

# Formation, Stability, and Protonation of Dihydropyridines. A MINDO/3 Study<sup>‡</sup>

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**Abstract:** A detailed MINDO/3 study of the formation, stability, and behavior of the various dihydropyridine isomers and related compounds was carried out. The order of stability of the seven dihydro isomers is as follows: 1,4 > 3,4 > 1,2 > 2,5 > 2,3 >> the two bicyclo structures. Protonation of the dihydropyridines occurs yielding preferentially enamine salts. The calculations of all these processes are in good agreement with experimental observations. The relative stabilities of the 1,4- vs. 1,2-dihydropyridines were well reproduced both for pyridine and its 1-methyl derivative. It is shown that the favorable electronic interactions (hyperconjugation, homoaromaticity) can indeed account for the increased stability of the 1,4-dihydro isomers. Excellent agreement between the calculated (adiabatic and vertical) and observed ionization potentials was obtained.

Although dihydropyridines<sup>2</sup> are of utmost importance in biological systems, particularly the NAD-NADH which is involved in biological oxidation-reduction, simple dihydropyridines have not been extensively studied due to their susceptibility to oxidation and various addition reactions and because of the lack of convenient methods for their preparation.

As a most recent important application,<sup>3</sup> the dihydropyridine  $\rightleftharpoons$  pyridine redox system was successfully applied for delivering a quaternary pyridinium salt, 1-methylpyridinium-2-carbaldoxime chloride (2-PAM), through the blood-brain barrier (BBB); the dihydropyridine derivative of 2-PAM (Pro-2-PAM) easily penetrated the BBB where it was rapidly oxidized to the active 2-PAM at the site of action. A generalized version of this redox system can be applied for target delivery of various drugs<sup>4</sup> which are otherwise inaccessible to the brain or to deep lipoidal tissues because of their polar ionic character.

The increasing importance of the dihydropyridine  $\rightleftharpoons$  pyridine redox system prompted us to initiate a detailed study on the formation, stability, and behavior of the various dihydropyridine isomers.

Theoretically, five isomeric dihydropyridines are capable of existence in addition to the two possible bicyclo structures, but most of the known dihydropyridines have either the 1,4- or the 1,2-dihydro structure, except in few cases, where steric hindrance or certain stabilizing groups lead to 2,3- or 3,4-dihydropyridines.<sup>2a</sup>

Experimental difficulties prompted investigators to probe the relative stability of few isomers by MO calculations. The most studied dihydropyridine derivative is certainly the 1-methyldihydropyridine, the model compound for NADH, investigated by simple Huckel,<sup>5a</sup> the PPP method,<sup>5b</sup> and very recently with the CNDO<sup>5c</sup> and EHT<sup>5d</sup> methods. A systematic study of the reduction process of pyridine and further properties of the various possible isomers must, however, use a more reliable quantum chemical approach in combination with an optimization procedure which allows complete minimization of the energies with respect to *all* geometrical variables, since the relative energy differences are expected to be small and simplifying assumptions would alter the results.

One very important experimental result was provided by Fowler,<sup>6</sup> who determined the relative stability of the 1-methyldihydropyridines. The results indicated that the 1,4-dihydro derivative is by  $2.29 \pm 0.01$  kcal/mol more stable than the 1,2 form. He suggested that the real reason for stability of

the 1,4 isomer is the "favorable electronic interaction". The present work will attempt to analyze this aspect of the problem, namely the reason for the relative stability of the isomers.

## Theoretical Procedure

The calculations reported here were carried out with the latest MINDO/3<sup>7</sup> program, which is an improved version in the series of MINDO<sup>8a</sup>-MINDO/2<sup>8b</sup>-MINDO/2<sup>8c</sup> methods. The major advantage of the latest MINDO/3 program is the use of the powerful and fast DFP<sup>7a</sup> optimization procedure which allowed us to calculate the various structures without any geometrical restrictions.

## Results and Discussion

The complex process of reduction of pyridine (1) and protonation of the dihydro isomers is presented in Scheme I.

The first step in the reduction process<sup>2b</sup> of pyridine (1) involves the attack of a hydride ion (H<sup>-</sup>), followed by the protonation of the possible negative ions 2 and 3 to form the dihydropyridines 4-10. Further protonation of the dihydropyridines leads to the possible ions 11-17. The various protonated forms can be formed from different dihydropyridine isomers, depending on the proton affinity of the various positions (kinetic product) and the relative stability of the protonated forms (thermodynamic product).

The results of the calculations on structures 1-17 are listed in Table I. In addition, the positive ions 18 and 19 were also included in order to compare the adiabatic ionization potentials of the two major dihydropyridine isomers.

First, the calculations on pyridine itself, obviously, reproduce well both the energetic and structural features of the molecule. Among the intermediars formed after the attack of the hydride ion, the 4-hydrido derivative 2 is by about 5 kcal/mol more stable than 3. An analysis of the HOMO's shows a much higher contribution of the N lone pair in 2 and in 3. There are three possible structures that can be formed from 2 by the addition of a proton to the positions 1-3. Based on the relative distribution of the negative charge, the order of preference is 1 > 3 >> 2. The stabilities of the products follow this order: the bicyclo structure 6 is much less stable than the 1,4- (5) and 3,4- (4) dihydropyridines, while the 1,4 isomer is the most stable, as expected. The protonation of 3 can lead to the four structures 7-10. Again, the bicyclo structure is much less stable than the other three, among which the classical 1,2-dihydropyridine (7) is the most stable.

The relative stability of the 1,4- and 1,2-dihydro isomers shows a difference of 4.5 kcal/mol, in good agreement with the experimental value.<sup>6</sup>

As expected based on X-ray studies of 1,4-dihydropyridine-

\* This paper is dedicated to Professor M. J. S. Dewar on the occasion of his 60th birthday.

**Table I.** Calculated Geometries, Heats of Formation ( $\Delta H_f$ , kcal/mol, 25 °C), Distribution of Formal Charges, and Ionization Potentials of Dihydropyridine Isomers and Related Compounds

