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Structure and Unimolecular Chemistry of Protonated Sulfur Betaines, $(CH_3)_2S^+(CH_2)_nCO_2H$ (n = 1 and 2)

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DMSA

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Figure S2: a) NPA charge distribution (from NBO calculation on Structure 5); b) hyperconjugative interaction as observed in the NBO analysis.

Figure S3: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for transition states relevant to fragmentation of [DMSA+H]+.

Figure S4: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ionmolecule complexes IMC relevant to fragmentation of [DMSA+H]+.

Figure S5: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the fragmentation of [DMSA+H]+.

Figure S6: B3LYP/6-311++G(2d,p) DFT calculation of all the competing fragmentation reactions found for [DMSA+H]+.



<u>^</u>	4 47005400	0 00004500	0 4 4 0 0 0 0 0 0	0	4 0 4 4 2 0 0 0 0	0 00000-00	0 04045500	0	4 0 4 4 2 0 0 0 0	0 00000000	0.04040400
C	-1.47635100	0.00021500	0.14633600	C	1.64139000	-0.02238500	-0.04245500	U	-1.64139900	-0.02236600	-0.04243100
С	-0.50275000	-0.00016300	-1.02822100	С	0.38121800	-0.82162600	0.26148200	С	-0.38122600	-0.82158300	0.26156900
0	-1.15862300	0.00092400	1.30493600	0	1.61897000	1.07561900	-0.53044700	0	-1.61897400	1.07566000	-0.53037300
0	-2.72086000	-0.00032500	-0.32180000	0	2.72132200	-0.70662100	0.31674800	0	-2.72133900	-0.70664600	0.31666300
S	1.27309100	-0.00036000	-0.60808400	S	-1.04850700	0.05572100	-0.46847300	S	1.04849400	0.05570000	-0.46847200
Н	-0.66137900	-0.87758400	-1.65878400	Н	0.42008200	-1.80599600	-0.20775200	Н	-0.23926300	-0.94739100	1.33615300
Н	-0.66109700	0.87712300	-1.65904900	Н	0.23926200	-0.94754300	1.33605400	Н	-0.42009000	-1.80599700	-0.20756800
Н	-3.34850000	0.00000600	0.42276800	Н	3.51779800	-0.17913500	0.12801100	Н	-3.51781500	-0.17916900	0.12789900
С	1.49200700	1.42917500	0.49615100	С	-2.41479000	-1.04160400	0.01764400	С	1.28743200	1.48072800	0.63500900
С	1.49142300	-1.42909000	0.49730300	С	-1.28736200	1.48071900	0.63506200	С	2.41477100	-1.04164300	0.01761700
Н	0.83908100	1.33847000	1.35896700	Н	-2.41040600	-1.21377600	1.09209900	Н	1.35119300	1.14956100	1.66979600
Н	1.27296600	2.31905400	-0.09254100	Н	-2.29612200	-1.97272200	-0.53435300	Н	0.44189400	2.14371400	0.46846100
Н	2.54470100	1.42950800	0.77647600	Н	-3.33447700	-0.54923300	-0.29544700	Н	2.21227400	1.96101400	0.31770300
Н	2.54415500	-1.42973200	0.77748400	Н	-2.21221900	1.96102200	0.31782800	Н	3.33445700	-0.54929700	-0.29551600
Н	1.27184400	-2.31934900	-0.09061500	Н	-0.44183000	2.14370500	0.46847700	Н	2.29606400	-1.97276900	-0.53435800
Н	0.83866700	-1.33734200	1.36013900	Н	-1.35105900	1.14952600	1.66984400	Н	2.41042400	-1.21379500	1.09207600

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C	1.59118100	0.06125900	-0.06028300	C
С	0.48101800	-0.35822900	-1.01898900	С
0	2.67505500	-0.43110800	-0.11675600	0
0	1.22394700	1.04160100	0.78768500	0
S	-1.26694600	-0.37647200	-0.46445300	S
Н	0.49156700	0.29078300	-1.89861200	Н
Н	0.68156900	-1.37512400	-1.35484900	Н
Н	2.00157200	1.29348900	1.31717800	Н
С	-1.20306000	-1.11022200	1.19692400	С
С	-1.70844500	1.35748000	-0.14679400	С
Н	-0.57573000	-0.51119700	1.85171600	Н
Н	-0.81861500	-2.12301600	1.08327400	Н
Н	-2.23124400	-1.14876600	1.55413900	Н
Н	-2.72755000	1.33981900	0.23806300	Н
Н	-1.69250900	1.86676900	-1.10940200	Н
Н	-1.01409800	1.80513100	0.55716000	Н

	0.20101100	0.000.0000
0.36917700	-0.84501900	0.24525000
2.73521800	-0.74304700	0.39634600
1.65973800	0.99506100	-0.57340600
-1.04108900	0.09155100	-0.46125700
0.36666100	-1.81188700	-0.26059300
0.20082400	-1.00668700	1.31053000
2.55953900	1.34519300	-0.70020100
-2.43376700	-1.00430200	-0.04996700
-1.26991100	1.45823600	0.71576500
-2.43586000	-1.24132900	1.01216400
-2.32769800	-1.90190500	-0.65729200
-3.34237500	-0.47620900	-0.33626600
-2.17559600	1.98141800	0.41189000
-0.40812000	2.11273800	0.60768100
-1.35962600	1.07212800	1.72946100

HF= -706.3636153 Zero-Point Correction= 0.1299439 HF= -706.3644437 Zero-Point Correction= 0.1298761 HF= -706.3644439 Zero-Point Correction= 0.1298799

-2.73628200 -0.74493500 0.39128200

-1.65936200 0.99782100 -0.56844400

1.04081300 0.09040800 -0.46151700

-0.20129400 -1.00121000 1.31411300

-0.36688500 -1.81254500 -0.25384900

-2.55909200 1.34763200 -0.69661700

1.27226000 1.45914100 0.71259400

2.43295600 -1.00592300 -0.04969600

1.36297300 1.07483700 1.72688300

0.41085500 2.11411800 0.60439600

2.17800400 1.98095300 0.40653900

3.34173000 -0.47910800 -0.33781600

2.32553200 -1.90449800 -0.65533900

2.43590500 -1.24108100 1.01284900

0

0

S

Н

Н

Н

С

С

Н

Н

Н

Н

Н

н

(14)



