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C−H and C−NO_2 Dissociation Energies in Some Azines and Nitroazines

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Structures and energies have been computed for six azines, their mononitro derivatives, and the radicals formed by loss of a hydrogen or a nitro group. A density functional procedure (B3P86/6-31+G**) was used. Relative stabilities within isomeric groups are compared, and 20 C−H and C−NO_2 dissociation energies are presented. The results are viewed as demonstrating the importance of the electron-attracting powers of the ring nitrogens.

Introduction

Our objective in this work has been to determine computationally and to compare the dissociation energies of the C−H bonds in benzene (**1**) and the azines **2**−**6**, and the C−NO_2 bonds in their nitro derivatives **7**−**16** (see Chart 1). C−H fission is viewed as an initiating step in the pyrolyses of aromatic azines,[1−6] which is relevant to the formation of NO_x species during some combustion processes. Considerable attention has accordingly been focused upon the ease of C−H bond breaking in such molecules.[3−6] C−NO_2 scission is significant with regard to the interest in polynitroazines as energetic materials (e.g., explosives and propellants).[7−14] For example, rupture of a C−NO_2 bond is believed to play a key role in the decompositions of such compounds;[15−23] in particular, their sensitivities to unintended shock or impact (which pose a serious problem) have been linked quantitatively to the properties of these bonds.[15,20,22−26] Quantitative data concerning the strengths of azine C−H and C−NO_2 bonds are therefore of considerable importance for establishing the combustion and decomposition mechanisms of these materials. Since the nitro group can undergo more complex interactions with the aromatic rings than can a hydrogen, it will also be interesting to note the similiarities or dissimiliarities in the trends shown by the C−H and C−NO_2 dissociation energies.

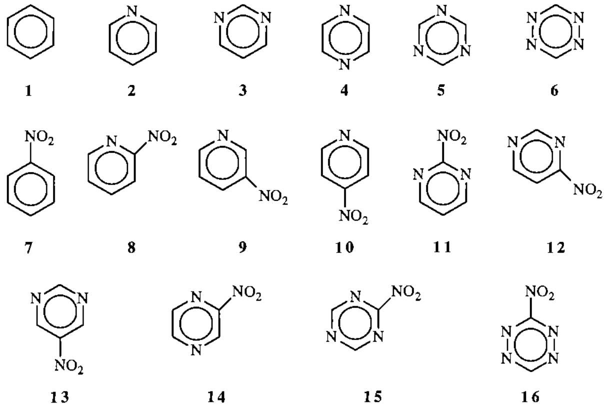
Methods

We have used a density functional procedure and the Gaussian 94 code[26] to compute optimized geometries, energy minima, and enthalpies at 298 K for **1**−**16** and for the products formed upon breaking the various C−H bonds in **1**−**6** and the C−NO_2 bonds in **7**−**16**. The functional combination was the Becke-3 (B3)[27] and Perdew-86 (P86),[28] with the 6-31+G** basis set. We have found the B3P86/6-31+G** procedure to be effective for calculating dissociation energies and heats of reaction.[29,30]

Results

(1) Structures. In Table 1 are the optimized bond lengths for **1**−**16** and for their radicals formed upon C−H or C−NO_2 bond rupture. Experimental values are given where available, and the overall agreement is very good. Among the unsubstituted azines, there is a general uniformity in the C−N bond distances and in the C−C as well; the latter are similar to those in benzene. The substitution of NO_2 slightly shortens the adjacent C−N and/or C−C bonds. This has been observed earlier[10,33] and was attributed to the electron-attracting power of the nitro group. The C−NO_2 distances are generally longest when ortho to a ring nitrogen, about 1.49 Å, and decrease to roughly 1.46 Å when meta.

