

J | A | C | S

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1997, 119(6), 1406-1415, DOI:[10.1021/ja963113k](https://doi.org/10.1021/ja963113k)

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

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 CH₂Cl₂) 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).

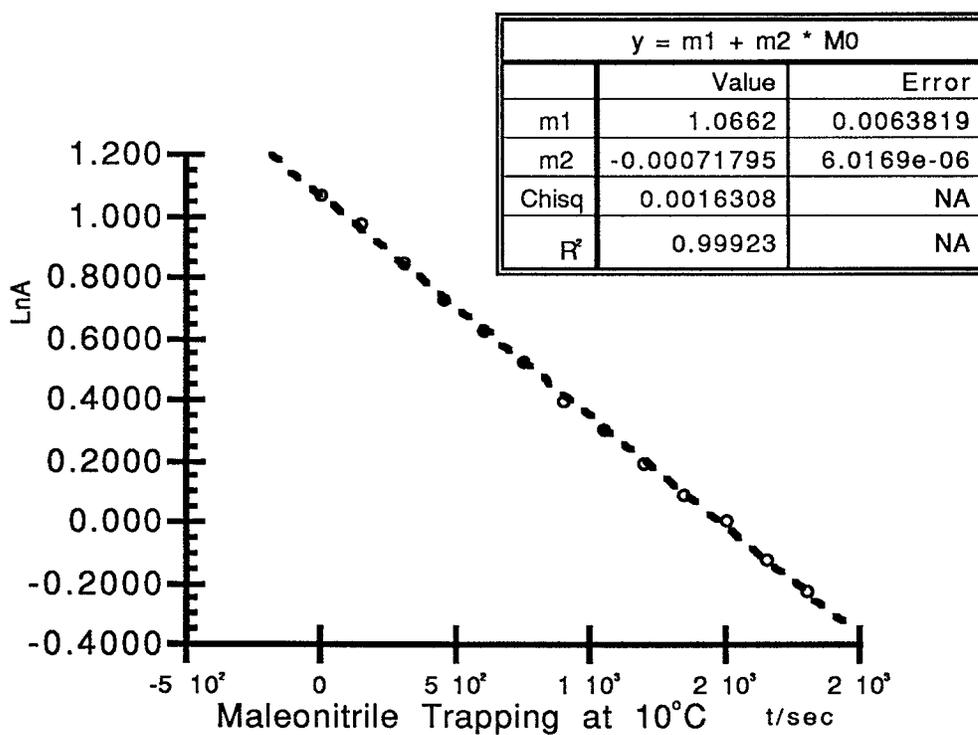
An NMR sample of diazene **17f** (0.007mmol, 0.5ml 14.15mM) in CDCl₃ and 2mg (0.026mmol) of maleonitrile was prepared at -20°C. The sample was 52 mM in MN. The sample was placed into the NMR probe which had been cooled at 10°C. The spectrometer was programmed to collect a spectrum every 2.5 minutes. The singlet due to the diazene methylenic protons (δ 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

Supporting Information

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 $7.18 \times 10^{-4} \text{ s}^{-1}$.

Supporting Information

EXP. LM 1-141-1.

V of diazene **17f**=0.5ml; c of diazene **17f**=14.5mM in CDCl₃

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

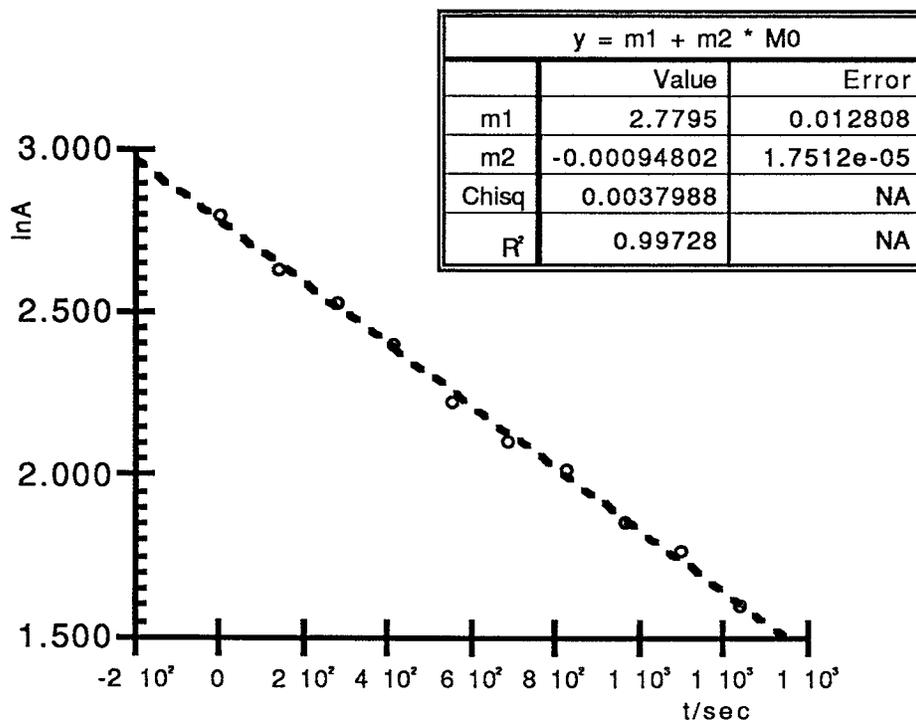
m of MN=3.9mg (0.05mmol; 100mM)

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

46

EXP. LM 1-140-1.

V of diazene **17f**=0.5ml; c of diazene **17f**=14.5mM in CDCl₃

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

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

T=10°C

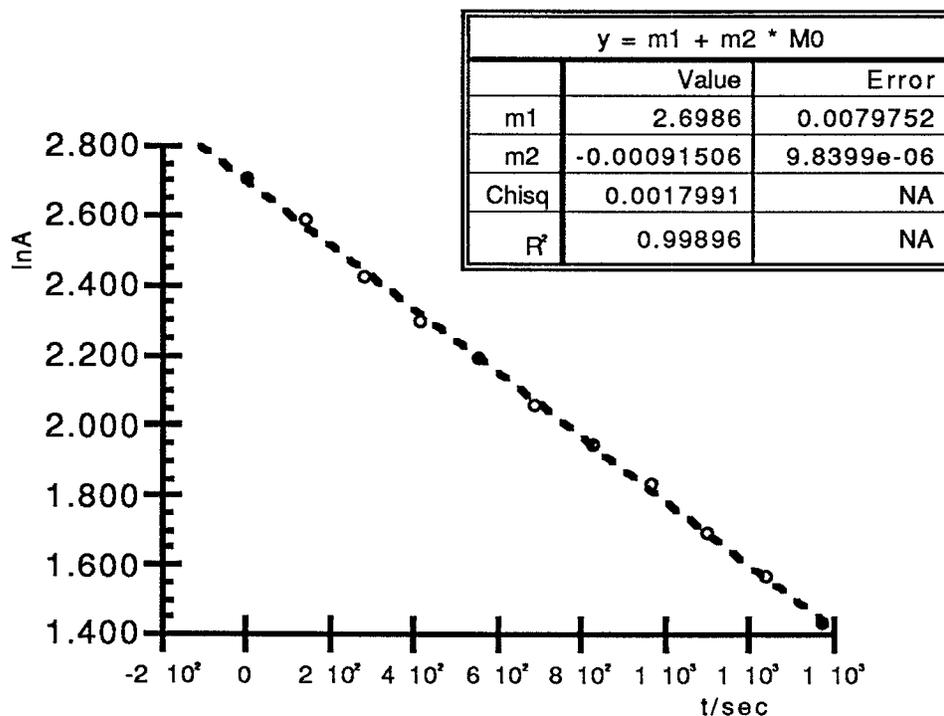
Time/sec	A	ln A
0	15.03	2.71
137	13.28	2.59

