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Supporting Information

S_N2 Regioselectivity in the Esterification of 5- and 7-Membered Azacycloalkane Quaternary Salts: A DFT Study to Reveal the Transition State Ring Conformation Prevailing over the Ground State Ring Strain

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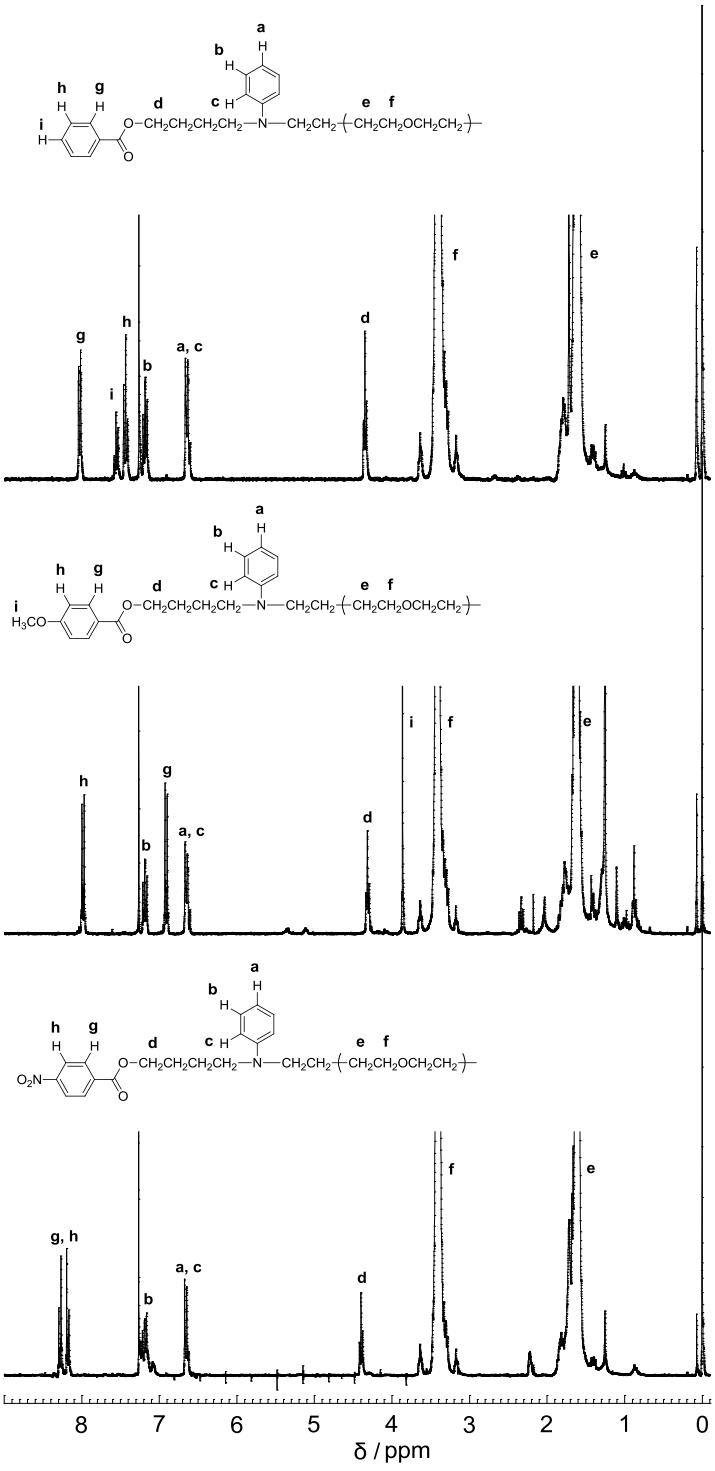


Figure S1. ^{1}H NMR spectra (300 MHz) of the reaction products of poly(THF) having *N*-phenylpyrrolidinium salt end groups (**1**) with (top) benzoate, (middle) *p*-methoxybenzoate, and (bottom) *p*-nitrobenzoate benzoate anions. ($CDCl_3$, 25 °C)

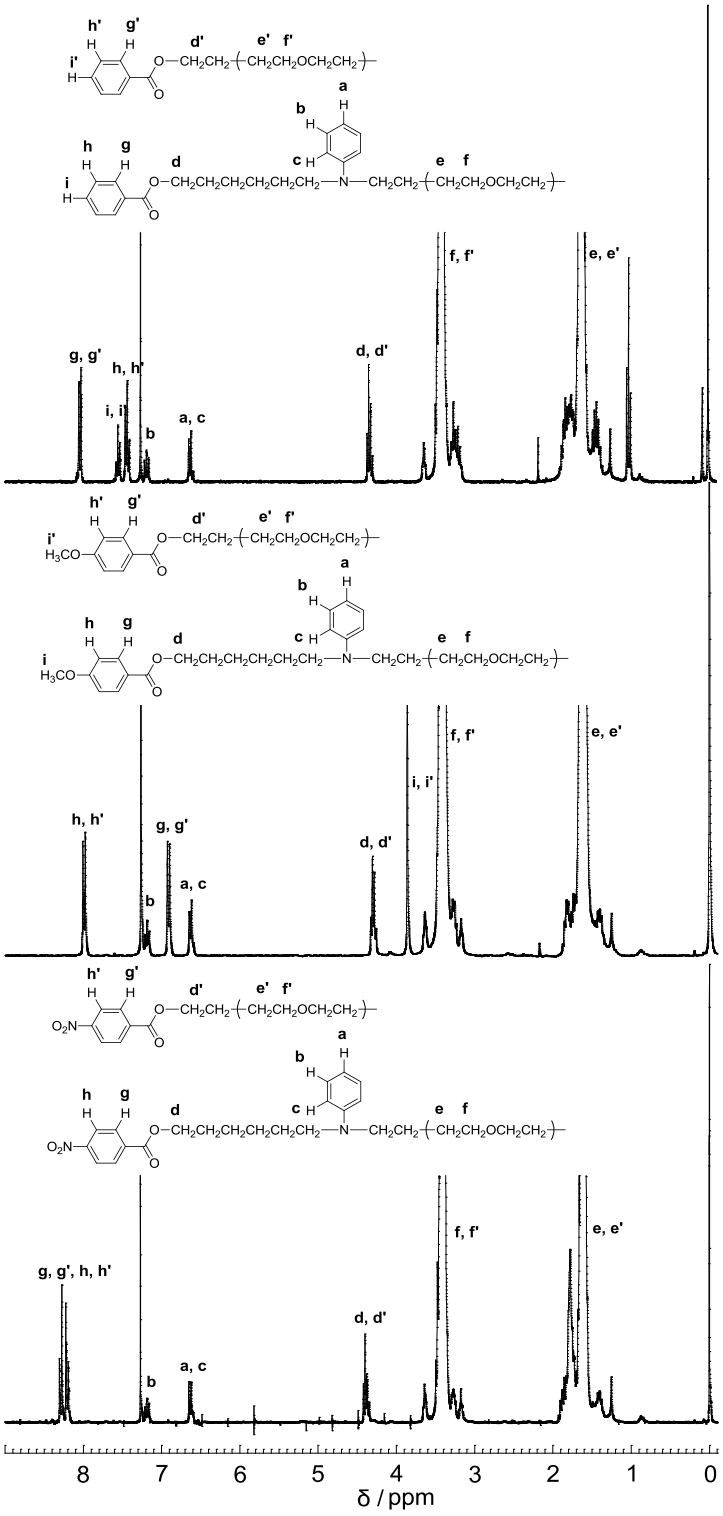


Figure S2. ^{1}H NMR spectra (300 MHz) of the reaction products of poly(THF) having *N*-phenylazepanium salt end groups (**2**) with (top) benzoate, (middle) *p*-methoxybenzoate, and (bottom) *p*-nitrobenzoate benzoate anions. ($CDCl_3$, 25 °C)

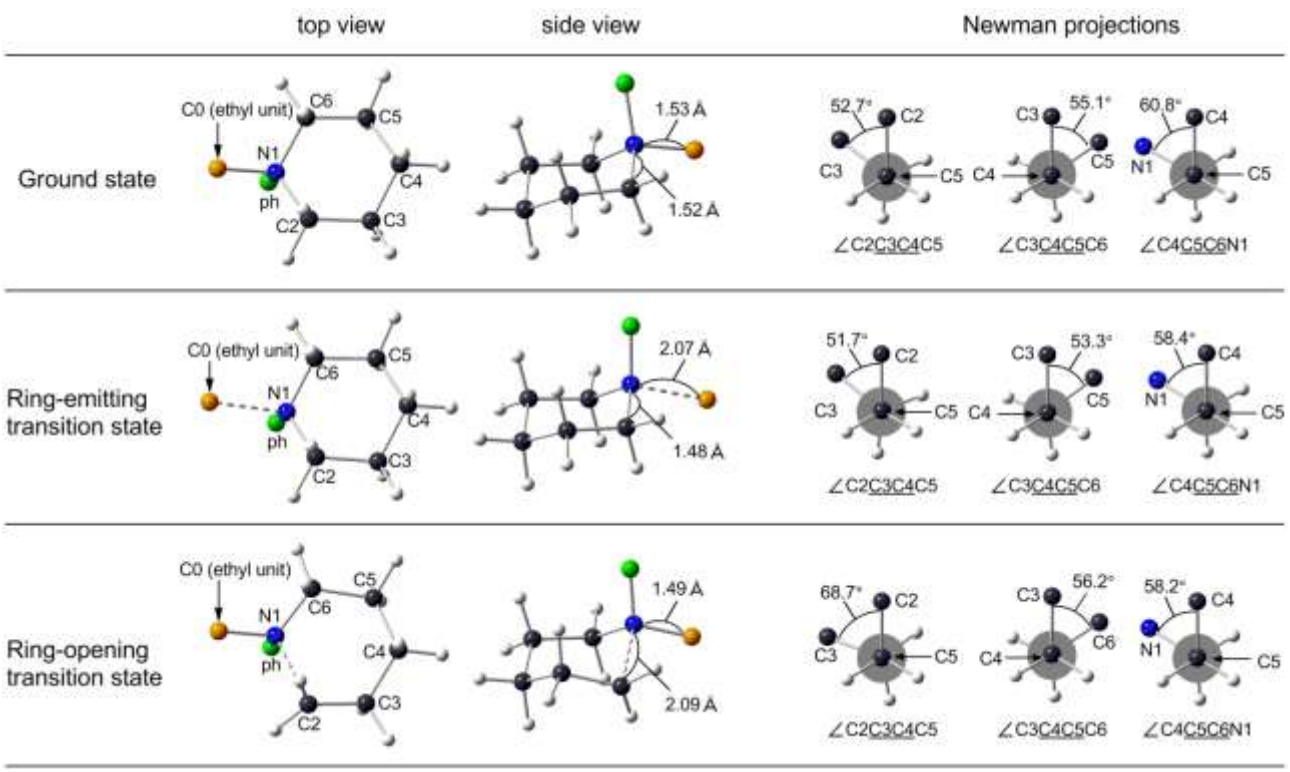


Figure S3. DFT-optimized ground state (**top)**, ring-emitting, **(middle)**, and ring-opening, **(bottom)**, transition state structures in the esterification of *N*-phenylazacyclohexane quaternary salt by benzoate, and the Newman projections along the skeletal C-C bonds. The benzoate anion is omitted for the sake of clarity. The projections of N1-C2, C2-C3 and C6-N1 bonds are not shown as these are involved in the esterification reactions.

