A combination of experimental and theoretical methods in evaluating triazole derivatives' mild steel corrosion inhibition ability in an acidic solution

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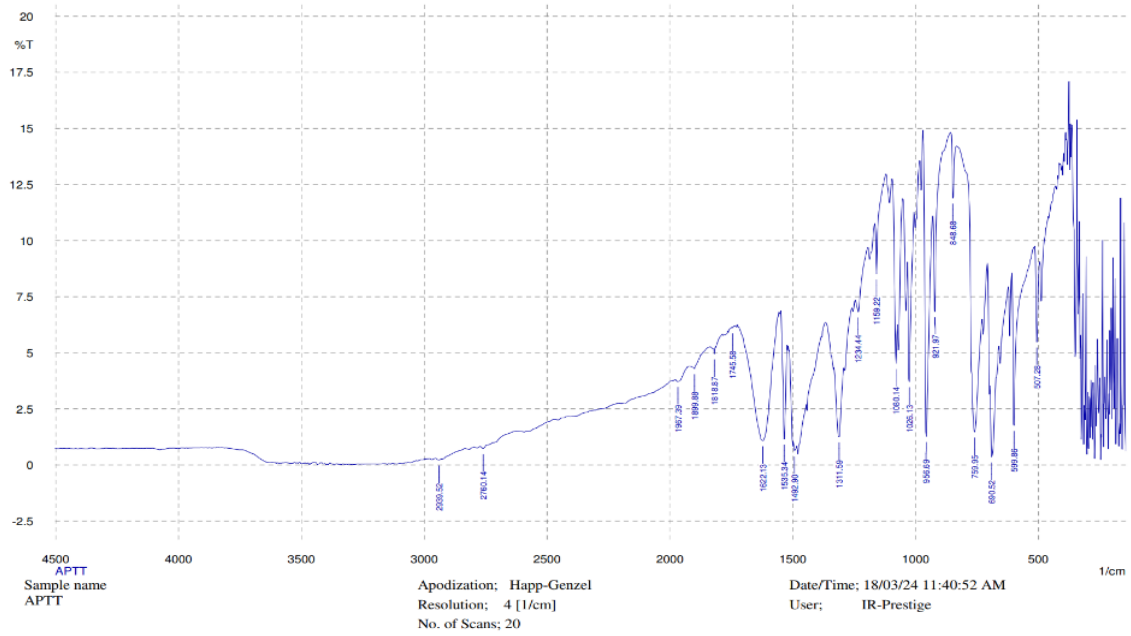
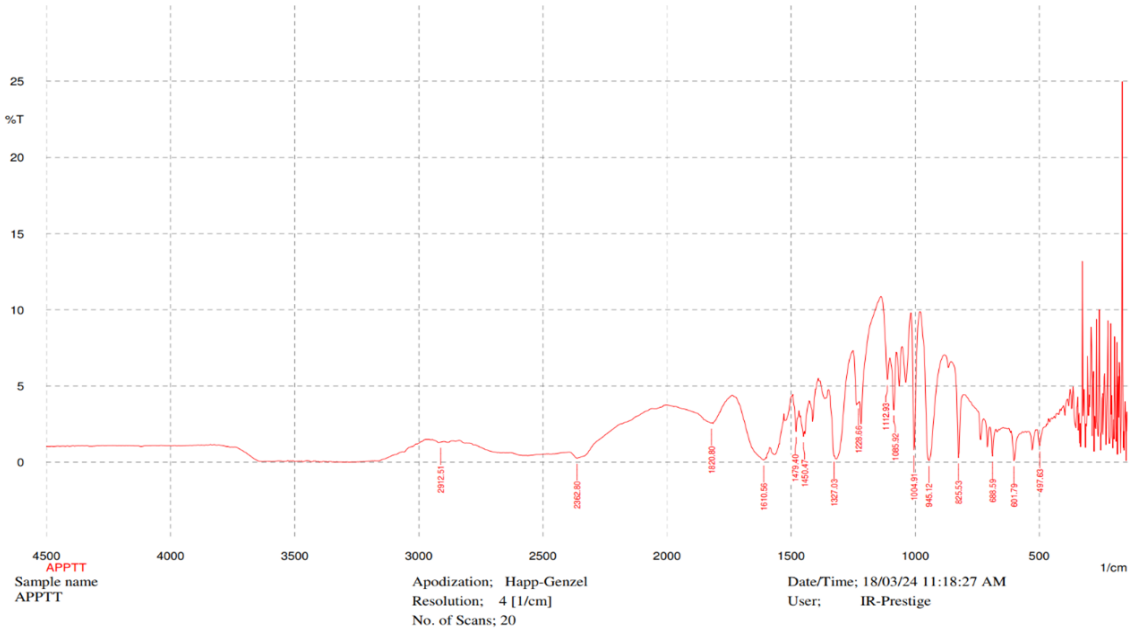
List of supporting information