С	1.64752900	-0.00072800	-0.05940000
С	0.39822200	-0.83337000	0.24532200
0	2.82032000	-0.53790600	0.27056500
0	1.55733400	1.08549200	-0.55608400
S	-1.03935100	0.05723700	-0.46303900
Н	0.42500800	-1.80681700	-0.24937100
Н	0.25202500	-0.97732600	1.31781000
Н	2.75937000	-1.42831800	0.64566300
С	-2.40646500	-1.04644300	0.00922300
С	-1.27713800	1.46116200	0.66847800
Н	-2.40388400	-1.23582800	1.08078000
Н	-2.29309300	-1.96879600	-0.55843000
Н	-3.32516500	-0.54637200	-0.29495200
Н	-2.20533100	1.94208100	0.36156900
Н	-0.43500100	2.13025100	0.51083900
Н	-1.33843400	1.11091800	1.69712900

HF= -706.3565229 Zero-Point Correction= 0.1296577

a)



b) Some important hyperconjugative interactions are observed in the NBO analysis of the minimum energy <u>structure 5</u>. These include normal hyperconjugative and negative hyperconjugative interactions.

Normal hyperconjugative interactions include:

Strong negative hyperconjugative interactions including:

Weaker negative hyperconjugative interactions including:

 $\sigma_{\text{C-S}} - \sigma_{\text{C-OH}}^*$: 2.99 kcal/mol $\sigma_{\text{O-H}} - \sigma_{\text{C-C}}^*$: 4.4 kcal/mol

 $\begin{array}{l} \mathbf{n}_{\mathrm{O(C=O)}} - \ \sigma \ast_{\mathrm{C-C}}: \mathbf{21} \ \mathrm{kcal/mol} \\ \mathbf{n}_{\mathrm{O(C=O)}} - \ \sigma \ast_{\mathrm{C-OH}}: \mathbf{31} \ \mathrm{kcal/mol} \end{array}$

 $n_{O(O-H, sp}^2) - \sigma^*_{C=O}$: 8 kcal/mol

These donor-acceptor interactions do not seem to have a major impact on the ions observed upon CID.

Figure S2: a) NPA charge distribution (from NBO calculation on Structure 5); b) hyperconjugative interaction as observed in the NBO analysis

TS₁₄₋₁₆ TS₄₋₁₅



TS_{5'-17}





C C O

ОЅНННССННННН

1.46560500	0.06170700	0.17285000	С	-1.96808100	-0.00064000	0.21643600	С	-1.62304900	0.28261100	0.01413500
0.65478000	-0.33494300	1.25734900	С	-1.58723900	0.00174100	-1.15902100	С	-0.41262900	-0.42975700	0.39696300
1.39268100	1.25235100	-0.33001700	0	-1.46895300	-0.00270000	1.37648300	0	-2.57861000	-0.89241500	0.37860300
2.21599800	-0.81909100	-0.44358700	0	-3.12510900	0.00047000	-0.22018500	0	-1.99034500	1.23635000	-0.55075000
-1.38403300	-0.01957600	0.44773200	S	1.17385300	-0.00015400	-0.06485700	S	1.05600800	0.08407500	-0.43630000
0.73990700	-1.36433500	1.58430300	Н	-1.51164300	-0.93700800	-1.69335700	Н	-0.30168000	-0.58083400	1.46932700
0.53820900	0.39672500	2.04619100	Н	-1.51101900	0.94243500	-1.68985400	Н	-1.51607000	-1.43647400	0.19710900
2.66050300	-0.42130900	-1.21357500	Н	-0.45543500	-0.00258900	1.28434200	Н	-3.34198300	-0.99059700	-0.21973900
-1.35476400	1.35562900	-0.47583200	С	2.30882400	-1.42761000	-0.02966900	С	2.14191200	-1.35213700	-0.19571700
-1.39685600	-1.40115900	-0.73711400	С	2.30690600	1.42872600	-0.02589300	С	1.85552900	1.33673500	0.62006300
0.42467100	1.60363400	-0.28362600	Н	2.93713300	-1.41242300	-0.91782700	Н	1.70995700	-2.17274000	-0.76433700
-1.74139400	2.24662600	0.00182400	Н	1.69736500	-2.32823100	-0.02681100	Н	2.21122100	-1.59887200	0.86183500
-1.30702500	1.28953700	-1.55430900	Н	2.91218100	-1.38998300	0.87538400	Н	3.11634000	-1.08535800	-0.60253100
-2.41885100	-1.47264900	-1.10662500	Н	2.91029900	1.38953200	0.87906800	Н	1.98314500	0.95090300	1.62968000
-1.12685700	-2.30529900	-0.19579300	Н	1.69425300	2.32852700	-0.02066800	Н	1.20895900	2.21249600	0.60955500
-0.70665800	-1.21319800	-1.55677700	Н	2.93526100	1.41674300	-0.91406900	Н	2.81503600	1.58008400	0.16440100

HF= -706.2913138 Zero-Point Correction= 0.1263891 Freq.= -351.656cm⁻¹ HF= -706.2768818 Zero-Point Correction= 0.1258316 Freq.= -253.789cm⁻¹ HF= -706.2588444 Zero-Point Correction= 0.1226296 Freq.= -1744.09cm⁻¹



