Didehydropyridines (pyridynes): An ab initio study

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Results and Discussion

We have calculated the bond energies of several homonuclear diatomic molecules through the proposed scheme, using the values of electronegativity, hardness, and covalent radius of the constituent atoms. The parameters k_1 and k_2 introduced through the modeling of bond electronegativity and bond hardness quantities are evaluated empirically by minimizing the error in predicted bond energies of nine single-bonded molecules, as compared to the experimental results.

For molecules involving multiple bonds, the bond order is larger in magnitude and one expects the bond charge to be higher, which corresponds to higher bond electronegativity and/or lower bond hardness. To mimic this, we propose an empirical relation for the constants k_1 and k_2 for multiple-bonded molecules given by

$$(k_2)_{mult} = (k_2)_{single} n^{-\alpha n^{1/2}} \qquad (13)$$

$$(k_1 k_2)_{mult} = (k_1 k_2)_{single} \qquad (14)$$

where n denotes the bond order and α is an empirical parameter determined by minimization of the overall error in the predicted bond energies of multiple-bonded molecules.

In the present calculation, the values of the coefficients are $(k_1)_{single} = 0.801$, $(k_2)_{single} = 1.467$, and $\alpha = 0.0786$. The value of k_1 is close to unity which indicates an approximate additivity of the chemical potentials (electrostatic potential at the Wigner–Seitz radius) in the bond region.

In Figure 1, we have plotted the calculated bond energies, using the parameters listed above, against the experimental results, which show good agreement. In Table I, the atomic electronegativity, hardness, and homonuclear diatomic bond length parameters used in the calculation are reported along with the calculated values of bond dissociation energies as well as the experimental ones. The average percentage error for bond energies for 19 molecules is 6.52, which reduces to 4.7 if the two molecules iodine and arsenic, for which the error is maximum, are excluded. Considering the fact that in certain cases the experimental error is high (above 5%), the prediction is very good. For the single-bonded systems (except hydrogen), the bond charges compare rather well with the usual bond order although the deviation is greater for the multiple-bonded systems.

Concluding Remarks

The present work has been concerned with a description of covalent binding in homonuclear diatomic molecules within the framework of an electronegativity-based picture through the electronegativity and hardness parameters of the constituent atoms. The novel feature has been the prediction of the bond energy by using the concepts of bond electronegativity and bond hardness. Further studies on improved R-dependent modeling and hence prediction of the potential energy curve as well as extension to polyatomic molecules are in progress.

Didehydropyridines (Pyridynes): An ab Initio Study

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(Received: October 22, 1990)

We report the first ab initio studies on the six DHP (didehydropyridine) isomers at the RHF, ROHF, and GVB levels, obtained with a 3-21G basis set. The geometries of all DHPs are fully optimized at each level of theory to determine their relative stability sequence as 3,4-(S) > 2,3-(S) $\approx$ 2,4-(S) > 3,5-(S) $\approx$ 2.6-(T) $\approx$ 2,5-(S), where (S) and (T) represent singlet and triplet, respectively. At the RHF level the hexagonal structures of the 2,n-DHPs (n = 3, 4, 5, 6) are severely distorted (for n = 3, 4, 6) or broken (for n = 5) by strong N1–C2 bonding, facilitated through a delocalized MO between the nitrogen lone pair orbital and its adjacent radical (C2) lobe orbital. At the GVB level the limited electron correlation between the two radical electrons lowers the RHF energies of the DHPs by 30–48 kcal/mol and the optimized geometries are much less strained hexagonal structures because the two radical electrons and the nitrogen lone pair tend to be confined to different regions. Only 2,6-DHP has a triplet ground state; it may be explained in terms of hindered through-space interaction by the nitrogen lone pair orbital, which stands between the two radical centers.

Introduction

Didehydropyridines (DHPs, commonly called pyridynes) have been the most studied of all known didehydroheteroarenes (or heteroarynes).[1-7] They have been proposed as likely intermediates in many organic reactions, principally those involving cyclo-

addition, cine-substitution, or tele-substitution.[6]

DHP has six possible isomers denoted as i,j-DHP, where i and j indicate the two dehydrogenated carbon centers indexed counterclockwise from the nitrogen.[5] Among the six DHPs, the 3,4-isomer is the most firmly established.[1-6] For example, diazabiphenylene, the dimer of 3,4-DHP, was identified in the time-of-flight mass spectrometric and kinetic UV spectroscopic analysis of the products formed by flash photolysis of pyridine-3-diazonium-4-carboxylate.[8] Recently, we have reported the infrared spectrum of 3,4-DHP generated via mild photolysis of 3,4-pyridinedicarboxylic anhydride (3,4-PDA) in N_2 or Ar matrices at 13 K.[9] These experiments provide convincing evidence that 3,4-DHP exists as a true reactive intermediate, not just as a transition state. On the other hand, the evidence for other DHP

