

The results presented here point to interesting aspects of both MNDO and ab initio methods. Both MO schemes often underestimate the primary stretch compliants. On the other hand, both approaches give reliable estimates of interaction coordinates, particularly symmetry interaction coordinates. The physical meaning is that MNDO and ab initio molecular orbital methods give reliable estimates of the initial part of a dissociation pathway since the interaction displacement coordinates are directly related to the MEP for unimolecular dissociation in the quadratic limit.<sup>27</sup> The fact that the molecular orbital schemes overestimate the relaxed force constant, the reciprocal of the primary compliant, indicates that they overestimate the restoring force for a distortion along this dissociation path.

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## References and Notes

- (1) L. H. Jones and B. I. Swanson, *Acc. Chem. Res.*, **9**, 128 (1976).
- (2) T. Shimanouchi in "Physical Chemistry, an Advanced Treatise", Vol. 4, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N.Y., 1970, Chapter 6.
- (3) J. L. Duncan, *Spec. Period. Rep., Mol. Spectrosc.*, **3** (1976).
- (4) L. H. Jones, R. S. McDowell, and B. I. Swanson, *J. Chem. Phys.*, **58**, 3757 (1973).
- (5) J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1965).
- (6) A. Müller and B. Krebs, *J. Mol. Spectrosc.*, **24**, 180 (1967).
- (7) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishi, *J. Mol. Spectrosc.*, **19**, 78 (1965).
- (8) J. Tyson, H. H. Claassen, and H. Kim, *J. Chem. Phys.*, **54**, 3142 (1971).
- (9) I. M. Mills, *Spectrochim. Acta*, **19**, 1583 (1963).
- (10) F. A. Cotton and C. J. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
- (11) J. W. Linnett and P. J. Wheatley, *Trans. Faraday Soc.*, **45**, 33, 39 (1949).
- (12) P. Pulay, "Modern Theoretical Chemistry", Vol II, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1976.
- (13) J. E. Boggs and S. Skaarup, *J. Mol. Struct.*, **30**, 389 (1976).
- (14) L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.*, **63**, 4750 (1975).
- (15) (a) P. Pulay and F. Torok, *Mol. Phys.*, **25**, 1153 (1973); (b) K. Kozmutza and P. Pulay, *Theor. Chim. Acta*, **37**, 67 (1975).
- (16) (a) C. E. Blom, P. J. Slingerland, and C. Altona, *Mol. Phys.*, **31**, 1359 (1976); (b) C. E. Blom and C. Altona, *ibid.*, **31**, 1377 (1976); (c) C. E. Blom, L. P. Otto, and C. Altona, *ibid.*, **32**, 1137 (1976); (d) C. E. Blom and C. Altona, *ibid.*, in press; submitted for publication; C. E. Blom, A. Oskam and C. Altona, submitted for publication.
- (17) B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976).
- (18) W. J. Taylor and K. J. Pitzer, *J. Res. Natl. Bur. Stand.*, **38**, 1 (1947).
- (19) J. C. Decius, *J. Chem. Phys.*, **38**, 241 (1963).
- (20) P. G. Maslou, *Dokl. Akad. Nauk SSSR*, **67**, 819 (1949).
- (21) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1046 (1939).
- (22) L. H. Jones, *Coord. Chem. Rev.*, **1**, 351 (1966).
- (23) L. H. Jones and R. R. Ryan, *J. Chem. Phys.*, **52**, 2003 (1970).
- (24) (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977). (b) M. J. S. Dewar and H. S. Rzepa, *ibid.*, following papers in this issue; M. J. S. Dewar and M. L. McKee, *ibid.*, **99**, 5231 (1977).
- (25) An earlier SCF-MO treatment based on the INDO approximation (MINDO/3) has been shown<sup>26</sup> to give potential constants which satisfactorily reproduce vibrational frequencies. Preliminary tests suggest that MNDO is somewhat better in this respect.
- (26) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
- (27) B. I. Swanson, *J. Am. Chem. Soc.*, **98**, 3067 (1976).
- (28) B. I. Swanson, J. J. Rafalko, H. S. Rzepa, and M. J. S. Dewar, *J. Am. Chem. Soc.*, **99**, 7829 (1977).
- (29) B. I. Swanson and R. S. Ottinger, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., No. 208.
- (30) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules, III", Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.
- (31) M. J. S. Dewar and Y. Yamaguchi, unpublished results.
- (32) C. A. Allen, Jr., and P. C. Cross, "Molecular Vib Rotors", Wiley, New York, N.Y., 1963; E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
- (33) P. Pulay, *Mol. Phys.*, **21**, 329 (1971).
- (34) P. Pulay and W. Meyer, *J. Chem. Phys.*, **57**, 3337 (1972).
- (35) W. Meyer and P. Pulay, *J. Chem. Phys.*, **56**, 2109 (1972).
- (36) W. Sawodny and P. Pulay, *J. Mol. Spectrosc.*, **51**, 135 (1974).
- (37) P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, **40**, 59 (1971).

