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and c,t-), 1.5 ml of diazene stock solution (10 mg, 0.036 mmol, 0.024 M) was rapidly transferred via a gas tight syringe to each tube at -78 °C. The tubes were degassed, sealed and each tube was photolyzed at 313 nm, -15 °C for one hour. At lower than -15 °C, the xanthone solidified and floated around. To maintain homogeneous solution, the proper temperature control was important. The tube was opened and capped with rubber septum quickly at -78 °C. To quench the reaction, freshly recrystallized 1 ml maleic anhydride solution (0.88 mmol, 86.24 mg/1ml CH<sub>2</sub>Cl<sub>2</sub>) was added and left at r.t. for 5 h.. The mixture was analyzed by HPLC and the peaks were compared with the authentic sample's. The results are listed in Table S-5.

**Table S-5.** Percentage of trapped product from HPLC analysis.

Trap	% c,c-trapped	% c,t-trapped
c,c-diene	87.3	12.7
c,t-diene	0	100

It seemed that there is no loss of stereospecificity in the adduct. Since c,c-hexadiene itself contained 3 % c,t-hexadiene and c,t-hexadiene reacts faster than c,c-hexadiene, it is no surprise that 13 % c,t-trapped product was formed and essentially there was no stereoscrumbling.

**Trapping of Biradical 3f Generated by Xanthone-Photosensitized Photolysis of Diazene 17f at 313 nm with Maleonitrile (MN) at Low Conversion.**

A solution of diazene **17f** (0.02625mmol, 3.5 ml 7.5mM) in methylene chloride, xanthone (100mg, 0.51mmol) and MN (11mg, 0.14mmol) was degassed and sealed in a square quartz tube equipped with a Pyrex extension. The sample was photolysed with 313nm light for 35 minutes at -20-30°C. The tube was opened at -78°C and treated with maleic anhydride 55mg, (0.56mmol, 0.5ml 1.12M) under nitrogen. The reaction mixture was allowed to warm to room temperature, and the product was analyzed by HPLC (20% EtOAc in hexane) and identified by comparison with the retention times of the pure trapping products, obtained by thermolyses of diazene with MN. Only cis products were observed. The ratio was bridged **28f-cis**/fused **27f-cis,endo** = 56/44. GC analyses of recovered maleonitrile indicated that MN/FN = 98.6/1.36.

**Xanthone-Photosensitized Photolysis of Diazene 17f at 313nm with Maleonitrile (MN) at Higher Conversion.**

A solution of diazene **17f** (0.016mmol, 2ml 8mM) in methylene chloride, xanthone (65mg, 0.33mmol) and MN (6.2mg, 0.08mmol) was degassed and sealed in a square quartz tube equipped with a Pyrex extension. The sample was photolysed with 313nm light for 60 minutes at -20,-30°C. The tube was opened at -78°C and treated with maleic anhydride 42mg (0.43mmol, 0.5ml 0.86M) under nitrogen. The reaction mixture was allowed to warm to room temperature, and the product was analyzed by HPLC (20% EtOAc in hexane) and identified by comparison with the retention times of the pure trapping products, obtained by thermolyses of diazene with MN. GC analyses of crude mixture showed that the ratio of MN/FN = 92.8/7.2. The ratio of trapped products observed after reaction is

**(28f-cis/27f-cis)/27f-trans** = (62/26)/12. The most likely source of the 12% of **27f-trans** is by trapping product of the biradical intermediate by FN.

**Kinetics of Thermal Reaction of Diazene 10f with maleonitrile (MN).**

An NMR sample of diazene **17f** (0.007mmol, 0.5ml 14.15mM) in CDCl<sub>3</sub> and 2mg (0.026mmol) of maleonitrile was prepared at -20°C. The sample was 52 mM in MN. The sample was placed into the NMR probe which had been cooled at 10°C. The spectrometer was programmed to collect a spectrum every 2.5 minutes. The singlet due to the diazene methylenic protons ( $\delta$  5.0ppm) was integrated for each spectrum. The plot of the natural log of those integrals vs. time gave the rate constant for diazene decomposition in the presence of MN as a trapping reagent.

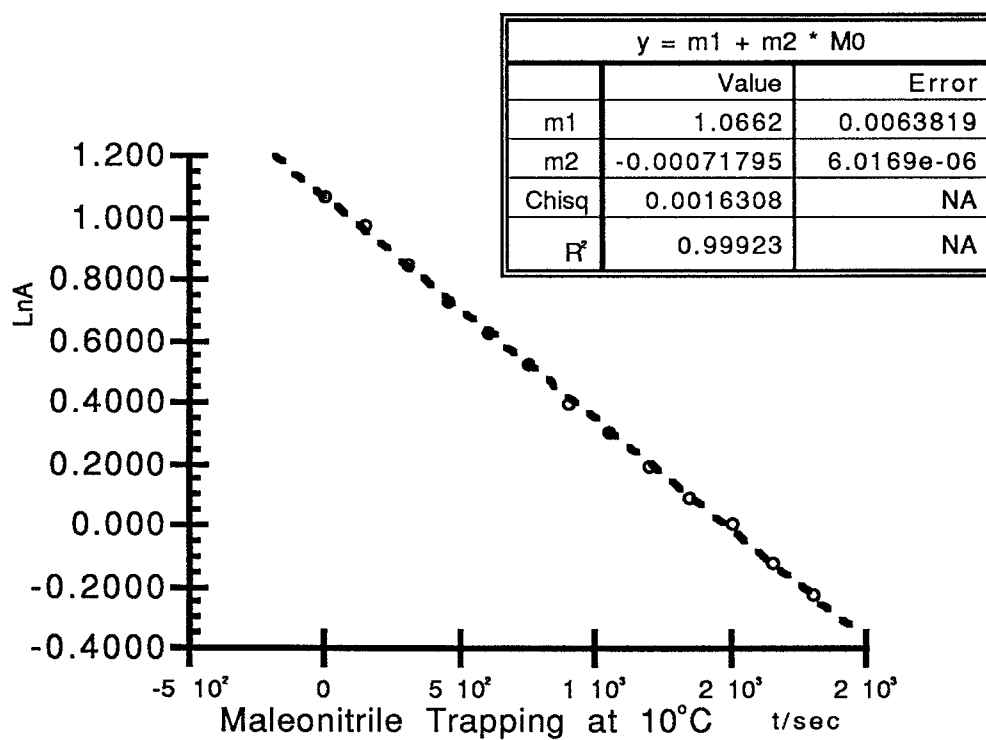
T=10°C

Time/sec	A	lnA
0	2.92	1.07
150	2.67	0.98
300	2.35	0.85
450	2.07	0.73
600	1.88	0.63
750	1.7	0.53
900	1.49	0.4
1050	1.36	0.31

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1200	1.22	0.2
1350	1.09	0.09
1500	1.01	0.01
1650	0.89	-0.12
1800	0.8	-0.22



The pseudo-first-order rate constant calculated from this data is 7.18  
 $\times 10^{-4} \text{ s}^{-1}$ .

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EXP. LM 1-141-1.

V of diazene **17f**=0.5ml; c of diazene **17f**=14.5mM in CDCl<sub>3</sub>

n of diazene **17f**=0.007mmol

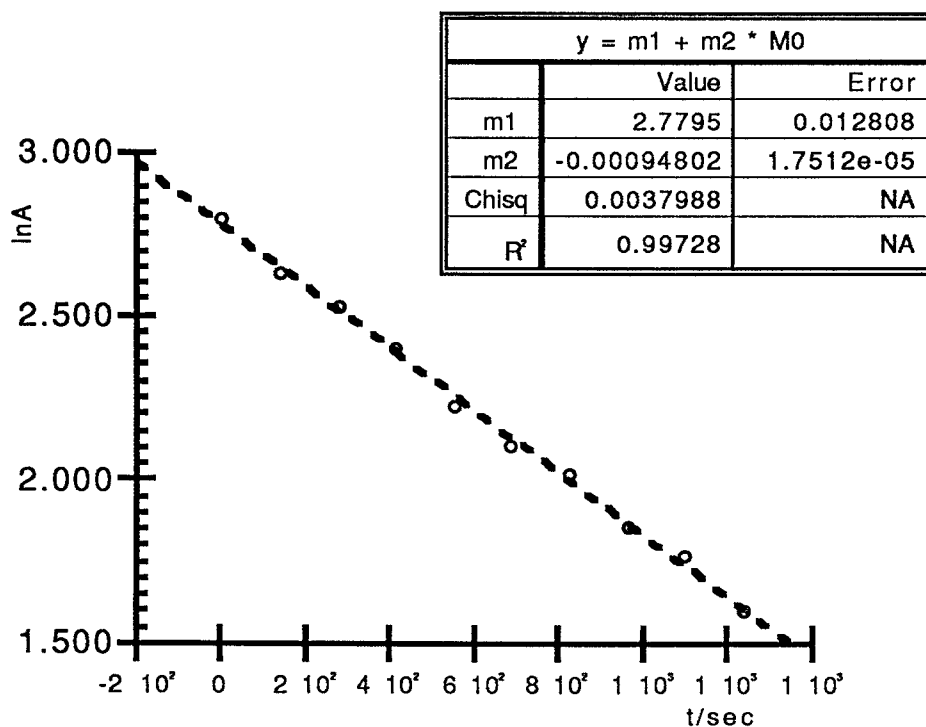
m of MN=3.9mg (0.05mmol; 100mM)

T=10°C

Time/sec	A	lnA
0	16.5	2.8
137	13.91	2.63
274	12.5	2.53
411	11.02	2.4
548	9.32	2.23
685	8.23	2.11
822	7.55	2.02
959	6.43	1.86
1096	5.87	1.77
1233	4.97	1.60

## Supporting Information

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EXP. LM 1-140-1.