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isomers, which are mostly based on organic trapping experiments, is somewhat inconclusive. The observation of cine-substituted products, Diels–Alder adducts, and tele-substituted products has been taken as evidence of intervening DHP species. These kinds of indirect evidence, however, possess severe limitations as other mechanisms, such as addition–elimination, transhalogenation, or addition ring opening–ring closure, can also account for the formation of the observed products from a given precursor.[6]

Theoretical calculations can provide valuable information regarding the structures and the detailed course of chemical reactions of reactive intermediates where experimental evidence does not exist or is inconclusive. Extended Hückel theory (EHT) calculations on the six DHPs have been carried out by Hoffmann et al. to determine their relative stability sequence as 3,4- > 2,4- > 2,5- > 2,3- > 3,5- > 2,6-DHP.[10] However, that study employed assumed geometries for the DHPs and made no distinction between singlet and triplet states. Energy calculations with optimized geometries in the MNDO approximation by Dewar and Ford suggest that all DHPs have singlet ground states with the relative energy ordering: 3,4- > 2,4- > 2,5- > 2,6- > 2,3- > 3,5-DHP.[11] In these calculations, 3,4-DHP emerges as the most stable isomer and 2,3-DHP is expected to be much less stable than the 2,4- or 2,5-isomer. Early Hückel MO calculations predicted that 2,3-DHP is more stable than the 3,4-isomer because the nitrogen lone pair would be delocalized over the two adjacent dehydrogenated carbon centers.[12] This argument has not been supported by higher level calculations.[10,11,13] Recent ab initio three-active-orbital CASSCF/3-21G calculations on 3,4- and 2,3-DHP with the RHF/3-21G optimized geometries favored 3,4-DHP over the 2,3-isomer by 13.9 kcal/mol and show that the weight of the nitrogen lone pair orbital in the total wave function is not significant.[13] No ab initio studies have been reported for other DHP isomers.

We report here calculations on all six DHP isomers at a sufficiently high level of ab initio theory that reliable predictions can be made. The geometries of all DHPs are optimized at the RHF, ROHF, and GVB levels with a 3-21G basis set and their relative stabilities are determined. We also treat the effect of limited electron correlation between the two radical centers with two-configuration wave functions, and the role of the nitrogen lone pair in that correlation with three-term separated-pair wave functions.[14] The results of these calculations are compared with those for the didehydrobenzenes (DHBs, or commonly called benzynes),[15] which are regarded as the paradigm of strained aromatic ring systems.

Computation

The calculations reported in this paper were carried out within the framework of ab initio MO theory with a 3-21G basis set, utilizing the GAUSSIAN86 program installed on an IBM/3090 system or a Micro Vax II.[16,17] The lowest singlet state of the DHPs was calculated initially at the RHF level and further refined at the GVB level of theory with two-configuration wave functions (equivalent to a TCSCF calculation).[14] The two-configuration wave functions employed approximately represent the symmetric and antisymmetric combinations of the two radical lobe orbitals.[18]
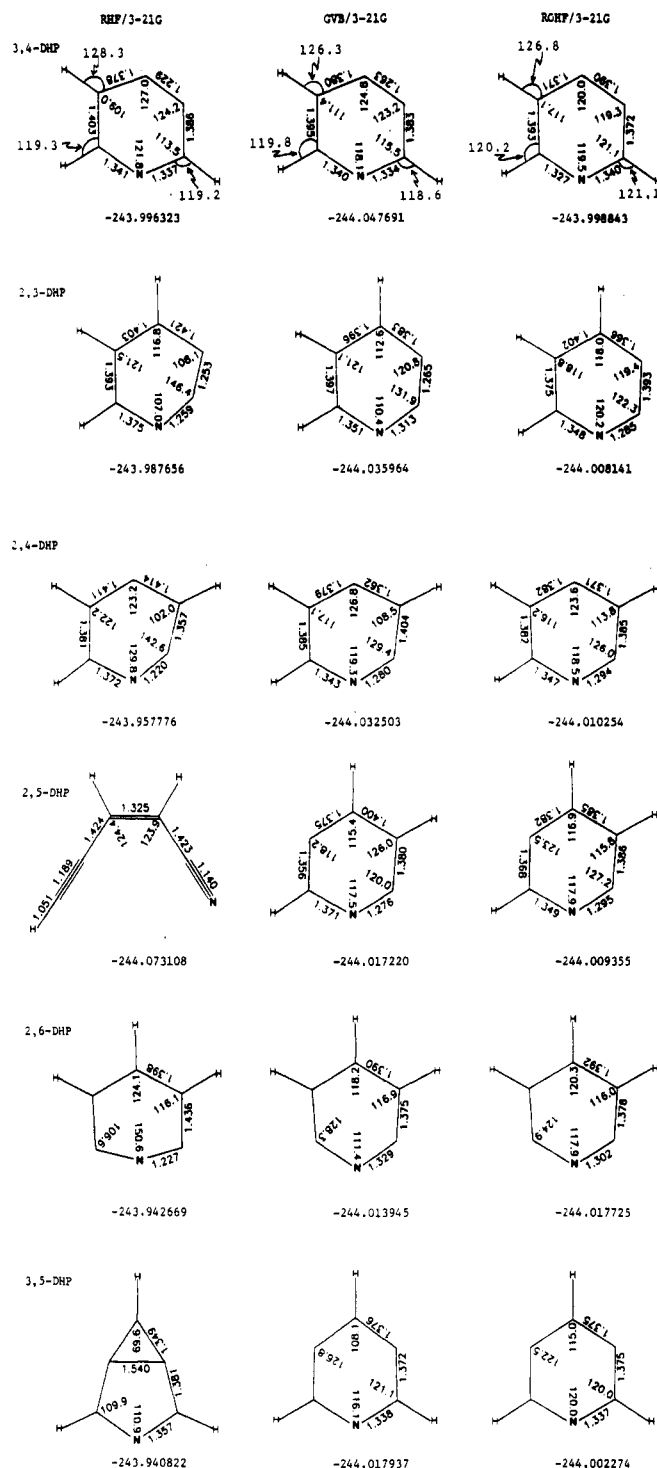
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Figure 1. Optimized geometries of DHPs with corresponding total electronic energies.

