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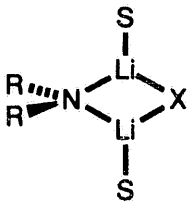
9187-9197

J9197-M1



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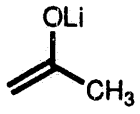

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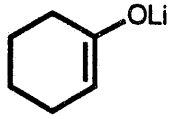

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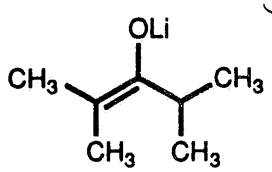

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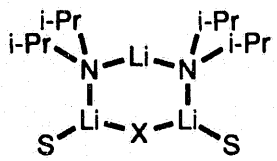
Table A. Calculated Heats of Formation of Mixed Cyclic Dimers.

R_2NLi	solvent, S	LiX = LiCl	LiX = **3**	LiX = **4**	LiX = **5**
LDA	unsolvated	-110.8	-116.3	-135.5	-146.0
	THF	-247.5	-248.6	-264.2	-264.5
	HMPA	-208.5	-206.8	-222.7	-220.7
LiTMP	unsolvated	-103.6	-113.9	-128.0	-137.7
	THF	-239.0	-240.2	-255.8	-255.6
	HMPA	-199.8	-198.3	-214.0	-211.7

[a]The heats of formation of THF and HMPA are -59.3 and -34.4, respectively.



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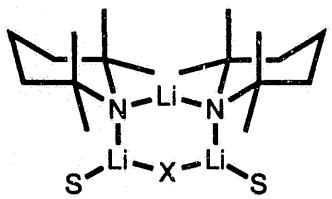
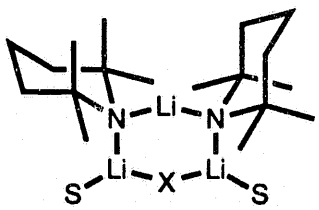


51, C_{2v}



52, C_s

Table B. Calculated Heats of Formation of Mixed Cyclic Trimers.[a]

R_2NLi	structure	solvent, S	LiX = LiCl	LiX = **3**	LiX = **4**	LiX = **5**
LDA	**27**	unsolvated	-174.4	-186.6	-200.6	-207.9
	27	THF	-297.6	-302.0	-309.8	-306.6
	27	HMPA	-257.1	-250.8	-264.9	-258.3
LiTMP	**51**, C_{2v}	unsolvated	-150.2	-163.6	-176.7	-185.1
	52, C_s	unsolvated	-150.9	-163.8	-177.5	-184.8
	51, C_{2v}	THF	-275.6	-273.7	-288.8	-282.6
	52, C_s	THF	-273.8	-272.3	-284.9	-280.0
	51, C_{2v}	HMPA	-234.2	-221.4	-238.8	-230.7
	52, C_s	HMPA	-233.7	-223.5	-237.3	-226.6

[a]The heats of formation of THF and HMPA are -59.3 and -34.4, respectively.

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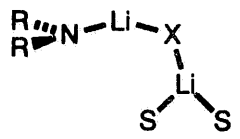

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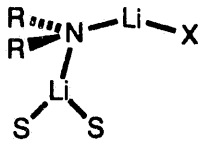

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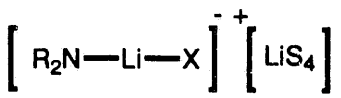

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Table C. Calculated Heats of Formation of Mixed Open Dimers and Triple Ions.[a]

R_2NLi	structure	solvent, S	LiX = LiCl	LiX = **3**	LiX = **4**	LiX = **5**
LDA	**41**	THF	-222.8	-244.8	-253.4	-261.6
	41	HMPA	-189.0	--[d]	-215.8	-220.0
	39	THF	-240.7	-241.3	-258.3	-220.0
	39	HMPA	-201.5	-200.9	-218.2	-219.7
	40[b]	THF	-255.1	-254.8	-273.2	-281.6
	40	THF	-338.0	-331.2	-349.4	-357.0
	40[b]	HMPA	-211.9	-211.6	-356.3	-238.4
	40	HMPA	-249.2	-247.2	-264.5	-272.3
LiTMP	**41**	THF	-216.9	-239.2	-251.0	-253.6
	41	HMPA	-184.2	--[d]	-212.4	-213.8
	39[c]	THF	-230.3	-228.6	-247.3	-250.1
	39[c]	HMPA	-190.1	-189.1	-206.3	-207.1
	40[b]	THF	-250.6	-250.2	-265.6	-275.9
	40	THF	-331.7	-327.8	-341.9	-351.3
	40[b]	HMPA	-207.4	-207.0	-222.4	-232.7
	40	HMPA	-246.4	-243.6	-256.4	-261.37

