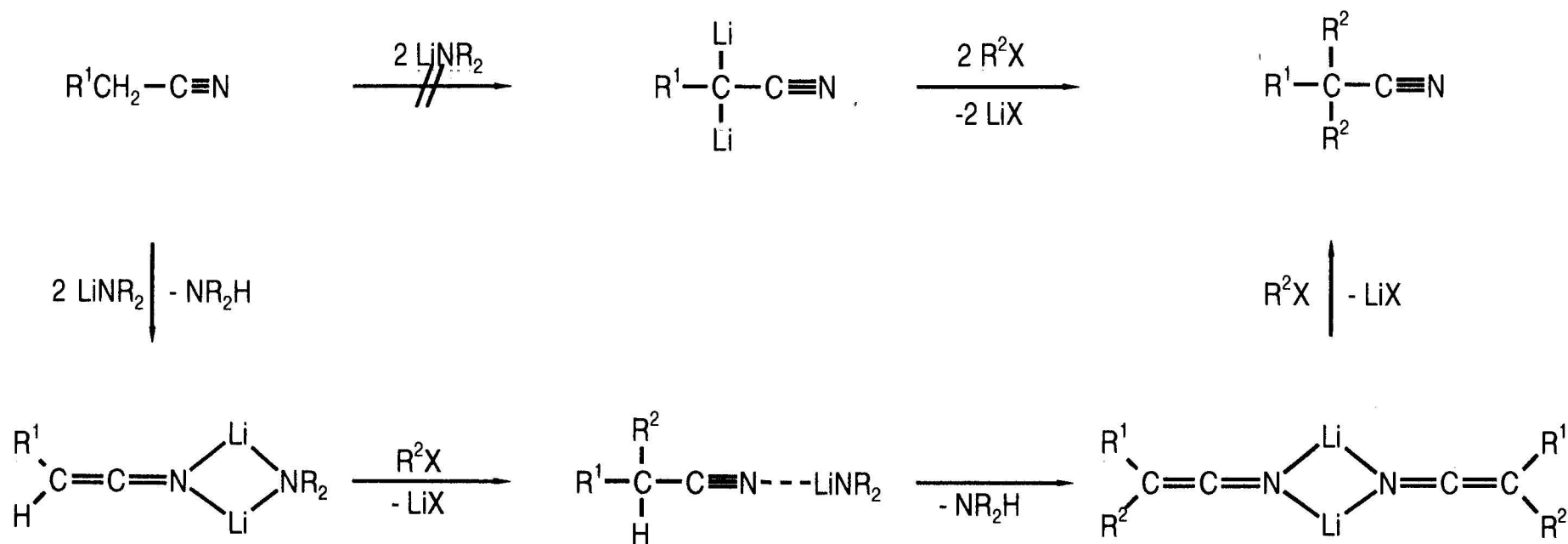
