Table II. Nucleophilic Reactivity Parameters for Selected Sulfur Nucleophiles[a]

nucleophile	n_{CH_3I}	ref
$^-SC_6H_5$	9.92	11
^-SH	8	11
$(bpy)_2Ru(SC_9H_6N)^+$	8.04	this work
$S(CH_3)_2$	5.54	11
HSC_6H_5	5.70	11
$(en)_2Co(SCH_2CH_2NH_2)^{2+}$	5.7	3
$S(CH_2C_6H_5)_2$	4.84	11

[a] $n_{CH_3I} = \log (k_{nuc}/k_{CH_3OH})$.[11] Conditions: 25 °C, CH_3OH, no ionic strength control.

of k_2 in DMF/H_2O is entirely consistent with previous observations,[3] and the well-established ability of DMF to stabilize the large transition states associtaed with S_N2 reactions.[10]

Table I lists values of k_2 for the reaction of a variety of thiolato complexes with CH_3I. The square-planar Ni(II) complex may constitute a special case since it can coordinate CH_3I in a preequilibrium step that is denied to the octahedral Co(III), Cr(III), and Ru(II) complexes, but it is nevertheless included in Table I since the corresponding k_2 value does not seem discordant with the other k_2 entries. As noted previously,[3] varying the metal ion center from Co(III) to Cr(III) does not significantly affect the reactivity of the coordinated thiolate, and coordinated arenethiolates are less nucleophilic than coordinated alkanethiolates. However, the Ru(II) entry in Table I shows that varying the metal center from Co(III) to Ru(II) markedly enhances the nucleophilicity of a coordinated thiolate; when arenethiolates are compared, k_2 for $[(bpy)_2Ru(SC_9H_6N)]^+$ is ca. 300 times larger than that of $[(en)_2Co(SC_6H_4NH_2)]^{2+}$. This large rate difference is not due to the different formal charges on the complexes since $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(SCH_2COO)]^+$ react at essentially the same rate.[3] Rather, this difference in reactivities undoubtedly resides in the greater π-back-bonding tendency of Ru(II); π-back-bonding from Ru(II) to sulfur places greater electron density on the coordinated thiolate and thus makes it a more efficient nucleophile. The efficacy of this π-back-bonding enhancement of nucleophilicity can be appreciated from the data of Table II, which compares values of the nucleophilic reactivity parameter, n_{CH_3I},[11] for a variety of sulfur nucleophiles. On this logarithmic scale it is seen that the positively charged Ru(II) complex is much more nucleophilic than are noncorrdinated thiols and thioethers and is about as nucleophilic as HS^-. Presumably, an anionic thiolato Ru(II) complex would be even more nucleophilic than HS^-.

π-Back-bonding from Ru(II) to nitrogen- and sulfur-containing ligands has often been invoked to explain the increased thermodynamic affinities of these ligands for protons[12-14] and the *reduced* susceptibility of these ligands toward attacks *by* nucleophiles.[15,16] In this work, π-back-bonding to a sulfur-containing ligand is seen to *enhance* it reactivity *as* a nucleophile. This result may be important in understanding the reactivity patterns of a variety of metal-sulfur systems, including the iron-sulfur cores in ferredoxins and related iron sulfur proteins. E.g., the nucleophilicity of a sulfur ligand in a $Fe_4S_4(SR)_4^{n-}$ core could be controlled by the degree of reduction of the iron atoms, the more highly reduced cores functioning as more efficient nucleophiles.

Acknowledgment. Financial support by National Science Foundation Grant No. CHE79-26497 is gratefully acknowledged. We also thank Dr. B. P. Sullivan and Prof. T. J. Meyer (The University of North Carolina, Chapel Hill, NC) for helpful discussions concerning synthesis of ruthenium thiolate complexes.

Registry No. $[(bpy)_2Ru(SC_9H_6N)]^+$, 88476-04-4; $[(bpy)_2Ru(SC_9H_6N)]PF_6$, 88476-05-5; $[(bpy)_2Ru(SC_9H_6N)]BF_4$, 88476-06-6; $[(bpy)_2Ru(S(CH_3)C_9H_6N)](PF_6)_2$, 88476-08-8; thiooxine, 491-33-8; iodomethane, 74-88-4.