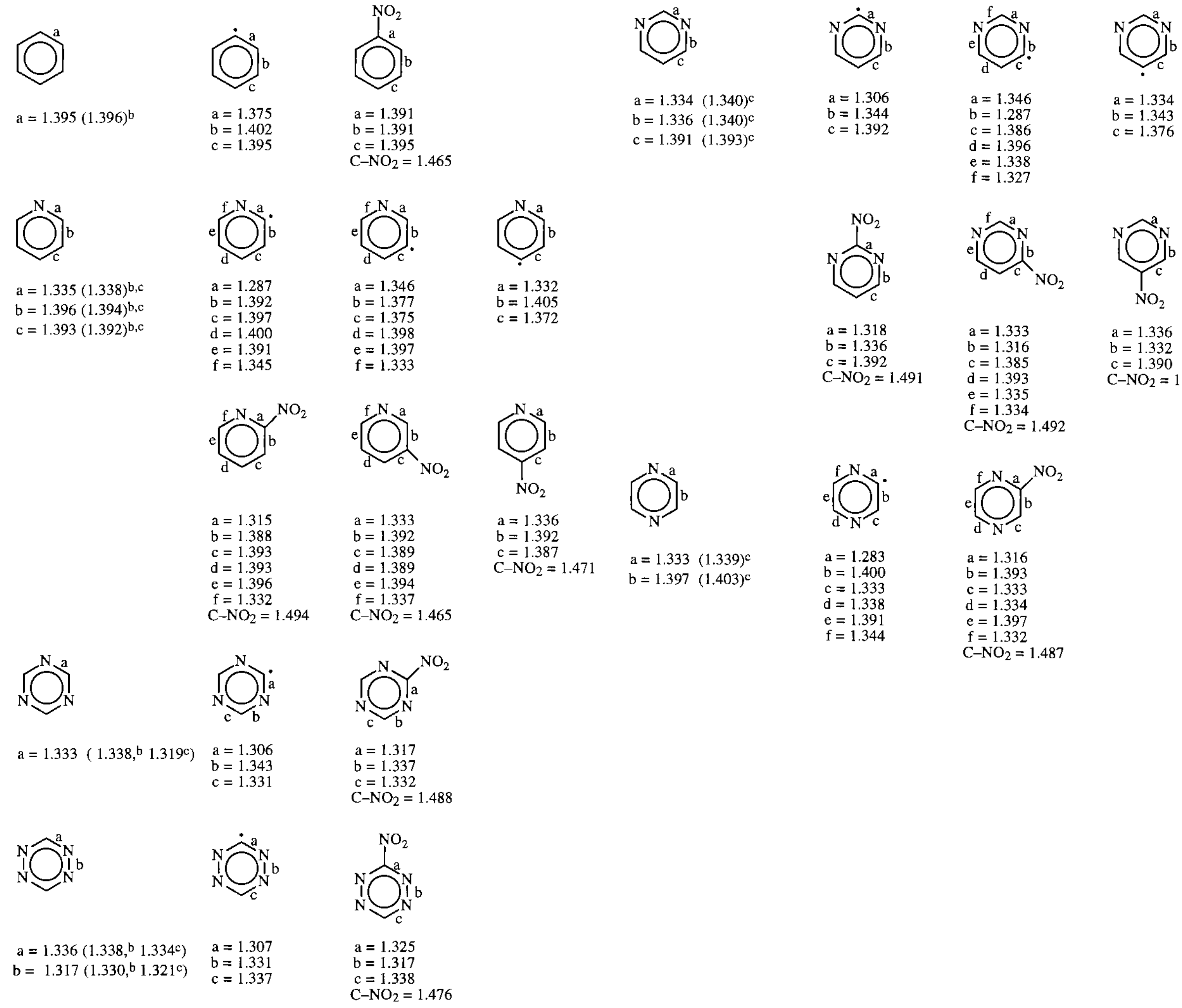
CHART 1



The changes in the structure upon C−H or C−NO_2 bond breaking are particularly interesting. $\dot{C}$−C bonds adjacent to the radical site are approximately 0.02 Å shorter than in the unsubstituted azine, except when the site is ortho to a ring nitrogen, in which case the major effect is a sizable decrease (about 0.05 Å) in the $\dot{C}$−N distance. This may be due to the unpaired electron being drawn somewhat into the bond region, in reponse to the higher electronegativity of the nitrogen. When the radical site is between two ring nitrogens, which are presumably competing for the electron, each $\dot{C}$−N shortening is only about 0.03 Å.