V of diazene **17f**=0.5ml; c of diazene **17f**=14.5mM in CDCl<sub>3</sub>

n of diazene **17f**=0.007mmol

m of MN=1mg (0.013mmol; 26mM)

T=10°C

Time/sec	A	ln A
0	15.03	2.71
137	13.28	2.59

## Supporting Information

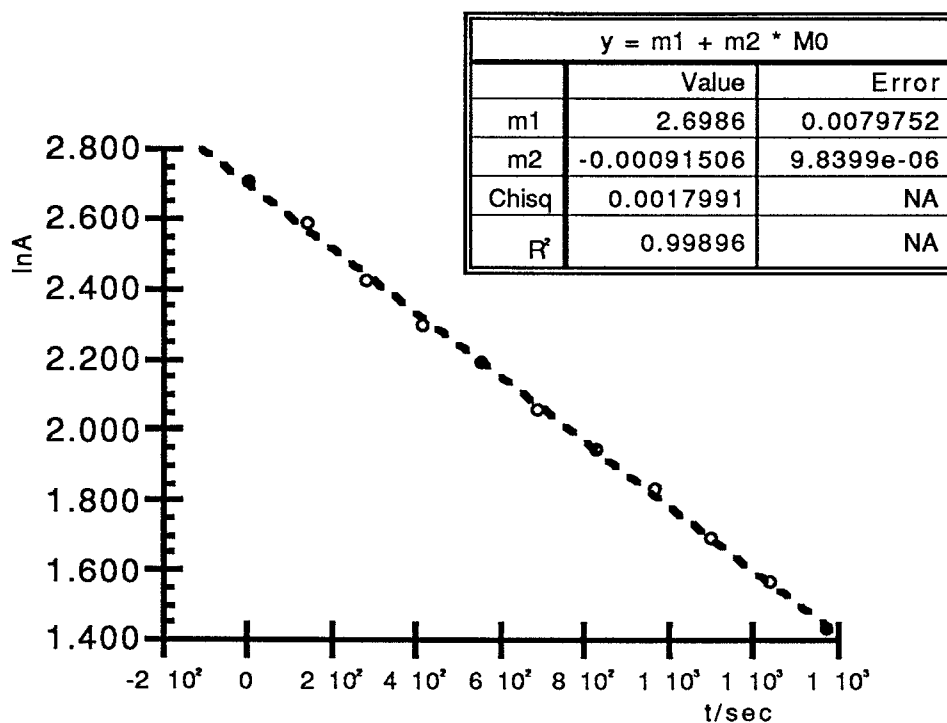
47

274	11.31	2.43
411	9.95	2.30
548	9.05	2.20
685	7.88	2.06
822	7.02	1.95
959	6.28	1.84
1096	5.48	1.70
1233	4.82	1.57
1370	4.23	1.44



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EXP. LM 1-139-1.V of diazene **17f**=0.5ml; c of diazene **17f**=14.5mM in CDCl<sub>3</sub>n of diazene **17f**=0.007mmol

m of MN=0g

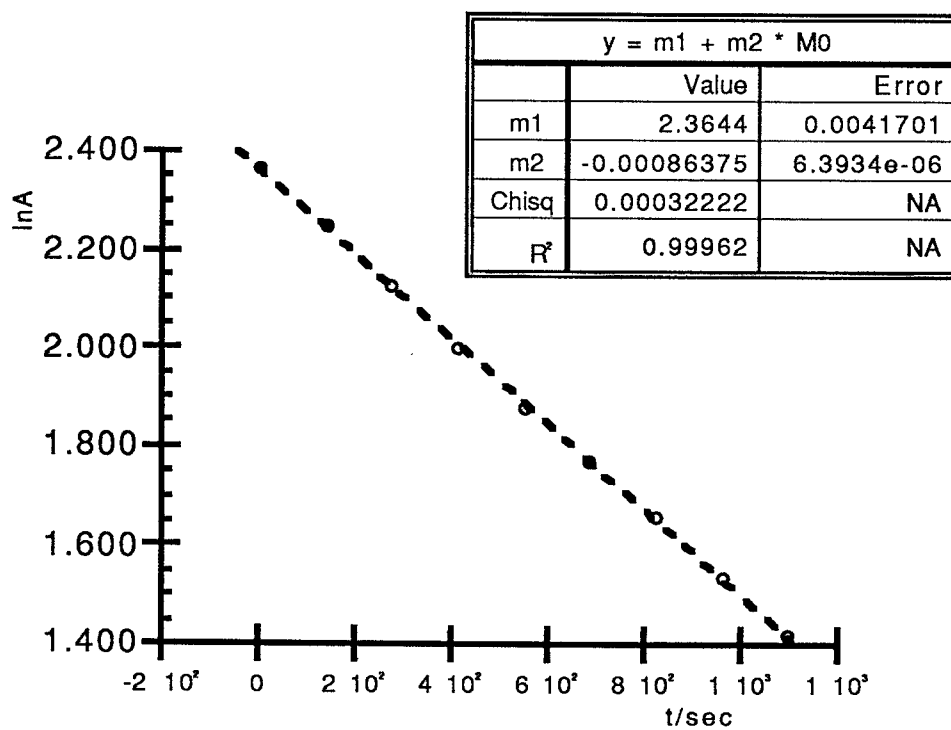
T=10°C

Time/sec	A	lnA
0	10.71	2.37
137	9.49	2.25

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274	8.4	2.13
411	7.41	2.00
548	6.54	1.88
685	5.89	1.77
822	5.24	1.66
959	4.65	1.54
1096	4.13	1.42



**Results of Kinetic Study**

Exp.	m MN/mg (c/mM)	k/mM <sup>-1</sup> s
1	0	8.6x10 <sup>-4</sup> *
2	1 (26)	9.2x10 <sup>-4</sup> *
3	2 (59)	7.2x10 <sup>-4</sup>
4	3.9 (100)	9.5x10 <sup>-4</sup> *

\* Experiments were done on the same day.

**Xanthone-Photosensitized Photolysis of Diazene 17f at 313nm with Maleonitrile (MN) at Low Conversion.**

A solution of diazene **17f** (0.02625mmol, 3.5 ml 7.5mM) in methylene chloride, xanthone (100mg, 0.51mmol) and MN (11mg, 0.14mmol) was degassed and sealed in a square quartz tube equipped with a Pyrex extension. The sample was photolysed with 313nm light for 35 minutes at -20-30°C. The tube was opened at -78°C and treated with maleic anhydride 55mg, (0.56mmol, 0.5ml 1.12M) under nitrogen. The reaction mixture was allowed to warm to room temperature, and the product was analyzed by HPLC (20% EtOAc in hexane) and identified by comparison with the retention times of the pure trapping products, obtained by thermolyses of diazene with MN. Only cis products were observed. The ratio was bridged **25f-cisendo** (X = X' = CN)/fused **24f-cis** (X = X' = CN) = 56/44. This ratio is essentially the same as that observed (57/43) in the trapping of thermally

generated **3f** see Table 1 of main text). GC analyses of recovered maleonitrile indicated that MN/FN = 98.6/1.36.

**Alkene Reactivity Ratios by Preparative Competition Experiments.  
Competitive Thermal Trapping (Table 3 of Main Text)**

The relative rates of thermal trapping of the diradicals **3e** and **3f** by alkenes were determined by competitive trapping experiments using procedures similar to those described previously (refs. 3b and 3d of main text). A typical photochemical run follows:

A CH<sub>2</sub>Cl<sub>2</sub> solution of diazene **3f** (0.0318 M), FN (0.122 M), and dimethyl fumarate (FE) (0.0681 M) was prepared at <-30 °C under the usual precautions to avoid thermal deazetation and irradiated at -30 °C for 50 min with monochromatic 370 nm light.

A typical thermal run was carried out as follows:

To a nitrogen purged solution of diazene **17f** (0.1125mmol, 10ml 11.25mM) in methylene chloride 17.6 mg (0.23mmol) of maleonitrile/fumaronitrile(1:1 mixture) in 2 ml of methylene chloride at -25 °C was added. The reaction mixture was allowed to warm to room temperature, and then stirred for 14 hours. The crude mixture of products was analyzed by HPLC (20% EtOAc in hexane) and identified by comparison with the retention times of pure trapping products, obtained by separate thermolyses of diazene with MN and FN. The relative percentages of the products were **24 trans** 29.1, **25 trans** 39.7, **24 cis** 28.5, **25 cis** 2.7. The overall FN:MN ratio is thus 2.2.

A typical photochemical run was carried out as follows: A  $\text{CH}_2\text{Cl}_2$  solution of diazene **17f** (0.0318 M), FN (0.122 M), and dimethyl fumarate (0.0681 M) was prepared at  $-30\text{ }^\circ\text{C}$  under the usual precautions to avoid thermal deazetation and irradiated at  $-30\text{ }^\circ\text{C}$  for 50 min with monochromatic 370 nm light. Excess MA in  $\text{CH}_2\text{Cl}_2$  was added, the reaction mixture was allowed to warm to room temperature, stored for several hours to complete the quenching of the diazene, and analyzed by HPLC.

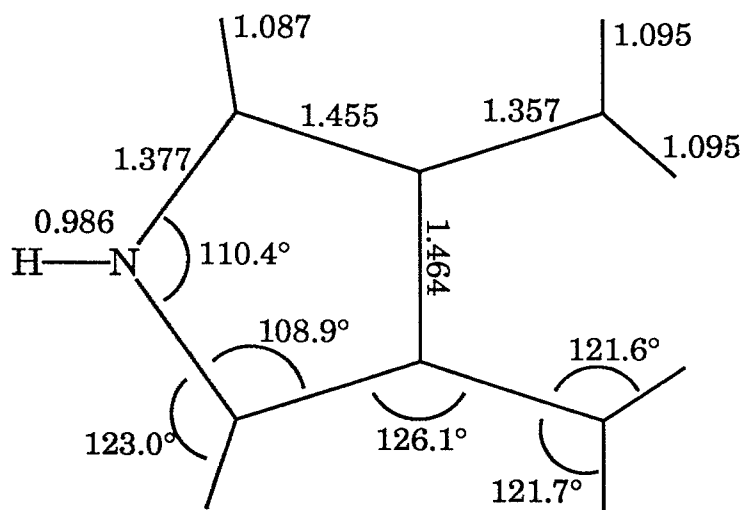
**Attempted Observation of the CIDNP Effect in Dimerization of *N*-Tosylpyrrole Biradical 3f.** Samples for CIDNP experiments were prepared as ca. 50 mM solutions of diazene **17f** in the following solvents:  $\text{CD}_2\text{Cl}_2$  (for deazetation at 298 K and 308 K), 1 : 3  $\text{CD}_2\text{Cl}_2$  :  $\text{CDCl}_3$  ( for deazetation at 313 K and 318 K),  $\text{CDCl}_3$  ( for deazetation at 328 K) or 1 : 1  $\text{CDCl}_3$  :  $\text{d}_6$ -DMSO (for deazetation at 348 K). Samples were placed in preheated NMR probes (250 MHz or 300 MHz), the instrument was locked, and acquisition was commenced without shimming, usually within ca. 5-15 s of insertion. Acquisitions (8) were collected up until the time of complete deazetation, but no emission or enhanced absorption signals were seen in any of the resonances of dimer **20f**.<sup>22</sup>

### Results of Semi-Empirical Calculations

The optimized geometry (using OPEN(4,4)/4 CI) and orbital coefficients of the HOMO and LUMO for the singlet and triplet of each biradical are given, as well as the calculated heat of formation.

