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Semiempirical Description of the C_6H_5N Reactive Intermediate in Phenyl Azide Photolysis

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The C_6H_5N intermediate generated by photolysis of phenyl azide in solution is studied by semiempirical computations separately parametrized for thermochemistry and spectra. We find that the intermediate which absorbs only weakly in the region 320-370 nm and which is trapped by amines is the bicyclic azirine singlet, as proposed by DeGraff, Gillespie and Sundberg. Other species such as azepinylidine, the distorted azallyl azacycloheptatetraene and pyridyl carbene seem less likely candidates, either because they would be expected to have a rich spectrum in the visible or because they are unstable relative to the azirine. The adduct formed during trapping by amines rearranges by a suprafacial [1, 3] sigmatropic shift, in contradiction to Woodward-Hoffman predictions. Details of the path are easily rationalized as due to specific orbital interactions.

Key words: Phenyl azide photolysis, C_6H_5N reactive intermediate in ~

1. Introduction

DeGraff, Gillespie and Sundberg [1] (DGS) have reported a flash photolysis study of the kinetics of phenyl azide decomposition and the reaction of an intermediate species with dialkyl amines in solution, leading to the production of azepines. DGS argue by reference to model systems that singlet phenyl nitrene is formed in the initial photolysis, but that a longer-lived bicyclic species is attacked by the amine.

In this report we wish to describe semi-empirical computations bearing on the geometry and spectra of the presumed intermediate C_6H_5N species. Two main types of computation are employed: bond lengths are determined by the MINDO scheme of Dewar [2], as incorporated into the OPTMO gradient search for the ground state geometry developed by Komornicki and McIver [3]. The spectrum is estimated by an INDO version of Del-Bene and Jaffé's scheme in which parameters are chosen to optimize predictions of spectra [4, 5] with multiconfigurational refinements [6, 7]. This variety of approach is adopted because no single set of parameters within the ZDO frame can account simultaneously for such diverse properties as spectra and ground state geometry.

2. Geometry of C_6H_5N and Rearrangement Products (Single Determinant Approximation)

Komornicki and McIver's OPTMO program, available from QCPE, computes the energy and its gradient, and alters molecular geometry following the gradient to the (nearest) minimum in the potential surface. The MINDO expression for the energy of a molecule describable by a single-determinant state produces excellent bond lengths except for bonds to hydrogen which are typically overestimated by 10%. The optimized structures we computed for ϕ-N, the azirine bicyclic rearrangement product, pyridyl carbene, aza-cycloheptatetraene and a 2-azabicyclic methylene (azapinylidene) are described in Fig. 1 and Table 1. The latter three species are not invoked by DGS to rationalize their kinetic data, but are suggested by gas phase studies and reports of analogous hydrocarbon species [8–10].

Several computations on the singlet C_6H_5N species or their hydrocarbon analogues have appeared previous to this work [11–13]. All these computations rely on the single-determinant approximation, and either use model geometries without optimization [13], or permit only limited geometry optimization.

Remarkably, the azepinylidine, azallene and pyridyl carbene are closely comparable in stability, and if phenyl nitrene is formed with a fair amount of vibrational energy, the less stable species could be formed in the course of the reaction. This implication is consistent with conclusions drawn by Wentrup from independent estimates of thermochemistry [10], although MINDO values of the energy differences are considerably lower than those of Wentrup.

We say this even though our geometry-optimized computations estimate that the bicyclo-azirine is 19 kcal more stable than singlet phenyl nitrene. Only if some mechanism exists

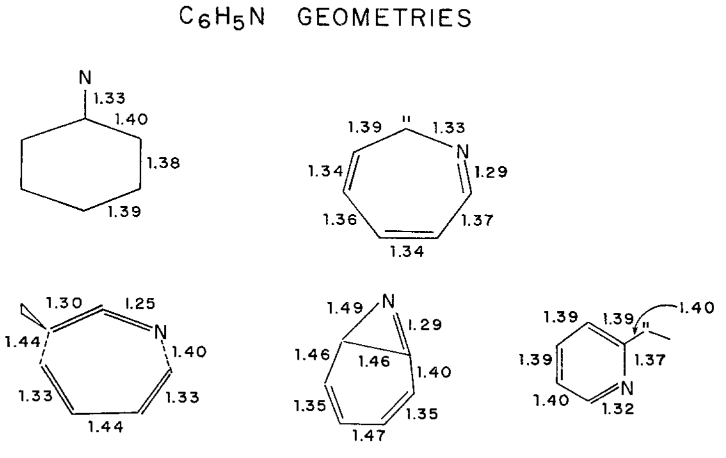

Fig. 1. MINDO-OPTMO optimized geometries for C_6H_5N species are shown, Phenyl nitrene, pyridyl carbene and 2-azacycloheptatrienylidene are planar, the azacycloheptatetraene allylic fragment is strongly twisted (20° from ⊥) and the 7-azabicyclo [4.1.0] hepta-3,5-diene has a dihedral angle of ~35°