Supplementary Material Available: Tables A and B listing the k_{obsd}-$[CH_3I]$ data (2 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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γ-Ray-Induced Linkage Isomerization of Tetrahedral Thiocyanato Complexes of Iron(II)

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It is well-known that the thiocyanate ion forms either thiocyanato (M-SCN) or isothiocyanato (M-NCS) metal complexes depending on the nature of the metal and this preference may be modified by other ligands being present or by the complex being in the solid state or in solution.[1-6] Many iron thiocyanate complexes have been reported, and most of them appear to be N bonded.[1,2,7-11] Several examples of linkage isomerization in iron thiocyanate complexes have been reported.[1,2] Both linkage isomers of $[(C_5H_5)Fe(CO)_2NCS]$ have been isolated by column chromatography.[12] in addition, the linkage isomerization of $[Fe(CN)_5NCS]^{3-}$ has been observed in solution,[13,14] and high-pressure-induced linkage isomerization has been reported to have been observed for $Fe(NCS)_3 \cdot 6H_2O$ and $K_3[Fe(NCS)_6]$.[2] So far γ-ray-induced thiocyanate linkage isomerization in a metal complex has not been found.

In the course of a Mössbauer investigation of the aftereffects of ^{57}Co-labeled $M_2[Co(NCS)_4]$ ($M = K^+, Et_4N^+, Me_4N^+$),[15] we have reported that two kinds of iron(II) species were observed on the basis of the emission Mössbauer spectra, which

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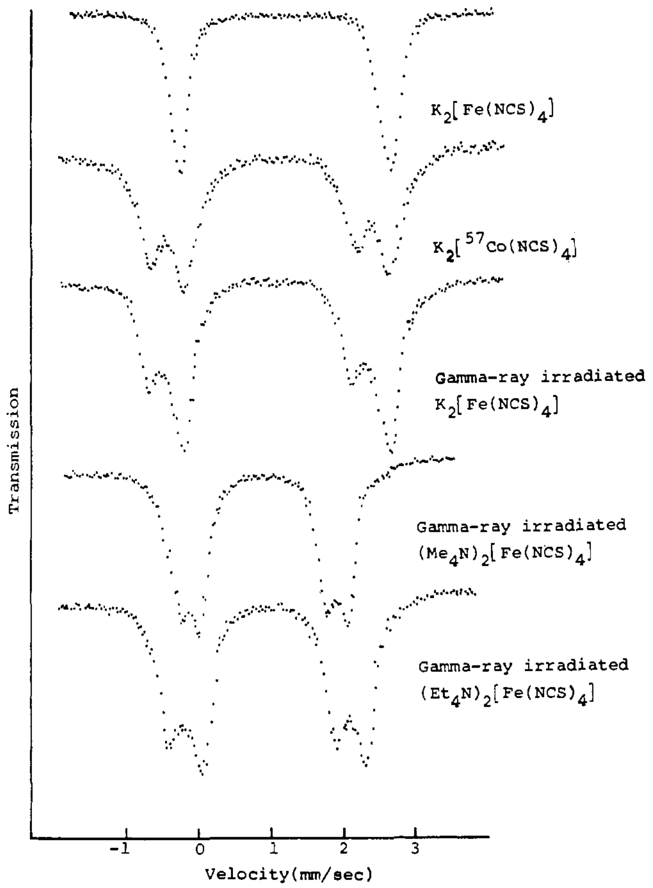

Figure 1. Mössbauer spectra of $K_2[^{57}Co(NCS)_4]$, $K_2[Fe(NCS)_4]$, and γ-ray-irradiated $M_2[Fe(NCS)_4]$ at 78 K.

showed two components of the quadrupole-split doublets. One of them was presumed to be a new S-bonded iron thiocyanate (Fe–SCN) species. In order to clarify the chemical environment of this new iron species, Mössbauer and infrared spectra of γ-ray-irradiated and -unirradiated $M_2[Fe(NCS)_4]$ (M = Me_4N^+, Et_4N^+, and K^+) and $(Et_4N)_2(FeCl_4)$ were studied. This work presents the first example of γ-ray-induced linkage isomerism for the tetrahedral $[Fe(NC)_4]^{2-}$. We also examined the Mössbauer emission spectrum of $(Et_4N)_2(^{57}CoCl_4)$.

