ISSN 0018-019X

Erscheint 8mal jährlich – Paraît 8 fois par an

235. On the Nature of the 7-Norbornadienyllithiums

Preliminary Communication

by **Melvin J. Goldstein**[1]* and **Timothy T. Wenzel**[2])

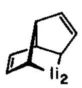
Department of Chemistry, Cornell University, Ithaca, New York 14853, USA

(19.VI.84)

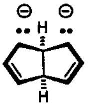
Summary

Lithium reductions of 7-chloronorbornadiene and of *bis*(7-norbornadienyl)mercury both provide $(C_7H_7)_2Li_2$ (**5a**). This product is accompanied by $C_7H_7Li_2Cl$ (**5c**) in the first case, and by C_7H_7Li (**5b**) in the second. The theoretically anticipated properties of all three organolithiums are apparent in the consistent C_s symmetry of their hydrocarbon ligands, their protolytic destruction by 12-crown-4, and their significant J(C(7),Li) (**5a**, 7.6; **5b**, 16.0; **5c** 8.9 Hz).

The recently synthesized dilithium semibullvalenide contains **1**[3]) as the common monomeric unit of two isomeric clusters [1]. The unusual lithium coordination – η^1 rather than η^3 to two otherwise symmetric allyl ligands [3] – was associated with the predicted bishomoantiaromaticity [4] of the corresponding C_{2v} dianion **2**. It was further suggested that the binary properties of organolithium compounds might more generally be used to test the binary predictions of qualitative theoretical models[4]); lithium



1



2

3

---

[1]) Present address: Research & Development, Bromine Compounds, Ltd., P.O.B. 180, Beer Sheva, Israel.

[2]) *Allen Seymour Olmstead* Fellow, 1981–1982. Taken in part from the Ph.D. Thesis of *T.T.W.*, Cornell University, 1984.

[3]) The deliberately ambiguous 'li' serves to indicate carbon-lithium covalency without specifying the full connectivity of the lithium atom or the composition of its cluster. 'Li' can then be reserved for a single lithium atom of fully specified connectivity, an increasingly common achievement of modern organolithium chemistry [2].

[4]) Quantitative theoretical models [5] reject the binary classification of carbanions and the algorithms [4] [6] [7] used to achieve it.

derivatives of 'stabilized' carbanions should be ionic while those of 'destabilized' carbanions should be covalent[5]).

The synthesis of 7-norbornadienyllithium [12] provides a propitious opportunity to test that suggestion. One of us had earlier associated failures to synthesize the 7-norbornadienyl anion **3** with its predicted antibicycloaromaticity [6]; **3** should be a destabilized *(2,2,2)* longicyclic [7]. If that were correct, 7-norbornadienyllithium should be covalent. We now demonstrate that it is.

Treatment of 7-chloronorbornadiene with Li in THF or $(CH_3)_2O$ at −78°C generated a solution whose subsequent treatment with CH_3OD afforded 77(5)% norbornadiene containing 0.96(1) atoms of deuterium at C(7)[6]). Alternative treatment with $HgCl_2$ afforded bis(7-norbornadienyl)mercury (**4**) whose covalency is as uneventful as it is unequivocal (m.p. 82.7°C[7])). Subsequent reduction of **4** (Li, $(CH_3)_2O$, −30°C) then generated the thermally unstable **5a**.

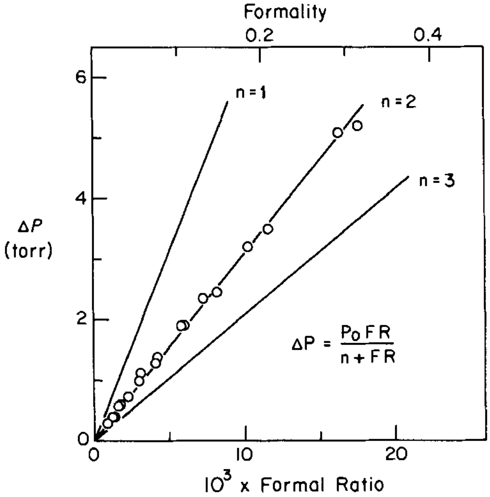


Fig. 1. *7-Norbornadienyllithium* **5a**. Raoult's *Law determination of cluster size (n) at −29°C. FR,* the formal ratio, is the number of titrimetrically determined equivalents per mole $(CH_3)_2O$. $P_0^{-29°C}$ = 618 Torr [13].

