of reaction with an olefin is much greater than in the presence of an equivalent amount of pyridine.

We have reevaluated β_1 and β_2 at 30° from the pyridine activity data and the absorbance changes of ref 1a, Table IV, using a nonlinear regression program. If the initial estimates for β_1 and β_2 of 0.24 and 0.05, respectively, for the lowest pyridine concentration are smoothly increased to the values 0.36 and 0.075 at 3.0 *M* pyridine, the observed absorbance changes fit to within 10% of the calculated values (ϵ_1 3800, ϵ_2 10,000 at 340 nm). That β values should increase with increasing pyridine concentration is not unreasonable in view of our observation that 1 *M* *p*-dioxane, which complexes OsO_4 only very weakly, increases the observed stability constant for the OsO_4–pyridine system by about 10%. This effect of solvent polarity is observed more dramatically in CCl_4 in which β_1 is about 12.[8]

The nature of the $OsO_4 \cdot 2py$ complex is not clear. Contact charge transfer[9] may occur as weak complexes between OsO_4 and aromatic molecules are known.[10]

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Registry No. OsO_4, 20816-12-0; pyridine, 110-86-1.

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Bis[bis(1,2-ethanedithiolato)ferrate(III)] Dianion, a μ_2-Thiolato Dimer. Synthesis and Properties

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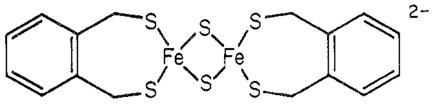
In the course of developing preparative routes to 2-Fe complexes which might serve as synthetic analogs[1] of the active sites of iron–sulfur proteins such as plant ferredoxins, adrenodoxin, and putidaredoxin,[2] the reactions of Fe(III) salts, sodium hydrosulfide, and various dithiols have been investigated. With *o*-xylene-α,α'-dithiol the centrosymmetric μ_2-sulfido-bridged dimer dianion **1** containing tetrahedrally coordinated Fe(III) is obtained. Its structure and electronic properties[3,4] reveal it to be a good representation of the oxidized forms of 2-Fe proteins. Under similar conditions with 1,2-ethanedithiol a dianionic complex has been isolated which contains no sulfide. This species has been identified as bis[bis(1,2-ethanedithiolato)ferrate(III)] dianion, $[Fe_2(edt)_4]^{2-}$ (**2**), whose structure[5] is schematically represented below. The complex is centrosymmetric with distorted trigonal-bipyramidal coordination, a planar and nearly square Fe_2S_2 bridging unit, and an Fe···Fe separation of 3.410 (3) Å. $[Fe_2(edt)_4]^{2-}$ is one of a small number[4] of centrosymmetric Fe(II) or Fe(III) dimers bridged by sulfur atoms included in chelate rings of the half-dimer. Of these, the dimeric Fe(II) complexes derived from *N*,*N*'-dimethyl-*N*,*N*'-bis(β-mercaptoethyl)ethylenediamine, $[FeL]_2$, and *N*,*N*'-dimethyl-*N*,*N*'-bis(β-mercaptoethyl)-1,3-propanediamine, $[FeL']_2$,[6] are structurally quite similar to **2**. In view of the current interest in Fe–S coordination compounds[7] and our own concern with various types of iron–thiolate complexes,[1] the X-ray structural characterization of $[Fe_2(edt)_4]^{2-}$ has been augmented by examination of certain chemical and electronic properties, which are reported herein.