In order to examine the role of the nitrogen lone pair in the correlation between the two singlet-coupled unpaired electrons, the GVB procedure was performed with a three-term separated-pair wave function whose third term roughly represents the in-plane nitrogen lone pair orbital.[14] The ROHF method was used to obtain the lowest triplet state. The energy separation between the lowest singlet and triplet states, ΔE_{S-T}, is compared at the GVB and ROHF level.[18] The UHF method was not employed due to large spin contamination.[19]

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TABLE I: Vibrational Frequencies (cm⁻¹) of Pyridine

symmetry	RHF/3-21G	expt[20]	expt/calc	av
in-plane				
A₁	689	601	0.87	
	1083	991	0.92	
	1138	1032	0.91	
	1199	1072	0.89	
	1354	1218	0.90	
	1654	1483	0.90	
	1749	1583	0.91	
	3364	3030	0.90	
	3378			
	3402	3094	0.91	
B₂	749	652	0.87	
	1158	1079	0.93	
	1191	1143	0.96	
	1327	1227	0.93	
	1529	1362	0.89	
	1607	1442	0.90	
	1742	1581	0.91	
	3370	3042	0.90	
	3393	3087	0.91	0.91
out-of-plane				
A₂	458	373	0.81	
	1039	871	0.84	
	1190	966	0.81	
B₁	486	403	0.83	
	822	700	0.85	
	875	744	0.85	
	1118	937	0.84	
	1213	1007	0.83	0.83

TABLE II: Comparison of Calculated and Experimental Frequencies (cm⁻¹) for 3,4-DHP

symmetry	¹A′ RHF	scaled[a]	expt[9]	GVB	³A′ ROHF
A′	535	487	489	674	668
	745	678		734	728
	952	866	848	1022	1067
	1079	982	996	1091	1129
	1146	1043	1055	1129	1152
	1254	1141		1264	1194
	1296	1179		1292	1249
	1365	1241	1216	1371	1364
	1502	1367	1355	1517	1530
	1525	1388	1385	1584	1579
	1576	1434	1558	1597	1676
	2189	1992	2085	1930	1703
	3392	3086		3391	3379
	3433	3124		3427	3396
	3441	3131		3431	3402
A″	464	393		474	463
	559	464		556	515
	756	627		798	806
	951	789	802	954	937
	1047	869	853	1090	1080
	1115	925		1157	1164

[a] Scaling factors: A′, 0.91; A″, 0.83.

The geometries of the DHPs were fully optimized at each level of theory mentioned above, under the assumption that they have planar structures. In order to investigate possible bicyclic structures of 2,4-, 2,5-, 2,6-, and 3,5-DHPs, the geometries of such isomers were initially optimized by fixing the distance between the dehydrogenated carbon centers at various lengths, and further refined with no constraints at the GVB level.

Vibrational frequencies have been calculated for 3,4- and 2,3-DHP at the RHF and GVB levels. In the case of 3,4-DHP, the calculated vibrations were compared with the known experimental frequencies by using the empirically determined scaling factors from the calculated and the experimental[20] frequencies of pyridine.