Table 1. Energies and spectra of C_6H_5N species

Species	Energy			Absorptions[d]
	MINDO/2[a]	INDO/P[a, b]	INDO/P/INO[a, c]	Position [nm] (Oscillator Strength)
7-Azabicyclo [4.1.0] hepta-2,4-diene singlet	−38.585 (−19 kcal[e])	−55.827 (−68.2)	−55.835 (−64.6)	398 (0.03), 313 (0.02), 252 (0.10)
7-Azabicyclo [4.1.0] hepta-2,4-diene triplet	–	−55.700 (+11.3)	–	382, 358, 315, 301, 284, 275
2-Pyridylcarbene[f]	−38.545 (+6.3 kcal[e])	–	–	–
4-Azacycloheptatetraene	−38.544 (+6.9 kcal[e])	–	–	–
2-Azacycloheptatrienylidene[g] triplet	−38.553 (+1.2 kcal[e])	−55.625 (+58.3)	−55.635 (+60.6)	422 (0.08), 354 (0.10), 262 (1.03)
	–	−55.602 (+72.6)	–	533, 433, 426, 328, 304
Phenyl nitrene singlet	−38.555 (0 kcal[e])	−55.718 (0 kcal)	−55.732 (0)	354 (0.17), 307 (0.03), 250 (0.13)[h]
Phenyl nitrene triplet	–	−55.747 (−18.4)	−55.756 (−15.0)	380[j], 330, 297, 274, 222

[a] At minimum energy geometries according to MINDO/2 – OPTMO

[b] INDO parametrization by Pople, chosen to mimic *ab initio* charge distributions.

[c] INDO-Pople parametrization with two iterations of Iterative Natural Orbital sequence with 27 single and double excitations chosen from five lowest SCI states.

[d] INDO with Jaffé-DelBene spectroscopic parameters, 80 single excitations in the CI representation of the excited state.

[e] Relative to singlet phenyl nitrene.

[f] Thermochemical estimate: +25 kcal.

[g] Thermochemical estimate: +14 kcal.

[h] Doublet.

[i] Valid only if the ground state is mainly a 6-pi electron system: however the 7-pi system also has appreciable absorption near 350 according to an INDO/S/INO computation.

[j] Experimental values [16] are 401, 368, 314, 304 and 240 nm; we observe a consistent 0.4 eV error in the triplet spectra.

for rapidly draining the excess energy away from the bicycloazirine will that species be long-lived. One expects products typical of the 7-membered rings in the gas phase where de-energization of the azirine is slow, and products typical of the azirine in condensed phases where energy transfer is efficient. This expectation is borne out in the hydrocarbon system [9]. The weakness of the azirine bonds which makes it short-lived in the gas phase makes its reaction with a scavenging base efficient in solution, in agreement with Sundberg's observations.

3. SCI and Iterative Natural Orbital Computations on C_6H_5N

We first sought to describe these species by moderately large (80 x 80) CI in the single-excitation approximation, using INDO/P orbitals determined in an SCF computation. INDO/P will describe singlet–triplet splittings even when the pair of electrons differently spin-coupled are on the same atom, in contrast to CNDO. Standard ground state INDO/P parameters were used since a) we wished to describe only the ground state of each multiplicity, rather than spectra, and b) no "correlation" is built into INDO parameters as is done in MINDO thermochemical parameters, since the INDO scheme mimics an *ab initio* SCF computation. Further, we restricted our attention to phenyl nitrene, bicycloazirine and azepinylidene, the three most stable species in this system. Geometries were as found by MINDO, except that we reduced all AH bond lengths by 10% to remove MINDO's systematic overestimate. We found the ground state of ϕN to be a triplet, some 18 kcal more stable than the singlet at the singlet equilibrium geometry, but all other species have singlet ground states.

In order to appreciate the extent of multiconfigurational character in the cyclic carbene, the nitrene, and the bicyclic species we performed iterative natural orbital (INO) computations [14,15] on these species, starting with the same INDO/P orbitals as we employed in the single-excitation CI computations.

As Table 1 indicates, the INO process had no drastic effect on the INDO energy differences: the bicyclic singlet is predicted to be most stable, followed by the nitrene triplet. Although MINDO leads us to consider the azepinylidene as an accessible species, INDO provokes a much dimmer view. In view of Wentrup's thermochemical estimate that singlet azepinylidene is 25 kcal less stable than the singlet nitrene, the azepinylidene is probably not accessible.

