THE JOURNAL OF
PHYSICAL CHEMISTRY
J. Phys. Chem., 1996, 100(25), 10580-10594, DOI:10.1021/jp9536514

H-10594-1

Supplementary Material

Dirk Bakowies and Walter Thiel, "Hybrid Models for Combined Quantum Mechanical and Molecular Mechanical Approaches".

The following pages provide supplementary material for sections 4.3 (Tables S1-S3) and 4.5 (Tables S4-S9).

References used in the supplementary material:

(1) Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.

(2) Olivella, S.; Urpi, F.; Vilarassa, J. *J. Comp. Chem.* **1984**, *5*, 230.

(3) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

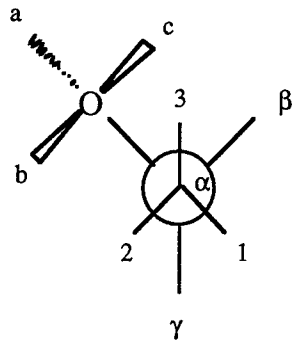
(4) Bartmess, J. E.; Scott, J. A.; McIver Jr., R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6046.

(5) Bakowies, D. *Hybridmodelle zur Kopplung quantenchemischer und molekülmechanischer Verfahren*; Ph.D. Thesis, Zürich, Hartung-Gorre Verlag: Konstanz, 1994.

(6) Paddon-Row, M. N.; Wu, Y.-D.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 10638.

Table S1

Energies and heats of formation of alcohols



Molecule					AM1	MNDO		QM(CH_3OH)/MM3 (3-7)				QM(H_2O)/MM3 (8-11)			
					1	2	3	4	5	6	7	8	9	10	11
R^{α}	R^{β}	R^{γ}	CS[b]	Conf.[c]											
H	H	H	d	x0	-38.50	-39.74	-	-	-	-	-	-7.55	-1.66	-1.66	0.43
Me	H	H	d	x0	-45.49	-45.30	-39.93	-39.21	-37.43	-39.89	-43.74	-9.82	-1.20	-1.20	-1.49
Et	H	H	d	x3	-53.14	-52.07	-37.25	-35.36	-33.70	-37.25	-40.51	-8.73	1.33	1.33	-0.39
				x1	-53.71	-51.75	-38.02	-36.71	-35.01	-37.92	-41.14	-10.67	-0.55	-0.55	-2.25
*t*Bu	H	H	d	x0	-63.48	-54.17	-33.34	-29.22	-27.70	-33.35	-35.34	-7.68	5.04	5.04	0.72
Me	Me	H	d	x0	-50.73	-48.02	-47.23	-45.85	-41.92	-47.32	-55.21	-11.91	-0.47	-0.47	-3.26
tBu	Me	H	d	x0	-66.07	-51.81	-34.94	-32.04	-28.41	-34.76	-41.40	-8.18	7.70	7.70	0.58
Et	*t*Bu	H	d	x3	-71.04	-55.28	-27.65	-23.95	-20.55	-27.40	-33.15	-4.07	13.07	13.07	4.73
				x1	-72.28	d	-29.05	-25.50	-22.10	-28.73	-34.41	-6.86	10.92	10.93	2.05
				x2	-73.19	-57.12	-30.98	-27.17	-23.68	-30.68	-36.57	-7.30	10.08	10.08	1.49
