THE ELECTRONIC SPECTRUM OF (−)-S-(pS)-2,5,3′,6′ -TETRAHYDRO[2.2]PARACYCLOPHANE- 2-CARBOXYLIC ACID

JAMES L. MARSHALL* and LINDSEY HALL

Department of Chemistry, North Texas State University, Denton, TX 76203, U.S.A.

Abstract—A new, efficient route was used in the synthesis of [2.2]paracyclophane-2-carboxylic acid. The chiral acid was then resolved and the Birch reduction performed yielding one enantiomer of tetrahydro[2.2]paracyclophane-2-carboxylic acid. The UV spectrum of tetrahydro[2.2]paracyclophane-2-carboxylic acid in isopentane shows one absorption at 206 nm ($\epsilon_{max} = 5271$). There are three bands observed in the CD spectrum in isopentane at 236 nm ($[\theta] = 1.8 \times 10^4$), 201 nm ($[\theta] = -16 \times 10^4$) and a positive band indicated below 180 nm but not observed; in ethanol the CD spectrum exhibits a band at 205 nm ($[\theta] = 1.5 \times 10^4$) and the UV spectrum shows a band at 208 nm ($\epsilon_{max} = 5915$). The bands were assigned and possible reasons for the occurrence of a $\pi \to \pi^*$ transition at unexpectedly long wavelengths are discussed.

[2.2]Paracyclophane (1) undergoes the Birch reduction to give the tetrahydro product (2), 2,5,3′,6′-tetra-hydro[2.2]paracyclophane.[1,2] It was observed[1] that the UV spectrum of 2,5,3′,6′-tetrahydro[2.2]paracy-lophane (2) consists of end absorption from 200 to 260 nm with ϵ_{max} above 10,000. This unusually low frequency absorption for isolated olefins suggested significant interaction between the olefins[3] of the two decks and accordingly it was postulated that the correct stereo chemistry for (2) was the "meso" geometry (3). Later it was shown[4] by means of an NMR study of the tetra-epoxide derivative that the correct geometry was in fact "D,L" (2). Further, a deuterium labeled study of the carboxylic acid analog (5) proved that in this compound also the correct geometry was "D,L".[5]

In the present study both UV spectroscopy and CD were employed to explore the nature of the electronic spectrum of the tetrahydro product (5) in an attempt[6] to assign excited states. Both compounds 3 and 5 are chiral and theoretically should be resolvable, but with 3 (with no functional groups), resolution should be difficult. Because 5 can rearomatize under certain conditions, the resolution step was conducted with compound 4. Additional corroboration for the "D,L" geometry of 5 would

be available from the CD spectrum of 5: the olefins are in a dissymetric environment and should absorb strongly, where with the "meso" geometry the olefins should absorb weakly, if at all.

In this study, the [2.2]paracyclophane-2-carboxylic acid (4) was prepared by a new method giving higher yields: [2.2]paracyclophane was brominated to give the 2-bromo[2.2]paracyclophane, which was converted to the Grignard reagent via activated magnesium and carboxylated on a vacuum system to give 4. Compound 4 was then resolved with *l*-(−)-α-methybenzylamine, and reduced via the Birch reduction in the normal manner to give resolved 5.

RESULTS

In taking the electronic spectrum of the tetra-hydro[2.2]paracyclophane system, the method of choice would be to take the spectrum in the vapor phase. Unfortunately, a polymer was formed from 5 under these conditions whose spectrum was the same as that for *p,p′*-dimethylbibenzyl.[10] Apparently, there was cleavage of the methylene bridge and rearomatization of the benzene moiety. Therefore, the UV and CD spectra were taken in solution, and the resulting data appear in Table
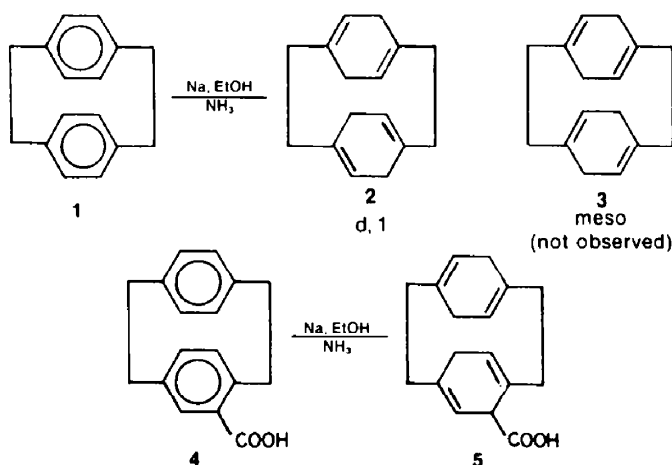
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Table 1. Ultraviolet and circular dichroism absorptions for 2,5,3',6'-tetrahydro[2.2]paracyclophane-2-carboxylic acid (5)