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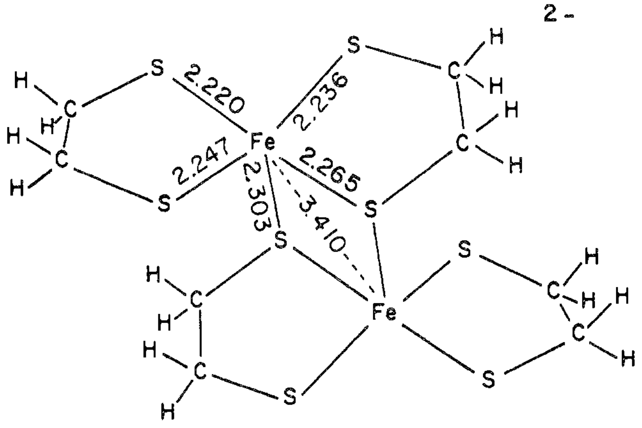


2

Experimental Section

Preparation of Compounds. All manipulations were performed with degassed solvents under a pure dinitrogen atmosphere.

$(n\text{-}Bu_4N)_2[Fe_2(S_2C_2H_4)_4]$. To a methanolic solution of 3.6 ml (42 mmol) of 1,2-ethanedithiol and 4.5 g (84 mmol) of sodium methoxide was added 8.24 g (20 mmol) of ferric chloride in methanol. An immediate dark red-brown color developed which became red-violet after the addition of ferric chloride was complete. Following stirring for 36 hr the reaction mixture was filtered and the collected solid was washed with water, leaving a small residue. The filtrate and wash were combined and treated with 9.2 g (29 mmol) of tetra-*n*-butylammonium bromide in water, yielding a precipitate of small black crystals. Two recrystallizations of this material from acetonitrile afforded the product in 35–50% yield as large, beautifully crystalline black blocks, mp 185–187°. Anal. Calcd for $C_{40}H_{88}N_2S_8Fe_2$: C, 49.76; H, 9.20; N, 2.90; S, 26.57; Fe, 11.57. Found: C, 49.90; H, 9.04; N, 2.95; S, 26.62; Fe, 11.68.

$[(CH_3)_3(PhCH_2)N]_2[Fe_2(S_2C_2H_4)_4]$. The above procedure was used with trimethylbenzylammonium bromide as the precipitant. The pure product was obtained as a black, finely crystalline solid, mp 196–198°. Anal. Calcd for $C_{28}H_{48}N_2S_8Fe_2$: C, 43.07; H, 6.20; N, 3.59; S, 32.85; Fe, 14.30. Found: C, 43.01; H, 6.27; N, 3.63; S, 32.57; Fe, 14.22.

Table I. Comparative Properties of Fe–S Dimers and Tetramers

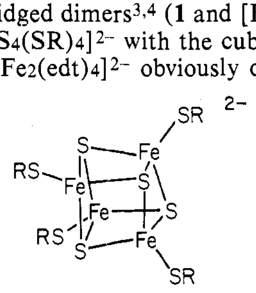
Property	$[Fe_2(edt)_4]_2^{2-}$ [a]	$[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ [b]	$[Fe_4S_4(SR)_4]^{2-}$ [c]
Fe· · ·Fe, Å	3.410	2.698	2.747[d,e]
Fe–SR, Å	2.242[f]	2.305	2.251[e]
S· · ·S, Å (bite)	3.16[f]	3.690	
∠SFeS, deg (bite)	89.6[f]	106.4	
λ_{max}, nm (ϵ_M)[g]	363 (23,100) 535 (6170) ~580 sh	338 (16,200) 414 (11,000) ~455 sh, 590 (4800)	298 (23,300)[o] 420 (17,200)
$E_{1/2}$,[g,h] V	−1.13[i]	−1.49 (2−, 3−) −1.73 (3−, 4−)	−1.33 (2−, 3−)[o] −2.04 (3−, 4−)
δ,[j,k] mm/sec	+0.25[l]	+0.17	+0.34[o]
ΔE_Q,[k] mm/sec	3.09[l]	0.36	1.10[o]
μ_{Fe},[k] BM	2.58	1.41	1.04[e]
J, cm^{-1}	−54	~−150[m]	n

[a] This work. [b] References 3 and 4. [c] References 10, 12–14. [d] Average of all values. [e] R = CH_2Ph. [f] In half-dimer. [g] DMF solution. [h] Vs SCE. [i] Irreversible two-electron reduction. [j] Relative to Fe metal. [k] Ambient temperture. [l] Data from W. D. Phillips and J. F. Weiher. [m] More accurate value being determined. [n] Not determined. [o] R = Et.