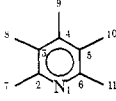
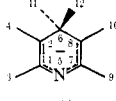
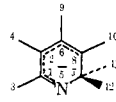
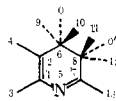
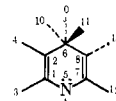
molecule name, <sup>a</sup> numbering, and heats of formation	molecule structure			at. charges, e		vert IP eV <sup>c</sup>
	bond lengths, Å	bond angles, deg	dihedral angles <sup>b</sup>	atom no.	charge	
 pyridine <sup>d</sup> (1) $\Delta H_f = 34.1$ kcal/mol (34.6 kcal/mol)	$\overline{12} = 1.336$ (1.340) <sup>e</sup>	$\overline{123} = 122.0$	planar	1	-0.1641	8.49 ( $\sigma$ )
	$\overline{23} = 1.402$ (1.395)	$\overline{234} = 118.2$		2	0.1351	9.13 ( $\pi$ )
	$\overline{34} = 1.406$ (1.394)	$\overline{345} = 119.8$		3	-0.0659	9.73 ( $\pi$ )
	$\overline{27} = 1.107$ (1.084)	$\overline{216} = 119.8$		4	0.0732	10.44 ( $\sigma$ )
	$\overline{38} = 1.105$ (1.081)	$\overline{723} = 120.6$		5	-0.0657	12.08 ( $\sigma$ )
	$\overline{49} = 1.114$ (1.077)	$\overline{832} = 120.6$		6	0.1348	
	$\overline{16} = 1.336$	$\overline{349} = 120.1$		7	-0.0151	
	$\overline{56} = 1.402$			8	0.0005	
	$\overline{45} = 1.406$			9	-0.0182	
				10	0.0001	
				11	-0.0147	
 (2) 4-hydropyridine $\Delta H_f = 27.1$ kcal/mol	$\overline{12} = 1.372$	$\overline{215} = 124.1$	planar within 0.5°	1	0.2172	1.53 ( $\pi$ )
	$\overline{15} = 1.367$	$\overline{126} = 123.5$		2	-0.2900	2.91 ( $\sigma$ )
	$\overline{26} = 1.479$	$\overline{268} = 110.5$		3	-0.1169	3.90 ( $\pi$ )
	$\overline{57} = 1.368$	$\overline{312} = 120.3$		4	-0.0656	4.66 ( $\sigma$ )
	$\overline{68} = 1.484$	$\overline{124} = 120.2$		5	-0.4262	6.31 ( $\pi$ )
	$\overline{78} = 1.377$	$\overline{8612} = 112.5$		6	0.3256	
	$\overline{13} = 1.126$	$\overline{8611} = 112.3$		7	0.2366	
	$\overline{24} = 1.113$	$\overline{6810} = 118.6$		8	-0.3163	
	$\overline{79} = 1.131$	$\overline{579} = 113.2$		9	-0.1288	
	$\overline{810} = 1.109$	$\overline{157} = 114.2$		10	-0.0519	
	$\overline{611} = 1.145$			11	-0.1919	
	$\overline{612} = 1.145$			12	-0.1918	
 (3) 2-hydropyridine $\Delta H_f = 32.0$ kcal/mol	$\overline{12} = 1.412$	$\overline{215} = 127.0$	$\theta = 11\ 7\ 5\ 1$ $= 128.0^\circ$	1	0.2791	1.38 ( $\pi$ )
	$\overline{15} = 1.313$	$\overline{126} = 114.9$		2	-0.3794	2.76 ( $\sigma$ )
	$\overline{26} = 1.426$	$\overline{268} = 121.6$		3	-0.1351	4.43 ( $\pi$ )
	$\overline{57} = 1.421$	$\overline{312} = 118.1$		4	-0.0403	4.97 ( $\sigma$ )
	$\overline{68} = 1.372$	$\overline{124} = 123.1$		5	-0.4143	5.78 ( $\pi$ )
	$\overline{78} = 1.485$	$\overline{269} = 118.4$		6	0.1807	
	$\overline{13} = 1.132$	$\overline{6810} = 120.7$		7	0.3767	
	$\overline{24} = 1.106$	$\overline{5711} = 109.9$		8	-0.2866	
	$\overline{69} = 1.119$	$\overline{5712} = 110.4$		9	-0.1215	
	$\overline{810} = 1.110$	$\overline{157} = 119.6$		10	-0.0538	
	$\overline{711} = 1.155$			11	-0.2020	
	$\overline{712} = 1.155$			12	-0.2035	
 (4) 3,4-dihydropyridine $\Delta H_f = 24.8$ kcal/mol	$\overline{12} = 1.350$	$\overline{215} = 122.4$	planar within 0.5°, except H <sub>13</sub> , which is out of plane by 2.3°	1	0.0897	8.52 ( $\sigma$ -p <sub>N</sub> )
	$\overline{15} = 1.403$	$\overline{126} = 121.8$		2	-0.0747	8.73 ( $\pi$ )
	$\overline{26} = 1.500$	$\overline{268} = 115.3$		3	-0.0059	10.38 ( $\sigma$ )
	$\overline{57} = 1.278$	$\overline{312} = 122.9$		4	0.0042	11.89 ( $\pi$ )
	$\overline{68} = 1.524$	$\overline{124} = 122.3$		5	-0.1547	
	$\overline{78} = 1.503$	$\overline{260} = 121.7$		6	0.1166	
	$\overline{13} = 1.112$	$\overline{680} = 124.0$		7	0.1460	
	$\overline{24} = 1.105$	$\overline{8713} = 116.5$		8	0.0308	
	$\overline{713} = 1.117$	$\overline{157} = 120.5$		9	-0.0421	
	$\overline{69} = 1.120$			10	-0.0425	
	$\overline{610} = 1.121$	HC <sub>6</sub> H = 101.4		11	-0.0258	
	$\overline{811} = 1.121$	HC <sub>8</sub> H = 102.0		12	-0.0260	
	$\overline{912} = 1.120$			13	-0.0157	
 (5) 1,4-dihydropyridine $\Delta H_f = 20.5$ kcal/mol	$\overline{12} = 1.359$	$\overline{215} = 120.3$	planar within 0.5° plane of 6 10 11 is perpendicular	1	0.1239	7.48 ( $\pi$ -p <sub>N</sub> )
	$\overline{15} = 1.370$	$\overline{126} = 120.1$		2	-0.1570	9.87 ( $\pi$ )
	$\overline{26} = 1.494$	$\overline{268} = 114.8$		3	-0.0124	10.32 ( $\sigma$ )
	$\overline{57} = 1.378$	$\overline{312} = 123.8$		4	0.0244	10.64 ( $\sigma$ )
	$\overline{68} = 1.493$	$\overline{124} = 120.7$		5	-0.0671	12.26 ( $\pi$ )
	$\overline{78} = 1.352$	$\overline{260} = 122.0$		6	0.2002	13.10 ( $\sigma$ )
	$\overline{13} = 1.113$	$\overline{6813} = 118.6$		7	0.1200	
	$\overline{24} = 1.100$	$\overline{8712} = 124.9$		8	-0.1459	
	$\overline{712} = 1.110$	$\overline{157} = 124.3$		9	0.0542	
	$\overline{814} = 1.102$	$\overline{159} = 117.0$		10	-0.0774	
	$\overline{610} = 1.126$			11	-0.0752	
	$\overline{611} = 1.120$	HCH = 100.8		12	-0.0079	
	$\overline{59} = 1.020$			13	0.0202	

Table I (Continued)