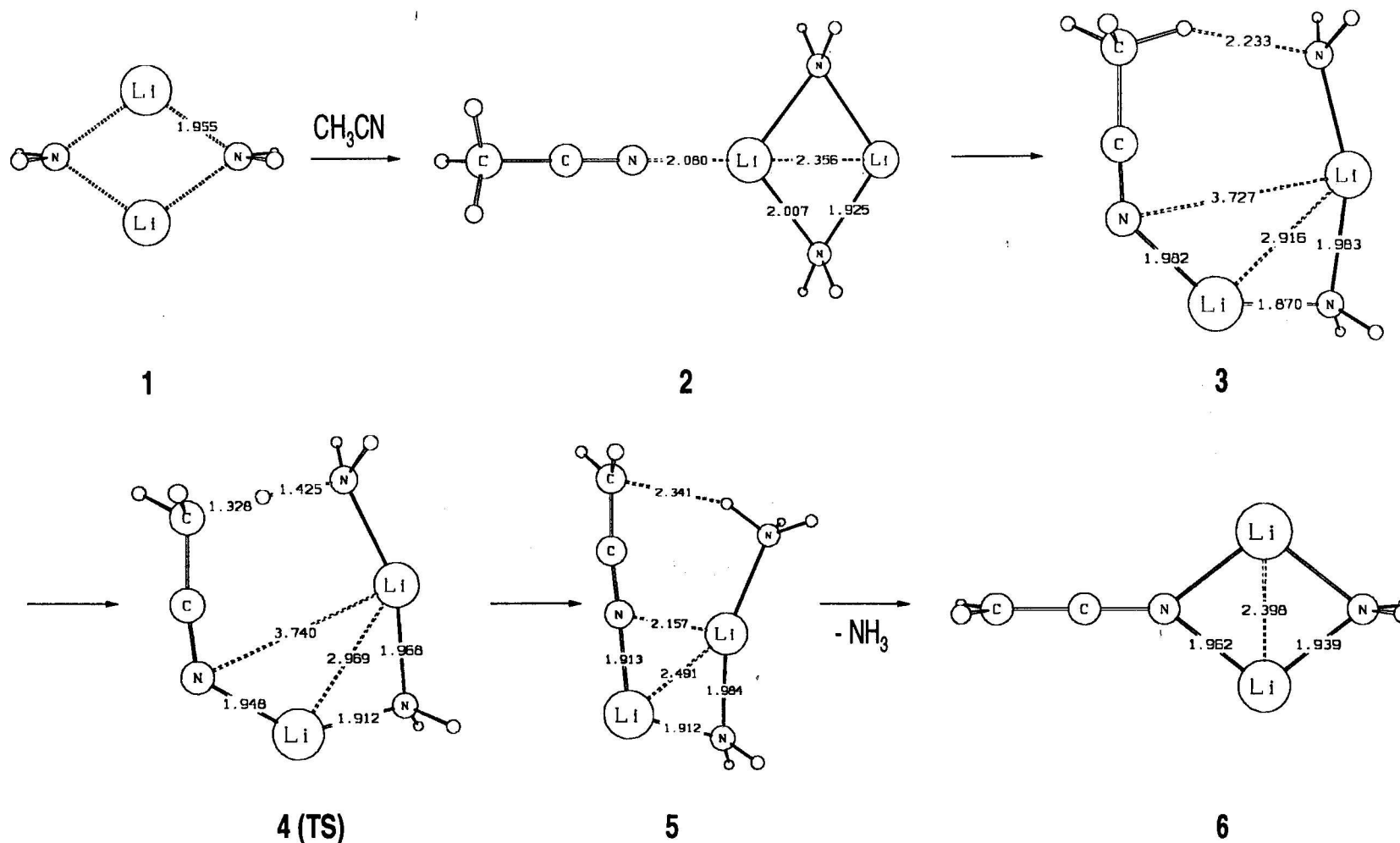