4. Spectra of Phenyl Nitrene and Rearrangement Products

4.1. Triplet Phenyl Nitrene

In our simplest series of computations of spectra, we represent a ground state by a single determinant and the excited states available from the ground state by combinations of single excitations from the reference determinant. CNDO and INDO parameterization schemes have been adapted to spectroscopic computation by Del Bene and Jaffé [4] and Zerner and Ridley [5] respectively: we used Jaffé parameters in the INDO scheme. Consider the phenyl nitrene triplet spectrum, for which experimental data is available

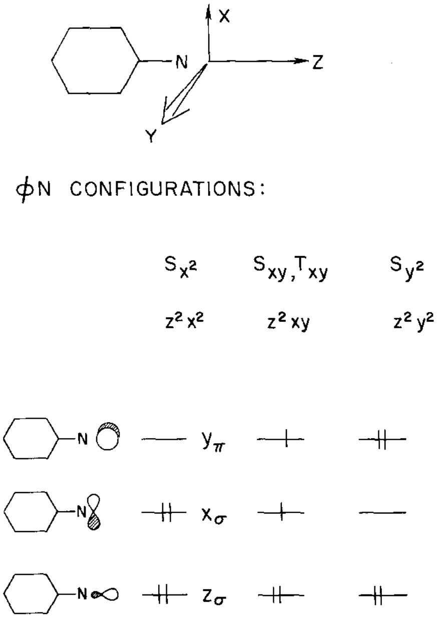

Fig. 2. The coordinate system for phenyl nitrene is shown. Configurations of phenyl nitrene are coded as follows: z^2 refers to an assignment of two electrons to the σ lone pair on N. The z^2y^2 state has eight pi electrons, the z^2xy state has seven pi electrons, and the z^2x^2 state has six pi electons

[16]. All computations agree that the $A_2(xy)$ triplet is the ground state. (The notation is defined in Fig. 2.) Iterative natural orbital computations in which double excitations are permitted indicate that the triplet state is well described by a single-excitation pair of determinants. We assign the first two transitions to $z^2xy(A_2) \rightarrow zxy^2(B_2)$ at 3.3 eV and $z^2xy(A_2) \rightarrow zx^2y(B_1)$ at 3.8 eV; these are to be compared with the experimental 3.1 and 3.3 eV. The remainder of the observed spectrum consists of absorptions at 3.95, 4.08, and 5.2 eV. We compute states at 4.2 (A_1), 4.45 (B_1) and 5.5 eV (A_1) in INDO/S. The INDO/S computed spectrum resembles the observed spectrum but seems consistently to overestimate transition energies. With this appreciation of the accuracy of the INDO/S computation, we will attempt to identify the reaction intermediate in the ϕN_3 photolysis. Chemical tests, in which it is presumed that singlet nitrenes insert into CH bonds while triplet nitrenes abstract H atoms, show that phenyl nitrene is generated from ϕN_3 primarily in the singlet state (50–95%) in hydrocarbon solvents, perhaps 85–90% in alcohols [16]. According to kinetic spectroscopy the intermediate trapped by amines does not absorb beyond the 320 nanometer region (<4.0 eV).

On the basis of qualitative arguments concerning cheletropic motion in ϕN_3 we presumed that singlet ϕN is initially produced in a state with 7π electrons, which absorbs throughout the visible. But regardless of the choice of nitrene state we compute substantial absorptions in the visible region. Therefore the species trapped by amines and nearly transparent in the 320–370 nm region seems not to be the singlet nitrene.

DGS argue that the large negative entropy of activation and the small – perhaps negative – activation energy of the amine trapping reaction suggests that a species more stable than the singlet nitrene and perhaps condensed into rings reacts with the amine.

The lack of effect on the transient signal of oxygenation or deoxygenation and a lack of effect on the rate of signal decay by 0.01 M piperylene implies that the rather stable triplet nitrene does not participate extensively in the reaction.

The triplet bicyclic azirine does not qualify as this intermediate since it is highly unstable relative to other C_6H_5N species and has a rich spectrum throughout the visible region according to INDO/S computations.

INDO/S and INDO/P SCI computations suggest that the ground state of the cyclic methylene (azepinylidene) species is a singlet, but that there is a low-lying triplet within 0.3–0.6 eV of the ground state. This triplet is predicted to have a strong absorption in the neighborhood of 3.8 eV, and a complex less intense absorption spectrum throughout the visible region. We conclude that the cyclic triplet is not the reactive intermediate.