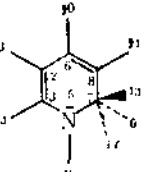
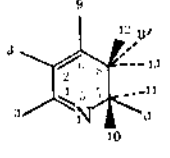
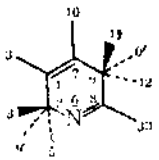
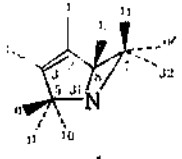
molecule name, <sup>a</sup> numbering, and heats of formation	molecule structure			at. charges, e		vert IP eV <sup>c</sup>
	bond lengths, Å	bond angles, deg	dihedral angles <sup>b</sup>	atom no.	charge	
 <p>(6) 1-azabicyclo[3.1.0]hex-2-ene <math>\Delta H_f = 52.7</math> kcal/mol</p>	$\overline{12} = 1.353$	$\overline{126} = 110.5$	$\theta = 4\ 2\ 1\ 3$ $= -3.2$	1	0.0944	8.23 ( $\pi$ -pN)
	$\overline{15} = 1.422$	$\overline{512} = 112.9$	$\theta = 5\ 1\ 2\ 3$ $= 175.1$	2	-0.1115	9.24 ( $\pi$ -pN)
	$\overline{26} = 1.506$	$\overline{158} = 105.9$	$\theta = 7\ 5\ 1\ 2$ $= 68.1$	3	0.0092	10.38 ( $\sigma$ )
	$\overline{58} = 1.516$	$\overline{124} = 127.1$	$\theta = 8\ 5\ 1\ 2$ $= 4.0$	4	0.0189	10.99 ( $\sigma$ )
	$\overline{57} = 1.446$	$\overline{213} = 129.6$	$\theta = 13\ 8\ 5\ 1$ $= 227.2$	5	-0.1358	11.45 ( $\pi$ )
	$\overline{68} = 1.520$	$\overline{157} = 123.3$		6	0.1235	
	$\overline{78} = 1.479$	$\overline{260} = 128.3$		7	0.1340	
	$\overline{13} = 1.106$	$\overline{5813} = 116.9$		8	0.0323	
	$\overline{24} = 1.101$	$\overline{570} = 146.8$		9	-0.0403	
	$\overline{69} = 1.119$	$\overline{268} = 110.8$		10	-0.0466	
	$\overline{610} = 1.120$	$\overline{586} = 103.5$		11	-0.0417	
	$\overline{711} = 1.116$	HC <sub>6</sub> H = 102.4		12	-0.0197	
	$\overline{712} = 1.116$	HC <sub>7</sub> H = 106.8		13	-0.0168	
$\overline{813} = 1.118$						
 <p>(7) 1,2-dihydropyridine <math>\Delta H_f = 25.0</math> kcal/mol</p>	$\overline{12} = 1.351$	$\overline{215} = 121.4$	essentially	1	0.1670	7.50 ( $\pi$ -pN)
	$\overline{15} = 1.363$	$\overline{126} = 120.1$	planar,	2	-0.1678	10.29 ( $\pi$ )
	$\overline{26} = 1.453$	$\overline{268} = 117.9$	within 1°	3	-0.0173	10.39 ( $\sigma$ )
	$\overline{68} = 1.357$	$\overline{312} = 122.9$	plane of	4	0.0184	10.69 ( $\sigma$ )
	$\overline{57} = 1.423$	$\overline{124} = 119.9$	12 7 13 is	5	-0.1174	11.56 ( $\pi$ )
	$\overline{78} = 1.492$	$\overline{2610} = 119.6$	perpendicular	6	0.0911	
	$\overline{13} = 1.113$	$\overline{6811} = 121.8$		7	0.2577	
	$\overline{24} = 1.101$	$\overline{570} = 123.2$		8	-0.1162	
	$\overline{610} = 1.105$	$\overline{157} = 124.0$		9	0.0663	
	$\overline{811} = 1.105$	$\overline{159} = 119.0$		10	0.0101	
	$\overline{712} = 1.134$			11	0.0083	
	$\overline{713} = 1.134$	HCH = 100.3		12	-0.0899	
	$\overline{59} = 1.019$			13	-0.0903	
 <p>(8) 2,3-dihydropyridine <math>\Delta H_f = 28.1</math> kcal/mol</p>	$\overline{12} = 1.469$	$\overline{215} = 122.5$	planar	1	0.1695	8.43 ( $\sigma$ -pN)
	$\overline{15} = 1.275$	$\overline{126} = 120.3$	within 0.4°	2	-0.0627	8.94 ( $\pi$ )
	$\overline{26} = 1.349$	$\overline{268} = 120.8$	planes 12	3	-0.0120	10.53 ( $\sigma$ )
	$\overline{57} = 1.432$	$\overline{312} = 119.1$	8 13 and 10	4	-0.0038	11.48 ( $\pi$ )
	$\overline{68} = 1.497$	$\overline{124} = 118.3$	7 11 are	5	-0.1871	
	$\overline{78} = 1.528$	$\overline{269} = 122.2$	perpendicular	6	0.0271	
	$\overline{13} = 1.115$	$\overline{780} = 123.3$	to frame	7	0.1728	
	$\overline{24} = 1.107$	$\overline{570} = 119.2$		8	0.0556	
	$\overline{69} = 1.106$	$\overline{157} = 123.3$		9	-0.0069	
	$\overline{710} = 1.127$			10	-0.0423	
	$\overline{711} = 1.127$	HC <sub>7</sub> H = 102.2		11	-0.0425	
	$\overline{812} = 1.122$	HC <sub>8</sub> H = 101.5		12	-0.0339	
	$\overline{813} = 1.122$			13	-0.0338	
 <p>(9) 2,5-dihydropyridine <math>\Delta H_f = 27.5</math> kcal/mol</p>	$\overline{12} = 1.495$	$\overline{126} = 116.9$	planar	1	-0.0482	8.52 ( $\sigma$ )
	$\overline{26} = 1.442$	$\overline{217} = 121.0$	within		0.1887	9.22 ( $\pi$ )
	$\overline{17} = 1.344$	$\overline{179} = 122.8$	0.8°	3	0.0028	10.57 ( $\sigma$ )
	$\overline{68} = 1.274$	$\overline{621} = 123.2$	planes 11	4	-0.0448	10.61 ( $\pi$ )
	$\overline{79} = 1.495$	$\overline{213} = 117.1$	9 12 and 4	5	-0.0448	11.78 ( $\sigma$ )
	$\overline{89} = 1.505$	$\overline{1710} = 121.2$	2 5 are	6	-0.1681	
	$\overline{24} = 1.129$	$\overline{790} = 124.7$	perpendicular	7	-0.0018	
	$\overline{25} = 1.127$	$\overline{9813} = 116.1$	to frame	8	0.1408	
	$\overline{13} = 1.106$	$\overline{268} = 120.7$		9	0.0602	
	$\overline{710} = 1.107$			10	-0.0122	
	$\overline{813} = 1.120$	HC <sub>2</sub> H = 102.1		11	-0.0263	
	$\overline{911} = 1.119$	HC <sub>9</sub> H = 103.1		12	-0.0264	
	$\overline{912} = 1.119$			13	-0.0200	
 <p>(10) 1-azabicyclo[3.1.0]hex-3-ene <math>\Delta H_f = 56.8</math> kcal/mol</p>	$\overline{12} = 1.351$	$\overline{156} = 105.8$	$\theta = 6\ 5\ 1\ 3$ $= 176.4^\circ$	1	0.0567	8.33 ( $\pi$ -pN)
	$\overline{15} = 1.506$	$\overline{215} = 110.9$	$\theta = 7\ 6\ 5\ 1$ $= 69.0^\circ$	2	-0.0096	9.57 ( $\pi$ )
	$\overline{28} = 1.495$	$\overline{128} = 108.5$	$\theta = 8\ 6\ 5\ 1$ $= 3.7^\circ$	3	0.0105	10.06 ( $\sigma$ )
	$\overline{68} = 1.512$	$\overline{286} = 105.3$	$\theta = 13\ 8\ 6\ 5$ $= 227.2^\circ$	4	0.0096	10.97 ( $\sigma$ )
	$\overline{56} = 1.458$	$\overline{568} = 107.9$		5	0.1956	11.24 ( $\pi$ )
	$\overline{67} = 1.447$	$\overline{567} = 122.8$		6	-0.1635	