---

[5]) The covalent/ionic dichotomy has unfortunately acquired different theoretical and experimental definitions. The *theoretical* distinction applies to *bonds, e.g.*, to the C–Li bond of monomeric, gaseous CH_3Li [8] [9]. We use an *experimental* definition that applies to *compounds*. A member of the covalent class is then defined, *inter alia* by: *a*) persistent stereoisomerism [1] [2j], *b*) a significantly noncoplanar R_3C ligand and a shorter C–Li distance in the solid state [2c, f, g, m], *c*) association into discrete clusters in donor solvents, rather than into a continuum of aggregates [10], *d*) a non-zero *J*(C, Li) [2a, d–k], *e*) a significantly lower *J*(C(α), H) [2q], *f*) greater solubility in alkane solvents, and *g*) greater reactivity towards ether solvents. All of these properties appear to coincide. *t*-BuLi is a typical covalent organolithium compound according to this definition; Ph_3CLi is a typical ionic one. As in all binary classifications, one expects to find examples that will not easily fit into either category. The power of the definition will depend upon the comparative number of such ambiguities. Thus far they are few [11]. The previous suggestion [1] had assumed that the abnormally high basicity of a 'destabilized' carbanionic ligand would force the corresponding organolithium compound into the covalent class, overwhelming all tendencies to the contrary.

[6]) Vinyl/bridgehead ^1H-NMR area ratio: 2.01(3); here and subsequently, standard deviations in the last significant figure appear in parentheses.

[7]) Complete elemental analysis agreed with expectation to within ±0.1%.

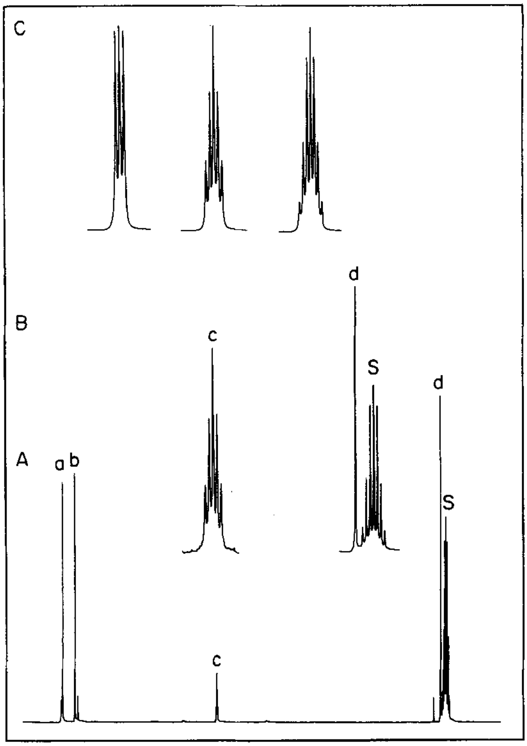
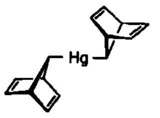
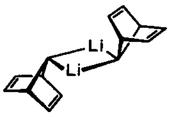


Fig. 2. A) *^{13}C-NMR spectrum of* **5a** *in* $(CD_3)_2O$ *at* -142°*C* (S is the solvent signal). B) *Expansion of* A. C) *Simulated expansion of* c *assuming splitting by one, two, and three atoms of* ^{6}*Li*