Results and Discussion

The optimized geometries of singlet (RHF and GVB) and triplet (ROHF) DHPs are shown in Figure 1, with their corresponding electronic energies. The six DHPs are described separately. In discussing the results, DHP atoms are indexed counterclockwise from the nitrogen atom (e.g., N1, C2, C3); and, in the same manner, DHB atoms are numbered from the first dehydrogenated carbon center. The term *strain* in the discussion is rather qualitative and is used to imply the extent of distortion of an optimized DHP geometry with respect to the equilibrium geometry of pyridine.

3,4-DHP. At the single-determinant SCF level, the lowest singlet 3,4-DHP lies 1.6 kcal/mol higher in energy than the triplet. However, consideration of correlation between the two unpaired electrons through a GVB calculation reverses this order, and 3,4-DHP has a singlet ground state with a singlet–triplet energy difference (ΔE_{S-T}) of 30.7 kcal/mol; this difference is very similar to that of 1,2-DHB (or *o*-benzyne), 29.9 kcal/mol,[15] when it is calculated at the same level of theory.

A comparison between the RHF and the GVB optimized structures of singlet 3,4-DHP shows large differences. The most significant change in bond distance is the lengthening of the C3–C4 triple bond (1.229 → 1.263 Å) as a consequence of the participation of the in-plane π^* antibonding character in the GVB description. The occupation number of the acetylenic in-plane π^* natural orbital in the GVB/3-21G optimized structure is 0.11. The same trends are found in the calculation of 1,2-DHB; similar triple bond lengthening (1.225 → 1.261 Å), and the same in-plane

π^* natural orbital occupation number (0.11).[13,21] This suggests that the bond between the two radical centers is almost identical for both 1,2-DHB and 3,4-DHP. On the other hand, the total atomic charges on the dehydrogenated carbon centers of 1,2-DHB have the same negative charges (−0.002) while those of 3,4-DHP have opposite charges (C3, −0.09; C4, +0.07). This unequal charge distribution in 3,4-DHP would explain the unequal rates of nucleophilic addition at the two ends of the dehydro bond.

Prior to the calculation of the vibrational frequencies of 3,4-DHP at the RHF/3-21G level, the performance of the theory was monitored by comparing the calculated and the observed vibrational frequencies of pyridine. The values are collected in Table I, from which it can be seen that the calculated in-plane (A₁, B₂) and out-of-plane (A₂, B₁) vibrations of pyridine are overestimated by 10.5% and 20.5% on average, respectively. The same trend is found for benzene: in-plane vibrations are overestimated by 10.5% and out-of-plane modes by 17.9%.[15] These results indicate that out-of-plane vibrations of aromatic systems are more overestimated than in-plane vibrations at the RHF level of theory.[22] Thus, we have applied two different scaling factors (0.91 for in-plane and 0.83 for out-of-plane vibrations) to the calculated vibrations of 3,4-DHP. The results are summarized in Table II. However, the RHF scaling factors are *not* applied to GVB frequencies since the transferability of an empirical factor between the two different levels of calculation cannot be justified.[21]

In general, the agreement between the scaled and the observed frequencies is quite satisfactory. However, the scaled (×0.91) vibrational frequencies of the C3–C4 stretch (ν_{C3C4}), 1992 cm⁻¹, and the ring stretching plus CH wagging mode ($\nu_{ring+CH}$) at 1434 cm⁻¹ are much lower than the corresponding assignments: 2085 and 1558 cm⁻¹, respectively.[9] The same pattern has been observed for the triple-bond stretch (ν_{C1C2}) and $\nu_{ring+CH}$ of 1,2-DHB; 2010 and 1469 cm⁻¹ are predicted after the RHF/3-21G frequencies are scaled by 0.91, while the experimental values are in the range 2082–2085 and 1596–1607 cm⁻¹, respectively.[13,23] The GVB method calculates the ν_{C3C4} of 3,4-DHP at 1930 cm⁻¹, which is

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very close to ν_{C1C2} of 1,2-DHB, 1931 cm^{-1},[21] obtained at the same level of calculation.

The triple-bond stretch of 1,2-DHB obtained from the laser photoelectron detachment spectrum of the 1,2-DHB anion of Leopold, Miller, and Lineberger is 1860 cm^{-1},[24] which is about 220 cm^{-1} lower than the value from diverse matrix isolation experiments.[23] Scheiner, Schaefer, and Liu predicted that the correct ν_{C1C2} of 1,2-DHB should lie in the range 1965–2010 cm^{-1}, based on their GVB and MP2 calculations with a DZ+P basis set, and questioned whether the ν_{C1C2} observed in inert matrices is really due to 1,2-DHB.[25] These controversies regarding 1,2-DHB raise a question about the assignment of the experimental results for 3,4-DHP, since the physical characteristics of the bonding between the two dehydrogenated carbon centers (e.g., bond length, diradical character, and vibrational frequency) are almost identical for both compounds.