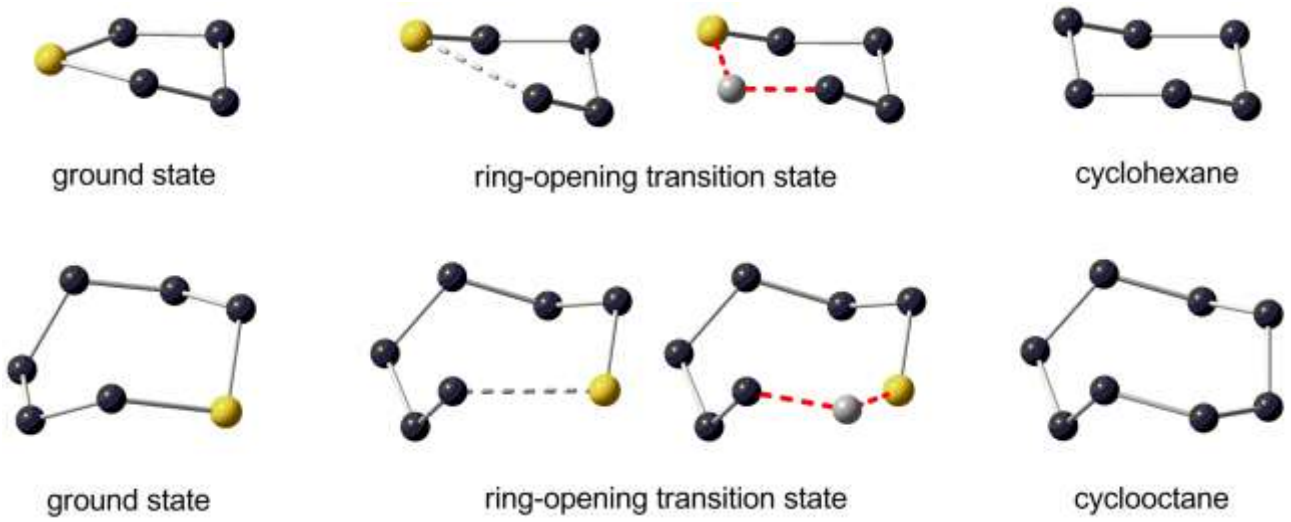


Figure S4. Skeletal conformation of (**top**) DFT-optimized 5-membered thiocyclopentane ground state, its ring-opening transition state, and with a hypothetical atom, and cyclohexane, and (**bottom**) DFT-optimized 7-membered thiocycloheptane ground state, its ring-opening transition state, and with a hypothetical atom, and cyclooctane

Electronic energy calculated by 6-311++G(d, p) and 6-311++G(2d, 2p) basis set

Method: B3LYP

	6-311++G(d, p)	6-311++G(2d, 2p)
I/benzoate(GS)	-943.1424245	-943.3617057
I/benzoate(TS, em)	-943.1089659	-943.3284778
I/benzoate(TS, op)	-943.1131464	-943.3328837
II/benzoate(GS)	-1021.764779	-1022.001067
II/benzoate(TS, em)	-1021.733870	-1021.970571
II/benzoate(TS, op)	-1021.734384	-1021.971234

Method: CAM-B3LYP

	6-311++G(d, p)	6-311++G(2d, 2p)
I/benzoate(GS)	-942.6324256	-942.8562696
I/benzoate(TS, em)	-942.5927958	-942.8169545
I/benzoate(TS, op)	-942.5970337	-942.8214772
II/benzoate(GS)	-1021.206325	-1021.447773
II/benzoate(TS, em)	-1021.168757	-1021.410680
II/benzoate(TS, op)	-1021.169666	-1021.411696

Method: ωB97X-D

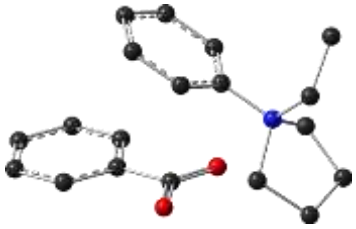
	6-311++G(d, p)	6-311++G(2d, 2p)
I/benzoate(GS)	-942.8504070	-943.0588185
I/benzoate(TS, em)	-942.8030722	-943.0115670
I/benzoate(TS, op)	-942.8061669	-943.0147696
II/benzoate(GS)	-1021.454060	-1021.679174
II/benzoate(TS, em)	-1021.410331	-1021.635296
II/benzoate(TS, op)	-1021.412874	-1021.638004

Method: M06-2X

	6-311++G(d, p)	6-311++G(2d, 2p)
I/benzoate(GS)	-942.7246703	-942.9672164
I/benzoate(TS, em)	-942.6786904	-942.9211982
I/benzoate(TS, op)	-942.6819204	-942.9243765
II/benzoate(GS)	-1021.306772	-1021.569510
II/benzoate(TS, em)	-1021.266133	-1021.528538
II/benzoate(TS, op)	-1021.267936	-1021.530336

Energies, Imaginary Frequencies, and Optimized Geometries

Ground state of an *N*-phenylpyrrolidinium end group model and benzoate, I/benzoate (GS)



electronic energy = -942.599709 Hartree

sum of electronic and zero-point energies = -942.251050

sum of electronic and thermal energies = -942.222310

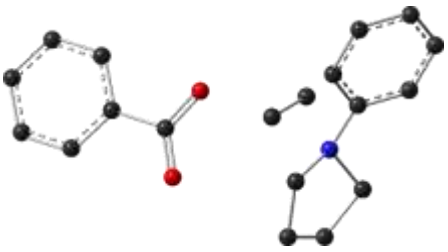
sum of electronic and thermal enthalpies = -942.221236

sum of electronic and thermal free energies = -942.318734

N	2.46258500	-0.20390300	0.07793000
C	2.15048900	-1.21385600	-1.01226300
C	2.79099300	-2.51281900	-0.53546300
C	2.75416200	-2.43213800	1.00754800
C	2.20574600	-1.04031000	1.32952800
H	2.52002700	-0.85200000	-1.96959100
H	1.06121700	-1.31622600	-1.03457600
H	2.21854800	-3.35898300	-0.92038100
H	3.81414500	-2.61932900	-0.90484700
H	3.74628000	-2.58645400	1.43824000
H	2.09110800	-3.18491800	1.43849800
H	2.68377300	-0.55867700	2.18137900
H	1.11905000	-1.05987700	1.45487400
C	1.59908800	1.00495100	0.04594900
C	0.04296200	3.30900700	0.03055200
C	0.86569800	1.33054500	-1.08706200
C	1.56935900	1.82702200	1.16924900
C	0.78828300	2.97667700	1.15883500
C	0.08604900	2.48527900	-1.08792800
H	0.88022900	0.70409400	-1.96868400
H	2.14011200	1.58357000	2.05787200
H	0.76227900	3.60964000	2.03978900
H	-0.49028200	2.73254800	-1.97345000
H	-0.56906800	4.20522200	0.02547100
H	4.51076000	-0.69896300	0.14959000
C	3.92594900	0.21491000	0.04810900
H	4.07927400	0.81237800	0.94733500
C	4.33971900	0.99181200	-1.18671500

H	5.39040200	1.27001100	-1.06541300
H	3.76141000	1.91058700	-1.30659800
H	4.26190500	0.40122900	-2.10238900
C	-1.51611400	-1.34044700	0.17385400
O	-0.98349300	-1.31635700	1.31580900
O	-0.98970100	-1.79824000	-0.87634500
C	-2.91982100	-0.75843200	0.04949600
C	-3.57912700	-0.75182700	-1.18146000
C	-3.56948100	-0.22508800	1.16461400
C	-4.86196300	-0.22252200	-1.29813500
H	-3.07058300	-1.16846100	-2.04424200
C	-4.85225800	0.30557600	1.05364300
H	-3.05369200	-0.23343100	2.11884200
C	-5.50238100	0.30816800	-0.17946100
H	-5.36368700	-0.22459200	-2.26197500
H	-5.34633400	0.71685900	1.92968300
H	-6.50353500	0.72082300	-0.26798900

Transition state of a ring-emitting reaction between an *N*-phenylpyrrolidinium end group model and benzoate, I/benzoate (TS, em)



electronic energy = -942.560211 Hartree

sum of electronic and zero-point energies = -942.214035

sum of electronic and thermal energies = -942.185492

sum of electronic and thermal enthalpies = -942.184418

sum of electronic and thermal free energies = -942.280627

560.39*i* (cm^{-1})

H	5.53026500	-3.41600300	-0.44153100
C	4.88036700	-2.54996500	-0.36663000
C	3.20393200	-0.30609300	-0.17581100
C	3.97286200	-2.25948400	-1.38237500
C	4.94463900	-1.71476400	0.74302300
C	4.11459800	-0.60055600	0.84312600
C	3.14021500	-1.14999400	-1.29144100
H	3.90900100	-2.89914100	-2.25732100
H	5.64719700	-1.92314800	1.54417100
H	4.19261500	0.03350200	1.71761000

H	2.44318600	-0.94674800	-2.09635400
N	2.30316800	0.80206200	-0.07056700
C	2.01006800	1.50557100	-1.35226900
H	1.26518800	0.94349200	-1.91873200
H	2.92675700	1.55088400	-1.94857500
C	1.51811500	2.91052500	-0.96086800
C	1.73272200	3.01562300	0.56171000
H	0.78684600	2.89959500	1.09823800
H	2.16109200	3.97417500	0.86234700
C	2.67583300	1.86600300	0.89142400
H	3.72268200	2.15038700	0.72536300
H	2.57572800	1.50861500	1.91668700
H	2.09661700	3.66720400	-1.49592600
H	0.46839500	3.05395500	-1.22570200
C	0.44804400	0.02490200	0.43780500
H	-0.00049100	0.96902900	0.17871000
H	0.59133100	-0.70062900	-0.34839800
C	0.67338700	-0.37829400	1.86002000
H	0.43414900	0.43199400	2.55236100
H	1.70605700	-0.69917600	2.02219700
H	0.03335200	-1.23047800	2.09295400
H	-4.53603600	1.75915400	-0.50239600
C	-4.81227500	0.72522100	-0.32563100
C	-5.48141400	-1.93643100	0.13531700
C	-3.81021200	-0.19167000	-0.00318000
C	-6.13963200	0.31690800	-0.41778600
C	-6.47689300	-1.01582300	-0.18728100
C	-4.15451500	-1.52521200	0.22636200
H	-6.91199900	1.03809100	-0.66941700
H	-7.51249300	-1.33593500	-0.25869400
H	-3.37237800	-2.23354100	0.47653000
H	-5.73958200	-2.97601700	0.31586900
C	-2.37078900	0.26979000	0.09239400
O	-2.10658800	1.47154700	-0.11762700
O	-1.51265700	-0.63045200	0.39094100