Table I (Continued)

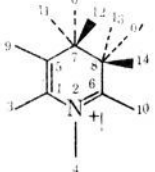
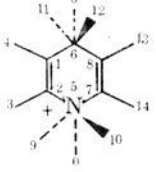
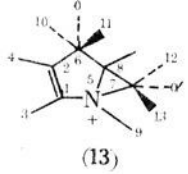
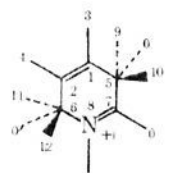
molecule name, <sup>a</sup> numbering, and heats of formation	molecule structure			at. charges, e		vert IP eV <sup>c</sup>
	bond lengths, Å	bond angles, deg	dihedral angles <sup>b</sup>	atom no.	charge	
 (11) C-protonated 1,4-dihydropyridine $\Delta H_f = 160.9$ kcal/mol	$\overline{78} = 1.480$	$\overline{312} = 126.5$		7	0.1260	
	$\overline{13} = 1.102$	$\overline{124} = 127.8$		8	0.0653	
	$\overline{24} = 1.101$	$\overline{150} = 128.7$		9	-0.0520	
	$\overline{59} = 1.124$	$\overline{6813} = 118.0$		10	-0.0452	
	$\overline{510} = 1.126$	$\overline{670} = 147.4$		11	-0.0412	
	$\overline{813} = 1.117$			12	-0.0184	
	$\overline{711} = 1.115$	HC <sub>5</sub> H = 102.9		13	-0.0205	
	$\overline{712} = 1.115$	HC <sub>7</sub> H = 106.1				
	$\overline{12} = 1.418$	$\overline{512} = 119.7$	$\theta = 4\ 2\ 1\ 3$ = 9.3°	1	-0.0263	14.38 ( $\pi$ )
	$\overline{15} = 1.347$	$\overline{157} = 122.6$	$\theta = 6\ 2\ 1\ 3$ = 191.3°	2	0.1743	15.92 ( $\sigma$ )
	$\overline{26} = 1.291$	$\overline{312} = 113.9$		3	0.0914	16.09 ( $\sigma$ )
	$\overline{57} = 1.496$	$\overline{951} = 118.8$	planes 11	4	0.1168	17.38 ( $\pi$ )
	$\overline{78} = 1.523$	$\overline{570} = 121.9$	7 12 and 13	5	0.0473	
	$\overline{68} = 1.496$	$\overline{7813} = 127.1$	8 14 are	6	0.1965	
$\overline{24} = 1.028$	$\overline{2610} = 118.4$	perpendicular	7	0.0515		
$\overline{13} = 1.108$	$\overline{126} = 124.0$	to frame	8	0.0265		
$\overline{59} = 1.106$	$\overline{124} = 115.45$		9	0.0824		
$\overline{610} = 1.113$	$\overline{268} = 121.5$		10	0.0708		
$\overline{711} = \overline{712} = 1.114$			11	0.0307		
$\overline{813} = \overline{814} = 1.117$	HC <sub>7</sub> H = 103		12	0.0377		
	HC <sub>8</sub> H = 102.4		13	0.0495		
			14	0.0509		
 (12) N-protonated 1,4-dihydropyridine $\Delta H_f = 174.0$ kcal/mol	$\overline{12} = 1.351$	$\overline{512} = 120.6$	everything	1	-0.0751	14.62 ( $\pi$ )
	$\overline{15} = 1.438$	$\overline{126} = 121.3$	planar	2	0.0763	15.64 ( $\pi$ )
	$\overline{26} = 1.502$	$\overline{268} = 114.5$	within 1°,	3	0.0932	15.80 ( $\sigma$ )
	$\overline{68} = 1.496$	$\overline{312} = 126.0$	except the	4	0.0833	16.16 ( $\sigma$ )
	$\overline{78} = 1.342$	$\overline{124} = 119.6$	perpendicular	5	0.3156	18.55 ( $\sigma$ )
	$\overline{57} = 1.437$	$\overline{260} = 122.7$	planes 11	6	0.0468	18.65 ( $\sigma$ )
	$\overline{59} = 1.046$	$\overline{6813} = 119.1$	6 12 and	7	-0.0733	
	$\overline{510} = 1.050$	$\overline{5714} = 114.1$	9 5 10	8	0.0767	
	$\overline{611} = \overline{612} = 1.116$	$\overline{157} = 121.2$		9	0.0989	
	$\overline{13} = 1.106$	$\overline{150} = 119$		10	0.0984	
	$\overline{24} = 1.103$	$\overline{9510} = 101$		11	0.0423	
	$\overline{714} = 1.106$	$\overline{11612} = 103.3$		12	0.0417	
	$\overline{813} = 1.104$	HN <sub>3</sub> H = 100.9		13	0.0778	
		HC <sub>6</sub> H = 103.2		14	0.0975	
 (13) protonated 1-azabicyclo[3.1.0]hex-2-ene $\Delta H_f = 189.6$ kcal/mol	$\overline{12} = 1.344$	$\overline{215} = 108.6$	$\theta = 4\ 2\ 1\ 3$ = 3.8°	1	-0.0030	14.72 ( $\pi$ )
	$\overline{15} = 1.444$	$\overline{126} = 113.7$	$\theta = 5\ 2\ 1\ 3$ = 175.8°	2	0.0181	16.14 ( $\sigma$ )
	$\overline{26} = 1.506$	$\overline{312} = 134.4$	$\theta = 6\ 2\ 1\ 3$ = 181.1°	3	0.1138	16.40 ( $\sigma$ )
	$\overline{58} = 1.524$	$\overline{124} = 124.7$	$\theta = 7\ 5\ 1\ 2$ = 68.5°	4	0.0960	17.06 ( $\sigma$ )
	$\overline{68} = 1.527$	$\overline{260} = 130.0$	$\theta = 8\ 5\ 1\ 2$ = 3.1°	5	0.1393	17.51 ( $\sigma$ )
	$\overline{57} = 1.473$	$\overline{5814} = 116.1$	$\theta = 9\ 5\ 1\ 2$ = 224.2°	6	0.0530	
	$\overline{78} = 1.480$	$\overline{570} = 140.9$	$\theta = 13\ 8\ 5\ 1$ = 228.9°	7	0.0977	
	$\overline{13} = 1.102$	$\overline{157} = 126.6$		8	0.0958	
	$\overline{24} = 1.100$	$\overline{158} = 109.4$		9	0.1077	
	$\overline{610} = 1.112$	$\overline{159} = 114.7$		10	0.0466	
	$\overline{611} = 1.114$			11	0.0463	
	$\overline{814} = 1.116$	H <sub>10</sub> C <sub>6</sub> H <sub>11</sub> = 104.6		12	0.0631	
	$\overline{712} = \overline{713} = 1.110$	H <sub>12</sub> C <sub>7</sub> H <sub>13</sub> = 108.5		13	0.0713	
	$\overline{59} = 1.032$			14	0.0544	
 (14) C-protonated 1,2-dihydropyridine $\Delta H_f = 164.4$ kcal/mol	$\overline{12} = 1.343$	$\overline{268} = 111.4$	essentially	1	0.0047	14.43 ( $\pi$ )
	$\overline{26} = 1.503$	$\overline{621} = 122.5$	planar,	2	-0.0357	15.69 ( $\sigma$ )
	$\overline{15} = 1.493$	$\overline{215} = 122.2$	max ~ 1.5°	3	0.0740	16.25 ( $\sigma$ )
	$\overline{57} = 1.481$	$\overline{157} = 155.0$	out, planes	4	0.0834	16.86 ( $\pi$ )
	$\overline{68} = 1.449$	$\overline{062} = 128.7$	9 5 10 and	5	0.0340	
	$\overline{78} = 1.290$	$\overline{421} = 123.3$	11 6 12 are	6	0.1268	
	$\overline{813} = 1.029$	$\overline{213} = 122.5$	perpendicular	7	0.2284	
	$\overline{13} = 1.103$	$\overline{150} = 124.7$	to frame	8	0.1198	
	$\overline{24} = 1.103$	$\overline{5714} = 122.1$		9	0.0554	