С	1.66275200	-0.50210500	0.03606000	С	1.09282600	0.94017400	0.40357400	С	-1.58906700	0.22308800	-0.24391300
С	0.44689900	-1.11297400	0.44478600	Н	0.14858800	0.55819400	0.86773300	С	0.22362700	-0.57810500	1.36509300
0	1.52191300	1.07644000	0.81184000	Н	1.61630100	1.56819000	1.12389400	0	-1.61769000	1.41647500	-0.26090400
0	2.57699900	-0.58498300	-0.66462900	Н	0.78011000	1.51605000	-0.46589100	0	-2.55831600	-0.62035400	0.09608000
S	-1.12358500	-0.05110700	-0.60305700	С	3.70664100	0.16036200	-0.26680100	S	1.41002200	-0.42399200	0.16945700
Н	0.39118300	-2.15053900	0.12424800	Н	4.02868700	0.65493300	0.65049700	Н	0.41892000	-0.01664700	2.27242500
Н	0.19459100	-0.93942800	1.48397200	Н	4.36254200	-0.68329600	-0.47425800	Н	-0.19927800	-1.57139900	1.46869900
Н	2.26522700	1.64021000	0.53206000	Н	3.71884100	0.85594900	-1.10405700	Н	-3.36588200	-0.11921000	0.31592600
С	-2.39765700	-0.73790500	0.50202300	С	-2.52366000	-0.02414200	-0.04248500	С	1.79639200	1.34908600	0.00909000
С	-1.04967600	1.56545900	-0.26681400	0	-3.37617800	-0.88092900	-0.12912200	Н	-0.71299300	-0.36483800	-0.81500200
Н	-2.29999800	-0.31178000	1.49836900	0	-2.58399500	1.26325700	-0.18938100	Н	2.52754000	1.43063100	-0.79312200
Н	-2.28650100	-1.82027500	0.52074300	Н	-3.49075200	1.55838400	-0.40355700	Н	2.23887400	1.64780200	0.95783000
Н	-3.35285600	-0.46202200	0.05790500	С	-1.31315000	-0.77389000	0.26323700	Н	0.87330500	1.88239200	-0.20303000
Н	-0.79585600	2.19507000	-1.10912300	Н	-0.76531900	-1.23393000	-0.55311900	С	0.77894300	-0.97168600	-1.31080200
Н	0.64792600	1.48597000	0.46662200	Н	-1.18518400	-1.15700500	1.27009800	Н	0.52823800	-2.02838700	-1.32297700
Н	-1.55156000	1.97399100	0.60009300	S	2.04322700	-0.53194500	-0.03177900	Н	1.27959200	-0.57973300	-2.19029200

HF= -706.2592861	E _{rel} = -706.2507609
Zero-Point Correction= 0.124654	Zero-Point Correction= 0.12385
Freq = -403.269cm ⁻¹	Freq = -174.625cm ⁻¹

HF= -706.2039434 Zero-Point Correction= 0.1215759 Freq = -483.015cm⁻¹



С	1.61672300	0.26979600	0.16335800	С	-2.19767200	0.00192200	0.01499400	С	-1.29023600	0.87910700	0.00002000
С	0.97306600	1.45388100	0.03734500	С	-3.46358800	-0.04007500	-0.67772100	С	-0.36504100	-0.07940600	-0.00021200
0	2.44215300	-0.29405200	-0.72491000	0	-0.99722800	0.01171400	0.07403200	0	-3.01289700	-1.39949800	0.00000700
0	1.36974400	-0.53573000	1.19607200	0	-3.19586800	0.03895900	0.84915600	0	-2.05814900	1.72433600	0.00005500
S	-1.33177800	-0.11338700	-0.66696100	S	2.04778700	-0.01190700	-0.63844300	S	1.30065000	0.40514200	-0.00000300
Н	0.47218800	1.87067300	0.89730700	Н	-3.89376600	-0.98749900	-0.97845700	Н	-0.68664800	-1.11263700	-0.00011400
Н	1.15706100	2.08850400	-0.81746400	Н	-3.90350700	0.86738700	-1.07282100	Н	-3.56318200	-1.60715200	-0.76513500
Н	2.02319200	-1.25284900	1.22285400	Н	0.67945600	-0.01489100	-0.62061900	Н	-3.56333000	-1.60871600	0.76461600
С	-1.24412400	-1.57483400	0.02800000	С	2.31110700	-1.42320000	0.48780300	С	2.03672600	-0.48110800	-1.41023700
С	-2.30212600	0.89662100	0.50265200	С	2.30264400	1.43760000	0.44026600	С	2.03645500	-0.48110700	1.41037700
Н	2.73647200	0.33868700	-1.39521200	Н	3.37083300	-1.44314700	0.73441300	Н	1.60481700	-0.04963300	-2.31084300
Н	-0.78634400	-2.37073400	-0.54608100	Н	2.04360200	-2.31977000	-0.06877000	Н	1.81761800	-1.54452400	-1.33702800
Н	-1.59216300	-1.77055200	1.03402600	Н	1.69247500	-1.30965000	1.37422600	Н	3.10991100	-0.29454000	-1.37966100
Н	-3.34697800	0.60950600	0.39570900	Н	1.68386500	1.34999700	1.32950300	Н	1.81743500	-1.54453100	1.33707300
Н	-2.16452700	1.93386100	0.20591000	Н	2.03012900	2.31338000	-0.14618800	Н	1.60429700	-0.04970000	2.31089700
Н	-1.94686800	0.73256400	1.51690100	Н	3.36214400	1.47184400	0.68625300	Н	3.10963400	-0.29445900	1.38006300

HF= -706.3057231 Zero-Point Correction= 0.127251 HF= -706.3046429 Zero-Point Correction= 0.125227 HF= -706.3291874 Zero-Point Correction= 0.1249165

Figure S4: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ion-molecule complexes IMC relevant to fragmentation of [DMSA+H]+.