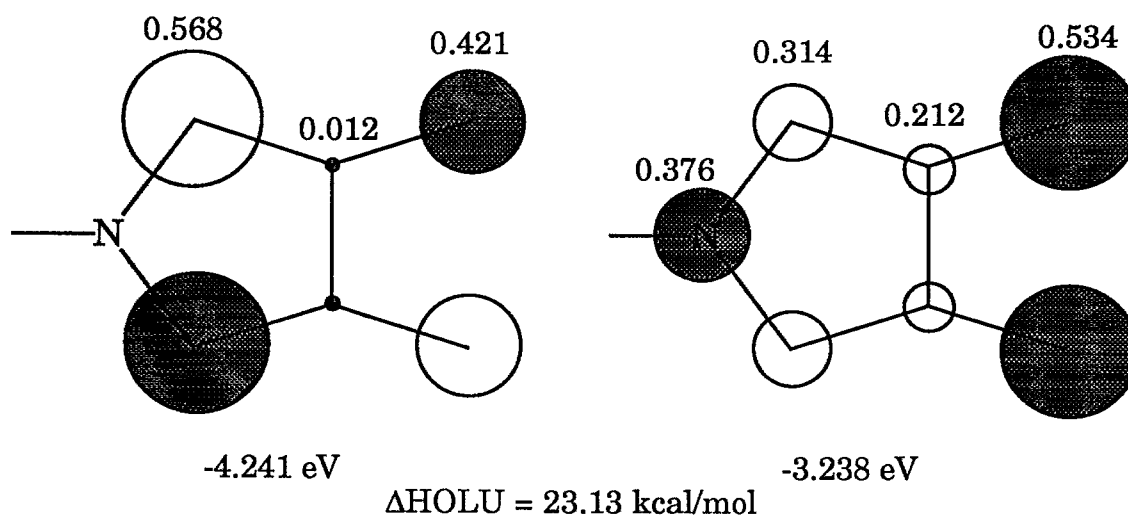
Of note is N-benzenesulfonyl-3,4-dimethylenepyrrole for which the unoccupied  $\pi$  MO nearest the HOMO is in the NLUMO position. Only  $\pi$  MOs are considered here.

**Singlet 3,4-Dimethylenepyrrole (3a) by AM1/CI**

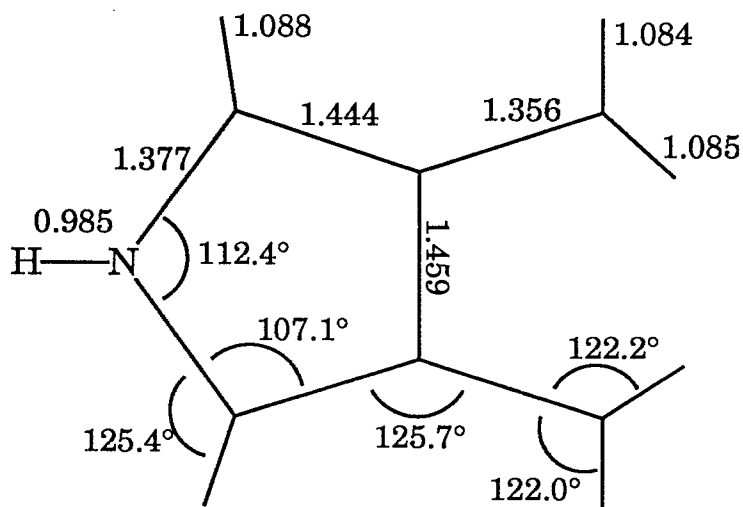


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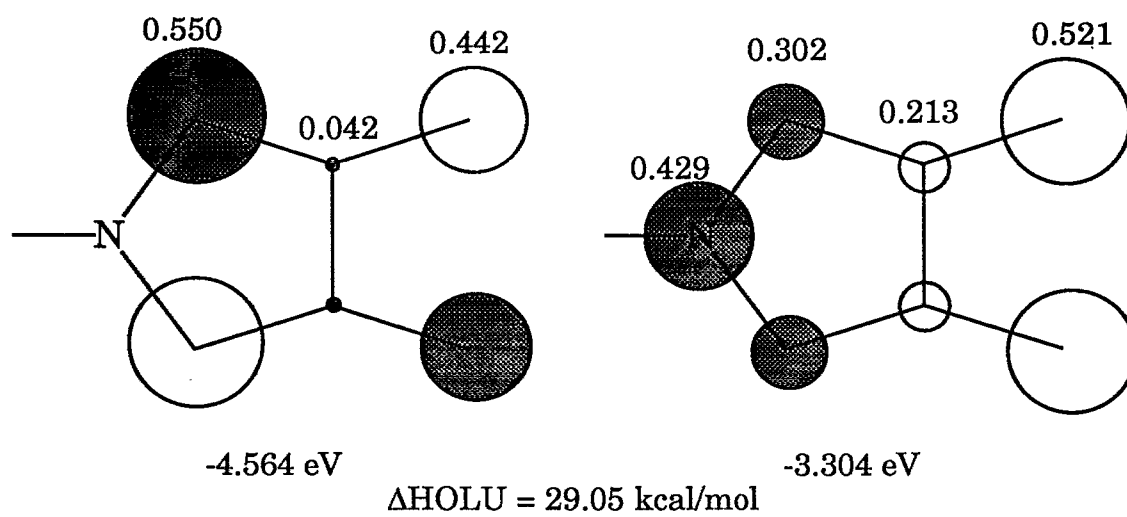


$H_f = 66.578 \text{ kcal/mol}$   
 singlet = -12.9705 eV  
 triplet = -12.3148 eV  
**Singlet 3,4-Dimethylenepyrrole (3a) by PM3/CI**



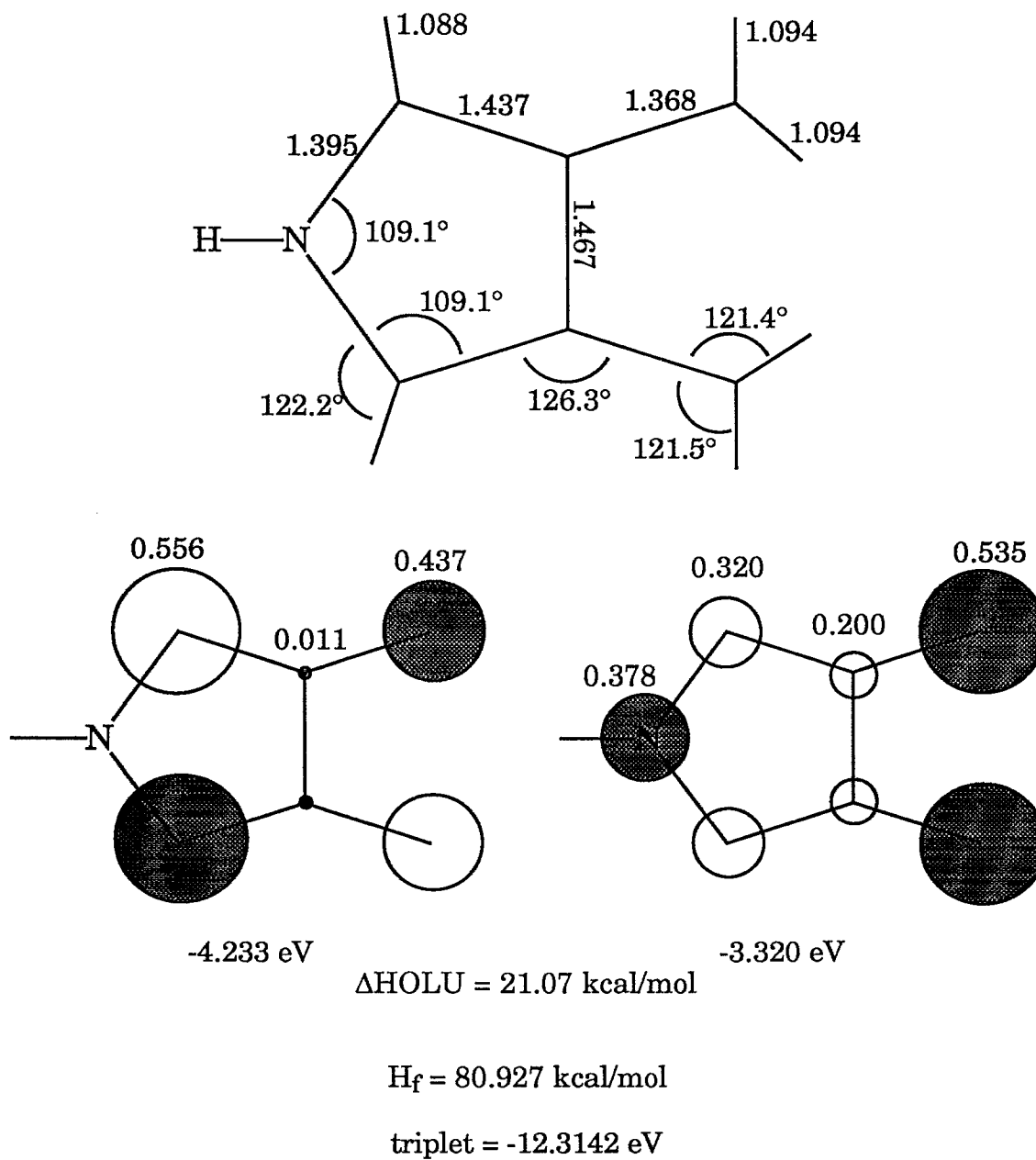
## Supporting Information

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$H_f = 54.941 \text{ kcal/mol}$   
singlet = -12.9659 eV  
triplet = -12.1667 eV

