for some $t_i^{TT} \in T^{TT}$. In other words, the number of right cosets Th_i contained in the sets of operations Th_oR and Th_pR equals the connectivity δ_R.

We first assume that h_o^{TR} is achiral. Then by definition, $Th_oR = Th_pR$. Thus δ_R is the number of right cosets Th_i in Th_oR. This number is calculated by eq A2.[23]

$$\delta_R = \frac{|R|}{|R \cap h_o^{-1}Th_o|} \qquad \text{(A2)}$$

If h_o is chiral and $h_p = \bar{l}_o \cdot h_o \cdot \bar{r}_o$, then the sets of operations Th_oR and Th_pR are mutually exclusive. We shall demonstrate that the number of right cosets Th_i in Th_oR equals the number of right cosets Th_j in Th_pR; *i.e.*, eq A3 holds.

$$\delta_R = \frac{2|R|}{|R \cap h_o^{-1}Th_o|} \qquad \text{(A3)}$$

We put the elements of h_oR and h_pR into a 1:1 correspondence by associating $h_o \cdot r_n$ with $\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o$. Proof of eq A3 involves showing that

$$h_o \cdot r_n = t_i \cdot h_o \cdot r_m$$

for some $t_i \in T$ if and only if

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

for some $t_j \in T$. This relation holds since: (i) for any given t_j and $\bar{l}_o$, $t_j \cdot \bar{l}_o = \bar{l}_o \cdot t_k$ for some $t_k \in T$ and, therefore, if

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

then

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = \bar{l}_o \cdot t_k \cdot h_o \cdot r_m \cdot \bar{r}_o$$

and consequently

$$h_o \cdot r_n = t_k \cdot h_o \cdot r_m$$

for some $t_k \in T$. (ii) $h_o \cdot r_n = t_i \cdot h_o \cdot r_m$ implies that

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = \bar{l}_o \cdot t_1 \cdot h_o \cdot r_m \cdot \bar{r}_o$$

Since $\bar{l}_o \cdot t_i = t_j \cdot \bar{l}_o$ for some $t_j \in T$

$$\bar{l}_o \cdot h_o \cdot r_n \cdot \bar{r}_o = t_j \cdot \bar{l}_o \cdot h_o \cdot r_m \cdot \bar{r}_o$$

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[23] For a proof, see ref 10. Note that Hall uses a different convention for naming right and left cosets from that used here.

Calculated and Observed Electronic Transitions in Organolithium Aggregates

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Abstract: The ultraviolet spectra of ethyl-, *n*-butyl-, *sec*-butyl-, and *tert*-butyllithium have been observed and found to have λ_{max} of 215 and 203 nm for ethyl (vapor phase) $\epsilon \sim 10^3$; *n*-butyl, λ_{max} 210 nm, ϵ 5.2 × 10^2 (hexane solution); *sec*-butyl, λ_{max} 206 nm (vapor phase); and *tert*-butyl, λ_{max} ~190 nm, $\epsilon \sim 10^3$ (vapor phase). The energies of the electronic transitions have been determined from CNDO/2 calculations on idealized tetrameric and hexameric methyllithium and on the basis of these transitions were predicted at 10.0 eV (124 nm) and at 7.26 eV (171 nm), respectively, in reasonable agreement with observed values.

In a review on organolithium compounds, Brown[2a] reported that alkyllithiums do not absorb in the ultraviolet region. This conclusion was based mainly on the work of Waack and Doran[2b] who studied a series of alkyllithium derivatives in tetrahydrofuran solutions and observed only end absorption.

Molecular orbital calculations by Weiss and Lucken[3] predict that the methyllithium tetramer should have a transition between the highest occupied molecular orbital (t_2) and the lowest unoccupied molecular orbital (a_1) occurring about 240 nm. More sophisticated calculations by Cowley and White[4] using SCC and CNDO/1 methods were used to predict transitions at 403 and 100.6 nm, respectively, for the methyllithium tetramer.

