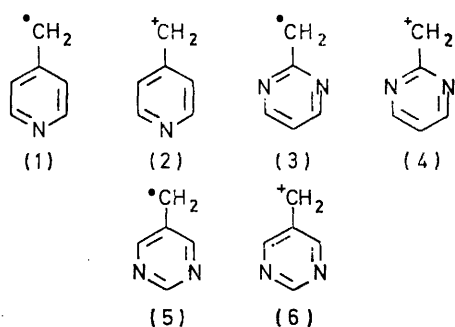


## Theoretical Study of the 4-Pyridylmethyl and the 2- and 5-Pyrimidylmethyl Cations and Radicals

By Charles U. Pittman, jun.,\* Maurice R. Smith, Gary D. Nichols, Shing K. Wu, and Lowell D. Kispert,\*  
Department of Chemistry, The University of Alabama, University, Alabama 35486

Geometry optimized SCF-MO calculations in the INDO approximation have been performed on the 4-pyridylmethyl (1), 2-pyrimidylmethyl (3), and 5-pyrimidylmethyl (5) radicals and their corresponding cations (2), (4), and (6). The spin distribution in (1), (3), and (5) and the charge distribution in (2), (4), and (6) provide evidence that mesomeric effects in these systems are similar to those in the benzyl radical and cation. The optimized geometries all have a quinonoid distortion which is more pronounced in the cation. The  $\pi$ -bond orders and the ring-CH<sub>2</sub><sup>•</sup> (or ring-CH<sub>2</sub><sup>+</sup>) rotational barriers were obtained. The results are discussed in terms of resonance hybrid structures. The ionization potentials of the radicals were obtained and found to be in the order (3) > (1) > (5). The calculated ionization potential of (1) was 8.71 V in good agreement with the experimental value of 8.40 V obtained by electron impact measurements.

It is well known that the methyl protons in 4-methylpyridine<sup>1,2</sup> and both 2- and 5-methylpyrimidine<sup>3</sup> are acidic. This is due to resonance, inductive, and field effects all of which operate to stabilize the corresponding anions. However, much less is known about the 4-pyridylmethyl and 2- and 5-pyrimidylmethyl cations and radicals (1)–(6). Solvolysis studies, so common for



benzyl derivatives,<sup>4</sup> are not available for evaluating the stability of cations (2), (4), and (6).

Competitive studies of  $\alpha$ -hydrogen abstraction from toluene and 4-methylpyridine showed that the 4-pyridylmethyl radical (1) was formed 0.29<sup>5</sup> (or 0.33<sup>6</sup>) times as fast as the benzyl radical. In these studies di-*t*-butyl peroxide was thermally decomposed to give *t*-butoxyl radicals as the hydrogen abstracting agent. The difference in reactivity between 4-methylpyridine and toluene was attributed, almost totally, to polar effects in

<sup>1</sup> R. A. Abramovitch and G. M. Singer, 'Properties and Reactions of Pyridines,' in 'Pyridine and its Derivatives,' Wiley, New York, 1974, vol. 14, suppl. part 1.

<sup>2</sup> J. A. Zoltewicz and L. S. Helmick, *J. Org. Chem.*, 1973, **38**, 658.

<sup>3</sup> D. J. Brown, 'The Pyrimidines,' vol. 16 of 'Heterocyclic Compounds,' ed. A. Weissberger, Interscience, New York, 1962.

<sup>4</sup> C. U. Pittman, jun., and S. P. McManus, 'Carbonium Ions' in 'Organic Reactive Intermediates,' ed. S. P. McManus, Academic Press, New York, 1973.

<sup>5</sup> K. M. Johnston and G. H. Williams, *Chem. and Ind.*, 1958, 358.

<sup>6</sup> K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1960, 1168, 1446.