Supporting Information

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

Supporting Information

48

EXP. LM 1-139-1.V of diazene 17f=0.5ml; c of diazene 17f=14.5mM in CDCl₃

n of diazene 17f=0.007mmol

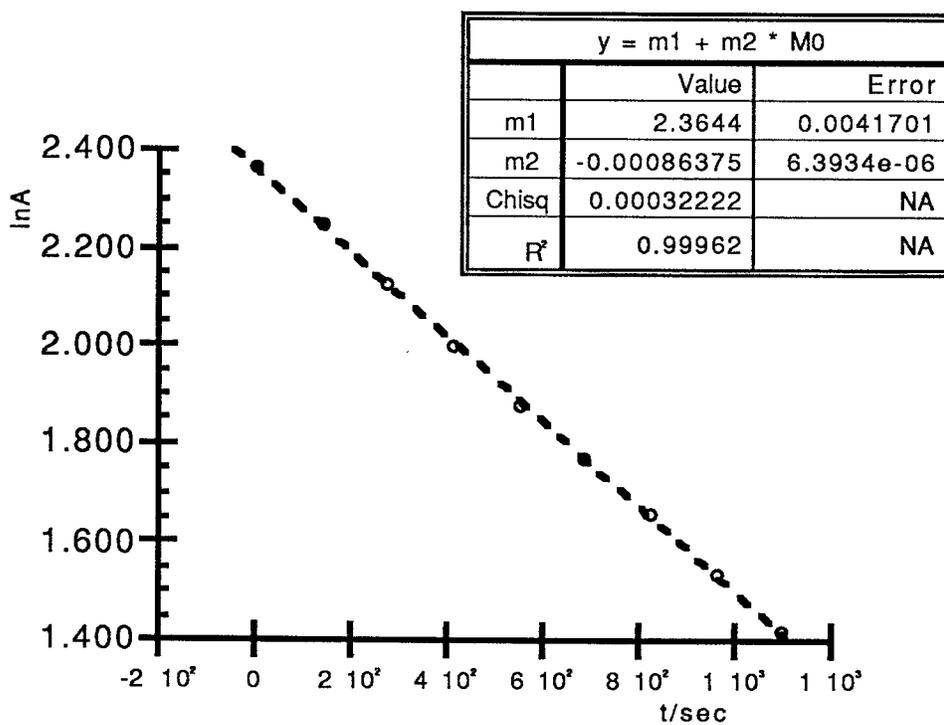
m of MN=0g

T=10°C

Time/sec	A	lnA
0	10.71	2.37
137	9.49	2.25

Supporting Information

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 ⁻¹ s
1	0	8.6x10 ⁻⁴ *
2	1 (26)	9.2x10 ⁻⁴ *
3	2 (59)	7.2x10 ⁻⁴
4	3.9 (100)	9.5x10 ⁻⁴ *

* 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 CH₂Cl₂ 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 CH_2Cl_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 CH_2Cl_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.

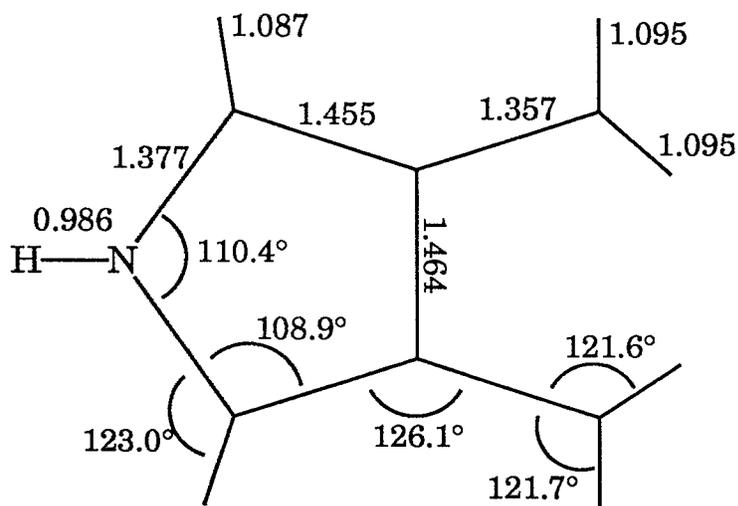
Attempted Observation of the CIDNP Effect in Dimerization of *N*-Tosylpyrrole Biradical **3f.** Samples for CIDNP experiments were prepared as ca. 50 mM solutions of diazene **17f** in the following solvents: CD_2Cl_2 (for deazetation at 298 K and 308 K), 1 : 3 CD_2Cl_2 : CDCl_3 (for deazetation at 313 K and 318 K), CDCl_3 (for deazetation at 328 K) or 1 : 1 CDCl_3 : 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**.²²

Results of Semi-Empirical Calculations

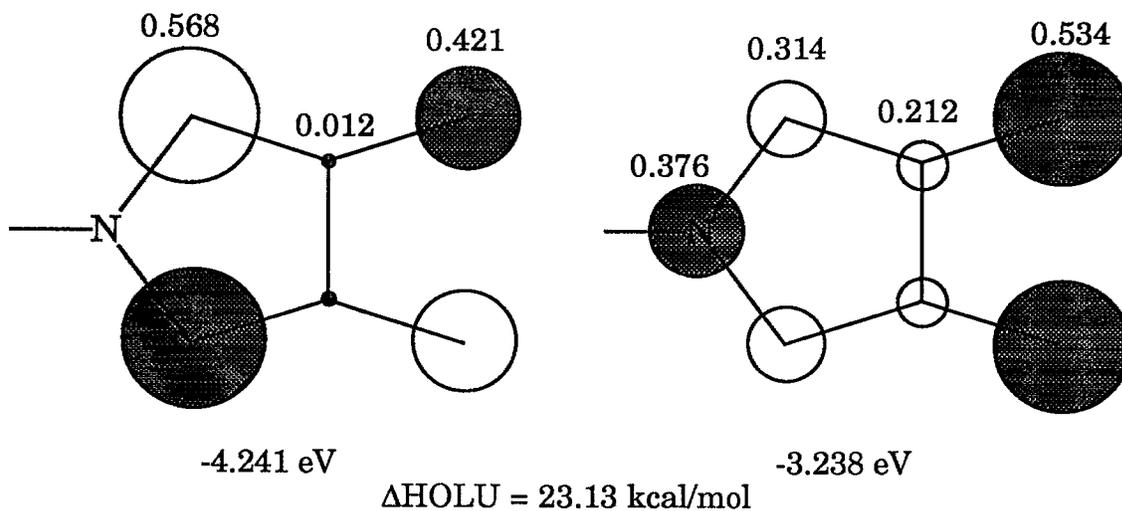
The optimized geometry (using OPEN(4,4)/4 CI) and orbital coefficients of the HOMO and LUMO for the singlet and triplet of each biradical are given, as well as the calculated heat of formation.

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

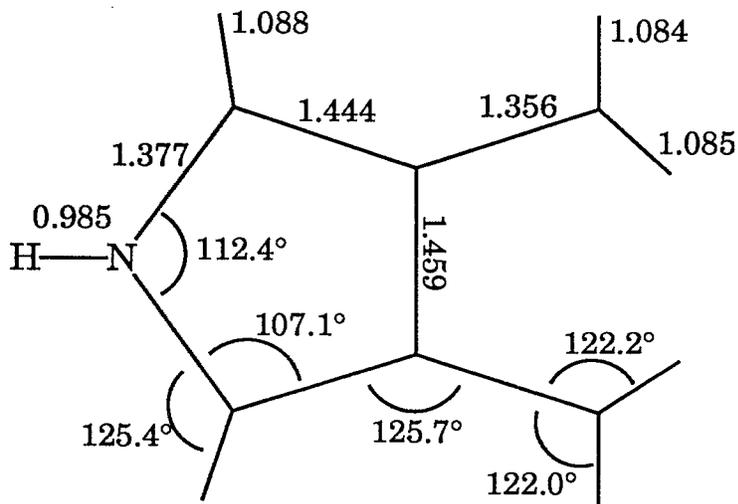
Singlet 3,4-Dimethylenepyrrole (3a) by AM1/CI



Supporting Information

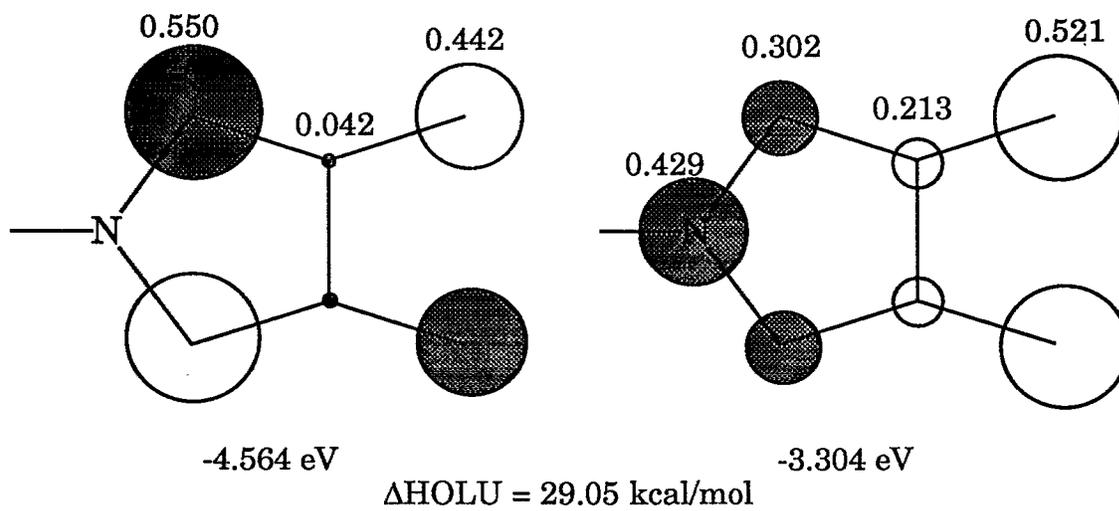


$H_f = 66.578 \text{ kcal/mol}$
 singlet = -12.9705 eV
 triplet = -12.3148 eV
Singlet 3,4-Dimethylenepyrrole (3a) by PM3/CI



