

Figure 2. A view of the  $[\text{Cr}_4(\text{OH})_4(\text{en})_4]^{6+}$  cation. The atoms are represented by ellipsoids whose principal axes were derived from the final values of the anisotropic temperature parameters. A crystallographic center of symmetry relates the primed and unprimed atoms.

XRD-6 diffractometer using 2155 reflections of which 252 were considered to have zero intensity. The compound crystallizes with four formula units in the orthorhombic space group  $D_{2h}^{15}$ -Pbca with unit cell dimensions  $a = 12.608$  (0.002) Å,  $b = 24.038$  (0.003) Å,  $c = 13.528$  (0.014) Å. The calculated density of the crystal is 1.612 g/cm<sup>3</sup>; the observed density (flotation) is 1.597 g/cm<sup>3</sup>. The structure was refined by least squares to an  $R$  value [ $R = (k|F_o| - |F_c|)/\sum k|F_o|$ ] of 0.092 and a goodness of fit  $(\sum w(F_o^2 - F_c^2/k^2)^2/(m - s))^{1/2}$  of 1.80.

The structure of the cation is shown in Figure 2. It is centrosymmetric and features a planar, rhomboid array of chromium atoms held together by oxygen atoms of four bridging hydroxo groups; the bridging angle Cr(1)-O(4)-Cr(2) is 131°, which is a large valence angle for three-coordinate oxygen. Furthermore, Cr(1) and Cr(1') are brought into close contact by O(3) and O(3') atoms of two more bridging hydroxo groups. The chromium-chromium distances are: Cr(1)-Cr(1'), 2.929 Å; Cr(1)-Cr(2), 3.606 Å; Cr(2)-Cr(2'), 6.554 Å. Each chromium atom is approximately octahedrally coordinated. The O(3)-Cr(1)-O(3') angle is 85.1°, whereas the O(4)-Cr(2)-O(5) angle is 95.1°.

Kambe's method<sup>6</sup> can be extended to derive an expression for the temperature dependence of the magnetism for the observed rhomboid structure of the four chromiums. Using this model and including all Cr(III)-Cr(III) interactions except Cr(2)-Cr(2'), we have been able to fit satisfactorily the experimental data points shown in Figure 1. Details of this treatment and further electronic structural interpretation will be the subject of a subsequent paper.<sup>7</sup>

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## Structures of $\text{B}_{20}\text{H}_{18}^{2-}$ and $\text{B}_{20}\text{H}_{18}\text{NO}^{3-}$ and Conformations of the Triethylammonium Ion

Sir:

Polyhedral<sup>1</sup>  $\text{B}_{10}\text{H}_{10}^{2-}$  is oxidized by  $\text{Fe}^{3+}$  to yield<sup>2,3</sup>  $\text{B}_{20}\text{H}_{18}^{2-}$ , in which we have located H atoms, and by  $\text{NO}_2$  to yield<sup>4</sup> a product called  $\text{B}_{14}\text{H}_{12}\text{NO}^{2-}$ , but which we show here to be  $\text{B}_{20}\text{H}_{18}\text{NO}^{3-}$ . Solutions of the disordered crystal structures of the triethylammonium salts of these ions also yield six conformations of this positive ion and precise interatomic distances for the  $\text{B}_{10}$  units in the negative ions (Figures 1 and 2).

Crystals of  $(\text{Et}_3\text{NH})_2\text{B}_{20}\text{H}_{18}$  are monoclinic, in the space group  $\text{P}2_1/a$ , and have unit cell parameters  $a = 17.52 \pm 0.02$ ,  $b = 7.60 \pm 0.01$ ,  $c = 11.72 \pm 0.01$  Å and  $\beta = 109.7 \pm 0.2^\circ$ . Two formula weights in the unit cell yield the calculated density of 0.991 g/cm<sup>3</sup> (observed 0.982). The Sayre method<sup>5</sup> as programmed by Long<sup>6</sup> provided a recognizable E map once the twofold disorders of both  $\text{B}_{20}\text{H}_{18}^{2-}$  and  $\text{Et}_3\text{NH}^+$  were recognized. Least-squares refinement of the 1874 intensities, measured on the Buerger automated diffractometer, has reached  $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.106$ . Hydrogen atoms of interest, located and refined in both disordered orientations, are 1.13 and 1.25 Å from apices near the center of the ion, but 2.34 and 2.27 Å to the nearest boron atoms of the opposite  $\text{B}_{10}$  units, respectively. This direct location of these H atoms thus supports the indications of the nuclear magnetic resonance study<sup>7</sup> in which the  $\text{B}_{10}$  units were linked by two three-center B-B-B bonds rather than by two hydrogen bridges. The  $\text{B}_{20}$  unit is similar to that found in Babcock's study<sup>8</sup> of  $[(\text{CH}_3)_3\text{S}]_2\text{B}_{20}\text{H}_{18}$  in which H atoms were not located and B-B distances have not yet appeared.