[a]Previously calculated heats of formation are as follows: THF, -59.3; HMPA, -34.4; +Li(THF), -135.0; +Li(HMPA)$_4$, -91.8. See Romesberg, F. E.; Collum, D. B., *J. Am. Chem. Soc.* **1992**, *114*, 2112. [b]Values correspond to heats of formation of triple ion at infinite ion separation. [c]LiTMP *X*-open dimers bear the doubly solvated lithium in the axial orientation. [d]Minima void of C-Li contacts could not be located.

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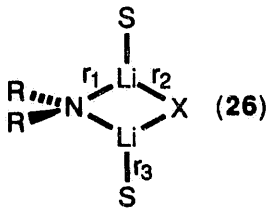


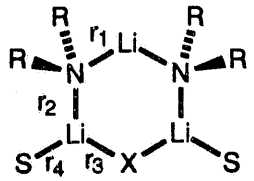
(26)

Table D. Mixed cyclic dimer calculated bond lengths (Å).

LDA dimer	solvent, S	r_1	r_2	r_3
LDA/LiCl	unsolv.	2.03	2.56	-
	THF	2.08	2.64	2.19
	HMPA	2.10	2.70	2.07
LDA/**3**	unsolv.	2.06	2.01	-
	THF	2.12	2.05	2.22
	HMPA	2.14	2.08	2.11
LDA/**4**	unsolv.	2.07	1.97/2.12[a]	-
	THF	2.07	2.11	2.21
	HMPA	2.14	2.10	2.11
LDA/**5**	unsolv.	2.10	2.05	-
	THF	2.12	2.09	2.23
	HMPA	2.14	2.14	2.15
LiTMP/LiCl	unsolv.	2.07	2.56	-
	THF	2.13	2.64	2.21
	HMPA	2.15	2.69	2.08
LiTMP/**3**	unsolv.	2.08	1.97/2.15[a]	-
	THF	2.16	2.06	2.24
	HMPA	2.18	2.09/2.13[a]	2.13
LiTMP/**4**	unsolv.	2.07	1.99/2.12[a]	-
	THF	2.15	2.07	2.23
	HMPA	2.18	2.11	2.12
LiTMP/**5**	unsolv.	2.12	2.02/2.06[a]	-
	THF	2.17	2.10	2.26
	HMPA	2.16/2.20	2.14	2.17

[a]Distortion causes unequal lengths for otherwise symmetry-equivalent bonds.

J9197-M4



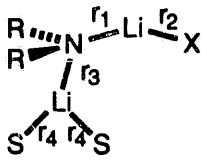
(27)

Table E. LDA mixed cyclic trimer calculated bond lengths (Å).

LDA trimer	solvent, S	r_1	r_2	r_3	r_4
LDA/LiCl	unsolv.	2.13	2.08	2.52	-
	THF	2.13	2.13	2.62	2.25
	HMPA	2.13	2.15	2.68	2.12
LDA/**3**	unsolv.	2.13	2.11	2.06/1.97[a]	-
	THF	2.14	2.19	2.09	2.19/2.36[a]
	HMPA	2.11	2.21	2.11	2.23
LDA/**4**	unsolv.	2.14	2.11	2.07/1.99[a]	-
	THF	2.12	2.18	2.10	2.34
	HMPA	2.11	2.20	2.14	2.21
LDA/**5**	unsolv.	2.14	2.12	2.08/2.05[a]	-
	THF	2.11	2.19	2.15	2.41
	HMPA	2.11	2.22	2.19	2.31/2.34[a]
LiTMP/LiCl	unsolv.	2.22	2.06/2.10[a]	2.52	-
	THF	2.12	2.13	2.63	2.26
	HMPA	2.21	2.16	2.69	2.11
LiTMP/**3**	unsolv.	2.20/2.23[a]	2.13	1.98/2.07[a]	-
	THF	2.19	2.18/2.22[a]	2.05/2.23[a]	2.31/2.53[a]
	HMPA	2.21	2.24	2.13	2.28
LiTMP/**4**	unsolv.	2.20/2.23[a]	2.10/2.13[a]	1.99/2.07[a]	-
	THF	2.18	2.20	2.11	2.35
	HMPA	2.17	2.25	2.15	2.46
LiTMP/**5**	unsolv.	2.21	2.13	2.04/2.07[a]	-
	THF	2.18	2.22	2.15	2.41
	HMPA	2.19	2.28	2.21	2.36

