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Molecular Structure and Vibrational Circular Dichroism of Tris(*trans*-1,2-cyclopropanediyl)dimethylene Diborate, a New, Stable Bridged Borate Ester

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In this paper are presented the preparation, properties, crystal structure, and infrared, Raman, and vibrational circular dichroism (VCD) spectra of the title compound, a novel triply bridged diborate ester, $B(OCH_2C_3H_4CH_2O)_3B$. This compound is unusually resistant to hydrolysis and crystallizes in the hexagonal system, space group $P6_3$, with $a = 11.294$ (3) Å, $c = 7.644$ (4) Å, and $Z = 2$. Its structure was solved by direct methods and refined to a conventional R factor of 0.074 for 1290 unique data. The molecule has C_3 symmetry with the cyclopropane bridges imposing helicity. The IR, Raman, and VCD spectra can be correlated to those of previously studied disubstituted cyclopropanes. Very large VCD signals were observed which appear to arise from coupling of the symmetry-related parts of the molecule.

Introduction

We have a continuing interest in obtaining small, stereochemically restricted chiral molecules as test cases for various proposed theoretical models of vibrational circular dichroism (VCD).¹ Toward this goal, we have prepared a series of *trans*-1,2-disubstituted cyclopropane compounds with either two identical² or two different³ substituents. In an effort to prepare *trans*-1,2-dimethylcyclopropane via reduction of *trans*-1,2-cyclopropanedicarboxylic acid (I) with diborane we have made a new borate ester in significant yield that is unusually resistant to hydrolysis. As will be shown in this paper, the compound consists of two boron atoms bridged with three *trans*-1,2-bis(oxy)methylcyclopropane groups to give an overall molecular formula of $B(OCH_2-C_3H_4-CH_2O)_3B$ (II).

The hydrolytic stability of this ester is of interest in terms of general organoboron chemistry. Normally, in the reduction of a carboxylic acid, $RCOOH$, by BH_3 an intermediate $(RCO)_2B$ is formed, which in the presence of excess BH_3 is further reduced to $(RCH_2O)_2B$. These borate esters are in turn typically easily hydrolyzed to the corresponding alcohols.⁴ For BH_3 reduction of a difunctional species such as I, the logic of the formation of a triply bridged double-borate intermediate is clear. The intermediate II, in this case, is not easily hydrolyzed to *trans*-1,2-bis(hydroxymethyl)cyclopropane (III) but actually crystallizes as a stable product after the hydrolysis reaction.

Data presented in this paper include results of Raman, infrared, and VCD spectral studies as well as a single-crystal X-ray structure determination which confirms the unusual molecular geometry. Its molecular symmetry (C_3) and apparent restricted conformational flexibility make this molecule an interesting model compound for future VCD analyses.

Experimental Section

Synthesis. In a typical reaction 6.5 g of the diacid (I) (0.05 mol) prepared as previously reported² was dissolved in 50 mL of THF and then added dropwise to 200 mL of a stirred, cooled 1 M BH_3 /THF solution (Aldrich). After it was stirred for 3 h at room temperature, the mixture was recooled in an ice bath and small pieces of ice were slowly added until the BH_3 was destroyed as determined by cessation of gas evolution. The THF was removed with a rotary evaporator, leaving an aqueous suspension of a white precipitate. Since we were primarily interested in obtaining III, dilute acid or base was then added, and the mixture was stirred with gentle heating (60 °C) for ~3 h in all of our reactions. Extraction with ether yielded a mixture containing the product II and III plus boric acid. II and III were

separated from the boric acid by extraction with chloroform. The borate (II) was then separated from any III by recrystallization from chloroform as colorless hexagonal needles with mp >200 °C. The yield of borate was approximately 22%, but since it was not the desired product and was always subjected to hydrolysis, the yield was clearly not optimized.

Product Characterization. Mass spectroscopic analysis of II revealed peaks at 322 and 321 in a ratio (approximately 2:1) consistent with the natural abundances of boron isotopes in a $C_{15}H_{24}O_6B_2$ formulation. Elemental analysis was consistent with this formulation. Anal. Calcd: C, 55.96; H, 7.51; B, 6.72; O, 29.81. Found: C, 55.87; H, 7.60; B, 6.40; O, 30.31. The compound was somewhat soluble in $CHCl_3$, CCl_4 , CS_2 , ether, and CH_3CN and was insoluble in water. In 1 M acid or base at high (reflux) temperatures, we obtained dissolution. The product extracted from these solutions with ether had an NMR spectrum different from that of either II or III, suggesting decomposition.