## Ground States of Molecules. 45. MNDO Results for Molecules Containing Beryllium

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**Abstract:** Calculations of heats of formation, molecular geometries, ionization potentials, and dipole moments are reported for more than 50 compounds containing beryllium. The two most stable structural forms of beryllium borohydride were calculated to be of  $D_{3d}$  and  $D_{2d}$  symmetry. The calculated molecular vibration frequencies for the former agree very well with assignments reported by Nibler, and additional frequencies observed by Nibler in the gas phase correlate well with the  $D_{2d}$  form. The most stable form of dicyclopentadienylberyllium is calculated to have one pentahapto and one monohapto ring, which agrees with the crystal but not the gas phase structure. The doubly face bridging isomer had calculated  $D_{5d}$  symmetry, with the metal atom at the center, in disagreement with the reported electron diffraction structure, where the metal is displaced by 0.22 Å. Several interesting structural features are reported for as yet unknown compounds containing BeO or BeN<sub>2</sub> units replacing the isoelectronic C<sub>2</sub> or C<sub>3</sub>. Singlet-triplet separations in BeO agree with those reported by Schaefer et al.

## Introduction

Previous papers<sup>1-4</sup> of this series have reported the development of a new semiempirical MO method (MNDO) and its application to numerous compounds of the first and second period elements, H, B, N, C, O, and F. The results were in very satisfactory agreement with experiment and definitely superior to those given by earlier treatments, in particular MINDO/3.<sup>5</sup> In view of this success, extension of MNDO to other elements,

in particular to metals, has become a matter of considerable interest. Here we report the first MNDO results for a metal, namely, beryllium.

One of the major obstacles encountered in developing treatments of this kind is the paucity of reliable experimental data needed for parametrization, in particular gas-phase heats of formation, and beryllium is typical in this respect. Indeed the situation here is especially bad because recognition of the

Table I. Optimized MNDO Parameters for Beryllium

| Optimized parameters       |             | Derived parameters                          |                    |
|----------------------------|-------------|---------------------------------------------|--------------------|
| $U_{ss}$ , eV              | -16.602 378 | $\Delta H_f^\circ$ , kcal mol <sup>-1</sup> | 76.96 <sup>a</sup> |
| $U_{pp}$ , eV              | -10.703 771 | $E_c$ , eV                                  | -24.2074           |
| $\zeta$ , au               | 1.004 210   | $D_1$ , Å                                   | 0.760 585          |
| $\beta_{sp}$ , eV          | -4.017 096  | $D_2$ , Å                                   | 0.645 378          |
| $\alpha$ , Å <sup>-1</sup> | 1.669 434   | $\rho_0$ , Å                                | 0.799 924          |
|                            |             | $\rho_1$ , Å                                | 0.788 356          |
|                            |             | $\rho_2$ , Å                                | 0.684 928          |

<sup>a</sup> W. V. Steel, *Annu. Rep. Prog. Chem., Sect. A*, 117 (1974).

extreme toxicity of beryllium compounds has led to increasingly severe restrictions on their study. Here again MNDO is superior to its predecessor, MINDO/3,<sup>5</sup> in that it uses only atomic parameters, not parameters for atom pairs. The number of parameters that have to be determined for each additional atom is therefore the same, regardless of the number of other elements already parametrized.

### Parametrization

The method previously described<sup>1-4</sup> was used, all the previously reported<sup>1</sup> parameters being held constant. Initial values were obtained by linear extrapolation of the parameters for B, C, N, O, and F and were refined by fitting selected properties of six compounds, including two heats of formation, two ionization potentials, one dipole moment, and 14 structural parameters. These were not sufficient for unambiguous estimation of the MNDO parameters for beryllium and as a result four different but equally good fits were obtained by using different sets of initial values. However, consideration of other properties (e.g., estimated heats of dimerization and the relative stabilities of  $\eta^5$  and  $\eta^1$  bridging species) enables us to reject three of these sets. The remaining set of parameters is listed in Table I. These are fairly close to the extrapolated values, with the exception of the orbital exponent  $\zeta$ . This was consistently low in all four sets and attempts to constrain it at a higher value led to unsatisfactory general behavior.

### Results and Discussion

Calculated heats of formation, ionization potentials, and dipole moments are presented in Table II, with experimental values where available. Selected structural information is given in Table III; full Cartesian coordinates for all the compounds studied are available as supplementary material. Some typical examples of charge distributions are shown in Table IV. Since there are insufficient experimental data available for a meaningful statistical analysis, we will discuss our results for specific groups of compounds.