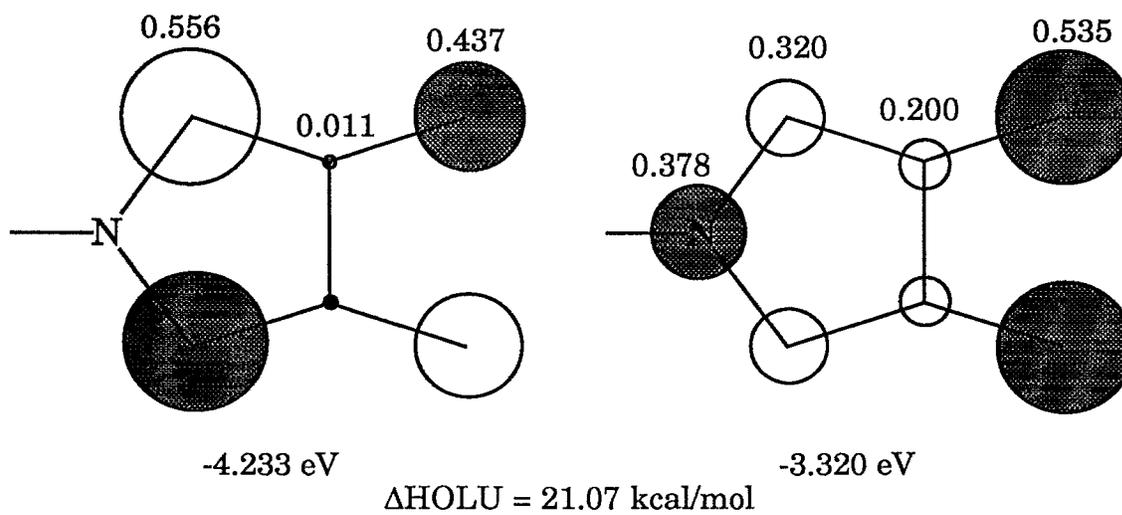
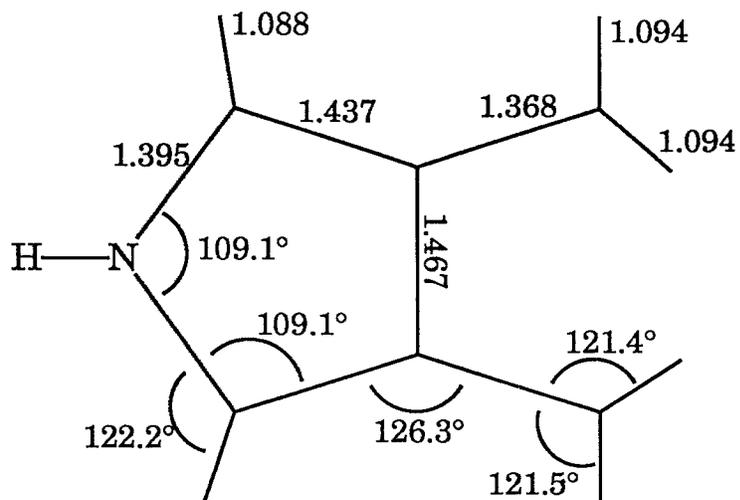
Supporting Information

55



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

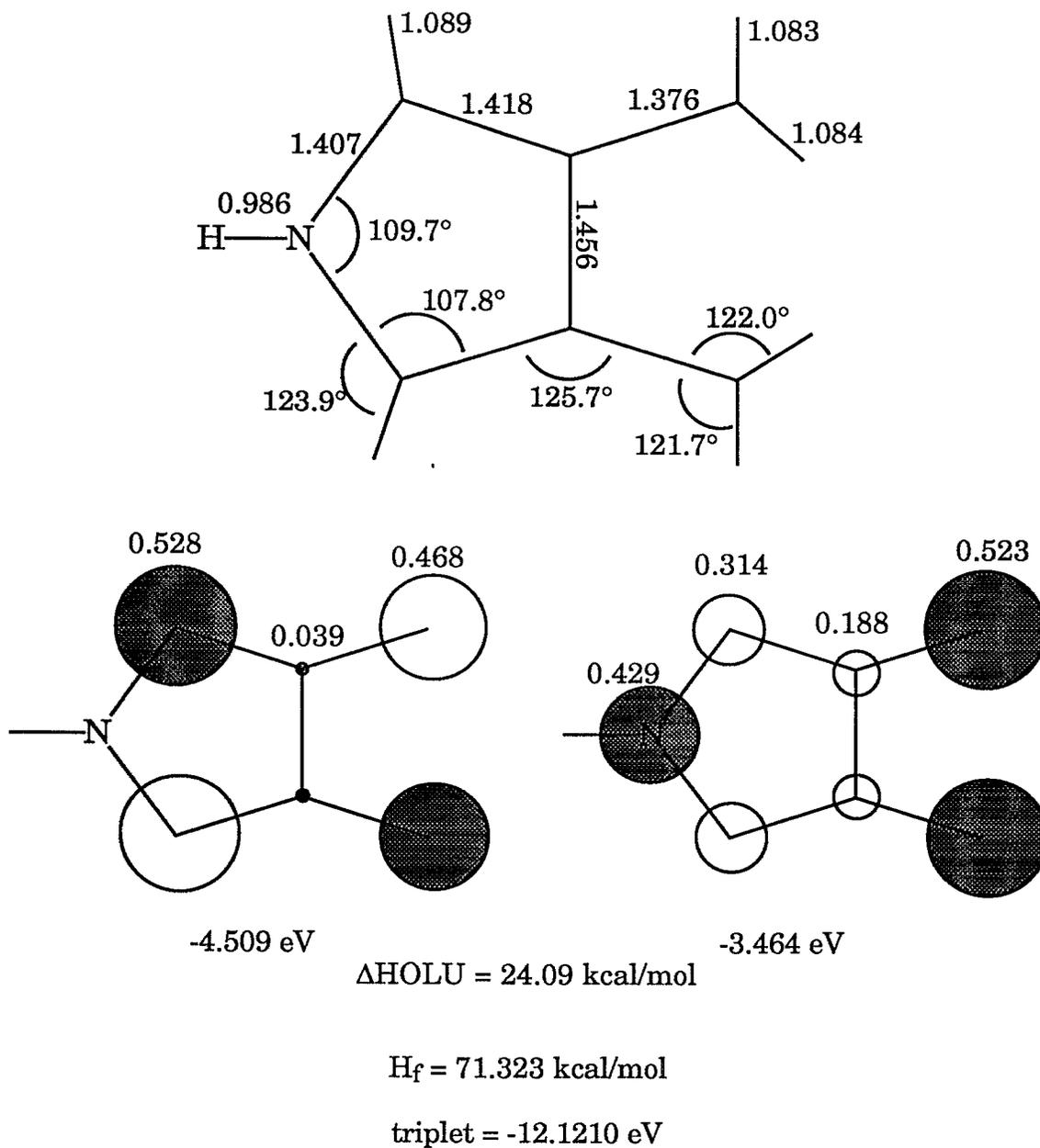
Triplet 3,4-Dimethylenepyrrole (3a) by AM1/CI



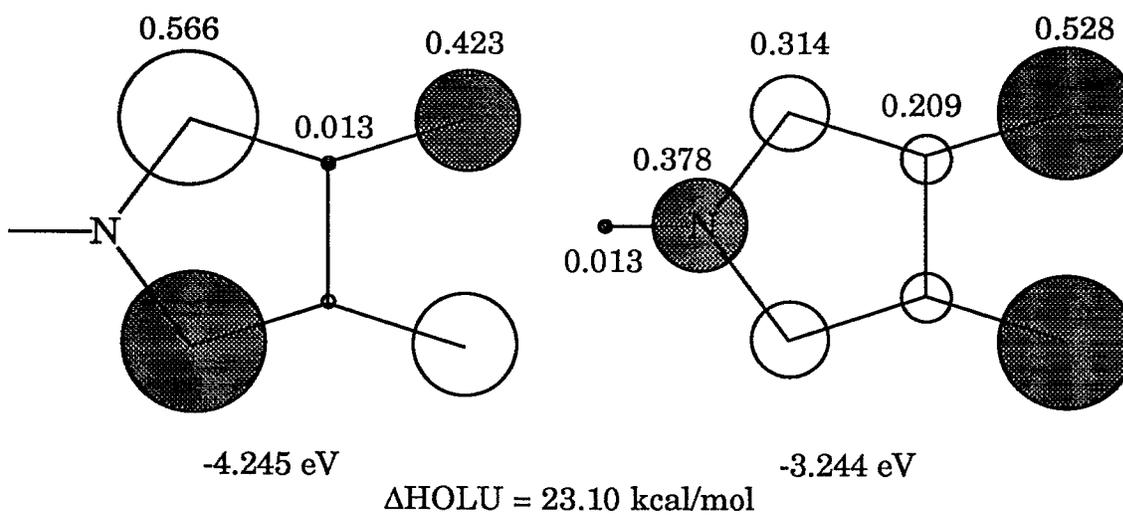
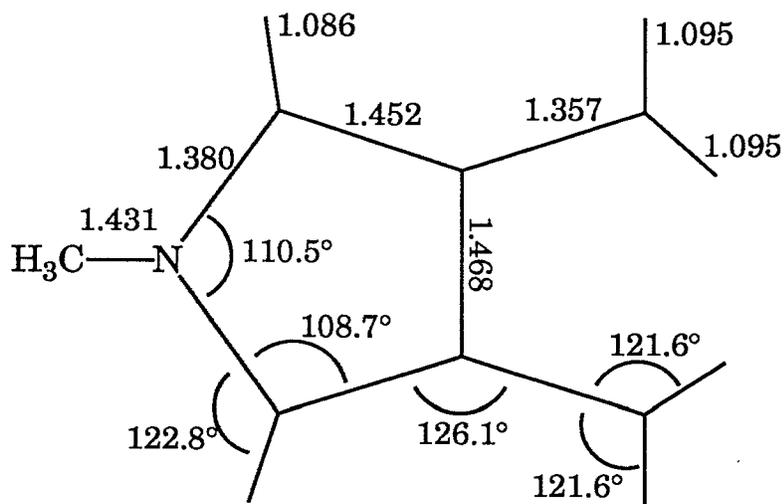
$$H_f = 80.927 \text{ kcal/mol}$$