С	1 30750200 -1 21054800	0 14572500	С	-1 38474800	0 19542800 (0 69907400	0	0 0 0 0 0 0 0 0 0 0	0 45404400	
ĉ	1 36160700 1 04731600	1 44580600	ц	2 00071200	1 64704700	1 01070500	C	-3.05975400	-0.45181400	0.00068900
0	1.30109700 -1.04731000	1.44509000		2.09071200	1.04/94/00 -	1.01979500	С	0.98682100	-1.42393600	0.20545100
0	1.91268900 1.87340700	-0.45442200	Н	-1.70316000	0.69241400	1.61011900	0	-1 90306700	-0 08804000	0 01105900
0	1.14429200 -1.33984700	-0.99434500	Н	-0.32415400	-0.02190300 (0.53230800	Õ	_4 10888500	0 33568800	-0 15955000
S	-1.65311300 -0.22898600	0.30997300	С	-4.08521000	0.21740400 (0.10764100	0	-4.100000000	0.0000000	-0.15355000
ŭ	1 10246900 1 00196200	2 00062000	ц Ц	4 04047400	0.60027600	1 00076100	5	1.86291900	-0.08795600	0.00756300
	1.19240600 -1.90166200	2.00002000		-4.04047400	0.69927600	1.06076100	Н	-0.08709800	-1.27601300	0.16523100
Н	1.76178800 -0.12941300	1.85399200	Н	-4.48919600	0.88768200 -(0.65175700	н	1 48355800	-2 38267700	0 21304800
Н	2.69734600 2.06657300	0.07395000	Н	-4.67844900	-0.69697700	0.14197400	11	2 02072400	1 25772000	0.27020200
C	-1 26261300 1 53544800	0 57104400	C	2 83644300	-0.08730300 -0	0 01733700	п	-3.62072100	1.25/72000	-0.27236300
0	-1.20201300 1.33344000	0.07 104400	0	2.03044300	-0.00733300 -0	0.01733700	С	0.95143300	1.44607900	0.23832500
С	-1.32678400 -0.51821500	-1.25493300	0	3.81049000	-0.77462000 -	0.06665200	н	-3 37678500	-1 49256000	0 12483300
Н	-0.24400900 1.73797600	0.23966000	0	1.58942500	-0.65196300	0.23071700	 Ц	1 27201000	2 12965000	0 54510100
н	-1 35951000 1 69959700	1 64281300	н	1 76147300	-1 60307600 (0 33621300	п	1.27201000	2.12003000	-0.54519100
	-1.00001000 1.00000100	1.04201000	0	0.70170000	1.000070000	0.00021000	Н	1.18944500	1.81876200	1.23285900
н	-1.99984000 2.13050400	0.03475000	C	2.76173900	1.39876000 -0	0.19512900	н	-0 10236400	1 17869000	0 14848500
н	-1.54915700 -1.50680800	-1.63761000	Н	3.75559300	1.78404200 -0	0.40514300	0	2 42055100	0.00250000	0.22562400
н	1 95975400 2 50525900	-1 18295500	н	2 37493700	1 86597800 (0 71323800	C	3.43055100	0.00359000	-0.32302400
	1.00070400 2.00020900	-1.10235500		2.01403100	0.00474500	0.11020000	Н	4.01895200	-0.78907500	-0.56558300
н	-0.94369600 0.23726600	-1.92905000	5	-2.41974700	-0.26174500 -0	0.45099600	Н	3.85680500	1.05910100	-0.14742600

HF= -706.2963215 Zero-Point Correction= 0.121044 E_{rel}= -706.331779 Zero-Point Correction= 0.126146

HF= -706.2399385 Zero-Point Correction= 0.1237046

Figure S4: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ion-molecule complexes IMC relevant to fragmentation of [DMSA+H]+.

 $CH_3S=CH_2 \qquad CH_2C(OH)_2 \qquad (CH_3)_2S^+H$







				(:
S	-0.14031700	-0.55222800	-0.00003800	Č
С	1.42450000	0.37771000	-0.00004200	0
С	-1.32874100	0.53694300	0.00022100	0
Н	1.23746200	1.44830500	-0.00379500	0
Н	1.97159700	0.06285500	-0.88957600	н
н	1,96787300	0.06849600	0.89383500	н
Н	-2 34737500	0 15904700	-0 00049300	н
н	-1 15903500	1 60903200	-0.00043000	н
	-1.13803300	1.00303200	-0.00043000	

3	0.00000000	-0.59327000	-0.10337200
1	0.00000000	-1.07486600	1.15892800
)	-1.44021500	0.52255000	0.02617300
)	1.44021500	0.52255000	0.02617300
ł	-1.33049700	1.18645400	0.87969200
ł	-2.31863600	-0.11423600	0.12121400
1	-1.48368200	1.07607600	-0.91043800
ł	1.48368200	1.07607700	-0.91043700
ł	2.31863600	-0.11423600	0.12121300
1	1.33049800	1.18645400	0.87969200

HF= -477.1545979	
Zero-Point Correction=	0.064007

HF= -229.1256226 Zero-Point Correction= 0.0605503

 -0.07746000
 -0.03552500
 0.00004400

 -1.39497100
 -0.22387100
 -0.00013200

 0.56906700
 1.16659500
 -0.00011300

 0.81583400
 -1.04722600
 0.00003800

 -2.07467500
 0.61536300
 -0.0005100

 -1.79613900
 -1.22486200
 0.00039200

 -0.07848700
 1.88088300
 -0.00087800

 1.70467700
 -0.66995900
 -0.0009000

HF= -478.3974031 Zero-Point Correction= 0.0858231



0

Н

Н





С	-0.32490500	-0.06727400	-0.00009900
0	-1.50631500	-0.16016900	0.00003400
0	0.60813100	0.88201800	0.00001700
С	1.02410500	-0.59383300	0.00001500
Н	1.49508300	-0.90406500	0.92527400
Н	1.49518900	-0.90408800	-0.92518000

С	-1.95112700	0.00000000	0.15727900
С	-0.72344600	-0.00001400	0.67078300
0	-3.00903000	-0.00000100	-0.27180100
S	0.62559200	0.00000000	-0.42679900
Н	-0.59188500	-0.00001300	1.74538700
С	1.64334000	-1.41493200	0.10056100
С	1.64332300	1.41494200	0.10056600
Н	1.07366500	-2.31310300	-0.12947300
Н	1.86096400	-1.34427200	1.16443900
Н	2.55646200	-1.38481500	-0.49363800
Н	1.86096600	1.34427100	1.16443900
Н	1.07362600	2.31310600	-0.12944500
Н	2.55643400	1.38485200	-0.49364900