Physical Measurements. Dc and differential pulse polarographic and cyclic voltammetric measurements were carried out with a Princeton Applied Research Model 170 Electrochemistry System at 25° using DMF solutions containing 0.05 M tetra-n-propylammonium perchlorate supporting electrolyte. Half-wave potentials were determined at a DME vs. a saturated calomel reference electrode. Magnetic measurements were performed with a vibrating-sample magnetometer operated in the temperature range 4.2–287°K. Measurements were made on two different samples and the results, corrected for diamagnetism and Curie-type paramagnetic impurity, were averaged. Data at $T \geq 28$°K were employed in fits to an antiferromagnetic coupling model.[8,9] The magnetic calibrant was pure nickel metal.

Results and Discussion

$[Fe_2(edt)_4]^{2-}$ is readily prepared by the reaction of $FeCl_3$ and 1,2-ethanedithiol in the presence of base in methanol. Quaternary cation salts are soluble in polar organic solvents to give intense red-brown, oxygen-sensitive solutions. This species is the third structural type which has been obtained from our synthetic studies of Fe–S complexes, the other types being the sulfide-bridged dimers[3,4] (**1** and $[Fe_2S_2(SAr)_4]^{2-}$) and tetramers $[Fe_4S_4(SR)_4]^{2-}$ with the cubane-like stereochemistry **3**.[10,11] $[Fe_2(edt)_4]^{2-}$ obviously differs from the dimers and **3** by its lack of sulfide and the presence of five-coordinate instead of approximately tetrahedral metal coordination sites. Some comparative structural[3,4,10] and electronic[3,4,12–14] properties of **1**, **2**, and **3** are collected in Table I.



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Two significant chemical properties of $[Fe_2(edt)_4]^{2-}$ are its failure to undergo thiolate ligand substitution reactions with aryl thiols under conditions allowing such reactions for **1**[4] and **3**[11] and its resistance to incorporation of sulfide. The latter property has been observed in synthetic reaction mixtures containing NaHS, in refluxing methanol solutions containing Na_2S_2,[15] and in reactions of the dithiol with **1**, $[Fe_4S_4(SEt)_4]^{2-}$, and 2-Fe and 8-Fe ferredoxin proteins.[16] In the latter instances the only identifiable product was $[Fe_2(edt)_4]^{2-}$, recognized by its absorption spectrum (Figure 1), which differs in detail from the spectra of **1** and **3** (Table I). Further, the spectrum of this complex is sufficiently similar to those of the unisolated reaction products of $FeCl_3$ with $HS(CH_2)_nSH$ in aqueous alkaline solution[17] to allow their identification as $[Fe_2(S(CH_2)_nS)_4]^{2-}$ (n = 2–6). The $FeCl_3$–dithiol systems with n = 2 or 3 did not react with sulfide. Systems with n = 4–6 did evidence reaction and developed species with absorption spectra similar to those of **1** and oxidized 2Fe-2S* proteins.[17] All of these results indicate considerable stability of $[Fe_2(edt)_4]^{2-}$ relative to the as yet undetected $[Fe_2S_2(edt)_2]^{2-}$ or other sulfide-bridged edt complexes. It would appear that one necessary condition for the formation of stable binuclear tetrahedral structures such as **1** from dithiols is structural flexibility of the latter adequate to allow near-tetrahedral angles around the metal while retaining normal Fe^{III}–S distances (ca. 2.3 Å). The markedly shorter bite distance of edt compared with o-xyl-S_2 (and $S(CH_2)_{4-6}S$) and its consequently smaller bite angle (Table I) are considered to be the principal geometric features preventing the formation of a stable binuclear structure similar to **1**.