*i*Pr	*t*Bu	H	d	x23	-76.40	-56.44	-23.92	-19.08	-15.78	-23.53	-28.67	-2.58	16.19	16.19	6.24
				x13	-72.74	-51.82	-22.16	-17.84	-14.61	-21.79	-26.67	-2.17	16.63	16.63	6.78
				x12	-74.92	d	-24.57	-19.78	-16.45	-24.19	-29.19	-4.46	15.24	15.24	4.45
*t*Bu	*t*Bu	H	d	x0	-75.29	-46.00	-17.94	-12.07	-8.88	-17.51	-21.84	0.61	21.50	21.50	9.53
Me	Me	Me	d	x0	-54.24	-47.25	-62.43	-57.15	-51.20	-63.29	-76.33	-13.42	0.58	0.58	-4.10
H	H	H	p	x0	138.29	134.87	-	-	-	-	-	129.96	133.33	134.30	118.29
Me	H	H	p	cb0	124.90	126.78	128.55	131.76	133.15	128.39	121.91	131.96	136.50	137.62	121.03
				ab0	125.78	126.80	129.01	131.23	133.24	128.82	122.72	133.75	137.72	138.85	122.03
Et	H	H	p	cb3	116.88	121.40	130.73	135.16	136.48	130.43	124.31	131.68	137.43	138.48	120.56
				cb1	117.70	121.02	131.37	135.13	136.51	131.20	124.98	132.68	138.13	139.22	121.46
				ac3	117.92	121.67	131.74	134.72	136.57	131.48	125.58	132.68	138.13	139.22	121.47
				ab3	0.00	121.45	132.29	134.85	136.68	132.08	125.86	133.87	138.44	139.51	121.89
				ac1	118.67	121.21	131.54	134.09	136.09	131.34	125.76	134.03	138.55	139.66	122.25
Me	Me	H	p	ac0	114.98	121.71	117.44	124.57	128.28	116.41	106.14	135.73	140.72	141.98	124.74
				ab0	116.31	122.08	118.58	124.56	128.89	117.65	107.31	137.44	141.78	143.07	125.46
Me	Me	Me	p	x0	107.80	120.60	105.21	118.54	123.84	103.25	86.22	139.14	144.28	145.69	127.92
H	H	H	n	x0	-57.03	-57.35	-	-	-	-	-	-59.58	-59.38	-59.29	-62.69
Me	H	H	n	c0	-64.21	-62.62	-59.07	-58.75	-58.23	-59.07	-62.77	-57.26	-56.95	-56.85	-59.94
				a0	-62.66	-62.99	-58.37	-58.20	-57.83	-58.37	-61.56	-56.40	-56.01	-55.92	-59.08
Et	H	H	n	b3	-70.59	-67.53	-55.60	-55.35	-54.80	-55.60	-58.86	-55.67	-55.31	-55.21	-58.47
				b1	-71.13	-67.62	-56.25	-56.05	-55.56	-56.25	-59.34	-56.29	-55.96	-55.87	-59.01
				c3	-70.89	-67.29	-55.65	-55.44	-54.93	-55.66	-58.90	-55.62	-55.28	-55.18	-58.40
				a3	-68.92	-67.71	-55.24	-55.03	-54.64	-55.24	-57.87	-55.19	-54.71	-54.62	-57.98
				a1	-69.53	-67.72	-56.08	-55.95	-55.57	-56.08	-58.56	-56.12	-55.67	-55.58	-58.84

