Intramolecular 1,5-Chalcogen Bond on the Conformational Preference of Carbonyl Thiocarbamate Species

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Electronic Supplementary Information

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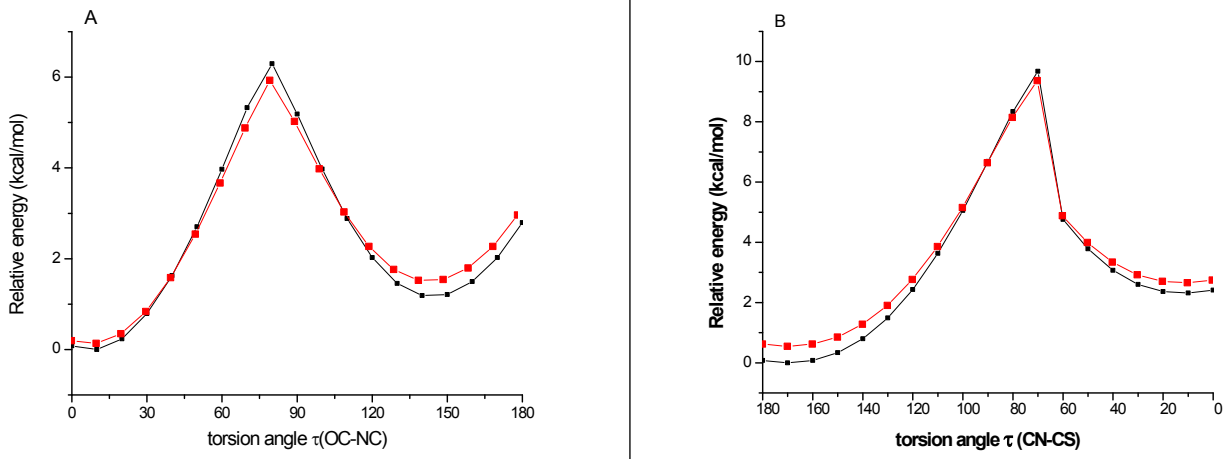
Figure S1. Potential energy curves calculated (B3LYP/6-311++G**) for internal rotation of O-methyl-N-4-fluorobenzoyl thiocarbamate (compound **I**, black line) and O-methyl-N-4-methylbenzoyl thiocarbamate (compound **II**, red line) as a function of the τ (OC-NC) (A) and τ (CN-CS) (B) torsion angle.

Figure S2. IR of O-methyl (4-fluorobenzoyl) carbamothioate

Figure S3. IR spectrum of *O*-methyl (4-methylbenzoyl) carbamothioate

Figure S4. Select region of Raman spectra of O-methyl-N-4-fluorobenzoyl thiocarbamate.



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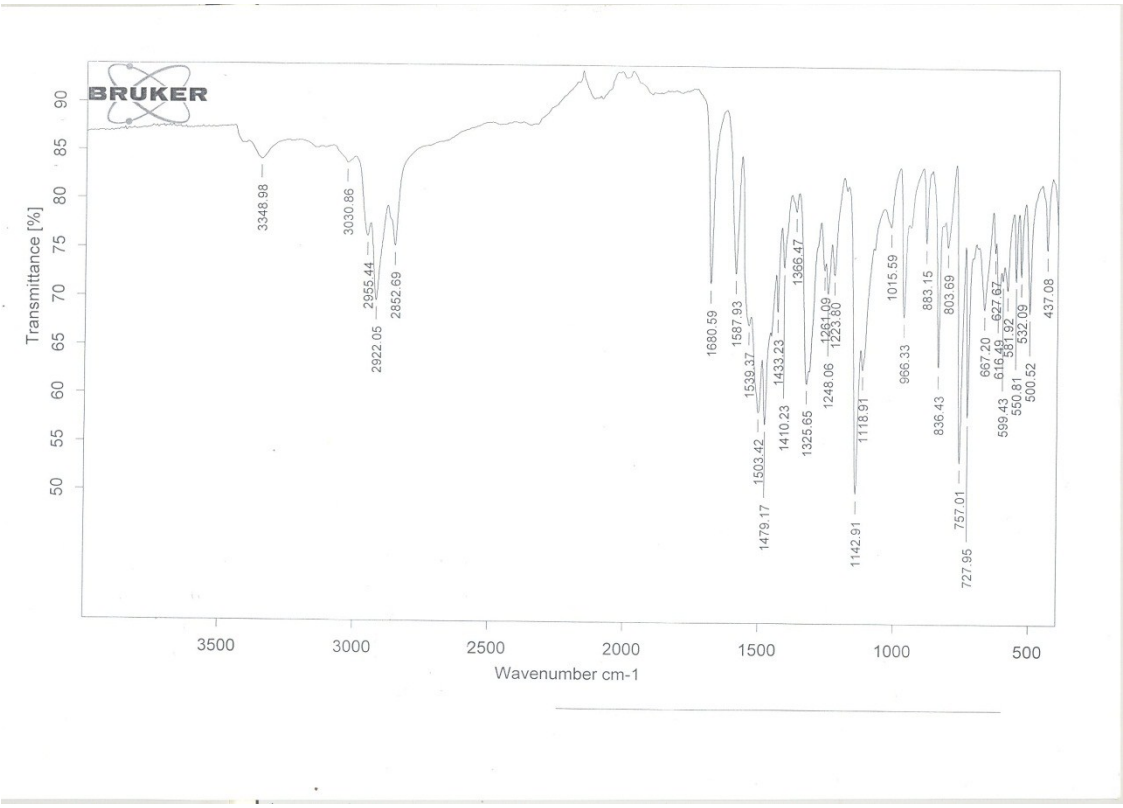

