An *Ab Initio* LCGO–MO–SCF Calculation of the Potential Energy Surface for an SN2 Reaction

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Abstract: An *ab initio* LCGO-MO-SCF study of the SN2 displacement of hydride ion by hydride ion on methane has been carried out. The portion of the potential energy surface for the CH_5 – system for which the approach of the hydride ion is toward the back side of the carbon, on line with the C-H bond to be broken, was explored. A single saddle point in this portion of the surface is found, corresponding to the CH_5 – system with D_{3h} symmetry, apical C-H distance of 3.30 au, and equatorial C-H distances of 2.01 au. The electron density on the carbon atom is found to decrease on going from methane to the saddle point.

The SN2 displacement reactions have been of considerable interest to both organic and inorganic chemists for a number of years. Stereochemical studies of these reactions have indicated a general back-side displacement process resulting in inversion of configuration about the atom on which the displacement occurs. It is generally assumed that the SN2 radio-exchange on saturated carbon compounds passes through a transition state with trigonal-bipyramidal geometry, but this assumption is open to question.¹

In a continuation of our previous work on the *ab initio* calculations of potential energy surfaces,² we have now explored a portion of the surface for the reaction of hydride ion with methane in which the product results from an SN2 displacement.

Methods and Results

The program used for the calculations has been described.² The Gaussian basis set used for all of the present work is the small basis set previously reported.³ It consists of four simple s-type functions, one "frozen core", and three of each p-type functions on carbon, and three s-type functions on each of the hydrogens.

The study was begun by locating the D_{3h} configuration of lowest energy. A minimum energy was found for this geometry having an apical C-H distance of 3.30 au and equatorial C-H distances of 2.01 au. Since this latter distance is only slightly less than that for methane, it was decided to carry out all further calculations with these "nonreacting" C-H distances constant at 2.06 au.

One calculation was carried out for a configuration with C_{3v} symmetry and with the incoming and outgoing hydrogens at equal distances from the carbon. The energy for this configuration is higher than that for D_{3h} symmetry.

Further calculations were restricted to configurations with C_{3v} symmetry. This restriction, along with the constancy of the "nonreacting" C-H distances, still leaves us with a surface on which the energy is a function of three variables: the angles between the "nonreacting" C-H bonds, the distance of the entering hydrogen from carbon, and the distance of the leaving hydrogen from carbon.

(1) R. G. Pearson and R. L. Burwell, J. Phys. Chem., 70, 300 (1966).

(2) C. D. Ritchie and H. F. King, J. Amer. Chem. Soc., 90, 825, 833, 838 (1968).

(3) C. D. Ritchie and H. F. King, J. Chem. Phys., 47, 564 (1967).

Calculations were carried out for three angles, spaced 1° apart, for each chosen pair of C-H distances. The minimum energy with respect to angle variation was then obtained by fitting the three points to a harmonic equation. In most cases, we were able to bracket the optimum angle in the three guesses, and the values obtained by the interpolation are highly reliable. In a few cases, however, our guesses were fairly far from the extrapolated optimum values. In these cases, notably points 5, 12, and 13 in Table I, the values for optimum angle and minimum energy may be in error by several degrees and perhaps 0.002 au, respectively.

The data obtained are reported in Table I, and a contour diagram of the surface constructed from these points is shown in Figure 1. A "reaction coordinate" diagram, obtained by interpolation of the points on the surface, and corresponding to the dashed line in Figure 1, is shown in Figure 2. The distance along the reaction coordinate in Figure 2 is defined as the perpendicular distance of the point from the 1,1 axis of Figure 1 (*i.e.*, $D_{\rm RC} = 2^{-1/2} [D(\rm CH_1) - D(\rm CH_2)]$). The energy difference between separated methane plus hydride and the saddle point is 0.078 au = 48.7 kcal/ mol.⁴

Gaussian and harmonic equation fits to the reaction coordinate are shown in Figure 2. It is interesting that the Gaussian function gives a far better fit than does the harmonic equation.

Mulliken population analyses of the wave functions for several configurations on, or near, the reaction coordinate are reported in Table II.

The reliability of calculations of the present type for constructing potential energy surfaces has been discussed thoroughly in earlier papers.²

Discussion

Only a small portion of the total potential energy surface for the CH_5^- system has been explored in this work. It seems pertinent to inquire, then, if we have explored the important regions for an SN2 process. Several lines of argument indicate that we have.

As Pearson and Burwell have pointed out,¹ there is no *a priori* reason to assume that the reaction path for an SN2 process passes through a structure with D_{3h}

⁽⁴⁾ In our earlier papers, we referred to this quantity loosely as the activation energy. This careless usage has been properly criticized: M. Menzinger and R. Wolfgang, Angew. Chem. Intern. Ed. Engl., 8, 438 (1969).