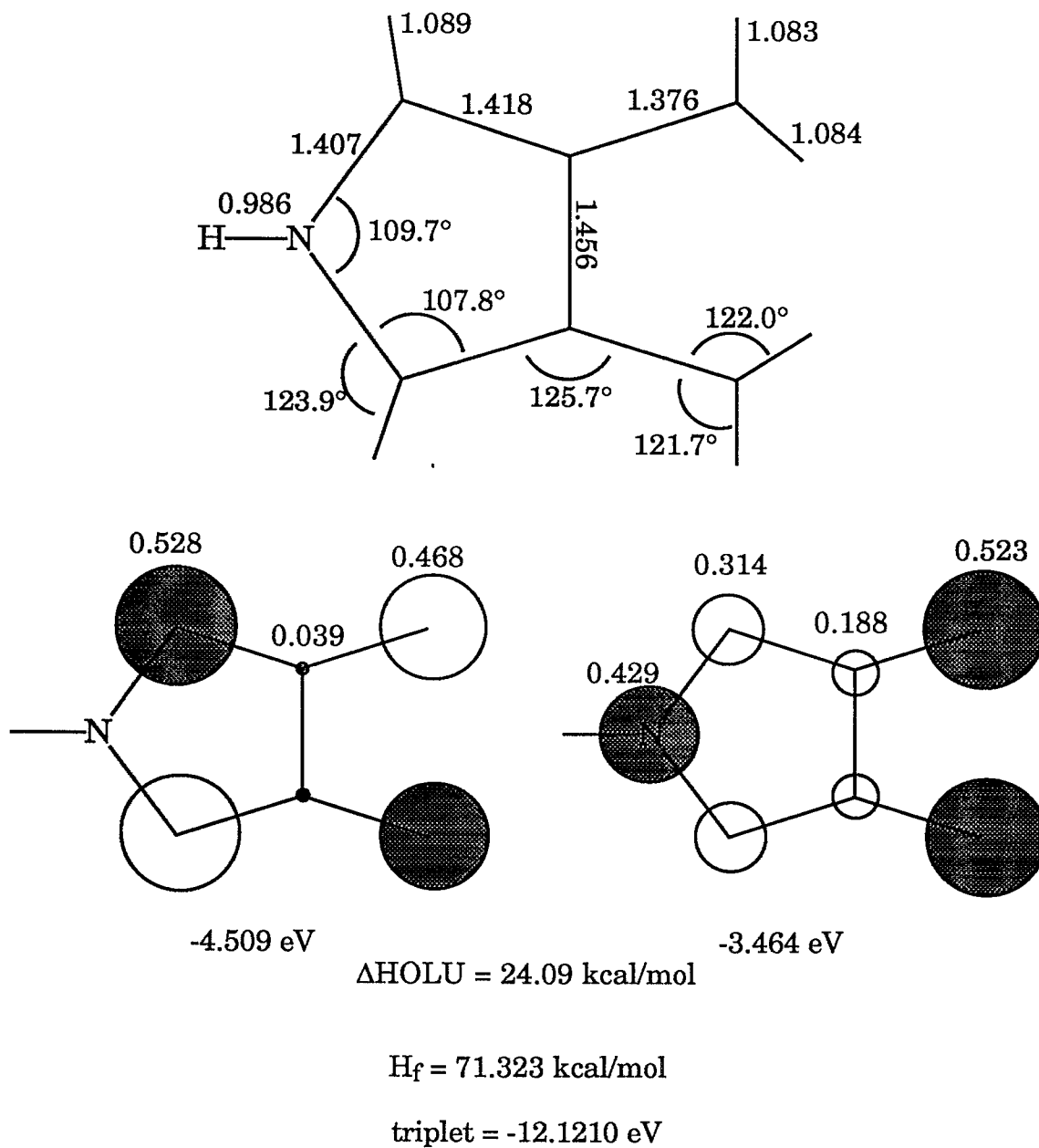


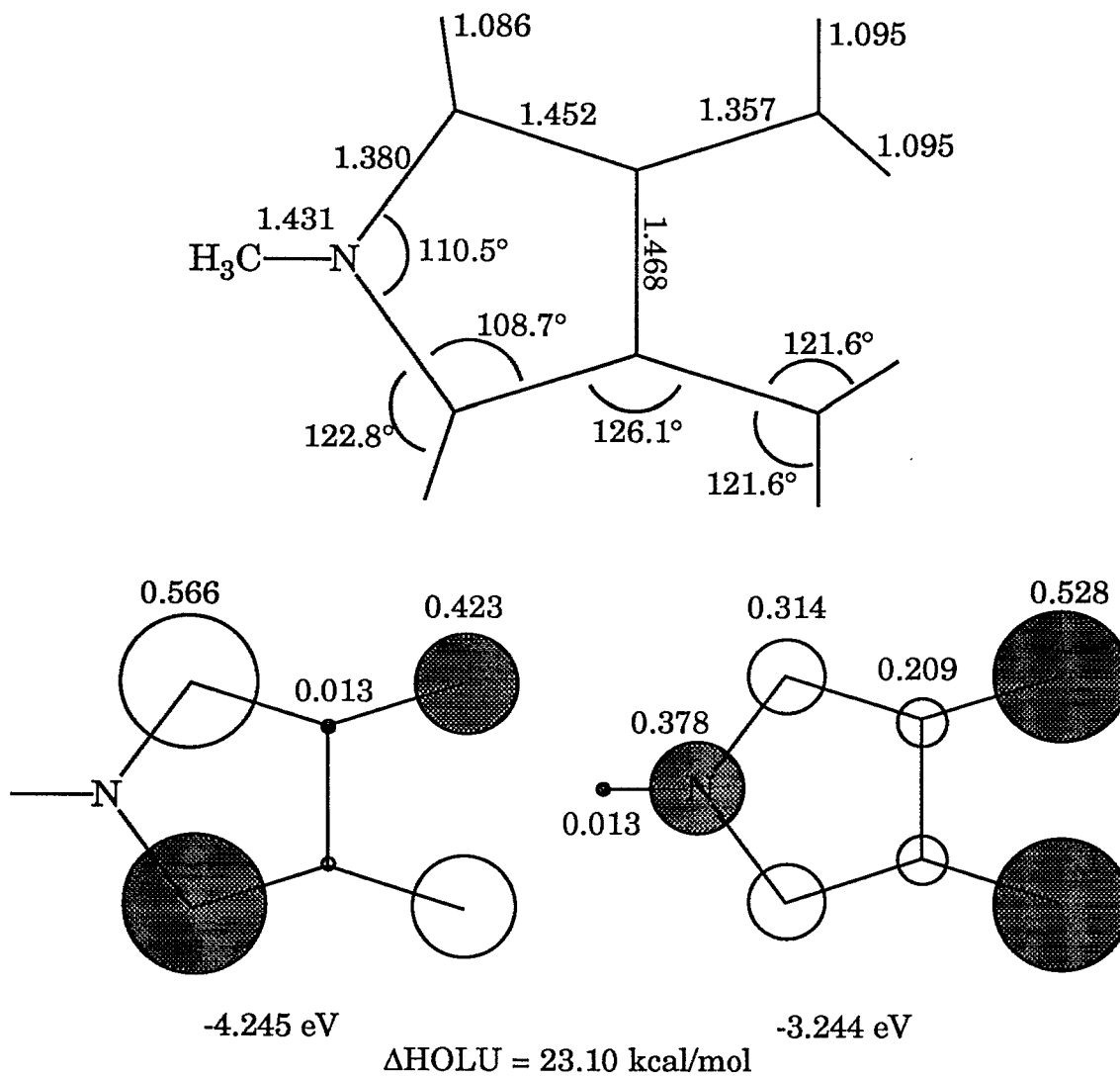
**Triplet 3,4-Dimethylenepyrrole (3a) by AM1/CI**