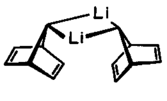
Two structural hypotheses, **5a1** and **5a2**[8], are consistent with: *a*) the $(CH_3)_2O$ vapor pressure determination of cluster size: $(C_7H_7Li)_n$, $n = 1.9(1)$, 0.016–0.316F at -29.5°C *(Fig. 1)*, *b*) the single ^{6}Li-NMR signal (δ_{Li} 1,45 ppm)[9]), *c*) the four ^{1}H- and ^{13}C-NMR signals, *d*) the J(C(7),H) 88.7 Hz, [2a, d, q], and *e*) the 1:2:3:2:1 splitting of the ^{13}C(7)-NMR signal by ^{6}Li ($I = 1$, J(C,Li) = 7.6 Hz, *Fig. 2*). A third hypothesis, **5a3**, would require rapid dyotropic [14] equilibration of the two Li atoms, perhaps proceeding through **5a1** as transition state. We prefer **5a1** as the energy minimum, both for steric reasons and because alkyllithiums are more often hypercoordinate than tetracoordinate in the solid state [10].



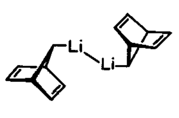
4



5a1



5a2



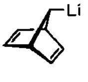
5a3

---

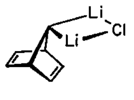
[8] Here and subsequently, we assume that 8-electron coordinative saturation of lithium is achieved by the appropriate number of ether molecules. Explicit illustration is avoided in the interests of clarity.

[9] Positive δ(Li) (at 44.165 MHz) *downfield* from 1M aq. LiCl at 27°C.

A second 7-norbornadienyllithium appeared in NMR spectra of the same solutions, but only at the lowest temperatures and the greatest dilutions. We assign a monomeric structure **5b**, both because the principal component is dimeric and because the ^{13}C-NMR signal at C(7) is split by ^{6}Li into a 1:1:1 triplet (J(C,Li) = 16.0 Hz)[10]). Area ratios (*ca.* 0.02–0.30F) provided $K_{\text{diss}}^{-140\,^{\circ}\text{C}} \simeq 2 \times 10^{-3}$M. To the best of our knowledge, *this represents the first experimental demonstration of a monomeric covalent organolithium compound in solution*[11]).



5b



5c

The third 7-norbornadienyllithium invariably accompanied the first (**5a**), but only in solutions that were prepared from 7-chloronorbornadiene, and increasingly so with increasing dilution[12]). The simplest consistent structural hypothesis (**5c**) also accommodates: a) the single ^{6}Li-NMR signal δ(Li) 1.10 ppm[9]), b) the four ^{1}H- and ^{13}C-NMR signals, and c) the 1:2:3:2:1 splitting of the ^{13}C(7)-NMR signal by ^{6}Li (J(C,Li) = 8.9 Hz). The distinct **5a** and **5c** ^{13}C-NMR signals reversibly broadened with increasing temperature and then coalesced into four averaged signals at −90 °C. These then sharpened, but did *not* collapse into three, even at temperatures sufficient to achieve thermolysis (*ca.* 25 °C, (D$_8$)THF)[13]). C(7) configuration remains intact.

Such solutions of **5a**/**5c** did, however, react irreversibly with 12-crown-4 [19], even at −45 °C. CH$_3$OD then provided deuterium-free norbornadiene (0.00(4) atoms at C(7)) as the exclusive isolable (71(2)%) or NMR-detectable product. Extraction of a lithium cation from its original environment apparently generates a base – perhaps **3** – sufficiently strong that it deprotonates the ether which set it free.

In this and other ways, the 7-norbornadienyllithiums mimic the dilithium semibullvalenides [1]. The two destabilized carbanions, **2** and **3**, have become preparatively accessible only within the coordination sphere of lithium, much like cyclobutadiene first become preparatively accessible only within the coordination sphere of nickel [20]. The alternative class – derivatives of stabilized [6] [7] carbanions – is represented by the lithium salts of bicyclo[3.2.2]nonatrienide and bullvalenide [21]. A qualitative binary theoretical model can hardly do better than that.