Table I (Continued)

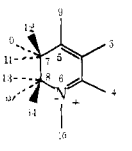
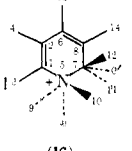
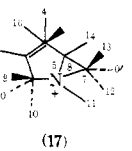
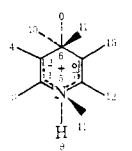
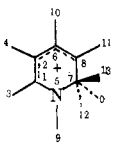
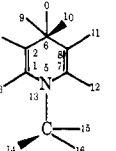
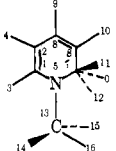
molecule name, <sup>a</sup> numbering, and heats of formation	molecule structure			at. charges, e		vert IP eV <sup>c</sup>
	bond lengths, Å	bond angles, deg	dihedral angles <sup>b</sup>	atom no.	charge	
 (15) C-protonated 1,2-dihydropyridine $\Delta H_f = 162.7$ kcal/mol	$\overline{611} = \overline{612} = 1.122$	$\overline{6813} = 113.4$		10	0.0536	
	$\overline{59} = \overline{510} = 1.117$			11	0.0355	
	$\overline{714} = 1.115$	HC <sub>5</sub> H = 102.8		12	0.0350	
		HC <sub>6</sub> H = 103.8		13	0.1135	
				14	0.0716	
	$\overline{12} = 1.450$	$\overline{751} = 120.6$	essentially	1	-0.1097	14.61 ( $\pi$ )
	$\overline{15} = 1.357$	$\overline{512} = 120.1$	planar,	2	0.2691	16.0 ( $\sigma$ )
	$\overline{26} = 1.296$	$\overline{126} = 121.2$	planes 11	3	0.0924	16.1 ( $\sigma$ )
	$\overline{57} = 1.498$	$\overline{862} = 126.5$	7 12 and	4	0.0622	17.2 ( $\pi$ - $\sigma$ )
	$\overline{68} = 1.449$	$\overline{780} = 127.1$	13 8 14 are	5	0.1400	
	$\overline{78} = 1.523$	$\overline{075} = 120.1$	perpendicular	6	0.0779	
	$\overline{610} = 1.026$	$\overline{951} = 121.9$	to frame	7	0.0110	
	$\overline{13} = 1.102$	$\overline{312} = 116.0$		8	0.1149	
	$\overline{24} = 1.115$	$\overline{124} = 120.7$		9	0.0681	
$\overline{59} = 1.102$	$\overline{2610} = 120.0$		10	0.1232		
$\overline{813} = \overline{814} = 1.123$		HC <sub>7</sub> H = 102.6	11	0.0454		
$\overline{711} = \overline{712} = 1.115$		HC <sub>8</sub> H = 103.3	12	0.0444		
			13	0.0310		
			14	0.0302		
 (16) N-protonated 1,2-dihydropyridine $\Delta H_f = 179.4$ kcal/mol	$\overline{12} = 1.348$	$\overline{215} = 120.0$	essentially	1	-0.0691	14.04 ( $\pi$ )
	$\overline{15} = 1.447$	$\overline{126} = 121.5$	planar	2	0.0965	15.77 ( $\sigma$ )
	$\overline{26} = 1.466$	$\overline{268} = 119.8$		3	0.0946	16.11 ( $\sigma$ )
	$\overline{68} = 1.349$	$\overline{157} = 121.8$		4	0.0776	16.70 ( $\pi$ )
	$\overline{78} = 1.494$	$\overline{312} = 127.1$		5	0.2592	18.26 ( $\sigma$ )
	$\overline{57} = 1.492$	$\overline{124} = 118.3$		6	0.0108	
	$\overline{59} = 1.044$	$\overline{2613} = 118.1$		7	0.0963	
	$\overline{510} = 1.044$	$\overline{6814} = 123.1$		8	-0.0100	
	$\overline{711} = 1.121$	$\overline{570} = 120.6$		9	0.1072	
	$\overline{712} = 1.121$	$\overline{150} = 118.3$		10	0.1064	
				11	0.0380	
				12	0.0389	
			HNH = 101.4	13	0.0743	
			HCH = 103.4	14	0.0793	
 (17) protonated 1-azabicyclo[3.1.0]hex-3-ene $\Delta H_f = 193.4$ kcal/mol	$\overline{12} = 1.351$	$\overline{567} = 127.2$	$\theta = 4\ 2\ 13$ = 0.8°	1	-0.0064	14.62 ( $\pi$ )
	$\overline{15} = 1.501$	$\overline{568} = 111.2$	$\theta = 5\ 2\ 13$ = 178.2°	2	0.0254	16.18 ( $\sigma$ )
	$\overline{28} = 1.495$	$\overline{051} = 133.3$	$\theta = 6\ 5\ 13$ = 175.3°	3	0.0950	16.50 ( $\sigma$ )
	$\overline{68} = 1.523$	$\overline{215} = 112.9$	$\theta = 7\ 6\ 5\ 1$ = 69.7°	4	0.1003	17.05 ( $\sigma$ )
	$\overline{56} = 1.476$	$\overline{312} = 127.7$	$\theta = 8\ 6\ 5\ 1$ = 3.0°	5	0.1222	
	$\overline{67} = 1.473$	$\overline{124} = 128.3$	$\theta = 11\ 6\ 5\ 1$ = 223.3°	6	0.0968	
	$\overline{78} = 1.481$	$\overline{6814} = 117.7$	$\theta = 14\ 8\ 6\ 5$ = 229.1°	7	0.0999	
	$\overline{13} = 1.099$	$\overline{5611} = 114.1$		8	0.1355	
	$\overline{24} = 1.097$	$\overline{670} = 140.7$		9	0.0409	
	$\overline{59} = 1.118$	$\overline{156} = 102.3$		10	0.0433	
	$\overline{510} = 1.117$			11	0.1117	
	$\overline{712} = \overline{713} = 1.110$		H <sub>9</sub> C <sub>5</sub> H <sub>10</sub> = 104.9	12	0.0618	
	$\overline{814} = 1.113$		H <sub>12</sub> C <sub>7</sub> H <sub>13</sub> = 108.3	13	0.0716	
	$\overline{611} = 1.031$			14	0.0529	
 (18) 1,4-dihydropyridinium ion $\Delta H_f = 183.4$ kcal/mol	$\overline{12} = 1.374$	$\overline{215} = 120.4$	planar	1	0.0645	
	$\overline{15} = 1.357$	$\overline{126} = 120.3$	within	2	0.0436	
	$\overline{26} = 1.480$	$\overline{268} = 114.3$	0.2°	3	0.0809	
	$\overline{57} = 1.363$	$\overline{312} = 123.7$	plane of	4	0.0827	
	$\overline{68} = 1.484$	$\overline{124} = 119.7$	6 10 11 is	5	0.1550	
	$\overline{78} = 1.375$	$\overline{260} = 122.9$	perpendicular	6	0.0590	
	$\overline{13} = 1.111$	$\overline{6813} = 119.0$		7	0.0610	
	$\overline{24} = 1.102$	$\overline{8712} = 124.5$		8	0.0439	
	$\overline{712} = 1.109$	$\overline{157} = 124.6$		9	0.1151	
	$\overline{813} = 1.104$	$\overline{159} = 117.8$		10	0.0642	
	$\overline{610} = 1.127$			11	0.0642	
	$\overline{611} = 1.127$			12	0.0871	
	$\overline{59} = 1.026$		HCH = 101	13	0.0788	