**1. The Metal.** Schaefer and co-workers<sup>6</sup> have recently reported ab initio studies of beryllium metal clusters. For tetrahedral  $\text{Be}_4$  they estimated<sup>6c</sup> a cohesive energy of about 10 kcal/mol per atom and an internuclear distance of 2.1 Å and for  $\text{Be}_{22}$  a cohesive energy of 35 kcal/mol per atom. Our MNDO calculations for  $\text{Be}_4$ , and for hexagonal close packed  $\text{Be}_{13}$ , gave cohesive energies of 67.5 and 86.7 kcal/mol, respectively, the experimental value for beryllium metal being 77.0 kcal/mol per atom (Table I). The Be-Be distance in  $\text{Be}_4$  was 1.85 Å and the geometry of  $\text{Be}_{13}$  agreed quite well with that found for the metal (Table III). While it is difficult to extrapolate to the metal from clusters, MNDO is clearly overestimating the cohesive energy. Possibly as a result of this, MNDO also finds a lower energy (by 2.4 kcal/mol per atom) for the cubic close packed  $\text{Be}_{13}$ .

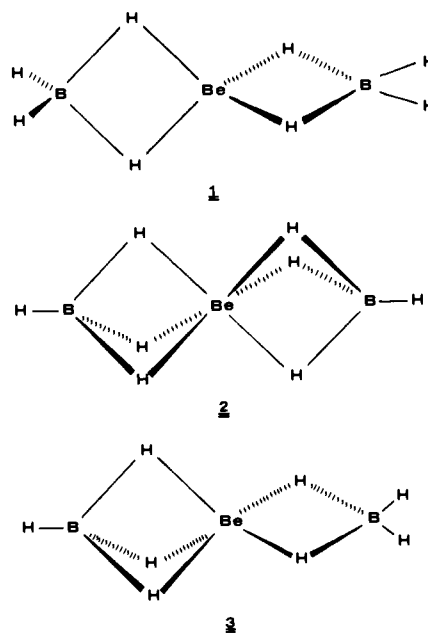
**2. The Beryllium Hydrides.** Recent ab initio studies<sup>7</sup> have appeared of the hydrides  $\text{BeH}^+$ ,  $\text{BeH}_3^+$ , and  $\text{BeH}_4$ . The reaction of  $\text{H}_2$  with  $\text{BeH}^+$  was predicted to be exothermic by -21.3 kcal/mol (UMP2/6-31G<sup>7a</sup>) or by -24.7 kcal/mol

(IEPA-PNO<sup>7b</sup>).  $\text{BeH}_4$  was found to be unbound with respect to  $\text{H}_2$  and  $\text{BeH}_2$ .<sup>7a</sup> MNDO predicts the heat of reaction for the former to be large (-32 kcal/mol) and  $\text{BeH}_4$  to be bound to the extent of 6.8 kcal/mol. The two methods predict qualitatively the same structure for  $\text{BeH}_3^+$ , but the MNDO BeH bond lengths are shorter by 0.04-0.05 Å. A similar difference was reported<sup>4</sup> between the MNDO and experimental lengths for BH bonds. The MNDO structure of  $\text{BeH}_4$  can be described as a weak  $\sigma$  complex of  $\text{BeH}_2$  and  $\text{H}_2$ .

Beryllium hydride itself is polymeric, with a cohesion energy estimated at 48 kcal/mol.<sup>8</sup> Ahlrichs,<sup>8</sup> using the R-H/IEPA method, calculated the energy of dimerization to be -31 kcal/mol. The addition of a further  $\text{BeH}_2$  unit was calculated to liberate a further 40 kcal/mol. The MNDO values are -57.0 and -67.2 kcal/mol, respectively. Compared with the R-H methods, therefore, MNDO overestimates the stability of beryllium hydrogen bridges by about 15-20 kcal/bridge. Unfortunately, no accurate experimental data are available.

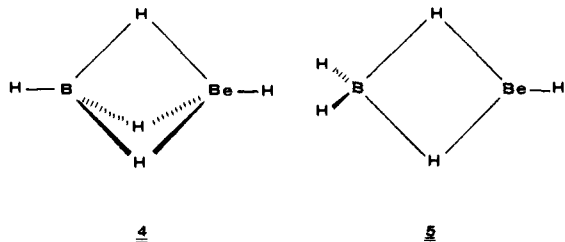
**3. The Beryllium Borohydrides.** The structure of beryllium borohydride has been the subject of much controversy over the last decade<sup>9-11</sup> and at least six structures have been suggested as prime candidates. Conflicting conclusions have been drawn from electron diffraction studies<sup>9i,j</sup> and it has been suggested<sup>9,11</sup> that the molecule may exist in at least two different forms in the gas phase. Beryllium borohydride has been reported<sup>9f,g</sup> to have a large dipole moment, but attempts to obtain a microwave spectrum have failed.<sup>9g</sup> This failure would be difficult to explain if the molecule were indeed polar. Problems have also arisen in assigning the infrared and Raman frequencies, owing to the instability of the vapor.

Recent R-H calculations by Ahlrichs,<sup>10c</sup> by Marynick and Lipscomb,<sup>10d</sup> and by Marynick<sup>10e</sup> have suggested that the only reasonable structures are those of  $D_{2d}$  (1),  $D_{3d}$  (2), and  $C_s$  (3)

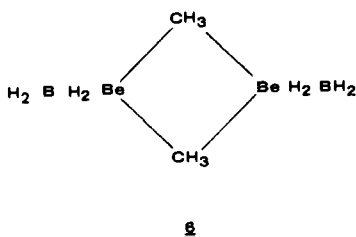


symmetry, with double or triple bridges. It is, however, difficult to account for the reported dipole moment on this basis.