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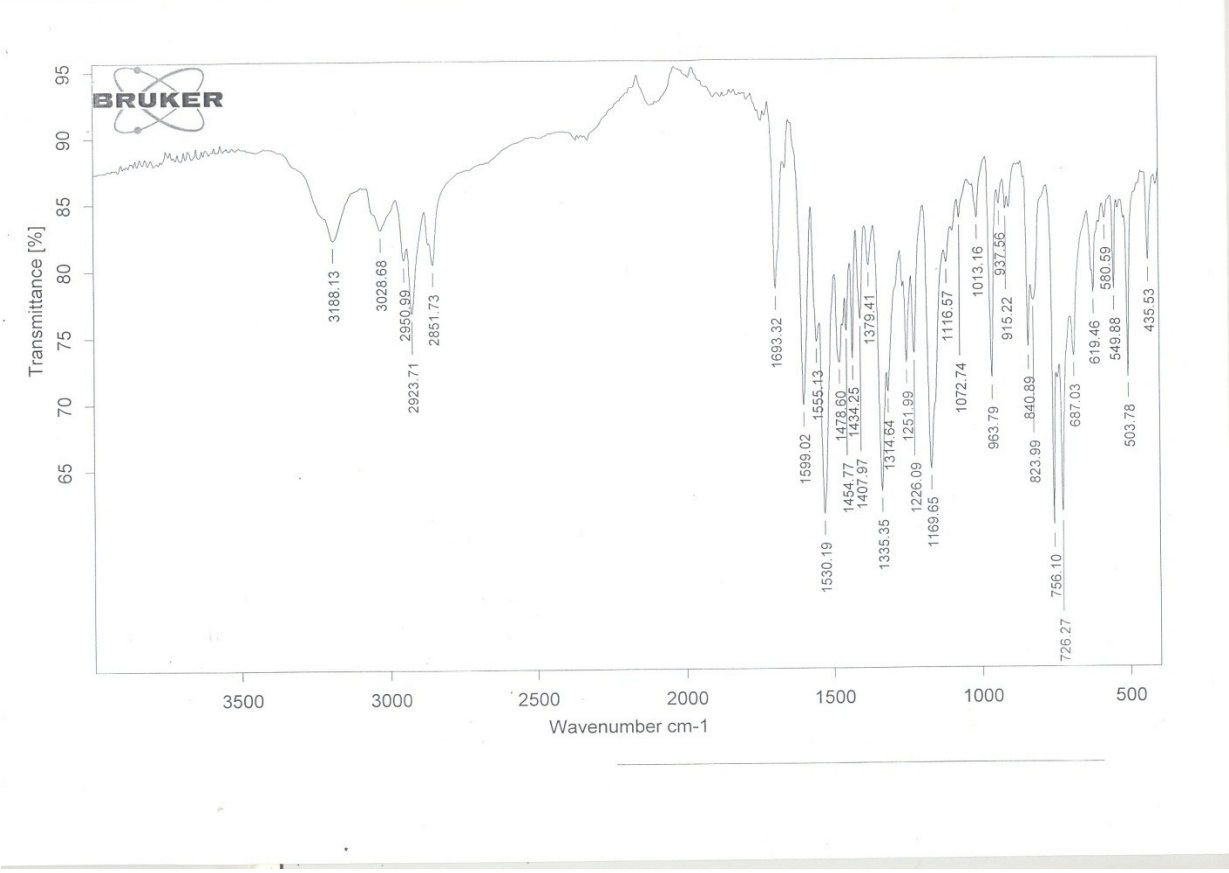