<sup>7</sup> H. H. Jaffé and H. L. Hones, 'Applications of the Hammett Equation' in 'Advances in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, 1964, vol. 3.

the transition state.<sup>6</sup> A  $\sigma^+$  value of 0.86 was assigned as the substituent constant for the 4-pyridyl function.<sup>6,7</sup>

The vertical ionization potential of the 4-pyridylmethyl radical (1) was shown to be 8.40 V by the electron impact method.<sup>8</sup> This may be compared to the values of the benzyl (7.74,<sup>8</sup> 7.73,<sup>9</sup> 7.81 V<sup>10</sup>) and allyl radicals (8.22<sup>8</sup> and 8.16 V<sup>10</sup>) to show that the substitution of N for CH in the benzyl radical brings about a significant increase in the vertical ionization potential. By fitting the ionization potential of the 4-pyridylmethyl radical (1) to the linear relationship between Hammett  $\sigma$ -constants and the ionization potentials of various benzyl radicals, a value of  $\sigma = 0.58$  was obtained. Attempts to determine the electron affinity of (1) by the magnetron method<sup>11</sup> failed because a phenyl type radical ( $\sigma$ -radical) was formed.<sup>12</sup> Roberts and Szwarc<sup>13</sup> reported the bond dissociation energy of the methyl C-H was 77.5 kcal mol<sup>-1</sup> for 4-methylpyridine and concluded that the resonance energy of (1) was within a few kcal of the resonance energy of the benzyl radical. However, this bond dissociation energy was *ca.* 20 kcal mol<sup>-1</sup> lower than that derived from appearance potential measurements of Palmer and Lossing.<sup>7</sup> In view of the small amount of experimental evidence available, we performed a series of geometry optimized SCF-MO calculations, in the INDO<sup>14,15</sup> approximation, on (1) and (2).

Even less is known about species (3)–(6). Side-chain bromination of 2-methylpyrimidine in HOAc and NaOAc gave 2-(tribromomethyl)-4-bromopyrimidine.<sup>16</sup> Monobromination of both 2,4,6-trichloro-5-methylpyrimidine and 4,6-dichloro-2,5-dimethylpyrimidine with *N*-bromosuccinimide gave their 5-bromomethyl derivatives in

<sup>8</sup> T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.*, 1963, **85**, 1733.

<sup>9</sup> F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, 1954, **22**, 621.

<sup>10</sup> J. B. Farmer, I. H. S. Henderson, C. A. McDowell, and F. P. Lossing, *J. Chem. Phys.*, 1954, **22**, 1948.

<sup>11</sup> F. M. Page, *Trans. Faraday Soc.*, 1960, **56**, 1742.

<sup>12</sup> R. L. Failes, J. T. Joyce, and E. C. Watton, *J.C.S. Faraday II*, 1973, 1487.

<sup>13</sup> J. S. Roberts and M. Szwarc, *J. Chem. Phys.*, 1948, **16**, 981.

<sup>14</sup> J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

<sup>15</sup> J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

<sup>16</sup> A. Holland and R. Slack, *Chem. and Ind.*, 1954, 1203.

good yields.<sup>17</sup> Presumably these reactions proceeded *via* pyrimidylmethyl radical intermediates. However, no physical measurements on the cations or radicals (3)—(6) have appeared, and few chemical reactions involving (3)—(6) as intermediates have been systematically studied. Thus, we performed geometry optimized INDO calculations on those species. In these studies all bond lengths and angles, with the exception of the ring carbon-hydrogen bond lengths, were fully optimized.

#### RESULTS AND DISCUSSION

The CINDO program,<sup>14,15</sup> QCPE number 141, was adapted for use on a Univac 1110 computer and used as previously described.<sup>18-24</sup> Initial calculations showed that the planar geometries of (1)—(6) were more stable than out-of-plane deformations. Then, each bond length was individually minimized followed by minimization of all angles (except that the ring C-H bond axes were assumed to bisect the ring C-C-C angles). This was