Lithiation of Nitriles I. General Mechanism

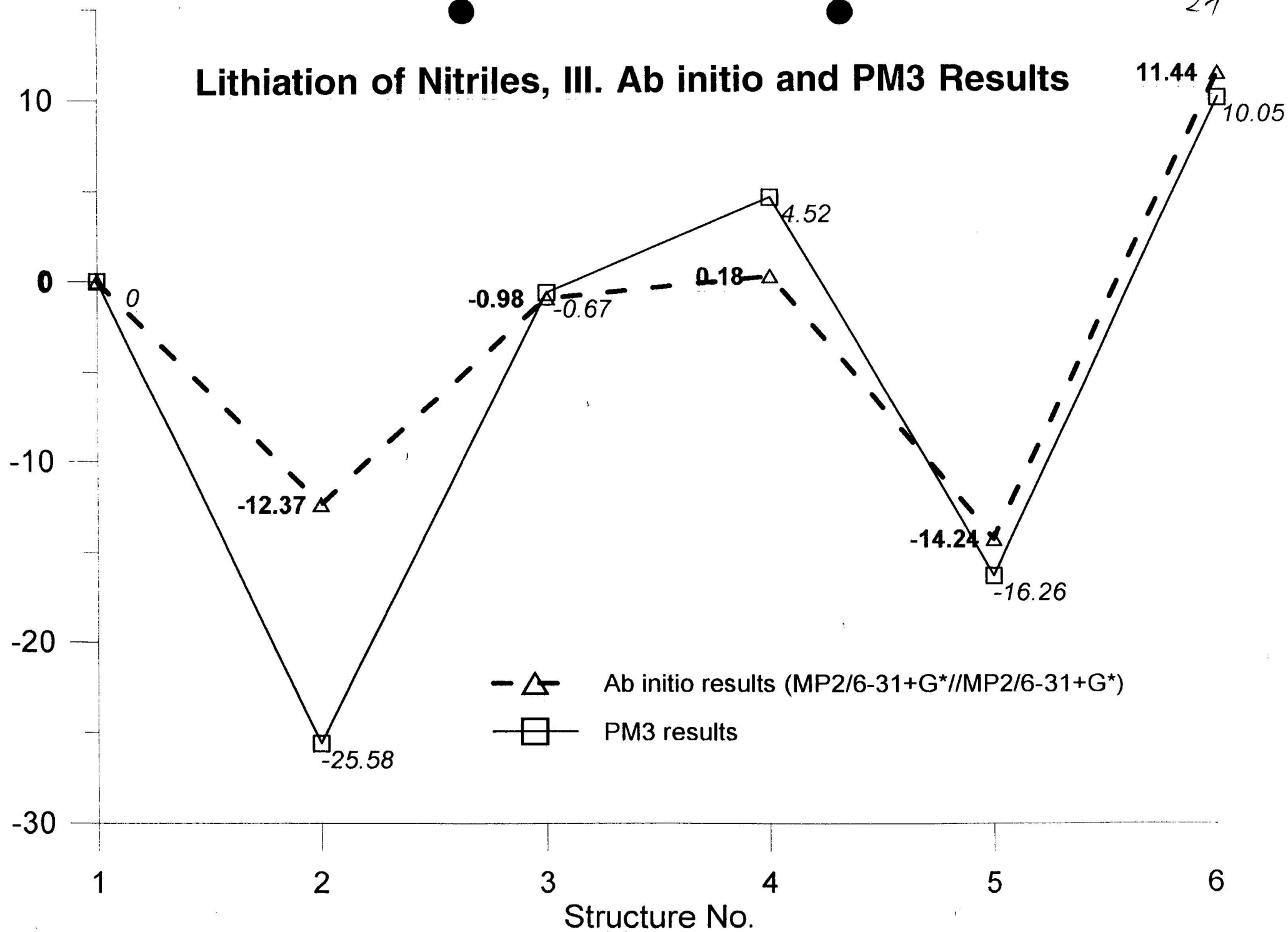


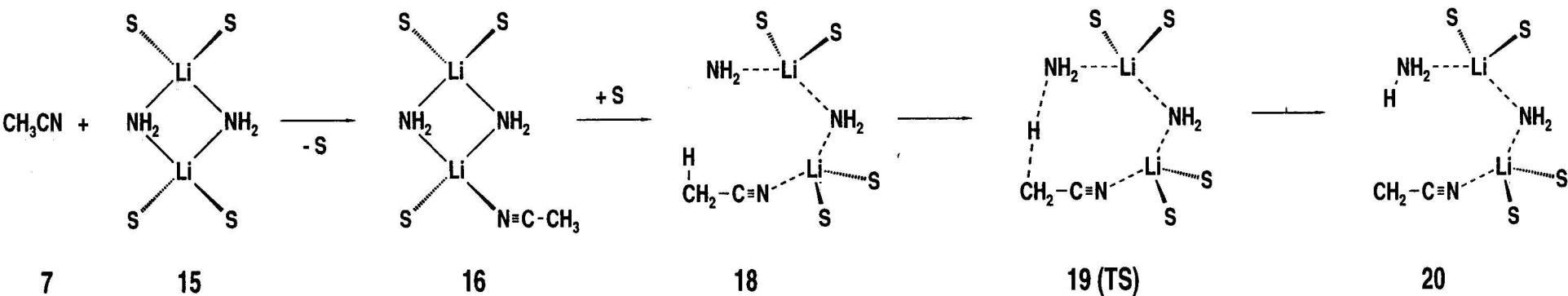
Lithiation of Nitriles, II. Proposed Deprotonation Mechanism