For the singlet azepinylidine SCI and INO computations show that the ground state is almost entirely a single determinant, implying that we may use the INDO/S transition energies to estimate the azapinlyidene spectrum. We expect a strong absorption (oscillator strength 1.03) at 4.7 eV and weaker absorptions near 3.5 and 2.95 eV. Since the sought intermediate does not absorb beyond 320 nm, and the cyclic methylene is transparent there, we cannot reject the singlet cyclic methylene as a candidate for the reactive intermediate.

The singlet bicyclic azirine is computed by INDO/S to have a weak transition (oscillator strength 0.02) lying at 4.0 eV or 310 nm. Some minor absorption beyond 320 nm could be observed, but the conclusion remains that the bicyclic azirine is very nearly a transparent species, and on energetic grounds is the leading candidate for the species trapped by the amine in solution.

4.2. Structure of the 1-H and 3-H Azepine Trapping Products

The 1-H azepine formed upon the trapping reaction rearranges rather slowly with a large negative ΔS to the 3-H azepine.

The large negative ΔS is accounted for [6] by the postulation of a bicyclic intermediate obtained from 1-H azepine by electrocyclic closure of the hexatriene fragment. OPTMO geometry determination of the structure of this species shows that it occupies a relative minimum on the potential surface. The 3- and 6-membered rings are more nearly coplanar (~30°) than models suggest (~60°) (see Fig. 3). The N–H bond is endo and inversion is difficult ($\Delta H_{\text{inv}} \sim 5$ kcal). The butadiene fragment is twisted relative to the bridge bond, with the carbon of the butadiene fragment nearest the NR_2 substituent somewhat depressed, and the other terminal carbon of the butadiene fragment elevated. Most significant, the NH bond is significantly tipped (~14°) from the plane perpendicular to the bridge bond, toward the 3-carbon, its eventual destination. Its tendency toward the 3-carbon rather than the 6-carbon is a substituent effect.

In the highest occupied molecular orbital of 1-H-azepine the *p* orbital of the substituent N is in phase with the ring N, C-3 and H1s AO's. That is, a weak bonding interaction is set up among the ring N, its hydrogen, the substituent N, and C-3: the substituent N

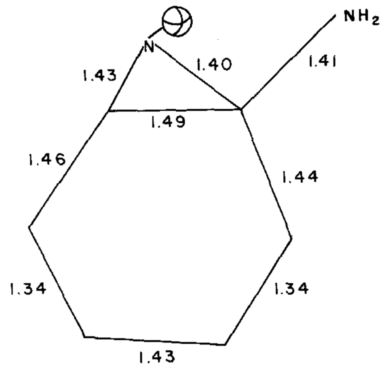

Fig. 3. MINDO/2-optimized structure of the 1-amino-7-azabicyclo-[4.1.0]hepta-3,5-diene, a possible intermediate in the 1-H to 3-H rearrangement of an aminoazepine

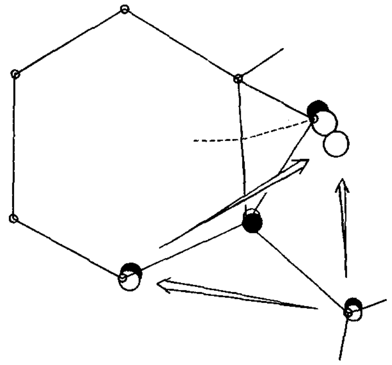

Fig. 4. Lobe diagram of the highest occupied MO in the 1-amino azabicyclo[4.1.0]heptadiene shows the 1-3 bonding interaction and the substituent influence described in the text. The tendency of the hydrogen to migrate suprafacially from the N to the C closest to the amino substituent can be seen to be a substituent effect

aids the suprafacial sigmatropic shift. If the amplitude of the orbital of the central carbon is small - as it is in the highest occupied MO of the bicyclic intermediate - then the [1, 3] suprafacial motion of hydrogen is aided by the substituent.

5. Conclusions

With the aid of MINDO-optimization of geometries, and INDO/S estimates of spectra in phenyl nitrene and conceivable rearrangement products pyridyl carbene, azepinylidene, azacycloheptatetraene and bicycloazirine, we are able to support Sundberg's reaction scheme, that although singlet phenyl nitrene absorbing in the 350-380 region is produced upon photolysis of phenyl azide in solution, under conditions of rapid energy transfer a bicycloazirine which is nearly transparent in the 320-370 region is formed and adds base to form a 1-H azepine. An alternate route involving the azepinylidene is feasible if energy transfer is slow; but the predicted absorption of the azepinylidene near 350 nm should have been detected by kinetic spectroscopy. The slow but stereospecific suprafacial [1, 3] rearrangement of the 1-H azepine formed by trapping with dialkyl amine is apparently aided by the basic substituent.

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