experimental values from ref 31. ^c From ref 27.

510 both in absorption and in VCD since the calculations follow
 511 the prediction of the $\Delta\nu = 1$ region, where they match
 512 experiment. Besides, the alternating features of VCD are
 513 calculated with an overall (-1) factor, although the alternation
 514 of bands seems to be correctly predicted.

515 In order to cope with the effects of electrical anharmonicity,
 516 we have run DFT calculations of electric dipole moment
 517 functions, whose results are shown in Figure 6 (B3LYPfunctional,
 518 6-31G**basis set). On the left, we provide the calculated
 519 components of the electric dipole moment functions along one
 520 CH bond of the aromatic moiety (C₁₂H in the scheme) and along
 521 one CH bond of the aliphatic moiety (C₁₀H in the scheme). Such
 522 functions have been evaluated by extending and shortening the
 523 two CH bonds in steps of 0.02 Å up to ± 0.4 Å; the calculated
 524 data have been fitted afterward to a fourth-order polynomial,
 525 in a similar way to what was done by Henry, Kjaergaard, et al.
 526 in ref 31. We have checked that the fourth-order polynomial
 527 coefficients do not significantly vary when the fitting polynomial
 528 order is increased up to seven. For sake of comparison, we have
 529 also performed calculations for ethylbenzene, and in Figure 6,
 530 we report the results for two aromatic CH bonds (one ortho
 531 and one para to the CH₂CH₃ group) and for the CH bonds of
 532 CH₂ and CH₃. As one may immediately see, the first derivatives
 533 of such functions, $(\partial\mu/\partial r)_0$, are negative and larger in magnitude
 534 for aliphatic CHs than for those for aromatic CHs; this fact
 535 justifies the observed feature of higher intensities (dipole and
 536 rotational as well) in the aliphatic region at $\Delta\nu = 1$. From the
 537 plots in Figure 6, we have derived the values for $(\partial\mu/\partial r)_0$ and

$(\partial^2\mu/\partial r^2)_0$ and compare them in Table 1 with experimentally
 538 derived values for toluene²⁷ and ethylbenzene.³² The comparison
 539 is rather encouraging. On the basis of eq 6 of refs 27 and 29,
 540 we may provide a further correction factor, which includes
 541 electrical anharmonicity, to go from $\Delta\nu = 1$ to $\Delta\nu = \nu$ local
 542 mode intensities
 543

$$\frac{\langle 0|\mu|\nu\rangle}{(\partial\mu/\partial r)_0\langle 0|r-r_0|1\rangle} \cong \frac{1}{\nu} \sqrt{\frac{\nu!}{(2K)^{\nu-1}}} \left\{ 1 - \frac{1}{a} \frac{(\partial^2\mu/\partial r^2)_0}{(\partial\mu/\partial r)_0} \left(1 + \frac{1}{2} + \dots + \frac{1}{\nu-1} \right) \right\} = \frac{1}{\nu} \sqrt{\frac{\nu!}{(2K)^{\nu-1}}} \left\{ 1 - \frac{1}{a} \frac{(\partial^2\mu/\partial r^2)_0}{(\partial\mu/\partial r)_0} F(\nu) \right\} = \frac{1}{\nu} \sqrt{\frac{\nu!}{(2K)^{\nu-1}}} f_{\text{anhar.}}(\nu)$$

544 In the latter term, the dimensionless parameter $f_{\text{anhar.}}(\nu)$ contains
 545 the corrections due to electrical anharmonicity. The Morse
 546 parameter $a = [8\pi^2 m c \chi / h]^2$ is 1.82 Å⁻¹ for aliphatic CHs and
 547 1.89 Å⁻¹ for aromatic CHs. In our case, the use of the values
 548 for $(\partial\mu/\partial r)_0$ and $(\partial^2\mu/\partial r^2)_0$ calculated for molecule **1** provide,
 549 with $f_{\text{anhar.}}(\nu) = -1.958$, for aliphatic CHs and, with $f_{\text{anhar.}}(\nu) =$
 550 -2.487 , for aromatic CHs at $\nu = 3$. By applying $f_{\text{anhar.}}(\nu)$, we
 551 obtain calculated absorption spectra that compare quite satis-

factorily with the observed ones (see the bottom left panel of Figure 5), both with respect to the overall intensities and with respect to the ratio of the aromatic to the aliphatic bands. Interestingly, $f_{\text{anhar.}}(\nu)$ is negative for both aromatic and aliphatic CHs; this result is due to the fact that $(\partial\mu/\partial r)_0$ and $(\partial^2\mu/\partial r^2)_0$ have the same sign (see Table 1 and Figure 6) and $|(1/a)(\partial^2\mu/\partial r^2)_0 F(\nu)| > |(\partial\mu/\partial r)_0|$. If we apply the calculated factor to the previous results of Figure 5, center right, we obtain the results for the bottom right panel. The calculated VCD spectrum is of much lower overall intensity than the experimental one, even though signs are in better correspondence with the experiment. We notice that in this treatment of calculated rotational strengths, we have introduced a correction for the electric dipole moment, but we have not taken into account the nonlinearities of the magnetic moment. We do not know yet if this is the only reason for underestimated rotational strengths.