$$\text{triplet} = -12.3142 \text{ eV}$$

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

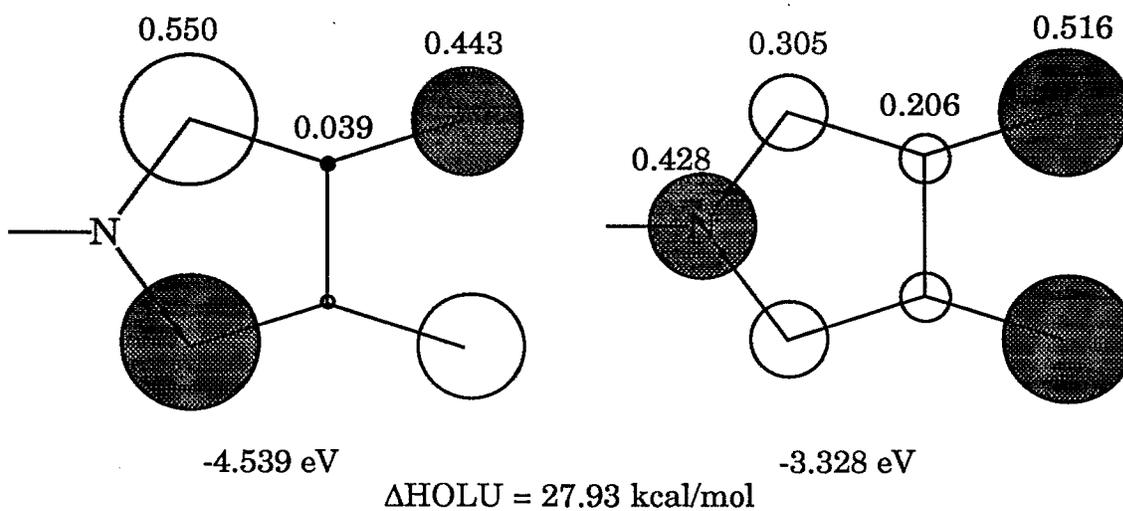
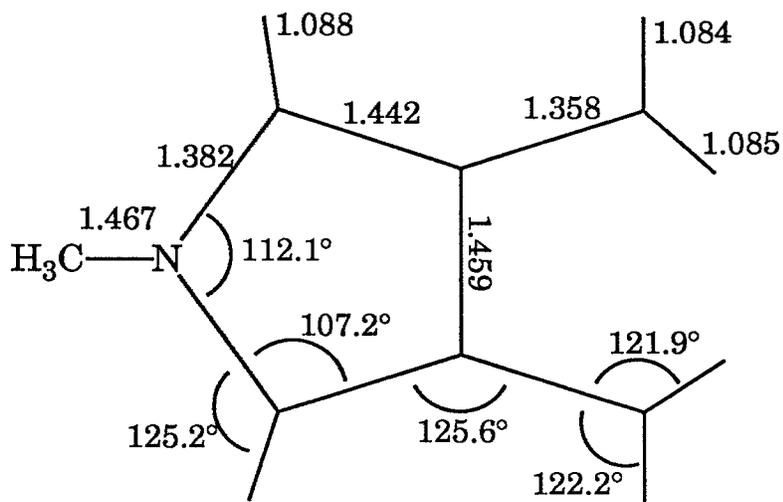


Singlet N-Methyl-3,4-dimethylenepyrrole (3b) by AM1/CI



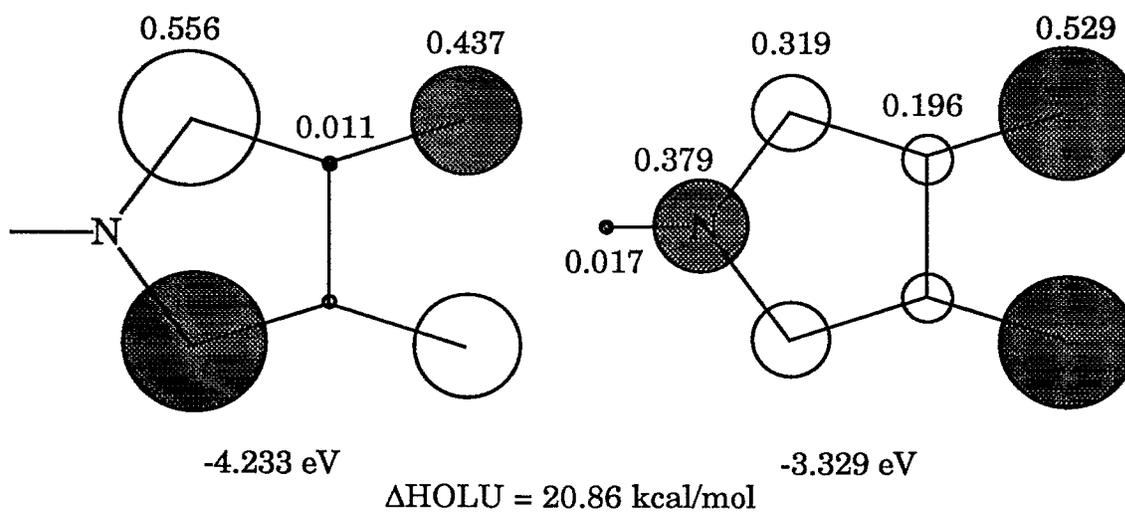
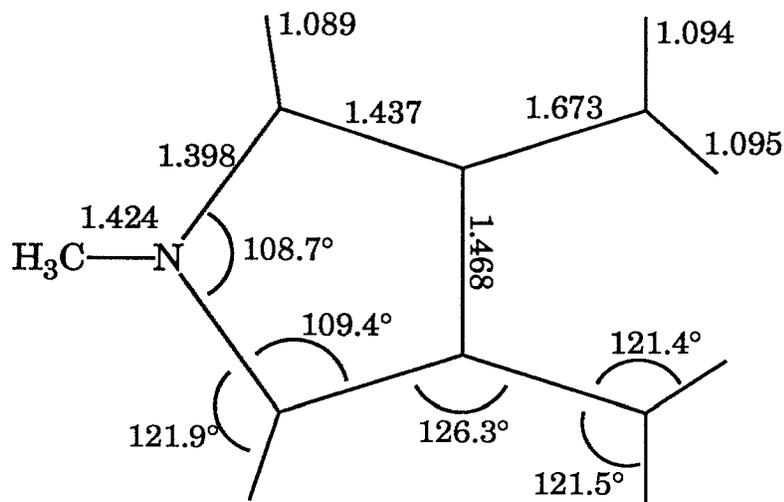
$H_f = 71.829 \text{ kcal/mol}$
 singlet = -12.8868 eV
 triplet = -12.2423 eV

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



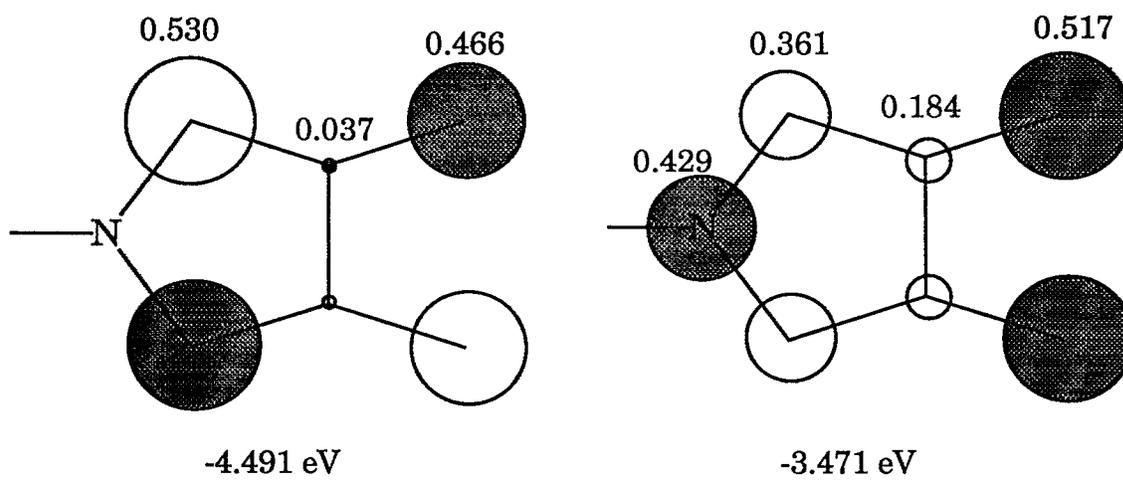
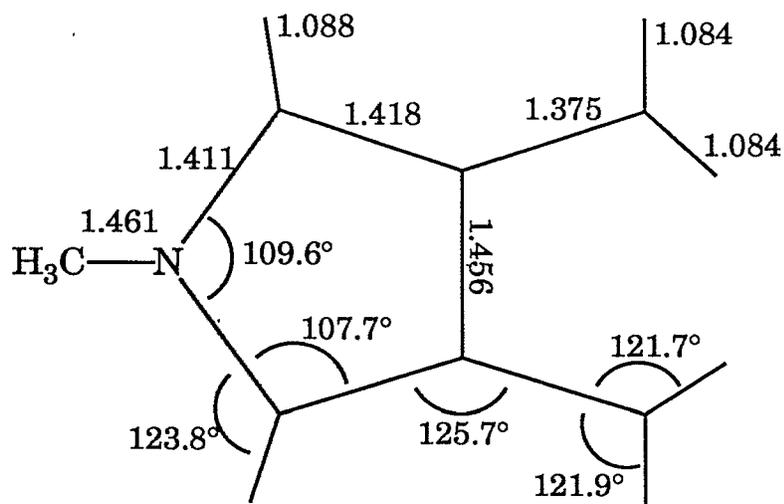
$H_f = 54.448 \text{ kcal/mol}$
 singlet = -12.8419 eV
 triplet = -12.0831 eV