Table I (Continued)

molecule name, <sup>a</sup> numbering, and heats of formation	molecule structure			at. charges, e		vert IP eV <sup>c</sup>
	bond lengths, Å	bond angles, deg	dihedral angles <sup>b</sup>	atom no.	charge	
 <p>(19) 1,2-dihydropyridinium ion <math>\Delta H_f = 186.3</math> kcal/mol</p>	$\overline{12} = 1.415$	$\overline{215} = 121.2$	planar	1	0.1763	
	$\overline{15} = 1.318$	$\overline{126} = 119.7$	within 0.1°	2	0.0108	
	$\overline{26} = 1.416$	$\overline{268} = 118.4$	plane of	3	0.0700	
	$\overline{57} = 1.436$	$\overline{312} = 121.6$	12 7 13 is	4	0.0847	
	$\overline{68} = 1.383$	$\overline{124} = 118.0$	perpendicular	5	0.0683	
	$\overline{78} = 1.479$	$\overline{2610} = 120.4$		6	0.0539	
	$\overline{15} = 1.113$	$\overline{6811} = 121.7$		7	0.1194	
	$\overline{24} = 1.100$	$\overline{570} = 122.3$		8	0.0495	
	$\overline{610} = 1.103$	$\overline{157} = 124.6$		9	0.1241	
	$\overline{811} = 1.104$	$\overline{159} = 120.3$		10	0.0756	
	$\overline{712} = 1.127$	HCH = 101.7		11	0.0739	
	$\overline{713} = 1.127$			12	0.0467	
	$\overline{59} = 1.025$			13	0.0468	
 <p>(20) 1-methyl-1,4-dihydropyridine <math>\Delta H_f = 38.6</math> kcal/mol</p>	$\overline{12} = 1.336$	$\overline{126} = 122.1$	planar	1	0.1062	7.51 ( $\pi$ -p <sub>N</sub> )
	$\overline{15} = 1.402$	$\overline{215} = 121.4$	within	2	-0.1327	9.92 ( $\pi$ )
	$\overline{26} = 1.492$	$\overline{157} = 119.4$	0.5°	3	-0.0088	10.27 ( $\sigma$ )
	$\overline{68} = 1.490$	$\overline{268} = 123.1$	$\theta = 14\ 13\ 5\ 1$ = 30.4°	4	0.0190	10.57 ( $\sigma$ )
	$\overline{78} = 1.354$	$\overline{213} = 122.6$	$\theta = 15\ 13\ 5\ 1$ = 150.2°	5	-0.0578	11.44 ( $\pi$ )
	$\overline{57} = 1.392$	$\overline{124} = 119.3$	$\theta = 16\ 13\ 5\ 1$ = 270.4°	6	0.1922	12.09 ( $\sigma$ )
	$\overline{13} = 1.112$	$\overline{5712} = 115.9$		7	0.1149	
	$\overline{24} = 1.104$	$\overline{6811} = 119.0$		8	-0.1410	
	$\overline{811} = 1.102$	$\overline{1513} = 120.0$		9	-0.0711	
	$\overline{712} = 1.114$	$\overline{51314} = 113.8$		10	0.0709	
	$\overline{69} = \overline{610} = 1.125$	$\overline{51315} = 113.8$		11	-0.0217	
	$\overline{513} = 1.424$	$\overline{51316} = 114.3$		12	0.0137	
	$\overline{1314} = 1.119$	HC <sub>6</sub> H = 101.1		13	-0.1661	
	$\overline{1315} = 1.119$	$\overline{062} = 123.1$		14	-0.0360	
	$\overline{1316} = 1.122$			15	-0.0364	
				16	-0.0518	
 <p>(21) 1-methyl-1,2-dihydropyridine <math>\Delta H_f = 41.8</math> kcal/mol</p>	$\overline{12} = 1.364$	$\overline{215} = 121.7$	planar	1	0.1490	7.51 ( $\pi$ -p <sub>N</sub> )
	$\overline{15} = 1.379$	$\overline{126} = 120.2$	within 0.4°	2	-0.1546	10.02 ( $\pi$ )
	$\overline{26} = 1.457$	$\overline{157} = 122.2$	$\theta = 11\ 7\ 0\ 8$ = 91.2°	3	-0.0130	10.30 ( $\sigma$ )
	$\overline{57} = 1.444$	$\overline{268} = 118.6$	$\theta = 12\ 7\ 0\ 8$ = 268.0°	4	0.0187	10.59 ( $\sigma$ )
	$\overline{68} = 1.354$	$\overline{213} = 121.8$	$\theta = 14\ 13\ 5\ 1$ = 27.8°	5	-0.0999	11.50 ( $\pi$ )
	$\overline{78} = 1.485$	$\overline{124} = 119.8$	$\theta = 15\ 13\ 5\ 1$ = 147.8°	6	0.0849	12.04 ( $\sigma$ )
	$\overline{13} = 1.113$	$\overline{269} = 119.1$	$\theta = 16\ 13\ 5\ 1$ = 267.8°	7	0.2457	
	$\overline{24} = 1.103$	$\overline{2810} = 121.8$		8	-0.1093	
	$\overline{69} = 1.104$	$\overline{078} = 121.3$		9	-0.0105	
	$\overline{810} = 1.105$	$\overline{1513} = 120.0$		10	0.0106	
	$\overline{711} = 1.132$	$\overline{51314} = 113.8$		11	-0.0825	
	$\overline{712} = 1.135$	$\overline{51315} = 113.8$		12	-0.0851	
	$\overline{513} = 1.426$	$\overline{51316} = 113.8$		13	0.1721	
$\overline{1314} = 1.118$	HC <sub>7</sub> H = 100.8		14	-0.0397		
$\overline{1315} = 1.117$			15	-0.0348		
$\overline{1316} = 1.121$			16	-0.0516		