Figure 1. Potential energy surface contour diagram constructed from data in Table I.



Figure 2. Reaction coordinate diagram: open circles, experimental points from Table I; filled circles, calculated from the equation, $E + 40.498 = -0.040D^2$; crosses, calculated from the equation, $E + 40.576 = 0.078 \exp(-0.26D^2)$.

symmetry. It is quite possible that such a path is not the one of lowest energy. The possibility of paths involving structures of very low symmetry cannot be ruled out by the present work. We believe, however, that paths involving a C_{4v} configuration, or a path passing through a configuration with C_{3v} symmetry and equal distances between carbon and both leaving and entering group, can be ruled out.

The latter statement is based on a comparison of the energies calculated for points 42 and 42b of Table I. The movement of the three equatorial hydrogens away from their positions in the configuration with D_{3h} symmetry raises the energy considerably.

Our belief that a path involving C_{4v} symmetry can be ruled out is based on the arguments recently presented by Pearson.⁵ It was argued there that two factors are of prime importance in determining the relative stabilities of D_{3h} and C_{4v} configurations for XY_5 molecules. These two factors are the symmetry species of the highest occupied and lowest unoccupied molecular orbitals, and the difference in orbital energies for these same orbitals.

Our calculations give the MO order: $(1A_1')^2(1E')^4$ - $(1A_2'')^2(2A_1')^2(2A_2'')^0$ for the valence shell of the CH₅⁻ species with D_{3h} symmetry (*i.e.*, point no. 45). The highest occupied orbital has an orbital energy of -0.023 au, and the lowest unoccupied orbital has an energy of

(5) R. G. Pearson, J. Amer. Chem. Soc., 91, 4947 (1969).

Table I. Potential Energy Surface Points for SN2 Reaction of Hydride with Methane^{α}