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



$$H_f = 85.884 \text{ kcal/mol}$$

$$\text{triplet} = -12.2241 \text{ eV}$$

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

$$\Delta\text{HOLU} = 23.50 \text{ kcal/mol}$$

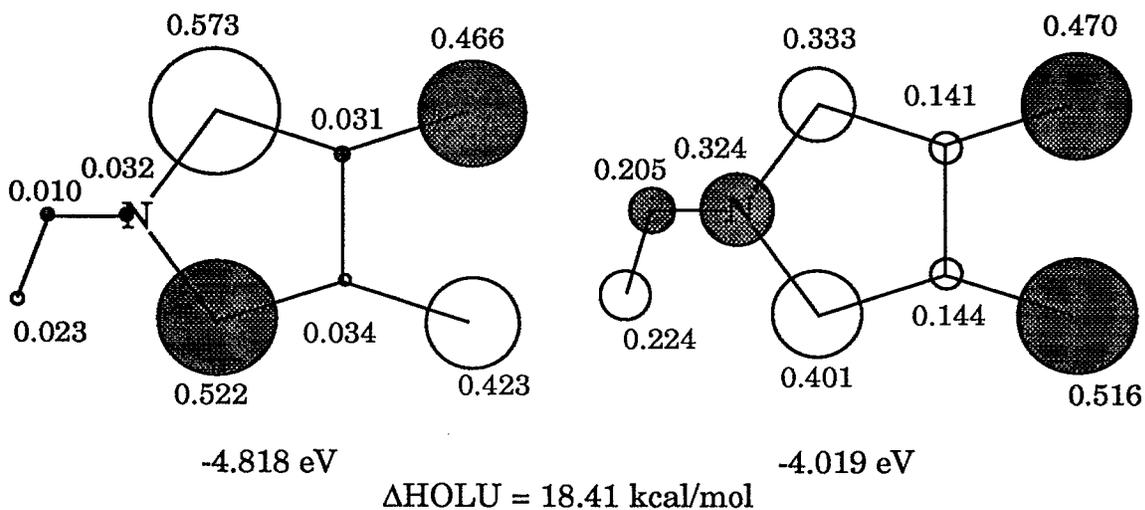
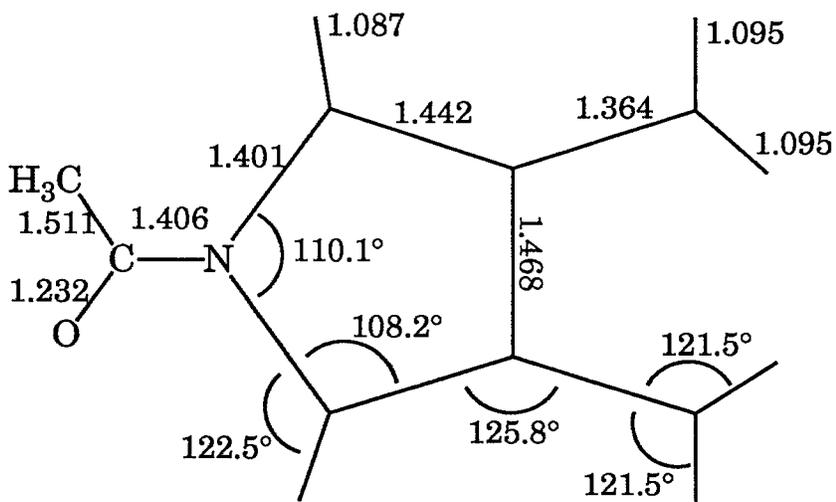
$$H_f = 70.146 \text{ kcal/mol}$$

$$\text{triplet} = -12.0490 \text{ eV}$$

Supporting Information

62

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



$H_f = 42.347 \text{ kcal/mol}$

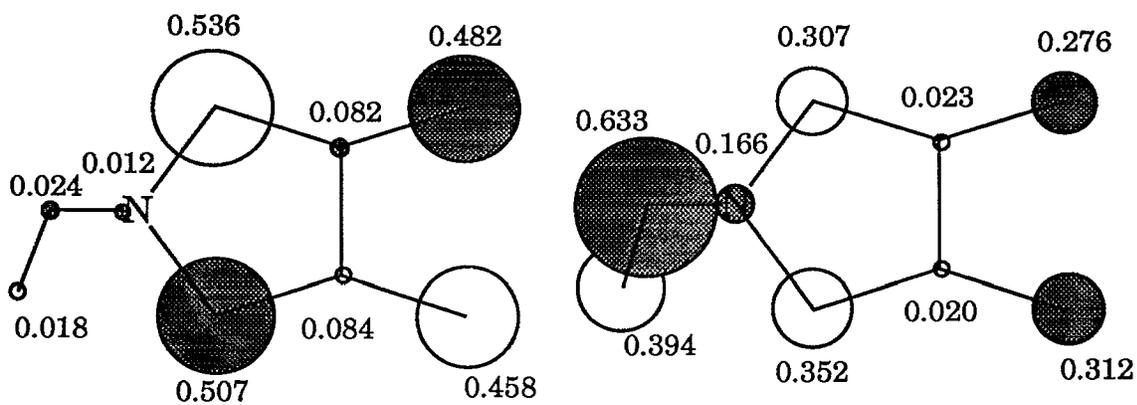
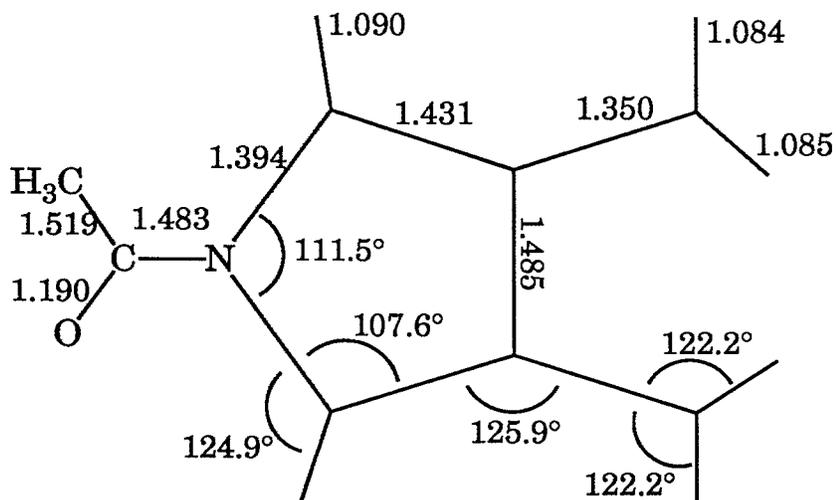
singlet = -12.1554 eV