We are grateful to *G. W. Klumpp* for his valuable encouragement and to the *National Science Foundation* for its support of research (CHE77-26482, CHE82-01052) and NMR instrumentation (CHE79-04825).

---

[10]) The increased J(C, Li) with decreased cluster size is consistent with INDO methyllithium computations [15]. STO-3G computations of monomeric, ether-free 7-norbornadienyllithium provided no similar information [16].

[11]) A 15 °K Ar matrix IR spectrum was attributed to CH$_3$Li [17]. Gas phase monomers have escaped mass spectrometric detection [18]. The analogous 1:1:1 NMR triplet pattern of α-haloorganolithium compounds was attributed either to monomers or to halide-bridged dimers [2a, d].

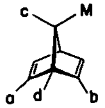
[12]) *Cf. Quantitative Appendix, Sect. 3.*

[13]) Thermolytic results will be described elsewhere.

Quantitative Appendix

1. Correlation of NMR Spectral Data *(Table 1).* – Most noteworthy is the close similarity between the four ^{1}H and four ^{13}C chemical shifts in the organomercury derivative **4** and in the three organolithium derivatives **5**. The a/b assignments follow from the general observation that $\delta(H_a) > \delta(H_b)$ in 7-substituted norbornadienes [12] [22a, b], and, in **4**, on the stereochemical dependence of $^3J(C, Hg)$ [22c] and $^4J(H, Hg)$ [22a].

Table 1. *NMR Spectral Data of 7-Metallonorbornadienes* **4** *and* **5a–c**^{a})



Substrate	Assignments			
	H_a	H_b	H_c	H_d
$(C_7H_7)_2{}^{199}Hg$ (**4**)^{b})				
$\delta(C)$	147.41	146.99	112.79	55.64
$J(C,H)^{e}$)	173.0	171.0	148.3	134.6
$J(C,M)^{c}$)	93.9	13.7	816.8	7.1
$J(H,M)^{c}$)	4.0	<1.0	22.0	22.0
$\delta(H)$	6.98	6.85	1.82	3.77
$(C_7H_7)_2{}^6Li_2$ (**5a**)^{c})^{d})				
$\delta(C)$	151.60	148.47	114.56	60.17
$J(C,H)^{c}$)	163.4	173.3	88.7	137.8
$J(C,M)^{f}$)			7.6	
$\delta(H)$	6.89	6.77	1.61	3.54
$C_7H_7{}^6Li$ (**5b**)^{c})				
$\delta(C)$	151.85	147.71	122.42	61.87
$J(C,M)^{f}$)			16.0	
$\delta(H)$	6.84	6.67	1.89	3.56
$C_7H_7{}^6Li_2Cl$ (**5c**)^{c})^{d})				
$\delta(C)$	151.89	147.22	113.36	59.66
$J(C,H)^{e}$)	165.4	165.4	94.5	145.7
$J(C,M)^{f}$)			8.9	
$\delta(H)$	6.90	6.70	1.42	3.54

[a]) ^{13}C-NMR spectra at 75.47 MHz, J in Hz. [b]) In $CDCl_3$ at ambient temperatures; ^{1}H-NMR spectra at 79.58 MHz; natural abundance sideband areas 16.4% ([23]: 16.8%). [c]) In $(CD_3)_2O$ at -142°C for ^{13}C-NMR spectra, -136°C for ^{1}H-NMR spectra at 300.14 MHz, δ relative to Me_4Si in 1:2 Me_4Si:Me_2O. [d]) ^{13}C and ^{1}H assignments were correlated by single-frequency heteronuclear decoupling. [e]) *Doublet.* [f]) *Pentuplet.* [g]) *Triplet.*

2. *Raoult's* Law Determination of Cluster Size *(Fig. 1).* – Equilibrium vapor pressure depression (ΔP) is a function of solvent vapor pressure (P_0) and the mole fraction of solution that is solute ($m_{solu}/(m_{solu} + m_{solv})$).