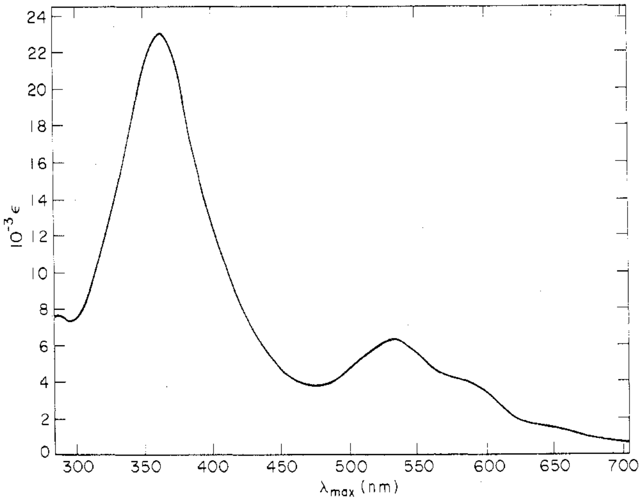

Figure 1. Ultraviolet-visible absorption spectrum of $(n\text{-}Bu_4N)_2[Fe_2(edt)_4]$ in DMF solution.

In contrast to the electrochemical behavior of **1** and **3**, which exhibit two one-electron reductions, $[Fe_2(edt)_4]^{2-}$ undergoes one two-electron reduction at a less cathodic potential (Table I). The two-electron nature of the reduction (i_d/C = 3.09 μA/mM) is supported by comparison of the diffusion current with the average diffusion currents (1.45 μA/mM) for the 2−, 3− reductions of a series of tetramer dianions measured at a DME under the same conditions.[13] The same conclusion is afforded by comparison with dimer reduction currents[4] and from data for $[Fe_2(edt)_4]^{2-}$ and tetramers obtained at a rotating Pt electrode. The reduction process was found not to correspond to reversible charge transfer as evidenced from a plot of log $[i/(i_d - i)]$ vs. E (−48 mV, DME, vs. −30 mV for n = 2) and from the results of differential pulse polarographic

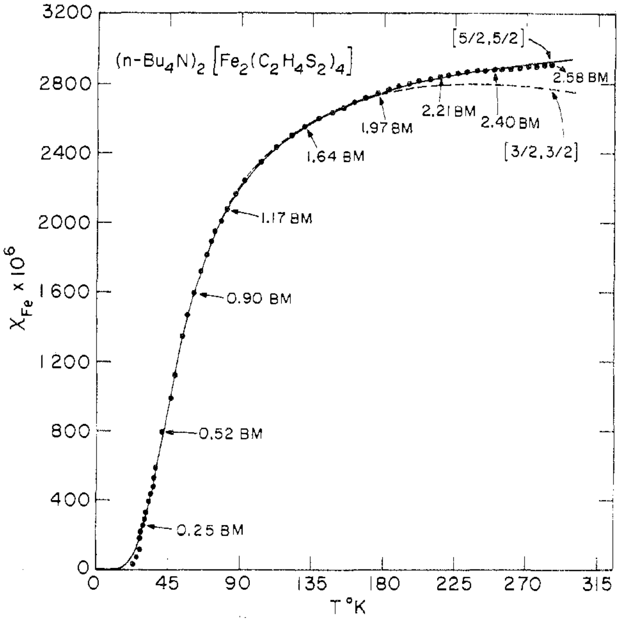

Figure 2. Temperature dependence of the magnetic susceptibility per iron of $(n\text{-Bu}_4\text{N})_2[\text{Fe}_2(\text{edt})_4]$: dots, experimental points; curves, calculated for two antiferromagnetically coupled Fe(III) ions with $S = {}^5/_2$ (——) and $S = {}^3/_2$ (- - - -) and with $J = -54$ cm^{-1}, $\bar{g} = 2.00$, and TIP = 0. Magnetic moments per iron at the various temperatures were calculated from the Curie law.

measurements and a series of cyclic voltammetric measurements (Pt electrode). The lack of stepwise reduction compared to **1** and **3** is ascribed to the effective isolation of the redox centers produced by structure **2**, in which the Fe···Fe distance is ca. 0.7 Å longer than in sulfide-bridged complexes.