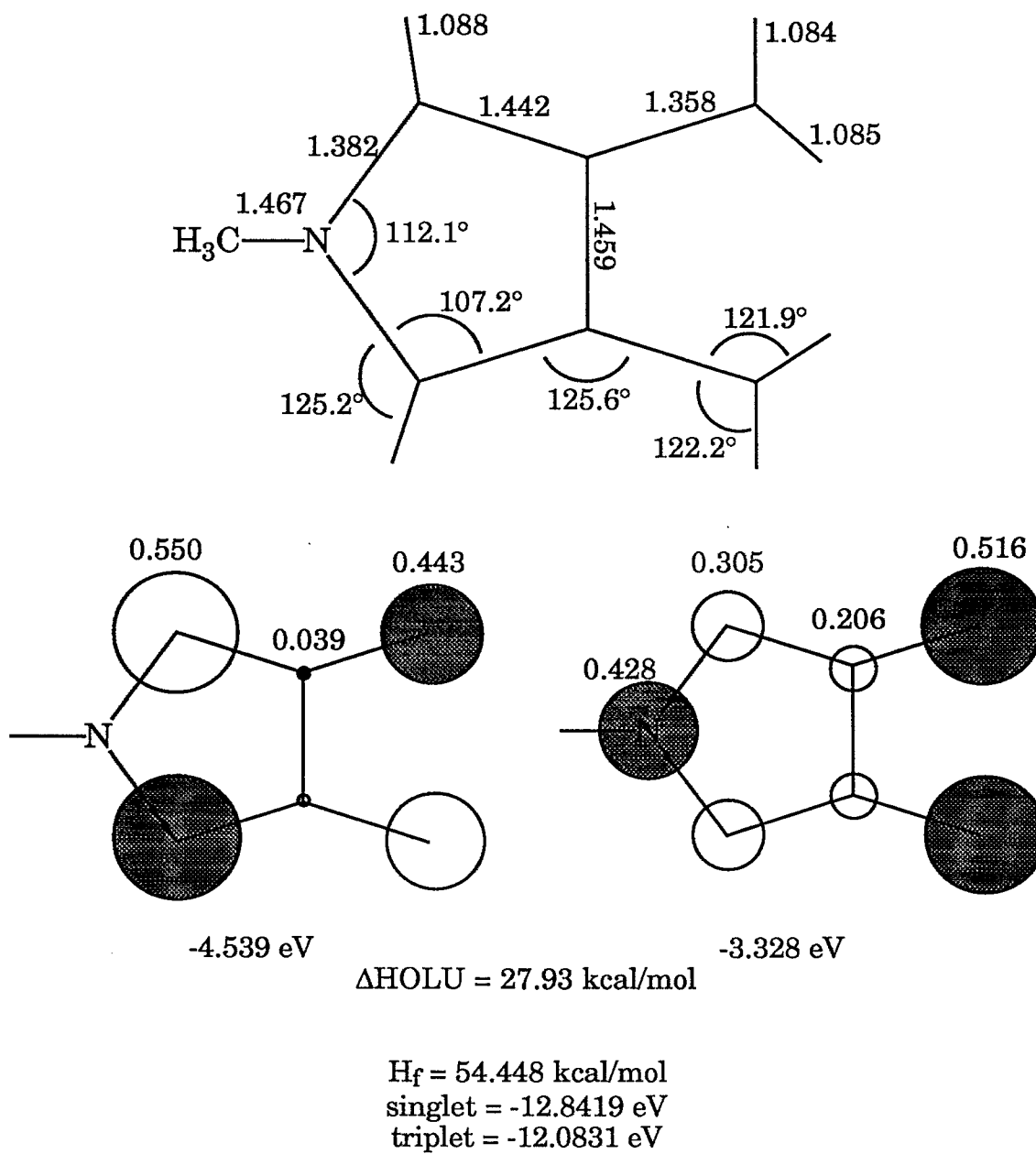
## Supporting Information

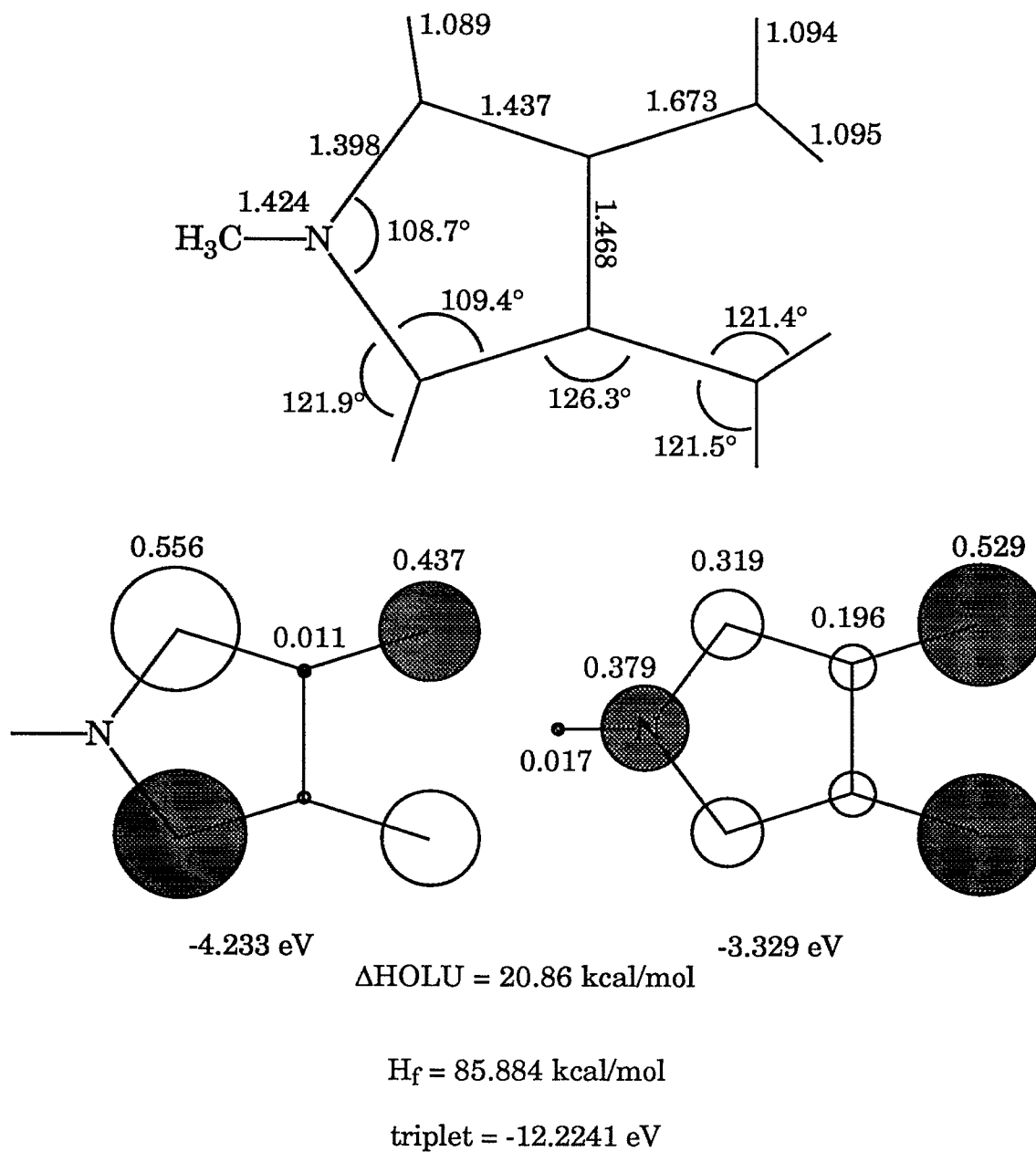
57

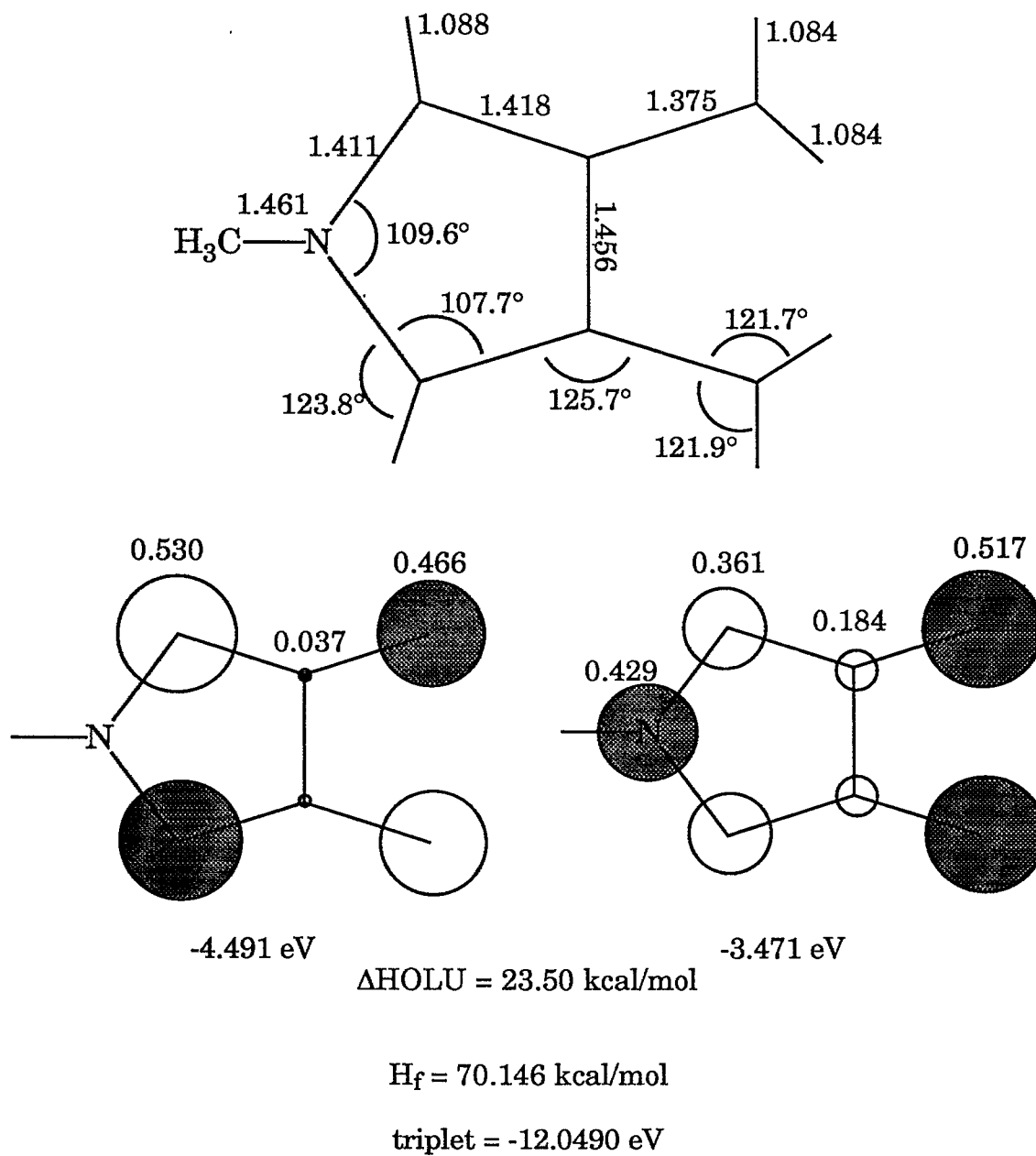
## Triplet 3,4-Dimethylenepyrrole (3a) by PM3/CI



**Singlet N-Methyl-3,4-dimethylenepyrrole (3b) by AM1/CI**

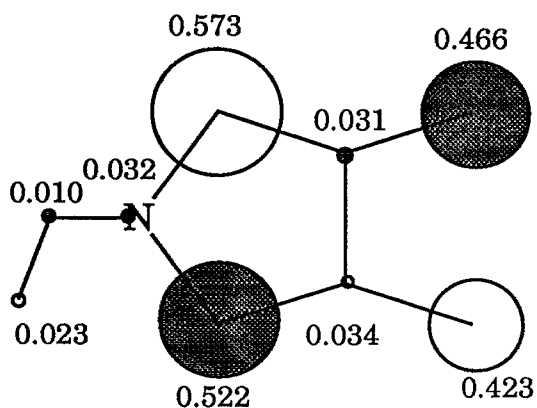
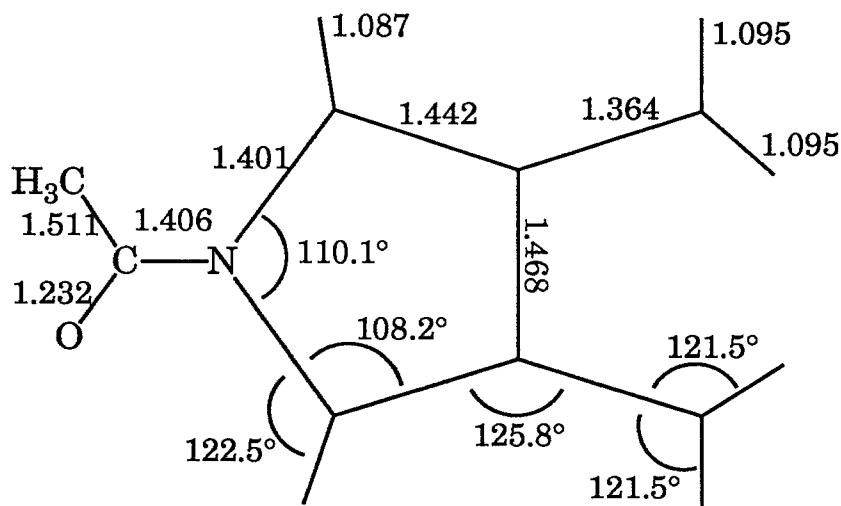
**Singlet N-Methyl-3,4-dimethylenepyrrole (3b) by PM3/CI**

**Triplet N-Methyl-3,4-dimethylenepyrrole (3b) by AM1/CI**

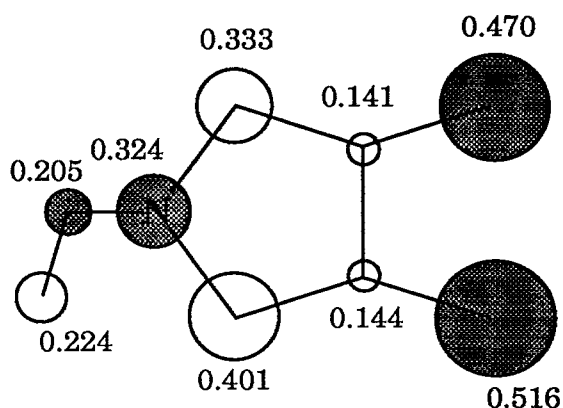
**Triplet N-Methyl-3,4-dimethylenepyrrole (3b) by PM3/CI**

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**Singlet N-Acetyl-3,4-dimethylenepyrrole by AM1/CI**