0.00000000	0.11696300	0.00000000
0.76520000	-0.46785100	0.00000000
-0.76520000	-0.46785100	0.00000000

 H_2O

HF= -227.882879	
Zero-Point Correction= 0.038345	

HF= -629.854065 Zero-Point Correction= 0.1011742 HF= -76.4595855 Zero-Point Correction= 0.021291

 $(CH_3)_2S=CH_3^+$

CH₃CO₂H



C C

0

Н

Н







-0.1021640	0 -0.	00003500	0.000	07900	Н	
1.2062430	0 0.	00000800	-0.000	29800	С	-
-1.2629030	0 0.	00001100	0.000	00300	0	-
1.7393180	0 0.	93895100	0.000	64200	0	-
1.7394350	0 -0.	93887000	0.000	64300	Н	-
					С	
					Н	

н

1.66714300	-0.71217300	0.88006100
-0.08855600	0.12695000	-0.00001800
-0.62188500	1.20623700	0.00000300
-0.79631600	-1.03160000	-0.00000400
-1.73488500	-0.78600100	0.00004800
1.39219600	-0.12776500	-0.00000800
1.92449700	0.81946600	-0.00071300
1.66701100	-0.71349600	-0.87922800

00	С	0.78943800	1.47056400	0.04815800
00	S	0.12862400	0.00165400	-0.01838700
00	Н	1.85376100	1.55887100	0.21074800
00	Н	0.16880700	2.29445300	-0.27193700
00	С	-1.67252500	-0.02825100	0.01337900
00	С	0.84146700	-1.44323300	-0.02504000
00	Н	-2.00686900	0.82909800	-0.56882500
00	Н	-1.98775400	0.04620000	1.05217700
	Н	-1.98016400	-0.96226400	-0.45209900
	Н	0.23023300	-2.29001400	0.25000800

Н

HF= -152.65479
Zero-Point Correction= 0.0314422

HF= -477.1545979 Zero-Point Correction= 0.064007 HF= -516.3896075 Zero-Point Correction= 0.0884789

1.91371800 -1.49729100 -0.14486700

$$(CH_3)_2S=CH_3^+$$
 ring HCO_2H





С	-1.16240900	0.33103700	0.73525000
S	0.22651500	-0.66701000	-0.00005200
Н	-0.81833100	1.20531700	1.27296300
Н	-1.86281300	-0.30446500	1.26327900
С	-1.16239800	0.33116400	-0.73520200
С	1.65174200	0.47832100	0.00004000
Н	-1.86279400	-0.30424500	-1.26335200
Н	-0.81831300	1.20553700	-1.27275800
Н	1.31255500	1.51126700	0.00033300
Н	2.23182200	0.25802600	-0.89467200
Н	2.23202700	0.25759400	0.89451300

0.13642900	0.39883000	0.00001200
-1.11743200	-0.08907300	-0.00002900
1.13371700	-0.26466200	-0.00001100
-1.05567500	-1.05892500	0.00017300
0.10682800	1.49583000	0.00007500

C O O H H

HF= -516.4967043 Zero-Point Correction= 0.0935491 HF= -189.8319498 Zero-Point Correction= 0.0336566



Reaction coordinate

Figure S6: B3LYP/6-311++G(2d,p) DFT calculation of all the competing fragmentation reactions found for [DMSA+H]+.

DMSP

Summary of Figures:

Figure S7: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for conformers of [DMSP+H]+.

Figure S8: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for transition state relevant to fragmentation of [DMSP+H]+.

Figure S9: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ionmolecule complexes IMC relevant to fragmentation of [DMSP+H]+.

Figure S10: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for products relevant to the fragmentation of [DMSP+H]+.

Figure S11: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for X-ray crystallography structures.



C	-1.95415200 (0.10505700	-0.05165900	C	1.95415200	0.10505700	-0.05165900	C	1 77381900	0 24277400	-0 04314000
С	-1.20892100 -1	1.17977500	0.23067700	С	1.20892100	-1.17977500	0.23067600	C	1 12622100	-1 11717500	-0.18965400
0	-1.41255800	1.18717600	-0.08661700	0	1.41255800	1.18717600	-0.08661700	0	1 1833/000	1 20216400	0.14060000
0	-3.24843600 -0	0.09786600	-0.27330400	0	3.24843600	-0.09786600	-0.27330300	0	2.07070900	0.12520000	-0.14900000
S	1.23101000 (0.06062500	-0.42514800	S	-1.23101000	0.06062500	-0.42514800	0	3.07070600	0.13369600	0.24016000
Ĉ	1 61646000	1 59197300	0 47681500	Ĉ	-2 82641700	-0.81082600	-0 34069200	5	-1.71708300	-0.40076000	-0.03295400
ĉ	2 82641700	0.81082600	0.34060200	Ĉ	1 61646000	1 50107300	0.47681500	C	-1.23198900	-0.05768500	1.68304500
0	2.02041700 -0	0.01002000	-0.34009200	0	-1.01040000	1.59197500	0.47001500	С	-1.90355300	1.26731700	-0.73307600
C	0.19800700 -0	0.93114400	0.75828400	C	-0.19800700	-0.93114400	0.75828400	С	-0.22484200	-1.11285200	-0.89283300
Н	-1.76279400 -1	1.76556700	0.96903600	Н	1.19981700	-1.78152600	-0.68269900	н	1 79154100	-1 75778600	-0 77569100
Н	-1.19981700 -1	1.78152600	-0.68269800	Н	1.76279400	-1.76556800	0.96903500	н	1 08088600	-1 58793500	0 79619600
Н	-3.67638100 (0.75219600	-0.47447500	Н	3.67638100	0.75219600	-0.47447500	и Ц	2 44025000	1.02509200	0.73013000
Н	2.04304500	1.35406600	1,44944900	н	-3.15949400	-0.90488000	0.69124500	п	3.44933000	1.02596200	0.34313700
н	0.68162200	2 13880400	0 56118100	н	-2 68776500	-1 78754000	-0.80146900	н	-0.40178900	0.64263600	1.70967400
	0.00102200 2	2.10000400	0.12847100		2.00770300	0.00107000	0.00761000	Н	-0.98958500	-1.00784800	2.15534900
	2.32756000 2	2.14172000	-0.13647100	п 	-3.53760300	-0.23127900	-0.92761900	Н	-2.11738300	0.36110200	2.16027500
Н	3.53760300 -0	0.23128000	-0.92762000	Н	-2.32758000	2.14172000	-0.13847000	н	-2 73004300	1 73127500	-0 19582200
н	2.68776500 -1	1.78754000	-0.80146900	Н	-0.68162200	2.13880400	0.56118100	Н	-2 180/5000	1 13533000	1 77796800
Н	3.15949500 -0	0.90487900	0.69124400	Н	-2.04304400	1.35406600	1.44945000	и Ц	0.07270700	1.01040400	0 62220700
н	0.73186200 -1	1 87012300	0 89650100	н	-0 19494400	-0.38205500	1 69850200	п	-0.97370700	1.01040400	-0.02339700
 Ц	0 10404400	0.38205400	1 60850200	 ப	0 73186200	1 87012300	0.80650000	Н	-0.53719500	-2.13635600	-1.09716300
11	0.15494400 -0	0.30203400	1.03030200	11	-0.73100200	-1.07012300	0.09000000	Н	-0.18868800	-0.57149000	-1.83801400