<sup>a</sup>O and O' are imaginary points helping to define structures. All structures were completely optimized using  $3N - 6$  variables ( $N$  is the number of atoms). <sup>b</sup>Clockwise. <sup>c</sup>Koopmans' theorem. <sup>d</sup>Observed bond lengths in parentheses, from B. Bak, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958). <sup>e</sup>Observed value: "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Mich., 1965.

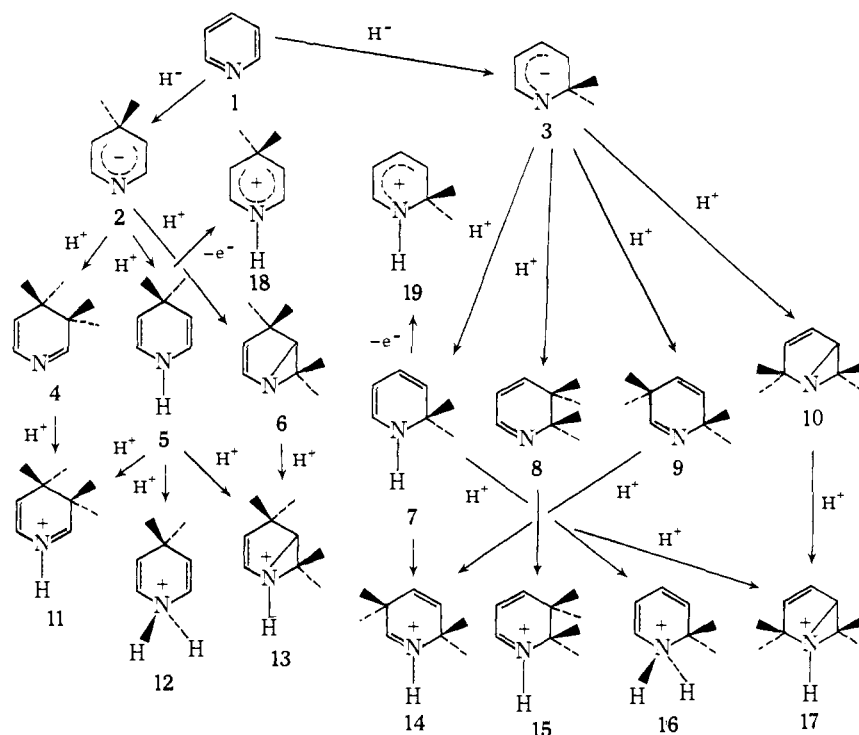
tinamide<sup>9</sup> and structural considerations, except for the bicyclo structures **6** and **10**, the ring system in the other dihydropyridine isomers is essentially planar.

In order to check if there is indeed a more "favorable electronic interaction"<sup>6</sup> in the 1,4-dihydro derivative **5** as compared to the 1,2 form **7**, the HOMO's and LUMO's in these molecules were examined. The HOMO's are, according to  $\phi_{16}^n = \sum \chi_i$ , as follows:

$$\phi_{16}^5 = 0.21p_z(C_1) + 0.48p_z(C_2) - 0.58p_z(N_5) + 0.20p_z(C_7) + 0.47p_z(C_8) - 0.10p_z(C_6) + 0.26s(H_{10}) - 0.25s(H_{11})$$

$$\phi_{16}^7 = 0.30p_z(C_1) + 0.53p_z(C_2) - 0.52p_z(N_5) - 0.20p_z(C_6) - 0.44p_z(C_8) + 0.06p_z(C_7) + 0.25s(H_{12}) - 0.25s(H_{13})$$

Scheme I. The Reduction and Protonation Processes of Pyridine



(The unrestricted optimization leads to the expected symmetrical structure of **5**. Small differences (within the error of the method) in the bond lengths or in the coefficients of  $H_{10}$  and  $H_{11}$  in the above  $\phi_{16}^5$  are due to the convergence criteria set.)

It is evident that there is a significant hyperconjugation<sup>10</sup> contribution of the  $-CH_2-$  group in both structures, as suggested in the case of the 1,4-dihydropyridine.<sup>5c,d</sup> It is also clear that both the  $-CH_2-$  hyperconjugation and the contribution of the N lone pair to the HOMO is stronger in the case of **5**, explaining the difference in stability. In addition, the low-lying LUMO in **7** [1.28 eV ( $\pi$ ) vs. 1.48 eV ( $\sigma$ ) and 1.76 eV ( $\pi$ ) in **5**] would indicate an increased electron affinity and thus sensitivity toward further reduction of **7**.

It is interesting to note the extremely good agreement between the calculated and observed<sup>11</sup> ionization potentials for the 1,4-dihydropyridine (**5**). As shown in Table II, the calculated values are in excellent agreement for the first and second IP's, both in values and in assignment, supporting the reliability of the calculation method used.

Table II. Calculated and Observed Ionization Potentials of Selected Dihydropyridines

	calcd <sup>a</sup> vertical IP's, eV	obsd <sup>c</sup>	calcd <sup>b</sup> adiabatic IP's, eV
 1,4-dihydropyridine ( <b>5</b> )	7.48 ( $\pi$ )	7.45 ( $\pi$ )	7.06
	9.87 ( $\pi$ )	9.77 ( $\pi$ )	
	10.21 ( $\sigma$ )		
	10.64 ( $\sigma$ )		
	12.26 ( $\pi$ )		
 1,2-dihydropyridine ( <b>7</b> )	7.50 ( $\pi$ )		7.00
	10.29 ( $\pi$ )		
	10.39 ( $\sigma$ )		
	10.69 ( $\sigma$ )		
	11.56 ( $\sigma$ )		

<sup>a</sup> Based on Koopmans' theorem. <sup>b</sup>  $IP_{ad} = (\Delta H_f(\text{mol}^+) - \Delta H_f(\text{mol}))$ . <sup>c</sup> Reference 11.

