

Supplementary Materials

Table S1. Relative energies (E, kJ mol⁻¹), dipole moments (μ , D), carbonyl frequencies (ν , cm⁻¹), and selected torsion angles (deg) calculated for the minimum energy conformations of 3-phenylthio-1-methyl-2-piperidone **4** at the MP2/6-31+G(d,p) level.

Method	Conf. ^a	E ^b	P ^c	μ	ν_{CO}	Torsion angles/ ^o ^d							
						α	β	γ	δ	θ	θ'	ω	ω'
MP2/6-31+G(d,p)	<i>ax</i>	0	77.7	3.68	1717.5	85.2	-104.3	55.5	4.16	161.8	-151.1	30.3	-52.6
	<i>eq</i>	3.09	22.3	5.89	1715.7	27.1	178.9	73.0	-6.20	-163.1	152.8	-31.1	52.2

^a Conformer designations *ax* and *eq* refers to the *axial* and *equatorial* conformers, respectively; ^b Relative energy; ^c Molar fraction in percentage; ^d See Scheme 1.

Table S2. Single point PCM solvent effect on the minimum energy gas phase for the conformations of **4** at the MP2/6-31+G(d,p) level; relative energies (E, kJ mol⁻¹) and dipole moments (μ , D).

Conf. ^a	C ₇ H ₁₄			CCl ₄			CHCl ₃			CH ₂ Cl ₂			CH ₃ CN		
	E ^b	P ^c	μ	E	P	μ	E	P	μ	E	P	μ	E	P	μ
<i>ax</i>	0	58.6	4.10	0	53.7	4.19	1.63	34.1	4.55	2.76	24.7	4.75	3.89	17.2	4.95
<i>eq</i>	0.86	41.4	6.59	0.37	46.3	6.74	0	65.9	7.35	0	75.3	7.69	0	82.8	8.04

^a Conformer designations *ax* and *eq* refers to the *axial* and *equatorial* conformers, respectively; ^b Relative energy; ^c Molar fraction in percentage.

Table S3. Mülliken charge (*e*) at selected atoms obtained at the B3LYP/6-31+G(d,p) level for 3-phenylsulfanyl-1-methyl-2-piperidone **4**.

Conf.	O(1)	C(2)	S(4)	N(6)	H(26)	H(30)	H(5)	H(11)	H(16)	H(17)
<i>ax</i>	-0.467	0.012	0.045	-0.057	0.181	0.131	0.213	0.195	0.148	0.167
<i>eq</i>	-0.458	-0.037	0.059	-0.182	0.131	0.135	0.196	0.195	0.149	0.154

Table S4. NBO occupancy of selected orbitals calculated at the B3LYP/6-31+G(d,p) level for the *ax* and *eq* conformers of 3-phenylthio-1-methyl-2-piperidone **3**.

Orbitals	<i>ax</i>		<i>eq</i>	
	DO ^a	AO ^b	DO	AO
LP _{N6} → π^* _{C2=O1}	1.666	0.320	1.674	0.284
LP _{O1} → σ^* _{C2-N6}	1.866	0.079	1.861	0.080
LP _{O1} → σ^* _{C2-C3}	1.866	0.070	1.861	0.068
LP _{O1} → σ^* _{C21-H26}	1.866	0.134	1.861	0.014
LP _{O1} → σ^* _{C10-H11}	1.866	0.009	1.861	0.011
LP _{S4} → π^* _{C2=O1}	1.892	0.320	1.925	0.284
LP _{S4} → π^* _{C20-C21}	1.892	0.388	1.925	0.368
σ _{C3-S4} → π^* _{C2=O1}	1.959	0.320	1.964	0.284
σ _{C3-S4} → σ^* _{C2-N6}	1.959	0.079	1.964	0.080
σ _{C3-S4} → σ^* _{C9-H18}	1.959	0.016	1.964	0.016
π _{C2=O1} → σ^* _{C3-S4}	1.989	0.037	1.989	0.034
π^* _{C2=O1} → σ^* _{C3-S4}	0.320	0.037	0.284	0.034

^{a,b} Donor and acceptor orbitals, respectively.

ax.gif

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Title Card Required

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C	1.56098700	0.85633300	0.24008800
C	3.60080300	-0.59046300	-0.05870300
C	1.63206400	-1.53087700	1.16724900
C	2.72495400	-1.82464300	0.13978100
C	0.75740000	-0.37324400	0.67499300
N	2.83652200	0.65386700	-0.21726500
H	4.23122400	-0.70952900	-0.94786400
H	1.01260000	-2.41162500	1.36015000
H	3.35978700	-2.65676400	0.46287400
H	0.07465600	-0.03551400	1.45626300
H	4.28189100	-0.47554100	0.80057600
H	2.09274800	-1.23942300	2.12252500
H	2.26832300	-2.12112500	-0.81228800
O	1.04343500	1.97548000	0.27788000
S	-0.32957100	-0.93395300	-0.73712100
C	3.62304000	1.81149800	-0.63061600
H	4.13679900	1.58870200	-1.57204700
H	4.37677800	2.06415700	0.12775900
H	2.95697900	2.66206400	-0.76435200
C	-1.94516800	-0.29200300	-0.29125800
C	-4.53480000	0.63169500	0.25421500
C	-3.04530900	-1.15043700	-0.43509500
C	-2.14258700	1.03488500	0.12047000
C	-3.43530800	1.48214200	0.40537300

C	-4.33594400	-0.68352900	-0.17349400
H	-2.88869400	-2.18037100	-0.74155600
H	-1.29298100	1.70518100	0.21154500
H	-3.58154200	2.50811000	0.73172200
H	-5.18208700	-1.35506500	-0.28933500
H	-5.53727900	0.99094700	0.46776400

eq.gif

%mem=15500MB

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freq rb3lyp/6-31+g(d,p) scrf=check guess=tcheck genchk geom=allcheck

Title Card Required

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C	-3.08388900	1.59452200	-0.09485700
C	-0.60957500	1.28662100	-0.29250800
C	-1.72165300	2.15297600	0.30055600
C	-0.72501900	-0.12752600	0.27964600
N	-3.19240100	0.14726500	0.11790400
H	-3.28495200	1.81569500	-1.15583100
H	-0.70114600	1.24919200	-1.38577200
H	-1.63092900	2.17992000	1.39423200
H	-0.49769700	-0.10026100	1.35352300
H	-3.87951500	2.07739600	0.48550500
H	0.37634700	1.70258000	-0.06662500
H	-1.64555100	3.18705900	-0.05359200
O	-2.29786500	-1.94857800	0.18249200
S	0.44377000	-1.35141500	-0.48961600
C	-4.54168000	-0.39595000	-0.00451000
H	-4.93140000	-0.24552800	-1.02055500
H	-5.20856400	0.10936500	0.70282600
H	-4.51473400	-1.46275300	0.21018800
C	2.01294800	-0.53285300	-0.16994000
C	4.52594500	0.63480000	0.29342200
C	2.74878100	0.01246700	-1.23191700
C	2.55348000	-0.50050800	1.12551400

C	3.79701600	0.09137500	1.35648100
C	4.00255400	0.58722700	-1.00080300
H	2.33666700	-0.01824500	-2.23576500
H	2.00465500	-0.95252400	1.94664100
H	4.20420800	0.11266000	2.36350800
H	4.56563600	1.00142300	-1.83247600
H	5.49814200	1.08465100	0.47284300