HF= -745.7075272 Zero-Point Correction= 0.1588988 HF= -745.7075272 Zero-Point Correction= 0.1588988 HF= -745.7026308 Zero-Point Correction= 0.1590468



								<u>^</u>	0 07004000	0 404 50500	0 0 4 7 5 0 0 0 0
Н	-1.91343400	-1.76521100	1.49343200	С	-2.37199400	-0.12154100	0.04753900	C	2.37201900	-0.12152500	0.04752800
Н	-3.27473700	-0.62077700	1.48238600	С	-1.03050700	0.50881500	-0.30146100	С	-0.08269200	-0.46331700	0.07447700
С	-2.20041900	-0.72626400	1.33799300	0	-2.49323900	-1.23700600	0.47880600	С	1.03052100	0.50888900	-0.30131900
Н	-1.65300000	-0.05885800	1.99883100	0	-3.37649700	0.72661700	-0.19331700	0	2.49326900	-1.23701500	0.47872800
Н	0.11173000	-1.58806900	-0.48116400	S	1.72212400	0.12300900	-0.50302300	0	3.37652600	0.72661200	-0.19338600
S	-1.87406000	-0.33836200	-0.40617500	С	2.13642600	1.45701400	0.65872800	Н	-0.14500900	-0.63870000	1.14824700
С	-0.05881800	-0.51707400	-0.60034000	С	2.81298800	-1.22101600	0.04931600	Н	0.05505100	-1.42333200	-0.42439200
Н	0.11173500	-0.29099700	-1.65416600	С	0.08270700	-0.46343300	0.07422400	Н	1.02922400	0.73485300	-1.37093100
Н	-3.26249500	1.57945300	-0.36238000	Н	-1.02931100	0.73477900	-1.37107200	Н	0.95269700	1.46114400	0.22722400
0	2.64208500	-0.82288400	-0.80114300	Н	-0.95259300	1.46106400	0.22708000	Н	4.21519100	0.28868200	0.03134800
С	-2.18786600	1.44876400	-0.48200300	н	-4.21515400	0.28872700	0.03152800	С	-2.13665900	1.45698500	0.65863900
Н	0.66284900	0.09092600	1.37225800	Н	2.01975800	1.11407300	1.68514900	S	-1.72207100	0.12298100	-0.50301300
С	0.83047000	0.31066900	0.31562100	Н	1.47701700	2.29533200	0.44243900	С	-2.81293100	-1.22110500	0.04918500
Н	-1.88975300	1.78472500	-1.47415600	Н	3.16638600	1.74610100	0.45432200	Н	-1.47725800	2.29533800	0.44246100
С	2.28950500	-0.00686100	0.00646100	Н	3.83526900	-0.91028500	-0.16068300	Н	-2.02015300	1.11405700	1.68508100
Н	-1.64299500	1.97622700	0.29694700	н	2.56634700	-2.09734800	-0.54806200	Н	-3.16659900	1.74600600	0.45404600
Н	0.68604900	1.38408100	0.18192000	Н	2.66848600	-1.41414500	1.11054800	Н	-3.83520500	-0.91038900	-0.16086900
Н	4.02591700	0.51223400	0.53977500	Н	-0.05496800	-1.42335600	-0.42484100	Н	-2.66850200	-1.41428800	1.11041700
0	3,10614800	0.74221500	0.75598400	н	0.14494900	-0.63900900	1.14796600	Н	-2.56622400	-2.09739900	-0.54822200

HF= -745.6983165	HF= -745.7012286	HF= -745.7012286
Zero-Point Correction= 0.1584627	Zero-Point Correction= 0.1584189	Zero-Point Correction= 0.1584187