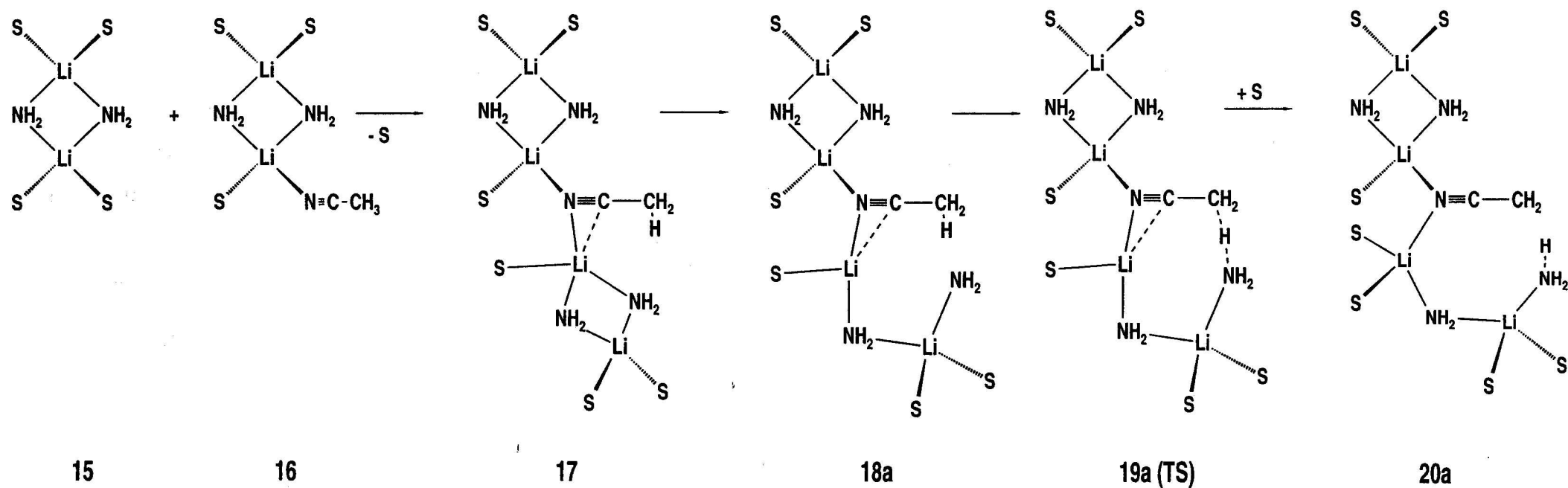
MP2/6-31+G**/MP2/6-31+G* results, R. Koch, E. Anders, in preparation.