(a) AT



b. AP

Figure S1. IR spectra of (a) AT and (b) AP

Table S1. Details of equivalent circuit models using Thales 4.5 sofware

To accurately match the impedance lines before and after the addition of inhibitors, an equivalent circuit model was employed by using Thales 4.5 software. When inhibitors are introduced into the solution, the composition and structure of the electrical double layer on the surface of mild steel undergo modifications. CPE is used in place of a double-layer capacitance (C_{dl}) to give a more accurate fit to the experimental results.The impedance of a CPE can be calculated as shown in equation (1'):

$$Z_{CPE} = Y_o^{-1}.(j\omega)^{-n} \quad (1')$$

Where Y_o, ω, j and n correspond to constant of CPE, angular frequency, imaginary number, and empirical exponent that reflects towards surface heterogeneity, respectively. CPE values are used for the estimation of double layer capacitance (C_{dl}) and are given as follows:

$$C_{dl} = Y_o.(\omega_{max})^{n-1} \quad (2')$$

In equation (2'):

$$\omega_{max} = 2\pi f_{max} \quad (3')$$

f_{max} represents the maximum impedance value ($-Z_{im}$) at the imaginary axis.

Table S2. Details of Temkin and Langmuir adsorption isotherm models

Adsorption isotherm models play a crucial role in understanding the interaction between the mild steel surface and the solution, particularly in characterizing the adsorption behavior of inhibitors on the metal surface. Various adsorption isotherms, such as Temkin, Frumkin, Freundlich, Langmuir, and Flory-Huggins, have been widely employed. Among them, two adsorption isotherm models, namely Temkin and Langmuir, were investigated in this study to examine the adsorption of AT and AP on mild steel surfaces.

In the Temkin model, the adsorbed inhibitor molecules do not interact with each other and the free energy of their position on the surface depends on the surface coverage (θ). θ is determined using Equation (4'):

$$\theta = \frac{H\%}{100} \quad (4')$$

In which H% is the corrosion inhibition efficiency obtained from the PP method.

The Temkin adsorption isotherm is described by Equation (5'), where a represents the adsorbate interaction parameter:

$$\ln K \times C = a \times \theta \quad (5')$$

The study also explores the Langmuir adsorption isotherm, which assumes that each adsorbate occupies only one position on the mild steel surface and the surface free energy remains constant at all substrate positions. The Langmuir adsorption isotherm model is mathematically represented by Equation (6'):

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (6')$$

In which, K is adsorption constant, C is inhibitor concentration.

Table S3 Detailed calculations of thermodynamic quantities

The relationship between adsorption constant (K) and adsorption-free energy (ΔG^o) can be expressed using Equation (7'), where 55.5 represents the molar concentration of water in the solution (M), and T denotes the temperature under investigation (K).

$$\Delta G^o = -R \times T \times \ln(55.5 \times K) \quad (7')$$

From the equation indicating the relationship between lnK and 1/T, adsorption enthalpy values (ΔH^o) are determined. Additionally, the adsorption entropy (ΔS^o) values are calculated from the obtained ΔH^o and corresponding ΔG^o using Equation (8'):

$$\Delta G^o = \Delta H^o - T \times \Delta S^o \quad (8')$$

In equation (8'), R denotes the gas constant with a value of 8.314 $J.mol^{-1}K^{-1}$.

Table S4. Optimized structure of AT and AP in gas phase using B3LYP/6-311++G(d,p).