-4.818 eV



-4.019 eV

 $\Delta\text{HOLU} = 18.41 \text{ kcal/mol}$  $H_f = 42.347 \text{ kcal/mol}$ 

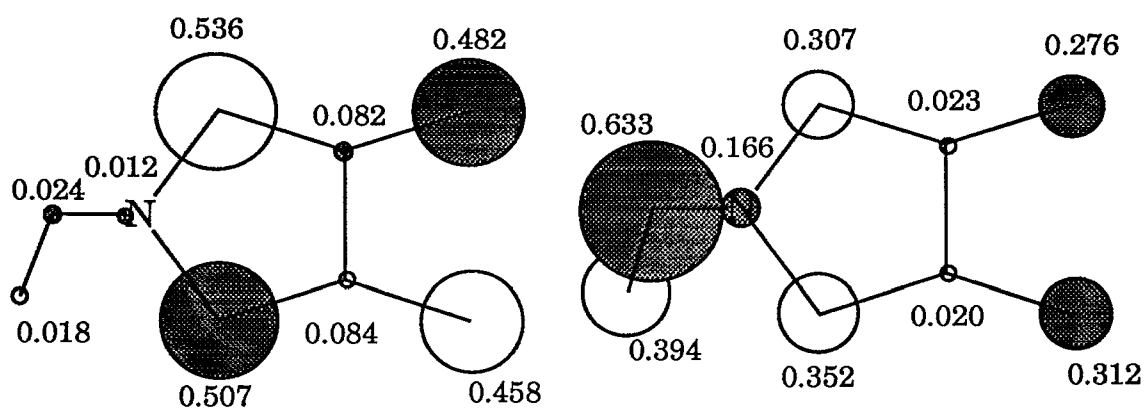
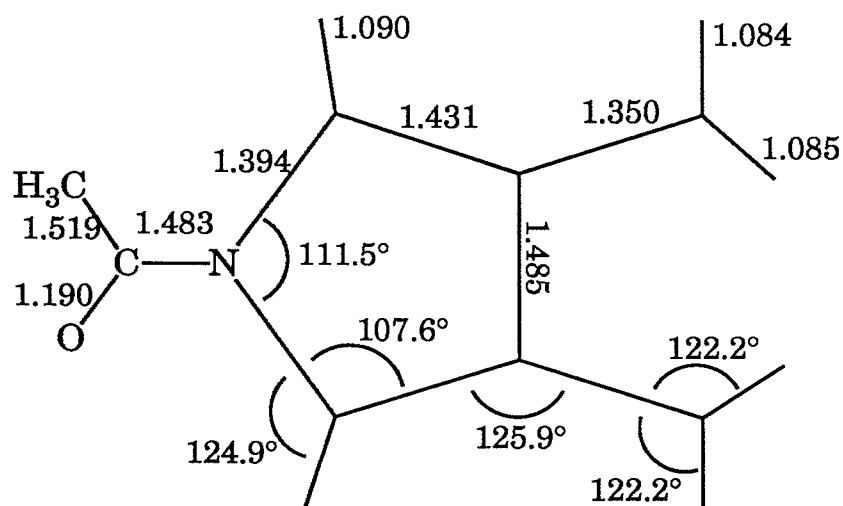
singlet = -12.1554 eV

triplet = -11.7751 eV

**Singlet N-Acetyl-3,4-dimethylenepyrrole by PM3/CI**

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-4.850 eV

-4.163 eV

 $\Delta\text{HOLU} = 15.84 \text{ kcal/mol}$  $H_f = 34.458 \text{ kcal/mol}$ 

singlet = -12.1645 eV

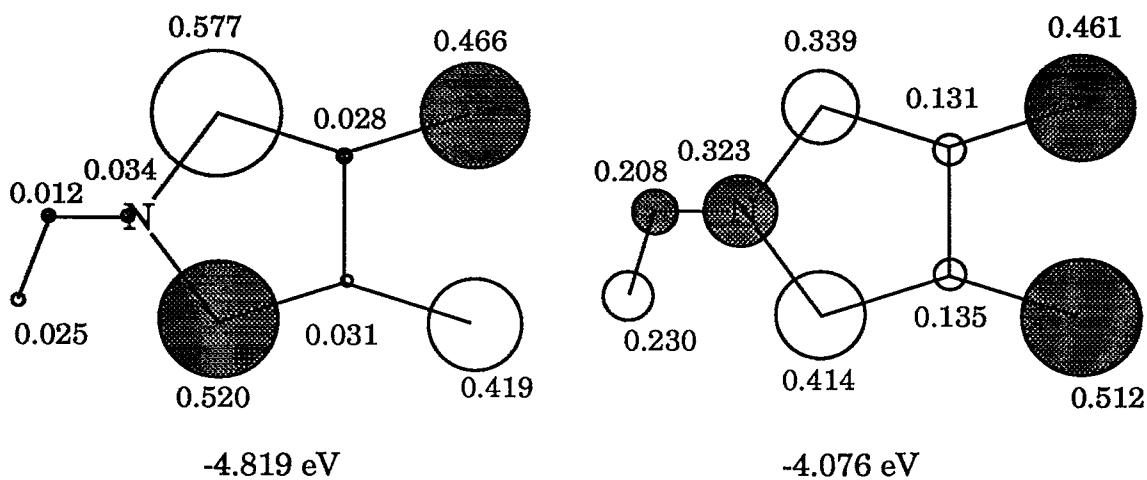
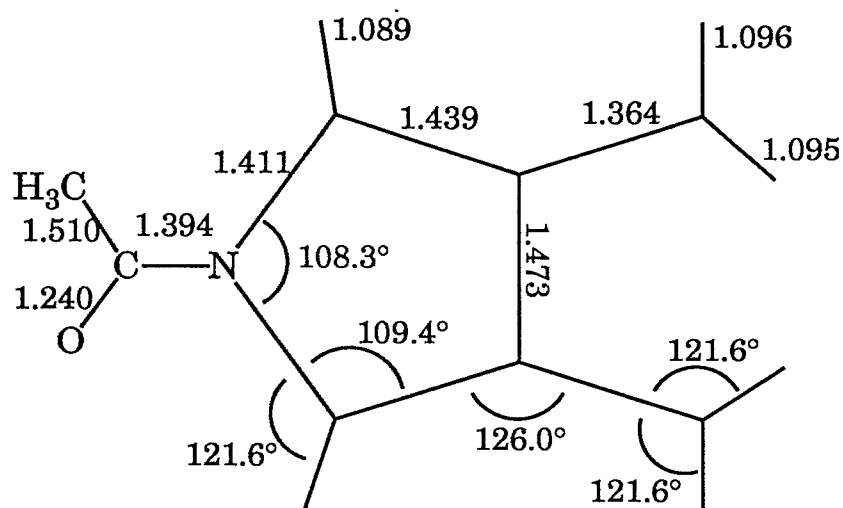
triplet = -11.6762 eV

**Triplet N-Acetyl-3,4-dimethylenepyrrole by AM1/CI**



## Supporting Information

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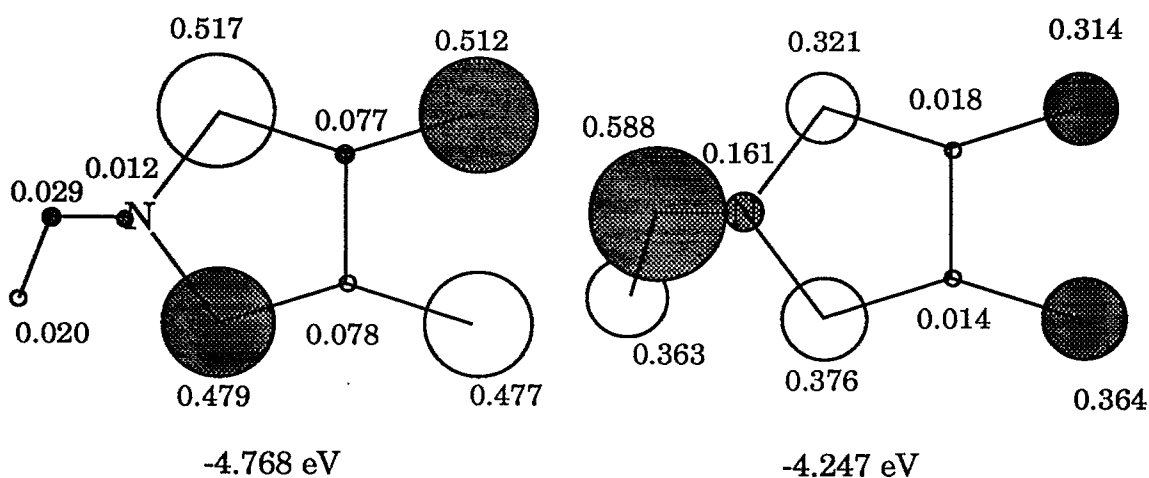
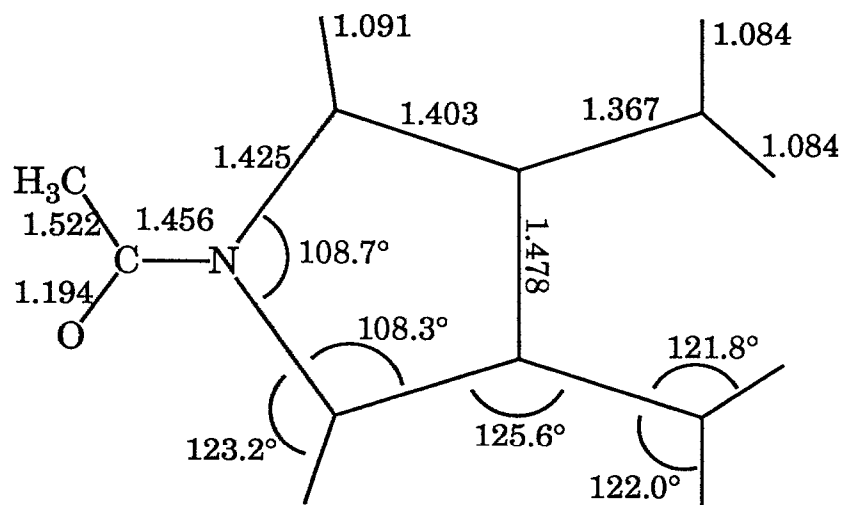
 $\Delta\text{HOLU} = 17.13 \text{ kcal/mol}$  $H_f = 50.481 \text{ kcal/mol}$ 

