

Supplementary Material (ESI) for Organic and Biomolecular Chemistry  
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**Pericyclic Rearrangements of *N*-Heterocyclic Carbenes of Indazole to  
Substituted 9-Aminoacridines**

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Calculations ..... S2- S12

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### Calculations

All density-functional theory (DFT)-calculations were carried out by using the Jaguar 7.7.107 software running on Linux 2.6.18-238.el5 SMP (x86\_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI 1.3.4. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP\* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6\* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima or first order saddle points by the absence of imaginary frequencies or occurrence of one imaginary frequency, respectively. Plots were obtained using Maestro 9.1.207, the graphical interface of Jaguar.

Thermodynamic corrections were estimated from unscaled frequencies, using standard formulae in the ideal gas harmonic oscillator approximation as implemented in Jaguar, and refer to a standard state of 298.15 K and 1 mol/dm<sup>3</sup> concentration. Charges were obtained using the natural atomic orbital and natural bond orbital analysis which is included in Jaguar NBO 5.0.<sup>1</sup>

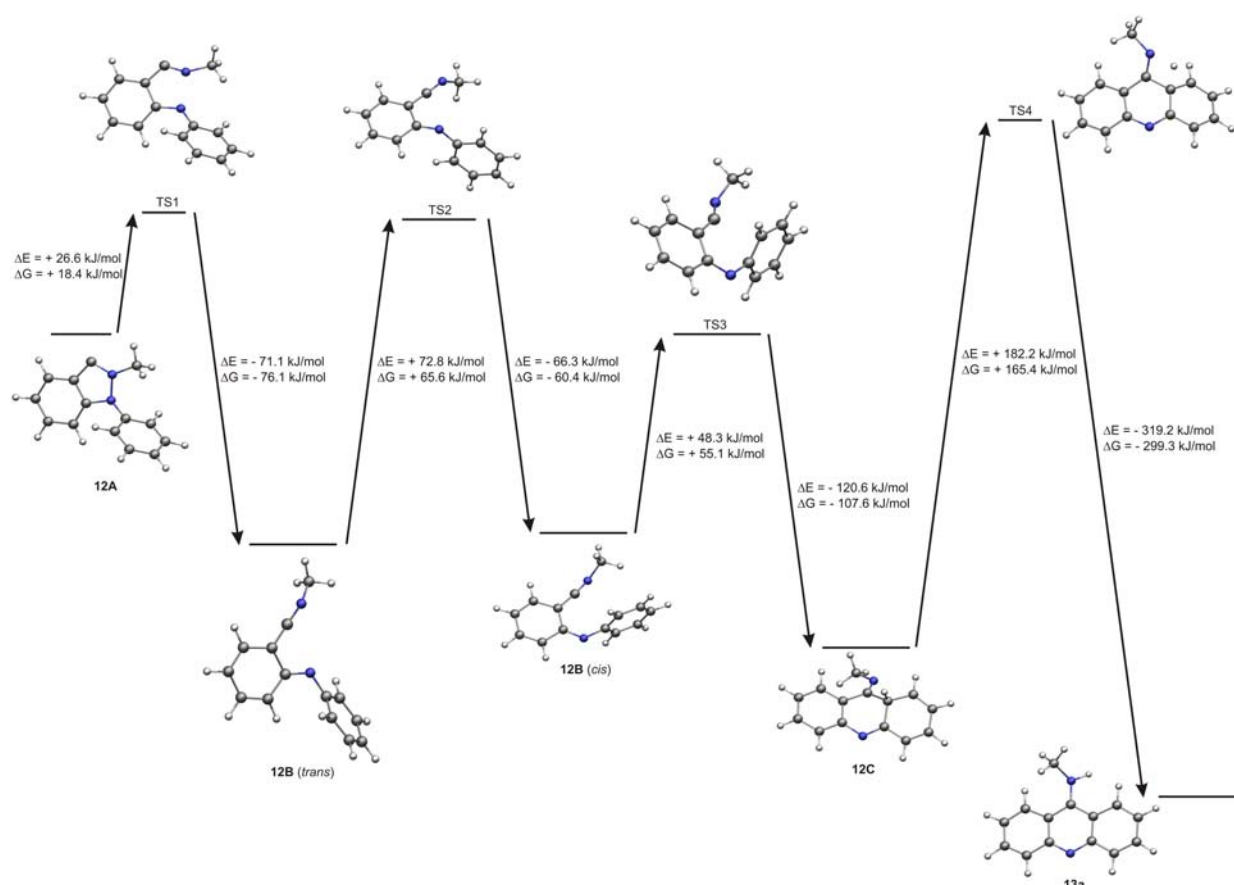
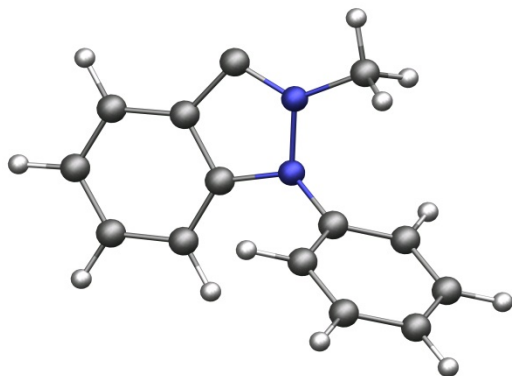