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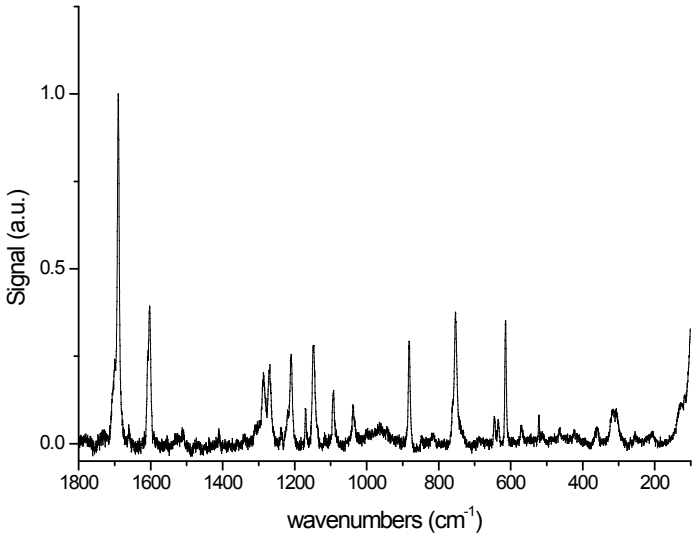

Figure S4. Select region of Raman spectra of O-methyl-N-4-fluorobenzoyl thiocarbamate.

Table S1. Theoretical energies calculations (B3LYP/6-311++G**) for the compound presents in the isodesmic reactions routes.

	Compound I		Compound II	
	Eº	Hº	Eº	Hº
1	-975.832439	-975.819621	-915.857498	915.843632
2	-607.409236	-607.402057	-607.409236	-607.402057
3	-1051.065611	-1051.051658	-991.090410	-991.075360
3′	-1051.063735	-1051.049802	-991.088099	-991.073120
3′′	-1051.062456	-1051.048503	-991.087210	-991.072142
4	-532.171206	-532.165763	-532.171206	-532.165763
Δ	3.04	2.68	3.21	2.86
Δ′	4.22	3.83	4.66	4.27
Δ′′	5.03	4.65	5.21	4.88

Table S2. Experimental and theoretical (B3LYP/6-311++G**) vibration frequencies of O-methyl-N-4-fluorobenzoyl thiocarbamate.