Transition state of a ring-opening reaction between an *N*-phenylpyrrolidinium end group model and benzoate, I/benzoate (TS, op)

electronic energy = -942.564420 Hartree

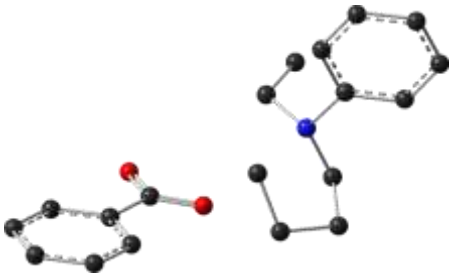
sum of electronic and zero-point energies = -942.217837

sum of electronic and thermal energies = -942.189652

sum of electronic and thermal enthalpies = -942.188578

sum of electronic and thermal free energies = -942.283634

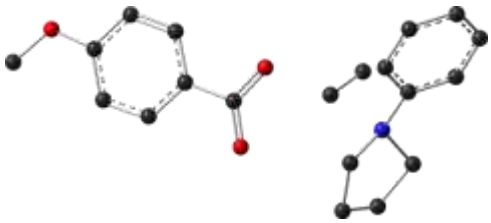
535.73*i* (cm^{-1})



H	4.71363300	3.86122000	-0.45019200
C	4.23513600	2.89110700	-0.36108500
C	3.00107400	0.37652400	-0.13103400
C	4.63947400	1.99266700	0.61847800
C	3.20126500	2.53167600	-1.22259800
C	2.58614900	1.29143800	-1.10648500
C	4.02972000	0.74456500	0.73691800
H	5.43975200	2.25455900	1.30394700
H	2.86165600	3.22218500	-1.98847400
H	1.77148200	1.04547800	-1.77855400
H	4.37449100	0.07672600	1.51539400
N	2.31239800	-0.89452100	-0.04120500
C	2.66651800	-1.75873900	1.10440100
H	3.74227600	-1.78523900	1.29064900
H	2.36243600	-2.77450500	0.84001200
C	1.84634700	-1.28345300	2.29030100
C	0.40172700	-1.17308300	1.79516800
H	-0.20086600	-0.59478900	2.49716400
H	-0.04894600	-2.16701400	1.71251000
C	0.35787900	-0.49109500	0.45188100
H	0.01408900	-0.99949300	-0.43518200
H	0.54073700	0.57045500	0.38683000
H	1.92548600	-1.98207000	3.12808500
H	2.20200600	-0.30883600	2.64074200
C	2.29488600	-1.64415000	-1.32712000
H	1.84228800	-1.00703300	-2.08725300
H	1.61976900	-2.49152700	-1.18361000
C	-2.40934300	-0.41974300	-0.22784800

O	-1.61046800	0.06358900	0.64701600
O	-2.09047000	-1.22599200	-1.12476800
C	-3.84887100	0.04391800	-0.13691500
C	-4.79183000	-0.44097800	-1.04503600
C	-4.25174700	0.95314600	0.84323400
C	-6.11813500	-0.02473500	-0.97572400
H	-4.47076300	-1.14684100	-1.80350300
C	-5.57766000	1.37139600	0.91496000
H	-3.51603500	1.32747000	1.54653100
C	-6.51385700	0.88310500	0.00522500
H	-6.84405800	-0.40819900	-1.68704900
H	-5.88132800	2.07906500	1.68112200
H	-7.54864200	1.20898600	0.06058300
C	3.66605000	-2.12236300	-1.78415700
H	3.56416200	-2.65752700	-2.73302900
H	4.34929900	-1.28258200	-1.94089000
H	4.11909400	-2.80683300	-1.06076400

Transition state of a ring-emitting reaction between an *N*-phenylpyrrolidinium end group model and *p*-methoxybenzoate, I/*p*-methoxybenzoate (TS, em)



electronic energy = -1057.044432 Hartree

sum of electronic and zero-point energies = -1056.668857

sum of electronic and thermal energies = -1056.636828

sum of electronic and thermal enthalpies = -1056.635754

sum of electronic and thermal free energies = -1056.740069

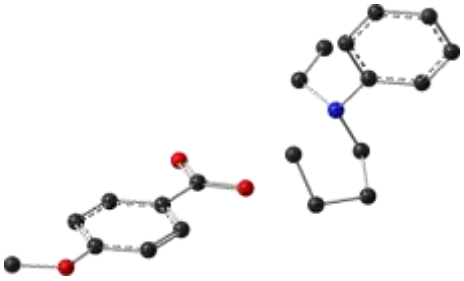
562.20*i* (cm^{-1})

H	6.19463400	-3.55370300	-0.46197600
C	5.57117000	-2.66837900	-0.38783100
C	3.96298800	-0.37484900	-0.19900200
C	4.66470000	-2.35765300	-1.39846400
C	5.66864800	-1.82843100	0.71579600
C	4.87263600	-0.68960000	0.81480700
C	3.86575000	-1.22355500	-1.30846200
H	4.57522100	-3.00064400	-2.26870800
H	6.37088000	-2.05237400	1.51302000
H	4.97585700	-0.05277900	1.68465400

H	3.16898600	-1.00507900	-2.10950200
N	3.09620700	0.76036600	-0.09368700
C	2.81303300	1.46365100	-1.37740300
H	2.05436700	0.91502900	-1.93864700
H	3.72865000	1.48733800	-1.97678100
C	2.35134200	2.87953200	-0.99007100
C	2.60216100	2.99749000	0.52654400
H	1.66396300	2.92330500	1.08347300
H	3.07056200	3.94413300	0.80436100
C	3.51143000	1.82015400	0.85560900
H	4.56509300	2.06913800	0.67689600
H	3.41040200	1.47424100	1.88471000
H	2.92642500	3.62210700	-1.54797900
H	1.29723400	3.03381100	-1.23042300
C	1.22589400	0.05095000	0.43777200
H	0.80628200	1.00978600	0.18438400
H	1.32995800	-0.68061300	-0.34915500
C	1.45304900	-0.36032200	1.85765300
H	1.24363800	0.45592400	2.55270100
H	2.47745200	-0.71084500	2.01059200
H	0.79063900	-1.19372100	2.09586100
H	-3.70530800	1.99669100	-0.37362600
C	-4.01514900	0.97189800	-0.19883800
C	-4.78791800	-1.65429300	0.25148500
C	-3.04242900	0.01776200	0.08659300
C	-5.36633900	0.63696900	-0.26322800
C	-5.75484800	-0.68434800	-0.03659200
C	-3.44995700	-1.30251500	0.31127900
H	-6.09594400	1.40553200	-0.48766900
H	-2.70009300	-2.05331900	0.53503400
H	-5.10868000	-2.67681500	0.42513700
C	-1.58774300	0.41239400	0.14966700
O	-1.27168400	1.60364200	-0.05751800
O	-0.76161500	-0.52758700	0.42023800
O	-7.04292900	-1.12097900	-0.07422900
C	-8.06944500	-0.18165400	-0.35882600
H	-7.93403300	0.26236600	-1.35086000

H	-9.00275400	-0.74353800	-0.33634500
H	-8.10090500	0.60965100	0.39779100

Transition state of a ring-opening reaction between an *N*-phenylpyrrolidinium end group model and *p*-methoxybenzoate, I/*p*-methoxybenzoate (TS, op)



electronic energy = -1057.048630 Hartree

sum of electronic and zero-point energies = -1056.672592

sum of electronic and thermal energies = -1056.640956

sum of electronic and thermal enthalpies = -1056.639882

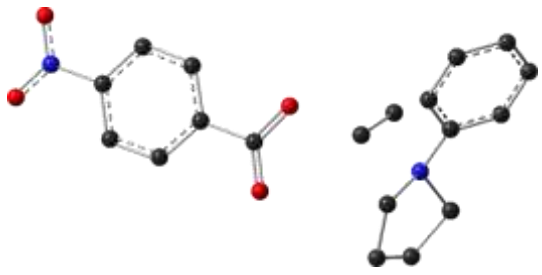
sum of electronic and thermal free energies = -1056.742893

537.88*i* (cm^{-1})

H	5.34417900	3.98672900	-0.48458000
C	4.90039800	3.00048700	-0.39296500
C	3.75661500	0.44426000	-0.15685600
C	5.34604500	2.11424200	0.57977300
C	3.87017700	2.60772200	-1.24421400
C	3.29953500	1.34668400	-1.12499100
C	4.78107800	0.84553400	0.70121000
H	6.14407400	2.40204000	1.25741500
H	3.49866000	3.28799100	-2.00441100
H	2.48660100	1.07432300	-1.78882900
H	5.15671800	0.18814400	1.47423800
N	3.11356700	-0.85045800	-0.06316100
C	3.51505100	-1.70657200	1.07319200
H	4.59377200	-1.69556400	1.24308400
H	3.24318600	-2.73134700	0.80840600
C	2.69586200	-1.26534000	2.27285500
C	1.24188900	-1.20190400	1.79738400
H	0.62956200	-0.64530500	2.50836800
H	0.82330800	-2.21005100	1.71825100
C	1.15768500	-0.51987100	0.45575300
H	0.81720900	-1.03965600	-0.42600300
H	1.29794500	0.54813300	0.39079800
H	2.81042800	-1.96501800	3.10565100
H	3.02287500	-0.28093200	2.62375900
C	3.10437100	-1.59513500	-1.35219800

H	2.61730700	-0.97208900	-2.10262700
H	2.46271600	-2.46697900	-1.20230600
C	-1.62650500	-0.58122200	-0.16515500
O	-0.83027800	-0.03747800	0.67779200
O	-1.28592400	-1.39601100	-1.04829300
C	-3.07866300	-0.18608200	-0.05191200
C	-4.02390000	-0.73810300	-0.91222000
C	-3.51117000	0.73508200	0.90944300
C	-5.37178200	-0.39345200	-0.83063200
H	-3.69523500	-1.45222200	-1.65977400
C	-4.84613200	1.09041000	1.00522100
H	-2.78335000	1.17181700	1.58442200
C	-5.78518600	0.52652000	0.13416900
H	-6.07959600	-0.84337600	-1.51621700
H	-5.18574200	1.80452100	1.74906600
C	4.48502800	-2.02131400	-1.83139500
H	4.38844700	-2.55652100	-2.78078700
H	5.13490200	-1.15670300	-1.99485300
H	4.97342000	-2.69135800	-1.11757100
O	-7.07261600	0.93370700	0.30228700
C	-8.07107100	0.39562700	-0.55238900
H	-9.00909100	0.85480300	-0.24159800
H	-7.87081500	0.64630300	-1.59960800
H	-8.14184700	-0.69166100	-0.44088300