Lithiation of Nitriles, III. Ab initio and PM3 Results

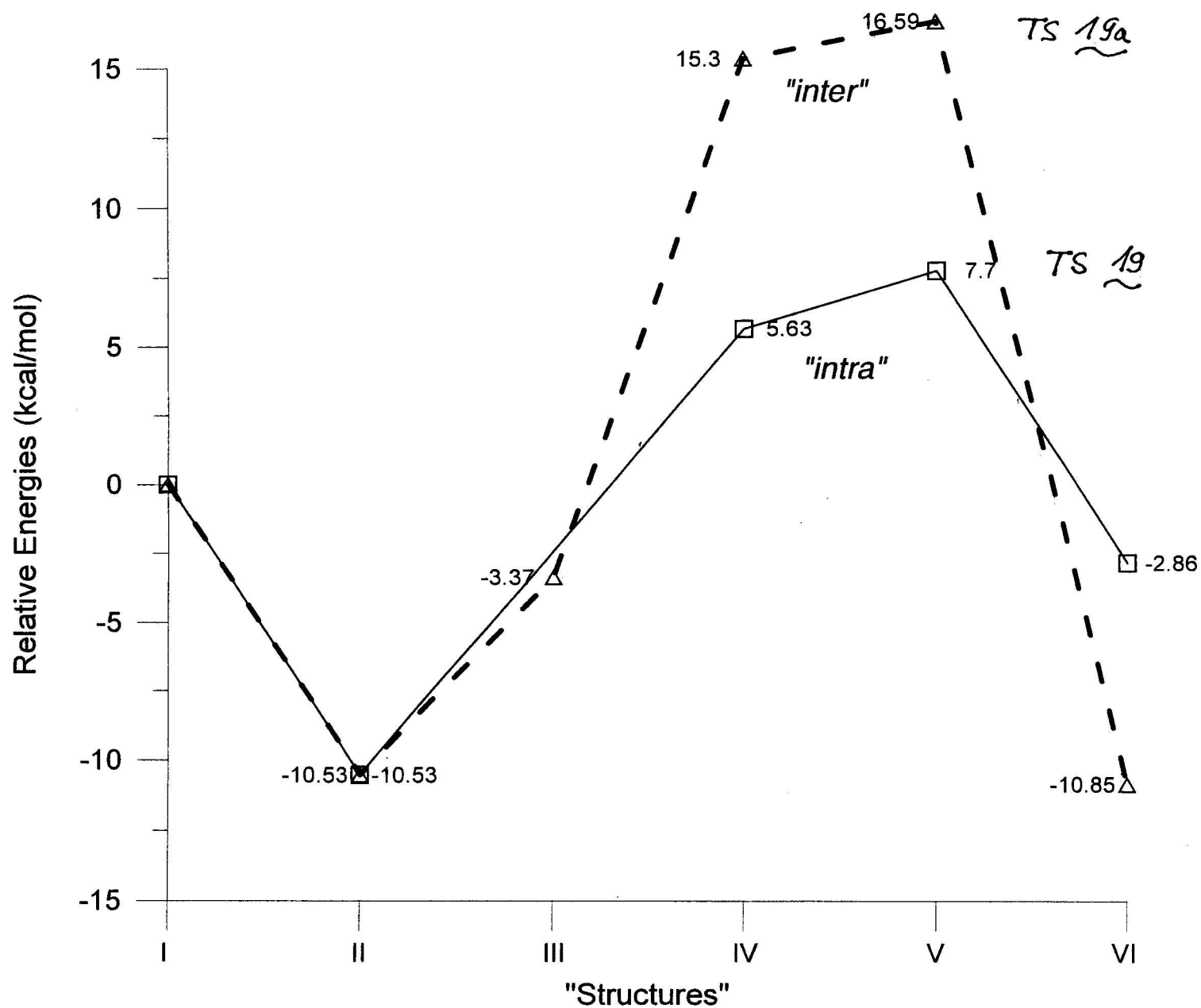




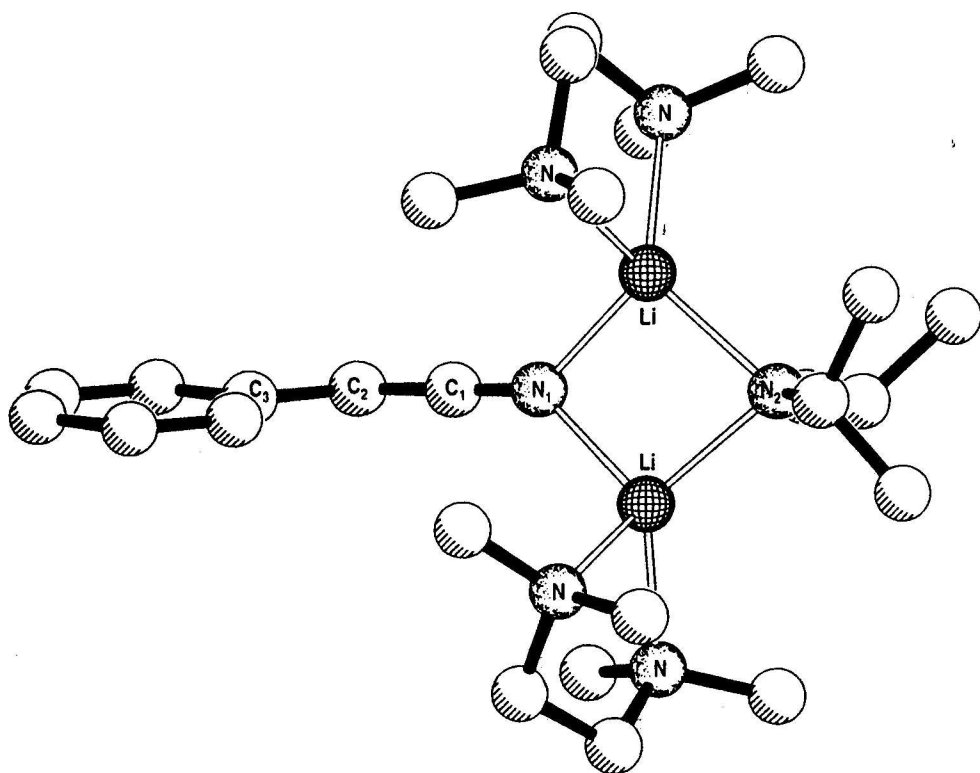
Lithiation of Nitriles: *Intra- vs. Intermolecular Deprotonation*