Before discussing this system in detail, we will first consider the monoborohydride, which has been studied by Ahlrichs<sup>10c</sup> using the IEPA PNO method. He finds the triply bridging form of  $C_{3v}$  symmetry (4) to be about 6 kcal/mol lower than the doubly bridging form (5). MNDO leads to similar conclusions, the difference in energy being 4.3 kcal/mol. The methyl monoborohydride is similarly calculated by MNDO to favor the triple bridge by 3.6 kcal/mol. Nibler and co-workers<sup>12</sup> have observed the latter compound to exist only as the dimer 6 in the gas phase, with double hydrogen bridges as



assigned from vibrational studies. MNDO confirms this, with a calculated heat of dimerization to **6** of 21.8 kcal/mol. The triply bridging form of the dimer is calculated to be 21 kcal/mol less stable than **6** as a result of nonbonding hydrogen interactions resulting from steric crowding. MNDO is therefore consistent with the available experimental and theoretical results.



In the case of the diborohydride, the calculations of Ahlrichs<sup>10c</sup> had predicted the three forms **1**, **2**, and **3** to be essentially isoenergetic, whereas Marynick and Lipscomb<sup>10d</sup> found **1** to be favored over **2** by 7.3 kcal/mol, with **3** close to **2** in energy. Our results show a smaller energy difference, **1** being only 1.4 kcal/mol lower than **2**. However, we do not find **3** to be a stable species, the diagonalized Hessian matrix having two negative eigenvalues.<sup>13</sup> Instead, **1** and **2** interconvert via a symmetrical transition state of  $C_2$  symmetry (Figure 1). The activation barrier for **2**  $\rightarrow$  **1** is only 0.7 kcal/mol, so the two forms should freely interconvert at room temperatures. This is in accord with the recent suggestion<sup>9j</sup> that the vapor contains at least two distinct isomers, and with the observation by Nibler<sup>11</sup> of a temperature-dependent infrared spectrum. However, the two structures **1** and **2** cannot explain the reported dipole moment of 2.1 D.<sup>9f,g</sup>

Clearly, a definite statement concerning the structure of this species cannot be made on the basis of the calculated SCF energies, since the differences are obviously smaller than the accuracy of the methods. A more promising approach is suggested by the elegant vibrational study by Nibler<sup>11</sup> of the molecule in the gas phase and in an argon matrix. He has assigned the normal frequencies in the matrix according to a  $C_{3v}$  model, similar to **2** but with the metal atom off center. We have calculated the vibrational frequencies of the two isomers **1** and **2**,<sup>14</sup> and a comparison with the experimental results is given in Table V for the triply bridging and Table VI for the doubly bridging form.

In our analysis of these results, we should first note that MNDO predicts  $\nu_{BH}$  and  $\nu_{BH_b}$  frequencies to be systematically too high by about 250–350  $\text{cm}^{-1}$ .<sup>16</sup> If this correction is applied, the agreement between the calculated frequencies for our  $D_{3d}$  model and Nibler's assignments based on a  $C_{3v}$  model becomes impressive. Particularly noteworthy is the small difference, both calculated and observed, between the  $\nu_{BH_t}$  symmetric and antisymmetric modes. Also in good agreement are the  $\nu_{BBeB}$  stretches and bends. Nibler located some additional frequencies in the gas-phase spectra, which were tentatively attributed to a  $D_{2d}$  model. These indeed match our calculated values nicely (Table VI). Again noteworthy is the appreciable difference of about 50  $\text{cm}^{-1}$  found between the symmetric and antisymmetric  $\nu_{BH_t}$  stretches.

One point of interest concerns the position of the metal atom.

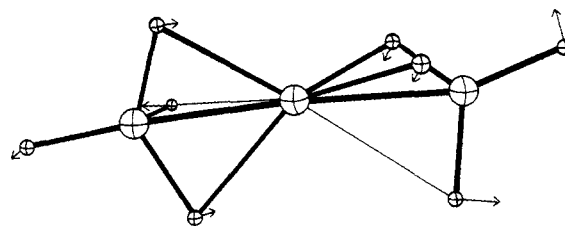


Figure 1. ORTEP plot of the transition state for the scrambling of **1** and **2**. Arrows indicate the motions of the atoms along the eigenvector of the negative eigenvalue.

Nibler<sup>11</sup> has observed *two* distinct  $\nu_{BH_b}$  stretches in the frequencies assigned to  $\text{BeB}_2\text{HD}_7$ , suggesting two distinct  $\text{BHBe}$  bridges. This, in conjunction with the apparent dipole moment and Raman depolarization data, led Nibler to the  $C_{3v}$  model. We find no stable minimum corresponding to  $C_{3v}$  symmetry, and Marynick<sup>10e</sup> likewise finds the model of  $D_{3d}$  symmetry to be an energy minimum, not maximum as suggested by Nibler. It is possible that one of the two weak bands observed by Nibler in the  $\nu_{BH_b}$  region for  $\text{BeB}_2\text{HD}_7$  might have been a combination band or overtone.