Transition state of a ring-emitting reaction between an *N*-phenylpyrrolidinium end group model and *p*-nitrobenzoate, I/*p*-nitrobenzoate (TS, em)



electronic energy = -1147.012573 Hartree

sum of electronic and zero-point energies = -1146.664227

sum of electronic and thermal energies = -1146.632249

sum of electronic and thermal enthalpies = -1146.631175

sum of electronic and thermal free energies = -1146.737130

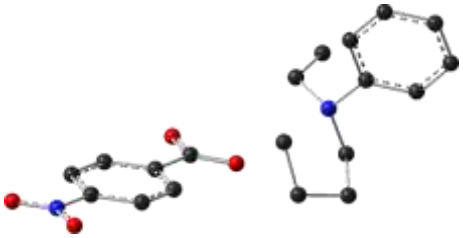
558.03*i* (cm^{-1})

H	6.22361200	-3.76403000	-0.44803500
C	5.65246800	-2.84391000	-0.37620600
C	4.17904400	-0.46064100	-0.19291400

C	4.77569600	-2.47687700	-1.39415200
C	5.78840000	-2.01480300	0.73153600
C	5.05956800	-0.83158400	0.82786500
C	4.04377400	-1.29824000	-1.30704800
H	4.65733500	-3.11025700	-2.26801100
H	6.46893000	-2.28207700	1.53422700
H	5.19236300	-0.20471300	1.70099500
H	3.36919200	-1.03617400	-2.11398400
N	3.37776800	0.72060000	-0.08998100
C	3.13754000	1.44061600	-1.37262100
H	2.34537700	0.94071800	-1.93359900
H	4.05127200	1.40752400	-1.97440900
C	2.76608400	2.88309800	-0.98502500
C	3.00142000	2.97833600	0.53528900
H	2.05338200	2.95187400	1.07983400
H	3.51598000	3.89689100	0.82544300
C	3.84118100	1.75157900	0.86782900
H	4.90884400	1.94358100	0.70163700
H	3.71045500	1.40796100	1.89452400
H	3.39949500	3.58716800	-1.52950800
H	1.72936900	3.11114000	-1.24221900
C	1.45057800	0.09806800	0.43173100
H	1.09715100	1.08471000	0.18503800
H	1.53361200	-0.62540000	-0.36499700
C	1.65230000	-0.33756000	1.84757900
H	1.45285700	0.47305600	2.55176800
H	2.66740300	-0.71173300	2.00571700
H	0.97178800	-1.16169500	2.06715000
H	-3.39310400	2.25164000	-0.35805200
C	-3.74215900	1.23770100	-0.20136100
C	-4.59085100	-1.39158100	0.21010700
C	-2.80838500	0.23598800	0.06813000
C	-5.09644400	0.94224100	-0.26777300
C	-5.49662400	-0.37262000	-0.06004400
C	-3.24077000	-1.07549900	0.27267900
H	-5.83118200	1.70963500	-0.47561300
H	-2.50857000	-1.84622000	0.48177400

H	-4.93996200	-2.40427400	0.36664300
C	-1.33151300	0.58766500	0.13574800
O	-0.99184700	1.76907700	-0.06003800
O	-0.54659200	-0.38454600	0.39660700
N	-6.92233200	-0.69569600	-0.12800000
O	-7.71215800	0.21091200	-0.36568100
O	-7.26333800	-1.85863200	0.05554300

Transition state of a ring-opening reaction between an *N*-phenylpyrrolidinium end group model and *p*-nitrobenzoate, I/*p*-nitrobenzoate (TS, op)



electronic energy = -1147.016851 Hartree

sum of electronic and zero-point energies = -1146.667994

sum of electronic and thermal energies = -1146.636457

sum of electronic and thermal enthalpies = -1146.635383

sum of electronic and thermal free energies = -1146.739085

535.07*i* (cm^{-1})

H	5.50378500	4.01331500	-0.78920400
C	5.08240700	3.02818300	-0.61618600
C	3.99659400	0.47436400	-0.16838100
C	5.51404800	2.25464800	0.45417700
C	4.09534000	2.52382700	-1.45972500
C	3.55328300	1.26423900	-1.23637400
C	4.97791600	0.98792300	0.68060100
H	6.27854100	2.63052000	1.12734300
H	3.73544700	3.11525800	-2.29602600
H	2.77353200	0.90444000	-1.89845200
H	5.34143300	0.42026000	1.52707900
N	3.38447200	-0.82190900	0.03169200
C	3.76106000	-1.54825700	1.26170400
H	4.83236800	-1.49395000	1.46773900
H	3.52104500	-2.60104700	1.09387600
C	2.89129400	-1.00894100	2.38321300
C	1.45051800	-1.03537400	1.86511900
H	0.80528000	-0.42948700	2.50319100
H	1.06112800	-2.05809100	1.87559300
C	1.38303400	-0.49049200	0.46185800

H	1.10125900	-1.10954500	-0.37492500
H	1.51225500	0.56710300	0.29055600
H	2.99566000	-1.61514100	3.28754600
H	3.18176600	0.01520400	2.63955200
C	3.43667400	-1.69088200	-1.17498700
H	2.96309300	-1.15867300	-2.00038300
H	2.80988400	-2.56012300	-0.96004200
C	-1.37022800	-0.73191700	-0.17913700
O	-0.60331300	-0.04137400	0.57312500
O	-1.01812600	-1.66137200	-0.92718200
C	-2.84252600	-0.35726400	-0.12930500
C	-3.75999900	-1.07143700	-0.90152100
C	-3.28700400	0.69115800	0.67829300
C	-5.10955500	-0.74961700	-0.87372400
H	-3.40229300	-1.88310200	-1.52406500
C	-4.63258200	1.02940300	0.71936100
H	-2.56774900	1.23971300	1.27462400
C	-5.52188900	0.29958200	-0.06049700
H	-5.83148500	-1.29588900	-1.46729700
H	-4.99077200	1.84035400	1.34064000
C	4.84244500	-2.12760100	-1.56380500
H	4.79143800	-2.75797700	-2.45664200
H	5.47794800	-1.26714200	-1.79269400
H	5.32051200	-2.70937500	-0.77003500
N	-6.94268100	0.64811100	-0.02434400
O	-7.29441600	1.57740000	0.69343700
O	-7.71809400	-0.00456600	-0.71356800

Ground state of an *N*-phenylpiperidinium end group model and benzoate

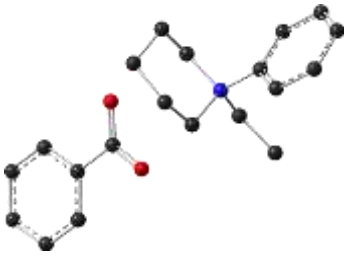
electronic energy = -981.894059 Hartree

sum of electronic and zero-point energies = -981.518720

sum of electronic and thermal energies = -981.488768

sum of electronic and thermal enthalpies = -981.487694

sum of electronic and thermal free energies = -981.586392



H	7.03600700	-0.59523600	-0.48591600
C	5.95962300	-0.49225500	-0.39398500

C	3.19083300	-0.21535800	-0.15452400
C	5.34839400	-0.59180000	0.84950400
C	5.17645200	-0.26624900	-1.52184000
C	3.79757200	-0.13148800	-1.40632500
C	3.96707900	-0.45912600	0.97303000
H	5.94098600	-0.77739900	1.73939800
H	5.63429000	-0.19576900	-2.50311300
H	3.21751000	0.03033500	-2.30613200
H	3.52769000	-0.55530600	1.95580300
N	1.70206600	-0.12757500	-0.07068800
C	1.14626000	1.03270400	-0.89390800
H	1.47632600	0.89202300	-1.92111300
H	0.05650100	0.91539300	-0.86832900
C	1.55742800	2.38596900	-0.34118800
H	1.13939400	3.14523500	-1.01010100
H	2.64725900	2.50319000	-0.37035400
C	1.03469500	2.56711600	1.08200900
H	-0.06119800	2.59596500	1.06454100
H	1.37841500	3.51810000	1.50054400
C	1.50650600	1.40701100	1.95588000
H	1.02023000	1.43562400	2.93675300
H	2.58209900	1.49568000	2.13673600
C	1.16208900	0.05546700	1.34180200
H	0.07992800	-0.06134600	1.22849400
H	1.52441200	-0.77174200	1.94865000
C	1.08847100	-1.40203700	-0.65706800
H	1.34709700	-1.39012400	-1.71711600
H	0.00941600	-1.27102500	-0.54498400
C	1.55217200	-2.69136500	-0.00734400
H	2.63041000	-2.84381800	-0.09500500
H	1.05491500	-3.51364700	-0.53004000
H	1.26699000	-2.75805100	1.04512700
H	-4.43775100	1.46318000	-1.54591800
C	-4.90247000	0.72630800	-0.89961300
C	-6.05969800	-1.17593200	0.76718400
C	-4.08153700	-0.10492100	-0.13476200
C	-6.28868900	0.61138900	-0.83387200

C	-6.87123400	-0.34126100	0.00053700
C	-4.67398700	-1.05613400	0.69843800
H	-6.91580700	1.26501300	-1.43395600
H	-7.95253800	-0.43284100	0.05304200
H	-4.03225300	-1.69964400	1.29064600
H	-6.50775400	-1.92067000	1.41928500
C	-2.56521400	0.02383800	-0.20920200
O	-2.09601300	0.88979500	-0.99391500
O	-1.88467500	-0.74871300	0.52133500

Transition state of a ring-emitting reaction between an *N*-phenylpiperidinium end group model and benzoate

electronic energy = -981.851668 Hartree

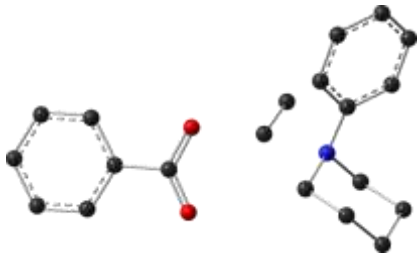
sum of electronic and zero-point energies = -981.478955

sum of electronic and thermal energies = -981.449168

sum of electronic and thermal enthalpies = -981.448094

sum of electronic and thermal free energies = -981.546545

557.48*i* (cm^{-1})



H	5.04418200	-3.82841200	-0.51287800
C	4.43648900	-2.93664300	-0.39743500
C	2.86454000	-0.61564500	-0.10210300
C	4.56159900	-2.13641100	0.73128100
C	3.51606400	-2.57541600	-1.37734900
C	2.73772900	-1.43298400	-1.23346500
C	3.78585200	-0.98901000	0.88168200
H	5.27083800	-2.39643400	1.51117800
H	3.39406900	-3.18755800	-2.26574600
H	2.02765600	-1.19577900	-2.01600100
H	3.92226100	-0.39486600	1.77525100
N	1.98590800	0.51736300	0.06263900
C	1.77672800	1.33036000	-1.16700400
H	1.47669600	0.68018900	-1.98696000
H	0.92718300	1.98876800	-0.96071100
C	3.00048000	2.16670300	-1.52813700
H	2.77722000	2.73487100	-2.43748900
H	3.84340300	1.50520600	-1.76281600
C	3.36713500	3.10505800	-0.37725200