Experimental Section

All operations were carried out in an inert-atmosphere glovebox filled with nitrogen. Solid reagent grade chemicals were used without further purification.

Preparation of $M_2[Fe(NCS)_4]$ (M = Me_4N^+, Et_4N^+, and K^+). $M_2[Fe(NCS)_4]$ (M = Me_4N^+, Et_4N^+, and K^+) were prepared by modifications of previously reported procedures.[1,11,16,17]

Preparations of $(Et_4N)_2(FeCl_4)$ and $(Et_4N)_2(^{57}CoCl_4)$. The compounds $(Et_4N)_2(FeCl_4)$ and $(Et_4N)_2(CoCl_4)$ were prepared directly according to the methods described previously by Forster and Goodgame.[18] The ^{57}Co-labeled $(Et_4N)_2(CoCl_4)$ was prepared by using a methanol solution of ligands and cobalt(II) chloride containing 1 mCi ^{57}Co. All the compounds gave satisfactory elemental analyses.

γ-Ray Irradiation of the Iron Complexes. γ-Ray irradiations were carried out at room temperature in a ^{60}Co γ-ray source (dose rate 1.0×10^6 rd h^{-1}) on species contained in sealed, evacuated, baked-out, Pyrex ampules and exposed up to a total dosage of 1.0×10^9 rd.

Physical Measurements. Magnetic susceptibility of the complexes at room temperature was measured on a Newport Gouy balance. Mössbauer absorption spectra of γ-ray-irradiated and -unirradiated iron complexes (sealed in an acrylic disk) were measured on an Austin Mössbauer spectrometer using a 10-mCi ^{57}Co (Pd) source. Mössbauer emission spectra were taken against an ^{57}Fe-enriched $K_4Fe(CN)_6{\cdot}3H_2O$ absorber moving in a mode of constant acceleration at room temperature. The isomer shift values are quoted relative to the center of the hyperfine pattern of the iron foil at room temperature.

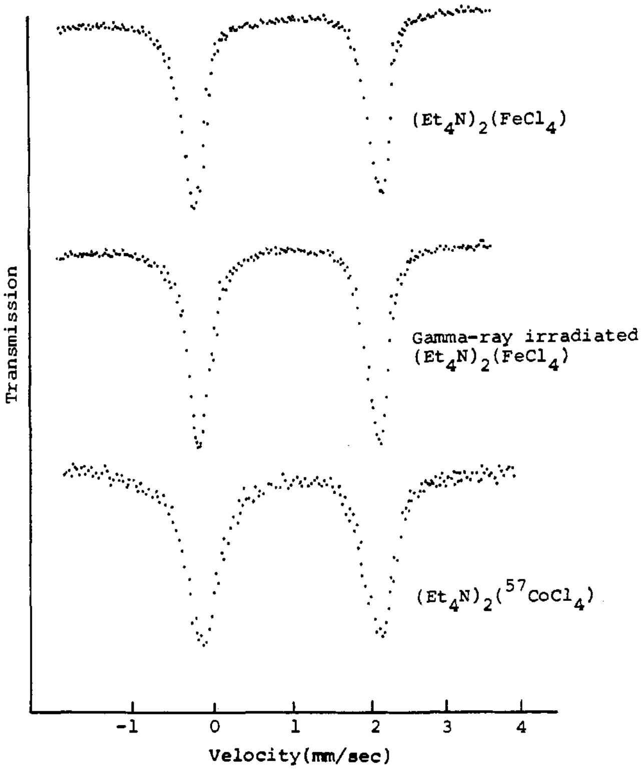

Figure 2. Mössbauer spectra of $(Et_4N)_2(FeCl_4)$, γ-ray-irradiated $(Et_4N)_2(FeCl_4)$, and $(Et_4N)_2(^{57}CoCl_4)$ at 78 K.