Point no. d_1 , au d_2 , au φ , deg $-E$, au 1 1.80 5.00 109.5 40.5554 2 2.20 5.00 109.5 40.5554 3 2.40 5.00 109.5 40.5625 4 2.60 5.00 109.5 40.5630 6 2.50 4.40 110.8 ⁵ 40.5446 7 2.60 4.30 111.8 ⁵ 40.5514 9 2.80 4.20 113.1 ⁵ 40.5264 10 3.80 4.20 115.0 40.7544 11 2.40 4.10 110.7 ⁵ 40.5444 13 2.10 4.00 108.3 ⁵ 40.5444 13 2.10 4.00 112.4 ⁵ 40.5176 16 2.20 3.90 110.7 ⁶ 40.5176 16 2.20 3.90 110.7 ⁶ 40.5176 17 2.40 3.80 114.4 ⁵ 40.5025 20			11		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Point no.	<i>d</i> 1, au	d₂, au	φ , deg	-E, au
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1	1.80	5.00	109.5	40.5554
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2	2.20	5.00	109.5	40.5713
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5 2.00 4.50 106.1^{5} 40.5630 6 2.50 4.40 110.8^{5} 40.5476 7 2.60 4.20 109.7^{5} 40.5399 8 2.30 4.20 113.1^{5} 40.5264 10 3.80 4.20 115.0 40.4754 11 2.40 4.10 110.7^{5} 40.5444 12 2.00 4.00 108.3^{5} 40.5444 13 2.10 4.00 108.0^{6} 40.5471 14 2.60 4.00 112.4^{5} 40.5417 17 2.40 3.80 111.8^{8} 40.5213 19 3.00 3.80 114.4^{5} 40.5213 19 3.00 3.80 116.8^{5} 40.5095 20 3.75 3.75 120.0 40.4895 21 2.90 3.70 116.6^{5} 40.5109 22 3.10 3.60 113.9^{5} 40.5032 23 2.20 3.60 11	4	2.60	5.00	109.5	40.54 9 4
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172.403.80111.8°40.5325182.703.80114.4°40.5325193.003.80116.8°40.5095203.753.75120.040.4895212.903.70116.6°40.5096223.103.70118.0°40.5248242.503.60110.1°40.5248242.503.60116.4°40.5110263.003.60117.8°40.5056273.103.60118.5°40.5031283.203.60119.5°40.5024313.003.50110.3°40.5125302.903.50117.7°40.5054313.003.50119.5°40.4982343.403.50119.5°40.4968353.503.50119.5°40.4968353.503.50120.040.4964362.603.40116.1°40.5072372.903.40119.5°40.4968353.503.50120.040.4981413.403.40120.040.4981413.403.40120.040.4981423.343.34120.040.4981433.103.30120.040.4982443.203.30120.040.4988453.303.30120.040.4988463.253.25 <td< th=""><td>16</td><td>2.20</td><td>3.90</td><td>110.7</td><td>40.5417</td></td<>	16	2.20	3.90	110.7	40.5417
182.703.80 114.4^{a} 40.5213 193.003.80 116.8^{b} 40.5095 203.753.75 120.0 40.4895 212.903.70 116.6^{b} 40.5046 232.203.60 110.1^{b} 40.5248 242.503.60 113.9^{b} 40.5198 252.803.60 116.4^{b} 40.5016 263.003.60 117.8^{b} 40.5031 283.203.60 119.5^{b} 40.5031 283.203.60 119.5^{b} 40.5033 302.903.50 110.3^{b} 40.5034 313.003.50 119.5^{b} 40.5033 323.103.50 119.5^{b} 40.4982 343.403.50 119.5^{b} 40.4982 343.403.50 119.5^{b} 40.4968 353.503.50 120.0 40.4964 362.603.40 116.1^{b} 40.5072 372.903.40 119.5^{b} 40.4968 353.503.50 120.0 40.4981 413.403.40 120.0 40.4981 423.343.34 120.0 40.4981 433.003.40 119.5^{b} 40.4990 403.30 3.90 3.00 40.978 42 3.43 3.41 120.0 40.4981 43 3.00 3.00	17	2.40	3.80	111.80	40.5325
19 3.00 3.80 116.8° 40.5095 20 3.75 3.75 120.0 40.4895 21 2.90 3.70 116.6° 40.5109 22 3.10 3.70 118.0° 40.5046 23 2.20 3.60 110.1° 40.5248 24 2.50 3.60 113.9° 40.5198 25 2.80 3.60 116.4° 40.5056 27 3.10 3.60 118.5° 40.5031 28 3.20 3.60 119.5° 40.5009 29 2.00 3.50 110.3° 40.5125 30 2.90 3.50 117.7° 40.5054 31 3.00 3.50 119.5° 40.5033 32 3.10 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4968 35 3.50 3.50 119.5° 40.4968 35 3.50 3.40 116.1° 40.5024 38 3.00 3.40 119.5° 40.4968 40 3.30 3.40 119.2° 40.4981 41 3.40 3.40 120.0 40.4981 42 3.34 3.30 120.0 40.4981 43 3.00 3.00 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 <td< th=""><td>18</td><td>2.70</td><td>3.80</td><td>114.4</td><td>40.5213</td></td<>	18	2.70	3.80	114.4	40.5213
20 3.75 3.75 120.0 40.4895 21 2.90 3.70 116.6^{b} 40.5109 22 3.10 3.70 118.0^{b} 40.5046 23 2.20 3.60 110.1^{b} 40.5248 24 2.50 3.60 113.9^{b} 40.5198 25 2.80 3.60 116.4^{b} 40.5056 27 3.10 3.60 117.8^{b} 40.5056 27 3.10 3.60 119.5^{b} 40.5029 29 2.00 3.50 110.3^{b} 40.5025 30 2.90 3.50 117.7^{b} 40.5054 31 3.00 3.50 119.3^{b} 40.5015 33 3.30 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4968 35 3.50 3.50 120.0 40.4984 36 2.60 3.40 116.1^{b} 40.5024 38 3.00 3.40 119.5^{b} 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 43 3.10 3.30 120.0 40.4981 44 3.20 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 <	19	3.00	3.80	116.80	40.5095
21 2.90 3.70 116.6° 40.5109 22 3.10 3.70 118.0° 40.5046 23 2.20 3.60 110.1° 40.5248 24 2.50 3.60 113.9° 40.5198 25 2.80 3.60 116.4° 40.5110 26 3.00 3.60 117.8° 40.5056 27 3.10 3.60 119.5° 40.5031 28 3.20 3.60 119.5° 40.5031 28 3.20 3.60 117.7° 40.5054 31 3.00 3.50 110.3° 40.5125 30 2.90 3.50 117.7° 40.5033 32 3.10 3.50 119.5° 40.4982 31 3.00 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4984 36 2.60 3.40 116.1° 40.5024 38 3.00 3.40 119.5° 40.4984 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.20 3.30 120.0 4	20	3.75	3.75	120.0	40.4895