Stable α-form (AT)			**$C_8H_8N_4S$**
0 1			
N	1.12077900	0.42538400	0.05243000
N	0.54130000	-1.66944900	-0.22283600
N	1.91039400	-1.61613500	-0.20056000
N	1.05390400	1.81045300	0.25597700
C	0.06322100	-0.44704900	-0.07419700
C	-1.37397200	-0.14085900	-0.02824300
C	-2.25360100	-1.20466900	0.23318700
C	-1.90221200	1.13583200	-0.26804300
C	2.25421200	-0.36813900	-0.02162900
C	-3.62639900	-0.99253200	0.25855600
C	-3.28017200	1.33899500	-0.24203100
C	-4.14621600	0.28061000	0.02213900

H	-1.84265700	-2.19043600	0.40891600
H	-1.23788100	1.96305900	-0.47054300
H	-4.29269400	-1.82268000	0.46400700
H	-3.67614700	2.33021200	-0.43251400
H	-5.21772000	0.44477600	0.04292700
S	3.89984900	0.27008500	-0.04154100
H	4.03369000	0.42296600	1.29571900
H	1.75040300	2.24925900	-0.34057800
H	1.29160800	2.01657600	1.22321500

Stable β-form (AT)	**$C_8H_8N_4S$**

0 1			
N	1.14530500	0.44048200	0.05177300
N	0.54044600	-1.66351000	-0.20280100
N	1.90052400	-1.53686400	-0.17798200
N	1.07140000	1.82336900	0.23614400
C	0.08034600	-0.44753800	-0.06034400
C	-1.35756300	-0.14309600	-0.01812800
C	-2.24385700	-1.20585500	0.22605600
C	-1.87618200	1.13939400	-0.24457500
C	2.34006900	-0.26573600	-0.02532500
C	-3.61519300	-0.98832200	0.24031700
C	-3.25378900	1.34742300	-0.22941800
C	-4.12671100	0.29010200	0.01223400
H	-1.84387900	-2.19623000	0.40156300
H	-1.20449700	1.96571400	-0.42275500
H	-4.28702200	-1.81706900	0.43243500

H	-3.64290600	2.34328000	-0.40842300
H	-5.19756000	0.45872100	0.02514800
S	3.88958000	0.34465200	0.04859800
H	1.71954600	2.24227700	-0.43048900
H	1.44720700	2.03266300	1.16035700
H	2.48939400	-2.34635100	-0.29025000

Stable α-form (AP)	**$C_7H_7N_5S$**

0 1			
N	1.11923500	0.43004800	0.03636000
N	0.53003000	-1.67361300	-0.13378800
N	1.89729800	-1.62569100	-0.12118400
N	1.05740100	1.82510300	0.15513500
C	0.05888400	-0.44378300	-0.04355600
C	-1.37819600	-0.13657100	-0.01774600
C	-2.27511100	-1.20114700	0.15192900
C	-1.91870900	1.14461900	-0.17590400
C	2.24782600	-0.37063400	-0.00552600
C	-3.63882500	-0.93713700	0.15942500
C	-3.30428300	1.29312200	-0.15215300
H	-1.90217900	-2.20964800	0.27149700
H	-1.28112600	2.00504500	-0.31232000
H	-4.34791600	-1.74915000	0.29130500
H	-3.74191500	2.28004500	-0.27428100
S	3.89692400	0.25607500	-0.06164000
H	4.03089000	0.47644600	1.26599700
H	1.72477000	2.22731000	-0.49795800

H	1.33620000	2.09150100	1.09620500
N	-4.16382200	0.28564400	0.01304500
Stable β-form (AP)			**$C_7H_7N_5S$**
0 1			
N	1.14365800	0.44672000	0.02463600
N	0.53057500	-1.66691000	-0.09347600
N	1.88748600	-1.54681800	-0.08442200
N	1.07548700	1.83904800	0.11235900
C	0.07658900	-0.44280200	-0.02697500
C	-1.36217200	-0.13922200	-0.00919800
C	-2.26608600	-1.20535000	0.11047900
C	-1.89262500	1.15011000	-0.12048600
C	2.33595100	-0.26866200	-0.01225000
C	-3.62775100	-0.93478600	0.11198900
C	-3.27854500	1.30426400	-0.10734900
H	-1.90569300	-2.22151500	0.20012600
H	-1.24643000	2.00996400	-0.20888900
H	-4.34237600	-1.74730200	0.20451200
H	-3.70926100	2.29778700	-0.19328800
S	3.88652400	0.33391000	0.02170400
H	1.66203600	2.21357000	-0.63294000
H	1.52320800	2.11338000	0.98624800
H	2.47195300	-2.36598800	-0.13740000
N	-4.14434700	0.29599400	0.00620300