A consistent electronic feature of the three types of complexes in Table I is antiferromagnetic interactions of metal centers. The temperature dependence of the paramagnetic susceptibility per iron of $(n\text{-Bu}_4\text{N})_2[\text{Fe}_2(\text{edt})_4]$ is shown in Figure 2, together with magnetic moments per iron calculated for various temperatures from the Curie law and theoretical susceptibility curves calculated by standard procedures from the usual antiferromagnetic coupling model based on the Hamiltonian $\mathcal{H} = -2J\bar{S}_1 \cdot \bar{S}_2$.[8,9] Satisfactory fits to experimental susceptibilities could not be obtained assuming $S_1 = S_2 = {}^1/_2$. The best fits for the $S_1 = S_2 = {}^3/_2$ and ${}^5/_2$ cases, both of which were obtained with $J = -54$ cm^{-1}, $\bar{g} = 2.00$, and TIP = 0, are shown in the figure. Inclusion of the intermediate spin case is necessitated in particular by the well-established quartet ground state of Fe(III) in the S_4X coordination units of mononuclear $\text{Fe}(\text{S}_2\text{CNR}_1\text{R}_2)_2\text{X}$ complexes.[18,19] The calculated susceptibility curves are essentially superimposable below ca. 170°K. Different behavior is encountered at higher temperatures due to a small fractional occupation of the $S' = 4, 5$ levels in the spin ${}^5/_2$ model with $J \approx -50$ cm^{-1}. In the temperature interval of ca. 190–290°K the experimental susceptibilities conform more closely to the spin ${}^5/_2$ than the spin ${}^3/_2$ model, although the calculated differences are not large. Hence, the magnetic data favor the high-spin configuration for the two Fe(III) centers. The isomer shift (Table I) is consistent with this description but is not a reliable means of distinguishing high- and intermediate-spin Fe(III). The quadrupole splitting is unusually large for Fe(III) and is tentatively ascribed to the low site symmetry and attendant asymmetry in charge distribution around the metal.

With the J values in Table I, together with the value for $[\text{Fe}(\text{salen})]_2\text{S}$,[20] and by assuming little effect of nonbridging ligands, the antiferromagnetic coupling sequence shown for three types of high-spin binuclear $\text{Fe}^{\text{III}}\text{–S}$ structural fragments is apparent ($-J$ values in parentheses). The analogous order

$\text{Fe(SR)}_2\text{Fe} < \text{Fe–S–Fe} < \text{Fe(S)}_2\text{Fe}$
(54 cm^{-1}) (75 cm^{-1}) (~160 cm^{-1})

$\text{Fe(OR)}_2\text{Fe}$ (8–20 cm^{-1} [21–23]) < Fe–O–Fe (85–105 cm^{-1} [24]) occurs in oxygen-bridged Fe(III) dimers. A comparison of coupling in $[\text{Fe}_2(\text{edt})_4]^{2-}$ and structurally defined $[\text{Fe}(\text{salen})\text{Cl}]_2$[25] is of some interest for both contain similar bridging units. In the former ∠FeSFe ≈ 91° while in the latter ∠FeOFe ≈ 95°, Fe···Fe ≈ 3.29 Å, and Fe–O distances are 0.3–0.5 Å shorter than corresponding Fe–S distances. Despite the latter two features J is much smaller (-7.5 cm^{-1} [26]) in $[\text{Fe}(\text{salen})\text{Cl}]_2$, suggesting that sulfur may be more effective than oxygen in effecting antiparallel spin coupling when bridging angles and metal separations (too long for appreciable direct interactions) are roughly constant. The generality of this effect remains to be tested. At this point it can only be observed that the order Fe–S–Fe < Fe–O–Fe (87–100 cm^{-1} [27]) is found for salen-type complexes, indicating sulfide to be somewhat less effective than oxide in this respect. An accurate structure of $[\text{Fe}(\text{salen})]_2\text{S}$ is required before a further assessment of magnetic coupling involving its sulfide bridge can be made. The much stronger coupling observed in the $\text{Fe(S)}_2\text{Fe}$ unit of **1** in the above Fe–S series must arise from exchange pathways involving both the Fe–S–Fe bridge and direct Fe···Fe interactions.