22 3.10 3.70 118.0^{9} 40.5046 23 2.20 3.60 110.1^{5} 40.5248 24 2.50 3.60 113.9^{5} 40.5198 25 2.80 3.60 116.4^{5} 40.5056 27 3.10 3.60 117.8^{5} 40.5031 28 3.20 3.60 119.5^{5} 40.5031 28 3.20 3.60 119.5^{5} 40.5033 30 2.90 3.50 110.3^{5} 40.5054 31 3.00 3.50 118.4^{5} 40.5033 32 3.10 3.50 119.5^{5} 40.4982 34 3.40 3.50 119.5^{5} 40.4982 34 3.40 3.50 119.5^{5} 40.4982 35 3.50 3.50 120.0 40.4982 36 2.60 3.40 116.1^{5} 40.5024 38 3.00 3.40 119.5^{5} 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 43 3.10 3.30 120.0 40.4981 44 3.20 3.30 120.0 40.4982 45 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4982 45 3.30 3.25 120.0 40.4982 46 3.25 3.25	21	2.90	3.70	116.6	40.5109
232.20 3.60 110.1° 40.5248 242.50 3.60 113.9° 40.5198 252.80 3.60 116.4° 40.5110 26 3.00 3.60 117.8° 40.5056 27 3.10 3.60 119.5° 40.5031 28 3.20 3.60 119.5° 40.50331 28 3.20 3.60 119.5° 40.50331 29 2.00 3.50 110.3° 40.5054 31 3.00 3.50 119.3° 40.5033 32 3.10 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4968 35 3.50 3.50 120.0 40.4964 36 2.60 3.40 116.1° 40.5072 37 2.90 3.40 119.5° 40.4964 38 3.00 3.40 119.2° 40.5011 39 3.20 3.40 119.5° 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.20 3.30 120.0 40.4982 45 3.30 3.30 120.0 40.4982 45 <	22	3.10	3.70	118.0	40.5046
24 2.50 3.60 113.9^{ab} 40.5198 25 2.80 3.60 116.4^{b} 40.5110 26 3.00 3.60 117.8^{b} 40.5056 27 3.10 3.60 118.5^{b} 40.5031 28 3.20 3.60 119.5^{b} 40.5031 28 3.20 3.60 119.5^{b} 40.5031 30 2.90 3.50 117.7^{b} 40.5054 31 3.00 3.50 119.3^{b} 40.5033 32 3.10 3.50 119.3^{b} 40.5033 32 3.10 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4968 35 3.50 3.50 120.0 40.4964 36 2.60 3.40 116.1^{b} 40.5072 37 2.90 3.40 119.5^{b} 40.4964 36 2.60 3.40 119.5^{b} 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.20 3.30 120.0 40.4978 42 3.34 3.34 120.0 40.4981 41 3.00 3.00 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 <td>23</td> <td>2.20</td> <td>3.60</td> <td>110.1°</td> <td>40.5248</td>	23	2.20	3.60	110.1°	40.5248
252.803.60 116.4^{ab} 40.5110 263.003.60 117.8^{b} 40.5056 273.103.60 118.5^{b} 40.5031 283.203.60 119.5^{b} 40.5009 292.003.50 110.3^{b} 40.5125 302.903.50 117.7^{b} 40.5054 313.003.50 119.5^{b} 40.5033 323.103.50 119.5^{b} 40.4982 343.403.50 119.5^{b} 40.4968 353.503.50 120.0 40.4964 362.603.40 116.1^{b} 40.5072 372.903.40 118.4^{b} 40.5024 383.003.40 119.5^{b} 40.4981 403.303.40 120.0 40.4978 413.403.40 120.0 40.4978 423.343.34 120.0 40.4978 433.103.30 119.5^{b} 40.4978 453.30 3.30 120.0 40.4981 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4983 47 3.00 3.00 120.0 40.4978 46 4.99^{d}	24	2.50	3.60	113.9	40.5198
26 3.00 3.60 117.8^{0} 40.505 27 3.10 3.60 118.5^{0} 40.5031 28 3.20 3.60 119.5^{0} 40.5009 29 2.00 3.50 110.3^{0} 40.5125 30 2.90 3.50 117.7^{0} 40.5054 31 3.00 3.50 119.5^{0} 40.5015 33 3.30 3.50 119.5^{0} 40.4982 34 3.40 3.50 119.5^{0} 40.4968 35 3.50 120.0 40.4964 36 2.60 3.40 116.1^{0} 40.5072 37 2.90 3.40 119.5^{0} 40.4964 36 2.60 3.40 119.5^{0} 40.4964 36 2.60 3.40 119.5^{0} 40.4964 36 3.50 120.0 40.4964 36 2.60 3.40 119.5^{0} 40.5072 37 2.90 3.40 119.5^{0} 40.4964 36 3.00 3.40 119.2^{0} 40.4964 43 3.00 3.40 120.0 40.4981 41 3.40 3.20 40.4981 41 3.40 3.20 40.4981 41 3.20 3.30 120.0 40.4981 41 3.20 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 <td>25</td> <td>2.80</td> <td>3.60</td> <td>115.4</td> <td>40,5110</td>	25	2.80	3.60	115.4	40,5110
27 3.10 3.60 118.3^{o} 40.5031 28 3.20 3.60 119.5^{b} 40.5009 29 2.00 3.50 110.3^{b} 40.5125 30 2.90 3.50 117.7^{b} 40.5054 31 3.00 3.50 118.4^{b} 40.5033 32 3.10 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4982 34 3.40 3.50 119.5^{b} 40.4964 36 2.60 3.40 116.1^{b} 40.5072 37 2.90 3.40 118.4^{b} 40.5024 38 3.00 3.40 119.2^{b} 40.4981 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 43 3.10 3.30 119.5^{b} 40.4978 42 3.34 3.30 120.0 40.4981 43 3.10 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4988 46 3.25 3.25 120.0 40.4988 46 1.94^{d} 3.25 3.25 120.0 40.4988 46 2.12^{d} 3.25 3.25 120.0 40.4988 46 3.25 3.25 120.0 40.4968 46 1.94^{d} 3.25 3.2	20	3.00	3.60	110.5	40.5056