Table S5. Optimized structures of protonated AT and AP in gas phase using B3LYP/6-311G(d,p)

pAT-N1			**$[C_8H_9N_4S]^+$**
1 1			
N	-1.09848800	-0.55859700	-0.11110600
N	-0.57183900	1.65271400	0.09083600
N	-1.93705500	1.51529900	0.02993000
N	-1.03103600	-1.59107400	0.89804500
C	-0.02206700	0.49628200	0.00913000
C	1.38821400	0.17504700	-0.01725900
C	2.30981000	1.22889100	0.15616600
C	1.85539700	-1.13232900	-0.24725100
C	-2.42057000	0.27358400	-0.12382200
C	3.66882200	0.96942700	0.09910800
C	3.22172300	-1.37546700	-0.30720700
C	4.12810200	-0.33020400	-0.13459700
H	1.94958300	2.23467200	0.33115300
H	1.16754800	-1.96109200	-0.35495900
H	4.37524200	1.77910800	0.23467500
H	3.57910900	-2.38216300	-0.48487100
H	5.19277700	-0.52627300	-0.17967000
S	-3.88378200	-0.38762600	-0.26386600
H	-1.92342200	-2.09023000	0.84722600
H	-0.97993700	-1.12478200	1.80375500
H	-2.50826100	2.34931800	0.08113100
H	-1.01980700	-1.03633100	-1.01613200
pAT-N2			**$[C_8H_9N_4S]^+$**
1 1			

N	-1.12086100	-0.45132900	0.10329700
N	-0.59356400	1.58088100	-0.35176700
N	-1.96951100	1.54568800	-0.18256100
N	-0.99882400	-1.81184800	0.37041000
C	-0.07066500	0.38208100	-0.09477000
C	1.35531800	0.11959200	-0.02718500
C	2.21661700	1.16178200	0.37111200
C	1.88859700	-1.12903400	-0.39380100
C	-2.36592700	0.23743000	-0.00749800
C	3.58749400	0.95629100	0.39540400
C	3.26476400	-1.31533100	-0.37743900
C	4.11294100	-0.28035900	0.01533200
H	1.82267200	2.11437300	0.70887400
H	1.23380800	-1.93433600	-0.69086200
H	4.24565400	1.75280100	0.71944900
H	3.67632500	-2.27309400	-0.67091400
H	5.18482500	-0.43796500	0.03315400
S	-3.85834700	-0.40284900	0.06677700
H	-1.62390600	-2.30803500	-0.26442700
H	-1.32849300	-1.98409400	1.31945100
H	-2.53804300	2.21838200	-0.68367700
H	-0.09479400	2.45909200	-0.40205800

pAT-N3			**$[C_8H_9N_4S]^+$**
1 1			
N	1.12039100	0.47474900	0.04807500
N	0.48380700	-1.66523800	-0.30980000

N	1.93876200	-1.56785700	-0.27186200
N	0.95518200	1.83344300	0.30976500
C	0.05962200	-0.44947200	-0.10733800
C	-1.36102600	-0.13961700	-0.02946000
C	-2.22809600	-1.18863600	0.33910000
C	-1.89144500	1.11878200	-0.36822100
C	2.34126300	-0.13187100	-0.02118200
C	-3.59649100	-0.97383200	0.38021200
C	-3.26646900	1.31374800	-0.33748900
C	-4.11802800	0.27623300	0.03999400
H	-1.82011800	-2.15640500	0.60057100
H	-1.24108300	1.92925900	-0.65743800
H	-4.25825200	-1.77792700	0.67756000
H	-3.67413500	2.27991400	-0.60828800
H	-5.18875200	0.44071600	0.07020800
S	3.85219600	0.40582000	0.11625300
H	1.55257400	2.36284800	-0.32208100
H	1.23575300	2.03022500	1.26903100
H	2.31281100	-2.17612700	0.46710100
H	2.32308800	-1.90331000	-1.16365200

pAT-N4	**$[C_8H_9N_4S]^+$**

1 1			
N	1.10580300	0.35421300	-0.04358500
N	0.56155700	-1.72763700	-0.42835900
N	1.92850000	-1.57218500	-0.37619600
N	1.17936600	1.65708400	0.46322000