H	2.57506700	3.85641600	-0.25820500
H	4.28996300	3.64886700	-0.60404300
C	3.52168500	2.31759400	0.92529400
H	3.64372100	2.99512500	1.77732700
H	4.42558100	1.70074200	0.87742700
C	2.29678200	1.43924600	1.18327100
H	1.41279400	2.07461000	1.30115600
H	2.39188400	0.86560000	2.10482900
C	0.08534900	-0.20836100	0.43423100
H	0.14854100	-0.76574000	-0.48764400
H	-0.26567100	0.80987400	0.39183600
C	0.28245800	-0.91820600	1.73717700
H	1.29649500	-1.31754100	1.82411900
H	-0.40213100	-1.76594200	1.78879200
H	0.08379900	-0.25989800	2.58555400
H	-4.74240200	2.07225000	-0.12200300
C	-5.09788500	1.04753200	-0.13503900
C	-5.97148200	-1.59443800	-0.16375900
C	-4.17117200	0.01354500	0.01017900
C	-6.45153400	0.76542200	-0.29359300
C	-6.89120600	-0.55726500	-0.30826400
C	-4.61806300	-1.30925200	-0.00545100
H	-7.16453600	1.57721200	-0.40584800
H	-7.94740500	-0.77904200	-0.43192700
H	-3.89514300	-2.10964100	0.10774600
H	-6.30939900	-2.62676000	-0.17458700
C	-2.70170100	0.34010600	0.18041000
O	-2.34504700	1.53563300	0.18251200
O	-1.91809100	-0.66254200	0.31437800

Transition state of a ring-opening reaction between an *N*-phenylpiperidinium end group model and benzoate

electronic energy = -981.849943 Hartree

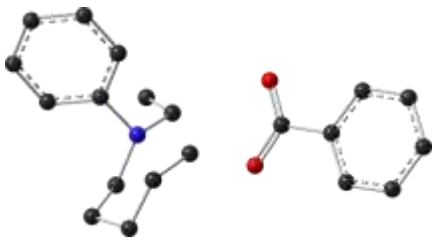
sum of electronic and zero-point energies = -981.477094

sum of electronic and thermal energies = -981.447460

sum of electronic and thermal enthalpies = -981.446386

sum of electronic and thermal free energies = -981.543278

557.01*i* (cm^{-1})



N	-2.15094500	0.55338800	0.73468900
C	-0.19790800	0.73508400	0.01296900
H	-0.01261000	1.39512400	0.84635900
H	-0.05268800	-0.31948200	0.16702500
C	-0.51944400	1.30647900	-1.33614900
H	-1.14094000	0.59537200	-1.89258600
H	0.42205900	1.39302800	-1.88236200
C	-1.20530400	2.67084400	-1.25528400
H	-1.25260400	3.10734300	-2.25847000
H	-0.59163700	3.34846400	-0.64721700
C	-2.61901900	2.58813500	-0.68415900
H	-3.26081900	2.05744200	-1.39403500
H	-3.03848000	3.59524900	-0.58166400
C	-2.68932500	1.93392800	0.69334300
H	-3.71368600	1.96243900	1.07969200
H	-2.07866600	2.51207800	1.39395100
C	2.42269900	-0.31243000	0.08635700
O	1.82982900	0.79344600	-0.17130000
C	3.93455300	-0.28290500	0.01302000
C	4.61692900	0.89261200	-0.30658000
C	4.66272600	-1.44636200	0.26795200
C	6.00754300	0.90506500	-0.37014100
H	4.04704300	1.79381600	-0.50422800
C	6.05300900	-1.43679400	0.20480600
H	4.12455600	-2.35500900	0.51528100
C	6.72849000	-0.26001900	-0.11451600
H	6.52971800	1.82437800	-0.61943800
H	6.61062800	-2.34731800	0.40464800
H	7.81359900	-0.25098100	-0.16406900
O	1.85109400	-1.38072400	0.38201200
C	-2.90048200	-0.44549600	-0.00280400
C	-4.20040800	-0.22456600	-0.46091100
C	-2.30936000	-1.69176100	-0.23881200
C	-4.88509300	-1.22088000	-1.15418100
H	-4.70261800	0.71680800	-0.27879900
C	-2.99791300	-2.68374700	-0.92698000
H	-1.30687700	-1.90464000	0.11541400

C	-4.28967600	-2.45357100	-1.39388000
H	-5.89510700	-1.02439700	-1.50096800
H	-2.51601000	-3.64122900	-1.09933400
H	-4.82502200	-3.22783100	-1.93438000
C	-1.90009600	0.11627200	2.13818400
H	-1.22966800	0.85532600	2.58522500
H	-1.35049900	-0.82602300	2.09357000
C	-3.14619100	-0.04766100	2.99942500
H	-3.83538100	-0.78271200	2.57414700
H	-2.84624200	-0.40152100	3.99044000
H	-3.68319700	0.89542700	3.13331900

Ground state of an *N*-phenylazepanium end group model and benzoate, II/benzoate (GS)

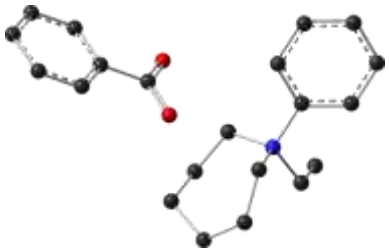
electronic energy = -1021.168069 Hartree

sum of electronic and zero-point energies = -1020.766024

sum of electronic and thermal energies = -1020.734586

sum of electronic and thermal enthalpies = -1020.733512

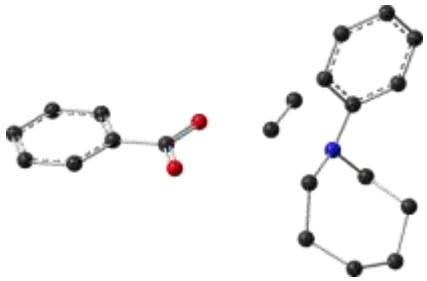
sum of electronic and thermal free energies = -1020.834295



C	-2.48853600	1.04033800	-0.07517500
C	-2.80558800	3.79449000	-0.39137700
C	-1.39137100	1.88623400	0.07710300
C	-3.73434000	1.56420500	-0.41018500
C	-3.88829500	2.94003200	-0.56091500
C	-1.56095300	3.25925100	-0.07786700
H	-0.39698300	1.50759600	0.30102200
H	-4.60197200	0.93730800	-0.55968700
H	-4.86701300	3.33499200	-0.81368700
H	-0.70042800	3.90945900	0.04475700
H	-2.92928600	4.86638000	-0.50901900
H	-3.30541200	-2.26382600	0.08719500
C	-3.57181600	-1.21279800	0.14881100
H	-4.15612200	-0.98747100	-0.74253200
C	-4.35633900	-0.96265100	1.42769600
H	-5.33217600	-1.44413900	1.31818800
H	-4.52663500	0.09611200	1.62938100
H	-3.86839900	-1.40542300	2.29848400

C	2.13773000	0.29654600	-0.08284800
O	1.61299300	-0.16335800	-1.13095400
O	1.50778300	0.73719800	0.91862000
C	3.65895800	0.32137400	-0.01357100
C	4.31030000	0.80776800	1.12177200
C	4.42566400	-0.14211900	-1.08470400
C	5.70107500	0.83088400	1.18773500
H	3.71013300	1.16697700	1.95079200
C	5.81670800	-0.12082500	-1.02398600
H	3.91523700	-0.51849600	-1.96481800
C	6.45836800	0.36619500	0.11368500
H	6.19534200	1.21176300	2.07724300
H	6.40158000	-0.48403100	-1.86457900
H	7.54355200	0.38363000	0.16294800
C	-1.38331700	-0.73238700	1.23725100
C	-1.54481700	-0.84522700	-1.26746100
C	-1.06990400	-2.19325500	1.52409200
H	-0.44290400	-0.20894000	1.06531000
H	-1.88476400	-0.26952400	2.08807300
C	-1.58916800	-2.30750900	-1.70500600
H	-0.51346600	-0.50322900	-1.13806500
H	-2.00861000	-0.24383900	-2.05084300
C	-0.26813000	-2.93937300	0.45202800
H	-1.96845500	-2.76393100	1.78630300
H	-0.47201500	-2.14907200	2.44193300
C	-1.11304100	-3.40696900	-0.73331600
H	-0.93617300	-2.30402700	-2.58548700
H	-2.58433400	-2.55633700	-2.08724400
H	0.56600000	-2.31586700	0.10901800
H	0.17401600	-3.82466600	0.92240700
H	-0.54208700	-4.14252500	-1.30951100
H	-1.97913500	-3.95530400	-0.34076100
N	-2.27354600	-0.44707300	0.02846900

Transition state of a ring-emitting reaction between an *N*-phenylazepanium end group model and benzoate, II/benzoate (TS, em)



electronic energy = -1021.130891 Hartree

sum of electronic and zero-point energies = -1020.731960

sum of electronic and thermal energies = -1020.700527

sum of electronic and thermal enthalpies = -1020.699453

sum of electronic and thermal free energies = -1020.801669

566.70*i* (cm^{-1})

H	4.31460600	-4.39210900	-1.08523000
C	3.85031800	-3.44296400	-0.83722300
C	2.64867000	-0.97866400	-0.19284900
C	4.27286600	-2.71782000	0.27012300
C	2.82472600	-2.92945100	-1.62627000
C	2.23054400	-1.71326300	-1.31124400
C	3.68211800	-1.49786400	0.59312900
H	5.07664000	-3.09352700	0.89595900
H	2.47747100	-3.47688300	-2.49717500
H	1.43556600	-1.34435600	-1.94803200
H	4.05728100	-0.96208900	1.45479600
N	1.96489400	0.24997200	0.13128100
C	0.05881000	-0.27197300	0.72463700
H	-0.03895700	-0.82351300	-0.19532000
H	-0.18093800	0.77681300	0.70222200
C	0.31584100	-0.99931500	2.00530700
H	1.21676300	-1.61471700	1.93326400
H	-0.52176300	-1.67057600	2.20028800
H	0.41250400	-0.31635700	2.85152700
C	2.52457300	1.01159100	1.26816400
H	2.66839400	0.30712200	2.08515500
H	1.74278300	1.69564400	1.60741200
C	3.80848100	1.80449100	0.98736600
H	4.41400700	1.29205600	0.23027000
H	4.40813000	1.81306300	1.90461000
C	3.53182200	3.24762600	0.56400300
H	4.47894900	3.79692100	0.50922400
H	2.93901600	3.73309000	1.35141200

C	2.80296000	3.38116100	-0.77212900
H	2.57698200	4.44006200	-0.94332600
H	3.47491400	3.07569600	-1.58597900
C	1.50176200	2.57921900	-0.89774500
H	0.98179900	2.91889600	-1.80036000
H	0.81897800	2.80133300	-0.06967000
C	1.68020500	1.07335400	-1.09299500
H	0.76530100	0.67703100	-1.53782600
H	2.49071000	0.90975000	-1.81056000
H	-4.17812800	-1.14171800	1.77829300
C	-4.78074800	-0.70060200	0.99193000
C	-6.30191800	0.44156300	-1.04017800
C	-4.14209300	-0.03959500	-0.05918000
C	-6.16956200	-0.79078300	1.02851100
C	-6.93324100	-0.21964900	0.01209900
C	-4.91329100	0.53026300	-1.07385800
H	-6.65693900	-1.30705600	1.85068700
H	-8.01693300	-0.28955300	0.03991800
H	-4.40954600	1.04229500	-1.88674800
H	-6.89276100	0.88836100	-1.83472800
C	-2.63121700	0.06826600	-0.11207200
O	-2.10061100	0.67271300	-1.06439900
O	-1.99674500	-0.48509000	0.85237400