Lithiation of Nitriles: *Intra-* vs. *Intermolecular* Deprotonation



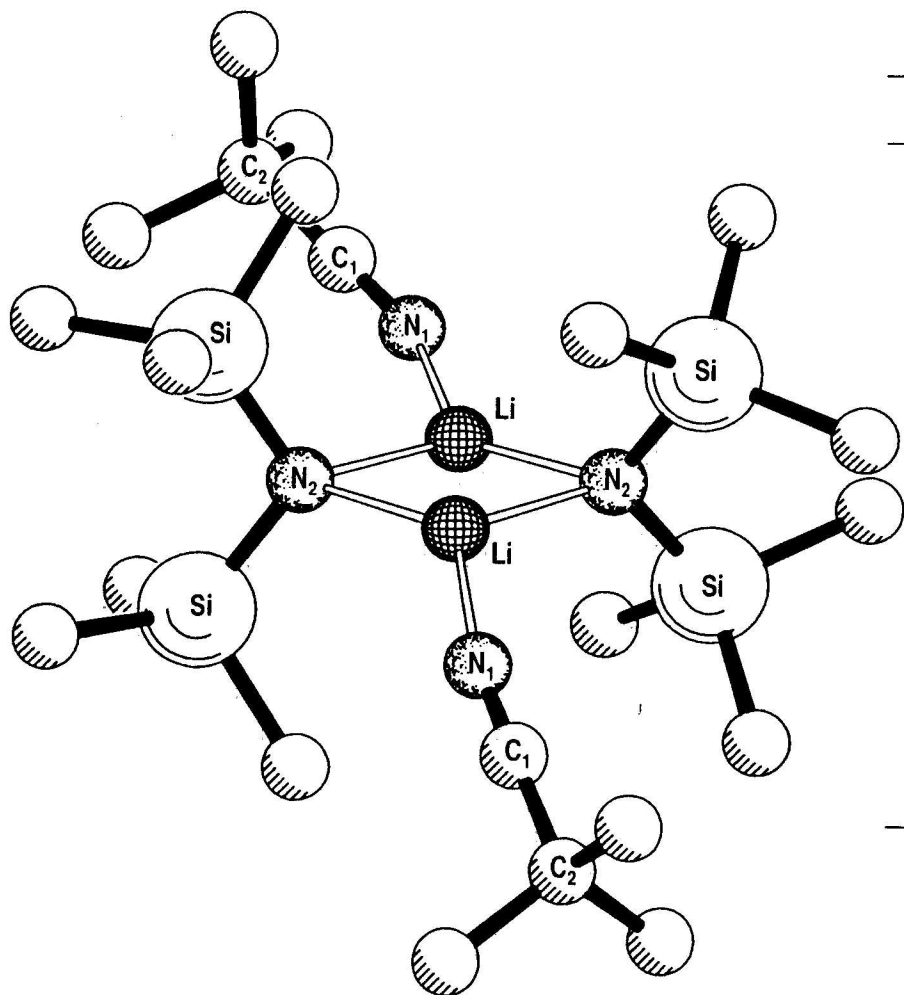
Lithiation of Nitriles, VI. X-Ray Structure 1



	X-ray	PM3	MNDO
Li-N ₁	2.092 (9)	2.059	2.225
Li-N ₂	2.035 (8)	2.127	2.236
Li-N _{TMEDA}	2.268 (9)	2.240	2.523
N ₁ -C ₁	1.173 (7)	1.209	1.193
C ₂ -C ₁ -N ₁	179.5 (7)	179.7	177.9
N ₁ -Li-N ₂	98.7 (4)	93.4	92.8
Li-N ₂ -Li	82.7 (3)	84.0	85.8
Li-N ₁ -Li	80.0 (3)	87.5	86.3
N ₁ -Li-N _{TMEDA}	104.7 (3)	111.1	111.4
N ₂ -Li-N _{TMEDA}	132.0 (4)	129.0	133.2

LiC₆H₅CHCN · LDA · 2 TMEDA: W. Zarges, M. Marsch, K. Harms, G. Boche, *Angew. Chem.*, **1989**, 101, 1424.