Table I. Mossbauer Parameters and Magnetic Data for the Complexes

compd	μ_{eff}, μ_B 295 K	isomer shift, mm/s 78 K	isomer shift, mm/s 293 K	quadrupole splitting, mm/s 78 K	quadrupole splitting, mm/s 293 K
$K_2[Fe(NCS)_4]$ (γ-ray irrad)	5.40	1.37	1.21	2.86	1.82
$K_2[Fe(NCS)_4]$	5.40	1.36	1.21	2.86	1.82
		0.91	0.85	2.83	1.94
$K_2[^{57}Co(NCS)_4]$		1.38	...	2.90	...
		0.90	...	2.85	...
$(Me_4N)_2[Fe(NCS)_4]$ (γ-ray irrad)	5.41	1.06	1.19	2.12	1.70
$(Me_4N)_2[Fe(NCS)_4]$	5.42	1.07	1.16	2.12	1.67
		0.92	0.83	2.05	1.73
$(Me_4N)_2[^{57}Co(NCS)_4]$[a]		1.05	...	2.20	...
		0.89	...	1.98	...
$(Et_4N)_2[Fe(NCS)_4]$ (γ-ray irrad)	5.42	1.31	1.22	2.25	1.79
$(Et_4N)_2[Fe(NCS)_4]$	5.42	1.34	1.25	2.30	1.79
		0.75	0.70	2.25	1.75
$(Et_4N)_2[^{57}Co(NCS)_4]$[a]		1.33	...	2.32	...
		0.76	...	2.44	...
$(Et_4N)_2(FeCl_4)$ (γ-ray irrad)	5.40	1.00	0.86	2.42	0.72
$(Et_4N)_2(FeCl_4)$	5.40	1.00	0.85	2.43	0.79
$(Et_4N)_2(^{57}CoCl_4)$		1.04	...	2.46	...

[a] Parameters taken from ref 15.

Infrared spectra between 4000 and 625 cm^{-1} were obatined on a Perkin-Elmer Model 257 spectrometer. Samples were taken as Nujol mulls on a NaCl plate or as KBr pellets.

Results and Discussion

Typical Mössbauer absorption spectra of γ-ray-irradiated iron complexes at 78 K are shown in Figures 1 and 2, together with spectra of the unirradiated compounds and the emission spectra of $K_2[^{57}Co(NCS)_4]$ and $(Et_4N)_2(^{57}CoCl_4)$ for the sake

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Table II. Infrared Spectra of Thiocyanate Complexes

compd	C-N str, cm^{-1}	C-S str, cm^{-1}	linkage isomer
$K_2[Fe(NCS)_4]$ (γ-ray irrad)	2053	830	Fe-NCS
$K_2[Fe(NCS)_4]$	2095 2056	830 720	Fe-NCS and Fe-SCN
$(Me_4N)_2[Fe(NCS)_4]$ (γ-ray irrad)	2053	830	Fe-NCS
$(Me_4N)_2[Fe(NCS)_4]$	2090 2053	830 710	Fe-NCS and Fe-SCN
$(Et_4N)_2[Fe(NCS)_4]$ (γ-ray irrad)	2053	829	Fe-NCS
$(Et_4N)_2[Fe(NCS)_4]$	2090 2053	829 710	Fe-NCS and Fe-SCN

of comparison. The Mössbauer parameters at 298 and 78 K for emission spectra of $M_2[^{57}Co(NCS)_4]$ and $(Et_4N)_2(^{57}CoCl_4)$ and absorption spectra of γ-ray-irradiated and -unirradiated corresponding iron complexes are given in Table I.