In addition to the work of Sugiura et al.[17] and that reported here, there have been a number of other investigations of the reactions of iron salts with thiols, some aspects of which have been reviewed recently.[28] Perhaps most closely related to the present work are the studies by Leussing et al.[29,30] on the systems Fe(II)– and Fe(III)–2,3-dimercapto-1-propanol (H_2dmp) in aqueous solution. The analog of **2** was not reported, "Fe(dmp)(OH)" being the only stable Fe(III) complex detected.[29] Evidence was presented for the possible existence of the dimer $[\text{Fe}_2(\text{dmp})_3]^{2-}$, potentially similar to $[\text{Fe}_2(\text{S}_2\text{-}o\text{-xyl})_3]^{2-}$ recently isolated in this laboratory and currently being characterized.[31] These results suggest that the stable forms of Fe(II) dimers containing only thiolate ligands are not necessarily the simple two-electron reduction products of stable Fe(III) dimers such as **2**.

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Registry No. $(n\text{-Bu}_4\text{N})_2[\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)_4]$, 36841-25-5; $[(\text{CH}_3)_3(\text{PhCH}_2)\text{N}]_2[\text{Fe}_2(\text{S}_2\text{C}_2\text{H}_4)_4]$, 54713-05-2.

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Rearrangement in Reduced Carboranes

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We recently discussed theoretical bases for the opening of deltahedral (closo) borane and heteroborane frameworks to nido and arachno molecules of lower symmetry upon addition of electrons to the polyhedral skeleton.[1] The potential energy surface along symmetry-allowed rearrangement coordinates was analyzed by extended Hückel MO calculations for $B_5H_5^{n-}$ (n = 2, 4, 6) molecules with the implication that these models were extendable to isoelectronic boranes and heteroboranes. Here we report similar work concerning the possible isomers of the known *closo*-carboranes $C_2B_3H_5$ and $C_2B_4H_6$,[2,3] isoelectronic with the unknown $B_5H_5^{2-}$ and the known $B_6H_6^{2-}$.[4] The results[5] have implications regarding the mode of intramolecular rearrangement and preferred geometry of the two-electron reduction products of these carboranes.