triplet = -11.7751 eV

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

Supporting Information

63



-4.850 eV

-4.163 eV

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

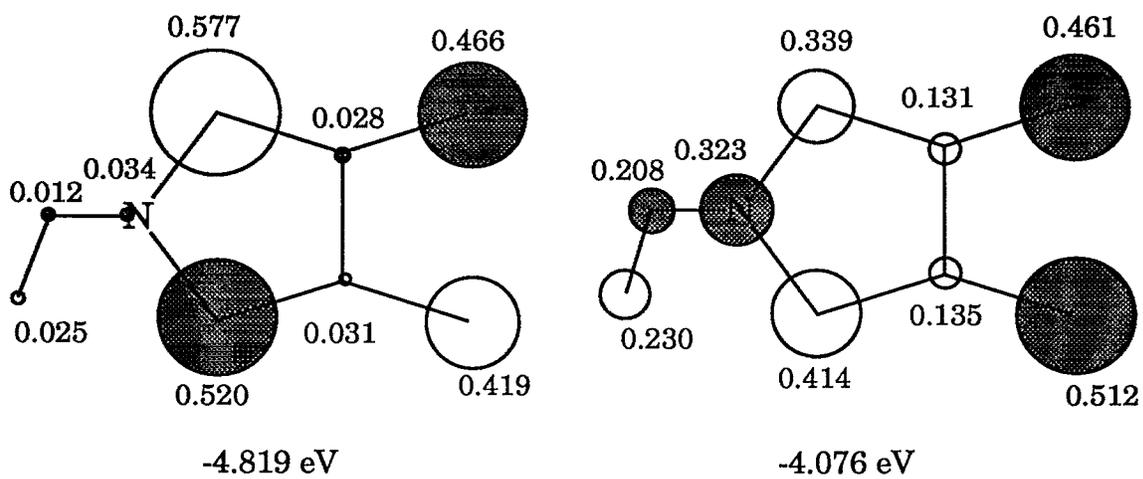
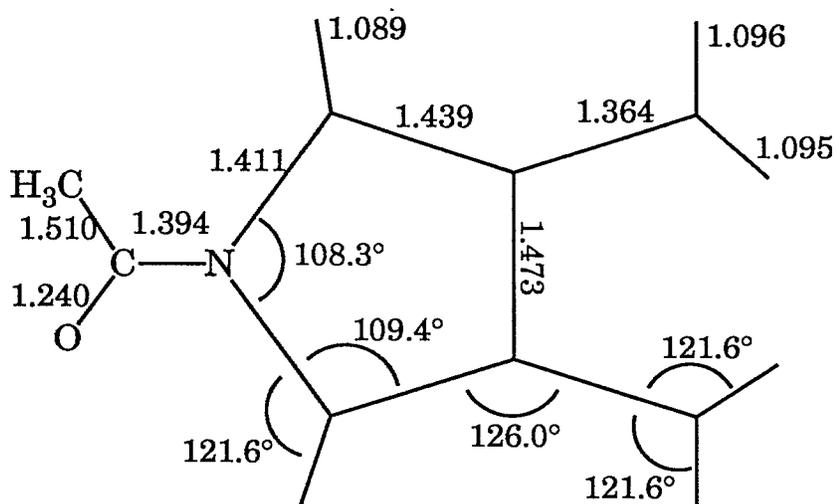
singlet = -12.1645 eV

triplet = -11.6762 eV

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

Supporting Information

64



-4.819 eV

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

-4.076 eV

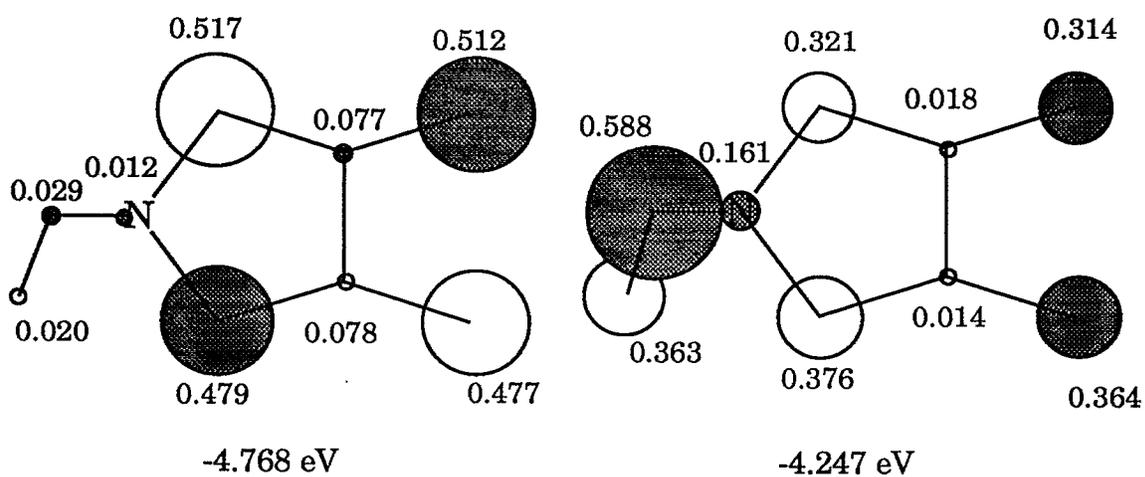
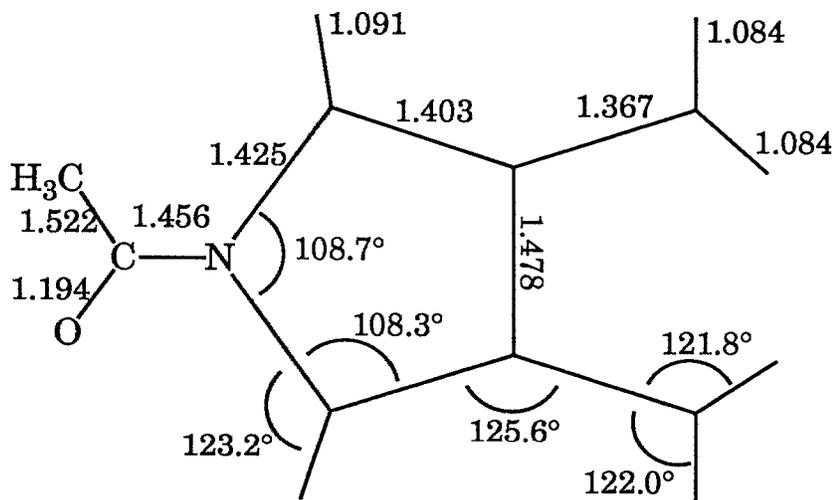
 $H_f = 50.481 \text{ kcal/mol}$

triplet = -11.8121 eV

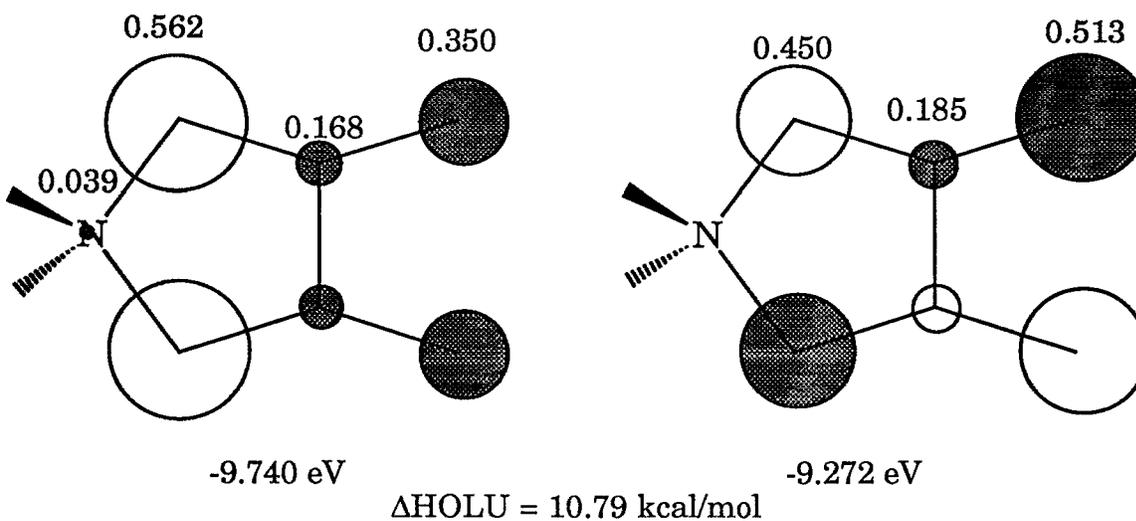
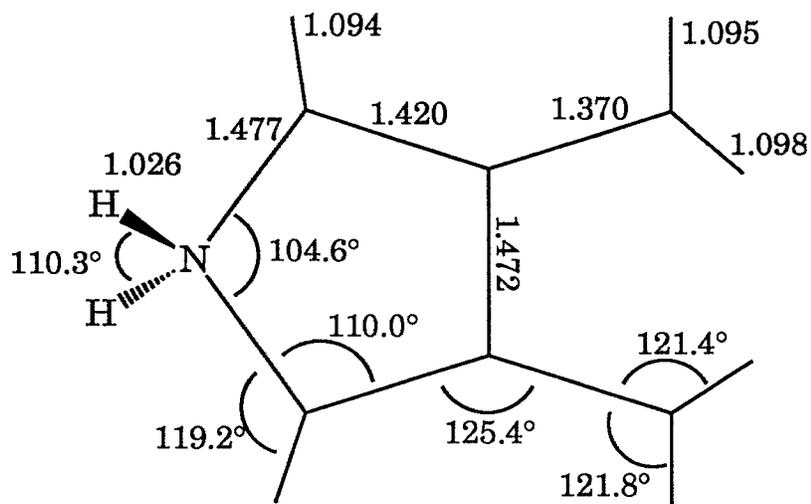
Triplet N-Acetyl-3,4-dimethylenepyrrole by PM3/CI