С	-2.11818000	-0.02107300	-0.08570600	С	2.11818700	-0.02107200	-0.08570200	С	-2.42820100	0.09967900	0.00810300
С	-1.20275600	-1.13635200	0.38899700	С	1.20275700	-1.13636900	0.38894500	С	-1.01935200	0.50154900	-0.42111700
0	-3.21420000	-0.19678300	-0.52189000	0	3.21423200	-0.19676200	-0.52183000	0	-3.29204300	0.88484700	0.26404500
0	-1.54499100	1.21053000	0.04003300	0	1.54497100	1.21052100	0.04001000	0	-2.57558600	-1.24151300	0.03085900
S	1.21397600	0.04696300	-0.41985700	S	-1.21398800	0.04696200	-0.41985900	S	1.72248800	0.00079700	-0.49457100
С	1.80487100	1.58220800	0.35239500	С	-2.71074700	-0.98542300	-0.40949000	С	2.14400000	1.53719300	0.38055700
С	2.71071000	-0.98545900	-0.40951400	С	-1.80483000	1.58221500	0.35242000	С	2.77366700	-1.22081000	0.34512700
С	0.16899200	-0.72567400	0.91007500	С	-0.16899200	-0.72571400	0.91004000	С	0.05279700	-0.42163200	0.15327500
Н	-1.72819600	-1.65032000	1.19957900	Н	1.13051900	-1.86465400	-0.42187700	Н	-1.00205100	0.47267400	-1.51496500
Н	-1.13052000	-1.86467700	-0.42178900	Н	1.72819400	-1.65038000	1.19950100	Н	-0.88713300	1.53637900	-0.10975000
Н	-2.19433200	1.86489500	-0.27098100	Н	2.19431500	1.86489700	-0.27097400	Н	-3.49649400	-1.44225800	0.27003700
Н	2.29058800	1.36500900	1.30177300	Н	-3.12846300	-1.04380800	0.59369900	Н	2.00657100	1.41204800	1.45318500
Н	0.92950900	2.21416600	0.48532000	Н	-2.42444600	-1.96984900	-0.77673700	Н	1.50321500	2.32416800	-0.01251500
Н	2.49879900	2.04378800	-0.34860000	Н	-3.41653900	-0.53038800	-1.10311200	Н	3.18185200	1.76275600	0.13943300
Н	3.41649300	-0.53045300	-1.10316500	Н	-2.49875700	2.04382000	-0.34855900	Н	3.80653800	-0.97376600	0.10409900
Н	2.42437400	-1.96988400	-0.77673600	Н	-0.92944900	2.21414800	0.48533700	Н	2.52413600	-2.19589200	-0.07025000
Н	3.12845400	-1.04383700	0.59366400	Н	-2.29053600	1.36501900	1.30180300	Н	2.60180100	-1.19302800	1.41949700
Н	0.72878400	-1.58713800	1.27183000	Н	-0.10413300	0.01509800	1.70417800	Н	-0.10259600	-1.45340200	-0.16251000
Н	0.10412800	0.01517000	1.70418300	Н	-0.72877800	-1.58719800	1.27176200	Н	0.10791400	-0.38499200	1.24197000

HF= -745.6976345	
Zero-Point Correction= 0.1585635	

HF= -745.6976345 Zero-Point Correction= 0.1585636 HF= -745.6973897 Zero-Point Correction= 0.158543

(13')



С	2.42855300	0.09925900	0.00785800
С	-0.05300600	-0.42248800	0.15174800
С	1.01945500	0.50218200	-0.41957100
0	2.57341600	-1.24210100	0.03690800
0	3.29464700	0.88398900	0.25737500
Н	-0.10809500	-0.38958400	1.24055400
Н	0.10191500	-1.45326700	-0.16745900
Н	1.00225800	0.47701800	-1.51352500
Н	0.88737800	1.53613900	-0.10518300
Н	3.49462300	-1.44338100	0.27449000
С	-2.14369300	1.53633500	0.38549600
S	-1.72250300	0.00276500	-0.49475100
С	-2.77422500	-1.22128400	0.34069400
Н	-1.50275200	2.32450400	-0.00491800
Н	-2.00633100	1.40756100	1.45770200
Н	-3.18149800	1.76290500	0.14511500
Н	-3.80698100	-0.97297000	0.10047800
Н	-2.60238400	-1.19725800	1.41515900
Н	-2.52509500	-2.19503900	-0.07802100

HF= -745.6973893 Zero-Point Correction= 0.1585435

TS_{10'-19}



С	-2.61439300	-0.00000300	-0.06853600
С	-0.67279400	0.00002000	0.62329700
С	-1.30838000	-0.00002400	-0.77079300
0	-2.29294600	0.00003500	1.15329700
0	-3.80606100	-0.00001800	-0.53887700
Н	-0.28181500	-0.91790800	1.03383000
Н	-0.28181600	0.91797300	1.03377300
Н	-1.12635200	0.88850800	-1.37472700
Н	-1.12635100	-0.88859400	-1.37467300
Н	-4.48857700	0.00000400	0.16091100
С	2.83254300	-1.40472300	0.25819400
S	1.98029900	-0.00001200	-0.53696000
С	2.83254200	1.40473200	0.25813700
Н	2.40218600	-2.31814900	-0.15012500
Н	2.70342800	-1.38481200	1.33987200
Н	3.89193000	-1.37271200	0.00789800
Н	3.89192900	1.37271400	0.00784200
Н	2.70342700	1.38486300	1.33981500
Н	2.40218300	2.31814100	-0.15021800