When the nitro group is adjacent to one ring nitrogen, its geometry departs from its usual symmetry in a manner that can be related to the negative character of the ring nitrogen. The N−O distances are now approximately 1.215 and 1.227 Å, the former being for the bond closer to the ring nitrogen; these are the extremes of the range of values obtained for the N−O bond lengths in **7**−**16**. This can be explained by invoking a larger contribution for structure **17A**, due to the greater repulsive

TABLE 1. Optimized Bond Lengths (Å)[a]



a = 1.395 (1.396)[b]

a = 1.375
b = 1.402
c = 1.395

a = 1.391
b = 1.391
c = 1.395
C–NO_2 = 1.465

a = 1.335 (1.338)[b,c]
b = 1.396 (1.394)[b,c]
c = 1.393 (1.392)[b,c]

a = 1.287
b = 1.392
c = 1.397
d = 1.400
e = 1.391
f = 1.345

a = 1.346
b = 1.377
c = 1.375
d = 1.398
e = 1.397
f = 1.333

a = 1.332
b = 1.405
c = 1.372

a = 1.315
b = 1.388
c = 1.393
d = 1.393
e = 1.396
f = 1.332
C–NO_2 = 1.494

a = 1.333
b = 1.392
c = 1.389
d = 1.389
e = 1.394
f = 1.337
C–NO_2 = 1.465

a = 1.336
b = 1.392
c = 1.387
C–NO_2 = 1.471

a = 1.333 (1.338,[b] 1.319[c])

a = 1.306
b = 1.343
c = 1.331

a = 1.317
b = 1.337
c = 1.332
C–NO_2 = 1.488

a = 1.336 (1.338,[b] 1.334[c])
b = 1.317 (1.330,[b] 1.321[c])

a = 1.307
b = 1.331
c = 1.337

a = 1.325
b = 1.317
c = 1.338
C–NO_2 = 1.476

a = 1.334 (1.340)[c]
b = 1.336 (1.340)[c]
c = 1.391 (1.393)[c]

a = 1.306
b = 1.344
c = 1.392

a = 1.346
b = 1.287
c = 1.386
d = 1.396
e = 1.338
f = 1.327

a = 1.334
b = 1.343
c = 1.376

a = 1.318
b = 1.336
c = 1.392
C–NO_2 = 1.491

a = 1.333
b = 1.316
c = 1.385
d = 1.393
e = 1.335
f = 1.334
C–NO_2 = 1.492

a = 1.336
b = 1.332
c = 1.390
C–NO_2 = 1.460

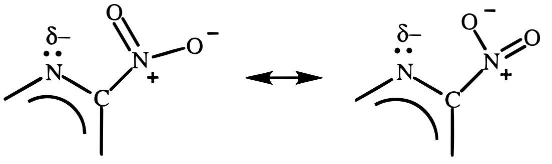
a = 1.333 (1.339)[c]
b = 1.397 (1.403)[c]

a = 1.283
b = 1.400
c = 1.333
d = 1.338
e = 1.391
f = 1.344

a = 1.316
b = 1.393
c = 1.333
d = 1.334
e = 1.397
f = 1.332
C–NO_2 = 1.487

[a] Experimental values are in parentheses. [b] Reference 31. [c] Reference 32.

interaction between the ring nitrogen and the nearby oxygen in **17B**.



17A **17B**

(2) Relative Stabilities. The computed energy minima and enthalpies at 298 K are listed in Table 2. Figure 1 shows the relative enthalpies at 298 K within the several groups of isomers. For a given azine, there is little or no difference in enthalpy between its various mononitro derivatives. However the enthalpy ranges among the corresponding radicals are significantly greater; the greatest stability is observed when the radical site is ortho to one nitrogen, and the least when it is meta. Analogous observations have been reported in earlier computational studies.[34,35]

(3) Dissociation Energies. The C−H and C−NO_2 dissociation energies of **1**−**16**, calculated from the data in Table 2, are given in Table 3 in decreasing order. There is good agreement with the experimental values that are available. Our results for the C−H bonds parallel those obtained by MP2/DZP//HF/3-21G computations[35] but are consistently about 5 kcal/mol higher.