H-10594-2

*t*Bu	H	H	n	c0	-78.76	-65.57	-50.18	-50.00	-49.48	-50.18	-52.33	-52.63	-52.17	-52.08	-55.51
				a0	-76.49	-65.63	-50.57	-50.19	-49.75	-50.58	-51.96	-52.90	-52.23	-52.14	-55.79
Me	Me	H	n	c0	-69.54	-65.09	-64.85	-62.79	-61.54	-64.96	-73.85	-54.73	-54.27	-54.15	-57.02
				b0	-68.04	-65.41	-63.01	-61.54	-60.72	-63.05	-71.51	-54.42	-53.87	-53.76	-56.70
*t*Bu	Me	H	n	c0	-81.83	-63.18	-51.85	-50.64	-49.35	-51.92	-59.46	-47.91	-47.24	-47.12	-50.33
				b0	-80.38	-63.49	-49.71	-48.93	-48.15	-49.72	-56.86	-47.06	-46.31	-46.21	-49.51
				a0	-79.71	-63.34	-51.19	-50.24	-49.35	-51.22	-57.97	-48.33	-47.42	-47.32	-50.76
Et	*t*Bu	H	n	c3	-85.64	-63.77	-44.00	-43.23	-41.93	-44.04	-50.54	-42.77	-42.09	-41.98	-45.24
				b3	-83.55	-64.54	-43.42	-42.71	-41.77	-43.42	-49.12	-43.27	-42.33	-42.22	-45.77
				a3	-83.98	-64.49	-42.34	-41.76	-40.92	-42.34	-48.25	-42.35	-41.51	-41.41	-44.84
				c1	-87.23	d	-44.67	-43.92	-42.66	-44.71	-51.12	-43.61	-42.95	-42.84	-46.04
				b1	-85.11	d	-44.19	-43.54	-42.68	-44.21	-49.80	-44.01	-43.07	-42.97	-46.44
				a1	-85.96	d	-43.52	-42.99	-42.17	-43.52	-49.37	-43.67	-42.75	-42.65	-46.10
				c2	-87.96	-66.79	-47.26	-46.44	-45.18	-47.30	-54.00	-46.05	-45.32	-45.20	-48.55
				b2	-86.13	d	-46.76	-46.07	-45.23	-46.78	-52.65	-46.39	-45.45	-45.34	-48.90
				a2	-86.33	-66.97	-45.85	-45.26	-44.47	-45.85	-51.92	-45.61	-44.75	-44.65	-48.15
*i*Pr	*t*Bu	H	n	c23	-90.56	-63.66	-39.85	-39.29	-38.03	-39.87	-45.70	-40.20	-39.52	-39.41	-42.79
				b23	-88.59	-64.36	-39.60	-39.04	-38.13	-39.61	-44.52	-40.94	-40.00	-39.90	-43.52
				a23	-88.32	-64.18	-38.66	-38.13	-37.30	-38.67	-43.81	-40.12	-39.15	-39.05	-42.71
				c13	-86.66	-59.80	-36.72	-36.24	-34.95	-36.74	-42.27	-37.35	-36.66	-36.55	-39.84
				b13	-84.75	-60.42	-36.66	-36.07	-35.19	-36.67	-41.41	-38.34	-37.30	-37.20	-40.82
				a13	-84.71	d	-36.39	-35.91	-35.05	-36.38	-40.45	-38.29	-37.31	-37.21	-40.74
				c12	-89.29	-60.47	-39.69	-39.13	-37.89	-39.71	-45.41	-40.42	-39.60	-39.50	-42.93
				b12	-86.91	d	-38.85	-38.29	-37.48	-38.86	-43.90	-40.49	-39.44	-39.34	-42.98
				a12	-87.19	d	-38.71	-38.19	-37.38	-38.72	-43.83	-40.45	-39.42	-39.32	-42.94
*t*Bu	*t*Bu	H	n	c0	-88.49	-51.40	-32.85	-32.41	-31.13	-32.86	-37.86	-34.60	-33.78	-33.67	-37.16
				b0	-86.32	-51.85e	-32.06	-31.44	-30.58	-32.08	-36.37	-34.83	-33.66	-33.56	-37.38
Me	Me	Me	n	x0	-71.60	-64.27	-72.74	-67.05	-65.76	-72.94	-89.13	-52.15	-51.45	-51.32	-54.06

a) All entries refer to minima on the potential surface if not stated otherwise. QM/MM energies and QM heats of formation are given in kcal/mol. For convenience, the QM/MM energies have been shifted by an additive constant *c* to yield tractable numbers. *c* equals the difference of the QM heat of formation and the QM total energy of the subunit *Y-L*. Columns 1 to 11 collect the results obtained with the following methods:

1:	AM1	2:	MNDO	3-6:	AM1(CH_3OH)/MM3
7:	MNDO(CH_3OH)/MM3	8-10:	AM1(H_2O)/MM3	11:	MNDO(H_2O)/MM3
3,7,8,11:	C//B	4,9:	B//B	5,10:	E^B_{pot}
6:	C//C				

b) Charge state: p (protonated), n (neutral), d (deprotonated).

c) Conformation: Letters and numbers refer to the position of hydroxy hydrogen atoms and methyl hydrogen atoms, respectively (see figure). "x" or "0" entries indicate that no such hydrogen atom is present or that the resulting conformations are identical.

d) Not a minimum on the potential surface (some of these conformations have been identified as transition states).

e) OH ecliptic with CH.