Figure 1. Energy profile of the rearrangement of **12A** to **13a**.

1. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001); <http://www.chem.wisc.edu/~nbo5>

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Reactant:



SCF-Energy: -650.116779, total Gibbs free energy (Htot-T\*S): -649.930222

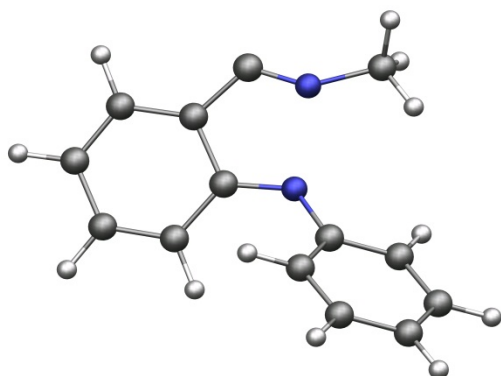
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Coordinates:

C1	-1.7111451354	2.7781423805	-2.5347349407
C2	-1.2317898623	1.5463269354	-3.0247841114
C3	-0.3862663947	0.7351328580	-2.2746242855
C4	-0.0278461400	1.1946604386	-1.0007859528
C5	-0.5082927041	2.4230290641	-0.4796150082
C6	-1.3520294629	3.2200794928	-1.2671789337
N7	0.8203623049	0.6306560975	-0.0702903415
N8	0.7204529284	1.5448501498	1.0772174172
C9	0.0003060336	2.6328192893	0.8673263045
C10	1.0201149776	-0.7704714778	0.1035871203
C11	-0.0721917137	-1.6470622344	0.1849350934
C12	0.1455753130	-3.0147482768	0.3452670904
C13	1.4476126389	-3.5143326423	0.4374401284
C14	2.5351919373	-2.6415465017	0.3596824719
C15	2.3245762453	-1.2736463513	0.1848171931
C16	1.5353459756	1.2369965831	2.2382449760
H17	-2.3673229116	3.3793961260	-3.1571411675
H18	-1.5277087125	1.2205568373	-4.0185705685
H19	-0.0193260973	-0.2093717002	-2.6640599584
H20	-1.7152606962	4.1645441209	-0.8727219961
H21	-1.0803433652	-1.2496107448	0.1179705391
H22	-0.7025034149	-3.6909861088	0.4041643299
H23	1.6134312905	-4.5802279523	0.5648456602
H24	3.5490317388	-3.0264616319	0.4209999279
H25	3.1618634753	-0.5882503260	0.0959819736
H26	1.3281513572	2.0175146568	2.9682407378
H27	1.2746797320	0.2582925204	2.6527468332
H28	2.6001307636	1.2426184128	1.9817435162

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TS1



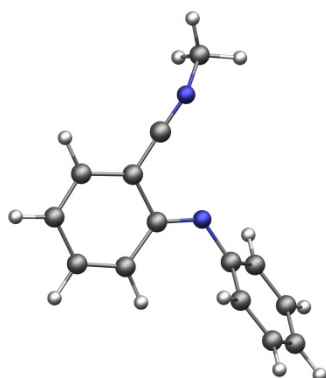
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Coordinates:

N1	0.0000000000	0.0000000000	0.0000000000
N2	0.0000000000	0.0000000000	2.0705460003
C3	2.1085675966	0.0000000000	-1.2751465175
C4	1.3324915801	-0.0709706369	-0.0847875197
C5	2.0700540316	-0.2910933894	1.1508248874
C6	3.4655058035	-0.4502337660	1.1588062538
C7	4.1752357462	-0.3847789700	-0.0255545162
C8	3.4806716549	-0.1620633136	-1.2342778135
C9	1.1784776775	-0.2847904958	2.2525708676
C10	-0.8179348437	0.7852530769	-0.7982229167
C11	-0.4180682553	2.0332060952	-1.3277941986
C12	-1.3027452540	2.7972186207	-2.0819092081
C13	-2.6067458598	2.3513849488	-2.3179810073
C14	-3.0176967208	1.1248535991	-1.7901649829
C15	-2.1372666990	0.3488200689	-1.0410082378
C16	-1.3174418279	-0.2003958415	2.5960049049
H17	5.2544675554	-0.5018028565	-0.0305535110
H18	4.0391768079	-0.1230724030	-2.1670140152
H19	1.5984997342	0.1507578008	-2.2217183104
H20	3.9677839090	-0.6174647657	2.1069286267
H21	0.5867342491	2.3945335022	-1.1294351612
H22	-0.9762560425	3.7549125403	-2.4806277789
H23	-3.2942862756	2.9547255001	-2.9045003750
H24	-4.0284138612	0.7670497742	-1.9706879042
H25	-2.4417914354	-0.6160399099	-0.6448837387
H26	-1.3733981086	0.2352515115	3.5989958780
H27	-2.0328628042	0.3086030722	1.9455827775
H28	-1.5652730947	-1.2659829753	2.6461804040

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Intermediate 1, trans



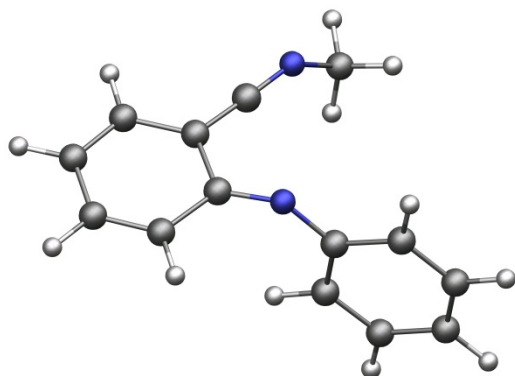
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Coordinates:

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C3	2.3586100536	0.0000000000	-0.7497172711
C4	1.2824863945	-0.0340987123	0.2317986805
C5	1.7316673405	-0.1908813033	1.6342269173
C6	3.1284029384	-0.3536912375	1.9631154451
C7	4.0677659341	-0.3284751961	0.9818713065
C8	3.6617424845	-0.1534000748	-0.3878596754
C9	0.7995542685	-0.1592862067	2.6109594049
C10	-0.5337605591	0.3155023234	-1.2504729128
C11	-0.1820666013	1.4789947539	-1.9652722299
C12	-0.8085144766	1.7893858551	-3.1710126965
C13	-1.7950646844	0.9520976675	-3.6945526487
C14	-2.1609565981	-0.1965418214	-2.9870942134
C15	-1.5499365708	-0.5058719007	-1.7755399888
C16	-0.9099912455	-0.9082817135	4.1717993805
H17	5.1203482268	-0.4434226243	1.2209367090
H18	4.4284763709	-0.1587814819	-1.1596908292
H19	2.0870185599	0.1026317297	-1.7941688088
H20	3.4051297045	-0.4833509253	3.0055946405
H21	0.5671474122	2.1476151449	-1.5497875661
H22	-0.5261663700	2.6958800031	-3.7017460608
H23	-2.2807697819	1.1963552162	-4.6353994011
H24	-2.9339838952	-0.8528335004	-3.3801075554
H25	-1.8391224833	-1.3898853170	-1.2140481773
H26	-0.7911786373	-0.7830063096	5.2512140232
H27	-1.9318393201	-0.6245211935	3.9049363840
H28	-0.7368562118	-1.9542590758	3.8960674435

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TS2



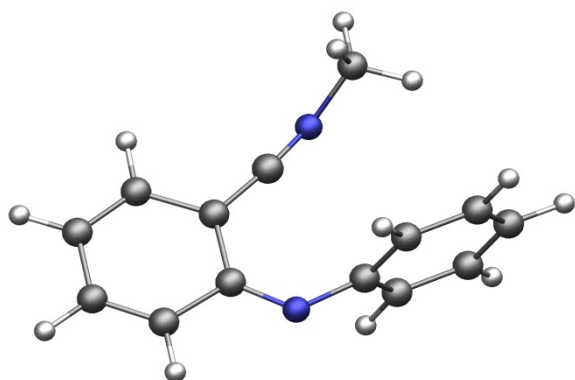
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Coordinates:

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C3	0.8703435588	0.0000000000	2.3158249179
C4	1.2464140857	-1.2460569235	3.0140267986
C5	1.5348985063	1.1835096393	2.8172529580
C6	2.1274100060	-1.2507455412	4.1501944198
C7	2.6752506430	-0.0788951391	4.5825412416
C8	2.3745974141	1.1417484413	3.8965027076
C9	0.7409944070	-2.4009253905	2.5043526102
N10	0.2182988354	-3.3915763398	2.1012457251
C11	-1.2196214406	0.0352150655	-0.7239574563
C12	-1.2263545275	0.0012083805	-2.1127182453
C13	-0.0356273446	-0.0786585399	-2.8447862988
C14	1.1731499626	-0.1144327026	-2.1450985352
C15	1.2038990555	-0.0699917887	-0.7540890604
C16	0.3947090895	-4.3699392714	1.0494485146
H17	3.3330867900	-0.0641372749	5.4458704370
H18	2.8312996895	2.0627659249	4.2515925295
H19	1.3086362512	2.1194883557	2.3154054993
H20	2.3334772435	-2.1895911594	4.6561136960
H21	-2.1497502135	0.0947175917	-0.1648254872
H22	-2.1801555414	0.0351285175	-2.6354847924
H23	-0.0513110696	-0.1091093920	-3.9305364682
H24	2.1139590915	-0.1719044459	-2.6901467862
H25	2.1533957925	-0.0907922874	-0.2247630122
H26	0.4987590475	-5.3596703614	1.5014798300
H27	-0.5030000071	-4.3650164522	0.4266734295
H28	1.2699863794	-4.1426316891	0.4333400395

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Intermediate 1, cis



SCF-Energy: -650.131264, total Gibbs free energy (Htot-T\*S): -649.950078

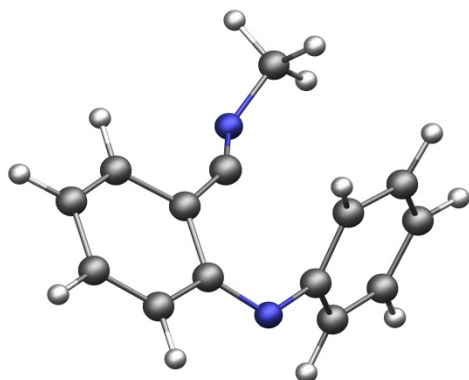
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C3	-2.2632016605	-2.4054062024	-0.7116450002
C4	-1.1294885961	-1.5223057836	-0.4679590592
C5	-1.4986468693	-0.1408159981	-0.0604455291
C6	-2.8986059714	0.2284132837	0.0765314692
N7	0.0744583747	1.8061176734	0.4042613261
C8	-0.5998548103	0.8265018146	0.2336007675
N9	0.0587252207	-2.0262646732	-0.6091382682
C10	1.2296501688	-1.2854368486	-0.4433926726
C11	1.9505663257	-1.3511816541	0.7649731430
C12	3.1729455211	-0.6927824399	0.8979951599
C13	3.7064858565	0.0377539640	-0.1668099004
C14	3.0023907489	0.0982412434	-1.3727941825
C15	1.7810509893	-0.5563136757	-1.5151183422
C16	0.8041069509	2.3377400950	1.5411065225
H17	-4.9301671012	-0.3704504477	-0.0808484940
H18	-4.3560142077	-2.7096413721	-0.7774424373
H19	-2.0076030373	-3.4161338741	-1.0132695070
H20	-3.1269643144	1.2476740680	0.3760847773
H21	1.5444923520	-1.9385396039	1.5840858794
H22	3.7173991669	-0.7611927035	1.8373310132
H23	4.6648000959	0.5402394227	-0.0639452248
H24	3.4111790359	0.6551703513	-2.2127432156
H25	1.2404560083	-0.5206648170	-2.4569406080
H26	0.5419521474	1.8303377688	2.4759583369
H27	1.8712035503	2.2099078748	1.3438967278
H28	0.5896066327	3.4064272342	1.6254239204



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TS3



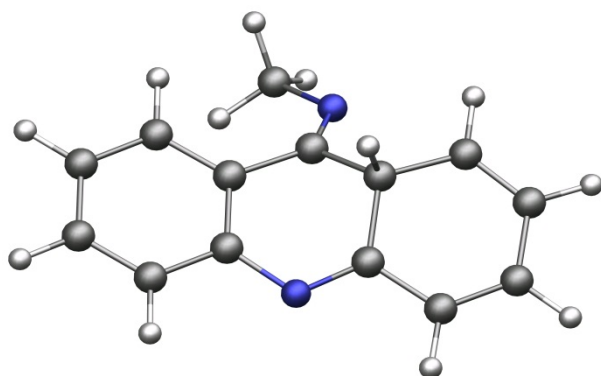
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Coordinates:

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C2	0.0000000000	0.0000000000	2.2954840531
C3	3.7583336340	0.0000000000	0.2326551984
C4	2.4050470753	0.2791696117	0.6597722825
C5	1.3444659902	-0.1657231340	-0.2512838104
C6	1.6818393077	-0.8190306176	-1.4922287973
N7	-1.1422275665	0.1017094333	-0.3776405998
C8	2.9810728057	-1.0413940909	-1.8374237790
N9	2.2013284504	0.9108815997	1.7902030606
C10	0.8873949498	1.0999156018	2.1774118121
C11	4.0273255899	-0.6223001695	-0.9490127115
C12	-1.2871846597	0.1869758871	2.8180879744
C13	-1.7634986945	1.4688764664	3.0875731997
C14	-0.9127955838	2.5672784551	2.9017205024
C15	0.3956522959	2.3883861633	2.4639244922
C16	-2.4488383812	-0.4337017244	-0.1193435169
H17	3.2265878004	-1.5283912898	-2.7759178844
H18	5.0612439808	-0.8069720094	-1.2316549921
H19	4.5497398103	0.3217890157	0.9022919069
H20	0.8688946486	-1.1194776813	-2.1478403702
H21	0.3941869143	-1.0076194767	2.2006210748
H22	-1.9170062917	-0.6783382432	3.0136582038
H23	-2.7691946825	1.6148002976	3.4721763138
H24	-1.2702554348	3.5701967381	3.1227581781
H25	1.0698384548	3.2318956340	2.3509162724
H26	-2.4157816957	-1.3059422387	0.5435468047
H27	-3.0747408721	0.3383301034	0.3367075882
H28	-2.9037750770	-0.7253251378	-1.0715534097

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Intermediate 2



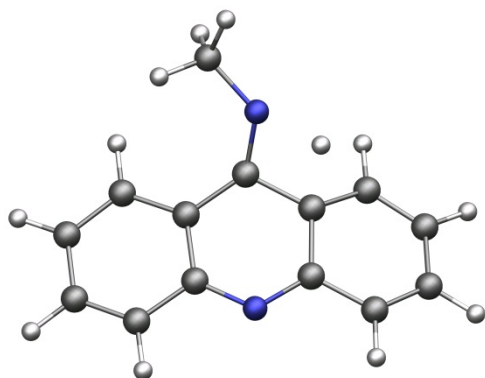
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Coordinates:

C1	-3.7162184038	-0.5186126475	-0.3873015190
C2	-3.5705147720	-1.8749525382	-0.0829643982
C3	-2.3083762062	-2.3982679389	0.1751271717
C4	-1.1672771227	-1.5823592111	0.1260103864
C5	-1.3154578480	-0.1937496426	-0.1475581402
C6	-2.5969895758	0.3121099786	-0.4088617671
N7	0.0614906602	-2.1933895335	0.3936049992
C8	1.1457352489	-1.5434533661	0.1027407010
C9	1.1333380337	-0.1876128912	-0.6062814442
C10	-0.0757326211	0.6279694174	-0.1600722215
C11	2.4297783651	-2.1371984013	0.4085561540
C12	3.5806419730	-1.4385242283	0.2489883922
C13	3.5836092068	-0.0624228221	-0.2233080294
C14	2.4415467699	0.5484132938	-0.5840710172
N15	0.1120139050	1.8513463604	0.1568352807
H16	0.9350744626	-0.4485267780	-1.6689950397
C17	-0.9405685420	2.7102226227	0.6663806779
H18	-4.6971840586	-0.1089837045	-0.6116489718
H19	-4.4421835773	-2.5234127183	-0.0526287176
H20	-2.1674833337	-3.4483728740	0.4121229720
H21	-2.7187467467	1.3568296868	-0.6718902643
H22	2.4163849314	-3.1436890489	0.8153209371
H23	4.5301713961	-1.8968348426	0.5145900389
H24	4.5289473984	0.4727718394	-0.2561209151
H25	2.4210960256	1.5868312688	-0.8947585949
H26	-0.4885379350	3.4225346485	1.3657930412
H27	-1.3761029545	3.3024176519	-0.1505091150
H28	-1.7547981942	2.1823481082	1.1804719489