The intense purple crystals of  $(\text{Et}_3\text{NH})_3\text{B}_{20}\text{H}_{18}\text{NO}$  are monoclinic in the space group  $\text{P}2_1/n$  and have unit cell parameters of  $a = 24.44 \pm 0.04$ ,  $b = 16.68 \pm 0.03$ ,  $c = 9.65 \pm 0.02$  Å, and  $\beta = 97.0 \pm 0.1^\circ$ . The four molecules per unit cell yield a calculated density of 0.972 g/cm<sup>3</sup> (observed 0.986). The structure was recognized in an E map after application of G. N. Reeke's direct methods program, and the largest 4555 independent reflections have been refined so far to  $R = 0.144$ . One  $\text{Et}_3\text{NH}^+$  ion has a twofold disorder. The N-O distance of 1.28 Å and B-N distances of 1.51 and 1.46 Å compare with values of N-O = 1.28 and 1.23 and of C-N = 1.51 and 1.44 Å in, respectively, the radicals di-*t*-butyl nitroxide<sup>9</sup> and di-*p*-anisyl nitroxide.<sup>10</sup> Although not a radical, the  $\text{B}_{20}\text{H}_{18}\text{NO}^{3-}$  ion appears to have a more satisfactory charge distribution if the N-O distance is between single- and double-bond distances, and if the B-N bonds have a bit more than single-bond character.

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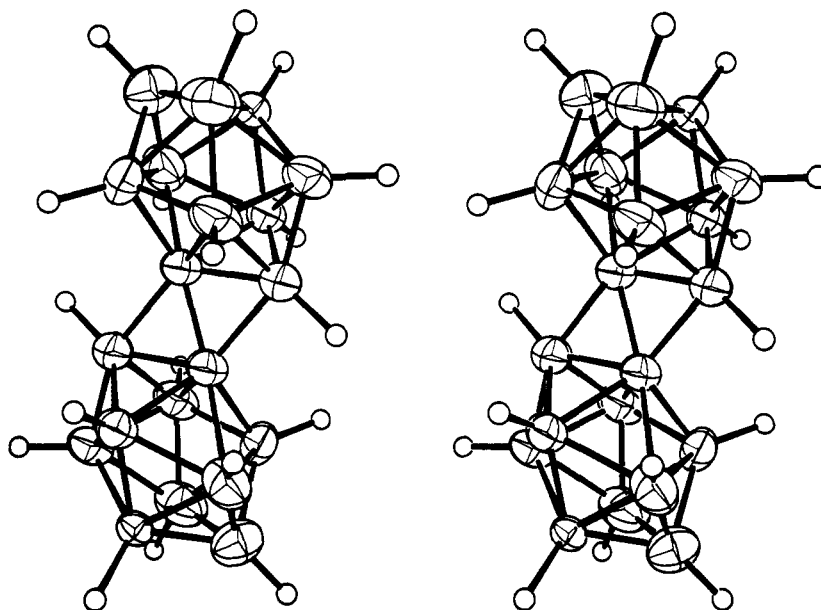
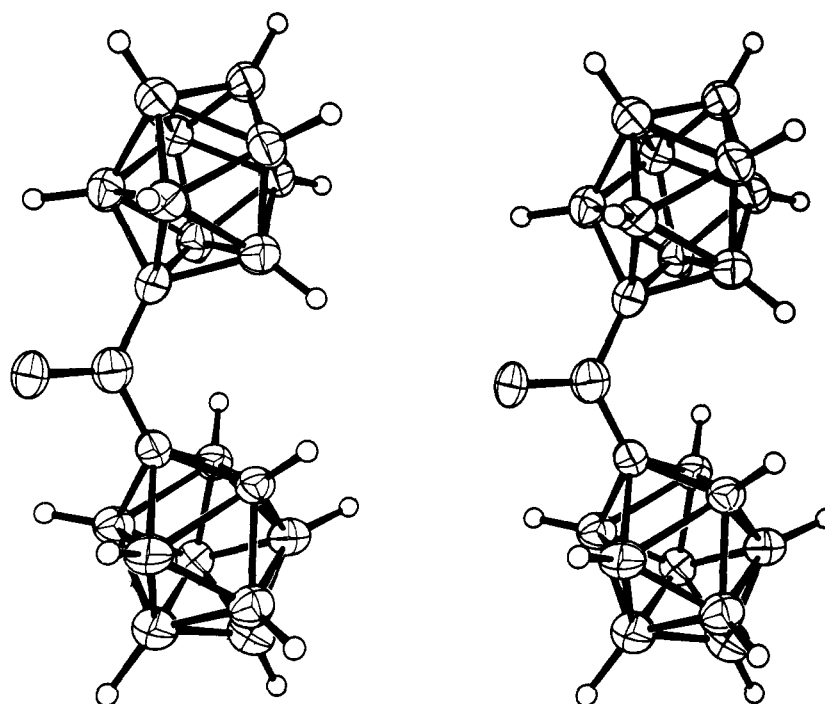
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Figure 1. Stereoview of the  $B_{20}H_{18}^{2-}$  ion.Figure 2. Stereoview of the  $B_{20}H_{18}NO^{3-}$  ion.