Supporting Information

65

 $\Delta\text{HOLU} = 12.01 \text{ kcal/mol}$ $H_f = 43.539 \text{ kcal/mol}$

triplet = -11.6886 eV

Singlet 3,4-Dimethylenepyrrolium Cation by AM1/CI

$H_f = 238.128$ kcal/mol

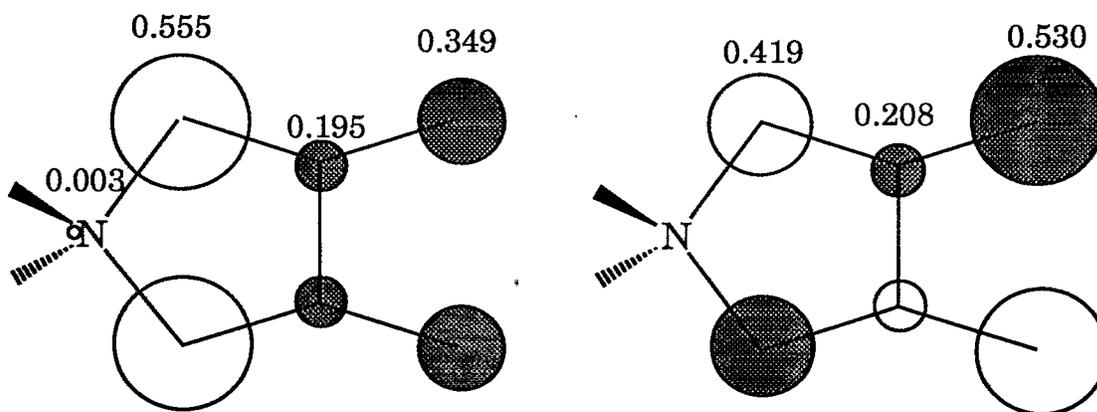
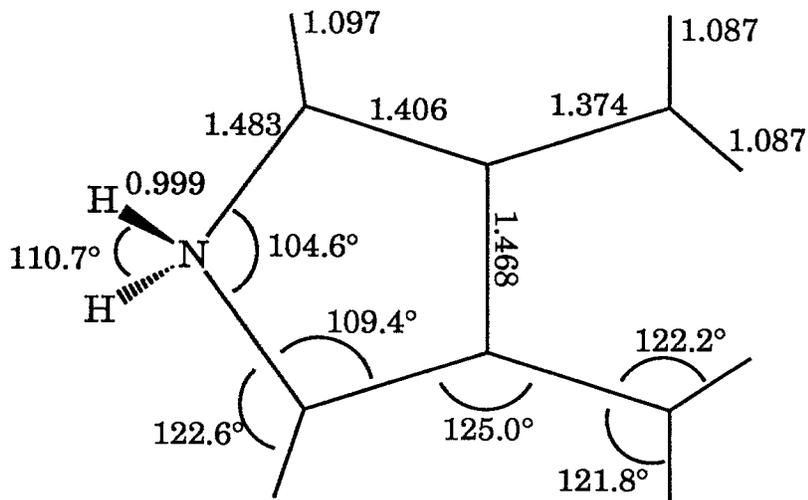
singlet = -12.5327 eV

triplet = -11.2910 eV

Singlet 3,4-Dimethylenepyrrolium Cation by PM3/CI

Supporting Information

67



-10.143 eV

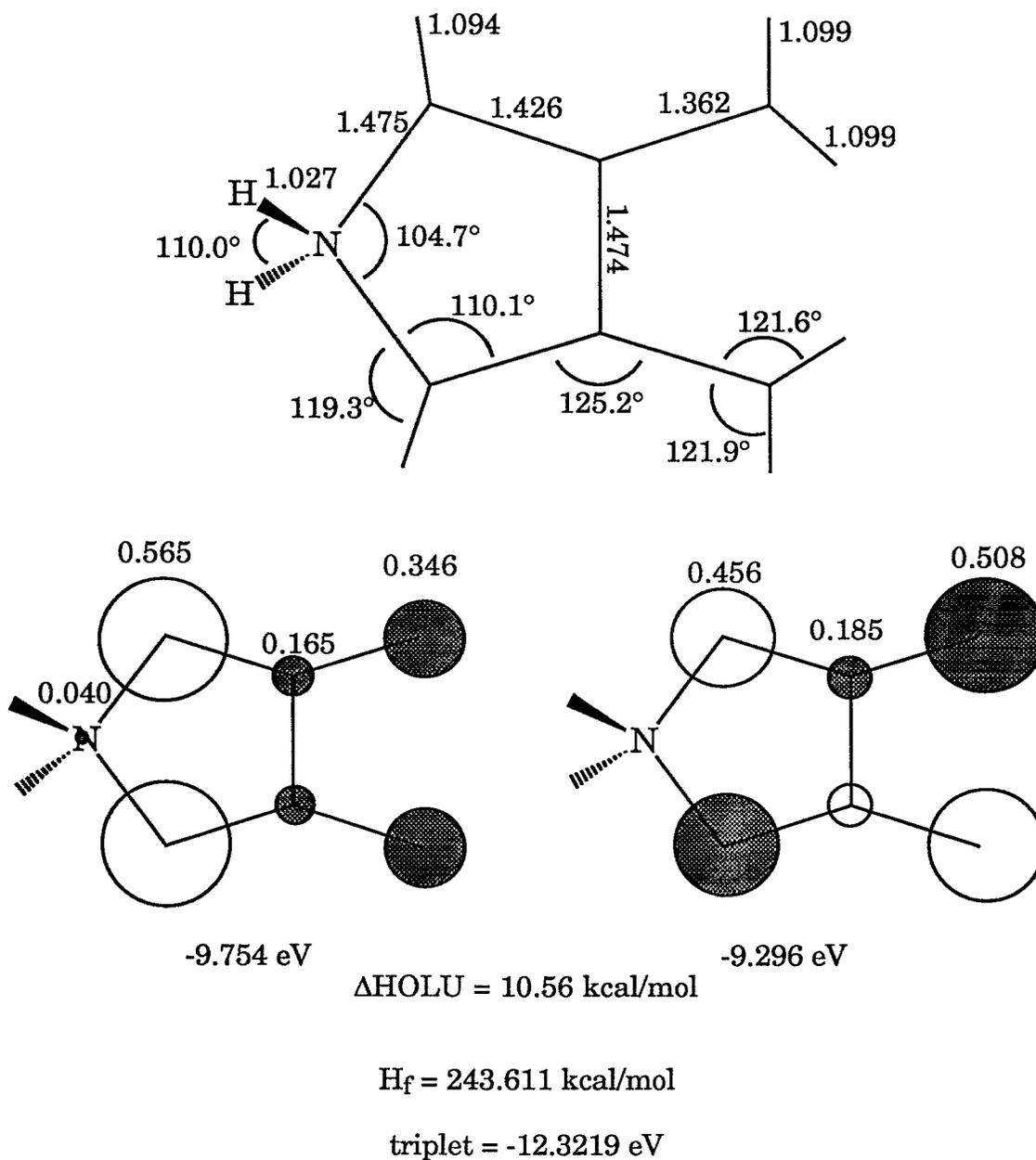
-9.584 eV

 $\Delta\text{HOLU} = 12.90 \text{ kcal/mol}$ $H_f = 228.3249 \text{ kcal/mol}$

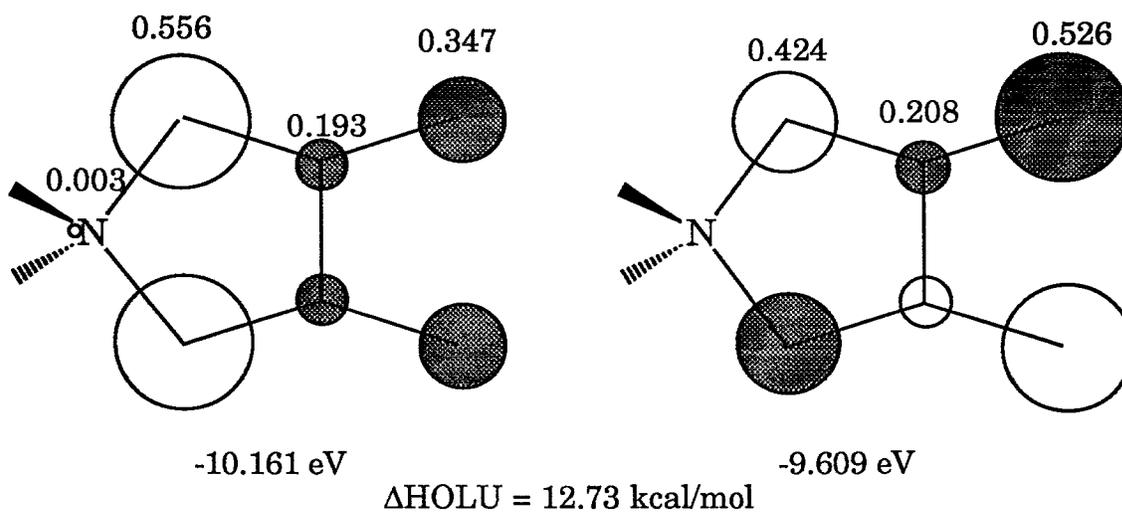
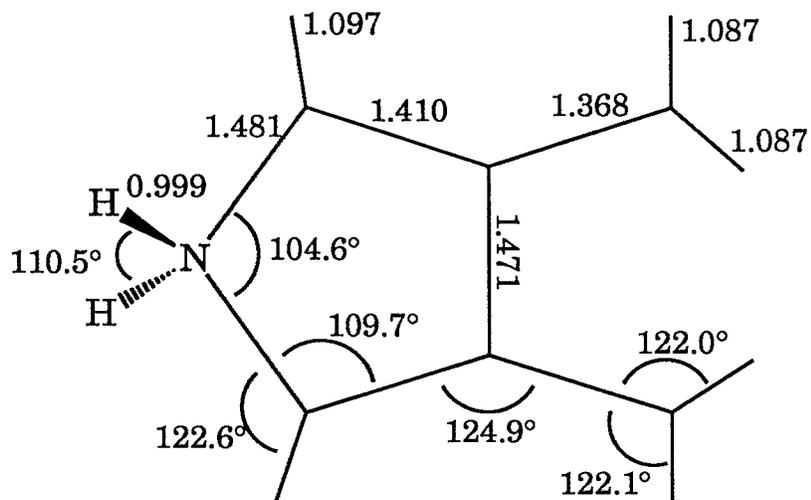
singlet = -12.4182 eV

