Bisdehydropyridines: MNDO (Modified Neglect of Diatomic Overlap) Molecular Orbital Calculations

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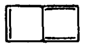
Summary Energy calculations in the MNDO approximation suggest that the biradical forms of 2,4-, 2,5-, and 2,6-bisdehydropyridine are comparable in stability with the known 2,3- and 3,4- bisdehydro compounds.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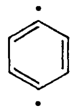
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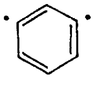
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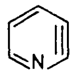
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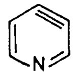
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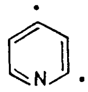
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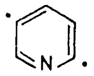
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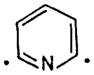
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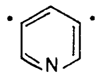
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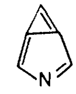
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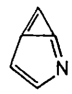
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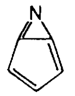
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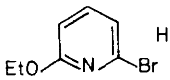
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$HC{\equiv}C{-}CH{=}CH{-}C{\equiv}N$

(16)

THE properties of benzyne itself are now well established[1] and experimental evidence for the other bisdehydrobenzenes (**1**)—(**4**) continues to accumulate.[2] In contrast, although the evidence for the intermediacy of 2,3- (**5**) and 3,4-bisdehydropyridine (**6**) seems fairly sound[3] almost nothing is known of the analogous *meta*- and *para*-bisdehydropyridines (**7**)—(**14**). We have therefore carried out semiempirical molecular orbital calculations[4] of these species with complete geometry optimisation and limited configuration interaction using our recently developed MNDO[5] method. The calculated heats of formation (kJ mol^{-1}) of bisdehydropyridines (with decreasing stability) are: (**6**) 549·6; (**7**) 551·7; (**8**) 556·3; (**9**) 581·9; (**5**) 587·3; (**10**) 596·1; (**11**) 622·5; (**12**) 623·7; (**13**) 643·4; and (**14**) 728·4. The calculated geometries of (**5**) and (**6**) were approximately as expected with 'C≡C' bond lengths of 1·297 and 1·285 Å, respectively. Those of the biradical forms (**7**)—(**10**) were similar to that of pyridine while the bicyclic analogues (**11**)—(**14**) were predicted to have distorted geometries as indicated with transannular bonds in the range 1·58—1·70 Å. All species were calculated to be ground-state singlets. For the *meta*- and *para*-dehydropyridines, the biradical forms were more stable than their bicyclic analogues in each case although since the latter are highly polarised molecules (being formally analogous to a fusion of the cyclopentadienyl anion and cyclopropenyl cations) they are expected to be substantially stabilized in polar solvents.

The most stable isomer was found to be (**6**) and, in agreement with the few known experimental facts,[6] is predicted to be considerably more stable than the 2,3-dehydro isomer (**5**). Very close in energy to (**6**) was the biradical form of 2,4-bisdehydropyridine. Derivatives of (**7**) (or **12**) may be involved in the *tele* amination of (**15**) by KNH_2 in liquid ammonia.[7] The only other isomer that has been discussed experimentally is a derivative of 2,6-bisdehydropyridine (**9**) or (**13**).[8]

We are now studying a number of possible gas-phase reactions of these compounds.† Thus a small activation energy of 15·9 kJ mol^{-1} was calculated for the highly exothermic ($\Delta H = -172{\cdot}0$ kJ mol^{-1}) conversion of (**14**) → (**8**). 2-Azabicyclo[2.2.0]hexa-1,3,5-triene (**14**) is therefore expected to undergo rapid unimolecular decay in the gas phase and, at least at low pressures, lead ultimately to 1-cyanobut-1-en-3-yne (**16**) which is separated from (**8**) by a calculated energy barrier of 115·2 kJ mol^{-1}.

The products of the gas-phase unimolecular decay of 3,4-bisdehydropyridine (**6**) are known to include HCN and diacetylene.[9] Thus we have located reaction paths corresponding to *retro* Diels–Alder reactions with activation energies of 226·0 and 225·6 kJ mol^{-1} *via* two unsymmetrical transition states corresponding to initial fission of either the 1,2- or 5,6-bonds of (**6**).

We thank the Air Force Office of Scientific Research for support and the Robert A. Welch Foundation for a post-doctoral fellowship (to G.P.F.). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Centre.

(*Received, 9th May* 1977; *Com.* 444.)

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† We studied reaction paths using an unrestricted Hartree-Fock version of our program since this allows a considerable saving of computer time. *Cf.* M. J. S. Dewar, S. Olivella, and H. S. Rzepa, *Chem. Phys. Letters*, 1977, **47**, 80.

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