HF= -745.6406972 Zero-Point Correction= 0.155989 Freq.= -199.618cm⁻¹



С	-2.61439300	-0.00000300	-0.06853600	С	1.69006600	0.33604000	0.16623500
C	-0.67279400	0.00002000	0.62329700	С	3.45699500	-0.55224500	-0.29964400
Ċ	-1 30838000	-0 00002400	-0 77079300	С	3.11611000	0.74022000	0.46024500
0	-2 29294600	0 00003500	1 15329700	0	1.99424000	-0.79131000	-0.49224300
õ	-3 80606100	-0 00001800	-0 53887700	0	0.58032100	0.76864800	0.38113500
н	-0 28181500	-0.91790800	1 03383000	Н	3.93748400	-0.44182600	-1.26722000
н	-0.28181600	0.01707300	1.000000000	Н	3.88548300	-1.36548800	0.27856300
н	-1 12635200	0.88850800	-1 37472700	Н	3.36295500	0.76059700	1.52064200
н	-1 12635100	-0.88859400	-1 37467300	Н	3.41897400	1.67541100	-0.00819700
н	-1.12000100	0.00000400	0 16001100	Н	-0.82533000	0.11948900	-0.20582900
C	2 8325/300	-1 40472300	0.10091100	С	-2.95473500	1.32326000	-0.09607200
ŝ	1 08020000	-0.00001200	-0.53696000	S	-2.13482800	-0.23752100	-0.56571700
0	2 83254200	1 40473200	0.25813700	С	-2.50304600	-1.33764700	0.84165300
с ц	2.03234200	2 2181/000	0.25015700	Н	-2.66336000	2.06292400	-0.83971100
	2.40210000	1 20401200	1 22097200	Н	-2.63877200	1.62632100	0.89883800
	2.70342000	1 27271200	1.33907200	Н	-4.02877500	1.15568400	-0.14210800
	3.09193000	-1.37271200	0.00704200	н	-3.56572800	-1.56851800	0.80741700
н	3.89192900	1.37271400	0.00784200	H	-2.23085300	-0.85450000	1.77676000
н	2.70342700	1.38486300	1.33981500	Н	-1 92365200	-2 24623200	0 68669200
н	2.40218300	2.31814100	-0.15021800			2.2.020200	0.00000200

HF= -745.641139 Zero-Point Correction= 0.1567481

HF= -745.6743372 Zero-Point Correction= 0.1550535

Figure S9: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for ion-molecule complexes IMC relevant to fragmentation of [DMSP+H]+.

	(CH ₃) ₂ S			(Cł	$H_2)_2 CO($)H+		(CH	l ₃)₂S⁺H		
									-0		
C S C H H	-1.39434100 0.00000000 1.39434200 -2.30706700 -1.37916200	0.51356600 -0.65968900 0.51356500 -0.08160200 1.13902800	0.00000300 0.0000200 0.0000300 -0.0028400 -0.89337500	C C C O O	0.49743100 -0.59846200 -1.48376200 -0.18543900 1.76221200	0.05461000 1.05231600 -0.21614500 -1.03273700 0.14678800	0.00000100 0.0000200 -0.0000300 -0.0000300 0.0000300	8 H C C H	0.0000000 0.0000000 -1.44021500 1.44021500 -1.33049700	-0.59327000 -1.07486600 0.52255000 0.52255000 1.18645400	-0.10337200 1.15892800 0.02617300 0.02617300 0.87969200
Н	-1.37948800	1.13869300	0.89362000	Ĥ	-0.63697400	1.67791500	-0.89264500	н	-2.31863600	-0.11423600	0.12121400
Н	1.37949100	1.13868700	0.89362300	Н	-0.63697600	1.67790900	0.89265300	Н	-1.48368200	1.07607600	-0.91043800

HF= -478.0713683
Zero-Point Correction= 0.0752424

1.37915800 1.13903200 -0.89337100

2.30706900 -0.08160000 -0.00029100

Н

Н

HF= -267.555646 Zero-Point Correction= 0.0808696

-2.02941900 -0.44870600 0.90821700

-2.02941600 -0.44870000 -0.90822500

2.22736000 -0.71551200 0.00000100

Н

Н

н

н

Н

н

HF= -478.3974031 Zero-Point Correction= 0.0858231

1.48368200 1.07607700 -0.91043700

2.31863600 -0.11423600 0.12121300

1.33049800 1.18645400 0.87969200

 $(CH_2)_2CO_2$



С	-0.62855000	0.02767200	-0.00000100
С	0.49253300	1.06503700	-0.00000200
С	1.40900200	-0.16493600	0.00000300
0	0.23039100	-1.04657600	0.00000300
0	-1.81483100	0.01040800	-0.00000300
Н	0.51630400	1.68915100	0.89191000
Н	0.51630700	1.68914600	-0.89191800
Н	2.00250200	-0.32779700	-0.89748000
Н	2.00249900	-0.32779200	0.89748900

HF= -267.2431781 Zero-Point Correction= 0.0683939

DMSP

DMSA





Н	-2.28367000	-1.87013900	-0.49390200
0	1.66042500	1.06815600	-0.56657400
S	-1.05344100	0.08387600	-0.48155300
Н	-3.22578600	-0.62390000	-0.14721400
Н	0.42024100	-1.69204000	-0.22426100
С	-2.35376600	-1.03858800	0.01993500
С	1.62428400	-0.02626800	-0.05559600
Н	3.33332900	-0.29557600	0.28098900
С	0.35446100	-0.79812800	0.19619900
0	2.66566100	-0.70714500	0.37372200
Н	-2.13034200	1.88701800	0.47858000
Н	-0.54385300	2.06167300	0.59602200
С	-1.28730000	1.42822400	0.67652400
Н	-2.26398700	-1.23647100	0.97561900
Н	0.22991400	-0.92420900	1.17029900
Н	-1.31555800	1.07209700	1.58916200

Н	-1.92762100	-1.80191200	1.29792000
Н	-2.93653100	-0.63528100	1.57829400
С	-2.05727600	-0.85149500	1.25938600
Н	-1.40145700	-0.41656000	1.80931900
Н	0.12516300	-1.41520700	-0.51354000
S	-1.88299500	-0.29648500	-0.42317100
С	-0.11029700	-0.49215700	-0.69654600
Н	0.07247300	-0.32705600	-1.63471500
Н	-3.02885800	1.60890600	0.11470500
0	2.62003700	-1.03468800	-0.47713100
С	-2.15532600	1.45525500	-0.25252500
Н	0.52148300	0.36005400	1.05662600
С	0.79422500	0.39981300	0.12665100
Н	-2.09198000	1.87438800	-1.11391400
С	2.22896800	-0.00542200	0.01658500
Н	-1.49189900	1.82666500	0.33352300
Н	0.69753700	1.31705100	-0.17370000
Н	4.09110400	0.47111200	0.60445700
0	3.04205600	0.89039200	0.56343700

Figure S11: B3LYP/6-311++G(2d,p) calculated Cartesian coordinates and energies (Hartrees) for X-ray crystallography structures.