However, although there remains some doubt about the experimental assignment, theoretical predictions of vibrational frequencies also have certain limitations: (1) The ratios between the experimental and RHF calculated in-plane vibrational frequencies of benzene and pyridine range from 0.87 to 0.98, and those of ν_{C1C2}(1,2-DHB) and ν_{C3C4}(3,4-DHP) do not deviate from this range. (2) It is known that electron correlation sometimes underestimates the vibrational frequency of multiple bonds.[26] (3) The level of accuracy that can be attained by purely computational methods, especially for a large molecule, is still less definitive than experimental determination.[19,27] Moreover, the matrix isolation experiments for 3,4-DHP and 1,2-DHB were highly reproducible.[15,23] Thus, we are inclined toward the interpretation that GVB or MP2 methods *underestimate* the frequency of the strained triple bond in aromatic ring systems.

The harmonic vibrations of the lowest 3,4-DHP triplet state are also listed in Table II. The most noticeable difference between the singlet and triplet involves the triple-bond-stretching vibration, which drops to 1703 cm^{-1}; this reveals that the C3–C4 triple bond character is essentially lost in the triplet state.

2,3-DHP. Experimental evidence supporting the generation of 2,3-DHP is neither as extensive nor as convincing as that for 3,4-DHP.[6] For example, the photolysis of 2,3-PDA in N_2 or Ar matrices leads to rupture of the ring structure and formation of a strong –C≡N bond. Infrared spectra of the products taken at various time intervals during photolysis provide no evidence for the intermediacy of 2,3-DHP.[9] This isomer seems particularly interesting, however, because of the various possible interactions among three adjacent lobe orbitals.

The total electronic energy of singlet 2,3-DHP at the GVB/3-21G level lies 7.4 kcal/mol higher than that of 3,4-DHP, but 17.5 kcal/mol below that of its lowest triplet state. Contrary to previous MNDO or EHT predictions,[10,11] this isomer is calculated to be the second most stable among all DHP isomers.

The RHF/3-21G optimized geometry indicates that there is a substantial delocalization of the nitrogen lone pair into the two dehydrogenated carbon centers. Jones and Beveridge suggested that this delocalization among the three lobe orbitals makes the 2,3-isomer more stable than 3,4-DHP.[12] However, this interaction severely strains the ring structure of 2,3-DHP by widening the bond angle at C2 (146.4°) to allow maximum overlap among the three lobe orbitals centered on N1–C2–C3, at the cost of increased angle strain at N1 (107.0°) and C3 (108.1°). Apparently, the system would gain little stabilization from such an interaction.

The RHF HOMO and LUMO of 2,3-DHP are approximately expressed as linear combinations of three lobe orbitals centered on N1–C2–C3. When these two orbitals are taken as a pair of initial GVB natural orbitals, the GVB SCF procedure minimizes

TABLE III: The C≡C Bond Length (Å) and Its Vibrational Frequency (cm^{-1}) of Vicinally Didehydrogenated Aromatic Systems

compound	$R_{C≡C}$ (GVB)^a	$R_{C≡C}$ (ROHF)^b	$\nu_{C≡C}$ (GVB)	$\nu_{C≡C}$ (exp)^9
1,2-DHB	1.261	1.389	1931	2082
3,4-DHP	1.263	1.390	1930	2085
2,3-DHP	1.265	1.393	1894	2044^c

^{a}Singlet. ^{b}Triplet. ^{c}Expected experimental value.

the magnitude of the nitrogen lobe orbital and leads to symmetric and antisymmetric combinations of the two radical lobe orbitals. Since the GVB method with a two-configuration wave function may underestimate the contribution of the nitrogen lone pair orbital, we have examined the three-term separated-pair wave function which adds the nitrogen lobe orbital as the third term in the correlation between the two singlet coupled electrons.[14] However, it turns out that the contribution from the third term to an overall wave function is negligible (0.04%). This result is consistent with the recent three-active-orbital CASSCF/3-21G calculation for 2,3-DHP, which also found that inclusion of the nitrogen lone pair orbital in the active space has only a marginal effect, even with the RHF optimized geometry.[13]

Thus, the bonding between C2 and C3 is determined primarily by the coupling of the two unpaired electrons and the nitrogen lone pair is mostly localized on nitrogen. The GVB optimized geometry clearly reflects this tendency: the bond length N1–C2 substantially increases (1.259 Å → 1.313 Å) while the bond angle at C2 correspondingly decreases (146.4° → 131.9°) from the RHF optimized geometry. The resultant geometry of 2,3-DHP is then much less strained than that from the RHF calculation and becomes rather close to other vicinally didehydrogenated aromatic systems. The entries in Table III show the similarity of the bonds between the two vicinal dehydrogenated carbon centers of 1,2-DHB, 3,4-DHP, and 2,3-DHP.