It is known that the compounds $M_2[Fe(NCS)_4]$ have the same crystal structures as $M_2[Co(NCS)_4]$ ($M = Me_4N^+$, Et_4N^+, and K^+), which have N-bonded thiocyanate (Fe-NCS),[18,19] although γ-ray-irradiated $M_2[Fe(NCS)_4]$ and ^{57}Co-labeled $M_2[Co(NCS)_4]$ show two sets of quadrupole-split doublets in both absorption and emission Mössbauer spectra. One of the two doublets is assigned to the N-bonded $[Fe(NCS)_4]^{2-}$ species on the basis of the values of the isomer shift and quadrupole splitting obtained in absorption spectra of the γ-ray-unirradiated species, which are typical of tetrahedral iron(II) compounds and $M_2[Fe(NCS)_4]$. These are in general agreement with values previously reported.[20] The other one has a quadrupole splitting similar to that of $[Fe(NCS)_4]^{2-}$ but of somewhat smaller isomer shift. In addition, the intensity of the absorption spectrum for this low-isomer-shift species increased with a decrease in temperature. The Mössbauer spectrum at 78 K presented in Figure 2 of ^{57}Co-labeled $(Et_4N)_2(CoCl_4)$ shows that only one kind of iron species has been found. The essentially identical Mössbauer spectral parameters observed for these tetrahalo complexes are typical of tetrahedral iron(II) compound and are in agreement with previous reports.[21] The results not only reveal that the $(Et_4N)_2(CoCl_4)$ is isomorphous with $(Et_4N)_2(FeCl_4)$, whose structure has been reported,[22-25] but also indicate that no γ-ray-induced structural changes occur and that no linkage isomerism occurred in the present system. In practice, however, isomerization of Fe-Cl bonds is impossible. Consequently, the new iron species, characterized by Mössbauer spectra of $M_2[^{57}Co(NCS)_4]$ and γ-ray-irradiated $M_2[Fe(NCS)_4]$, are recognized as being induced from the recombination between iron atoms and NCS ligans after γ-ray radiolysis. This observation indicates that this new iron species has therefore the possibility of being the S-bonded thiocyanato (Fe-SCN) isomer. It does seem reasonable that the isomer shift values (as shown in Table I) of the S-bonded Fe-SCN isomer be lower than those of N-bonded Fe-NCS complexes. This low shift is probably the result of a somewhat increased 3d delocalization to covalently bonded sulfur. This results in a higher s-electron density at the iron nucleus and a lower isomer shift, since the 3d-electron shielding of s electrons will be reduced.

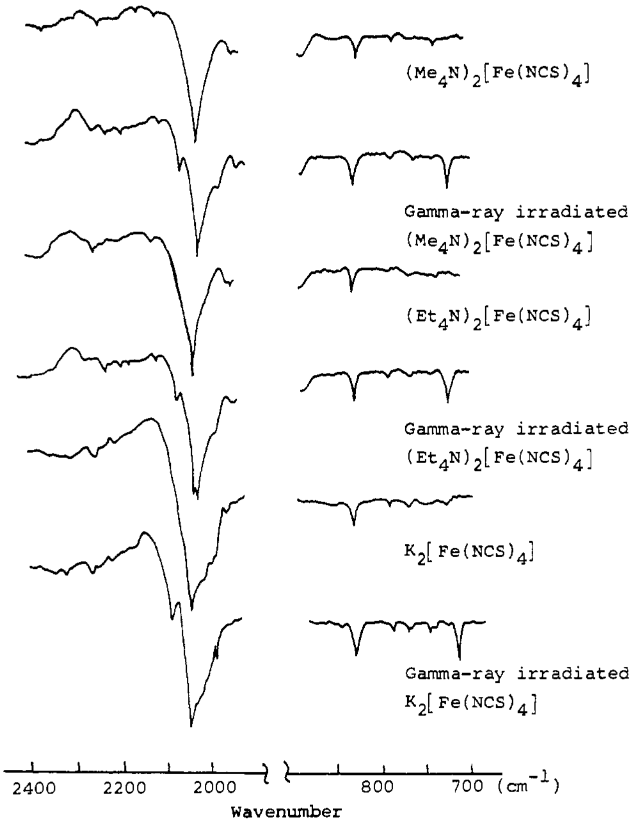

Figure 3. Infrared spectra of $M_2[Fe(NCS)_4]$ and γ-ray-irradiated $M_2[Fe(NCS)_4]$.