TABLE I

Rotational barriers for optimized geometries

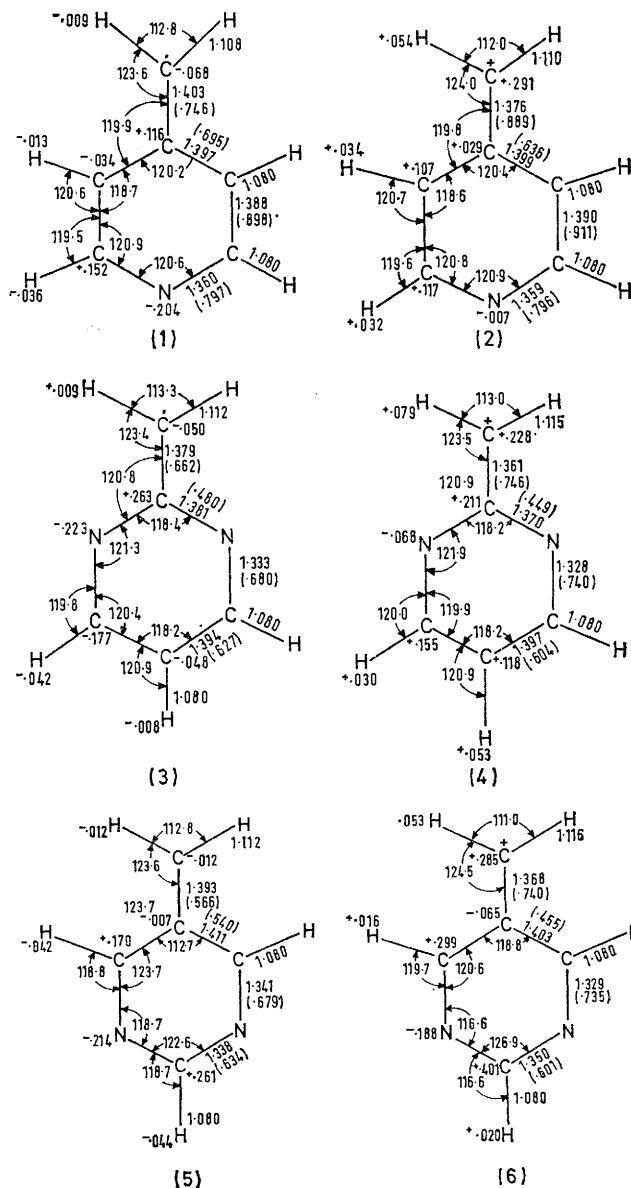
| Species | Ring-CH <sub>2</sub> rotational barriers (kcal mol <sup>-1</sup> ) | Length (Å) | $\pi$ -Bond order |
|---------|--|------------|-------------------|
| (1)     | 13.7   | 1.403      | 0.746             |
| (2)     | 15.6   | 1.376      | 0.889             |
| (3)     | 23.7   | 1.379      | 0.662             |
| (4)     | 35.4   | 1.361      | 0.738             |
| (5)     | 18.9   | 1.393      | 0.566             |
| (6)     | 21.2   | 1.368      | 0.740             |

followed by a second iteration after which no further minimizations were needed. These geometries are summarized in the Figure and the energy minimum obtained by this procedure was stationary to *ca.* 5 cal.

The major conclusions which can be drawn from the calculations include the following items. (1) The calculated energy difference between cation (2) and radical (1) is 8.99 V. The difference between radical (1) and the corresponding cation, having the same geometry as (1) is 8.71 V. This difference is the vertical ionization potential and may be compared to the experimental value of 8.40 V.<sup>8</sup> Similarly, radicals (3) and (5) are more stable than cations (4) and (6) by 9.21 and 8.61 V respectively. The calculated vertical ionization potential of (3) is 9.36 and that of (5) is 8.71 V.

(2) The 4-pyridylmethyl radical exhibits a slight quinonoid type geometrical deformation. The magnitude of this deformation is even more pronounced in the 4-pyrimidylmethyl cation. Similar deformations were exhibited by pyrimidylmethyl radicals (3) and (5) and

cations (4) and (6). The Figure summarizes these geometries. A similar phenomena was noted by Beveridge and Guth who found small quinonoid deformations in the benzyl radical led to lower calculated energies in the INDO approximation.<sup>25</sup>



Optimized geometries of radicals (1), (3), and (5) and cations (2), (4), and (6)

(3) The  $\pi$ -bond orders between the ring carbon and the CH<sub>2</sub> group are large in radicals (1), (3), and (5) and larger

<sup>17</sup> T. Hasegawa, *Chem. and Pharm. Bull. (Japan)*, 1953, **1**, 287.

<sup>18</sup> L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 6948.

<sup>19</sup> L. D. Kispert, C. U. Pittman, jun., D. L. Allison, T. B. Patterson, jun., C. W. Gilbert, jun., C. F. Hains, and J. Prather, *J. Amer. Chem. Soc.*, 1972, **94**, 5979.