	CD		UV	
	λ (nm)	$[\theta] \times 10^4$	λ (nm)	ϵ_{max}
Isopentane Solvent	236	-1.825	206.3	5271
	201	-16.38		
	180	?		
Ethanol Solvent	205	-15.28	208.2	5915

1. For 5 in isopentane, the UV spectrum consisted of a peak at 206.3 nm and the CD spectrum had peaks at 236 nm and 201 nm with another peak indicated below 180 nm. From the CD spectrum, it can be seen that the electronic spectrum consists of three transitions. The absolute geometry of chiral 5 was correctly predicted by +XYZ sector rule for wavelength absorption.[11]

The lowest energy transition is tentatively assigned as a $\pi x \to 3s(\delta^*)$ Rydberg-like transition. This transition was identified as $\pi x \to 3s$ on the basis of its weakness relative to the next lower energy transition[11] and its apparent shift upon a change of solvents.[11,12] For isolated olefins, this Rydberg-like transition has been observed to be on the lower energy wing of the first low energy transition.[12] In ethanol, the Rydberg-like transition appears to have shifted under the first low energy transition where it is not readily observable. In isopentane, the Rydberg-like transition is observed as a shoulder on the stronger absorption at 201 nm.

The next two transitions observed in the CD (isopentane) are an oppositely signed couplet. One band of the couplet is observed at 201 nm with the other band indicated below 180 nm. The UV spectrum should have bands corresponding to those seen in the couplet. The first band in the UV is seen at 206.3 nm (isopentane) and the second is indicated below 180 nm.[11] This couplet is assigned to mixing of $\pi x \to \pi x^*$ and $\pi x \to \pi y^*$. An oppositely signed CD couplet comes from the interaction of the collinear transition moments in a chiral molecule when one is an electric and the other a magnetic multipole of the same order. It has been implied that the oppositely signed couplet of chiral olefins arises from the mixture of an electric- and a magnetic- dipole zero-order excitation through perturbation. For ethylene the $\pi x \to \pi x^*$ transition with a Z-polarized electric dipole moment is accompanied by a near-degenerate quadrupole transition and if this is $\pi x \to \pi y^*$, or $\pi y \to \pi x^*$, it could have the XY- component of an electric quadrupole and the Z-component of a magnetic dipole as the leading transition moments.[11] On energy grounds, in chiral alkenes $\pi x \to \pi y^*$ is virtually degenerate with $\pi x \to \pi x^*$, easily allowing mixing. The couplet in chiral olefins arises mostly from the mixing of the zero-order excitations $\pi x \to \pi x^*$ and $\pi x \to \pi y^*$.[11] The absorption bands in both the UV and the CD are expected to have similar areas and these bands which come from the virtual degeneracy of the $\pi x \to \pi x^*$ and $\pi x \to \pi y^*$ transitions in substituted olefins.[11] The absence of spectra below 180 nm makes this hard to determine, but the trends are present. The major absorption around 200 nm and the absorption indicated below 180 nm are assigned to a mixing of the $\pi x \to \pi x^*$ and $\pi x \to \pi y^*$ transitions.