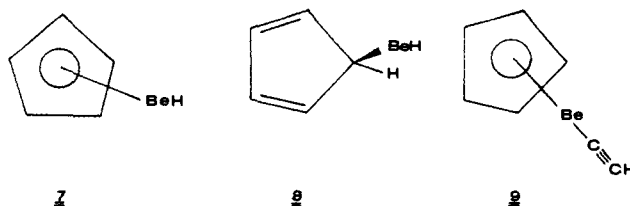
**4. The Beryllium Alkyls.** The structure of dimethylberyllium is well known from the electron diffraction studies of Haaland and co-workers.<sup>17</sup> MNDO reproduces this quite well, although the C–Be bond length is about 0.03 Å too short (Table III). The observed antisymmetric C–Be stretching frequency of 1081  $\text{cm}^{-1}$ <sup>18</sup> is less than that calculated by MNDO (1250  $\text{cm}^{-1}$ ),<sup>14</sup> reflecting the error in the calculated bond length.

The ionization potential<sup>19</sup> of dimethylberyllium is calculated very well, but not the large difference (1.1 eV) reported<sup>19</sup> between the values for dimethyl- and dimethylberyllium.

Qualitative observations of the dimer concentration in the gas phase<sup>18–20</sup> suggest that the enthalpy of dimerization of dimethylberyllium is probably not more than about 10–15 kcal/mol. The MNDO value of –25.1 kcal/mol (Table II) is somewhat too negative, again suggesting that MNDO overestimates the beryllium–beryllium energy of interaction, as indeed we also found in the case of the metal and the beryllium hydride dimers (vide supra). We were unfortunately unable to include compounds with Be–Be bonds in the parametrization since no accurate thermochemical data are available. The calculated structure of the dimer shows a  $\text{BeC}_b$  bond length about 0.18 Å longer than the terminal BeC length. This is similar to the situation found in trimethylaluminum.<sup>17a</sup>

A recently reported R-H calculation for the hypothetical  $\text{C}(\text{BeH})_4$  gave a barrier to inversion via a  $D_{4h}$  planar form of 32 kcal/mol using the 3G basis set.<sup>21</sup> The MNDO value of 25.5 kcal/mol is in close agreement, particularly since the use of a larger basis set would lower the ab initio value.

**5. Cyclopentadienyl Derivatives.** There has been considerable interest in the structures of cyclopentadienyl derivatives of beryllium.<sup>7a</sup> The structure of the simplest derivative has been shown by microwave spectroscopy<sup>22</sup> to contain a pentahapto bridging ring (7). The MNDO method is in agreement, al-



though an  $\eta^1$  isomer (**8**) is calculated to be stable and 9.1 kcal higher in energy. This difference may well be too low because