H-10594-3

Table S2

Proton affinities of alcohols[a]

H-10594-4

Molecule	R^{α}	R^{β}	R^{γ}	exp.[b]	AM1	MNDO	QM(CH_3OH)/MM3[c]		QM(H_2O)/MM3[c]	
							AM1[d]	MNDO	AM1	MNDO
H_2O	-	-	-	166.5	163.0	170.6	-	-	163.0[e]	170.6[e]
R_3COH	H	H	H	181.9	170.4	173.5	170.4[e]	173.5[e]	176.2	184.7
R_3COH	CH_3	H	H	188.3	176.6	175.9	178.1	181.0	176.5	184.7
R_3COH	C_2H_5	H	H	190.8	177.7	177.0	178.7	182.1	177.7	186.1
R_3COH	CH_3	CH_3	H	191.2	181.2	178.6	183.4	185.7	175.2	183.9
R_3COH	CH_3	CH_3	CH_3	193.7	186.3	180.8	187.8	190.3	174.4	183.7

a) All entries are in kcal/mol. The AM1 and MNDO values for H_2O have been taken from refs. 1,2.

b) See ref. 3.

c) C//B results.

d) AM1/MM3/C//C results for R_3COH in corresponding order: 170.4, 178.2, 179.0, 184.3, 189.5 kcal/mol.

e) QM/MM and QM description are identical by definition.

H-10594-5

Table S3

Deprotonation enthalpies of alcohols[a]

Molecule	R^{α}	R^{β}	R^{γ}	exp.[b]	AM1	MNDO	QM(CH_3OH)/MM3[c]		QM(H_2O)/MM3[c]	
							AM1[d]	MNDO	AM1	MNDO
H_2O	-	-	-	390.8	410.8	420.8	-	-	410.8[e]	420.8[e]
R3COH	H	H	H	379.2	384.2	383.3	384.2[e]	383.3[e]	417.7	428.8
R3COH	CH_3	H	H	376.1	384.4	383.4	384.8	384.7	413.1	424.1
R3COH	C_2H_5	H	H	374.7	383.1	381.4	383.9	383.9	411.3	422.5
R3COH	*t*-C_4H_9	H	H	371.8	381.0	377.2	382.9	382.7	410.9	422.2
R3COH	CH_3	CH_3	H	374.1	384.5	383.1	383.3	384.3	408.5	419.5
R3COH	CH_3	*t*-C_4H_9	H	370.7	381.5	377.4	382.6	383.8	405.8	417.0
R3COH	C_2H_5	*t*-C_4H_9	H	369.6	380.5	375.5	382.0	383.1	404.8	416.1
R3COH	*i*-C_3H_7	*t*-C_4H_9	H	368.5	379.9	373.6	381.0	382.2	402.2	413.7
R3COH	*t*-C_4H_9	*t*-C_4H_9	H	367.3	378.9	371.6	380.6	381.7	401.1	412.6
R3COH	CH_3	CH_3	CH_3	373.3	383.1	382.7	376.0	378.5	404.4	415.7

a) Alle entries in kcal/mol. The AM1 und MNDO values for H_2O have been taken from refs. 1,2.

b) See ref. 4 (± 2 kcal/mol). The deprotonation enthalpies of alcohols (entries 2-11) have been obtained from ion cyclotron resonance experiments.

c) C//B results.

d) AM1/MM3/C//C results for R3COH in corresponding order: 384.2, 384.9, 384.0, 382.9, 383.3, 382.9, 382.3, 381.4, 381.0, 375.4 kcal/mol.

e) The QM/MM and the QM treatments are identical by definition.

H-10594.6

Table S4

Conformational energies of 2,3-endo,endo-diformyl-7-norbornanone **5**[a]