28 3.20 3.60 119.3° 40.5009 29 2.00 3.50 110.3° 40.5125 30 2.90 3.50 117.7° 40.5054 31 3.00 3.50 118.4° 40.5033 32 3.10 3.50 119.3° 40.5015 33 3.30 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4968 35 3.50 3.50 120.0 40.4964 36 2.60 3.40 116.1° 40.5072 37 2.90 3.40 118.4° 40.5024 38 3.00 3.40 119.2° 40.4990 40 3.30 3.40 119.2° 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4978 42 3.34 3.34 120.0 40.4978 43 3.10 3.30 120.0 40.4978 45 3.30 3.00 120.0 40.4982 46 3.25 3.25 120.0 40.4920 $42b^{\circ}$ 3.34 3.34 119.0 40.4920 $42b^{\circ}$ 3.34 3.25 120.0 40.4920 46 2.25 3.25 120.0 40.4920 46 3.25 3.25 120.0 40.4920 46 42.5 3.25 3.25 120.0 40.4920	2/	3.10	3.60	118.5	40.5031
292.00 3.50 110.3° 40.5123 30 2.90 3.50 117.7° 40.5054 31 3.00 3.50 118.4° 40.5033 32 3.10 3.50 119.3° 40.5015 33 3.30 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4982 34 3.40 3.50 119.5° 40.4968 35 3.50 3.50 120.0 40.4964 36 2.60 3.40 116.1° 40.5072 37 2.90 3.40 119.2° 40.5011 39 3.20 3.40 119.5° 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 43 3.10 3.30 119.5° 40.4979 44 3.20 3.30 120.0 40.4978 45 3.30 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4920 $42b^{\circ}$ 3.34 3.34 119.0 40.4920 $42b^{\circ}$ 3.34 3.25 3.25 120.0 40.4920 46 3.25 3.25 120.0 40.4920 46 4.25 3.25 120.0 40.4922 46 4.25 3.25 120.0 40.4922 46 4.25 3.25 3.25 120.0 40.4922 46	20	3.20	3.60	119.5	40.5009
302.903.50 111.7^{12} 40.503313.003.50 118.4^{b} 40.5033323.103.50 119.3^{b} 40.5015333.303.50 119.3^{b} 40.4982343.403.50 119.5^{b} 40.4968353.503.50 120.0 40.4964362.603.40 116.1^{b} 40.5072372.903.40 119.5^{b} 40.4990403.303.40 119.5^{b} 40.4990403.303.40 120.0 40.4981413.403.40 120.0 40.4981433.103.30 119.5^{b} 40.4978423.343.34 120.0 40.4981433.103.30 120.0 40.4982463.253.25 120.0 40.4982463.253.25 120.0 40.492042b^{c}3.343.34 119.0 40.495846 1.25 3.25 120.0 40.492042b^{c} 3.34 3.25 3.25 120.0 40.495846 $(2.10)^{d}$ 3.25 3.25 120.0 40.495846 $(2.12)^{d}$ 3.25 3.25 120	29	2.00	3.50	110.5°	40.5125
313.003.50110.4*40.503323.103.50119.3*40.5015333.303.50119.5*40.4982343.403.50119.540.4982353.503.50120.040.4964362.603.40116.1*40.5072372.903.40118.4*40.5024383.003.40119.5*40.4981403.303.40120.040.4981413.403.40120.040.4981413.403.40120.040.4981433.103.30119.5*40.4978443.203.30120.040.4978453.303.30120.040.4982463.253.25120.040.4982463.253.25120.040.492042b°3.343.34119.040.495846 (1.94)*3.253.25120.040.492042b°3.343.253.25120.040.492046 (2.10)*3.253.25120.040.496846 (2.12)*3.253.25120.040.492246 (2.18)*3.253.25120.040.4938 $\infty*$ 2.12 ∞ 109.540.576	30	2.90	3.50	117.7	40.5034
32 3.10 3.50 119.5^{3} 40.4982 33 3.30 3.50 119.5^{3} 40.4982 34 3.40 3.50 119.5^{3} 40.4968 35 3.50 3.50 120.0 40.4968 36 2.60 3.40 116.1^{5} 40.5072 37 2.90 3.40 118.4^{5} 40.5024 38 3.00 3.40 119.5^{5} 40.4990 40 3.30 3.40 119.5^{5} 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 43 3.10 3.30 119.5^{5} 40.4978 43 3.10 3.30 120.0 40.4978 45 3.30 3.20 3.40 120.0 40.4978 43 3.10 3.30 120.0 40.4978 45 3.30 3.20 40.4979 44 3.20 3.30 120.0 40.4982 45 3.30 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4920 $42b^{c}$ 3.34 3.34 119.0 40.4958 46 40.253 3.25 120.0 40.4920 $42b^{c}$ 3.25 3.25 120.0 40.4968 46 $(2.12)^{d}$ 3.25 3.25 120.0 40.4922 46 $(2.12)^{d}$ 3.25 3.25 120.0 </th <td>22</td> <td>3.00</td> <td>3.50</td> <td>110.4</td> <td>40.5055</td>	22	3.00	3.50	110.4	40.5055
343.403.50112.340.496835 3.50 3.50 119.5 40.4968 35 3.50 3.50 120.0 40.4964 36 2.60 3.40 116.1^{b} 40.5072 37 2.90 3.40 118.4^{b} 40.5024 38 3.00 3.40 119.5^{b} 40.4981 40 3.30 3.40 119.5^{b} 40.4981 41 3.40 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4978 42 3.34 3.34 120.0 40.4978 43 3.10 3.30 120.0 40.4978 45 3.30 3.30 120.0 40.4978 45 3.30 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4958 46 (1.94)^{d} 3.25 3.25 120.0 40.4958 46 (2.00)^{d} 3.25 3.25 120.0 40.4958 46 (2.12)^{d} 3.25 3.25 120.0 40.4920 46 (2.18)^{d} 3.25 3.25 120.0 40.4922 46 (2.18)^{d} 3.25 3.25 120.0 40.4938 ∞^{d} 2.12 ∞ 109.5 40.576	32	3.10	3.50	119 5	40.3013
35 3.50 3.50 112.5 40.4964 36 2.60 3.40 116.1^{b} 40.4964 36 2.60 3.40 118.4^{b} 40.5072 37 2.90 3.40 118.4^{b} 40.5024 38 3.00 3.40 119.2^{b} 40.4964 39 3.20 3.40 119.2^{b} 40.5011 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4978 42 3.34 3.34 120.0 40.4978 43 3.10 3.30 119.5^{b} 40.4979 44 3.20 3.30 120.0 40.4981 45 3.30 3.30 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 1.94^{a} 3.25 3.25 120.0 40.4958 46 $(1.94)^{a}$ 3.25 3.25 120.0 40.4958 46 $(2.10)^{a}$ 3.25 3.25 120.0 40.4968 46 $(2.12)^{a}$ 3.25 3.25 120.0 40.4922 46 $(2.12)^{a}$ 3.25 3.25 120.0 40.4938 46 $(2.18)^{a}$ 3.25 3.25 120.0 40.4839 ∞^{a} 2.12 ∞ 109.5 40.576	34	3 40	3.50	119.5	40.4962