The harmonic C2–C3 stretching frequency at the RHF/3-21G level is predicted to be 1936 cm^{-1}, which is reduced to 1762 cm^{-1} by a scaling factor 0.91. This value suggests that the C2–C3 bond in the RHF optimized geometry of 2,3-DHP is essentially a strained allenic bond. The calculated value of ν_{C2C3} at the GVB level is 1894 cm^{-1}. Since the GVB method apparently underestimates the vibrational frequency of the strained triple bond in 1,2-DHB or 3,4-DHP by about 7.3% (see Table III), the ν_{C2C3} stretching frequency in 2,3-DHP may be up-scaled to 2044 cm^{-1}. Thus, we expect that, if 2,3-DHP is ever formed in a matrix isolation experiment, the C≡C stretching frequency would be observed at about 40 cm^{-1} below that of 3,4-DHP.

2,4-DHP. 2,4-DHP has been proposed as a likely intermediate in the tele-substitution of 6-substituted-2-bromopyridines with KNH_2.[28] Two previous theoretical calculations predicted that 2,4-DHP is the second most stable isomer of DHP.[10,11] The MNDO calculation estimates that the heat of formation of 2,4-DHP is only 0.5 kcal/mol higher than that of 3,4-DHP but 8.6 kcal/mol lower than that of 2,3-DHP.[11]

At the GVB/3-21G level, the lowest singlet state of 2,4-DHP lies 9.6 kcal/mol higher in energy than that of 3,4-DHP. Contrary to previous semiempirical calculations,[10,11] 2,4-DHP is less stable than 2,3-DHP by 2.2 kcal/mol. The ground electronic state of 2,4-DHP is singlet with a predicted ΔE_{S-T} of 14.0 kcal/mol.

RHF/3-21G calculations on 1,3-DHB (or *m*-benzyne) yield a bicyclic structure with a C1–C3 separation of 1.514 Å.[15] Since the two dehydrogenated carbons of 2,4-DHP are also meta, one might expect the RHF calculations to predict a bicyclic structure for 2,4-DHP. However, as noted in the example of 2,3-DHP, at the RHF level the nitrogen lone pair tends to delocalize over the adjacent dehydrogenated carbon lobe orbital, which considerably weakens the C2–C4 interaction. Thus, the RHF optimized geometry of 2,4-DHP has short N1–C2 bond length (1.220 Å) and a rather close C2–C4 distance (2.153 Å) compared to the normal

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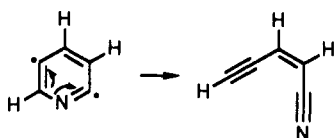
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SCHEME I

pyridine geometry (2.378 Å), but much longer than the C1–C3 distance of 1,3-DHB. The total overlap population between the two radical centers (–0.10) is negative, which is indicative of no effective bonding between them. No bicyclic 2,4-DHP was found in our calculation, while the previous MNDO calculation predicts it to be 17.3 kcal/mol higher in energy than the singlet 2,4-DHP diradical.

The GVB SCF procedure with either two-configuration or three-term separated-pair wave functions restricts the delocalization of the nitrogen lone pair on the adjacent radical center. A comparison between the RHF and the GVB optimized structures of singlet 2,4-DHP shows large difference in the N1–C2 bond length (RHF, 1.220 Å, GVB, 1.280 Å) and its adjacent bond angle (RHF, 142.6°; GVB, 129.4°). The resultant GVB geometry is less strained than the RHF structure and has much lower energy. Thus, we conclude that 2,4-DHP exists as a diradical, with a more stable structure when the nitrogen lone pair is localized.

2,5-DHP. Although the heat of formation of 2,5-DHP (133.5 kcal/mol) calculated by the MNDO method is only 1.6 kcal/mol higher than that of 3,4-DHP,[11] no experimental evidence for 2,5-DHP has been reported.[6] On the other hand, our GVB calculation predicts a substantially large energy difference, 19.1 kcal/mol, between the two isomers. The singlet 2,5-DHP lies 4.9 kcal/mol lower in energy than the triplet state.

The most interesting question about 2,5-DHP pertains to the stability of its ring structure, since C6–N1 bond scission readily leads to a more stable acyclic isomer, β-ethynylacrylonitrile (Scheme I). Such a ring-opening mechanism would become facile if the nitrogen (N1) lone pair is allowed to interact with its neighboring radical center (C2) to form a strong –C≡N bond. Indeed, RHF geometry optimization of 2,5-DHP converges to the β-ethynylacrylonitrile structure. As we have observed from the examples of 2,3- and 2,4-DHP, the RHF method tends to exaggerate the delocalization of the nitrogen lone pair and consequently it fails to retain the cyclic structure for 2,5-DHP.