4. Conclusions

As previously reported by Furo et al.,⁴ this work on 4-X-substituted paracyclophanes shows, once more, the possibility to assign the correct AC by VCD in the mid-IR region combined with ab initio/DFT calculations. The currently commercially available softwares are based on the double harmonic approximation, that is, the assumption of mechanical and electrical harmonicity. However, our study of the IR-VCD spectra in the CH stretching region has led us to evaluate FR, which determines the 2800–2900 cm^{-1} portion of the IR and IR-VCD spectra and is due to mechanical anharmonicity. This has been done by transferring an interaction force constant, which has been demonstrated to account well for methylenic signals. The ab initio determination of such an anharmonic force constant is beyond the scope of the present work and is deferred to work like that of Barone et al.²⁶ In any case, we may conclude that the use of transferred anharmonic force constants or of ab initio-calculated anharmonic interactions permits one to exploit also the full CH stretching region to assign AC.

Moreover, in this work, we examined NIR-VCD data, which allowed to shed some light on phenomena related to electrical anharmonicity terms, as pointed out a long time ago on the basis of intensity data of CH stretching fundamental and overtone transitions.²⁷ The procedure proposed here is inevitably approximate due to the complexity of the problem, and in particular, further work needs to be done on the magnetic dipole moment function.

In any case, we think that treating CH stretchings as isolated Morse oscillators in a chiral field, as proposed some time ago by Polavarapu³³ and applied in a few studies,^{10,17} is a good starting point for the analysis of NIR-VCD spectra. The correct frame to tackle the problem of electrical and magnetic anharmonicity together with correct handling of mechanical anharmonicity is that proposed by Bak et al.³⁴

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Appendix

Construction of FR Matrices. Due to the form of the anharmonic interaction Hamiltonian, we need to consider the following harmonic wave functions for interacting matrices: $|1,0,0,0\rangle = \psi_1(Q_{\text{SS}})\psi_0(Q_{\text{AS}})\psi_0(Q_{\text{BS}})\psi_0(Q_{\text{BA}})$, $|0,0,2,0\rangle = \psi_0(Q_{\text{SS}})\psi_0(Q_{\text{AS}})\psi_2(Q_{\text{BS}})\psi_0(Q_{\text{BA}})$, $|0,0,0,2\rangle = \psi_0(Q_{\text{SS}})\psi_0(Q_{\text{AS}})\psi_0(Q_{\text{BS}})\psi_2(Q_{\text{BA}})$, $|0,1,0,0\rangle = \psi_0(Q_{\text{SS}})\psi_1(Q_{\text{AS}})\psi_0(Q_{\text{BS}})\psi_0(Q_{\text{BA}})$, $|0,0,1,1\rangle = \psi_0(Q_{\text{SS}})\psi_0(Q_{\text{AS}})\psi_1(Q_{\text{BS}})\psi_1(Q_{\text{BA}})$. Two FR interacting matrices are to be considered for moiety (1,2)

$$\begin{array}{lll} & |1,0,0,0\rangle & |0,0,2,0\rangle & |0,0,0,2\rangle \\ \langle 1,0,0,0| & \omega_{\text{SS}} - 2\chi_{\text{str}} & \Lambda_1 & \Lambda_2 \\ \langle 0,0,2,0| & \Lambda_1 & 2\omega_{\text{BS}} - 6\chi_{\text{b}} & 0 \\ \langle 0,0,0,2| & \Lambda_2 & 0 & 2\omega_{\text{BA}} - 6\chi_{\text{b}} \end{array}$$

and

$$\begin{array}{lll} & |0,1,0,0\rangle & |0,0,1,1\rangle \\ \langle 0,1,0,0| & \omega_{\text{aS}} - 2\chi_{\text{str}} & \Lambda_3 \\ \langle 0,0,1,1| & \Lambda_3 & \omega_{\text{BS}} + \omega_{\text{BA}} - 4\chi_{\text{b}} \end{array}$$