362.603.40112.1040.5072372.903.40116.1 ^b 40.5074383.003.40119.2 ^b 40.5024393.203.40119.2 ^b 40.4990403.303.40120.040.4981413.403.40120.040.4978423.343.34120.040.4978433.103.30119.5 ^b 40.4979443.203.30120.040.4978453.303.30120.040.4982463.253.25120.040.4988473.003.00120.040.495846 (1.94) ^d 3.253.25120.040.496846 (2.12) ^d 3.253.25120.040.496846 (2.12) ^d 3.253.25120.040.496846 (2.18) ^d 3.253.25120.040.4989 ∞^{d} 2.12 ∞ 109.540.576	35	3.50	3 50	120.0	40.4964
37 2.90 3.40 118.4^{b} 40.5024 38 3.00 3.40 119.2^{b} 40.5024 39 3.20 3.40 119.2^{b} 40.5011 39 3.20 3.40 119.5^{b} 40.4990 40 3.30 3.40 120.0 40.4981 41 3.40 3.40 120.0 40.4981 42 3.34 3.34 120.0 40.4978 42 3.34 3.30 119.5^{b} 40.4979 44 3.20 3.30 120.0 40.4978 45 3.30 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4980 47 3.00 3.00 120.0 40.4920 $42b^{c}$ 3.34 3.34 119.0 40.4920 $42b^{c}$ 3.25 3.25 120.0 40.4920 46 2.12^{d} 3.25 3.25 120.0 40.4922 46 $(2.12)^{d}$ 3.25 3.25 120.0 40.4922 46 $(2.18)^{d}$ 3.25 3.25 120.0 40.4922 46 $(2.18)^{d}$ 3.25 3.25 120.0 40.4839 ∞^{d} 2.12 ∞ 109.5 40.576	36	2 60	3 40	116 10	40.5072
383.003.40119.2b40.5011393.203.40119.5b40.5011393.203.40119.5b40.4990403.303.40120.040.4981413.403.40120.040.4978423.343.34120.040.4981433.103.30119.5b40.4979443.203.30120.040.4978453.303.30120.040.4982463.253.25120.040.4980473.003.00120.040.4980463.253.25120.040.492042bc3.343.34119.040.495846(2.00)^d3.253.25120.040.492246(2.12)^d3.253.25120.040.492246(2.12)^d3.253.25120.040.492246(2.18)^d3.253.25120.040.492246(2.18)^d3.253.25120.040.4839 ∞^d 2.12 ∞ 109.540.576	37	2 90	3.40	118.4	40.5024
393.203.40119.5b40.4990403.303.40120.040.4981413.403.40120.040.4981423.343.34120.040.4978423.343.34120.040.4981433.103.30119.5b40.4979443.203.30120.040.4982453.303.30120.040.4982463.253.25120.040.4980473.003.00120.040.492042bc3.343.34119.040.495846 (1.94)d3.253.25120.040.496846 (2.00)d3.253.25120.040.499746 (2.12)d3.253.25120.040.492246 (2.18)d3.253.25120.040.492246 (2.18)d3.253.25120.040.4839 ∞^d 2.12 ∞ 109.540.576	38	3.00	3.40	119.2	40.5011
403.303.40120.040.4981413.403.40120.040.4981423.343.40120.040.4978433.103.30119.5 ^b 40.4979443.203.30120.040.4978453.303.30120.040.4982463.253.25120.040.4982473.003.00120.040.492042bc3.343.34119.040.495846 (1.94) ^d 3.253.25120.040.495846 (2.00) ^d 3.253.25120.040.495846 (2.12) ^d 3.253.25120.040.492246 (2.18) ^d 3.253.25120.040.492246 (2.18) ^d 3.253.25120.040.4922 ∞^{d} 2.12 ∞ 109.540.576	39	3.20	3.40	119.5	40,4990
413.403.40120.040.4978423.343.34120.040.4978433.103.30119.5 ^b 40.4979443.203.30120.040.4978453.303.30120.040.4982463.253.25120.040.4982473.003.00120.040.492042bc3.343.34119.040.495846 (1.94) ^d 3.253.25120.040.496846 (2.00) ^d 3.253.25120.040.495846 (2.12) ^d 3.253.25120.040.492246 (2.18) ^d 3.253.25120.040.492246 (2.18) ^d 3.253.25120.040.4839 ∞^{d} 2.12 ∞ 109.540.576	40	3.30	3.40	120.0	40.4981
42 3.34 3.34 120.0 40.4981 43 3.10 3.30 119.5^{b} 40.4979 44 3.20 3.30 120.0 40.4978 45 3.30 3.30 120.0 40.4978 46 3.25 3.25 120.0 40.4982 46 3.25 3.25 120.0 40.4982 47 3.00 3.00 120.0 40.4920 $42b^{c}$ 3.34 3.34 119.0 40.4958 46 ($1.94)^{a}$ 3.25 3.25 120.0 40.4968 46 ($2.00)^{a}$ 3.25 3.25 120.0 40.4997 46 ($2.12)^{a}$ 3.25 3.25 120.0 40.4922 46 ($2.18)^{a}$ 3.25 3.25 120.0 40.4839 ∞^{a} 2.12 ∞ 109.5 40.576	41	3.40	3.40	120.0	40.4978
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	42	3.34	3.34	120.0	40.4981
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	43	3.10	3.30	119.5%	40.4979
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	44	3.20	3.30	120.0	40.4978
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	45	3.30	3.30	120.0	40.4982
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46	3.25	3.25	120.0	40.4980
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	47	3.00	3.00	120.0	40.4920
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	42b°	3.34	3.34	119.0	40.4958
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46 (1.94) ^a	3.25	3.25	120.0	40.4968
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46 (2.00) ^d	3.25	3.25	120.0	40.4997
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	46 (2.12) ^d	3.25	3.25	120.0	40.4922
∞^{e} 2.12 ∞ 109.5 40.576	46 (2.18) ^a	3.25	3.25	120.0	40.4839
	^ه ه	2.12	æ	109.5	40.576