triplet = -11.8121 eV

**Triplet N-Acetyl-3,4-dimethylenepyrrole by PM3/CI**

## Supporting Information

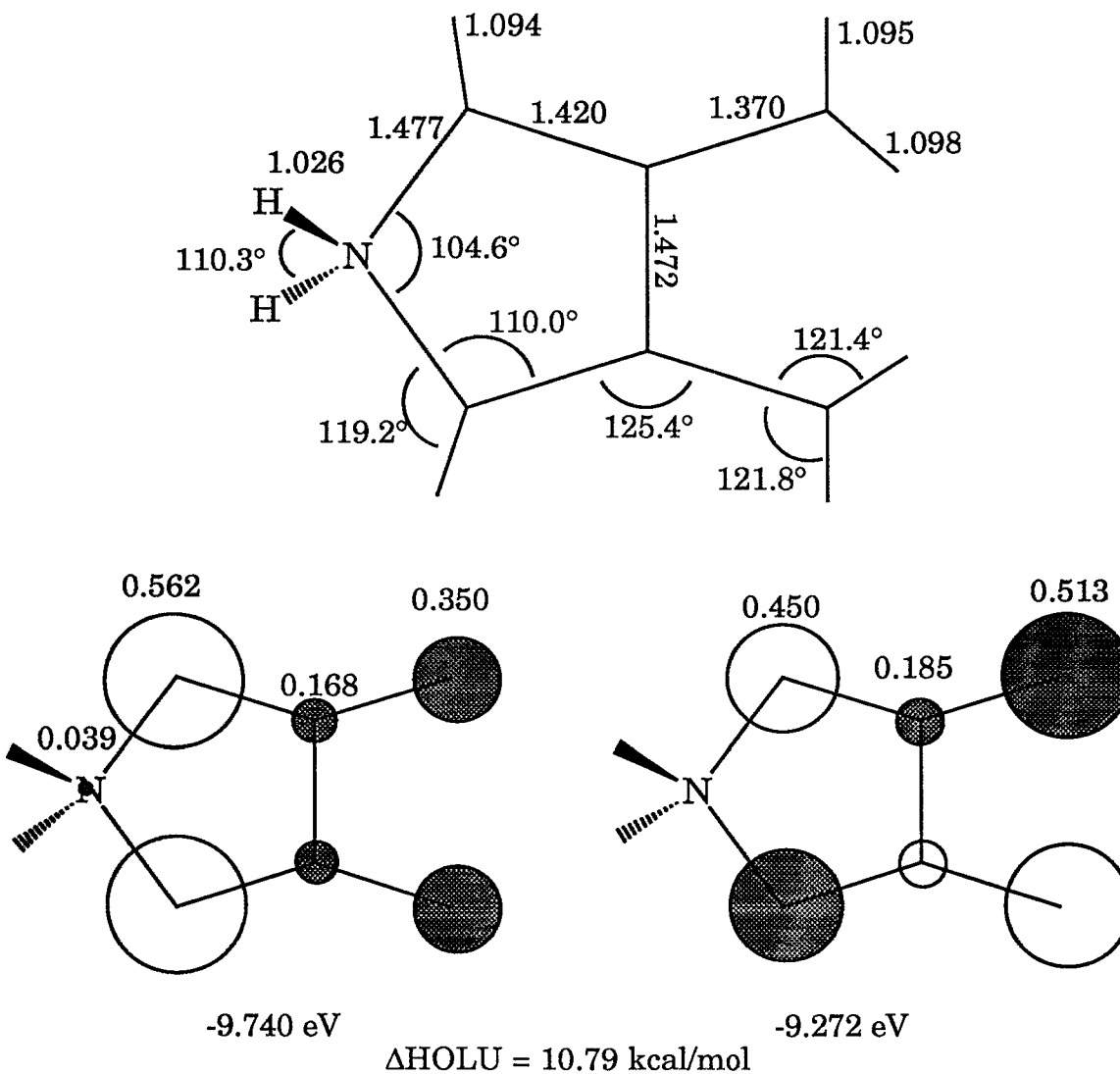
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$$\Delta\text{HOLU} = 12.01 \text{ kcal/mol}$$

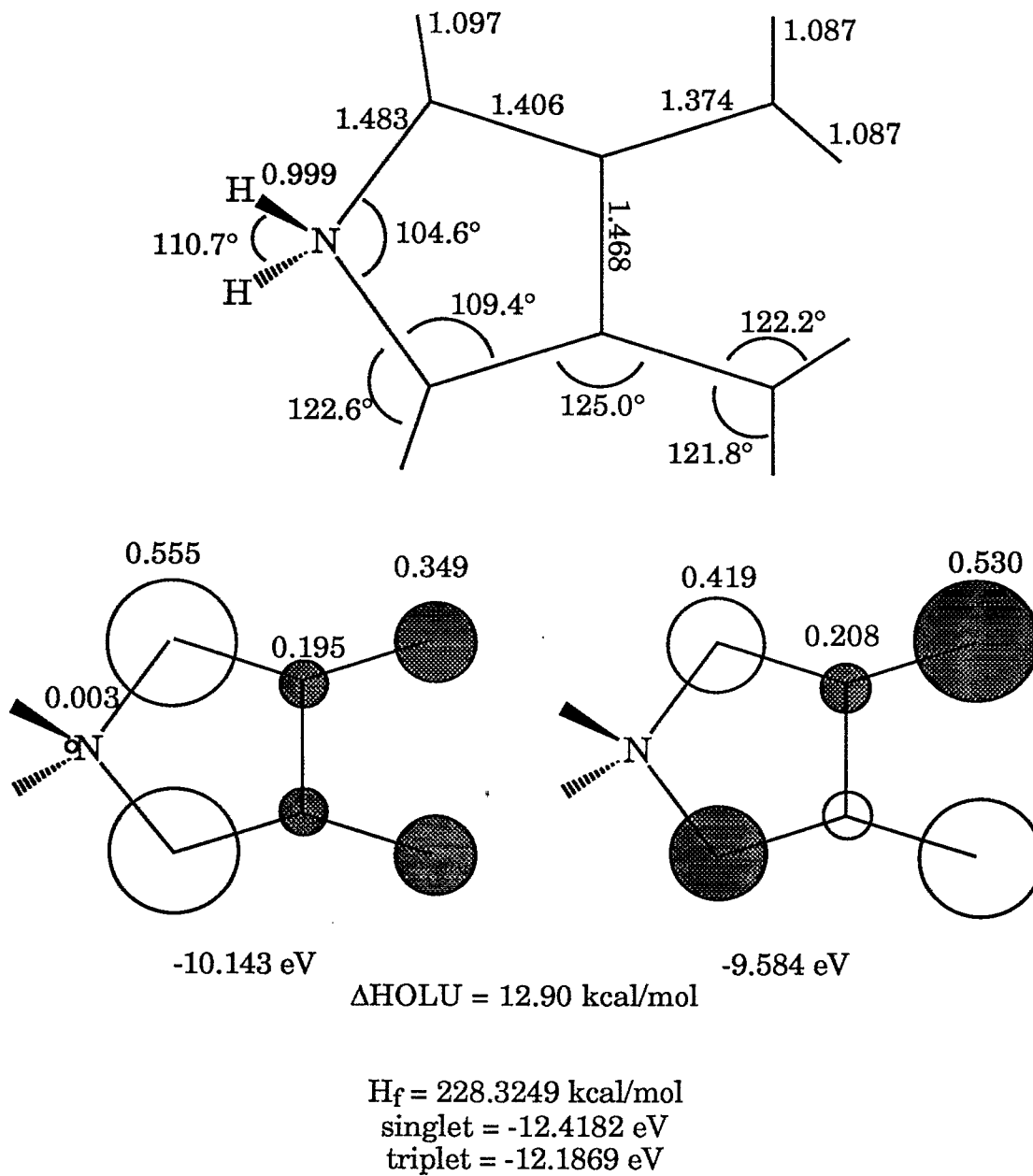
$$H_f = 43.539 \text{ kcal/mol}$$

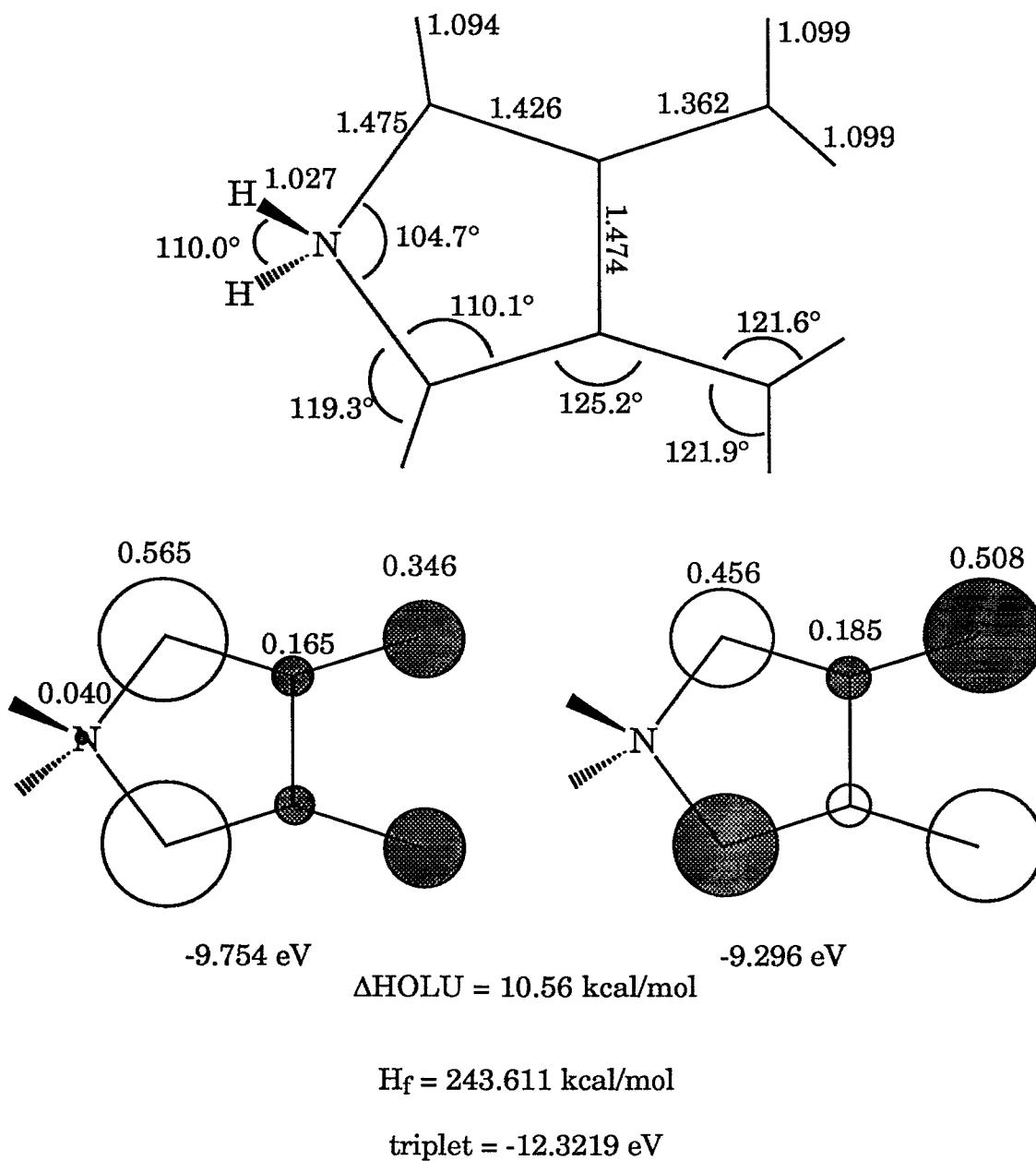
$$\text{triplet} = -11.6886 \text{ eV}$$