Oliver, *et al.*,[5] have reported a transition for *n*-butyllithium in hexane occurring at λ_{max} 220 nm, while Glaze and Brewer[6] have observed a transition for ethyllithium in isooctane with λ_{max} 210 nm. Due to the extreme reactivity of these compounds and the difficulty in obtaining solvents which are completely free of moisture, oxygen, and olefinic impurities, these results have been viewed with skepticism (see for instance the referee's comment in ref 6).

In an effort to establish whether these reported transitions were due to the alkyllithium species both vapor phase and solution studies of the ultraviolet spectra of organolithium derivatives were initiated. Additional molecular orbital calculations were carried out using the CNDO/2 method since it is reported that these calculations give better results than the earlier CNDO/1 scheme.[7]

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(1) (a) Xavier University; (b) Wayne State University.

(2) (a) T. L. Brown, *Advan. Organometal. Chem.*, 3, 365 (1965); (b) R. Waack and M. Doran, *J. Amer. Chem. Soc.*, **85**, 1651 (1963).

(3) K. Weiss and E. A. C. Lucken, *J. Organometal. Chem.*, **2**, 197 (1964).

(4) A. H. Cowley and W. D. White, *J. Amer. Chem. Soc.*, **91**, 34 (1969).

(5) J. P. Oliver, J. B. Smart, and M. T. Emerson, *ibid.*, **88**, 4101 (1966).

(6) W. H. Glaze and T. L. Brewer, *ibid.*, **91**, 4490 (1969).

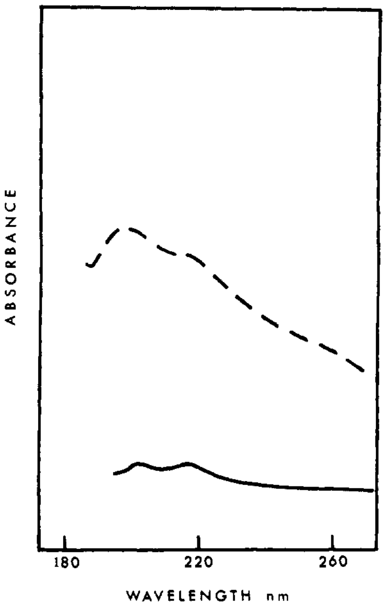

Figure 1. Ultraviolet spectra of ethyllithium vapor (——) and of the vapor–solid equilibrium mixture (- - -).

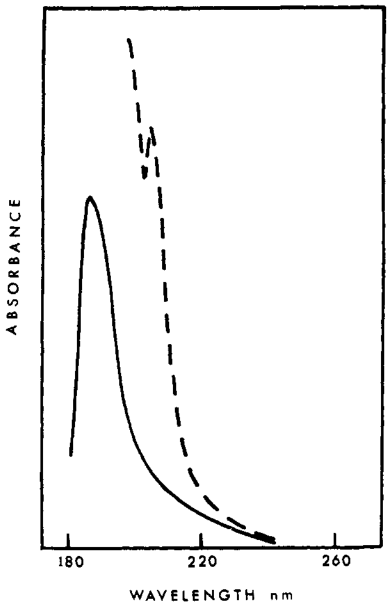

Figure 2. Ultraviolet spectra of *sec*-butyllithium (- - -) and *tert*-butyllithium (——) in the vapor phase.

Experimental Section

All reactions and transfers of organolithium compounds were carried out under an argon atmosphere or in a high-vacuum system to ensure the purity of all compounds. Ethyllithium was prepared under vacuum by cleavage of diethylmercury with lithium metal in hexane. The diethylmercury was obtained from Eastman Organic Chemicals or from the reaction of ethyl Grignard with mercuric chloride. Purification was accomplished by trap to trap distillation in the vacuum system. *n*-Butyllithium was prepared in the same manner from the mercury compound, but was purified only by filtration from the excess lithium metal. *sec*-Butyllithium was obtained from Matheson Coleman and Bell (15% hexane solution) and purified by a distillation in the high-vacuum system yielding a colorless liquid product. *tert*-Butyllithium was obtained from Foote Mineral Co. (15% in pentane solution) and purified in an analogous manner yielding a white crystalline product. The vapor pressure of *tert*-butyllithium was estimated to be ~0.1 mm at 25° by exposing *tert*-butyllithium vapor to a Hastings DV-43 vacuum gauge. On exposure for several minutes the *tert*-butyllithium vapor reacted with the detector filament leaving a coating on it and greatly decreasing the response.