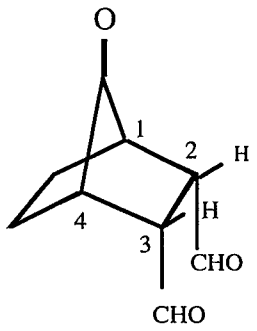
Type	C=O ecliptic with		MNDO	MM3	MNDO/MM3	RHF/6-31G*	MP2/6-31G*[b]
a	C_1C_2	C_3C_4	0.0	0.0	0.0	0.0	0.0
b	C_2H	C_3H	-0.8[c]	3.2	2.3	2.5[c]	2.7
c	C_1C_2	C_3H	-1.4	0.2	-0.3	-0.7	-0.8
d	C_1C_2	C_2C_3	-1.0	-0.6	-1.9	-3.6	-4.1
e	C_2H	C_2C_3	-1.4	1.3	-0.5[d]	-1.8	-2.5

a) Relative energies in kcal/mol. Conformations **a** and **b** possess C_S symmetry, conformations **c**, **d**, and **e** are unsymmetric (C_1). The reaction path has been studied for conformation **a.** Additional information about any of the calculations may be found elsewhere [5].

b) Single point energy calculations for RHF/6-31G* geometries.

c) The hessian shows one negative eigenvalue.

d) The rotation of the QM subunit along the CO axis refers to a negative eigenvalue of the hessian. The minimum shows orthogonal CH_2O (QM) and CC_2O (MM) subunits and is 0.2 kcal/mol lower in energy.



2,3-endo,endo-diformyl-7-norbornanone **5**

H-10594:-7

Table S5

Selected geometrical parameters of the transition structures for the nucleophilic addition of LiH to **6** – **10**[a]

		Distances (Å)				Angles (deg.)			
		CO	OLi	LiH	HC	COLi	OLiH	LiHC	HCO
MNDO	**6**[b]	1.255	2.081	1.468	2.037	83.5	93.4	80.5	102.6
	7	1.276	2.018	1.503	1.873	84.8	88.3	84.5	102.4
	8	1.259	2.014	1.495	1.920	89.3	86.4	86.6	97.6
	9	1.260	2.010	1.497	1.919	90.0	85.9	87.1	96.9
	10a	1.258	2.018	1.505	1.913	90.1	85.3	87.4	97.2
MNDO/MM3	**6**[b]	1.255	2.081	1.468	2.037	83.5	93.4	80.5	102.6
	7	1.265	2.011	1.498	1.853	85.9	86.9	85.9	101.4
	8	1.264	2.007	1.491	1.868	87.5	86.2	86.8	99.4
	9	1.264	2.006	1.494	1.860	87.7	85.8	87.2	99.3
	10a	1.267	2.009	1.501	1.848	87.3	85.6	87.3	99.9
RHF/6-31G*	**6**	1.205	1.917	1.680	2.690	99.9	108.6	62.7	88.8
	7	1.245	1.795	1.705	1.953	93.7	90.7	75.6	100.0
	8	1.235	1.798	1.689	2.052	95.5	92.8	74.3	97.4
	9	1.236	1.792	1.687	2.043	95.7	92.6	74.5	97.1
	10a	1.233	1.799	1.699	2.029	95.6	91.8	74.8	97.8

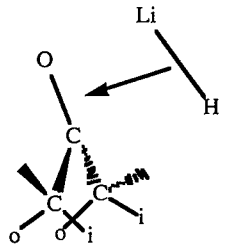
a) Syn oriented attack.

b) The QM/MM and QM treatments are identical by definition.

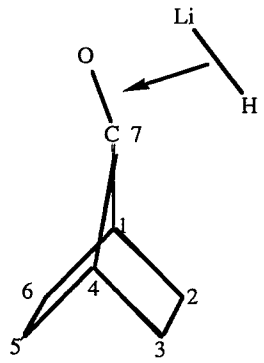
Table S6

Selected bond lenghts and non-bonded distances in **7** and **8** (in Å)[a]

Method	R(7)		T(7)			P(7)		
	C-C	$H_i \cdot\cdot H_i$	C-C	$H_i \cdot\cdot H_i$	$H_o \cdot\cdot H_o$	C-C	$H_i \cdot\cdot H_i$	$H_o \cdot\cdot H_o$
MNDO	1.527	2.718	1.543	2.580	2.969	1.561	2.621	2.766
Model A[b]	1.516	2.689	1.520	2.618	2.794	1.539	2.716	2.705
Model B[b]	1.492	2.669	1.494	2.692	2.643	1.513	2.693	2.663
RHF/6-31G*	1.514	2.671	1.510	2.534	2.784	1.532	2.604	2.588