[a]Distortion causes unequal lengths for otherwise symmetry-equivalent bonds.

J9197-m5



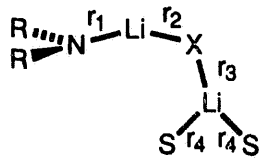
(39)

Table F. LDA mixed *X*-open dimer calculated bond lengths (Å).

open dimer	solvent, S	r_1	r_2	r_3	r_4[a]
LDA/LiCl	THF	2.12	2.34	2.09	2.24
	HMPA	2.13	2.37	2.14	2.18
LDA/**3**	THF	2.15	1.82	2.09	2.25
	HMPA	2.15	1.84	2.15	2.16
LDA/**4**	THF	2.14	1.83	2.09	2.25
	HMPA	2.15	1.86	2.15	2.16
LDA/**5**	THF	2.15	1.97	2.10	2.29
	HMPA	2.14	2.87	2.16	2.16
LiTMP/LiCl	THF	2.18	2.39	2.11	2.26
	HMPA	2.16	2.39	2.18	2.17
LiTMP/**3**	THF	2.18	184	2.11	2.26
	HMPA	2.21	1.85	2.18	2.18
LiTMP/**4**	THF	2.18	1.84	2.11	2.26
	HMPA	2.20	1.86	2.18	2.18
LiTMP/**5**	THF	2.21	1.96	2.11	2.28
	HMPA	2.21	1.88	2.18	2.17

[a]Corresponds to average of two inequivalent bonds

J9197-m6



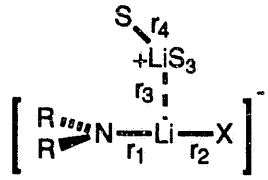
(41)

Table G. *N*-open dimer calculated bond lengths (Å).

open dimer	solvent, S	r_1	r_2	r_3	r_4[a]
LDA/LiCl	THF	1.90	2.58	2.45	2.13
	HMPA	1.89	2.55	2.54	2.03
LDA/**3**	THF	1.90	2.06	2.08	2.16
	HMPA	1.91	2.07	2.01	2.05
LDA/**4**	THF	1.91	2.08	1.98	2.16
	HMPA	1.93	2.12	2.03	2.07
LDA/**5**	THF	1.93	2.09	2.19	2.20
	HMPA	1.95	2.13	2.06	2.10
LiTMP/LiCl	THF	1.92	2.59	2.43	2.13
	HMPA	1.94	2.60	2.54	2.01
LiTMP/**3**	THF	1.92	2.06	2.04	2.16
	HMPA	1.94	2.07	2.08	2.07
LiTMP/**4**	THF	1.92	2.07	2.04	2.16
	HMPA	1.94	2.08	2.08	2.07
LiTMP/**5**	THF	1.97	2.13	2.00	2.19
	HMPA	1.99	2.14	2.08	2.07

[a]Corresponds to an average of two inequivalent bonds.

J9187-M7



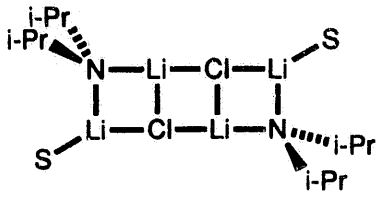
(40)

Table H. Mixed triple ion calculated bond lengths (Å).