The ^{11}B NMR spectrum of II consisted of a single peak near δ 47 (boron trifluoride etherate external standard). This is indicative of a tris(organyloxy)boron compound in which the boron atoms are bound to three equivalent oxygen atoms and in which all borons are equivalent.⁵ The low-resolution proton NMR spectrum showed three broad bands of equal areas at δ 4.2, 3.0, and 1.4 and a sharp complex multiplet centered at δ ~0.4 (all referenced to Me_4Si). The last two features correlate well with those we have observed for other *trans*-substituted cyclopropanes.² The higher δ peaks must be due to the oxygen-bound CH_2 's, whose hydrogens are not equivalent. All of these data are consistent with a molecular formula of $B(OCH_2C_3H_4C-H_2O)_3B$. Infrared spectra and Raman spectra also support this formulation and will be discussed in more detail below. Of interest to the structural characterization is that no $C=O$ bands occur and that sharp bands characteristic of substituted cyclopropanes are evident.²

The optically active borate complex was prepared by starting with resolved diacid I, which was obtained as previously described,² and proceeding as described above. In this case, white, hexagonal prismatic crystals were also formed. Solutions of (+)II were prepared by reaction of BH_3 with (-)-1*R*,2*R*-I, ~84% ee, and gave an oppositely signed optical rotation, $[\alpha]^{25} = +234^\circ$ ($c = 1.07$, $CHCl_3$). (If this were corrected for the partial racemization of the starting material, this would indicate $[\alpha]_D \approx +279^\circ$.) These results, along with the virtually identical IR spectra of the racemic and resolved species, suggest that only one structurally isomeric form of the borate exists (two optical enantiomers). We have made no further attempt to determine the

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Table I. Experimental Data for the X-ray Diffraction Study

Unit Cell Data on $B(OCH_2C_3H_4CH_2O)_3B$	
$a = 11.294 (3) \text{ \AA}$	mol wt: $321.977 \text{ g mol}^{-1}$
$c = 7.622 (4) \text{ \AA}$	$\rho(\text{calcd}) = 1.270 \text{ g cm}^{-3}$
$V = 842.1 (7) \text{ \AA}^3$	$\rho(\text{obsd}) = 1.27 (2) \text{ g cm}^{-3}$
space group: $P6_3$ (No. 173)	$F_{000} = 344 \text{ e}$
$Z = 2$	

Details of Collection and Refinement

radiation: Mo $K\alpha$ ($\lambda = 0.71069 \text{ \AA}$), graphite monochromator
 abs coeff: $\mu(\text{Mo } K\alpha)$, 0.88 cm^{-1}
 cryst shape: hexagonal prism
 cryst dims: $0.3 \times 0.3 \times 0.7 \text{ mm}$
 scan speed: variable, $3.91\text{--}299.30^\circ \text{ min}^{-1}$
 scan range: 1.10° below 2θ ($K\alpha_1$) to 1.15° above
 bkgd counting time: $0.5 \times$ scan time
 2θ limits: $2.0\text{--}55.0^\circ$
 refltns collected: 1550 (including 51 stds)
 unique refltns: 1290
 unique data used: 1285 with $F_o^2 > 2.5\sigma(F_o^2)$
 no. of variables: 101
 goodness of fit: 0.663
 $R = 0.0743$
 $R_w(F) = 0.0950$

structural purity of the racemic material.

Spectroscopy. Infrared absorption and VCD spectra from 3200 to 900 cm^{-1} were obtained on the UIC spectrometer with use of techniques that have been previously described.^{1,6} This is one of the first reports of VCD spectra in the $1000\text{--}cm^{-1}$ region now made accessible by implementation of previously proposed optical changes.⁶ These include substitution of a ZnSe modulator (Hinds) and ZnSe lens (Laser Power Optics) for the CaF_2 ones and use of a $9\text{-}\mu\text{m}$ blaze, 100 groove/mm grating (Bausch and Lomb).⁷ Spectra were run on solution samples held in a variable path length cell with NaCl windows. CS_2 and CCl_4 solutions were used to cover the entire region. VCD spectra were calibrated with a CdS (II–IV optics) birefringent plate and grid polarizer combination,¹ and signs were determined by comparison to spectra of 3-methylcyclohexanone.^{1,6}

Laser Raman spectra were run on a single crystal of the borate in two crystal orientations with a conventional instrument. Fourier transform infrared (FT IR) spectra were obtained on a Nicolet MX1 instrument at 2-cm^{-1} resolution.

X-ray Crystal Structure Data Collection. White crystals of the (+) borate (II) were grown by slow precipitation from chloroform. The data crystal was mounted on a thin glass fiber affixed to the 001 face of the hexagonal prism.