The purity of the compounds was checked by examination of their infrared and nmr spectra. The infrared spectra were obtained on thin films using a Perkin-Elmer 237B spectrophotometer. The nmr spectra were obtained on either a Varian A-60-A or HA60IL spectrometer. The nmr samples of the alkyllithium were prepared either by sublimation or distillation directly into the nmr tube attached to the vacuum system followed by addition of solvent or in the argon-filled drybox. No unassignable peaks were observed in the nmr spectra of these compounds indicating that any impurity present is less than 1%.

Ultraviolet studies were made using Cary Models 14 and 15 and a Beckman DB spectrophotometer. The Beckman instrument was calibrated to benzene and holmium oxide; the reported values are accurate to ±3.0 nm. The vapor-phase spectra were obtained using a specially constructed high-vacuum cell with a 1-mm path length and 90% transmission at 180.0 nm. The cells were evacuated for 24 hr before use to ensure that traces of moisture adhering to the walls would be removed. The purified lithium compounds stored in the vacuum system were then sublimed or distilled directly into the cell by immersing the side arm of the cell in liquid nitrogen. All spectra were obtained at ambient temperature (unless otherwise noted) with the solid or liquid in equilibrium with its vapor *vs.* a matched cell containing air.

The solution spectra of *n*-butyllithium and lithium *n*-butoxide were obtained by making solutions of the lithium compounds in an argon-filled drybox, scavenged with sodium–potassium alloy. The hexane solvent was dried over sodium–potassium alloy and then distilled into another vessel on the high-vacuum system which in turn was sealed off by means of a constriction. The concentrations were determined either by weight of the alkyllithium and of the solvent used or by titration of lithium hydroxide following hydrolysis of an aliquot of the solution. The 10-mm liquid cells and all other glassware that was used to handle the lithium compounds in the glove box were placed in a vacuum chamber for 24 hr prior to use or dried at 140° for a similar period to remove traces of moisture adhering to the glass.

The validity of the absorbing species was established by first observing the spectrum with the sample in the cell. The sample was then distilled out of the cell into a high-vacuum system and the spectrum recorded again. The second spectrum was observed to be a duplication of the cell blank. The reintroduction of the sample into the cell again produced the original spectrum. Finally, the sample was frozen in the side arm of the cell with liquid nitrogen and a small amount of water vapor was introduced into the cell from the vacuum system. After allowing the cell to warm to room temperature the spectrum was scanned again. The absorption observed initially was now absent and only the cell blank was observed.

Results

Ethyllithium vapor showed a very broad absorption in the region of 220–200 nm (Figure 1) with two maxima, *ca.* 215 and 203 nm. These data are collected in Table I. The solid (obtained by subliming ethyllithium onto the face of the cell) displayed the same type of broadened spectrum but now a definite λ_{max} was observed at 203 nm, with a shoulder appearing at 215 nm. Based on a vapor pressure of 10^{-3} mm at 60°,[2a] a value of 10^3–10^4 can be estimated for the extinction coefficient. This corresponds to the value of 2.0×10^3 l./(mol cm) obtained by Glaze and Brewer for ethyllithium in isooctane.[6]

tert-Butyllithium vapor showed a single λ_{max} at *ca.* 190 nm (Figure 2). The reliability of the uv instrument in this region is variable; however the observed peak was reproducible from different *tert*-butyllithium samples and was never observed in cell blank scans. At 25° *tert*-butyllithium was observed to have a vapor pressure of 0.1 mm. As with the ethyllithium the extinction coefficient was estimated to be around 10^3–10^4.