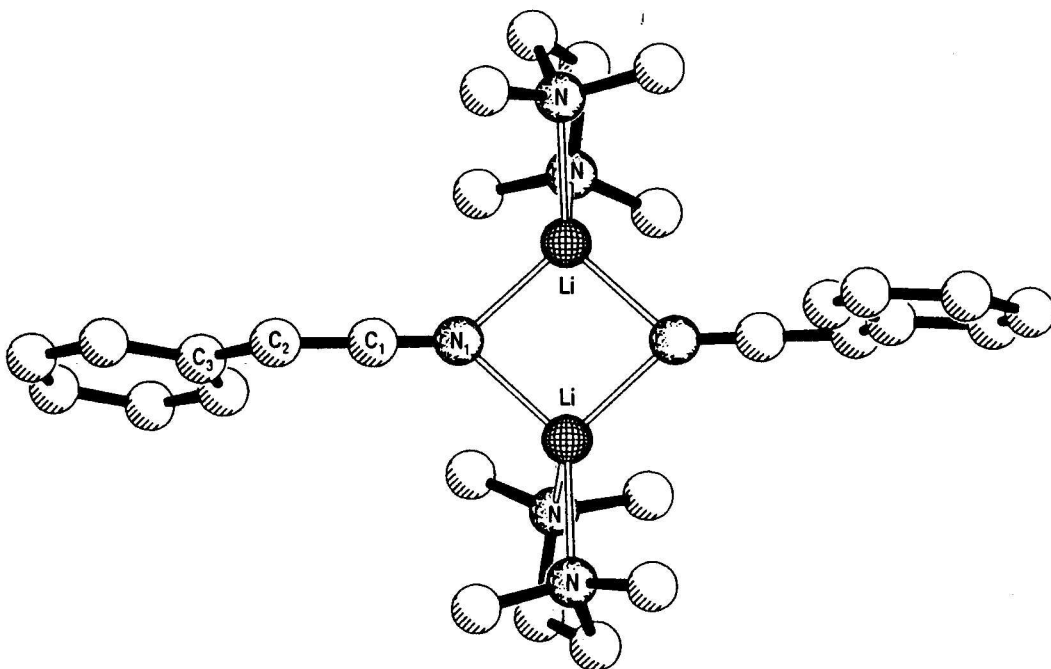
Lithiation of Nitriles, VII. X-Ray Structure 2



	X-ray	PM3	MNDO
Li-N ₁	2.049 (8)	1.987	2.232
Li-N ₂	2.030 (7)	2.040	2.171
N ₂ -Si	1.700 (3)	1.782	1.712
N ₁ -C ₁	1.139 (6)	1.161	1.161
C ₁ -C ₂	1.461 (7)	1.468	1.474
N ₁ -C ₁ -C ₂	179.6 (4)	177.8	179.9
N ₂ -Li-N _{2a}	105.1 (3)	103.7	110.5
Li-N ₂ -Li	74.9 (3)	76.3	69.5
C ₁ -N ₁ -Li	161.5 (4)	158.3	179.1
N ₁ -Li-N ₂	115.9 (3)	115.0	123.6
	139.0 (4)	135.9	125.8

[*t*-BuCN · Li(NSiMe₃)₃]₂: G. Boche, I. Langlotz, M. Marsch, K. Harms, G. Frenking, *Angew. Chem.*, **1993**, *105*, 1207.

Lithiation of Nitriles, VIII. X-Ray Structure 3



	X-ray	PM3	MNDO
Li-N ₁	2.04 (3)	2.035	2.167
Li-N _{TMEDA}	2.05 (4)	2.181	2.312
Li-Li	2.64 (5)	2.731	3.011
N ₁ -C ₁	1.17 (7)	1.212	1.196
C ₁ -C ₂	1.38 (2)	1.342	1.360
C ₂ -C ₃	1.43 (2)	1.437	1.442
C ₃ -C ₂ -C ₁	124.5 (1)	123.9	127.3
C ₂ -C ₁ -N ₁	178.4 (1)	178.4	177.3
N ₁ -Li-N _{1a}	98.2 (0.5)	93.3	92.0
Li-N ₁ -Li	80.9 (0.5)	84.3	88.0

$[(\text{LiC}_6\text{H}_5\text{CHCN} \cdot \text{TMEDA})_2 \cdot \text{C}_6\text{H}_6]$: G. Boche, M. Marsch, K. Harms, *Angew. Chem.*, **1986**, 98, 373.