Experimental		Calculated	Assigment
IR	Raman		
3348 m		3623 (8)	ν_{N-H}
		3209 (<1)	ν_{C-H}(sym,Ph)
		3206 (<1)	ν_{C-H}(sym,Ph)
		3197 (<1)	ν_{C-H}(asym,Ph)
3030 w		3177 (1)	ν_{C-H}(asym,Ph)
2955 m		3163 (3)	ν_{C-H} (asym, CH_3)
2922 s		3132 (3)	ν_{C-H} (asym, CH_3)
2852 s		3054 (6)	ν_{C-H} (sym, CH_3)
1680 s	1690 s	1774 (70)	$\nu_{C=O}$
1587 s	1603 m	1640 (31)	ν_{CC}
		1628 (1)	ν_{CC}
1539 m		1543 (54)	δ_{N-H}
1503 s		1529 (97)	$\delta_{N-H} + \delta_{C-H}$ (Ph)
1479 s		1491 (4)	δ_{C-H} (CH_3)
		1478 (4)	δ_{C-H} (CH_3)
1433 (80)		1473 (67)	δ_{C-H} (CH_3) + δ_{N-H}
1410 w		1436 (<1)	$\nu_{CC} + \delta_{C-H}$ (Ph)
1366 vw		1341 (15)	$\nu_{C-C} + \nu_{N-C(S)}$
1325 s	1285 m	1327 (100)	$\nu_{N-C(S)} + \delta_{C-H}$ (Ph)
1320 sh		1321 (47)	δ_{C-H} (Ph) + $\nu_{N-C(S)}$
1261 m	1270 m	1265 (49)	$\nu_{C-C(O)} + \nu_{C=S}$
1248 m	1235 vw	1250 (21)	$\nu_{C-F} + \delta_{C-H}$ (Ph)
1223 m	1209 m	1227 (71)	$\delta_{N-H} + \nu_{O-C(S)}$
1142 vs	1169 w	1179 (19)	δ_{C-H} (Ph)
1118 s	1146 m	1167 (51)	δ_{C-H} (CH_3) + $\nu_{C=S}$
		1125 (5)	δ_{C-H} (Ph)
		1102 (4)	ν_{O-CH3}
1015 s		1048 (28)	$\nu_{O-CH3} + \nu_{N-C(O)}$
966	1091 w	1028 (7)	δ_{ccc}
	1037 w	989 (<1)	δ_{C-H} (oop, Ph)
883 m	884 m	884 (11)	$\delta_{OCN} + \delta_{C-H}$ (oop, Ph)
		866 (10)	δ_{C-H} (oop, Ph)
836 s		832 (1)	δ_{C-H} (oop, Ph)
803 m		830 (<1)	δ_{C-H} (oop, Ph)
757 vs	754 m	771 (10)	$\delta_{CC(O)}$ (oop) + δ_{C-H} (oop, Ph)
727 vs		760 (1)	$\delta_{CC(O)}$ (oop) + $\nu_{C=S}$

667 m		658 (8)	δ_{N-H} (oop)
		644 (1)	$\delta_{ccc} + \delta_{N-H}$ (oop) + $\delta_{NC(S)}$ (oop)
627 sh	645 w	631 (5)	$\delta_{NC(S)}$ (oop) + δ_{N-H} (oop)
616 w	635 w	616 (12)	$\delta_{CCC} + \delta_{OCS}$
599 vw	614 m	576 (2)	δ_{OCS}
581 w	570 w		
550 m	520 vw	516 (3)	δ_{CCC} (oop)
532 m		459 (<1)	τ_{CCCC}
500 m		426 (<1)	δ_{CCC} (oop)
437 m		402 (<1)	δ_{FCC}
	359 vw	348 (<1)	τ_{OCNC}
	310 w	288 (<1)	τ_{SCOCH3}

Table S3. Experimental and theoretical (B3LYP/6-311++G**) vibration frequencies of O-methyl-N-4-methylbenzoyl thiocarbamate.