where $\Lambda_1 = (L_{\text{str}}L_{\delta}^2 f_{\text{d}\delta\delta})/(2H\omega_{\text{SS}}^{1/2}\omega_{\text{BS}}) = 22.96 \text{ cm}^{-1}$, $\Lambda_2 = (L_{\text{str}}L_{\delta}^2 f_{\text{d}\delta\delta})/(2H\omega_{\text{SS}}^{1/2}\omega_{\text{BA}}) = 22.32 \text{ cm}^{-1}$, $\Lambda_3 = (L_{\text{str}}L_{\delta}^2 f_{\text{d}\delta\delta})/(\sqrt{2}H\omega_{\text{aS}}^{1/2}\omega_{\text{BS}}^{1/2}\omega_{\text{BA}}^{1/2}) = 32.82 \text{ cm}^{-1}$, and $H = (8\pi^3 c^5/2 \cdot 10^{-13}/N_0^3/2h^{1/2})$. The frequencies ω , anharmonicities χ , and interaction constants Λ are in wavenumbers; c is the light velocity, N_0 is Avogadro's number, and h is Planck's constant. The constant H given above is such that the anharmonicity constant is $\text{mdyne}/\text{rad}^2$ and the eigenvectors' constants L_{str} and L_{δ} are in $\text{amu}^{-1/2}$ and in $(\text{amu}^{-1/2} \text{ \AA})$. We evaluate them from the Wilson G matrix diagonal elements $L_{\text{str}} \approx G_{\text{rr}}^{1/2}$ and $L_{\delta} \approx G_{\phi\phi}^{1/2}$ (Wilson, E.B., Jr.; Decius, J.C.; Cross, P.C. *Molecular Vibrations*; Dover Books: New York, 1980). The matrices above are formally valid for both moieties (1,2) and (9,10); for the latter, small adjustments are needed for slightly different values of ω 's. By diagonalizing them, one obtains three (two) eigenvalues, which are the frequencies bearing the anharmonic contribution, and for each eigenvalue, normalized eigenvectors with three (two) coefficients, each element of which describes the involvement of each state in the final state. The first coefficient, in all cases, is relative to the fundamental CH stretching state, and it is the coefficient to consider as responsible for redistributing dipole and rotational strength to anharmonically perturbed bending overtone and combination states.²²

As pointed out in the main text, the interacting anharmonic Hamiltonian is most probably not complete; following ref 25, in both moieties (1,2) and (9,10), one should also consider

$$V'_{\text{anh}}(1,2) = \frac{1}{2} (\partial G_{\varphi\varphi}/\partial r_{\text{CH}})_0 [(d_{1\text{I}} + d_{2\text{I}})p_{\delta\text{I}}^2 + (d_{1\text{II}} + d_{2\text{II}})p_{\delta\text{II}}^2] \quad (\text{A1})$$

where $p_{\delta\text{I}}$ is the momentum conjugate to the coordinate δ_{I} . One has

$$(\partial G_{\varphi\varphi}/\partial r_{\text{CH}})_0 = G' \approx -2r_{\text{CH}}^{-3} [1/m_{\text{H}} + (1 - \cos(\text{HCH})/m_{\text{C}})] \quad (\text{A1}')$$

From eq A1, following the same methodology in the text, we obtain

$$V'_{\text{anh}}(1,2) = \frac{1}{2} (\partial G_{\varphi\varphi}/\partial r_{\text{CH}})_0 L_{\text{str}} L_{\delta}^{-2} (Q_{\text{SS}} P_{\text{BS}}^2 + Q_{\text{SS}} P_{\text{BA}}^2 + 2Q_{\text{AS}} P_{\text{BS}} P_{\text{BA}}) \quad (\text{A2})$$

where P_{BS} and P_{BA} are the momenta conjugated to the normal coordinates Q_{BS} and Q_{BA} . Use of eqs A2 and A1' allows one to evaluate $\Lambda'_1 = -(L_{\text{str}}L_{\delta}^{-2}G')(\omega_{\text{BS}}/\omega_{\text{SS}}^{1/2})/8H' = 39.92 \text{ cm}^{-1}$, $\Lambda'_2 = -(L_{\text{str}}L_{\delta}^{-2}G')(\omega_{\text{BA}}/\omega_{\text{SS}}^{1/2})/8H' = 39.41 \text{ cm}^{-1}$, $\Lambda'_3 = -(L_{\text{str}}L_{\delta}^{-2}G')/(\omega_{\text{BS}}\omega_{\text{BA}}/\omega_{\text{AS}})^{1/2}/4\sqrt{2}H' = 56.24 \text{ cm}^{-1}$, and $H' = (\pi c^{1/2} 10^{-8}/N_0^{1/2} h^{1/2})$. These values are on the same order of magnitude as those for Λ_1 , Λ_2 , and Λ_3 that we have used above. These and other kinetic contributions²⁵ are always present; 615

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652 however, as stated in the text, the ad hoc value $f_{\delta\delta\delta} = 0.201$
 653 $\text{mdyne}\cdot\text{rad}^{-2}$ has guaranteed that the “effective” Λ values used
 654 in the interacting matrices reproduce the FR scheme well in
 655 several molecules containing CH_2 groups.^{22,23} For this reason,
 656 in the text, we report results ignoring kinetic contribution.

657 **Supporting Information Available:** Additional experimen-
 658 tal and theoretical results. This material is available free of
 659 charge via the Internet at <http://pubs.acs.org>.

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