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TS4



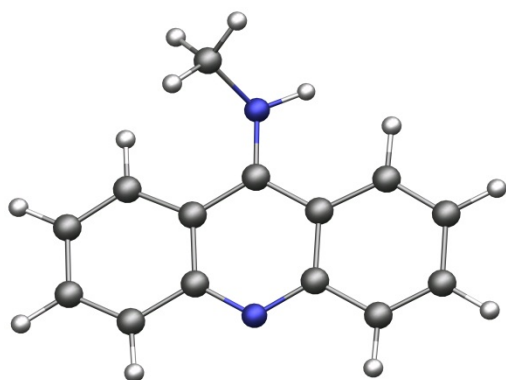
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Coordinates:

N1	0.0520316792	0.1080994059	0.0905244715
H2	-0.1547376058	0.1663259730	1.5362627639
C3	4.8289682072	0.0594608267	0.6011812580
C4	3.5001847156	0.2745423480	1.0420134137
C5	2.5257304215	0.6168628100	0.0391901597
C6	2.9108726643	0.7833842679	-1.3068210966
N7	3.2487980979	0.1493452104	2.3880302523
C8	2.0683765060	0.5368593298	2.8505159866
C9	0.9548360613	0.9028097695	1.9767469230
C10	1.1745947108	0.6139201735	0.5406757703
C11	1.8743987926	0.7399322341	4.2586172990
C12	0.8449343204	1.5240660798	4.7073330116
C13	-0.0751821371	2.1517720612	3.8069437139
C14	0.0037310665	1.8945074038	2.4682311372
C15	4.2307765652	0.6085741110	-1.6874806662
C16	5.1855773723	0.2305407218	-0.7239047874
C17	-0.2451438960	-0.2545674542	-1.2808891278
H18	4.5252054629	0.7533018784	-2.7228999176
H19	6.2192422065	0.0784594789	-1.0248019253
H20	5.5615549578	-0.2176954913	1.3527123800
H21	2.1678963053	1.0775222788	-2.0425323443
H22	2.6351706717	0.3569337731	4.9317736974
H23	0.7495747665	1.7205205024	5.7725935494
H24	-0.8334883681	2.8267511409	4.1913238007
H25	-0.7024933498	2.3224658921	1.7611090187
H26	-1.0608424159	-0.9830291079	-1.2852027384
H27	0.6335326593	-0.7016495947	-1.7652892855
H28	-0.5626870773	0.6127919282	-1.8760608271

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Product **9a**



SCF-Energy: -650.210954, total Gibbs free energy (Htot-T\*S): -649.021279

Coordinates:

C1	-3.6806809439	-0.4145567350	-0.0787907087
C2	-3.5635186199	-1.7860317805	0.2786085341
C3	-2.3279462774	-2.3629119445	0.4018198738
C4	-1.1319113516	-1.6060348088	0.1947931562
C5	-1.2496283903	-0.1957436262	-0.0867146998
C6	-2.5580677600	0.3535479922	-0.2563601206
N7	0.0354706292	-2.2674473075	0.2446411207
C8	1.1570583610	-1.5647740891	0.0183472044
C9	1.1853337698	-0.1406168426	-0.2099558473
C10	-0.0553739470	0.5577697220	-0.2416923013
C11	2.3956390244	-2.2797898988	0.0328266228
C12	3.5910192356	-1.6366050062	-0.1467148149
C13	3.6231974143	-0.2281805593	-0.3356732004
C14	2.4561599698	0.4932763614	-0.3587434318
C15	-0.8641120989	2.8669051168	0.3469228614
N16	-0.0889907471	1.9254460514	-0.4629957939
H17	-4.6650360678	0.0206608018	-0.2287586784
H18	-4.4612160778	-2.3806820448	0.4278753616
H19	-2.2059103500	-3.4156101406	0.6373153375
H20	-2.6658798034	1.3852750080	-0.5696115019
H21	2.3384023529	-3.3517486251	0.1945401210
H22	4.5216873262	-2.1978889226	-0.1329686908
H23	4.5774076226	0.2789202686	-0.4492291835
H24	2.5228719494	1.5716786825	-0.4787087431
H25	-1.6223917098	3.3957284485	-0.2444315155
H26	-0.1956968919	3.6162307109	0.7877427858
H27	-1.3659683975	2.3433051600	1.1632883970
H28	0.7944531465	2.3061942890	-0.7663864206