Another band which is expected to be present in both the UV and the CD is the carboxylic acid absorption. Carboxylic acids usually absorb weakly between 200 and 210 nm when they are not conjugated.[11,12] There is an indication that the carboxylic acid $n \to \pi^*$ absorption is buried under the stronger $\pi \to \pi^*$ absorption of the olefin in the same region. The intensity of the absorption in this region is greater for 2,5,3',6'-tetrahydro[2.2]paracyclo-phane-2-carboxylic acid (5) than for 2,5,3',6'-tetra-hydro[2.2]paracyclophane (2).[1] The carboxylic acid would be expected to show a CD absorption since it is located in a dissymmmetric environment. Since there is no resolved 2,5,3',6'-tetrahydro[2.2]paracyclophane available (2), it is not possible to compare the CD spectra. Since in the UV region intensities are additive, the increased absorption of the acid compared to the hydro-carbon is taken as evidence that the acid $n \to \pi^*$ lies under the stronger $\pi \to \pi^*$. The major absorption around 200 nm also experiences a blue shift upon going from a polar to a nonpolar solvent, which does not indicate a $n \to \pi^*$ transition, but is indicative of a $\pi \to \pi^*$ transition. Also, the weak CD band at 236 nm is not assigned as a red-shifted acid $n \to \pi^*$ transition since 1,4-dihydroben-zoic acid shows no abosption above 200 nm.[15] This effectively rules out the assignment of the 236 nm absorption as originating from an $n \to \pi^*$ transition. The $n \to \pi^*$ transition of the acid is therefore believed to lie under the strong $\pi \to \pi^*$ transition on the high energy side of the band.

The rotational and dipole strengths and the anistropy factor were not determined because the overlapping of these bands makes it difficult to determine these values from experimental data. The Rydberg band appears to be on the order of 0.1, the strength of the first major low energy band, but it is partly obscured by the low energy wing of this band. The occurrence of both the acid $n \to \pi^*$ and the first low energy olefin transition make it difficult to separate the two transitions. The values for the highest energy olefin transition cannot be obtained since the complete band is not observed.

The UV spectrum of 5 absorbs at 208.2 nm in ethanol and 206.3 nm is isopentane. This is a lower energy absorption than might be expected for a trisubstituted ethylene present in a 1,4-cyclohexadiene moiety, because the $\pi \to \pi^*$ transition of trisubstituted ethylenes is about 184 nm,[10,14] and 1,4-cyclohexadiene absorbs at 156 nm[17] (the $\pi \to \pi^*$ transition of ethylene is at 165 nm). Since 5 absorbs at longer wavelengths, then there must be other considerations in this system.

A possible effect that could account for the long wavelength $\pi \to \pi^*$ transition is twisting around a double bond. Steric strain can be most efficiently relieved by

twisting of the double bond in olefins. The steric inter-
ferences raises the potential energy of both the ground
and excited states, but this effect is probably larger in the
ground than in the excited state because of the larger
bond order of the ground state. The transition thus
requires less energy moving it to longer wavelengths.[18]
2,5,3',6'-Tetrahydro[2.2]paracyclophane-2-carboxylic acid
(5) is not predicted to have twisted olefin groups because
of the flexibility of the 1,4-cyclohexadiene moiety and
the lack of very bulky groups on the olefins. The 1,4-
cyclohexadiene rings found in 2,5,3',6'-tetra-
hydro[2.2]paracyclophanes can easily flex and are not
forced into rigid conformation which would strain the
double bonds.[4,5] The groups immediately around the
olefins in 2,5,3',6'-tetrahydro[2.2]paracyclophane are
methylenes which are relatively small groups. A trisub-
stituted olefin endocyclic to a somewhat constrained
cyclohexane ring is α-pinene. Electron diffraction studies
indicate that the double bond of α-pinene is not dis-
torted.[19] There is apparently enough flexibility in the ring
and the substituents small enough that there is no steric
strain placed on the double bond. A compound with a
1,4-cyclohexadiene ring locked into a rigid conformation
is anti-7-norbornenyl p-bromobenzoate which has a very
slight twist (1°) of the double bond.[20] The olefins in
2,5,3',6'-tetrahydro[2.2]paracyclophane are certainly not
as strained a system as is anti-7-norbonenyl p-bromoben-
zoate and should not have any twisting of its olefin
groups. Hence, twisting of the olefin groups should not
account for the long wavelengths absorption of 2,5,3',6'-
tetrahydro[2.2]paracyclophane.

The mixing of excited states in chiral olefins appears to
be responsible for absorptions at long wavelengths. The
α-(−)-pinene CD absorption shows transitions at 201 nm
and 177 nm.[11] α-(−)-Pinene would be expected to show
a strong $\pi \to \pi^*$ absorption at 184 nm, as would be
expected for nonchiral trisubstituted olefin.[18] For α-(−)-
pinene it has been suggested that the couplet of
oppositely signed CD bonds in the far UV regions arise
from the mixing of the excited states under either a static
or a dynamic perturbation of the symmetric olefin
chromophore by dissymetrically located substituents.[6]
The perturbation of the olefin chromophore in chiral
olefins gives two $\pi \to \pi^*$ transitions of almost equal
intensity with one appearing at longer than expected
wavelengths.