C	0.04616400	-0.55919300	-0.19213000
C	-1.37036200	-0.22073200	-0.09023000
C	-2.24591000	-1.13622100	0.51148200
C	-1.86610300	0.98741500	-0.60614300
C	2.32991100	-0.32244600	-0.10767800
C	-3.59959000	-0.83418100	0.60539300
C	-3.22177400	1.28055900	-0.50667100
C	-4.08724100	0.37244000	0.10350300
H	-1.86074600	-2.07032900	0.90107700
H	-1.21840100	1.67010400	-1.14824100
H	-4.27485600	-1.54098800	1.07194000
H	-3.60612500	2.20429100	-0.92171800
H	-5.14338700	0.60198400	0.17857700
S	3.77434600	0.45545400	0.19359600
H	2.31035000	1.72318400	0.56062900
H	0.71178800	1.75473400	1.37183000
H	2.52482900	-2.37446100	-0.52620000
H	0.82986700	2.35805800	-0.19614200

pAT-S18	**$[C_8H_9N_4S]^+$**

1 1			
N	1.10587600	0.43002000	0.05756900
N	0.50784200	-1.66299600	-0.32386700
N	1.86650600	-1.53492300	-0.26974200
N	1.00405700	1.78622700	0.34624300
C	0.03029500	-0.45972600	-0.11399600
C	-1.39388400	-0.14833500	-0.04117300

C	-2.26223800	-1.18488600	0.34503900
C	-1.91718200	1.10721700	-0.38828300
C	2.25559500	-0.28732300	-0.04637100
C	-3.63117600	-0.96117900	0.39040800
C	-3.29093300	1.31578700	-0.34580400
C	-4.14781200	0.28814300	0.04529500
H	-1.85831200	-2.15328400	0.61159000
H	-1.26488400	1.91115300	-0.69527300
H	-4.29544600	-1.76027100	0.69596700
H	-3.69297400	2.28301900	-0.62167100
H	-5.21715300	0.45981800	0.08018700
S	3.83352600	0.42787400	0.11273000
H	1.47525200	2.35003100	-0.35413900
H	1.32540800	1.98968300	1.28769900
H	2.44111200	-2.35347900	-0.42201300
H	4.50463400	-0.71913500	-0.12812200

pAP-N1			**$[C_7H_8N_5S]^+$**
1 1			
N	1.09649200	0.56290100	-0.11933000
N	0.56572400	-1.64183600	0.11270500
N	1.92801200	-1.51663800	0.04879700
N	1.02442600	1.61254200	0.87080900
C	0.02194800	-0.48703800	0.01672500
C	-1.39659300	-0.17153800	-0.01601600
C	-2.32223700	-1.21507600	0.14832700
C	-1.87870600	1.12518300	-0.23995700

C	2.41907000	-0.27550700	-0.11988200
C	-3.67536000	-0.90710900	0.07996400
C	-3.25931000	1.31256600	-0.29298600
H	-1.99485000	-2.23208700	0.32043300
H	-1.22133600	1.97800100	-0.34544900
H	-4.41869100	-1.68783200	0.20344400
H	-3.66642900	2.30373500	-0.46497600
S	3.88324200	0.37290100	-0.26623400
H	1.90024100	2.13632200	0.79238500
H	1.00303800	1.16546100	1.78748100
H	2.49413600	-2.35367200	0.11392400
N	-4.14309800	0.32722000	-0.13750200
H	1.01825800	1.02544700	-1.03290600

pAP-N2	**$[C_7H_8N_5S]^+$**

1 1			
N	-1.11206000	-0.44783200	0.11545800
N	-0.59196500	1.57912100	-0.36684800
N	-1.96680800	1.53887000	-0.21673000
N	-0.97373400	-1.80254700	0.40184900
C	-0.07226600	0.38632500	-0.09809000
C	1.36211200	0.12235400	-0.03327600
C	2.22418600	1.12739100	0.43028900
C	1.90668400	-1.09390000	-0.46049900
C	-2.36456100	0.23407100	-0.01196900
C	3.59174400	0.86757000	0.43927000
C	3.29299000	-1.23533400	-0.41714000

H	1.85774900	2.07023900	0.82042000
H	1.28343100	-1.90103700	-0.81552300
H	4.28822800	1.61574800	0.80345400
H	3.75448900	-2.15945900	-0.74941200
S	-3.85215600	-0.40926400	0.07559400
H	-1.59136500	-2.31672500	-0.22607000
H	-1.29915000	-1.96606800	1.35403000
H	-2.53811200	2.21855000	-0.70519900
N	4.11997100	-0.28450800	0.02116000
H	-0.09393200	2.45439200	-0.46693300

pAP-N3	**$[C_7H_8N_5S]^+$**

1 1			
N	1.11170900	0.47220000	0.05867400
N	0.48123000	-1.66363600	-0.33011700
N	1.93830000	-1.56433300	-0.29510000
N	0.92749700	1.82449400	0.33663600
C	0.06305700	-0.45320200	-0.11326100
C	-1.36674300	-0.14411100	-0.03784900
C	-2.23612800	-1.15963200	0.38731500
C	-1.90809600	1.08763500	-0.42585700
C	2.33916100	-0.12859700	-0.02016100
C	-3.60011800	-0.88921300	0.41687100
C	-3.29270300	1.23851600	-0.36773300
H	-1.86022000	-2.12636100	0.69544500
H	-1.28868100	1.90370600	-0.76403100
H	-4.30050900	-1.64759600	0.75112400