Table II. Calculated (Observed) Properties of Beryllium Compounds

| Compd                                                                             | Point group           | $\Delta H_f^{\text{calcd}}$ , kcal mol <sup>-1</sup> | IP <sub>1</sub> , <sup>a</sup> eV | $\mu$ , D                |
|-----------------------------------------------------------------------------------|-----------------------|------------------------------------------------------|-----------------------------------|--------------------------|
| Be <sub>4</sub>                                                                   | <i>T<sub>d</sub></i>  | 37.9                                                 | 8.97                              |                          |
| Be <sub>13</sub>                                                                  | <i>D<sub>3h</sub></i> | -127.1                                               | 5.70                              |                          |
| Be <sub>13</sub>                                                                  | <i>D<sub>3d</sub></i> | -159.0                                               | 6.59                              |                          |
| BeH <sup>+</sup>                                                                  | <i>C<sub>∞v</sub></i> | 238.5                                                | 19.6                              |                          |
| BeH <sub>3</sub> <sup>+</sup>                                                     | <i>C<sub>2v</sub></i> | 207.1                                                | 19.0                              |                          |
| BeH ( <sup>2</sup> Σ <sup>+</sup> )                                               | <i>C<sub>∞v</sub></i> | 60.2 <sup>b</sup>                                    |                                   | 1.38                     |
| BeH <sub>2</sub>                                                                  | <i>D<sub>∞h</sub></i> | 5.6 (-8 <sup>c</sup> )                               | 12.26                             |                          |
| Be <sub>2</sub> H <sub>4</sub>                                                    | <i>D<sub>2h</sub></i> | -45.8                                                | 12.10                             |                          |
| Be <sub>3</sub> H <sub>8</sub>                                                    | <i>D<sub>2d</sub></i> | -107.4                                               | 12.17                             |                          |
| HBH <sub>3</sub> BeH                                                              | <i>C<sub>3v</sub></i> | -31.0                                                | 12.88                             | 0.03                     |
| H <sub>2</sub> BH <sub>2</sub> BeH                                                | <i>C<sub>2v</sub></i> | -26.7                                                | 12.90                             | 0.78                     |
| HBH <sub>3</sub> BeH <sub>3</sub> BH                                              | <i>D<sub>3d</sub></i> | -54.6                                                | 12.86                             |                          |
| H <sub>2</sub> BH <sub>2</sub> BeH <sub>2</sub> BH <sub>2</sub>                   | <i>D<sub>2d</sub></i> | -56.0                                                | 13.17                             |                          |
| H <sub>2</sub> BeH <sub>2</sub> BH <sub>2</sub> BH <sub>2</sub>                   | <i>C<sub>2v</sub></i> | -6.5                                                 | 11.40                             | 4.04                     |
| Me <sub>2</sub> Be                                                                | <i>D<sub>3d</sub></i> | -47.2                                                | 10.77 (10.67) <sup>d</sup>        |                          |
| Me <sub>4</sub> Be <sub>2</sub>                                                   | <i>C<sub>2h</sub></i> | -119.5                                               | 10.67                             |                          |
| Et <sub>2</sub> Be                                                                | <i>C<sub>2h</sub></i> | -58.7                                                | 10.42 (9.46) <sup>d</sup>         |                          |
| C(BeH) <sub>4</sub>                                                               | <i>T<sub>d</sub></i>  | -125.9                                               | 11.69                             |                          |
| C(BeH) <sub>4</sub>                                                               | <i>D<sub>4h</sub></i> | -100.4                                               | 10.26                             |                          |
| η <sup>5</sup> -CpBeH                                                             | <i>C<sub>5v</sub></i> | 12.77                                                | 9.88 (9.64) <sup>e</sup>          | 2.02 (2.08) <sup>f</sup> |
| η <sup>1</sup> -CpBeH                                                             | <i>C<sub>s</sub></i>  | 21.9                                                 | 8.82                              | 0.43                     |
| η <sup>5</sup> -CpBeC≡CH                                                          | <i>C<sub>5v</sub></i> | 33.9                                                 | 9.45                              | 1.27                     |
| η <sup>1</sup> -CpBeC≡CH                                                          | <i>C<sub>s</sub></i>  | 41.5                                                 | 8.66                              | 1.52                     |
| (η <sup>5</sup> -Cp) <sub>2</sub> Be                                              | <i>D<sub>5d</sub></i> | 47.6                                                 | 8.42                              |                          |
| (η <sup>5</sup> -Cp) <sub>2</sub> Be                                              | <i>D<sub>5h</sub></i> | 47.8                                                 | 8.42                              |                          |
| η <sup>5</sup> -CpBe-η <sup>1</sup> -Cp                                           | <i>C<sub>s</sub></i>  | 31.8                                                 | 8.38                              | 2.53                     |
| (η <sup>1</sup> -Cp) <sub>2</sub> Be                                              | <i>C<sub>2h</sub></i> | 38.8                                                 | 8.76                              |                          |
| MeBeH <sub>3</sub> BH                                                             | <i>C<sub>3v</sub></i> | -55.6                                                | 11.46                             | 0.49                     |
| MeBeH <sub>2</sub> BH <sub>2</sub>                                                | <i>C<sub>2v</sub></i> | -52.0                                                | 11.57                             | 1.35                     |
| H <sub>2</sub> BH <sub>2</sub> BeMe <sub>2</sub> BeH <sub>2</sub> BH <sub>2</sub> | <i>C<sub>2h</sub></i> | -133.0                                               | 11.48                             |                          |
| HBH <sub>3</sub> BeMe <sub>2</sub> BeH <sub>3</sub> BH                            | <i>C<sub>2h</sub></i> | -112.0                                               | 11.04                             |                          |
| η <sup>5</sup> -CpBeH <sub>3</sub> BH                                             | <i>C<sub>s</sub></i>  | -5.9                                                 | 9.67                              | 2.58                     |
| η <sup>5</sup> -CpBeH <sub>2</sub> BH <sub>2</sub>                                | <i>C<sub>s</sub></i>  | -6.4                                                 | 9.70                              | 3.46                     |
| BeNH ( <sup>1</sup> Σ <sup>+</sup> )                                              | <i>C<sub>∞v</sub></i> | 84.7                                                 |                                   | 3.56                     |
| BeNH ( <sup>3</sup> Π)                                                            | <i>C<sub>∞v</sub></i> | 90.3 <sup>b</sup>                                    |                                   |                          |
| Be(NH <sub>2</sub> ) <sub>2</sub>                                                 | <i>D<sub>2d</sub></i> | -32.45                                               | 9.99                              |                          |
| Be(NH <sub>2</sub> ) <sub>2</sub>                                                 | <i>D<sub>2h</sub></i> | -28.5                                                | 9.09                              |                          |
| BeO ( <sup>1</sup> Σ <sup>+</sup> )                                               | <i>C<sub>∞v</sub></i> | 38.2 (31) <sup>g</sup>                               | 11.25                             | 5.32                     |
| BeO ( <sup>3</sup> Π)                                                             | <i>C<sub>∞v</sub></i> | 54.6 <sup>b</sup>                                    |                                   | 1.64                     |
| BeO ( <sup>3</sup> Σ <sup>+</sup> )                                               | <i>C<sub>∞v</sub></i> | 75.6 <sup>b</sup>                                    |                                   |                          |
| BeO ( <sup>3</sup> Σ <sup>-</sup> )                                               | <i>C<sub>∞v</sub></i> | 102.9 <sup>b</sup>                                   |                                   |                          |
| Be <sub>2</sub> O <sub>2</sub>                                                    | <i>D<sub>2h</sub></i> | -49.3 (-98) <sup>g</sup>                             | 9.88                              |                          |
| Be(OH) <sub>2</sub>                                                               | <i>C<sub>2h</sub></i> | -136.6 (-156.4) <sup>g</sup>                         | 11.19                             |                          |
| HBeOH                                                                             | <i>C<sub>∞v</sub></i> | -73.9                                                | 12.71                             | 1.96                     |
| (HBeOH) <sub>3</sub>                                                              | <i>D<sub>3h</sub></i> | -325.0                                               | 11.80                             |                          |
| H <sub>2</sub> BeOH <sub>2</sub>                                                  | <i>D<sub>2h</sub></i> | -74.4                                                | 10.73                             | 6.20                     |
| H <sub>2</sub> BeOH <sub>2</sub>                                                  | <i>D<sub>2d</sub></i> | -70.4                                                | 10.57                             | 6.05                     |
| C <sub>8</sub> H <sub>8</sub> BeO                                                 | <i>C<sub>2v</sub></i> | -21.3                                                | 8.87                              | 3.75                     |
| BeF ( <sup>2</sup> Σ <sup>+</sup> )                                               | <i>C<sub>∞v</sub></i> | -52.9 <sup>b</sup> (-48) <sup>h</sup>                |                                   | 1.63                     |
| BeF <sub>2</sub>                                                                  | <i>D<sub>∞h</sub></i> | -192.3 (-190.3) <sup>g</sup>                         | 14.45                             |                          |
| Be <sub>2</sub> F <sub>4</sub>                                                    | <i>D<sub>2h</sub></i> | -453.3                                               | 14.38                             |                          |
| BeF <sub>4</sub> <sup>2-</sup>                                                    | <i>T<sub>d</sub></i>  | -344.9                                               |                                   |                          |
| FBeOBeF                                                                           | <i>D<sub>∞h</sub></i> | -286.7 (-287.9) <sup>g</sup>                         | 12.76                             |                          |
| HBeOF                                                                             | <i>C<sub>s</sub></i>  | -15.3                                                | 12.08                             | 1.42                     |
| FBeOH                                                                             | <i>C<sub>∞v</sub></i> | -166.0                                               | 12.43                             | 2.57                     |
| FBeOF                                                                             | <i>C<sub>s</sub></i>  | -110.4                                               | 12.07                             | 1.02                     |