Another important interaction is embodied in the 1,4-
cyclohexadiene moiety itself. The $\pi \to \pi^*$ transition for

1,4-cyclohexadiene is located at 156 nm and for ethylene
at 165 nm.[17] 1,4-Cyclohexadiene absorbs at higher energy
because of the parallel electric dipole interaction of the
isolated olefins, predicted from the vector addition of the
electric dipoles.[17] 2,5,3',6'-Tetrahydro[2.2]paracyclo-
phane-2-carboxylic acid (5) contains 1,4-cyclohexadiene
moieties with a significant difference. 1,4-Cyclohexadiene
itself is flat[21] whereas the 1,4-cyclohexadiene moiety in
2,5,3',6'-tetrahydro[2.2]paracyclophane systems is
puckered,[5,7] which relieves the steric strain present in
the parent compound.[22] 2.5-[2.2.2]Bicyclooctadiene and
2,5-[2.2.1]bicycloheptadiene can be examined as models
for the effects of puckering on a non-conjugated cyclo-
hexadiene. 2,5-[2.2.2]Bicycloheptadiene absorbs at
198 nm[23] and 2,5-[2.2.1]bicycloheptadiene absorbs at
211 nm.[3a] Both of these molecules contain a puckered
cyclohexadiene ring and absorb at much longer
wavelengths than does flat 1,4-cyclohexadiene. None of
these molecules is optically active ruling out mixing of
the $\pi x \to \pi x^*$ and $\pi x \to \pi y^*$ excited states. A possible
explanation is that the puckered conformation in the
ground state[24] is somewhat unstable, decreasing the
transition energy in going from the ground to the excited
state. This possible puckering effect can also be seen in
2-[2.2.2]bicyclooctene and 2-[2.2.1]bicycloheptene: these
molecules absorb at 190.3 and 195 nm, respectively;[3,23] at
longer wavelengths than for 1,2-cis-disubstituted ethy-
lenes which absorb at 175 nm.[16] These ideas are further
supported by CNDO/2 calculations done in this study on
flat and puckered 1,4-cyclohexadiene[17] (Table 2), which
show the ground state of the flat molecule is more stable
than that for the puckered molecule. Also, flat 1,4-
cyclohexadiene is correctly predicted to absorb at higher
energy than ethylene[17] by ca 8 nm, and puckered 1,4-
cyclohexadiene is correctly predicted to absorb at
several tens of nm lower energy than ethylene. Thus,
CNDO/2 calculations predict that the $\pi \to \pi^*$ transition
of non-conjugated cyclohexadiene is shifted to longer
wavelengths when forced into the "boat" conformation.

Implicit in the consideration of 1,4-cyclohexadiene in
the "boat" conformation is the non-conjugated inter-
action[3] between olefins in the same ring. Both 2,5-
[2.2.2]bicyclooctadiene and 2,5-[2.2.1]bicycloheptadiene
absorb at longer wavelengths than do their mono-olefin
counterparts (8 and 17 nm, respectively). The difference
in the diene absorption could be that the π-bonds are
closer in 2,5-[2.2.1]bicycloheptadiene giving more efficient
overlap and lowering the energy of the $\pi \to \pi^*$ transition.

Table 2. CNDO/2 calculations for ground and πx^* excited states and wavelength of $\pi x \to \pi x^*$ absorption for flat
1,4-cyclohexadiene, puckered 1,4-cyclohexadiene and ethylene

	1,4-Cyclohexadiene		
	Flat	Puckered (20°)	Ethylene
Ground State (In Atomic Units)	−47.5765	−46.5791	−17.0677
πx^* Excited State (In Atomic Units)	−47.1196	−46.2353	−16.6442
Energy Difference (In Atomic Units)	0.4569	0.3438	0.4235
Calculated Wavelength of Absorption (nm)	99.7	132.5	107.6

The "puckering effect" can be attributed to the energy difference between ground and excited states becoming smaller and to non-conjugated interaction.