^a Unless specified otherwise, the three identical nonreacting carbon-hydrogen bonds have a distance of 2.06 au. ^b Optimum angle obtained from interpolation or extrapolation as described in text. ^c This point establishes that the D_{3h} geometry of the transition state is stable toward the motion into C_{3v} symmetry. ^d In these calculations, the nonreacting carbon-hydrogen bond distances are varied. The distances are given in the parentheses. ^e This value, for separate methane and hydride systems, was reported in an earlier study, ref 2.

+0.425 au. The direct product of A_1' and A_2'' does not contain E', the symmetry species of the vibration carrying D_{3h} into C_{4v} configuration. It is informative to note that the A_2'' transition symmetry is consistent

	Center population			Bond orders					
Point no.	С	$\mathbf{H}_{\mathbf{E}^{a}}$	- H _L ^b	H _{NR} ^e	$CH_{L^{b}}$	$CH_{E^{a}}$	CH _{NR} ^c	d_1^d	d_{2^e}
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	6.54	2.00	0.869	0.869	0,387	0.00	0.387	2.06	∞
14	6.36	1.904	1.187	0.853	0.254	-0.05	0.411	2.60	4.00
21	6.27	1.818	1.359	0.852	0.184	-0.006	0.417	2.90	3.70
26	6.24	1.773	1.422	0.851	0.161	0.008	0.418	3.00	3.60
32	6.23	1.730	1.484	0.851	0.137	0.035	0.419	3.10	3.50
39	6.22	1.691	1.532	0.852	0.115	0.055	0.420	3.20	3.40
45	6.22	1.613	1.613	0.852	0.086	0.086	0.420	3.30	3.30