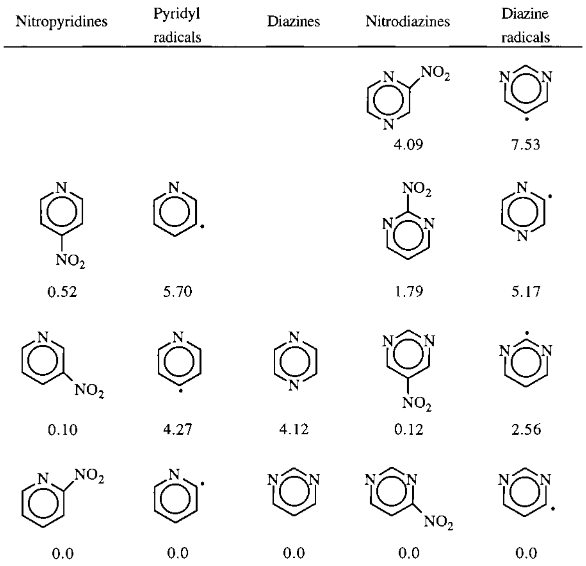
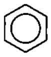
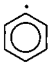
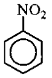
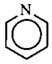
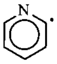
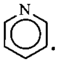
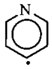
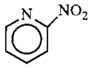
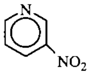


Figure 1. Relative enthalpies at 298 K, in kcal/mol, within groups of isomers.

Discussion

The C−NO_2 dissociation energies in Table 3 vary over nearly twice as large a range as do the C−H, presumably reflecting

TABLE 2. B3P86/6-31+G Computed Energy Minima and Enthalpies at 298 K**

Molecule	E_{min},[a] hartrees	H(298 K), hartrees
	−233.02094	−232.91479
	−232.31229	−232.21925
	−437.91800	−437.80664
	−249.05372	−248.95943
	−248.35333	−248.27198
	−248.34417	−248.26289
	−248.34625	−248.26517
	−453.94643	−453.84716
	−453.94642	−453.84700
	−453.94572	−453.84633
	−265.08925	−265.00666
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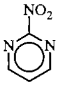
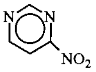
	−264.37808	−264.30845
	−469.97472	−469.88736
	−469.97759	−469.89022
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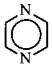
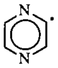
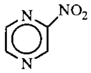
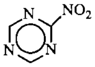
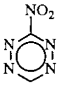
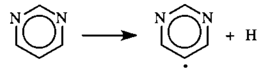
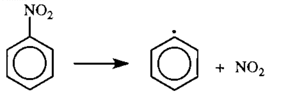
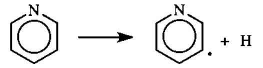
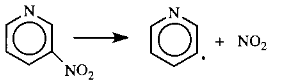
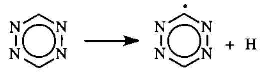
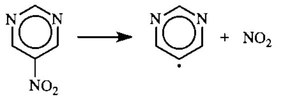
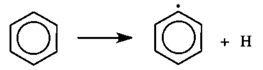
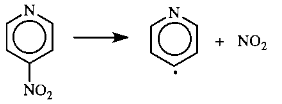
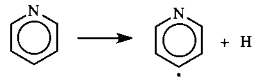
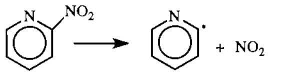
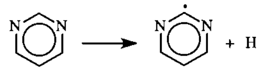
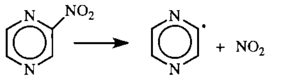
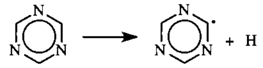
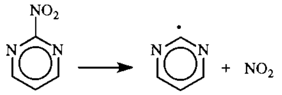
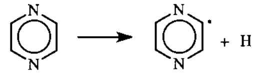
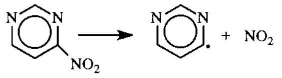
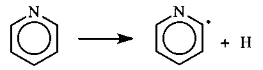
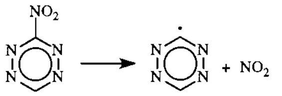
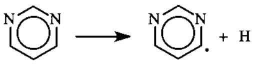
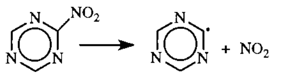
	−265.08231	−265.00009
	−264.38162	−264.31221
	−469.97088	−469.88371
	−281.12720	−281.05635
	−280.42510	−280.36749
	−486.00910	−485.93351
	−297.07996	−297.02297
	−296.37015	−296.32680
	−501.95518	−501.89358
H	−0.51682	−0.51446
NO_2	−205.48462	−205.47178