Preliminary precession photographs had indicated Laue symmetry $6/m$ and the systematic absence $00l$ for $l = 2n + 1$. Because the compound was chiral, having been synthesized from (–)I, the otherwise possible space group $P6_3/m$ was ruled out and the noncentrosymmetric, polar space group $P6_3$ was unambiguously indicated. Data collection was carried out with a Syntex (Nicolet) P3/F automatic diffractometer equipped with a graphite-crystal monochromator.⁸ Lattice parameters were accurately determined by least-squares procedures using the angular positions of 25 independently centered reflections well separated in reciprocal space. Crystal and diffractometer data are summarized in Table I. Data collection was carried out at approximately 26°C with Mo $K\alpha$ radiation using $\theta\text{--}2\theta$ scans. One-sixth of a sphere of data was collected, $h, k, \pm l$, out to $2\theta = 55^\circ$. The intensities of 3 standard reflections, measured every 93 reflections, showed no significant decay. Neutral-atom scattering factors from Cromer and Mann⁹ were used for all nonhydrogen atoms. Those from Stewart et al.¹⁰ were used for hydrogen atoms. The net intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied.¹¹

Solution and Refinement of the Structure. The structure determination and refinement were carried out with use of the SHELXTL

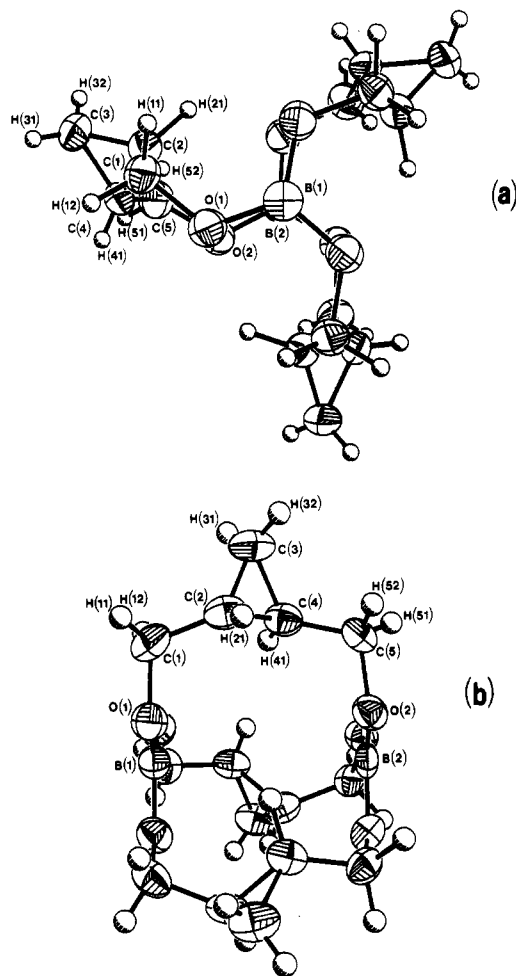


Figure 1. ORTEP perspective views of a molecule of $B(OCH_2C_3H_4CH_2O)_3B$. The top view (a) shows left-handed helicity and eclipsed BO_3 groups; the side view (b) shows near-coplanarity of $\text{B}(\text{OC})_3$ groups. Hydrogens are represented by small arbitrarily sized spheres.

series of programs,¹² revision 3.0. All calculations were performed on a Syntex (Nicolet) R3 crystallographic computing unit. The E map with the highest combined figure of merit yielded the positions of all the non-hydrogen atoms. Several cycles of isotropic refinement, applying unit weights to the reflection data and ending in a difference map, gave the locations of all the hydrogen atoms. At this point the model gave $R = 0.1249$, where $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The hydrogen atoms were inserted, and all the non-hydrogen atoms were converted to anisotropic temperature factors. Eight cycles of full-matrix least-squares refinement then converged with $R = 0.074$ and $R_w = 0.0962$, where $R_w^2 = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$. The refinement minimized $\sum w(|F_o| - |F_c|)^2$ and used counterweights where $w^{-1} = \sigma^2(F_o) + cF_o^2$, and c was refined as a parameter whose final value was 0.019 . There was no correction for secondary extinction. The largest peak in the final difference map was 0.55 e/\AA^3 , located 0.33 \AA from O(2). Refinement using enantiomorphic coordinates converged equally well. The $1R,2R$ absolute configuration at the substituted cyclopropane, represented in Figure 1 and the stereoview of the unit cell shown in the supplementary material, is that of the predominant enantiomorph of the starting material, I.¹³ The final fractional coordinates and thermal parameters of the refined atoms are given in Table II. A listing of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Crystal Structure. The molecular geometry is illustrated in Figure 1. The molecule has C_3 symmetry. The two non-equivalent borons lie on special positions on the crystallo-