<sup>a</sup> Calculated using Koopman's theorem. <sup>b</sup> Calculated using the half-electron approximation. <sup>c</sup> M. Ducros, R. Levy, and G. Mehava, *Bull. Soc. Chim. Fr.*, 2763 (1970). <sup>d</sup> D. B. Chambers, G. E. Coates, and F. Glonkling, *J. Chem. Soc. A*, 741 (1970). <sup>e</sup> W. Goodman, personal communication. <sup>f</sup> T. Bartke, A. Bjørseth, A. Haaland, K. M. Marstokk, and H. Møllendal, *J. Organomet. Chem.*, **85**, 271 (1975). <sup>g</sup> D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", NSRDS-NBS 37, 2nd ed, 1971. <sup>h</sup> M. Farber and R. D. Srivastava, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1581 (1974).

analogous face-bridging structures for boron hydrides<sup>5</sup> are calculated to be much too unstable.

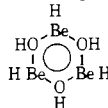
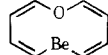
The HOMO is a degenerate e<sub>1</sub> type. The beryllium is sp hybridized, with the two empty 2p orbitals acting as acceptors from the cyclopentadienyl e<sub>1</sub> orbitals, as first suggested by Drew and Haaland<sup>23</sup> for methylcyclopentadienylberyllium.

The acetylide derivative **9** is similar to the hydride, the η<sup>5</sup> isomer being 7.6 kcal/mol more stable than the η<sup>1</sup> form. In

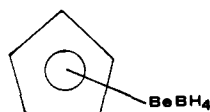
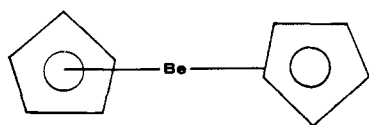
both **7** and **9**, the metal to ring carbon distance is too long by about 0.07 Å, whereas in **9** the BeC≡ distance is too short by 0.025 Å. This reflects the relative instability of face-bridging species in the MNDO method. The HOMO in **9** is similar to that in the hydride, with the next lower an e-type orbital localized mainly on the triple bond, but with appreciable p<sub>π</sub> overlap with the beryllium.