To confirm the proposed the linkage isomerism of iron complexes, we have recorded infrared spectra of all the γ-ray-irradiated and -unirradiated iron complexes, the results of which are shown in Figure 3 and Table II. The nature of the thiocyanate bonding in these two isomers was determined on the basis of the position of the thiocyanate C-S and C-N stretching requencies for the complex in question. It has been shown[1,26,27] that the C-S stretching vibrations of coordinated thiocyanates fall into two ranges: M-SCN, 690-720 cm^{-1}; M-NCS, 780-860 cm^{-1}. The frequencies of the C-N vibrations were also observed to vary. In most cases the thiocyanate group (M-SCN) exhibited very sharp, well-formed C-N stretching peaks at about 2080-2130 cm^{-1}, whereas the isothiocyanato (M-NCS) complexes exhibited relatively broad, more intense peaks at about 2040-2080 cm^{-1}.

The infrared spectra of the unirradiated $M_2[Fe(NCS)_4]$ complexes (as shown in Figure 3) showed the complete absence of the S-bonded C-S stretching peaks near 710 cm^{-1}. The C-N stretching peaks, found only at a lower frequency (ca. 2055 cm^{-1}), are characteristic of N-bonded complexes. After a total dose of 10^9 rd of γ-ray irradiation to the corresponding isothiocyanato iron(II) complexes, the new infrared absorption bands at ca. 710 and ca 2095 cm^{-1}, which are characteristic of the C-S and C-N absorptions of the S-bonded thiocyanato iron(II) isomer, were found. Use of these criteria show that the partial linkage isomerization of thiocyanate takes place in the γ-ray-irradiated $M_2[Fe(NCS)_4]$ solid samples.

It would have been desirable, of course, to investigate the mechanism of isomerization in the solid state of these and other systems. to this end work is now in progress on the synthesis and Mössbauer and infrared spectroscopic studies of the

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analogous linkage isomers of the type M–SeCN and M–NCSe and possibly M–NCO and M–OCN.

Acknowledgment. We gratefully acknowledge the use of the laboratory facilities of the Radiochemical Research Institute of National Cheng-Hwa University for preparation of ^{57}Co-labeled complexes and ^{60}Co γ-ray irradiation in this work.

Registry No. $K_2[Fe(NCS)_4]$, 88295-75-4; $(Me_4N)_2[Fe(NCS)_4]$, 13978-34-2; $(Et_4N)_2[Fe(NCS)_4]$, 14127-42-5; $K_2[^{57}Co(NCS)_4]$, 88295-76-5; $(Et_4N)_2(FeCl_4)$, 15050-84-7; $(Et_4N)_2(^{57}CoCl_4)$, 88295-80-1; ^{57}Co, 13981-50-5.

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An ab Initio Study of the $B_2H_7^-$ Anion

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Shore et al.[1] have reported an X-ray diffraction study on the $B_2H_7^-$ anion as a part of the $[(Ph_3P)_2N]^+[B_2H_7]^-\cdot CH_2Cl_2$ compound. In disagreement with previous ab initio calculations carried out in the gas phase[2] on $B_2H_7^-$, Shore et al. found the ion to exhibit a bent B–H–B central linkae as well as to feature a certain asymmetry in the lengths of the boron distances from the bridging hydrogen. They report an overall C_s symmetry for the anion, with two hydrogens set trans to each other (one on each boron) and set in the same plane as the two borons and the central hydrogen.

A similar compound, $[Me_3Al(\mu\text{-}H)AlMe_3]^-$, as reported by Atwood et al.,[3] also through X-ray diffraction data and confirmed by our ab initio calculations[4] using a 3-21G basis set, reveals a linear Al–H–Al bond.