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Table II. Final Positional Parameters for B(OCH₂C₃H₄CH₂O)₃B

atom	x	y	z
B(1)	1/3	2/3	0.4713 (10)
B(2)	1/3	2/3	1
O(1)	0.1937 (2)	0.6041 (2)	0.4712 (9)
O(2)	0.1965 (2)	0.6206 (2)	0.9994 (9)
C(1)	0.1240 (5)	0.6799 (5)	0.4751 (10)
C(2)	0.0708 (3)	0.6786 (3)	0.6552 (11)
C(3)	0.0648 (4)	0.8020 (4)	0.7193 (12)
C(4)	0.1669 (4)	0.7689 (4)	0.7952 (10)
C(5)	0.1453 (3)	0.7137 (3)	0.9776 (10)
H(11)	0.0467 (49)	0.6448 (48)	0.4114 (70)
H(12)	0.1642 (44)	0.7432 (52)	0.4511 (71)
H(21)	0.0065 (33)	0.6018 (35)	0.6961 (45)
H(31)	0.1000 (53)	0.8699 (55)	0.6579 (80)
H(32)	-0.0049 (47)	0.7860 (46)	0.7855 (59)
H(41)	0.2704 (38)	0.8402 (36)	0.7576 (49)
H(51)	0.1984 (44)	0.7951 (45)	1.0641 (66)
H(52)	0.0456 (46)	0.6644 (40)	1.0012 (66)

graphic threefold axis. Each boron is bound to three oxygens in an undistorted planar array. These BO₃ groups are bridged by three -CH₂C₃H₄CH₂- groups, which, due to their trans substitution, lower the potential molecular symmetry and make the molecule chiral. The carbons C(1) and C(5) corresponding to the trans-CH₂ groups are nearly coplanar with their respective BO₃ groups. But, since the P₆ space group is polar, these B(OCH₂)₃ groups are not equivalent and, in fact, C(5) deviates by ~0.15 Å from its BO₃ plane. We have not determined if this asymmetry also occurs in the solution structure or if other crystal phases exist.

As seen in Figure 1, the two B(OCH₂)₃ groups in the molecule have the same spiral sense with regard to the crystal C₃ axes and are approximately mirror images of each other, being only slightly twisted from an eclipsed geometry. The -C₃H₄- bridging groups, however, destroy any possible mirror plane due to their helicity, which results from their trans substitution. This pseudosymmetry has implications for the VCD interpretation (vide infra). Additionally, the cyclopropane rings give the molecule a definite helicity with a pitch of 44.5° and the sense of a left-handed screw as illustrated in Figure 1 and in the stereoview of the unit cell shown in the supplementary material. (Pitch here is defined as the angle between the B(1)-B(2) axis and the plane of the cyclopropane ring.¹⁴) Furthermore, we find that each cyclopropane ring makes angles of 76.2 and 103.8° with respect to its two symmetry-equivalent neighbors in the molecule. This molecule thus provides an unusual example of a conformationally stable C₃ system with several degenerate vibrations for which VCD can be studied.

Table III lists unique bond lengths, angles, and contact distances. Angles involving the hydrocarbon H atoms are omitted, as they are within normal limits. In particular, the short B-O bond length is consistent with previous electron diffraction results on B(OCH₃)₃.¹⁵ This has been interpreted in the past to indicate π-back-bonding to the boron and to explain the weak Lewis acidity of borate esters compared to that of other borates. Along these lines, it is interesting to note that the BO₃ groups are stacked in the crystal in a nearly eclipsed inter- as well as intramolecular arrangement. This arrangement might give rise to the possibility of a π-electron interaction between the molecules. However, if the Lewis acidity were strong, we might expect a more staggered and less symmetrical arrangement. The large B-B distances (~3.5 Å intermolecular and ~3.9 Å intramolecular) presumably minimize such an interaction. The intermolecular space is partially occupied by the hydrogen from the trans-CH₂ groups

Table III. Selected Interatomic Distances (Å) and Angles (deg) for B(OCH₂C₃H₄CH₂O)₃B with Estimated Standard Deviations in Parentheses^a

B(1)-O(1)	1.368 (2)	C(1)-H(11)	0.91 (5)
B(2)-O(2)	1.362 (2)	C(1)-H(12)	0.65 (5)
O(1)-C(1)	1.423 (8)	C(2)-H(21)	0.87 (3)
O(2)-C(5)	1.440 (6)	C(3)-H(31)	0.81 (6)
C(1)-C(2)	1.496 (11)	C(3)-H(32)	0.87 (5)
C(4)-C(5)	1.492 (10)	C(4)-H(41)	1.08 (3)
C(2)-C(3)	1.511 (8)	C(5)-H(51)	1.04 (5)
C(3)-C(4)	1.495 (8)	C(5)-H(52)	0.99 (5)
C(2)-C(4)	1.500 (9)		
O(1)-B(1)-O(1)'	120.0	C(4)-C(2)-C(1)	119.7 (4)
O(2)-B(2)-O(2)'	120.0	C(3)-C(2)-C(4)	59.6 (4)
C(1)-O(1)-B(1)	122.0 (2)	C(2)-C(4)-C(3)	60.6 (4)
C(5)-O(2)-B(2)	121.0 (2)	C(2)-C(4)-C(5)	117.8 (4)
O(1)-C(1)-C(2)	110.7 (6)	C(3)-C(4)-C(5)	118.6 (5)
O(2)-C(5)-C(4)	111.8 (5)	C(2)-C(3)-C(4)	59.9 (4)
C(3)-C(2)-C(1)	119.4 (5)		

^a Primed atoms generated by a rotation about a 3-fold axis.