^a  $H_E$  is the entering hydrogen, *i.e.*, the hydrogen farthest from the carbon. ^b  $H_L$  is the leaving hydrogen, *i.e.*, the hydrogen along the  $H_E$ -C bond extension. ^c  $H_{NR}$  refers to the nonreacting hydrogens. ^d The distance between C and  $H_L$  is  $d_1$ . ^c The distance between C and  $H_E$  is  $d_2$ .

with the symmetry of the vibration carrying  $CH_5^-$  into  $CH_4 + H^-$ .

Assuming that we have explored the path corresponding to an SN2 reaction, it is interesting to note the population analyses in Table II. The interesting feature is that the electron densities on both carbon and the nonreacting hydrogens decrease on going from methane to the saddle point. This rather surprising result appears to be consistent with the experimental observation that electron donating substituents on carbon increase the rates of SN2 reactions.⁶

Quite recently, Berthier⁷ has reported *ab initio* LCGO-MO-SCF calculations pertaining to the SN2 reaction of  $F^-$  with  $CH_3F$ . Only the two regions corresponding to reactants and  $D_{3h}$  species were examined closely. In agreement with the present study, it was found that the electron densities on carbon and

(6) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 3 ff; C. K. Ingold, *Quart. Rev.* (London), 11, 1 (1957).

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on the hydrogens decrease on going from reactants to "transition state." The density on carbon decreased by 0.123 unit, and the densities on each of the hydrogens decreased by 0.008 unit. In the present study, the corresponding decreases are 0.32 and 0.017 unit, respectively.

In contrast to the present results, Berthier finds the  $CH_3F_2^-$  transition state to be 8.8 kcal/mol more stable than the separated reactants. It should be recalled that the same situation was encountered in our earlier work² on the reactions of H⁻ and F⁻ with hydrogen molecules. The H⁻ reaction showed a transition state less stable than separated reactants, while the F⁻ reaction gave the opposite result. We are still unable to understand the origin of these unusual results, but note that positive "excitation energies" have been found for ion-molecule reactions only in the cases where hydride ion is both the entering and leaving group.

Acknowledgments. We are grateful to the Computer Center, State University of New York at Buffalo, for the donation of massive amounts of computer time.

## A Semiempirical Description of the Diamagnetic Susceptibilities of Aromatic Molecules

### Patricia S. O'Sullivan¹ and H. F. Hameka

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Abstract: A semiempirical description of the diamagnetic susceptibilities of conjugated organic molecules has been derived. The susceptibility is represented as a sum of three terms, namely the contributions from the  $\sigma$  electrons and from the  $\pi$  electrons and the contribution from  $\sigma - \pi$  interactions. The  $\pi$ -electron contribution is derived from London's theory and the other terms are expressed in terms of atomic susceptibilities, bond susceptibilities, and bond-bond interactions. As an example the polyacenes are discussed, where satisfactory agreement with experiment is obtained.

I n previous work² the authors have put forward a semiempirical theory of the diamagnetic susceptibilities of saturated organic molecules. The present paper extends this theory to conjugated molecules.

It should be noted that in deriving the theory for saturated molecules we made a few assumptions which are not valid in the case of conjugated systems and it is therefore necessary to reconsider the theoretical derivation. The first assumption was that the molecular eigenfunctions of the ground and excited states may be approximated as single-determinant LCAO-MO functions. The second assumption was that the

⁽¹⁾ Supported by the National Science Foundation Undergraduate Participation Program.

^{(2) (}a) H. F. Hameka, J. Chem. Phys., 34, 1996 (1961); (b) P. S. O'Sullivan and H. F. Hameka, J. Amer. Chem. Soc., 92, 25 (1970).