Transition state of a ring-opening reaction between an *N*-phenylazepanium end group model and benzoate, II/benzoate (TS, op)

electronic energy = -1021.131657 Hartree

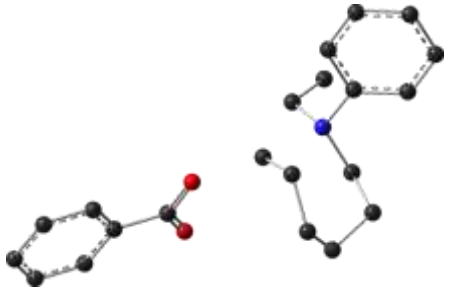
sum of electronic and zero-point energies = -1020.732628

sum of electronic and thermal energies = -1020.701346

sum of electronic and thermal enthalpies = -1020.700272

sum of electronic and thermal free energies = -1020.800910

546.57*i* (cm^{-1})



H	-5.88971600	2.91168600	-0.90305100
C	-5.11932500	2.21653300	-0.58469000
C	-3.12259300	0.41475200	0.23663200
C	-3.93772700	2.68507000	-0.01413500

C	-5.29649000	0.84777300	-0.74051600
C	-4.30962400	-0.04898800	-0.33273200
C	-2.95047000	1.79596300	0.39014100
H	-3.77723000	3.75100700	0.11514600
H	-6.21128400	0.46091700	-1.17914100
H	-4.49222900	-1.10741500	-0.46220000
H	-2.03969300	2.19255100	0.82400300
N	-2.06376000	-0.47124200	0.67830200
C	-1.81854000	-0.33999300	2.14656400
H	-1.59440600	0.70822400	2.35016500
H	-0.90994800	-0.90774900	2.36438500
C	-2.23710700	-1.90360200	0.32058900
H	-3.20580000	-2.24920200	0.69440400
H	-1.47999200	-2.44671700	0.89340400
C	-2.09274300	-2.29625300	-1.15534600
H	-2.72387400	-1.67306800	-1.79738500
H	-2.51576200	-3.30556700	-1.21437400
C	-0.65758300	-2.33953900	-1.70449500
H	-0.59823200	-3.12270000	-2.46848900
H	0.02336500	-2.65598500	-0.90517900
C	-0.15706600	-1.03143000	-2.32884400
H	0.92839800	-1.09461400	-2.46178800
H	-0.58970000	-0.91661500	-3.32999800
C	-0.49894200	0.22216000	-1.52405100
H	-1.55437200	0.47809200	-1.65538000
H	0.05742900	1.08129200	-1.90780000
C	-0.20937500	0.10739600	-0.05911200
H	-0.24989000	0.98604600	0.56356000
H	0.19327500	-0.79084400	0.37987900
C	2.61066300	-0.21419100	0.21895400
O	1.77605500	0.62365200	-0.26834100
C	4.06884800	0.19235300	0.15761100
C	4.45233200	1.41669700	-0.39334500
C	5.04892700	-0.66620000	0.65891800
C	5.79602300	1.77757600	-0.44267400
H	3.68750600	2.08044800	-0.78144700
C	6.39302900	-0.30815900	0.61075400

H	4.74196500	-1.61494600	1.08575100
C	6.76938600	0.91550900	0.05930800
H	6.08458800	2.73223500	-0.87322200
H	7.14793400	-0.98340900	1.00337700
H	7.81801100	1.19649300	0.02094300
O	2.31172800	-1.31448800	0.72582600
C	-2.96060600	-0.80158300	3.04301400
H	-2.69414500	-0.59701000	4.08433300
H	-3.88745600	-0.26443200	2.82131900
H	-3.15079700	-1.87439200	2.95551000

Transition state of a ring-emitting reaction between an *N*-phenylazepanium end group model and *p*-methoxybenzoate, II/*p*-methoxybenzoate (TS, em)

electronic energy = -1135.615138 Hartree

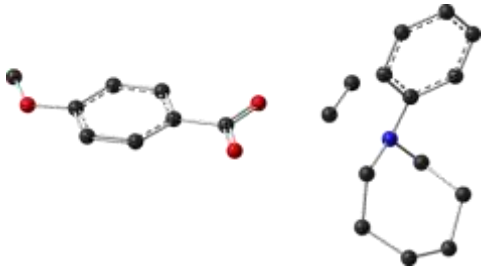
sum of electronic and zero-point energies = -1135.186689

sum of electronic and thermal energies = -1135.151849

sum of electronic and thermal enthalpies = -1135.1507775

sum of electronic and thermal free energies = -1135.260169

568.59*i* (cm^{-1})

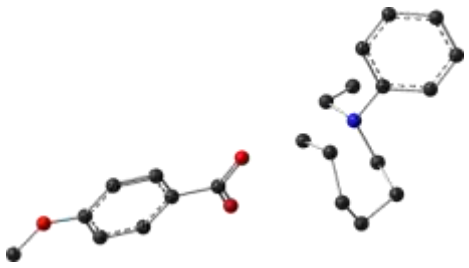


H	4.91198900	-4.47960100	-1.07262700
C	4.47549800	-3.51801800	-0.82205400
C	3.34569200	-1.02183100	-0.17094200
C	4.90439500	-2.81803600	0.29895600
C	3.47983700	-2.96321100	-1.62142300
C	2.92119200	-1.73116500	-1.30310400
C	4.34909500	-1.58242100	0.62537200
H	5.68547400	-3.22619600	0.93315300
H	3.12831400	-3.49034300	-2.50306600
H	2.14877300	-1.32999600	-1.94808900
H	4.72801400	-1.06771700	1.49816500
N	2.69742100	0.22563500	0.15527600
C	0.76870800	-0.23754400	0.70710500
H	0.66813400	-0.77723900	-0.21930000
H	0.56124600	0.81824400	0.69065200
C	0.97651600	-0.98317500	1.98632700
H	1.85538700	-1.63084000	1.92507300

H	0.11127000	-1.62414100	2.16142500
H	1.08356800	-0.31051300	2.83956100
C	3.26337200	0.95650200	1.30918200
H	3.37114300	0.23900400	2.12034700
H	2.49874000	1.66185400	1.64394200
C	4.57665000	1.71003900	1.05703800
H	5.17701200	1.18619900	0.30363000
H	5.16170100	1.68906300	1.98344100
C	4.35408700	3.16603400	0.64570600
H	5.31942200	3.68448000	0.61219400
H	3.76477100	3.66219900	1.42906200
C	3.65169800	3.33782800	-0.70020400
H	3.46252500	4.40528000	-0.86270300
H	4.32662200	3.01981600	-1.50673000
C	2.32794400	2.57935100	-0.85550500
H	1.83358700	2.94531800	-1.76222600
H	1.63952500	2.81422500	-0.03565600
C	2.46177400	1.07074700	-1.06488500
H	1.54284000	0.70871300	-1.53006600
H	3.27985700	0.88890900	-1.76933200
H	-3.53618700	-0.92999800	1.67424300
C	-4.09450600	-0.49332200	0.85331300
C	-5.51457500	0.62791300	-1.25060200
C	-3.39781000	0.10609900	-0.19266000
C	-5.48766400	-0.54204200	0.86569500
C	-6.20166900	0.02174800	-0.19255300
C	-4.13065000	0.66656200	-1.24524000
H	-5.99666500	-1.01645900	1.69589800
H	-3.59449100	1.13555300	-2.06330400
H	-6.08640500	1.06143700	-2.06527600
C	-1.88916700	0.16001000	-0.20643200
O	-1.30995500	0.71397900	-1.16295600
O	-1.29735200	-0.38259900	0.79239300
O	-7.55948000	0.03036400	-0.28210600
C	-8.31181900	-0.57083400	0.76156000
H	-9.35829200	-0.45020500	0.48286500
H	-8.07846400	-1.63710000	0.85255500

H	-8.12865700	-0.07076400	1.71867400

Transition state of a ring-opening reaction between an *N*-phenylazepanium end group model and *p*-methoxybenzoate, II/*p*-methoxybenzoate (TS, op)



electronic energy = -1135.615940 Hartree

sum of electronic and zero-point energies = -1135.187468

sum of electronic and thermal energies = -1135.152727

sum of electronic and thermal enthalpies = -1135.151653

sum of electronic and thermal free energies = -1135.260656

548.23*i* (cm^{-1})

H	-6.51087800	3.07396400	-0.86708200
C	-5.76305400	2.35279300	-0.55281100
C	-3.82494200	0.48348000	0.25784300
C	-4.55482400	2.78101300	-0.00686300
C	-5.99615200	0.99037100	-0.68919000
C	-5.03844700	0.06024100	-0.28660400
C	-3.59653700	1.85848900	0.39217900
H	-4.35071900	3.84121500	0.10725000
H	-6.93252500	0.63477200	-1.10830500
H	-5.26432600	-0.99161000	-0.40033200
H	-2.66430300	2.22396200	0.80735600
N	-2.79394400	-0.43835100	0.69255000
C	-2.51623100	-0.29702900	2.15425000
H	-2.24712500	0.74405900	2.33878200
H	-1.62675700	-0.89726500	2.36343000
C	-3.03182900	-1.86766600	0.35978800
H	-4.00707600	-2.16727600	0.75542200
H	-2.28761200	-2.43287800	0.92808900
C	-2.92976200	-2.28838900	-1.11185000
H	-3.54652100	-1.65019900	-1.75309300
H	-3.39400600	-3.28055500	-1.14719800
C	-1.50734900	-2.39800200	-1.68417300
H	-1.49239900	-3.19457400	-2.43637800
H	-0.82615600	-2.72928700	-0.89107300
C	-0.96617600	-1.12040700	-2.33718000
H	0.11390500	-1.22757400	-2.48464300

H	-1.40923500	-1.00487300	-3.33370200
C	-1.24733800	0.15804000	-1.54821500
H	-2.29447000	0.45144900	-1.66725800
H	-0.66529700	0.98885900	-1.95538100
C	-0.93739900	0.05646000	-0.08631600
H	-0.93228500	0.94695200	0.52055500
H	-0.55651700	-0.84743000	0.36072100
C	1.87647400	-0.35268800	0.16760800
O	1.06431400	0.49743300	-0.33917100
C	3.34087000	0.00344200	0.08820800
C	3.77140600	1.19393700	-0.50940600
C	4.29964400	-0.85691900	0.61614800
C	5.11787600	1.51062400	-0.57569100
H	3.03312300	1.87159500	-0.92392400
C	5.65897100	-0.55520100	0.55947800
H	3.97161900	-1.78061200	1.08081100
C	6.07036200	0.63591000	-0.04064200
H	5.45637900	2.43245100	-1.03856400
H	6.37698100	-1.24806200	0.98117300
O	1.54182800	-1.42843300	0.70734800
C	-3.65883600	-0.70071400	3.07751100
H	-3.36534000	-0.49240600	4.11078800
H	-4.56778600	-0.13042100	2.86465300
H	-3.89258000	-1.76627500	3.00906100
O	7.36822400	1.02919200	-0.15138300
C	8.38055200	0.18177000	0.37220100
H	9.32511900	0.68769200	0.17438800
H	8.25941100	0.04293500	1.45184700
H	8.37638600	-0.79300400	-0.12723700