In this work, the $B_2H_7^-$ anion is subjected to an investigation by ab initio (Hartree–Fock) methods, in order to elucidate its geometry and to report eventual differences in the compound description introduced by the use of Gaussian basis sets with and without polarization functions. For comparison purposes, calculations are also carried out on the $B_2H_6F^-$ anion.

Method

The $B_2H_7^-$ ion is subjected to total geometry optimization using a split-valence 6-31G[5a] and a 6-31G**[5b] basis set, as implemented by the GAUSSIAN-80 computer program.[6c] The 6-31G** basis set adds d orbitals on the boron and p orbitals on the hydrogen. The optimization technique used is the Berny optimization technique,[5c] which determines singular points by minimizing the energy with all the parameters to be optimized simultaneously.

The initial value assigned to the B–H–B angle for the 6-31G minimization procedure was 150°.

In the 6-31G** calculations, two initial values were used: 136° (the experimental value reported by Shore et al.[1]) for one optimization and 180° for the second. The purpose of this procedure was to avoid local minima that could be misleading. An almost identical procedure is applied to the $B_2H_6F^-$ anion, again performing two sets f optimizations, one starting with a B–F–B angle of 136° and the other setting the B–F–B angle at 180° and optimizing the other paramters. Since the studies of the $B_2H_6F^-$ anion need further refinement, only the general conclusions are reported here.

Table I displays the energies corresponding to the optimum geometries, together with the geometrial parameters.

In Table II, the net atomic charges are displayed, as obtained for the lowest energy states. Figure 1a, b shows the bent and linear structures of the B_2H_7 anion. Figure 2 shows the $B_2H_6F^-$ anion.

Table I. Energies (au) and Geometrical Parameters[a]

	6-31G E = −53.37002	6-31G** E = −53.40258
Distances		
B_1H_1	1.33	1.34
B_2H_1	1.33	1.32
B_1H_2	1.21	1.21
$B_1H_3 = B_1H_4$	1.21	1.21
$B_1\text{–}B_2$	2.57	
B_2H_5	1.21	1.21
$B_2H_6 = B_2H_7$	1.21	1.22
Angles		
$B_1H_1B_2$	179.9	149.9
$H_2B_1H_1$	104.2	101.3
$H_3B_1H_1 = H_4B_1H_1$	104.2	104.3
$H_5B_2H_1$	104.2	106.9
$H_6B_2H_1 = H_7B_2H_1$	104.2	104.3
$H_3B_1H_2 = H_4B_1H_2$	114.2	114.0
$-H_6B_2H_5 = H_7B_2H_5$		
Dihedral Angles		
$H_2B_1H_1$ with $B_1H_1B_2$	180.0[b]	180.0
$H_5B_2H_1$ with $B_1H_1B_2$	0.0[b]	0.0

[a] Bond lengths in angstroms; bond angles in degrees. [b] Set values.

Table II. Net Atomic Charges (eu) As Obtained by 6-31G** Calculations for the Optimum Geometry

B_1	0.211	H_4	−0.189
B_2	0.206	H_5	−0.187
H_1	−0.226	H_6	−0.208
H_2	−0.209	H_7	−0.208
H_3	−0.189		

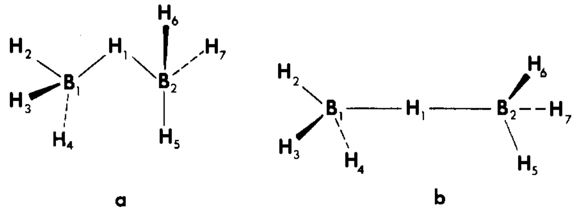

Figure 1. (a) Bent structure of $B_2H_7^-$. (b) Linear structure of $B_2H_7^-$.

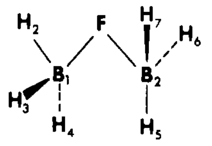

Figure 2. Structure of $B_2H_6F^-$.

Discussion of the Results

The 6-31G calculations predict a linear B–H–B bond. However, in disagreement with previous ab initio calculations, including those carried out with a large basis set with polar-

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