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(7) A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

Table I. Electronic Transitions Calculated by CNDO/2 Procedures

Compound	Symmetry allowed, eV	Oscillator strength[a]	Electronic symmetry forbidden, eV	Transitions molecular orbitals	Symmetry of excited state
Tetramer	10.00	0.783		(14, 15, 16)-17	T_2
			10.27	(14, 15, 16)-(18, 19, 20)	T_1
			10.27	(14, 15, 16)-(18, 19, 20)	E
			10.29	(14, 15, 16)-(18, 19, 20)	A_1
	10.74	0.005		(14, 15, 16)-(18, 19, 20)	T_2
			13.00	(14, 15, 16)-(21, 22)	T_1
	13.14	0.899		(14, 15, 16)-(21, 22)	T_2
Hexamer			5.69	(23, 24)-25	E_g
	7.26	0.479		(23, 24)-26	E_u
	7.62	0.935		22-25	A_{2u}
			8.69	22-26	A_{1g}
			8.97	(23, 24)-27	E_g
	9.01	0.851		(20, 21)-25	E_u
			9.72	(20, 21)-26	E_g
	11.52	0.975		(23, 24)-(28, 29)	E_u

[a] Oscillator strength for each of a set of degenerate transitions.

sec-Butyllithium vapor showed a single λ_{max} at 206 nm and then an infinite end absorption as shown in Figure 2.

n-Butyllithium in hexane has a λ_{max} at 210 nm with an extinction coefficient of 5.2×10^2 l./(mol cm). Exposing the sample briefly to air caused a new peak to appear at 245 nm which we attribute to the formation of lithium butoxide. This is shown in Figure 3. We observed a similar appearance of longer wavelength absorptions in ethyllithium through exposure of a hexane solution of ethyllithium to air. This exposure resulted in the appearance of several new absorptions with λ_{max} about *ca.* 260 nm. In accordance with the data on lithium butoxide it seems reasonable to assign this new band to the presence of lithium ethoxide. In a more general sense, it appears that alkoxide contamination yields new absorptions at longer wavelengths. Since no absorption observed in this work was above 220 nm, it seems reasonable to conclude its absence in sufficient amount to influence our studies, which is in agreement with our nmr studies.

Molecular orbital calculations on electronic transitions have been carried out on idealized tetrameric and hexameric methyllithium species. In the model used for the tetramer,[8,9] the lithium atoms are at the corners of a regular tetrahedron with a Li-Li distance of 2.55 Å. The carbon atoms are located above each face of the tetrahedron at a distance of 2.3 Å from each of three lithium atoms. These sp^3 hybridized carbons are bonded to three hydrogens with C-H bond length of 1.09 Å as observed for normal C-H bonds. The fourth sp^3 orbital points directly to the center of the tetrahedron. The model used for calculations on the hexameric species has the lithium atoms placed at the corners of a regular octahedron with carbon atoms located above six of the eight faces. The two empty faces were chosen opposite each other giving the molecule D_{3d} symmetry. The bond lengths were assumed to be the same in the hexamer as in the tetramer with the hexameric structure based on the model proposed by Brown.[2a]

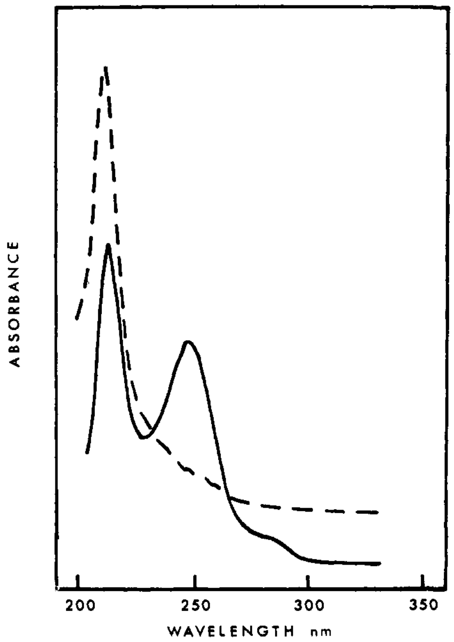

Figure 3. Ultraviolet spectra of *n*-butyllithium in hexane solution before (- - -) and after (——) exposure to air.