Transition state of a ring-emitting reaction between an *N*-phenylazepanium end group model and *p*-nitrobenzoate, II/*p*-nitrobenzoate (TS, em)

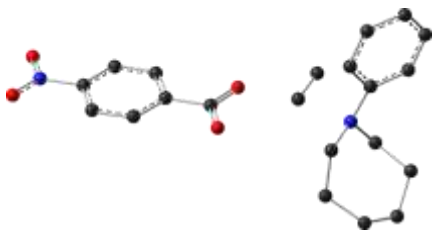
electronic energy = -1225.583433 Hartree

sum of electronic and zero-point energies = -1225.182291

sum of electronic and thermal energies = -1225.147491

sum of electronic and thermal enthalpies = -1225.146417

sum of electronic and thermal free energies = -1225.257151



563.99*i* (cm^{-1})

H	5.16578300	-4.44685300	-1.17415100
C	4.72924200	-3.48980300	-0.90691900
C	3.59911200	-1.00466000	-0.21256800
C	5.16700000	-2.80307600	0.21886200
C	3.72466200	-2.92717500	-1.68946700
C	3.16594700	-1.70083300	-1.34992700
C	4.61183500	-1.57323800	0.56658100
H	5.95534100	-3.21715900	0.84010900
H	3.36618300	-3.44364200	-2.57463000
H	2.38665800	-1.29353400	-1.98270300
H	4.99852400	-1.06855000	1.44181900
N	2.95077800	0.23485600	0.13696600
C	1.01412800	-0.25686400	0.72142400
H	0.91711800	-0.78639300	-0.21160100
H	0.81120900	0.80006700	0.71811500
C	1.25653700	-1.01386500	1.98698200
H	2.14889900	-1.64007000	1.90311600
H	0.41032500	-1.67887600	2.16628300
H	1.36087200	-0.34995700	2.84720400
C	3.52638800	0.95512500	1.29204600
H	3.64916100	0.22897300	2.09340100
H	2.76234700	1.65203200	1.64550800
C	4.83192400	1.71956200	1.03222700
H	5.42590800	1.20706300	0.26603400
H	5.42852000	1.69291000	1.95109100
C	4.59503800	3.17815700	0.63867100
H	5.55672600	3.70266700	0.59640000
H	4.01429100	3.66305300	1.43538500
C	3.87226200	3.35956900	-0.69516800
H	3.67642100	4.42771100	-0.84460900
H	4.53653800	3.05213800	-1.51451300
C	2.54920500	2.59736800	-0.83862400
H	2.03953500	2.97152500	-1.73347000
H	1.87276400	2.82033400	-0.00547300
C	2.68593200	1.09179300	-1.06742200

H	1.76001300	0.73064900	-1.51987500
H	3.49003500	0.92290700	-1.79108800
H	-3.21779100	-1.04373800	1.75917600
C	-3.81178900	-0.59175400	0.97385200
C	-5.30706100	0.58682300	-1.07097700
C	-3.16582600	0.06086600	-0.07767600
C	-5.19738700	-0.66258600	1.01646500
C	-5.92164800	-0.06944400	-0.01084200
C	-3.92089100	0.64672200	-1.09494800
H	-5.71095600	-1.16523600	1.82611500
H	-3.40707100	1.15031300	-1.90545200
H	-5.90436300	1.03724700	-1.85346900
C	-1.64849500	0.14404500	-0.12952000
O	-1.11670100	0.73957500	-1.08251000
O	-1.03376200	-0.42099400	0.83742000
N	-7.38288300	-0.13766500	0.02509000
O	-7.91417300	-0.71643500	0.96598000
O	-8.01098100	0.38706500	-0.88731800

Transition state of a ring-opening reaction between an *N*-phenylazepanium end group model and *p*-nitrobenzoate, II/*p*-nitrobenzoate (TS, op)

electronic energy = -1225.584132 Hartree

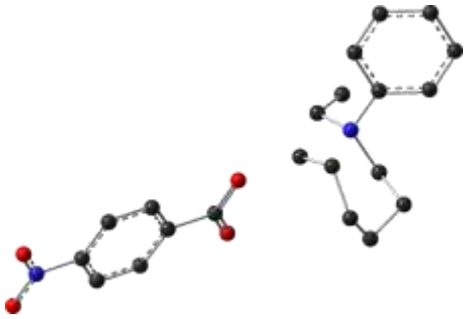
sum of electronic and zero-point energies = -1225.182815

sum of electronic and thermal energies = -1225.148178

sum of electronic and thermal enthalpies = -1225.147104

sum of electronic and thermal free energies = -1225.256564

544.24*i* (cm^{-1})



H	-6.60238500	3.30427800	-0.67094300
C	-5.89101300	2.52809900	-0.40718300
C	-4.04669600	0.51642700	0.27291700
C	-4.68769700	2.85497400	0.21447300
C	-6.16633800	1.19524800	-0.68429200
C	-5.25542100	0.19485100	-0.34689300
C	-3.77576200	1.86249700	0.54897800
H	-4.45102800	3.89053700	0.43878300
H	-7.09983400	0.91773000	-1.16435500

H	-5.51360200	-0.83159500	-0.57052500
H	-2.84599600	2.15083300	1.02601300
N	-3.06346700	-0.48111600	0.64266700
C	-2.81943500	-0.49167000	2.11636000
H	-2.51664300	0.51516600	2.40808200
H	-1.95894100	-1.14412600	2.28742800
C	-3.33950200	-1.86102200	0.16524300
H	-4.33629000	-2.16255100	0.50224000
H	-2.63269000	-2.50607800	0.69504200
C	-3.20622800	-2.14122300	-1.33735000
H	-3.78144800	-1.42249800	-1.93016400
H	-3.70181600	-3.10792900	-1.48204500
C	-1.77171600	-2.24642100	-1.88004000
H	-1.76026000	-2.96974400	-2.70288200
H	-1.12433800	-2.67381100	-1.10468500
C	-1.17140800	-0.93382100	-2.39786700
H	-0.09270000	-1.06645100	-2.53558500
H	-1.58781700	-0.70835000	-3.38689700
C	-1.42562700	0.27415100	-1.49679300
H	-2.46017400	0.61329200	-1.60285200
H	-0.81044500	1.12014800	-1.81444600
C	-1.14922700	0.02611900	-0.04657300
H	-1.14390300	0.85157700	0.64614900
H	-0.82701800	-0.93300200	0.32437200
C	1.62936100	-0.50599300	0.21434400
O	0.85600200	0.41685000	-0.20981300
C	3.11495400	-0.18840300	0.16289400
C	3.56697300	1.04659200	-0.30538300
C	4.03708300	-1.14513700	0.59008400
C	4.92484100	1.33098100	-0.34942800
H	2.84400000	1.78300600	-0.63522400
C	5.39881700	-0.88043400	0.55372800
H	3.67257300	-2.09961600	0.95139300
C	5.81849900	0.35819700	0.08267700
H	5.28911700	2.28449000	-0.71007300
H	6.12452000	-1.61359500	0.88204300
O	1.27378600	-1.61494500	0.65264200

C	-4.00027900	-0.93727500	2.96992200
H	-3.72753000	-0.84117900	4.02518000
H	-4.88166000	-0.31407600	2.79224700
H	-4.27102800	-1.98135600	2.79257500
N	7.25219600	0.64845200	0.04031100
O	7.61049900	1.74430400	-0.37583600
O	8.03110800	-0.21706700	0.42292700

Ground state of a thiolanium end group model and benzoate

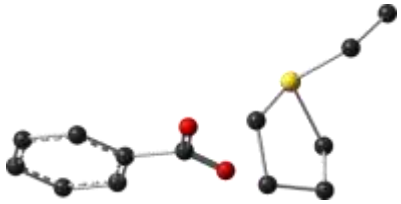
electronic energy = -1054.529154 Hartree

sum of electronic and zero-point energies = -1054.270295

sum of electronic and thermal energies = -1054.247201

sum of electronic and thermal enthalpies = -1054.246127

sum of electronic and thermal free energies = -1054.330201



C	2.23285500	1.33136100	-1.09431700
H	1.40869300	1.36073900	-1.80401900
H	3.17227100	1.56931200	-1.59746600
C	1.98358400	2.19209600	0.14911200
H	2.37062600	3.20133000	-0.01672200
H	0.90710400	2.25410000	0.31897500
C	2.65757400	1.51136300	1.34136400
H	2.30887800	1.92672400	2.29131400
H	3.74418700	1.64538500	1.30481600
C	2.28676100	0.03253600	1.26479500
H	1.24390400	-0.15415200	1.54417900
H	2.95334700	-0.63555700	1.81327000
C	4.15386600	-0.72220900	-0.74433900
H	4.32212000	-0.60082400	-1.81759100
H	4.72226200	0.04703800	-0.21685700
S	2.36705100	-0.40504700	-0.51017700
C	4.52836300	-2.12623300	-0.29167400
H	5.58878000	-2.29319100	-0.50051200
H	4.37592800	-2.26772800	0.78165800
H	3.95306700	-2.88598700	-0.82782000
C	-1.19559200	-0.15594600	0.43224300
O	-0.40317700	0.16636500	-0.49613700

O	-0.85940600	-0.47401000	1.60352000
C	-2.68382600	-0.15773300	0.10701700
C	-3.62128200	-0.49282100	1.08613100
C	-3.13412000	0.17368000	-1.17254600
C	-4.98289100	-0.49599200	0.79450400
H	-3.26632800	-0.74982400	2.07839300
C	-4.49462900	0.17135700	-1.46962200
H	-2.40284900	0.43261000	-1.93070700
C	-5.42328000	-0.16388000	-0.48567800
H	-5.70176600	-0.75817100	1.56588600
H	-4.83153600	0.43087200	-2.46950900
H	-6.48513800	-0.16623100	-0.71545600

Transition state of a ring-opening reaction between a thiolanium end group model and benzoate

electronic energy = -1054.497144 Hartree

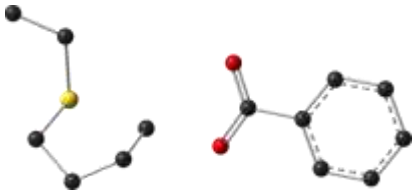
sum of electronic and zero-point energies = -1054.239581

sum of electronic and thermal energies = -1054.216840

sum of electronic and thermal enthalpies = -1054.215766

sum of electronic and thermal free energies = -1054.298849

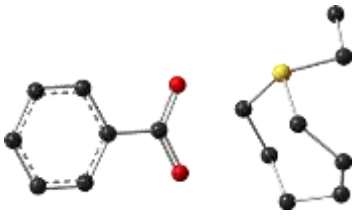
490.75*i* (cm^{-1})