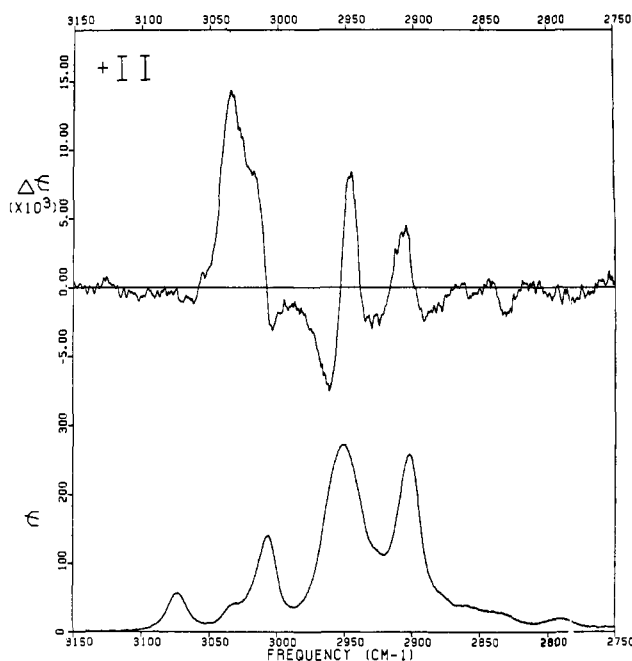


Figure 2. VCD and absorption spectra of (+)II in the CH stretching region. VCD spectra shown are an average of six 3-s time constant scans taken on a 0.003 M CCl₄ solution with a 0.35-cm path length at ~11-cm⁻¹ resolution.

whose closest contacts are ~3.0 Å, H(12) to H(51).

Close inspection of the molecular geometry via a model shows that any possible variation in the separation between borons is limited in range by the particular manner in which the three -CH₂C₃H₄CH₂- bridges bind the BO₃ groups. The resistance to alteration of intramolecular boron-boron distance appears to be due to torsional barriers about the O(1)-C(1), O(2)-C(5), C(1)-C(2), and C(4)-C(5) single bonds. The observed molecular conformation involves approximately staggered vicinal geometries (C-H with C-C). Efforts to create more compact structures using models have resulted in only small changes of the B-B distance even with large rotations about the B-O and C-O bonds. Such changes moreover would entail short oxygen-hydrogen (cyclopropane) contacts. Hence, the molecular structure appears to be quite conformationally stable. An alternative D₃ borate structure can be constructed by bridging staggered rather than eclipsed oxygens. From a model, this geometry does not seem to have abnormal contacts or torsion angles. It may have been formed as an alternate product or may be kinetically unfavorable. Since the B(OCH₂)₃ groups have opposite chiral sense in this

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Table IV. Observed Infrared and Raman Bands for the Borate Ester

FT IR ^a		Raman ^b			FT IR ^a		Raman ^b		
freq, cm ⁻¹	intens, cm ⁻¹ M ⁻¹	freq, cm ⁻¹	rel intens ^f	group freq assignt	freq, cm ⁻¹	intens, cm ⁻¹ M ⁻¹	freq, cm ⁻¹	rel intens ^f	group freq assignt
3089 ^c	11				1185	30			
3069	71	3062	8	CH ₂ as str (cyclo)	1172	80	1178	20	CO sym str
3050	24				1158 ^c	40			
3030	36	3032	15	C*H str	1117	180	1120 ^h		C*H bend (?)
		3021	20	C*H str			1103	8	
3008 ^c	sh				1089	120	1080 ^h		
3003	148	2997 ^g	80	CH ₂ sym str (cyclo)	1068	150			
		2971	sh		1041	270			
		2961 ^g	70	CH ₂ as str	1029	2130 (1330) ^c	1027 ^h		CO as str
2948	296	2951 ^g	70	CH ₂ as str	1010 ^c	60	1008	3	CH ₂ wag (?) (cyclo)
2924	sh	2924 (?)	sh		992	240	997	5	C-C str (?)
2900	273	2902 ^g	65	CH ₂ sym str	969	180	973	4	ring def (cyclo)
2857	59	2860	3				942	4	
2828 ^d		2820	3		873 ^c	sh	871	4	
1729 ^c	132				868	170			
1580 ^e	470				848 ^c	11			
					813 ^c	103			
1484	950			CH ₂ def			815	10	CH ₂ rock (?) (cyclo)
1479	1130			CH ₂ def			796 ^g	230	BO sym str
1473	sh	1472	sh				785	sh	
1465	120	1464 ^g	100	CH ₂ def	691 ^c	30	742	65	C-C str (?)
1458	180				675	90			
1437	650			CH ₂ def (cyclo)	667	150			
1431	830	1432 ^h		CH ₂ def (cyclo)	654	504 (271) ^c			BO ₃ out of plane
1423	120				604	150	602 ^h		
1416	360						570	1	
1393	2610 (1620) ^c	1399 ^h		BO ₃ as str (?)	565 ^c	17	562	1	
1381	sh	1364	3		531	90	525 ^h		BO ₃ def in plane (?)
1345	120	1343 ^h					487		
1324	3490 (2060) ^c	1321 ^h		BO ₃ as str (?)			415	15	
1315 ^c	sh						407 ^h		
1302	240	1305	2	C*H bend (?)			397	12	
1290	60						368	3	
1270	120	1271	2				304	25	BOC def (?)
1251	1070 (880) ^c	1258	1				228	10	
1200	230	1203	75	ring breathe (cyclo)			213	8	
							199	8	
							189	sh	
							147	7	
							105	65	
							85	20	