7



8

Method	R(8)			T(8)					P(8)				
	C_1C_7	C_1C_2	C_2C_3	C_1C_7	C_1C_2	C_1C_6	C_2C_3	C_5C_6	C_1C_7	C_1C_2	C_1C_6	C_2C_3	C_5C_6
MNDO	1.550	1.560	1.559	1.571	1.559	1.565	1.557	1.560	1.598	1.559	1.558	1.556	1.556
Modell A[b]	1.500	1.557	1.573	1.506	1.550	1.564	1.573	1.576	1.519	1.550	1.564	1.575	1.575
Modell B[b]	1.495	1.556	1.572	1.501	1.548	1.563	1.571	1.574	1.515	1.550	1.563	1.573	1.574
RHF/6-31G*	1.523	1.542	1.565	1.518	1.535	1.550	1.560	1.567	1.547	1.537	1.540	1.560	1.555

a) Reactants **R**, transition states **T**, and products **P**.

b) MNDO/MM3.

H-10594-9

Table S7

Dipole complexes of 2,3- endo, endo-diformyl-7-norbornanone **10** with LiH[a,b]

Method	Type	CO	OLi	LiH	HC	COLi	OLiH	N_{imag}[c]	E_{rel}
MNDO[d]	**D**	1.219	2.093	1.403		174	164	1[e]	-
MNDO/MM3	**D**	1.225	2.058	1.402		179	178	2[f]	0.0
C//B	**DI**	1.234	2.083	1.418	3.217	110	120	0	-2.3
RHF/6-31G*	**D**	1.196	1.871	1.661		174	174	1[g]	0.0
	DI	1.202	1.902	1.683	3.350	117	122	0[h]	-1.2[i]

a) Conformation **a** as specified in Table S4. Distances, angles, and relative energies are given in Å, degrees, and kcal/mol, respectively.

b) See figure for a visual comparison of dipole complex **DI** and transition state **T**.

c) Number of imaginary frequencies.

d) MNDO only locates dipole complex **D**.

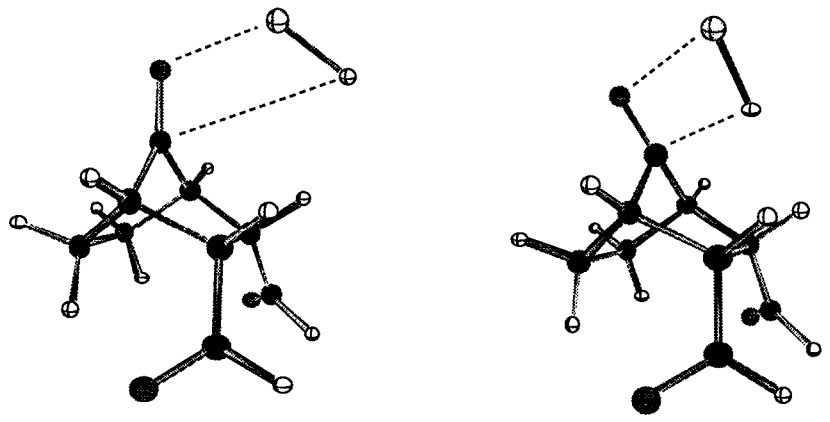
e) The imaginary frequency (36 i cm^{-1}) corresponds to a normal mode which describes the conrotatory movement of the formyl groups.

f) The imaginary frequencies (15 i und 18 i cm^{-1}) correspond to normal modes which describe movements of the LiH molecule.

g) The imaginary frequency (42 i cm^{-1}) corresponds to a normal mode which describes the movement of the LiH molecule.

h) The force constant matrix has seven eigenvalues equal to zero. The seventh of these eigenvalues corresponds to an antisymmetric (a") bending vibration involving the LiH molecule and the keto group.

i) MP2/6-31G*//RHF/6-31G*: -2.1 kcal/mol.



DI **T**

MNDO/MM3/B geometries of **DI** (**10a**) and **T** (**10a**). The link atoms are not shown.