triple ion	solvent, S	r_1	r_2	r_3	r_4[a]
LDA/LiCl	unpaired	1.94	2.39	-	-
	HMPA	1.90	2.47	6.75	2.20
	HMPA	1.90	2.47	8.21	2.18
LDA/**3**	unpaired	1.90	1.99	-	-
	THF	1.92	1.90	7.90	2.19
	HMPA	1.94	1.88	8.81	2.18
LDA/**4**	unpaired	1.90	1.99	-	-
	THF	1.95	1.88	6.44	2.19
	HMPA	1.93	1.89	7.08	2.18
LDA/**5**	unpaired	1.97	2.00	-	-
	THF	2.01	1.99	7.13	2.19
	HMPA	1.97	2.02	8.89	2.18
LiTMP/LiCl	unpaired	1.96	2.39	-	-
	THF	1.93	2.46	7.22	2.19
	HMPA	1.94	2.41	7.90	2.18
LiTMP/**3**	unpaired	1.98	1.86	-	-
	THF	1.97	1.88	6.70	2.19
	HMPA	1.98	1.88	8.19	2.18
LiTMP/**4**	unpaired	1.97	1.88	-	-
	THF	1.97	1.89	6.57	2.19
	HMPA	1.98	1.90	8.36	2.18
LiTMP/**5**	unpaired	1.99	2.00	-	-
	THF	2.00	2.02	6.74	2.19
	HMPA	2.01	2.02	8.94	2.21

[a]Corresponds to the average Li-O bond length.

J9197-M8



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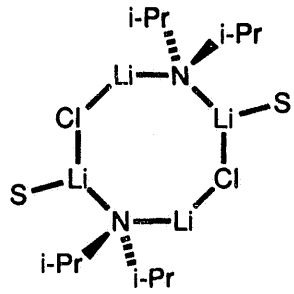
30 (S = THF); H_f = -378.27



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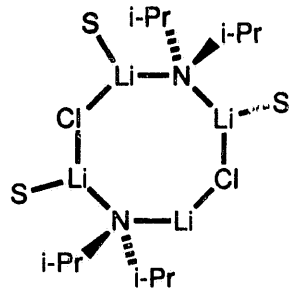
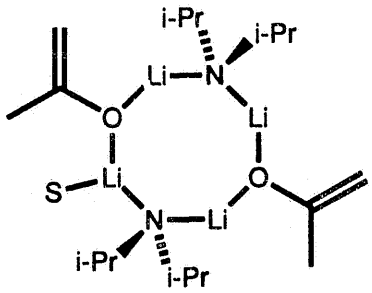
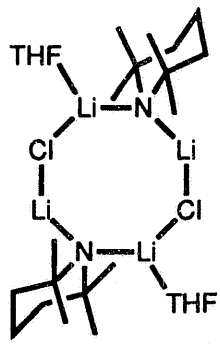


(S = THF); H_f = -433.85



33 (unsolvated); H_f = -288.97
(S = THF); H_f = -342.61



H_f = -358.78

Chart A. Heats of formation of mixed tetramers.

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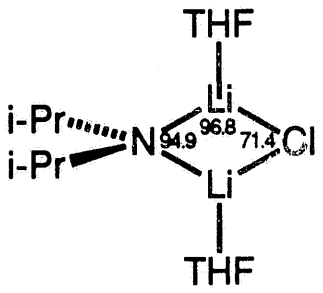

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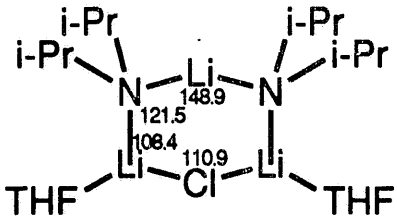

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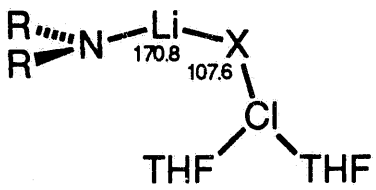

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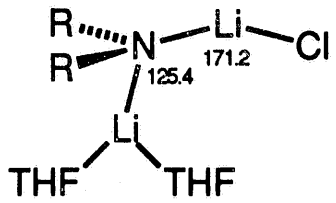

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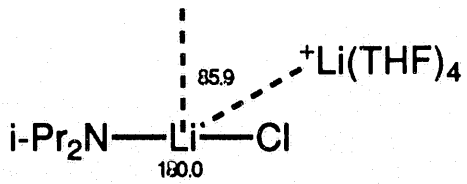

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Chart B. Selected bond angles: LDA/LiCl