H	-3.74843300	2.17653200	-0.66797000
S	3.84509800	0.41291600	0.12398600
H	1.50534600	2.37340300	-0.29670100
H	1.21159400	2.01728700	1.29559700
H	2.31183000	-2.18719800	0.43214700
N	-4.12477200	0.28273400	0.04831400
H	2.31916300	-1.88500900	-1.19419500

pAP-N4	**$[C_7H_8N_5S]^+$**

1 1			
N	1.10381000	0.35318000	-0.02833200
N	0.54566200	-1.72709600	-0.40101800
N	1.91128200	-1.58212400	-0.35975300
N	1.19930000	1.66896800	0.43861100
C	0.04093500	-0.55379300	-0.17308200
C	-1.38013600	-0.21549700	-0.08485100
C	-2.26750000	-1.11761100	0.50862900
C	-1.88492300	0.98576600	-0.59693200
C	2.32243400	-0.33209500	-0.10142900
C	-3.61497300	-0.76695300	0.57288000
C	-3.25149300	1.23298100	-0.47762400
H	-1.91874200	-2.06010700	0.91090200
H	-1.26398100	1.69244600	-1.13774900
H	-4.33253000	-1.44129700	1.02899600
H	-3.67903800	2.14863200	-0.87404300
S	3.77168100	0.44429400	0.17570300
H	2.34669600	1.71392100	0.51565500

H	0.75235500	1.80090900	1.35288200
H	2.50060700	-2.39020000	-0.50927300
N	-4.10150600	0.38335500	0.10076000
H	0.85183100	2.35622200	-0.23604900

pAP-N20			**$[C_7H_8N_5S]^+$**
1 1			
N	1.18502000	0.46983000	-0.00005400
N	0.57116500	-1.65267000	-0.00007300
N	1.90389900	-1.54772800	-0.00006500
N	1.10685400	1.86373600	0.00015600
C	0.12101000	-0.41756200	-0.00003500
C	-1.30375400	-0.14297700	-0.00002100
C	-2.20084600	-1.23617100	0.00008600
C	-1.84226800	1.16096600	-0.00010600
C	2.37995400	-0.25441200	-0.00003800
C	-3.55294800	-1.01217400	0.00010400
C	-3.20681400	1.33292100	-0.00008800
H	-1.82560000	-2.25010400	0.00014300
H	-1.18786500	2.02053200	-0.00019000
H	-4.28700900	-1.80621100	0.00017600
H	-3.67850400	2.30629400	-0.00015400
S	3.92204800	0.31022800	0.00003200
H	1.61761800	2.20202600	-0.81599400
H	1.61801400	2.20177400	0.81616800
H	2.48345300	-2.37672000	-0.00004700
N	-4.02801100	0.25932500	0.00002900

H	-5.03136500	0.40777000	0.00002700

pAP-S16			**$[C_7H_8N_5S]^+$**
1 1			
N	1.10087000	0.42998000	0.05758900
N	0.50273300	-1.66375300	-0.31440000
N	1.86053800	-1.53637800	-0.26702600
N	0.99141500	1.78828600	0.33372500
C	0.03007600	-0.46101200	-0.11014400
C	-1.39958800	-0.14883400	-0.04275000
C	-2.27628000	-1.16677800	0.35475800
C	-1.93370000	1.09401700	-0.39870900
C	2.25123200	-0.28701000	-0.04552600
C	-3.63958900	-0.88999300	0.38371200
C	-3.31679300	1.25552300	-0.33561200
H	-1.90711900	-2.14398300	0.63755000
H	-1.31029100	1.91532300	-0.71861500
H	-4.34487000	-1.65512400	0.69166900
H	-3.76448000	2.20570400	-0.60909500
S	3.82790500	0.42771900	0.11138300
H	1.46062500	2.34803200	-0.37152200
H	1.31080400	2.00214200	1.27375700
H	2.43431000	-2.35660800	-0.41637700
N	-4.15793600	0.29446800	0.04867700
H	4.49905900	-0.72269900	-0.11382500