The GVB calculation with a two-configuration wave function, on the other hand, localizes the nitrogen lone pair and yields a cyclic 2,5-DHP (see Figure 1). However, GVB geometry optimization of 2,5-DHP with a three-term separated-pair wave function again fails to obtain a cyclic structure, while such calculations for 2,3-, 2,4-, and 2,6-DHP converge to essentially the same geometry as with the two-configuration wave function. From these results, we conclude that the stability of 2,5-DHP depends critically on the degree of interaction between the nitrogen lone pair and its neighboring radical center and that the ring-opening reaction of 2,5-DHP would proceed with very low energy barrier.

While GVB/3-21G calculation predicts two bicyclic 1,4-DHB structures,[15] no bicyclic 2,5-DHP was found in this calculation.

2,6-DHP. The intermediacy of a 2,6-DHP derivative has been tentatively considered to account for the formation of 2-piperidinyl-3-aminopyridine from the reaction of 2-bromo-5-aminopyridine with lithium piperidine in liquid ammonia solution.[29]

Among the six DHPs, in our predictions only 2,6-DHP has a triplet ground state, which lies 2.4 kcal/mol lower in energy than the lowest singlet. This result is not in accord with calculations for 1,3-DHB[15] and 3,5-DHP, which have the same type of symmetrically identical radical centers as those of 2,6-DHP; both have singlet ground states with rather large ΔE_{S-T} values (1,3-DHB, 10.5; 3,5-DHP, 9.8 kcal/mol). While the ground electronic state for formal diradicals which have a pair of degenerate or nearly degenerate orbitals is triplet, through-space or through-bond interactions can significantly split the energy levels of such orbitals

TABLE IV: Relative Energies (kcal/mol) of DHPs with Respect to GVB Energy of 3,4-DHP

DHP	RHF (singlet)	GVB (singlet)	ROHF (triplet)
3,4-	32.2	0.0	30.7
2,3-	37.7	7.4	24.8
2,4-	56.4	9.5	23.5
2,5-	–15.9[a]	19.1	24.1
2,6-	65.9	21.2	18.8
3,5-	67.1	18.8	28.5

[a] β-Ethynylacrylonitrile.

and make the singlets more stable.[18,30] In 1,3-DHB and 3,5-DHP, it has been suggested that through-space interaction between the atomic orbitals of the two radical centers is responsible for the sizable stabilization of the singlet with respect to the triplet.[18] In the case of 2,6-DHP, although the same type of interaction stabilizes the singlet state, it is largely hindered by the nitrogen lone pair orbital which stands between the two radical centers C2 and C6. This is a qualitative rationale for 2,6-DHP having a triplet ground state and for the small energy difference between the ground triplet and lowest singlet states.

3,5-DHP. No experimental evidence for 3,5-DHP has been reported.[6] At the GVB level, 3,5-DHP has a singlet ground state with a predicted ΔE_{S-T} of 9.8 kcal/mol. Its stability is comparable to singlet 2,5-DHP or triplet 2,6-DHP.

3,5-DHP, unlike 2,4-DHP, is remarkably similar to 1,3-DHB in many respects. The RHF geometry optimization yields a bicyclic equilibrium structure with a C3–C5 separation of 1.540 Å. The positive C3–C5 overlap population indicates the formation of weak bonding between them. The GVB optimized structure increases the C3–C5 distance to 2.229 Å, which is only 0.06 Å shorter than that of pyridine. The overlap population becomes negative, which is indicative of no effective bonding between the dehydrogenated carbon centers in the GVB singlet structure. No bicyclic structure was found at the GVB level.

Summary and Conclusion

The results of primary interest are the relative energetics among the six isomers of DHP. These are summarized in Table IV. At the RHF level, the ground states of all six DHPs are predicted to be triplets. However, at the GVB level the limited electron correlation between the two unpaired electrons lowers the RHF energies of DHPs by 30–48 kcal/mol and the ground states of all DHPs except the 2,6-isomer are predicted to be singlets. Considering the limitations of the small basis set (3-21G) used in this calculation, and attributing little significance to total energy differences less than 5 kcal/mol,[31] the difference in ground-state energy between, 2,3- and 2,4-DHP and between 2,6- and 2,5 (or 3,5)-DHP are too small to specify the relative energy ordering with confidence. However, the splitting between 3,4- and 2,3-DHP and between 2,4- and 3,5-DHP are sufficiently large (7.4 and 9.3 kcal/mol, respectively) that their relative stability is probably independent of the level of the computations. Thus, the ground-state stabilities of the DHPs decrease in the order 3,4-(S) > 2,3-(S) $\approx$ 2,4-(S) > 3,5-(S) $\approx$ 2,6-(T) $\approx$ 2,5-(S), where (S) and (T) represent singlets and triplets, respectively.