The last interaction which must be considered is that between the decks of 2,5,3',6'-tetrahydro[2.2]paracyclophane-2-carboxylic acid. Interaction between decks is significant in paracyclophane system as evidenced by the spectra of several paracyclophanes with various sizes of methylene bridges. Interaction is significant for the smaller paracyclophanes, but when the number of methylenes in each bridge reaches four, then the spectrum becomes similar to that found for the open chain analog p,p-bibenzyl.[25] To explore the nature of the interaction between the decks of 2,5,3',6-tetrahydro[2.2]paracyclophane systems, CNDO/2 calculations (Table 3) on two ethylenes were performed with the orientation of two interacting olefins of structure 2 as the two olefins were allowed to approach one another. The energy of the overall system decreases as the two ethylenes become close, but to the extent of less than 0.004 atomic units (corresponding to a change of less than 1 nm). Therefore, it hardly seems likely that interdeck interactions contribute significantly to the bathochromic shift of the main electronic absorption of 2,5,3',6-tetrahydro[2.2]paracyclophane-2-carboxylic acid.

CONCLUSIONS

The main reasons for the unexpectedly low frequency absorption of 2,5,3',6'-tetrahydro[2.2]paracyclophane-2-carboxylic acid (5) appear to be due to the puckering of the 1,4-cyclohexadiene moiety. Interaction between the two decks appears to be minimal and contributes substantially nothing to the electronic transitions of 5. Mixing of states makes an important contribution to the spectra of chiral olefins but it is not known how this will affect the shifting of the $\pi \rightarrow \pi^*$ transition. Mixing of states probably affects the spectrum since chiral alkyl substituted olefins absorb at longer wavelengths than do achiral alkyl substituted olefins. The interaction of the parallel electric dipoles in the 1,4-cyclohexadiene moieties should move the $\pi \rightarrow \pi^*$ transition to higher energy. Twisting of double bonds is not believed to occur and therefore should not make a contribution to the spectrum. Thus, the long wavelength absorption of 2,5,3',6'-tetrahydro[2.2]paracyclophane is attributed to a $\pi \rightarrow \pi^*$ transition bathochromically shifted by mixing of orbitals, substituent and puckering effects and with a smaller blue shift contribution from parallel dipole interaction. The low energy side of this band is extended to longer wavelengths since a $\pi \rightarrow 3s$ Rydberg-like transition is partially hidden under this low energy wing. The absorption bands for 2,5,3',6'-tetrahydro[2.2]paracyclophane-2-carboxylic acid were assigned as follows: a) 236 nm as $\pi \rightarrow 3s$, b) 201 nm as $\pi x \rightarrow \pi x^*$, c) the absorption indicated below 180 nm as $\pi x \rightarrow \pi y^*$. The n $\rightarrow \pi^*$ absorption of carboxylic acid is believed to lie under the $\pi x \rightarrow \pi x^*$ transition, probably on the high energy side of this band. 2,5,3',6'-Tetrahydro[2.2]paracyclophane-2-carboxylic acid obeys the +XYZ sector rule for the long wavelength absorption and the +XYZ sector rule for the short wavelength absorption of the CD couplet.

EXPERIMENTAL

All reagents were reagent-grade commercial chemicals unless otherwise indicated. $l-(-)$-αMethylbenzylamine, spectrophometric grade 2-methyl-butane, and [2.2]paracyclophane were obtained from Aldrich Chemical Co., Milwaukee, WI 53233 and were used as received. Anhyd AlCl$_3$, Br$_2$, and I$_2$ were of analytical reagent grade and were purchased from Mallinckrodt Chemical Works, St. Louis, MO 63160. Na and K were cut into small pieces and washed free of oil with dried ether or hexane. Anhyd ammonia (Dixie Chemical, Houston, Texas) was of refrigeration grade and condensed directly into the reaction vessel. EtOH was refluxed continuously over CaO and freshly distilled prior to use. THF was refluxed continuously over a mixture of two parts Na to one part K and was freshly distilled prior to use. Optical rotation data were obtained from a Rudolph Model 80 polarimeter. CD spectra were obtained from a JASCO J-40A Automatic Recording Spectropolarimeter, while purging with nitrogen. UV spectra were taken on a Beckman Model 25 Spectrophotometer with a one centimeter length cell. M.ps were taken on a Thomas Hoover Capillar M.P. Apparatus and are uncorrected for atmospheric pressure. 2-Bromo[2.2]paracyclophane was prepared by the procedure of Cram.[7]