triplet = -12.1869 eV

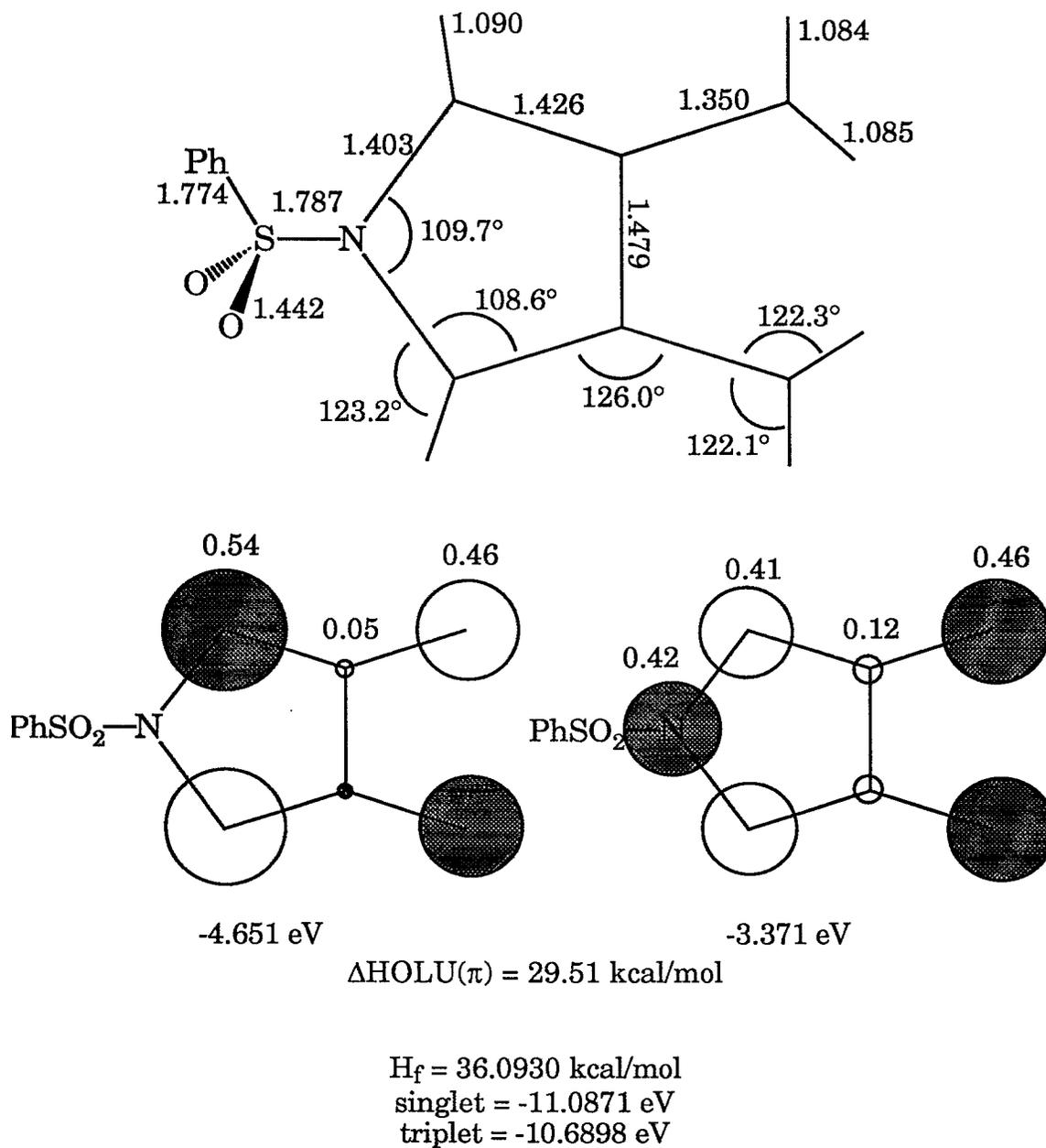
Triplet 3,4-Dimethylenepyrrolium Cation by AM1/CI



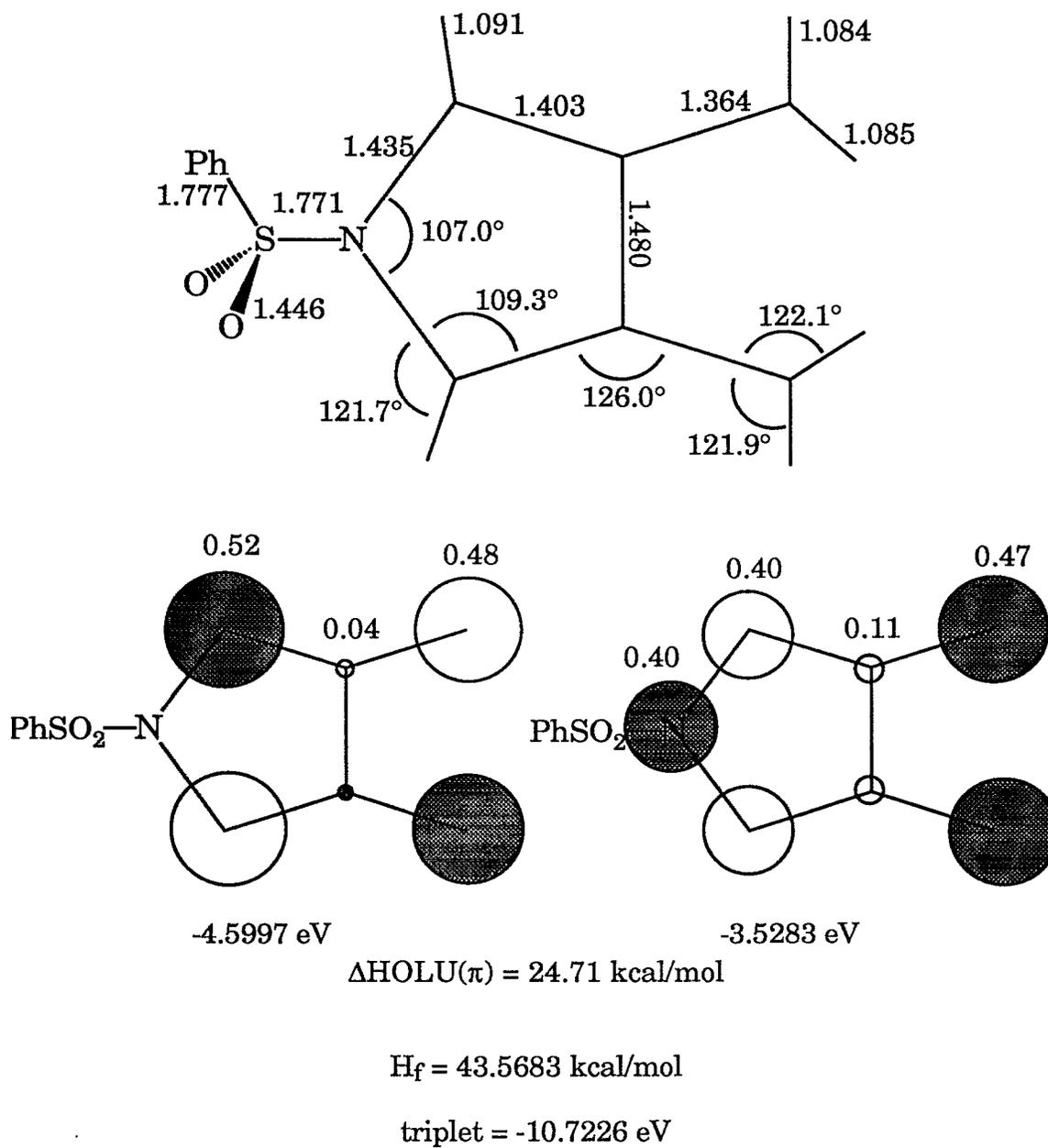
Triplet 3,4-Dimethylenepyrrolium Cation by PM3/CI



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.