<sup>20</sup> C. U. Pittman, jun., C. Dyas, C. Engelman, and L. D. Kispert, *J.C.S. Faraday II*, 1972, 345.

<sup>21</sup> C. U. Pittman, jun., T. B. Patterson, jun., and L. D. Kispert, *J. Org. Chem.*, 1973, **38**, 471.

<sup>22</sup> C. U. Pittman, jun., L. D. Kispert, and T. B. Patterson, jun., *J. Phys. Chem.*, 1973, **77**, 494.

<sup>23</sup> C. U. Pittman, jun., A. Kress, T. B. Patterson, P. Walton, and L. D. Kispert, *J. Org. Chem.*, 1974, **39**, 373.

<sup>24</sup> C. U. Pittman, jun., A. Kress, and L. D. Kispert, *J. Org. Chem.*, 1974, **39**, 378.

<sup>25</sup> D. L. Beveridge and E. Guth, *J. Chem. Phys.*, 1971, **55**, 458.

in the corresponding cations (2), (4), and (6). Furthermore, the distribution of  $\pi$ -bond orders in the rings alternates, further reflecting the quinonoid distribution. Thus, the geometrical distortions and  $\pi$ -bond orders agree with a significant contribution for hybrid structures

The values of  $a_{15\text{N}}$  in (1) and (3) were substantially larger than those in (5). This is in further agreement with the quinonoid geometry distortions.

(5) The delocalization of charge, *via* the mesomeric effect, in cations (2), (4), and (6) is remarkably similar to

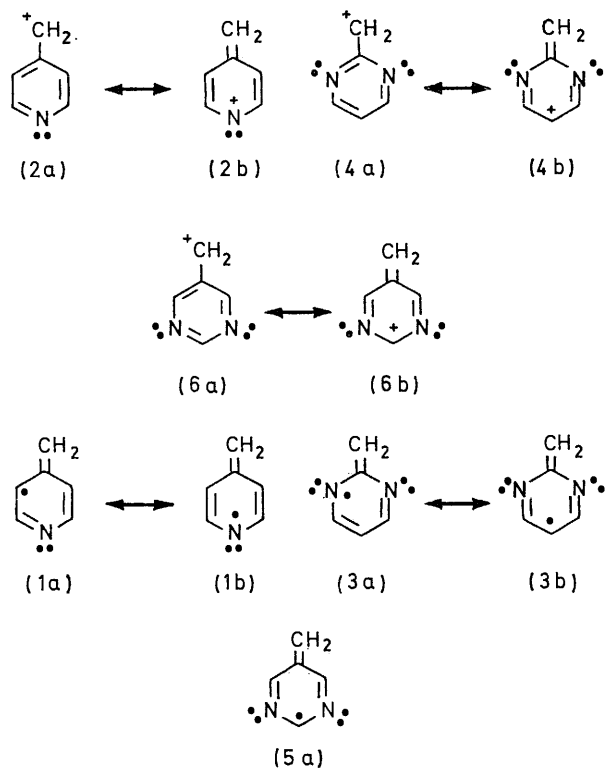
TABLE 2

Calculated hyperfine coupling constants

| Species               | CH <sub>2</sub> |                 | 1-C             | <i>ortho</i> -C-H |                   | <i>meta</i> -C-H |                    | <i>para</i> -C-H |                   |
|-----------------------|-----------------|-----------------|-----------------|-------------------|-------------------|------------------|--------------------|------------------|-------------------|
|                       | <sup>1</sup> H  | <sup>13</sup> C | <sup>13</sup> C | <sup>1</sup> H    | <sup>13</sup> C   | <sup>1</sup> H   | <sup>13</sup> C    | <sup>1</sup> H   | <sup>13</sup> C   |
| (1)                   | -16.40          | 32.10           | -13.00          | -6.76             | 12.16             | +3.68            | -10.58             |                  | 5.82 <sup>a</sup> |
| (3)                   | -15.86          | 28.45           | -17.02          |                   | 6.53 <sup>a</sup> | +4.85            | -12.66             | -7.42            | 13.78             |
| (5)                   | -17.66          | 32.45           | -13.68          | -6.82             | 14.37             |                  | -3.46 <sup>a</sup> | -6.29            | 13.31             |
| Benzylic <sup>b</sup> | -17.01          | 32.62           | -12.32          | -6.43             | 11.71             | 3.60             | -8.5               | -5.64            | 10.47             |
| Benzylic <sup>c</sup> | -16.61          |                 |                 | -6.61             |                   | 3.85             |                    | -6.13            |                   |