[2.2] Paracyclophane-2-carboxylic acid (4) via activated Grignard

Mg (1.5 g), a catalytic amount of I$_2$ and 10 g 1-chlorobutane was added to a 3-neck round bottom flask equipped with a dropping funnel, mechanical stirrer and condenser under an argon atomsphere. The mixture was heated until a while solid was formed (MgCl$_2$) and white smoke was present in the flask (octane). Dry THF (250 ml) and 3.2 g K were added, and the mixture was brought to reflux while stirring. After 3 hr a small aliquot was tested to make sure all K was consumed. 2-Bromo[2.2]paracyclophane (2.37 g) was dissolved in 50 ml dry THF and added dropwise to the soln. The soln was stirred for a 0.5 hr and allowed to reflux for 16 hr. The soln was then poured into a flask equipped with a stirring bar, degassed and placed on a vacuum line. The soln was frozen (liquid N$_2$) and a large excess (1.75 g) of CO$_2$ was then frozen on top of the Grignard reagent. The flask was packed in dry ice and stirred. When the dry ice had sublimed, the mixture was removed from the vacuum line, diluted with water, concentrated by a rotary evaporator, and poured into 200 ml of a 5% HClaq. NaCl was added and the mixture was extracted with ether. The ether layer was then extracted with brine and 10% NaOH. The 10% NaOH layer was acidified yielding a while fluffy solid, 1.022 g (97.5%), after sintering, m.p. 210–221 (Lit. 223.5–224.5).[7]

Resolution of [2.2]paracyclophane-2-carboxylic acid

[2.2]Paracyclophane-2-carboxylic acid (0.551 g) and 0.2884 g $l-(-)$-α-methylbenzylamine were stirred in 20 ml CHCl$_3$ for 1 hr. Ether was added and the soln was placed in an ice bath for 48 hr. The soln was filtered and the filtrate washed with ether yielding 0.7316 g of a dusty white salt. The salt was dissolved in 12 ml anhyd EtOH and was allowed to precipitate in an ice bath. Thereby, 0.2041 g of salt was obtained and dissolved in 3.4 ml abs EtOH and allowed to precipitate, with 0.17 g salt being recovered, $[\alpha] = +95.44$ (0.68, CHCl$_3$), Lit.[8] $[\alpha]_D = +97°$. The salt

Table 3. CNDO/2 calculations for the energy of ground states of two ethylenes situated at various distances with geometry as in structure 2

Distance Between Ethylenes (A)	Energy (Atomic Units)
2.83	−34.1372
3.55	−34.1345
4.27	−34.1347
5.76	−34.1348
10.0	−34.1348

was stirred in a mixture of $CHCl_3$ and dil HCl. The $CHCl_3$ layer was separated and extracted with 10% NaOH. The aqueous extract was acidified, and cooled in an ice bath, and extracted with $CHCl_3$; the $CHCl_3$ extract was concentrated on a rotatory evaporator giving the free carboxylic acid, $[\alpha]_D = +164.1$ (0.372, $CHCl_3$), Lit.[8] $[\alpha]_D = +164°$; CD $\lambda, [\theta]$: 203, -3.03×10^4; 216, 3.33×10^4; 237, -1.53×10^5; 273, 8.48×10^4; 297, -8.48×10^3, 327, 2.24×10^4, Lit.[8,9] the same.

2,5,3',6'-Tetrahydro[2.2]paracyclophane-2-carboxylic acid (5)

(+)-2-Carboxy[2.2]paracyclophane (0.0654 g) was dissolved in 30 ml dry THF and placed in a 250 ml 3-neck flask equipped with a magnetic stirrer. Liquid ammonia (75 ml) was condensed into the flask. Na (0.120 g) and 1.2 ml dry EtOH were added over a period of 30 min. The reaction was conducted and worked up as before[5] to give 0.0635 g (95.6%) white crystals. The crystals were washed with petroleum ether, m.p. 157.5–159 (Lit.[5] 158–159, $[\alpha]_D = -101°$ (0.326 $CHCl_3$); UV and CD in Table 1.

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