^a Unless otherwise indicated, data are from 0.0025 M CCl₄ solution, 1.35-mm path, taken at 2 cm⁻¹ resolution over 10 min. ^b Unless otherwise indicated, data are from a single crystal with laser excitation and scattering perpendicular to the *c* axis, with resolution of ~2 cm⁻¹. ^c Determined from 5-min data collection on 0.0054 M CS₂ solution at 1.35-mm path. ^d Seen only in VCD (Figure 2). ^e May be an artifact of correction for solvent absorption. ^f Values above and below 2000 cm⁻¹ determined with different system gains. ^g Band intensity very sensitive to orientation. ^h Band seen with laser parallel to *c* axis and light scatter perpendicular to *c* axis.

hypothetical structure, its VCD could be quite different from that of II.

The expected Lewis acidity of the BO₃ groups (even if small) coupled with the apparent open nature of the molecular structure suggests that II might act as a cage for stabilization or transport of small basic molecules. (The H(41)–H(41)' intramolecular contacts are ~4.1 Å.) Studies to test this idea are now under way.

Vibrational Spectroscopy Results. The VCD and low-resolution IR absorption spectra for the borate II are shown in Figure 2, for the CH stretching region, and in Figure 3, for the mid-IR region down to ~900 cm⁻¹. The region below 1365 cm⁻¹ was run on a CS₂ solution and that above on a CCl₄ solution. Only very small differences in frequencies and line widths were noted between the solutions in the region where these spectra overlapped, but large differences in ϵ were found. These were confirmed to be characteristic of the entire spectrum by comparison of higher resolution FT IR spectra run on samples in each solvent. The borate ester modes expected from analogy to the B(OCH₃)₃ results^{16–19} appear as intense

IR peaks at 653, 1028, and 1390 cm⁻¹. Additional strong bands are found at 1250, 1320, 1430, and 1480 cm⁻¹ in the mid-IR region and 2900, 2950, 3010, and 3075 cm⁻¹ in the CH stretching region. As discussed below, these all correlate well with our previous work on trans-substituted cyclopropanes.^{2,20}

With the aid of the Raman and FT IR spectra many of the bands seen in the VCD can be associated with internal coordinates which should be major components of the normal modes involved. These results are summarized in Table IV. More definite assignments and normal-coordinate analysis demand data from isotopically substituted molecules and will be published separately.

Qualitative comparison of the VCD spectra with data obtained on other optically active cyclopropanes² is of interest here. Perhaps the most striking aspect of such a comparison is that of the relative magnitudes. The borate $\Delta\epsilon$ values are

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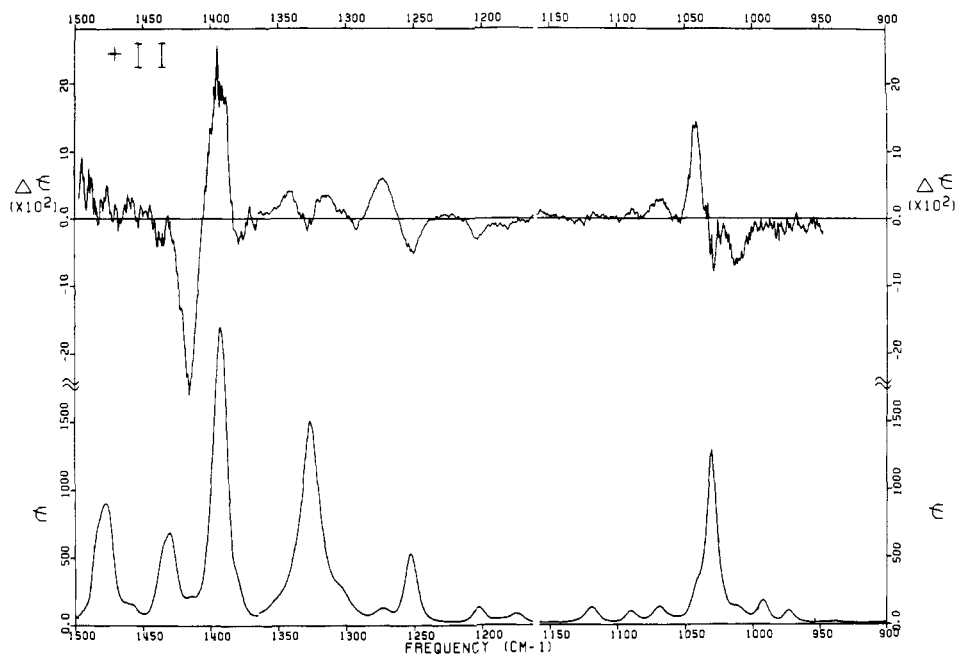