The calculation of the electronic transitions for the lithium tetramer and hexamer were carried out using the CNDO/2 method.[10] To avoid biasing these calculations, the original parameterization of Pople and Segal[11] was used rather than any of the special reparameterizations specifically modified to better reproduce electronic transitions. The energy required to promote an electron from an occupied molecular orbital, ψ, to an unoccupied orbital, ϕ, was predicted using the virtual orbital approximation[12] when either orbital ψ or ϕ is a member of a nondegenerate set of orbitals. In this method, the excitation energy for the singlet-singlet transition is given by

$$\Delta E = \epsilon_{\psi} - \epsilon_{\phi} - J_{\psi\phi} + 2K_{\psi\phi} \qquad (1)$$

where ϵ_{ψ} and ϵ_{ϕ} are the energy of orbital ψ and ϕ, respectively, and $J_{\psi\phi}$ and $K_{\psi\phi}$ are the Coulomb and exchange type integrals over the molecular orbitals.

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(8) E. Weiss and G. Henchen, *J. Organometal. Chem.*, **21** 265 (1970).

(9) H. Dietrich, *Acta Crystallogr.*, **681**, 16 (1963).

(10) Quantum Chemistry Program Exchange Indiana University, Bloomington, Indiana 47401.

(11) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

(12) H. W. Kroto and D. P. Santry, *ibid.*, **47**, 792 (1967).

Since the tetrameric and hexameric species have high symmetry, many sets of degenerate orbitals occur. When both ψ and ϕ are members of degenerate sets of orbitals, it is necessary to use first-order configuration interaction methods to calculate the transitions. The procedures for these calculations have been published.[13,14]

The results of these calculations are presented in Table II. Symmetry forbidden transitions are reported since they may become allowed as the molecular symmetry is reduced in going from the methyl to the ethyl compound or due to distortion of the regular polyhedra. The lowest energy allowed transitions for the tetramer is calculated at 10.0 eV and observed at 6.1–6.5 eV. For the hexamer the calculated transition occurs at 7.26 eV and occurs experimentally at 5.8–5.9 eV. This overestimation of the transition energies is characteristic of the method of calculation.[12,15,16] Using the original parameterization for the π–π^* transitions in benzene,[15] the calculated value is 14.4 eV *vs.* 6.82–6.39 eV for the transition to the $^1E_{1u}$ state, 10.26 *vs.* 6.09 eV to the $^1B_{1u}$ state, and 10.07 *vs.* 4.72 eV to the $^1B_{2u}$ state.

Table II. Ultraviolet Spectral Parameters of Alkyllithium Compounds

			λ_{max}		
Compound	Solvent	Aggregation	eV	nm	ϵ
Methyl		Tetramer	9.98	123.98	(calcd)
		Hexamer	7.25	170.73	(calcd)
Ethyl	Isooctane[a]	Hexamer	5.90	210	2.0×10^3
	Vapor[b,c]	Hexamer	5.76	215	$\sim 10^3$
		Tetramer	6.09	203	
n-Butyl[d]	Hexane	Hexamer	5.90	210	5.2×10^2
sec-Butyl	Vapor[b]		6.01	206	
tert-Butyl	Vapor	Tetramer	6.25	~190	$\sim 10^3$

[a] Reference 3. [b] Gas-phase equilibrium mixture of hexamer and tetramer. [c] Broad absorption from 220 to 200 nm. [d] Exposure to air resulted in absorption at 245 nm.

Discussion

The lowest energy transition in the tetramer provides an interesting result in that the electron goes from a molecular orbital centered 73% on the carbons to one which is 83% on lithium. In the hexamer the lowest energy symmetry allowed transitions do not show this charge transfer behavior. However, two of the low-energy transitions which are symmetry forbidden for the methyllithium hexamer do display this characteristic. The first of these is at the lowest transition energy calculated for the hexamer, 5.96 eV, and involves electron transfer from an orbital 80% on carbon to one 48% on lithium. In the second of these transitions at 8.97 eV, the electron is promoted from an orbital 77% on carbon to one 83% on lithium.

The electronic spectra of alkyllithium derivatives in the vapor phase seem to be determined by two factors: (a) the state of aggregation and (b) the nature of the carbon α to the lithium, *i.e.*, the relative ability of an α-carbon to release electron density.