Hoffmann and Lipscomb[6] also have employed LCAO calculations to speculate on the nature of reduced carboranes. They noted that in D_{3h} symmetry (both C atoms axial in a trigonal-bipyramidal structure) $C_2B_3H_5^{2-}$ has orbital degeneracy and should not be stable. However, the isomeric forms of $C_2B_3H_5^{2-}$ of different symmetry were deemed "energetically inaccessible". Our results confirm this "inaccessibility" *if* the isomeric forms which are considered retain a nominally trigonal-bipyramidal framework and the symmetry is lowered from D_{3h} by varying the C atom placement to axial–equatorial (C_s) or equatorial–equatorial (C_{2v}). However, if descent in symmetry is realized by distortion from the trigonal-bipyramidal geometry to a square-pyramidal skeleton, we find that all of the isomeric forms of $C_2B_3H_5^{2-}$ are energetically accessible. The isomeric forms of square-pyramidal $C_2B_3H_5^{2-}$ are interconvertible by sds (square–diamond–square) rearrangements.[6] With the aid of symmetry considerations such as those discussed by Pearson[7] and Bartell[8] we find sds rearrangements to be symmetry allowed; however, on the basis of our EHMO calculations they appear to be relatively high-energy paths and alternate, symmetry-allowed, low-energy paths are proposed. Figure 1 summarizes the results for $C_2B_3H_5^{2-}$. The symmetry-allowed "low-energy" mode of interconversion between the isomeric square-pyramidal forms of $C_2B_3H_5^{2-}$ amounts to an arcing of one atom position as shown in Figure 1. These EHMO results suggest that the nominally square-pyramidal isomers of $C_2B_3H_5^{2-}$ decrease in stability in the order trans basal–basal, cis basal–basal, and apical–basal (−377.32, −376.34, and – −375.67 eV, respectively). This result appears to be in direct conflict with the fact that the only known isomer of $C_2B_3H_7$ (isoelectronic with $C_2B_3H_5^{2-}$) has the C atoms in apical and basal positions.[9] However, addition of protons to the "square" face of $C_2B_3H_5^{2-}$ so as to give two bridge hydrogens in the apical–basal isomer and two BH_2 groups in the basal–basal isomers changed the relative stabilities to apical–basal > trans basal–basal > cis basal–basal (−390.30, −389.70, and −389.46 eV, respectively). These results corroborate Williams' empirical observation that the placement of extra hydrogens as bridging hydrogens in heteroboranes appears to have precedence over the placement of electron-rich heteroatoms at low-coordinate vertices.[10] In the present case of $C_2B_3H_7$, even though a trans basal placement of the carbon atoms would be anticipated, such placement would preclude the possibility of bridge hydrogens since they have never been observed to bridge other than boron positions and bridge preferentially on nontrigonal faces. The apical–basal placement of the carbon atoms is the only one which can accommodate both extra hydrogens in bridging positions in the nido deltahedral fragment.[11]

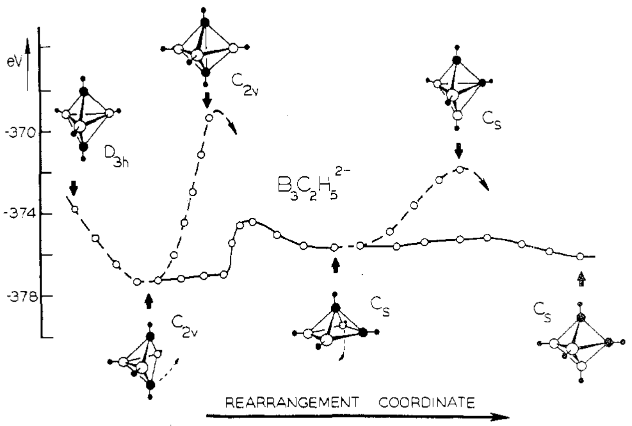

Figure 1. Energy as a function of geometry for $C_2B_3H_5^{2-}$. The solid line represents the interconversion of the isomeric forms of $C_2B_3H_5^{2-}$ via symmetry-allowed arcing movements of the designated atoms. The broken line designates the inconversion via a dsd mechanism. During the rearrangements all interatomic distances were maintained at their idealized values[5] except for that portion of the structure where the major rearrangement occurred.

The interconversion of the two isomeric forms of $C_2B_4H_6$ (cis and trans carbons in a nominally octahedral framework) has been suggested to occur through either a pentagonal-pyramidal intermediate or perhaps a trigonal prism.[6] However, one study mitigates against either of the latter intermediates and suggests a more complex potential surface.[12] In the case of $C_2B_4H_6^{2-}$ instability was implied for the trans isomer because of orbital degeneracy and it was suggested that the cis isomer was energetically accessible.[6] Our EHMO results suggest that *cis*- and *trans*-$C_2B_4H_6^{2-}$ are very similar in energy (ca. −430.5 eV). Likewise, the three trigonal-prismatic forms