[a] Zero-point energy not included in E_{min}.

the greater complexities of the interactions between the nitro groups and the azine rings. The ordering of the two types of dissociation energies is also quite different; for example, the C−H value for the tetrazine **6** is one of the highest, but the C−NO_2 for the nitrotetrazine **16** is one of the lowest. However, the dissociation energies for the three types of C−H bonds in pyridine (**2**) decrease in the same sequence as do the corresponding C−NO_2 bonds, meta > para > ortho. There is an analogous parallel between the three C−H and C−NO_2 dissociation energies for pyrimidine (**3**): 5 > 2 > 4.

For pyridine (**2**), pyrimidine (**3**), and their nitro derivatives, the order in which the several C−H and C−NO_2 dissociation energies decrease exactly parallels the increasing stabilities of the respective pyridyl and pyrimidyl radicals (Figure 1). Since the isomeric nitro derivatives of these azines are very similar in energy, it follows that the variation in the magnitudes of the

TABLE 3. Calculated C−H and C−NO_2 Dissociation Energies, in kcal/mol[a]

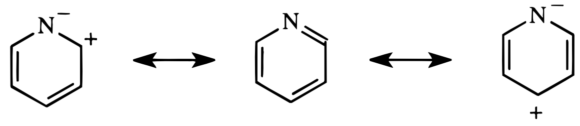
Reaction	ΔH(298 K)	Reaction	ΔH(298 K)
C-H Bonds		*C-NO_2 Bonds*	
	115.3		72.5 (71.3,[b] 71[c])
	114.3		70.5
	114.0		68.9
	113.6 (110.9,[b] 111.3,[b] 111[c])		68.6
	112.8		64.9
	110.3		62.6
	109.4		62.3
	108.8		61.5
	108.6		59.6
	107.8		59.1

[a] Experimental values are in parentheses. [b] Reference 36. [c] Reference 37.

C−H and C−NO_2 dissociation energies can be attributed largely to the relative stabilities of the products.

As a partial explanation of the observed trends, it has been suggested that there is an interaction between azine nitrogen lone pairs and adjacent carbon radical sites.[6,34,35] However such delocalization of the lone pairs should make the 2-pyrimidyl radical more stable than the 4-pyrimidyl.[5,6] We find the reverse to be true (Figure 1), as did Jones et al.[35] We investigated the possibility that our result may be an artifact of the computational approach by repeating the calculations[36,37] for these two radicals using the Perdew/Wang-91 functional[38] instead of the Perdew-86 and considerably increasing the basis set, to 6-311++G-(3df,3pd). The 4-pyrimidyl was again more stable than the 2-pyrimidyl, by nearly the same amount as at the B3P86/6-31+G** level.

The relative stabilities of the radicals can also be interpreted in terms of the withdrawal of electronic charge that is known to be associated with an azine nitrogen.[10,12,32,33] (Striking examples of this have been observed in a computational study of chloro and dinitramino derivatives of *s*-tetrazine, **6**.[12]) This particularly affects the ortho and para positions, as is illustrated below for pyridine, **2**. The greater stability of the ortho and para radicals may accordingly reflect the more positive environment of the unshared electron.



2A **2** **2B**

Summary

We have computed the structures and energies of six azines and their mononitro derivatives, as well as the radicals formed by the loss of a hydrogen from the former and the nitro group from the latter. The corresponding 20 C−H and C−NO_2 dissociation energies are presented. While these do not show any obvious overall trends, their variations within two isomeric groups can be interpreted in terms of the relative stabilities of the product radicals. Our results indicate the importance of the electron-attracting powers of the ring nitrogens in determining the properties of these systems, such as the stabilization of ortho radicals.

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References and Notes

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