When the radical centers are nonadjacent to the nitrogen atom (N1), such as 3,4- or 3,5-DHP, the nitrogen lone pair has little influence on the structure determination at any level of calculation. When one of the radical centers is adjacent to N1, we have two contradictory descriptions: at the RHF level the nitrogen lone pair and the adjacent radical lobe are delocalized; on the other hand, at the GVB level they are localized and the nitrogen lone pair has limited interaction with the adjacent radical center. This difference between the two methods is well illustrated in the optimized structures of the 2,n-DHPs (n = 3, 4, 5, 6); while the RHF method strongly binds N1 and C2 and obtains an extremely strained ring (for n = 3, 4, 6) or open cyclic structure (for n =

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5), the GVB calculation obtains hexagonal structures modestly distorted from the equilibrium structure of pyridine. Thus, the GVB method not only lowers the total electronic energies of the system by correlating the two radical electrons but also significantly reduces the angle strain of the DHPs by limiting the interaction of nitrogen lone pair with the neighboring radical center.

At the RHF level, only 3,5-DHP has a bicyclic structure. In the cases of 2,4-, 2,5-, and 2,6-DHP, a strong interaction between the nitrogen lone pair and its adjacent radical electron keeps the two radical centers from forming a transannular bond. We have not been successful in obtaining bicyclic structures for the 2,4-, 2,5-, 2,6-, and 3,5-DHPs at the GVB level, while both mono- and bicyclic structures were predicted by MNDO calculations. Our GVB calculations indicate that they have monocyclic structures with significant diradical character.

GVB calculations which employ a three-term separated-pair wave function slightly improve the total electronic energies of 2,n-DHPs by 0.2–0.6 kcal/mol. The weight of the third term,

which corresponds roughly to the in-plane nitrogen lobe orbital, is less than 0.04% for all 2,n-DHPs. Geometry optimization with this wave function converged to the same structure as with the two-configuration wave function, except for the 2,5-DHP, which did not retain its cyclic structure. Thus, at the current level of theory the nitrogen lone pair plays a limited role in determining the overall geometry and energetics of 2,3-, 2,4-, and 2,6-DHP, but it substantially destabilizes the 2,5-isomer.

Ab Initio Study of Aluminum Hydrides

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Structures and heats of formation of aluminum hydrides up to Al_6H_{10} have been predicted by ab initio molecular orbital calculations. Classical and nonclassical structures modeled on the analogous boron hydride, are considered for Al_3H_7, Al_4H_{10}, Al_5H_9 and Al_5H_{11}, while only the nonclassical structure is considered for Al_6H_{10}. The energy difference between classical and nonclassical structures is smaller for the aluminum hydrides than for the boron hydrides. In fact, for the aluminum hydride Al_4H_{10} the bisdiborane structure is more stable than the "butterfly" structure, whereas the opposite ordering is found for B_4H_{10}. Estimated heats of formation suggest that formation of aluminum hydrides from aluminum clusters plus hydrogen is thermodynamically feasible.

Introduction

Little is known about larger aluminum hydrides, either experimentally or theoretically. Since aluminum has the same number of valence electrons as boron, one could expect some similarities in the structure of the hydrides.[1-4] Electron-deficient bonding might occur since aluminum is orbitally rich and electron poor. However, if one considers the lithium/sodium pair,[5] one finds that, in contrast to extensive bridging characteristic of lithium complexation, bridging in sodium complexes is less favorable. In aluminum hydrides a similar trend might indicate that classical structures with 2c–2e bonding and corresponding vacancies on aluminum would prevail.

Two experimental approaches have been used to form aluminum hydrides. In the first, H_2 is allowed to flow past an aluminum vapor.[6] The products, identified by mass spectrometry, suggest the neutral precursors AlH_3 and Al_2H_6. A very recent approach by Hara et al.[7] used a thermal desorption technique under ultrahigh vacuum. Hydrogen atoms are deposited on an Al(111) single crystal surface at 150 K. At 340 K desorption peaks are observed that are attributed to aluminum hydrides such as AlH_3 or Al_2H_6.

A starting point for this study is a consideration of the aluminum clusters, Al_n ($n = 2$–6). Considerable work has been done on small aluminum clusters both experimentally[8] and theoretically.[9] The recent review by Jarrold and co-workers[8] on aluminum clusters indicates a constant linear decrease in cohesive energy per atom as the neutral cluster decreases in size by the negative one-third power of n ($n^{-0.33}$) when n is 7 atoms or larger. Below that value, the cohesive energy per atom decreases more rapidly. Theoretical studies of the small neutral clusters predict a smaller cohesive energy per atom than experiment but a similar trend of decreasing cohesive energy as the size of the cluster decreases. However, there is disagreement over the geometry and multiplicity of the ground states of the individual clusters.

Method

All calculations have been made by using the GAUSSIAN 88 program system.[10] Geometries have been optimized at the

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