The B-B distances are comparable with the values found in  $Cu_2B_{10}H_{10}^{11}$  (Table I).

Table I. Averaged Bond Distances (Å) with Standard Deviations

Boron cage	Apex-edge	Basal edge-edge	Belt edge-edge
$B_{20}H_{18}^{2-}$ (disorder A)	$1.70 \pm 0.07$	$1.85 \pm 0.07$	$1.84 \pm 0.09$
$B_{20}H_{18}^{2-}$ (disorder B)	$1.71 \pm 0.09$	$1.83 \pm 0.10$	$1.79 \pm 0.05$
$B_{20}H_{18}NO^{3-}$ (cage I)	$1.72 \pm 0.01$	$1.88 \pm 0.04$	$1.81 \pm 0.02$
$B_{20}H_{18}NO^{3-}$ (cage II)	$1.71 \pm 0.02$	$1.86 \pm 0.04$	$1.84 \pm 0.02$
$B_{10}H_{10}^{2-}$	$1.73 \pm 0.02$	$1.86 \pm 0.03$	$1.82 \pm 0.02$

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The five conformations of the  $Et_3NH^+$  ion in these studies are summarized in Table II, where angles of rotation about C-N bonds are listed relative to the ide-

Table II. Triethylammonium Rotation Angles (Degrees) from  $C_3$  Model to Actual

$(Et_3NH)_2B_{20}H_{18}$		$(Et_3NH)_3B_{20}H_{18}NO$			
Dis <sup>a</sup> A	Dis B	Dis A, I	Dis B, I	II	III
14	10	12	31	22	26
8	9	0	-2	6	-9
-4	1	-4	-9	-103	-107

<sup>a</sup> Dis = disorder.

alized  $C_3$  model which has all single bonds perfectly staggered and all  $CH_3$ 's a maximum distance from one

another. A positive rotation brings the methyl carbon towards eclipse with N-H, while a negative rotation brings the methyl carbon toward a methylene carbon. All angles are fairly near  $0^\circ$ , except for two near  $120^\circ$  which represent another staggered conformation in which one methyl carbon projects axially from the methylene carbon in a direction opposite from that of the N-H bond. No previous studies of the conformations of  $\text{Et}_3\text{NH}^+$  ions have appeared, and we do not recommend them as ordered positive ions in the studies of structures of the negative ions, unless the location of H atoms is a critical part of the study.

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### Detection of Cyclobutadienocyclopentadienyl Anion

Sir:

In principle, cyclic antiaromatic systems of four  $\pi$  electrons, such as cyclobutadiene, can be stabilized in two ways by fusion to other conjugated rings. Fusion to rings with six  $\pi$  electrons, as in biphenylene, is stabilizing because of diminished bond order in the cyclobutadiene ring even though the over-all system retains  $4n$   $\pi$  electrons.<sup>1</sup> On the other hand, fusion of two  $4n$   $\pi$  electron systems produces a composite with  $4n + 2$   $\pi$  electrons on the periphery; a number of examples are known<sup>2</sup> in which cyclooctatetraene is fused to another  $4n$   $\pi$  electron ring, but the energetic situation for such compounds is not yet completely clear.