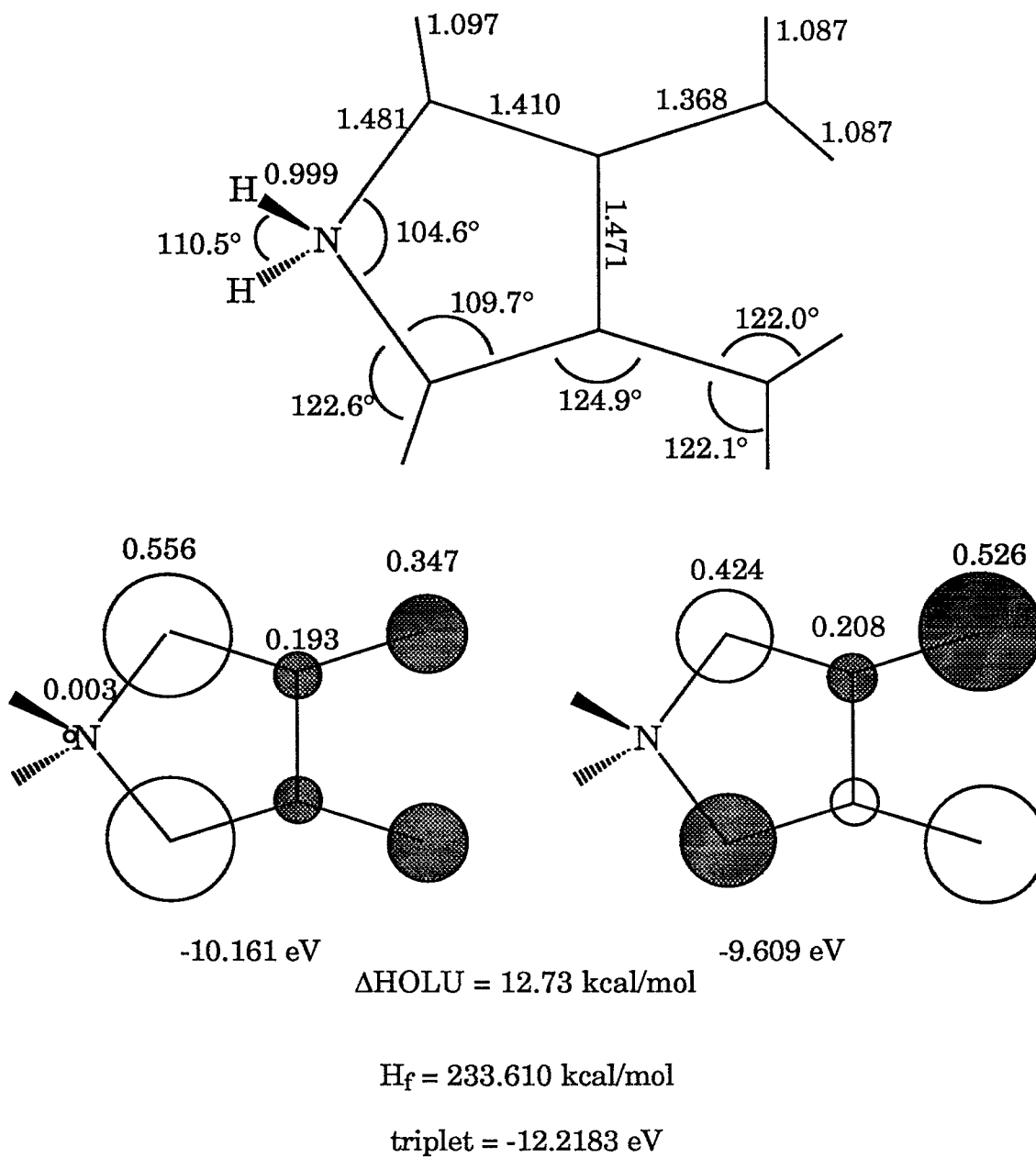
**Singlet 3,4-Dimethylenepyrrolium Cation by AM1/CI****Singlet 3,4-Dimethylenepyrrolium Cation by PM3/CI**

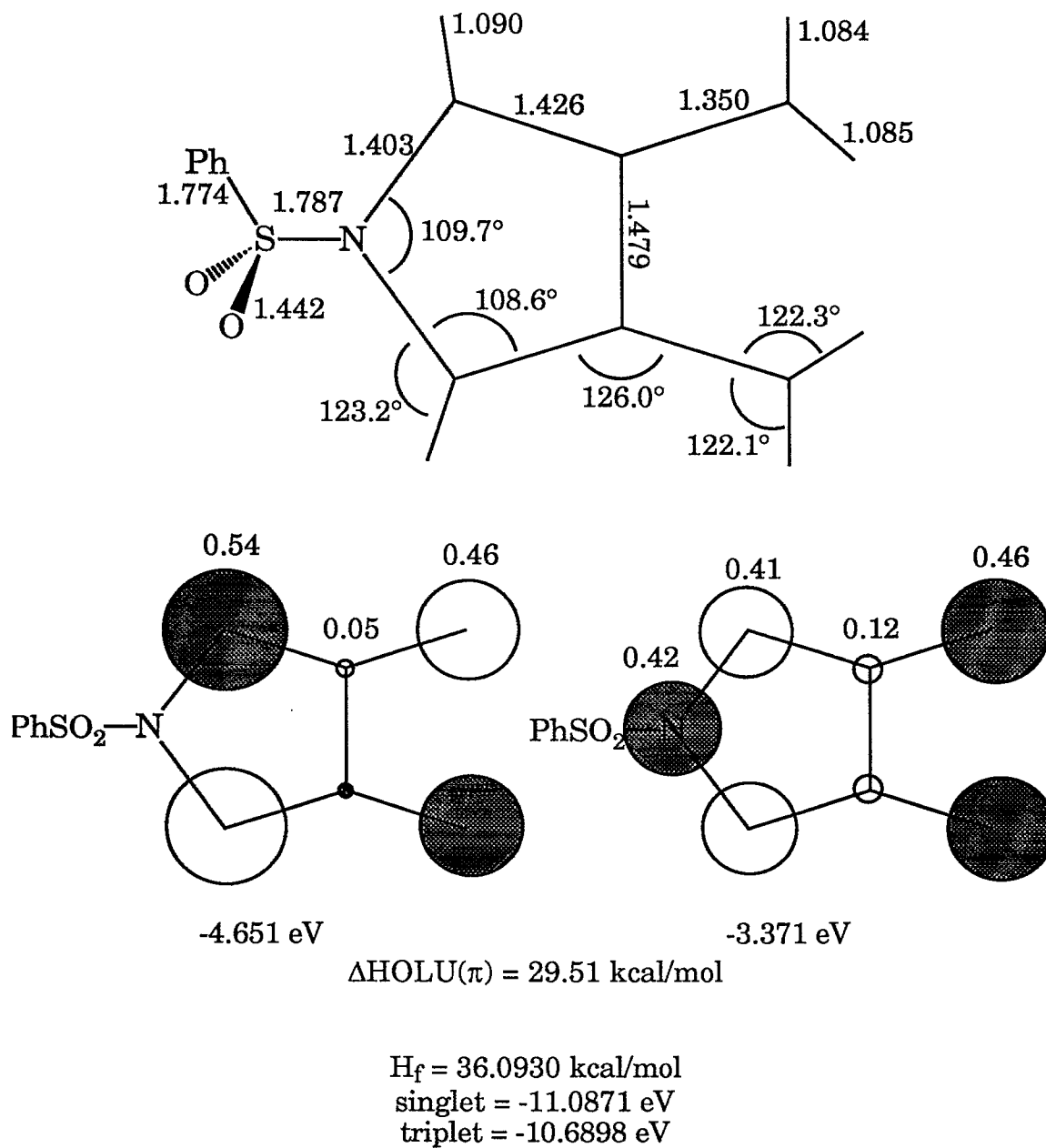
## Supporting Information

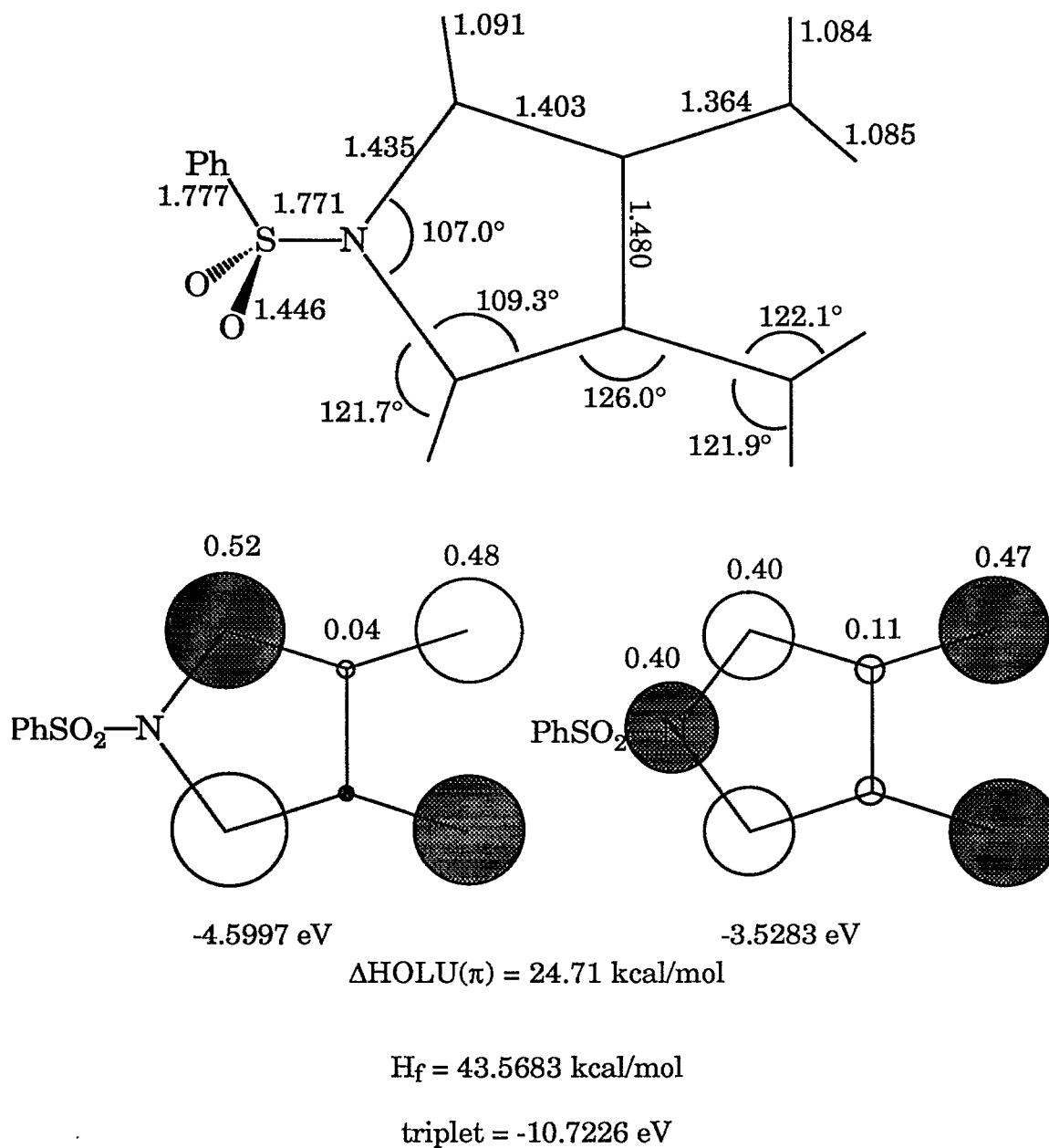
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**Triplet 3,4-Dimethylenepyrrolonium Cation by AM1/CI**

**Triplet 3,4-Dimethylenepyrrolonium Cation by PM3/CI**

**Singlet N-Benzenesulfonyl-3,4-Dimethylenepyrrole by PM3/CI**

**Triplet N-Benzenesulfonyl-3,4-Dimethylenepyrrole by PM3/CI**



The optimized conformations of the singlet and the triplet are similar to that shown in Fig. 3 of the main text.

## References

(S-1) Stone, K.J.; Greenberg, M.M.; Blackstock, S.C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659.