<sup>a</sup>  $a_{15\text{N}}$  (not  $a_{13\text{C}}$ ). <sup>b</sup> Calculated using standard bond lengths and angles, see J. A. Pople and D. L. Beveridge, *J. Chem. Phys.*, 1968, **49**, 4725. <sup>c</sup> Calculated after a partial geometry optimization of the energy hypersurface, see ref. 25

(2b), (4b), and (6b) in the cations. Similar hybrids contribute in the radical series.



(4) The calculated <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N hyperfine coupling constants for (1), (3), and (5) are remarkably similar to those of the benzyl radical (see Table 2). Apparently, replacement of CH by N causes little change in the overall spin distribution. INDO Calculations have proved remarkably successful in predicting the magnitude and sign of hyperfine couplings,<sup>26</sup> especially when geometry optimizations are performed,<sup>25</sup> as in this work. The magnitudes of the splittings is in accord with major contributions by hybrids (1a), (1b), (3a), (3b), and (5a).

that observed in the benzyl cation. Thus, like the distribution of spin density, the charge is distributed mainly to the '*ortho*' and '*para*'-positions. Thus, in (2) the '*ortho*'-carbon bears a significant positive charge (+0.107). The nitrogen maintains only a slight (-0.007) negative charge, but this is due to strong polarization of the nitrogen-carbon  $\sigma$  bonds ( $N_{q_{p_z}}$  1.23 *versus meta*-C $_{q_{p_z}}$  0.885) which compensates for the loss of  $\pi$ -electron density ( $N_{q_{p_z}}$  0.812) from nitrogen. The same is seen in cation (4) where the '*ortho*'-nitrogens carry a total charge of only -0.068 [*versus* -0.223 in radical (3)]. Again, the  $N_{p_z}$  orbital donates  $\pi$ -electron density ( $N_{q_{p_z}}$  0.868). These values may be compared to that of the '*meta*'-nitrogen of cation (6) where little  $\pi$ -density is lost ( $N_{q_{p_z}}$  1.08).

The extent of  $\pi$ -delocalization is more apparent upon noting that the charge on the '*para*'-carbon of (4) (+0.118) is similar to that on the '*meta*'-carbon (+0.155) despite the strong inductive polarization of the '*meta*'-carbon-nitrogen bond. Overall, the presence of nitrogen in (2), (4), and (6) does not greatly perturb the  $\pi$ -electron distribution relative to the benzyl cation. Thus, the charge densities are in agreement with significant contribution by structures (2b), (4b), (6b) and their *ortho*-equivalents.

(6) The calculated rotational barriers of the CH<sub>2</sub> group in (2), (4), and (6) are higher than the respective barriers in (1), (3), and (5) (see Table 1). These barriers in (3) and (4) are substantially greater than those of (1) and (2) while those of (5) and (6) are only moderately higher than (1) and (2) respectively.

(7) In both the radicals and cations the calculated polarization of the nitrogen-carbon  $\sigma$  bonds is virtually the same. The electron densities in the carbon atomic orbital involved in the C-N bonds, range only slightly from 0.905 to 0.875. Similarly, those of the corresponding nitrogen atomic orbital varied only from 1.196 to 1.244 in (1)-(6).

Overall, the distribution of spin in (1), (3), and (5) and charge in cations (2), (4), and (6) resemble that found in

<sup>26</sup> J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

the benzyl radical and cation, respectively. If this is true, one would expect this to be reflected in the stability of the cations. Thus, the ionization potential order, predicted for the radicals, would be (3) > (1) > (5). The two 'ortho'-nitrogens in (4) would destabilize this cation [relative to radical (3)] more than the single 'para'-nitrogen would destabilize (2) relative to (1). In (6), the 'meta'-nitrogens are not in a conjugating position to destabilize this cation [relative to (5)] by

resonance. It is satisfying that the calculated vertical ionization potentials fit this predicted order perfectly: 9.36 for (3) > 8.99 for (1) > 8.71 V for (5).

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