The relative stability of the 1,4- and 1,2-dihydro isomers is not, as expected, affected by the introduction of a 1-methyl group. The fully optimized 1-methyl-1,4-dihydropyridine (**20**) is by about 5 kcal/mol more stable than the corresponding 1,2 isomer (**21**). The most stable conformation for the methyl group in **20** is the one in which two of the H atoms are rotated by about 30° out of the plane of the ring while the third one is in a perpendicular plane. There is a significant contribution to the HOMO in **20** of the third H and less by the other two. The conformation of the *N*-methyl in **21** does not differ significantly from that in **20**, although it is somewhat rotated toward a position of decreased repulsion with the neighboring  $-CH_2-$  hydrogen atoms.

The IP's of **20** and **21** vs. the homologues **5** and **7** are essentially the same, in very good agreement with the literature.<sup>11</sup>

The dihydropyridine isomers undergo further protonation and other electrophilic addition reactions under conditions of synthetic and biological importance.<sup>2b</sup> The attack of the electrophile on the dienamine system could occur at the terminal carbon of the central double bond or at the end of the dienamine system. It was suggested by Lyle<sup>2b</sup> that the protonation of dienamines seems to be correlated by the rule developed by Ingold for the protonation of  $\alpha,\beta$ -unsaturated esters. We have, however, examined all possibilities for the attack of a proton on the various dihydropyridine isomers.

The protonation of 1,4- and 3,4-dihydropyridine (**5** and **4**) can result in three possible protonated forms (**11**–**13**). The bicyclo derivative **13** can also be formed directly from **6**. It is evident that **13** is a highly unstable form energetically, besides that the position ortho to the N is highly unfavorable for the attack of the proton. Both the relative charge distributions of **5** and the heats of formation of **4** and **5** indicate that the N-protonated form **12** is much less stable than the classical enamine salt **11**, which is the most stable protonated form. If, however, **4** would be forming, the protonation on the N is favored, leading again to a structure like **11**, in very good agreement with the experimental finding of the structure of the protonated dihydropyridines.

The protonation of the four possible isomers formed from **3** could lead again to four isomers (**14**–**17**). Again, the bicyclo

form **17** is much less stable, as well as the unfavorable N-protonation would result in an unstable structure. The choice is then between the C-protonated structures **14** and **15**. The relative heats of formation would indicate that **15** is more stable. This is somewhat in contradiction with the concept of protonation of **7** in the middle,<sup>2b</sup> as well as with our findings on the structure of the protonated dihydropyridine formed upon the reduction of 2-PAM.<sup>3a,b</sup> However, analyzing the possibilities of the formation of the more stable form **15**, it can be seen that it can be formed primarily from the protonation of less stable 2,3-dihydropyridine (**8**), by protonation on the N. The formation of **15** from the classical 1,2-dihydropyridine structure **7** is unfavorable from the point of view of the relative charge distribution. It seems, thus, that the protonation of 1,2-dihydropyridine (**7**) would result in the kinetically more favorable **14**, which, however, would equilibrate under appropriate conditions to the thermodynamically more stable **15**.

In conclusion, the detailed MINDO/3 study of the reduction and related processes has accurately described the relative energies and behavior of the various dihydro isomers. It can be seen that the relative energy differences among the simple isomers are not too large, and under certain conditions any of the isomers could form. The bicyclo structures **6**, **10**, **13**, and **17**, although not clearly dihydropyridines, are of interest and the structures certainly represent minima in the potential surface.

The energetic and conformational problems of the related biologically important dihydropyridines, such as the various N-alkyl pyridinium aldoximes<sup>3,4</sup> are currently being studied and the results will be published elsewhere.

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## Theoretical Study of Li<sub>2</sub>H. 3. Approximate Natural Orbital Contour Diagrams and Occupation Numbers for the Formation and Dissociation of Li<sub>2</sub>H

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**Abstract:** Approximate natural orbital contour diagrams and occupation numbers are used to analyze ab initio potential energy curves along pathways that lead to the formation and dissociation of Li<sub>2</sub>H: H + Li<sub>2</sub> → Li<sub>2</sub>H → LiH + Li. In addition to the ground state, the three lowest excited states are analyzed. The analysis revealed extensive charge transfer intermediates of the type Li<sub>2</sub><sup>+</sup>H<sup>-</sup>. The species LiH<sup>-</sup>...Li<sup>+</sup> was also found to be an intermediate. The natural orbital description predicts in general that charge transfer is more gradual than is expected on the basis of uncorrelated molecular orbitals. However, rather abrupt natural orbital charge transfer was also encountered.

Previous theoretical work on Li<sub>2</sub>H has been largely concerned with determining the characteristics of the ground<sup>1-4</sup> and low-lying excited state<sup>2-4</sup> potential energy surfaces. Ab initio results<sup>1-3</sup> predict the existence of stable Li<sub>2</sub>H with a C<sub>2v</sub> geometry, while diatomics-in-molecules work<sup>4</sup> predicts a linear symmetric ground state. The discrepancy with the ab initio results is apparently due to the neglect of ionic and p-symmetry terms in the diatomic states used in ref 4.<sup>5</sup> Li<sub>2</sub>H is ionic in most of its low-lying states, so it seems reasonable that ionic curves should be required in the diatomic input. The p symmetry is probably necessary to stabilize the C<sub>2v</sub> geometries by enabling the Li contributions to "point" toward the incoming H atom.

A mass spectrometric identification of Li<sub>2</sub>H has recently been reported.<sup>6</sup> The diatomics-in-molecules results<sup>4</sup> are used

to establish that Li<sub>2</sub>H has a linear symmetric geometry. However, since more accurate ab initio calculations<sup>1,2</sup> predict that the C<sub>2v</sub> symmetry is most stable, the "experimental" geometry should be viewed as questionable. The original motivation for our own calculations<sup>2,3</sup> was to provide potential curves for the interpretation of ongoing molecular beam experimental work.<sup>7</sup> There are many interesting charge transfer processes taking place in Li<sub>2</sub>H within energies accessible to the molecular beams. The purpose of the present work is to provide a description of these processes. Correlated wave functions are required for two reasons. First, uncorrelated molecular orbital (MO) wave functions are less accurate. Any interpretation based on them is therefore questionable. Second, the MO (single configuration) wave functions for excited states which have the same symmetry as lower states do not usually satisfy the variational principle.<sup>8</sup> This occurs because higher single configuration states are not orthogonal to any state which is itself an upper bound to the true ground state. Therefore the

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