Ethyllithium provides a good model from which to study aggregation effects because the degree of association has been determined in the solid, solution and vapor phases. Brown has shown that ethyllithium in the vapor phase exists in both the hexameric and tetrameric forms.[17] In accordance with these observations, two absorptions at 203 and 215 nm were observed for the ethyllithium vapor. Based on our calculations, we assigned the absorption at 203 nm to the tetrameric species. This assignment is further supported by the increased absorption at 203 nm when a thin film of solid ethyllithium (tetramer) was present in equilibrium with its vapor. The absorption at 215 nm is close to the value of 210 nm observed by Glaze[6] for ethyllithium in isooctane and ethyllithium[18] has been shown to be hexameric in nonpolar solvents. *n*-Butyllithium has also been shown to be hexameric in solution.[5] Our assignment of the lower energy transition to the hexamer is consistent with the observed transition for the *n*-butyl case (λ_{max} 210 nm).

sec-Butyl- and *tert*-butyllithium have been shown to be tetrameric in nonpolar solvents and in vapor.[19,20] These derivatives have electronic transitions which occur at 206 and 190 nm, respectively. This again is consistent with our calculation which shows that transitions in the tetramer framework occur at higher energy.

Aggregation effects alone do not account for the difference observed by individual hexameric and tetrameric species. The ethyl-, *sec*-butyl-, and *tert*-butyllithium have electronic transitions in the vapor occurring at 203, 206, and 190 nm, respectively. The differences within these tetrameric species may be related to the degree of substitution on the α-carbon atom. Our calculations indicate that the lowest energy transition in the tetrameric unit corresponds to an electron leaving an orbital centered mainly on the carbon atoms to one centered on the lithium aggregate. For this charge transfer transition, the inductive effect of adding methyl groups to the α-carbons should lower the energy of the excited state. Therefore one would predict that the energy of the electronic transitions will follow the order primary > secondary > tertiary. The observed order is *tert*-butyl- > ethyl- > *sec*-butyllithium.

The anomalous occurrence of the *tert*-butyllithium transition at higher energy than ethyl- or *sec*-butyllithium may be accounted for in terms of the distortion introduced in the structure of *tert*-butyllithium due to steric interactions. Let us assume that the Li–Li distance in the tetramer unit is kept at 2.55 Å and that the closest approach permitted between the methyls of the *tert*-butyl groups is 4.0 Å,[21] *i.e.*, twice the van der Waals radius. Then the Li–α-carbon bond length must be increased by 0.10 Å, and the dihedral angle formed by lithium, the center of the tetramer, and the α- and β-carbon must be kept at 17.5°. If one wanted to allow any rotation of the *tert*-butyl under these assumptions, the distance must be increased further. Primary and secondary α-carbon atoms do not experience this elongation because they can slide slightly off the center of the face to relieve steric repulsions.

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(13) J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 81 (1967).

(14) J. N. Murrell and L. Salem, *J. Chem. Phys.*, **34**, 1914 (1961).

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(18) T. L. Brown and M. T. Rogers, *J. Amer. Chem. Soc.*, **79**, 1859 (1957).

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(21) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1948, p 190.

The observed results can now be explained in terms of inductive effects and the bond elongation. Although the α-carbon in *tert*-butyllithium is potentially more capable of transferring electron density to the lithium than the α-carbon in ethyl- and *sec*-butyllithium based on inductive effects, it is in actuality less capable because of the drastically increased Li–C bond distance. Ethyl- and *sec*-butyllithium, therefore, absorb at a lower energy than *tert*-butyllithium and our rationale of predicting the order of transitions within a specific aggregate unit seems justifiable.

Thus the alkyllithium aggregates have been shown to have electronic transitions observable in the ultraviolet region which may be generally associated with a charge transfer from the alkyl group to the lithium framework. Both the experimentally observed spectra and the transitions calculated using CNDO/2 procedures support these conclusions and also support the relative energies of the transitions observed.

Based on these conclusions, one may further predict that the photochemical reactions of alkyllithiums will occur primarily at high energy and involve formation of radicals by the charge transfer process. This contention is supported by Glaze[6] who postulates an interaggregate disproportionation mechanism, *e.g.*, (2),

$$(C_2H_5Li)_6^* \longrightarrow \cdot C_2H_5(C_2H_5Li)_5 + Li \qquad (2)$$

$$\cdot C_2H_5(C_2H_5Li)_5 \longrightarrow C_2H_6 + \cdot C_2H_4Li(C_2H_4Li)_4 \qquad (3)$$

$$\cdot C_2H_4Li(C_2H_5Li)_4 \longrightarrow C_2H_4 + (C_2H_5Li)_4 + Li \qquad (4)$$

(3), and (4) to account for the photodecomposition products of ethyllithium. The $(C_2H_5Li)_4$ may in turn equilibrate to form more hexamer or eliminate LiH and ethylene or both. This "not so free" radical-type intermediate may be common to all photolytic reactions of alkyllithiums at high energy.