$$\Delta P = \frac{P_0 m_{solu}}{m_{solu} + m_{solv}} \tag{1}$$

We define FR, the experimental formal ratio, to be the moles of monomer units ((nm_{solu}); by acidimetric titration) divided by the moles of solvent (m_{solv}; by weight).

$$FR = \frac{nm_{solu}}{m_{solv}} \tag{2}$$

From *Eqns. 1* and *2*:

$$\Delta P = \frac{P_0\, FR}{FR + n} \tag{3}$$

The reliability of both the technique and the assumed $P_0^{-29°C}$ (618 torr) [13] were tested by determining the 'cluster size' of benzophenone in $(CH_3)_2O$: $n = 0.98(6)$.

3. Composition of 5c

$$\nu_1(\mathrm{RLi})_{\nu_2} + \nu_1\nu_2\nu_3\mathrm{LiCl} \overset{K}{\rightleftarrows} \nu_2(\mathrm{RLi}_{1+\nu_3}\mathrm{Cl}_{\nu_3})_{\nu_1}$$

5a **5c**

3.1. Formal (*c*) and Relative Formal (*RC*) Concentrations. – It was experimentally convenient to assay the formal concentration of monomer units (*c*) by dividing the H_c ^{1}H-NMR areas of **5a** or **5c** by those of residual $(D_5)(CH_3)_2O$. The expected linear relationship between such experimental relative formal concentrations *RC* and *c* was evaluated in two steps.

First, the yield of **5a** and **5c** from 7-chloronorbornadiene was determined to be 0.77(5), independent of initial 7-chloronorbornadiene concentration (*ccnb*) by ^{1}H-NMR integration of the H_c areas against those of an internal neopentane standard. Then, the sum of the relative formal concentrations (*RC*(**5a** + **5c**)) was shown to be a linear function of *ccnb* (*Fig. 3* and *Eqn. 4*).

$$RC = 1.5(2)\ ccnb + 0.03(7) \tag{4}$$

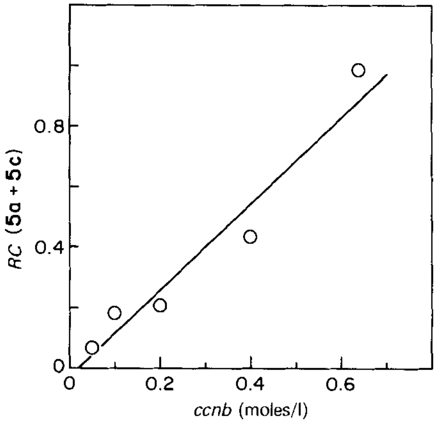


Fig. 3. *Relative formal concentration (RC) at varying initial concentrations of 7-chloronorbornadiene (ccnb); $(CD_3)_2O$, –143 °C*

The linearity and zero intercept show that the yield of **5** is independent of precursor concentration and that area ratios faithfully reflect proton ratios. In practice, the latter condition was satisfied only with delay times > 150 s.

$$\text{Since } c = 0.77\ ccnb\text{: } c = 0.51\ RC \tag{5}$$

3.2. Composition by Direct Comparison of ^{1}H- and ^{6}Li-NMR Area Ratios. – *Eqns. 6a* and *6b* follow from the definitions of R^H and R^{Li}: the NMR area of H_c of **5c** divided by that of **5a** and of the **5c** ^{6}Li nucleus divided by that of **5a**.

$$R^H = \nu_1[\mathbf{5c}]/\nu_2[\mathbf{5a}] \tag{6a}$$

$$R^{Li} = \nu_1(1 + \nu_3)[\mathbf{5c}]/\nu_2[\mathbf{5a}] \tag{6b}$$

$$R^{Li}/R^H = (1 + \nu_3) \tag{7}$$

It is apparent that the quotient should be independent of *c* or *RC*, as it is (*Table 2*). Because the result ($\nu_3 = 1.6(2)$) was both ambiguous and imprecise, we also investigated a potentially more powerful fitting procedure.