Experimental	Calculated	Assignment
IR		
3188 m	3624 (7)	ν_{N-H}
	3199 (<1)	ν_{C-H}(sym,Ph)
	3178 (2)	ν_{C-H}(sym,Ph)
	3162 (1)	ν_{C-H}(asym,Ph)
	3161 (3)	ν_{C-H}(asym,Ph)
	3162 (2)	ν_{C-H} (asym, CH_3)
3028 m	3131 (2)	ν_{C-H} (asym, CH_3)
	3107 (2)	ν_{C-H} (asym, CH_3, Ph)
2951 sh	3077 (3)	ν_{C-H} (asym, CH_3, Ph)
2924 m	3053 (5)	ν_{C-H} (sym, CH_3)
2852 m	3027 (5)	ν_{C-H} (asym, CH_3, Ph)
1693 s	1772 (60)	$\nu_{C=O}$
1599 s	1649 (12)	ν_{CC}
	1607 (1)	ν_{CC}
1555 m	1544 (35)	$\delta_{N-H} + \delta_{C-H}$ (Ph)
1530 vs	1531 (84)	$\delta_{N-H} + \delta_{C-H}$ (Ph)
	1494 (1)	δ_{C-H} (CH_3, Ph)
	1492 (3)	δ_{C-H} (CH_3)
	1485 (1)	δ_{C-H} (CH_3, Ph)
	1477 (1)	δ_{C-H} (CH_3)
1479 w	1473 (54)	δ_{C-H} (CH_3) + δ_{N-H}
1455 w	1435 (<1)	δ_{C-H} (Ph) + δ_{C-H} (CH_3, Ph)
1408 w	1414 (<1)	δ_{C-H} (CH_3, Ph)
1379 w	1341 (11)	δ_{C-H} (Ph)
1335 vs	1337 (32)	$\nu_{C-C} + \nu_{N-C(S)}$
1314 m	1326 (100)	$\nu_{N-C(S)} + \nu_{C-C}$
1252 m	1267 (33)	$\nu_{C-C(O)} + \nu_{C=S}$
1226 m	1236 (17)	$\nu_{C-CH3} + \delta_{N-H}$
	1224 (28)	$\nu_{C-C} + \nu_{C-CH3} + \nu_{C-C(O)}$
	1209 (18)	δ_{C-H} (Ph)
1170 vs	1167 (31)	δ_{C-H} (CH_3) + δ_{N-H}
1117 w	1143 (10)	δ_{C-H} (Ph)
	1102 (2)	ν_{O-CH3}
	1062 (1)	δ_{C-H} (CH_3, Ph)
1073 w	1049 (23)	$\nu_{O-CH3} + \nu_{N-C(O)}$
1013 w	1034 (10)	δ_{ccc}
964 m	997 (<1)	δ_{C-H} (oop, Ph)
938 vw	971 (<1)	δ_{C-H} (oop, Ph)

915 vw		
841 m	882 (6)	$\delta_{OCN} + \delta_{C\text{-}H}$ (oop, Ph)
	860 (2)	$\delta_{C\text{-}H}$ (oop, Ph)
824 m	843 (2)	$\delta_{C\text{-}H}$ (oop, Ph)
756 vs	759 (10)	$\delta_{CC(O)}$ (oop) + $\delta_{C\text{-}H}$ (oop, Ph)
726 vs	705 (3)	$\delta_{CC(O)}$ (oop) + $\nu_{C=S}$
687 m	661 (5)	$\delta_{N\text{-}H}$ (oop)
619 w	635 (3)	$\delta_{ccc} + \delta_{N\text{-}H}$ (oop) + $\delta_{NC(S)}$ (oop)
581 vw	617 (3)	$\delta_{ccc} + \delta_{COC}$
550 w	577 (3)	δ_{COCH3}
504 m	499 (1)	δ_{CCC} (oop) + $\delta_{C\text{-}H}$ (oop, Ph)
436 w	444 (1)	τ_{CCCC}

Table 4. Crystal data and structure refinement result for compounds **I** and **II**.

	Compound **I**	Compound **II**
Crystal data		
Chemical formula	$C_9H_8FNO_2S$	$C_{10}H_{11}NO_2S$
Formula weight	213.2	209.3
Crystal system	Monoclinic	monoclinic
space group	***P 2$_1$/c***	***P 2$_1$/c***
a (Å)	11.7032 (18)	11.7767(16)
b (Å)	8.7287(13)	9.1218(13)
c (Å)	9.8686(15)	9.7623(14)
β (°)	111.415(3)	106.287(3)
Volume (Å^3)	938.5(2)	1006.6(2)
Z	4	4
Density (mg/m^3)	1.509	1.381
μ (mm^{-1})	0.331	0.293
F(000)	440	400
Crystal size (mm^3)	0.32 x 0.22 x 0.15	0.45 x 0.22 x 0.18
Data collection		
Diffractometer	Bruker SMART APEX CCD	Bruker SMART APEX CCD
Radiationtype	Mo K_α	Mo K_α
Wavelength (Å)	0.71073	0.71073
Temperature (K)	130 (2)	130 (2)
Reflection collection	8674	9276
Θ range for data collection (°)	1.9 to 27.9	1.8 to 27.9
Independent reflections	2240 (R_{int} = 0.022)	2400 (R_{int} = 0.022)
Refinement		
Refinement method	full-matrix least-squares F^2	full-matrix least-squares F^2
R[F^2 > 2_(F^2)], wR(F^2), S	0.033, 0.090, 1.04	0.034, 0.098, 1.02
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e. Å^{-3})	0.38, -0.21	0.36, -0.19

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