Figure 3. VCD and absorption spectra of (+)II in the mid-IR region: above 1365 cm⁻¹, average of six 10-s time constant scans on a 0.03 M CCl₄ solution at 0.10-cm path length and ~9-cm⁻¹ resolution; below 1365 cm⁻¹, average of four 10-s time constant scans on a 0.0055 M CS₂ solution at 0.10-cm path length and ~7-cm⁻¹ resolution.

nearly an order of magnitude larger than were found for the simple trans-substituted cyclopropanes in both the CH stretching and the mid-IR regions.² In the 1400-cm⁻¹ region, these values correspond to apparent rotational strengths²¹ in excess of 6×10^{-42} esu cm², which makes them among the largest *R* values observed to date for VCD.²²

With regard to individual features, some additional comments are in order. In the CH stretching region, the pattern of the apex CH₂ stretches giving positive VCD (1*S*,2*S*) is not maintained. Higher resolution scans show that the symmetric CH₂ (apex) stretching modes at 3010 cm⁻¹ and the asymmetric (2950 cm⁻¹) and symmetric (2900 cm⁻¹) CH₂ (substituent) stretching modes give derivative-shaped spectra. Coupling of three degenerate modes related by the C₃ axis gives rise to an A and an E mode. To the extent that the VCD is only dependent on this coupling, these will result in a conservative, bisignate line shape.²³ That the bisignate shape of the 2900- and 2950-cm⁻¹ bands has the opposite sense is reasonable since they correlate to local symmetry coordinates with orthogonal transition dipole moments.

At lower energies we find several other bisignate features but, surprisingly, see little VCD associated with the CH₂ scissor modes.² The largest VCD feature occurs near 1400 cm⁻¹ while the largest absorption is at 1324 cm⁻¹ (Table IV). Two intense bands are seen in absorption at 1390 and 1320 cm⁻¹. Since most of the cyclopropanes had an intense IR band between 1290 and 1350 cm⁻¹, it is reasonable to associate the lower frequency band with that mode and the higher with the asymmetric BO₃ stretching mode. We then expect the BO₃ feature to have a shoulder to higher energy due to the ¹⁰B isotope effect. Higher resolution absorption scans indicate a band at 1416 cm⁻¹, which seems too weak for this assignment, and an unresolved shoulder at ~1400 cm⁻¹, which could be the ¹⁰B-¹¹B band. The large 1400-cm⁻¹ VCD could be due to coupling of the BO₃ groups, but the nearly mirror image

symmetry of these groups (see Figure 1) should minimize this.

At lower energies, the 1250-cm⁻¹ band can be associated with a cyclopropane deformation while the 1030-cm⁻¹ band can be associated with the C–O stretching motion. The simple chiral cyclopropanes also show large VCD in the 1000–1050-cm⁻¹ region so that the VCD at 1030 cm⁻¹ may be due to overlapping cyclopropane vibrations.² At present, we can obtain VCD data neither for the 654-cm⁻¹ BO₃ out-of-plane deformation nor for the weaker sharp bands at 813, 691, and 604 cm⁻¹, which for the present we leave unassigned. Since the BO₃ groups have such high symmetry and have vibrations with such high extinction coefficients, it is possible that the observed VCD correlates with small features due to the cyclopropane bridges and not the more obvious large B(OC)₃ type peaks.

This preliminary analysis does indicate that II may be an useful molecule for modeling coupled oscillator effects in VCD.²⁴ In particular it offers a rigid system with a variety of isotopic species and a correlation between the VCD of subunits and that of the coupled complex. The C₃ symmetry offers a new extension from previously studied C₂ systems.

Conclusion

We have presented the synthesis, crystal structure, and vibrational spectra for a new bridged, stable borate ester, tris(*trans*-1,2-cyclopropanediyl)dimethylene diborate. This molecule's high symmetry and low conformational flexibility make it of interest for detailed vibrational optical activity studies that can probe the relationship between local chirality and coupled oscillator effects. The molecule may also be of interest due to its unusual stability with respect to hydrolysis and to its potential as a cage compound.