Table 2. *Chloride Composition of* **5c** *by Direct Comparison*

RC[a])	*c*[b])	R^{Li}	R^{H}	R^{Li}/R^{H}
0.0446	0.0227	1.26	0.424	2.97
0.0451	0.0230	1.06	0.427	2.48
0.113	0.0576	0.719	0.267	2.69
0.120	0.0612	0.735	0.315	2.33
0.128	0.0653	0.671	0.253	2.65
0.131	0.0668	0.641	0.256	2.50
0.246	0.125	0.417	0.178	2.34
0.262	0.134	0.441	0.179	2.46
0.291	0.148	0.377	0.140	2.41
0.337	0.172	0.375	0.126	2.98
			mean standard deviation	2.6(2)

[a]) As evaluated by ^{1}H-NMR, in LiCl-saturated $(CD_3)_2O$, – 130°C.

[b]) From *Eqn. 5.*

3.3. Composition by Nonlinear Least Squares Fitting. – The formal concentration of monomer units (c) is given by:

$$
\begin{aligned}
c &= \nu_2[\mathbf{5a}] + \nu_1[\mathbf{5c}]\\
c &= \nu_2[\mathbf{5a}][1 + (\nu_1[\mathbf{5c}]/\nu_2[\mathbf{5a}])]\\
c &= \nu_2[\mathbf{5a}](1 + R^{H})
\end{aligned}
\tag{8a}
$$

and, from *Eqn. 6b*:

$$c = \nu_2[\mathbf{5a}][1 + (R^{Li}/1 + \nu_3)] \tag{8b}$$

At equilibrium:

$$K = [\mathbf{5c}]^{\nu_2}/[\mathbf{5a}]^{\nu_1} = ([\mathbf{5c}]/[\mathbf{5a}])^{\nu_2}[\mathbf{5a}]^{-(\nu_1 - \nu_2)} \tag{9}$$

where K implicitly includes (LiCl) as an undetermined K_{sp}(LiCl). The subsequent derivation proceeds in parallel for R^{H}, using *Eqn. 8a*, and for R^{Li}, using *Eqn. 8b*. Only the former is given in detail. Using *Eqn. 6a*:

$$([\mathbf{5c}]/[\mathbf{5a}]^{\nu_2} = \nu_2^{\nu_2}\,(R^{H})^{\nu_2}\,(\nu_1)^{-\nu_2}$$

Using *Eq. 8a:*

$$[\mathbf{5a}]^{(\nu_2 - \nu_1)} = c^{(\nu_2 - \nu_1)}\nu_2^{-(\nu_2 - \nu_1)}(1 + R^{H})^{-(\nu_2 - \nu_1)}$$

Substituting into *Eqn. 9*:

$$
\begin{aligned}
K &= c^{(\nu_2 - \nu_1)}(\nu_2)^{\nu_1}(\nu_1)^{-\nu_2}(R^{H})^{\nu_2}(1 + R^{H})^{-(\nu_2 - \nu_1)}\\
c^{(\nu_2 - \nu_1)} &= K(\nu_2)^{-\nu_1}(\nu_1)^{\nu_2}(R^{H})^{-\nu_2}(1 + R^{H})^{(\nu_2 - \nu_1)}\\
c^{(1 - \nu_1/\nu_2)} &= K'(R^{H})^{-1}(1 + R^{H})^{(1 - \nu_1/\nu_2)}
\end{aligned}
\tag{10a}
$$