The bicyclo[3.2.0]heptatrienyl system is particularly interesting in this regard. The cation Ia, a bridged tropylium ion, is the formal product of fusion of cyclobutadiene and cyclopentadienyl cation; the anion Ib is on its periphery a cycloheptatrienyl anion, but it is also a cyclopentadienyl anion. HMO calculations predict a total  $\pi$  energy of  $8.906\beta$  for both species, and a  $\Delta\text{DE}$  of  $1.918\beta$  for ionization of a covalent bicycloheptatriene (e.g., Ic) to either species. The HMO calculated  $\Delta\text{DE}$  for converting cyclopentadiene to its anion is only  $2.000\beta$ , so Ic should be comparably acidic. As an approach to Ia and Ib we have generated the hydrocarbon Ic. This strained triene is so labile that we have not yet been able to isolate it undimerized, but it has still been possible to demonstrate that the ionization of Ic to the anion Ib is a facile process.

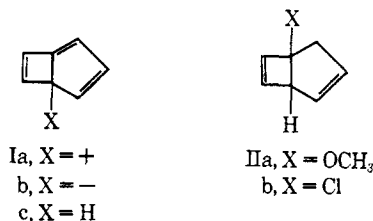
Treatment of 1-methoxybicyclo[3.2.0]hepta-3,6-diene (IIa)<sup>3</sup> with  $\text{BCl}_3$  at  $-75^\circ$  afforded the chlorodiene IIB<sup>4</sup>

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(4) Mass and nmr spectra consistent with the assigned structure.



in 63% yield. On standing for 3 hr at  $25^\circ$  with 0.2  $M$   $\text{KO}-t\text{-Bu}$  in tetrahydrofuran, IIB eliminates  $\text{HCl}$  to produce a dimer of the triene Ic,  $m/e$  180; the nmr data are consistent with a structure derived by 1,4 addition of the cyclopentadiene in Ic to the strained trisubstituted double bond of a second molecule of Ic. Triene Ic can also be trapped as an adduct with diphenylisobenzofuran, present during the base treatment of IIB. The adduct,  $m/e$  360, is from the nmr data a mixture of the two stereoisomers formed by addition across the new strained double bond in Ic.

The same dimer, as well as the adduct with diphenylisobenzofuran, can be prepared by reaction of IIB with  $N$ -bromosuccinimide and dehalogenation of the resulting bromo-IIB<sup>4</sup> with  $\text{Li}(\text{Hg})$  in ether.

Dimerization of Ic is fairly rapid: treatment of a  $5 \times 10^{-4} M$  solution of IIB with 0.1  $M$  potassium  $t$ -butoxide in tetrahydrofuran for 5 min at  $25^\circ$ , followed by neutralization, leads to partial development of a new chromophore,  $\lambda_{\text{max}}$  316 nm, which decays with second-order kinetics,  $t_{1/2} \sim 3$  hr. Assuming that this uv absorption is due to triene Ic, at preparative concentrations it would have a half-life of a few minutes at best. Nonetheless, when the elimination of  $\text{HCl}$  from IIB is performed by stirring with 0.2  $M$   $\text{KO}-t\text{-Bu}$  in 74 ml of tetrahydrofuran and 6 ml of  $t\text{-BuOD}$  for 4 hr at  $25^\circ$ , a 40% yield of the dimer was formed containing 65% of 2.0 D/dimer. The 60% of recovered IIB has no deuterium, and the dimer does not exchange under these conditions. When some dimethyl- $d_6$  sulfoxide is added to the dehydrochlorination mixture the product dimer has 100% of 2.0 D/dimer. The nmr spectrum of deuterated dimer is consistent with dimerization of I ( $X = \text{D}$ ). Apparently hydrocarbon Ic exchanges *via* anion Ib at a rate comparable to its rapid dimerization; while it is difficult to relate this observation to a precise  $\text{p}K_a$  for Ic, it does suggest that the HMO prediction of acidity in Ic is correct.

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### Cations and Cation Radicals of Porphyrins and Ethyl Chlorophyllide a

Sir:

The polarographic oxidation of a variety of porphyrins has been studied in butyronitrile<sup>1</sup> and in methylene chloride.<sup>2</sup> Oxidation proceeds *via* two well-defined one-

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