C	-3.98473000	-1.21909100	0.40506300
H	-4.92088900	-1.67948200	0.08526200
H	-4.15209600	-0.71071200	1.35824000
C	-2.84254800	-2.22415900	0.50733100
C	-1.51553200	-1.48645600	0.69779400
H	-0.69811800	-2.21011200	0.71675200
H	-1.50793300	-0.95912000	1.65735600
C	-1.22328400	-0.51299500	-0.41592600
H	-0.97739100	0.52171400	-0.23143700
H	-1.09609900	-0.88040400	-1.42376400
H	-3.02175100	-2.90766400	1.34343900
H	-2.80019800	-2.83363000	-0.40295700
C	-3.63523900	1.59956600	0.08510900
H	-3.09403900	2.32979900	-0.52226400
H	-3.10871800	1.50403900	1.03867300
C	1.50067700	0.32770000	-0.05737900

O	0.85760400	-0.75180000	-0.29226800
O	0.98113700	1.44564800	0.14033100
C	3.01089100	0.20749000	-0.02062900
C	3.78982100	1.33358200	0.25166600
C	3.64101300	-1.01590600	-0.25684000
C	5.17800000	1.23978600	0.28883200
H	3.29251700	2.28033300	0.43309400
C	5.02938900	-1.11266100	-0.22107400
H	3.03192300	-1.88782200	-0.46862400
C	5.80093400	0.01544600	0.05218200
H	5.77498800	2.12189400	0.50212400
H	5.51037100	-2.06882700	-0.40662100
H	6.88429000	-0.05923600	0.08051000
C	-5.08376500	2.02330000	0.28286300
H	-5.11246900	2.98327100	0.80819500
H	-5.59583800	2.14182300	-0.67606600
H	-5.63944600	1.29688700	0.88329500
S	-3.46704900	0.02580300	-0.82210400

Ground state of a thiepanium end group model and benzoate



electronic energy = -1133.098726 Hartree

sum of electronic and zero-point energies = -1132.787668

sum of electronic and thermal energies = -1132.761152

sum of electronic and thermal enthalpies = -1132.760078

sum of electronic and thermal free energies = -1132.852397

C	-1.62859600	-0.00000700	0.00025300
O	-1.09225500	-1.13483900	-0.13029000
O	-1.00119200	1.08564600	0.13303500
C	-3.14946100	0.06245500	-0.00426800
C	-3.81033200	1.28295700	0.14836100
C	-3.90645300	-1.10024900	-0.16156400
C	-5.20157500	1.34227800	0.14472200
H	-3.21742800	2.18309900	0.27020300
C	-5.29790100	-1.04626500	-0.16674600
H	-3.38780900	-2.04565300	-0.27933000
C	-5.94934900	0.17651200	-0.01331800
H	-5.70374700	2.29827900	0.26498200

H	-5.87537700	-1.95828600	-0.29046100
H	-7.03487800	0.22074100	-0.01686800
C	1.75853800	0.31237000	-1.35796900
C	1.61724000	-0.28426600	1.42616700
C	2.56781200	-0.92579200	-1.71958800
H	0.68727800	0.09915300	-1.32433100
H	1.92360000	1.12245000	-2.07295100
C	2.65567300	-1.37431400	1.67238700
H	0.68351000	-0.67307300	1.00456100
H	1.37264200	0.22323600	2.36258500
C	2.37725200	-2.16076000	-0.82753300
H	3.63497000	-0.68524600	-1.80123700
H	2.24350300	-1.17363300	-2.73751800
C	3.20813300	-2.15937500	0.46329800
H	2.13858500	-2.07039100	2.34343300
H	3.48861800	-0.97145300	2.25810100
H	1.31185200	-2.30135000	-0.61129600
H	2.69034200	-3.03035300	-1.41553100
H	3.34531000	-3.19627300	0.78735300
H	4.21642200	-1.80311200	0.21824500
S	2.02254700	1.07130600	0.27585300
C	3.82310200	1.30151600	0.42145700
H	4.33434600	0.35887600	0.22906700
H	3.98064100	1.57223300	1.46871500
C	4.30589100	2.40892900	-0.50660100
H	5.37088500	2.57798600	-0.32570800
H	4.18690000	2.14167800	-1.55992200
H	3.77681400	3.34779200	-0.32205500

Transition state of a ring-opening reaction between a thiepanium end group model and benzoate

electronic energy = -1133.067886 Hartree

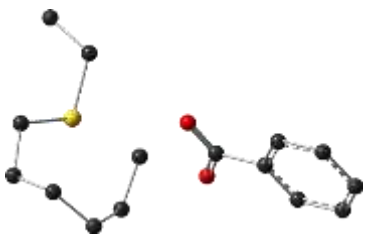
sum of electronic and zero-point energies = -1132.758210

sum of electronic and thermal energies = -1132.732161

sum of electronic and thermal enthalpies = -1132.731087

sum of electronic and thermal free energies = -1132.821319

508.96*i* (cm^{-1})



C	3.14863600	-2.19380500	-0.16646300
H	2.61377200	-2.71627700	-0.96423600
H	2.52171900	-2.22323900	0.72956400
C	3.88146800	0.37811500	0.76734600
H	4.96845100	0.27179700	0.75079200
H	3.49855100	-0.16169800	1.63878200
C	3.49495500	1.85625500	0.85525500
H	3.79317400	2.38462200	-0.05880400
H	4.11992100	2.27188100	1.65316700
C	2.01412000	2.11924500	1.18661000
H	1.95622200	2.93984100	1.90990500
H	1.60344900	1.24549300	1.70751600
C	1.10541100	2.49225100	0.00814200
H	0.07547600	2.54781500	0.37813400
H	1.36477000	3.49922500	-0.34080800
C	1.14309100	1.55732500	-1.20216400
H	2.06213900	1.70863700	-1.77732000
H	0.32846300	1.81601500	-1.88380800
C	0.99182700	0.09570100	-0.87257200
H	0.88170200	-0.61683100	-1.67774200
H	0.80500100	-0.25962000	0.12942200
C	-1.68431800	-0.25903200	0.11473600
O	-1.10534300	0.16214000	-0.94346000
C	-3.19954200	-0.26930500	0.08337000
C	-3.89790200	0.16723400	-1.04417600
C	-3.91401900	-0.71978900	1.19490500
C	-5.28991900	0.15447900	-1.06043700
H	-3.33864400	0.51626300	-1.90527200
C	-5.30575100	-0.73406400	1.18147400
H	-3.36412900	-1.05721500	2.06686400
C	-5.99691400	-0.29651100	0.05282700
H	-5.82414000	0.49661300	-1.94224100
H	-5.85224700	-1.08656200	2.05159000
H	-7.08309800	-0.30682700	0.04097000
O	-1.10084500	-0.65031700	1.14716400
C	4.50793400	-2.83448200	0.08051800
H	4.36736300	-3.88121900	0.36825300

H	5.12797600	-2.80776800	-0.82000300
H	5.05064800	-2.33728500	0.88937600
S	3.24865600	-0.46374600	-0.72812300

cyclohexane

electronic energy = -235.735450 Hartree

sum of electronic and zero-point energies = -235.581775

sum of electronic and thermal energies = -235.573658

sum of electronic and thermal enthalpies = -235.572584

sum of electronic and thermal free energies = -235.614811

C	-1.26522400	0.73047800	0.22964300
C	0.00000000	1.46095500	-0.22964300
C	1.26522400	0.73047800	0.22964300
C	1.26522400	-0.73047800	-0.22964300
C	0.00000000	-1.46095500	0.22964300
C	-1.26522400	-0.73047800	-0.22964300
H	2.15806100	1.24595700	-0.14464700
H	0.00000000	1.52517300	-1.32734600
H	0.00000000	2.49191400	0.14464700
H	-1.32083800	0.76258600	1.32734600
H	-2.15806100	1.24595700	-0.14464700
H	1.32083800	-0.76258600	-1.32734600
H	2.15806100	-1.24595700	0.14464700
H	0.00000000	-2.49191400	-0.14464700
H	0.00000000	-1.52517300	1.32734600
H	-1.32083800	-0.76258600	-1.32734600
H	-2.15806100	-1.24595700	0.14464700
H	1.32083800	0.76258600	1.32734600

cycloheptane

electronic energy = -275.013042 Hartree

sum of electronic and zero-point energies = -274.833499

sum of electronic and thermal energies = -274.824475

sum of electronic and thermal enthalpies = -274.823401

sum of electronic and thermal free energies = -274.869100

C	1.00735400	1.29465300	-0.26772900
C	-1.53023200	0.77584200	-0.21132400

C	1.73713700	0.00000000	0.09283300
H	0.85661200	1.34318600	-1.35618700
H	1.66618000	2.13508200	-0.01443800
C	-1.53023100	-0.77584300	-0.21132500
H	-1.60888600	1.13504800	-1.24547500
H	-2.44113600	1.12597900	0.28904900
C	1.00735400	-1.29465300	-0.26772900
H	1.93773900	0.00000000	1.17414700
H	2.71855900	0.00000000	-0.39925200
C	-0.34139500	-1.49605900	0.43490900
H	-1.60888500	-1.13504700	-1.24547500
H	-2.44113600	-1.12598000	0.28904700
H	0.85661300	-1.34318600	-1.35618600
H	1.66618100	-2.13508200	-0.01443800
H	-0.57758600	-2.56774600	0.43402800
H	-0.24910700	-1.21176500	1.49194100
C	-0.34139600	1.49605900	0.43490900
H	-0.57758600	2.56774600	0.43402800
H	-0.24910700	1.21176400	1.49194100

cyclooctane

electronic energy = -314.283578 Hartree

sum of electronic and zero-point energies = -314.078023

sum of electronic and thermal energies = -314.067033

sum of electronic and thermal enthalpies = -314.065959

sum of electronic and thermal free energies = -314.117133

C	-1.67482200	0.61442900	0.47391700
C	-0.53102500	-1.49678000	-0.55863900
C	-0.74252500	1.62879200	-0.21103800
H	-1.35221700	0.49296700	1.51669500
H	-2.68039100	1.05074800	0.53255700
H	-0.11134000	-1.04716100	-1.46622600
H	-0.79006500	-2.52526000	-0.83726900
C	0.53110200	-1.49673900	0.55866400
C	0.74244900	1.62881200	0.21105000
H	-0.80856300	1.52037200	-1.30388500
H	-1.13303300	2.62966700	0.01237500

C	1.82830400	-0.76050800	0.19427300
H	0.11140500	-1.04710200	1.46623600
H	0.79018000	-2.52519900	0.83733300
C	1.67478300	0.61449800	-0.47393400
H	1.13292600	2.62970600	-0.01233500
H	0.80849000	1.52036800	1.30389400
H	2.42129000	-1.39303400	-0.48119100
H	2.42777400	-0.64412900	1.10768100
H	1.35215200	0.49302300	-1.51670200
H	2.68032500	1.05087200	-0.53259900
C	-1.82826100	-0.76058400	-0.19429200
H	-2.42770000	-0.64422800	-1.10772400
H	-2.42125800	-1.39312500	0.48114900