Similarly:

$$c^{(1 - \nu_1/\nu_2)} = K'[R^{Li}/(1 + \nu_3)]^{-1}[1 + (R^{Li}/1 + \nu_3)]^{(1 - \nu_1/\nu_2)} \tag{10b}$$

$$K' \equiv K^{1/\nu_2}\nu_1(\nu_2)^{-\nu_1/\nu_2} \tag{11}$$

Conventional least-squares programs require the dependent variable – R^{H} and R^{Li} – to be expressed as an explicit function of the independent variable (c). *Eqns. 10* show this to be impossible. We therefore modified such a program, but in a way that retained the conventional least squares criterion: the minimization of $(R^{i}_{calcd} - R^{i}_{obsd})^2$. R^{i}_{calcd} was obtained by the numerical solution of *Eqns. 10*, using the utility program ZEROIN. This was done for each set of adjustable parameters (K, ν_1, and ν_3) at each value of the independent variable (c) using the independently determined $\nu_2 = 2$. This provided:

$$K = 6.6(6) \times 10^{-3},\ \nu_1 = 1.03(3),\ \nu_3 = 1.6(1),\ R = 0.095\ [24]$$

Although ν_1 is gratifying close to one, the resulting ν_3 is no less ambiguous than it was previously. A mixture of $\nu_3 = 1$ and 2 is difficult ro reconcile with the ^{13}C- and ^6Li-NMR requirement that the Li atoms be magnetically and chemically indistinguishable. Neither can $\nu_3 = 2$ (*i.e.*, three Li atoms per cluster) accommodate this requirement. We therefore choose $\nu_3 = 1$. The experimental discrepancy may be due to salt effects, to the difficulty of achieving full equilibration under heterogeneous conditions at such low temperatures, *etc.*

REFERENCES

[1] *M.J. Goldstein, T.T. Wenzel, G. Whittaker & S.F. Yates,* J. Am. Chem. Soc. *104,* 2669 (1982).

[2] a) *D. Seebach, H. Siegel, J. Gabriel & R. Hässig,* Helv. Chim. Acta *63,* 2046 (1980); b) *D. Dietrich & D. Rewicki,* J. Organomet. Chem. *205,* 281 (1981); c) *R. Amstutz, W.F. Schweitzer, D. Seebach & J.D. Dunitz,* Helv. Chim. Acta *64,* 2617 (1981); d) *D. Seebach, R. Hässig & J. Gabriel,* ibid. *66,* 308 (1983); e) *R. Hässig & D. Seebach,* ibid. *66,* 2269 (1983); f) *D. Seebach, J.D. Dunitz, R. Amstutz, J. Gabriel & R. Hässig,* ibid., in press; g) *R. Amstutz, T. Laube, W.B. Schweizer, D. Seebach & J.D. Dunitz,* ibid. *67,* 224 (1984); h) *D. Seebach, J. Gabriel & R. Hässig,* ibid. *67,* 1083 (1984); i) *G. Fraenkel, M, Henrichs, J.M. Hewitt & B.M. Su,* J. Am. Chem. Soc. *102,* 3345 (1980); j) *G. Fraenkel, M. Henrichs, M. Hewitt & B.M. Su,* ibid. *106,* 255 (1984); k) *G. Fraenkel & P. Pramanik,* J. Chem. Soc., Chem. Commun. *1983,* 1527; l) *W. Schubert, W. Nuegebauer & P.v.R. Schleyer,* ibid. *1982,* 1184; m) *G.W. Klumpp, P.J.A. Geurink, A.L. Spek & A.J.M. Duisenberg,* ibid. *1983,* 814; n) *H. Hope & P.P. Power,* J. Am. Chem. Soc. *105,* 5320 (1983); o) *B. Schubert & E. Weiss,* Angew. Chem. *95,* 493 (1983); Angew. Chem. Int. Ed. *22,* 496 (1983); p) *E. Weiss, G. Sauermann & G. Thirase,* Chem. Ber. *116,* 74 (1983); q) *J.P.C.M. van Dongen, H.W.D. van Dijkman & M.J.A. de Bie,* Recl. Trav. Chim. Pays-Bas *93,* 29 (1974).

[3] *T. Clark, C. Rohde & P.v.R. Schleyer,* Organometallics *2,* 1344, (1983) and references there cited.