Table S8

Dipole complexes of formaldehyde **6** and 7-norbornanone **8** with LiH[a]

H-10594-10

Method	Molecule	Type[b]	CO	OLi	LiH	HC	COLi	OLiH	N_{imag}[c]	E_{rel}
MNDO[d]	**1**	**D**	1.223	2.064	1.403	4.690	180	180	0	-
	3	**D**	1.219	2.084	1.404	4.708	179	180	0	-
MNDO/MM3	**3**	**D**	1.222	2.051	1.405	4.678	180	180	0	0.0
C//B	**3**	**DII**	1.226	2.075	1.408	3.952	130	141	0	0.1
RHF/6-31G*	**1**	**D**	1.192	1.896	1.657	4.744	180	180	1	0.0
	1	**DII**	1.197	1.933	1.661	3.787	121	138	0	-0.6[e]
	3	**D**	1.197	1.864	1.664	4.725	180	180	1	0
	3	**DII**	1.200	1.895	1.664	4.346	135	163	0	-0.5[f]

a) Distances, angles, and relative energies are given in Å, degrees, and kcal/mol, respectively.

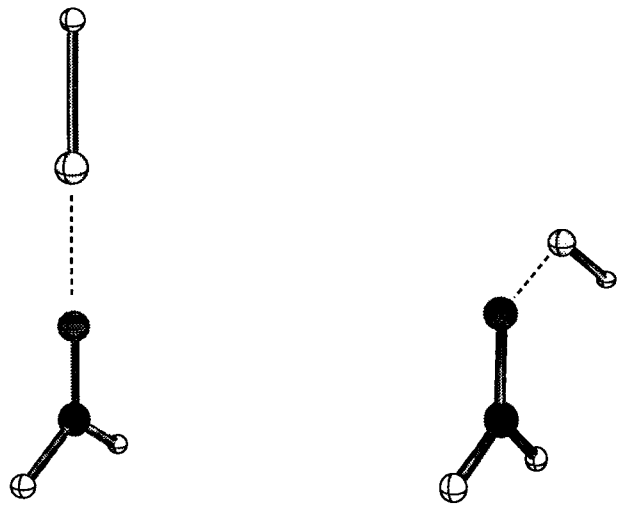
b) See figure for a visual comparison of dipole complexes **D** and **DII**.

c) Number of imaginary frequencies. The normal coordinates corresponding to imaginary frequencies always describe movements of the LiH molecule.

d) MNDO only locates dipole complex **D**.

e) MP2/6-31G*//RHF/6-31G*: -0.8 kcal/mol.

f) MP2/6-31G*//RHF/6-31G*: -0.9 kcal/mol.



D **DII**

Dipole complexes **D**(**6**) und **DII** (**6**) (RHF/6-31G* geometries)

H-10594-11

Table S9

Relative energies of transition states **T** and products **P** formed from syn or anti attack of LiH[a]

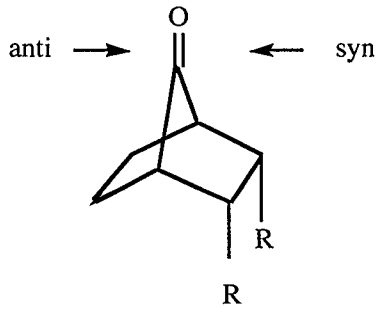
Method	Molecule[b]	T	P
MNDO	**9**	-0.4	0.6
	10a	0.8	0.5
	10b	-0.3	0.2
MNDO/MM3	**9**	0.8	-0.2
C//B	**10a**	0.3	-0.4
	10b	0.9	-0.9
RHF/6-31G*	**9**	-0.5[c]	0.2
	10a	3.0[c]	-0.8
	10b	-0.2[c]	-1.2
MP2/6-31G*[d]	**9**	-0.6[c]	0.0
	10a	4.0[c]	-1.1
	10b	-0.6[c]	-1.3

a) Energy differences $E_{(anti)}$-$E_{(syn)}$ in kcal/mol.

b) The specification of conformations refers to Table S4.

c) See ref. 6.

d) MP2/6-31G*//RHF/6-31G*.



9 R = CH_3
10 R = CHO