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Registry No. I, 696-75-3; (-)-1R,2R-I, 34202-45-4; II, 86022-60-8; (+)II, 85976-95-0; III, 2345-75-7.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms, bond angles involving hydrogen atoms, and observed and calculated structure factors and a stereoview of the unit cell (11 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Dinuclear Trihydride Complexes of Platinum with Chelating Ligands. Crystal and Molecular Structure of $[\text{Pt}_2\text{H}_3(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)_2][\text{BPh}_4]$

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A series of cationic dinuclear trihydride complexes of platinum have been prepared and isolated as the different salts $[\text{Pt}_2\text{H}_3(\text{L-L})_2][\text{A}]$: **1a**, L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dpe), A = BF_4 ; **1b**, L-L = dpe, A = I; **1c**, L-L = dpe, A = NO_3 ; **1d**, L-L = dpe, A = BPh_4 ; **1a-d**₃, L-L = dpe, A = BF_4 ; **2a**, L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dpp), A = BF_4 ; **3a**, L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb), A = BF_4 ; **3c**, L-L = dpb, A = NO_3 ; **4a**, L-L = *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ (dpct), A = BF_4 ; **5a**, L-L = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{AsPh}_2$ (dpae), A = BF_4 . Raman spectroscopic data (for **1a**) indicate the presence of both terminally bonded and bridge-bonded hydride while only the terminal hydride absorptions are seen in the IR spectra. ¹H, ³¹P, and ¹⁹⁵Pt NMR studies indicate fluxional behavior down to -95 °C. Crystal and molecular structure determination of **1d** was undertaken at 115 K. The salt crystallizes in the monoclinic space group $C_{2h}^2-P2_1/n$ with cell dimensions $a = 11.107(2)$ Å, $b = 29.118(4)$ Å, $c = 19.646(2)$ Å, and $\beta = 97.62(1)^\circ$. There are four $[\text{Pt}_2\text{H}_3\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]$ cations and four BPh_4 anions per unit cell. The bidentate phosphine groups are chelated each to a separate metal atom, and two hydrogen atoms are observed to be bridging between the two metal atoms. If the bridging hydrogen atoms are ignored, coordination around one of the two metal atoms, Pt(1), is close to a square plane while that around Pt(2) is trigonal. The square plane around Pt(1) consists of two *cis*-coordinated phosphorus atoms, Pt(2), and the terminally bonded hydrogen atom. The trigonal coordination around Pt(2) is composed of two *cis*-coordinated phosphorus atoms and Pt(1). The Pt-Pt distance (bridged by two hydrogen atoms) is 2.728 Å with Pt-H_μ distances estimated to be in the range 1.4 (1)-2.0 (1) Å.

Introduction

The chemistry of the platinum hydrides has been almost completely dominated for many years by mononuclear species of the types *trans*- $[\text{Pt}(\text{H})(\text{PR}_3)_2(\text{L})]^{n+}$ ($n = 1$, L = neutral ligand; $n = 0$, L = anionic ligand)² and *trans*- $[\text{Pt}(\text{H})_2(\text{Pr}'_3)_2]$, where R' is a bulky substituent.³ *cis*-Dihydride complexes with chelating ligands were reported first in 1976 by Shaw et al.⁴ and later by Otsuka, Ibers, and co-workers.⁵

Dinuclear species were unknown until the same year, when the neutral species $[\text{Pt}_2(\text{X})_2(\mu\text{-H})_2(\text{L})_2]$ (L = $\text{P}(\text{C}_6\text{H}_{11})_3$; X = H, SiR₃, GeR₃) were described by Stone et al.⁶ In 1977, two reports, one by members of our group⁷ and the other by Brown, Puddephatt, et al.,⁸ gave account of the isolation of the cations $[\text{Pt}_2\text{H}_3(\text{dpe})_2]^+$, dpe = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, and $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dpm})_2]^+$, dpm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, respectively. Since then, several other papers have described complexes

containing the $\text{Pt}_2\text{H}_3\text{P}_4$ unit^{9,10} as well as different aspects of their reactivity.¹¹⁻¹⁴ Dinuclear cationic complexes are seen to derive from mononuclear Pt(II) complexes in reactions of the type shown in Scheme I. These reactions involve the displacement by PtH_2L_2 of X⁻ or solvent (S) on $\text{Pt}(\text{H})\text{XL}_2$ ¹⁰ or $[\text{Pt}(\text{H})(\text{S})\text{L}_2]^+$.^{9c} These derivatives may also be considered to arise from the oxidative addition of PtH_2L_2 at a Pt^0L_2 center, followed by protonation, indicated in eq 3 of Scheme I. Some of the dinuclear species are known to be fluxional,^{7,8,10} and the structure for the salt of $[\text{Pt}_2\text{H}_3(\text{L-L})_2]^+$, L-L = $(t\text{-Bu})_2\text{P}(\text{CH}_2)_3\text{P}(t\text{-Bu})_2$, has been determined.¹⁰

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