[4] *S. Winstein,* J. Am. Chem. Soc. *81,* 6524 (1959); *S. Winstein,* Quart. Rev. Chem. Soc. *23,* 141 (1969): *P. Warner,* in 'Topics in Nonbenzenoid Aromatic Chemistry', Vol. 2, eds. T. Nozoe, R. Breslow, K. Hafner, S. Ito and I. Murata, Hirokawa, Tokyo, 1977, p. 283.

[5] *J.B. Grutzner & W.L. Jorgensen,* J. Am. Chem. Soc. *103,* 1372 (1981); *E. Kaufman, H. Mayr, J. Chandresekhar & P.v.R. Schleyer,* ibid. *103,* 1375 (1981).

[6] *M.J. Goldstein,* J. Am. Chem. Soc. *89,* 6357 (1967).

[7] *M.J. Goldstein & R. Hoffmann,* J. Am. Chem. Soc. *93,* 6193 (1971).

[8] *S.M. Bachrach & A. Streitweiser, Jr.,* J. Am. Chem. Soc. *106,* 228, (1984) and references there cited.

[9] a) *J.D. Dill, P.v.R. Schleyer, J.S. Binkley & J.D. Pople,* J. Am. Chem. Soc. *99,* 6159 (1977); b) *G.D. Graham, D.S. Marynick & W.N. Lipscomb,* ibid. *102,* 4572 (1980); c) *L. Herzig, J.M. Howell, A.M. Sapse, E. Singman & G. Snyder,* J. Chem. Phys. *77,* 429 (1982).

[10] a) *B.J. Wakefield,* 'The Chemistry of Organolithium Compounds', Pergamon, Oxford, 1976, Chapter 1; b) *J.L. Wardell,* 'Comprehensive Organometallic Chemistry', eds. G. Wilkinson, F.G.A. Stone and E.W. Abel. Pergamon, Oxford, 1982, Vol. 1, p. 43.

[11] *E.g., P.R. Peoples & J.B. Grutzner,* J. Am. Chem. Soc. *102,* 4709 (1980).

[12] *G.W. Klumpp & J. Stapersma,* Tetrahedron *37,* 187 (1981).

[13] *R.M. Kennedy, M. Sagenkahn & J.G. Aston,* J. Am. Chem. Soc. *63,* 2267 (1941).

[14] *M.T. Reetz,* Angew. Chem. *84,* 161, 163 (1972); Angew. Chem. Int. Ed. *11,* 129, 131 (1972).

[15] *T. Clark, J. Chandresekhar & P.v.R. Schleyer,* J. Chem. Soc., Chem. Commun. *1980,* 672.

[16] *S. Nagase & K.N. Houk,* Tetrahedron Lett. *23,* 19 (1982).

[17] *L. Andrews,* J. Chem. Phys. *47,* 4834 (1967).

[18] *M.Y. Darensbourg, B.Y. Kimura, G.E. Hartwell & T.L. Brown,* J. Am. Chem. Soc. *92,* 1236 (1970).

[19] *F.A.L. Anet, J. Krane, J. Dale, K. Daasvatn & P.O. Kristiansen,* Acta Chem. Scand., Ser. B *27,* 3395 (1973).

[20] *R. Criegee & G. Schröder,* Ann. *623,* 1 (1959).

[21] *M.J. Goldstein, S. Tomoda & G. Whittaker,* J. Am. Chem. Soc. *96,* 3676 (1974).

[22] a) *E.I. Snyder & B. Franzus,* J. Am. Chem. Soc. *86,* 1166 (1964); b) *R.K. Lustgarten & J.G. Richey, Jr.,* J. Am. Chem. Soc. *96,* 6393, (1974); c) *W. Kitching, D. Praeger, D. Doddrell, F.A.L. Anet & J. Krane,* Tetrahedron Lett. *1975,* 759.

[23] *D. Strominger, J.M. Hollander & G.T. Seaborg,* Rev. Mod. Phys. *30,* 585 (1958).

[24] *W.C. Hamilton,* 'Statistics in Physical Science', Ronald Press, New York, 1964, p. 157.