Acknowledgments. The authors would like to express their thanks to the Formica Co., Ethyl Corporation, and Wayne State University for aid in the form of fellowships (to R. J. H.) and to the Research Corporation and the Greater Cincinnati Foundation for direct financial assistance. The authors also wish to thank Dr. Darrell Ebbing for helpful discussions. The National Science Foundation, Grant GP-8323 and 19299, also provided partial support for this work.

Preparation and Characterization of an Inorganic Analog for the Active Site of the Reduced 2Fe–S* Iron–Sulfur Proteins[1]

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Received May 31, 1972

Abstract: The reaction of $[(CF_3)_2C_2S_2]$ (ligand) with $Fe(CO)_5$ in the presence of H_2S produces a black crystalline solid, I (apparent space group $P4_332$ or $P4_132$), which, when dissolved in hydrocarbon solvents, exhibits many of the physical properties of the reduced two-iron iron–sulfur proteins. A frozen solution of I in hexane exhibits an epr spectrum which upon addition of isopropyl disulfide narrows and has an axial g tensor ($g_\perp = 1.988_0$, $g_{||} = 2.009_8$, from computer simulation) similar to that observed in reduced adrenodoxin and putidaredoxin. The integrated intensity of the epr corresponds to one unpaired electron per two Fe. The magnetic susceptibility measured between 20 and 300°K exhibits non-Curie behavior which can be described using the antiferromagnetic interaction Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$ with $J = -95$ cm^{-1} and $S_1 - S_2 = 1$. An endor measurement gave values for the ^{19}F hyperfine constant of $A_{||}' = 1.25$ MHz and $A_\perp' = 0.78$ MHz, from which it was concluded that the unpaired electron resides almost exclusively on the Fe–S center. There is a hydrogen in the molecule which acts as a counterion allowing the complex to be soluble in nonpolar solvents while having the irons in different formal oxidation states. The instability of the complex to Lewis bases parallels the chemistry of hydrogen polysulfides. Spectral properties of the complex were determined from 55,000 to 200 cm^{-1}. Changes were observed following addition of isopropyl disulfide in ^{19}F nmr, Mössbauer, and epr spectra but not in the optical measurements. The near-infrared electronic and far-infrared vibrational spectra of $\{Fe[S_2C_2(CF_3)_2]_3\}_2$, $\{CO[S_2C_2(CF_3)_2]_2\}_2$, and $[(CF_3)_2C_2S_2]_2$ and the Raman spectra of I and $[(CF_3)_2C_2S_2]_2$ are reported. A convenient method for obtaining Raman spectra of highly colored solutions is described.

The iron–sulfur proteins (ferredoxins) are an intriguing and biologically significant class of compounds with the characteristic property that, when reduced, they exhibit an electron paramagnetic resonance (epr) spectrum with both g_{av} and $g_{x,y} < 2$. A subclass of this group of proteins which contain two atoms of both iron and inorganic sulfide (*e.g.*, spinach ferredoxin) has been extensively characterized by chemical and physical methods and a probable structure deduced.[2]

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(1) Acknowledgment is made for the receipt of Predoctoral Fellowship 5-F01-GM-37,338 from the National Institute of General Medical Sciences, USPHS from July 1969 through Oct 1971, and NIH Research Grant GM12176. The Raman spectrometer (Spex Ramalog system) was provided to the Chemistry Department, University of Michigan, with the help of funds from NSF Grant GP-8345. The X-ray diffractometer (Syntex P1) was made possible by NSF Grant 18277.

(2) W. R. Dunham, G. Palmer, R. H. Sands, and A. Bearden, *Biochem. Biophys. Acta*, 253, 373 (1971).