The borohydride **10** is interesting since Nibler and co-

Table III. Molecular Geometries

| Molecule                                                                            | Point group           | Calcd <sup>a</sup> (obsd) values for geometrical variables                                                                                                                    | Ref      |
|-------------------------------------------------------------------------------------|-----------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| Be <sub>4</sub>                                                                     | <i>T<sub>d</sub></i>  | BeBe, 1.850                                                                                                                                                                   |          |
| Be <sub>13</sub>                                                                    | <i>D<sub>3h</sub></i> | <i>a</i> 2.090 (2.287), <i>c</i> 3.704 (3.584)                                                                                                                                | <i>b</i> |
| Be <sub>13</sub>                                                                    | <i>D<sub>3d</sub></i> | <i>a</i> 2.264, <i>c</i> 3.1364                                                                                                                                               |          |
| BeH <sup>+</sup>                                                                    | <i>C<sub>∞v</sub></i> | BeH 1.247 (1.312)                                                                                                                                                             | <i>c</i> |
| BeH <sup>•</sup>                                                                    | <i>C<sub>∞v</sub></i> | BeH 1.291 (1.343)                                                                                                                                                             | <i>c</i> |
| BeH <sub>3</sub> <sup>+</sup>                                                       | <i>C<sub>2v</sub></i> | BeH 1.253, BeH' 1.708, H'H' 0.726                                                                                                                                             |          |
| BeH <sub>4</sub>                                                                    | <i>C<sub>2v</sub></i> | BeH 1.291, BeH' 1.862, H'H' 0.690                                                                                                                                             |          |
| BeH <sub>2</sub>                                                                    | <i>D<sub>∞h</sub></i> | BeH 1.278                                                                                                                                                                     |          |
| Be <sub>2</sub> H <sub>4</sub>                                                      | <i>D<sub>2h</sub></i> | BeH <sub>t</sub> 1.285, BeH <sub>b</sub> 1.504, BeBe 2.055                                                                                                                    |          |
| Be <sub>3</sub> H <sub>6</sub>                                                      | <i>D<sub>2d</sub></i> | BeH <sub>t</sub> 1.285, BeH <sub>b</sub> 1.490, BeBe 2.018                                                                                                                    |          |
| HBH <sub>3</sub> BeH                                                                | <i>C<sub>3v</sub></i> | HB 1.156, BeH <sub>t</sub> 1.277, BeH <sub>b</sub> 1.711, BeB 1.752                                                                                                           |          |
| H <sub>2</sub> BH <sub>2</sub> BeH                                                  | <i>C<sub>2v</sub></i> | HB 1.164, BeH <sub>t</sub> 1.276, BeH <sub>b</sub> 1.543, BeB 1.903, HBBE 121.2                                                                                               |          |
| HBH <sub>2</sub> BeH <sub>2</sub> BH                                                | <i>D<sub>3d</sub></i> | BH <sub>t</sub> 1.157 (1.16) BH <sub>b</sub> 1.242 (1.303), BeB 1.779 (1.790), H <sub>b</sub> BH <sub>t</sub> 111.4 (117.5)                                                   | <i>d</i> |
| H <sub>2</sub> BH <sub>2</sub> BeN <sub>2</sub> BH <sub>2</sub>                     | <i>D<sub>2d</sub></i> | BH <sub>t</sub> 1.164, BH <sub>b</sub> 1.309, BeB 1.911, H <sub>t</sub> BH <sub>t</sub> 118.6                                                                                 |          |
| Me <sub>2</sub> Be                                                                  | <i>D<sub>3d</sub></i> | BeC 1.660 (1.698) BeCH 111.8 (113.9)                                                                                                                                          | <i>e</i> |
| Me <sub>4</sub> Be <sub>2</sub>                                                     | <i>C<sub>2h</sub></i> | BeC <sub>t</sub> 1.698, BeC <sub>b</sub> 1.878, CH <sub>t</sub> 1.114, 1.117, CH <sub>b</sub> 1.125, 1.130                                                                    |          |
| Et <sub>2</sub> Be                                                                  | <i>C<sub>2h</sub></i> | BeC 1.669, CC 1.527, BeCC 115.9, CH 1.121, 1.111, CCH 108.4, 111.9                                                                                                            |          |
| C(BeH) <sub>4</sub>                                                                 | <i>T<sub>d</sub></i>  | CBe 1.636 (1.630)                                                                                                                                                             | <i>f</i> |
| C(BeH) <sub>4</sub>                                                                 | <i>D<sub>4h</sub></i> | CBe 1.656 (1.622)                                                                                                                                                             | <i>f</i> |
| η <sup>5</sup> -CpBeH                                                               | <i>C<sub>5v</sub></i> | BeH 1.285 (1.320), BeC 1.991 (1.919), CC 1.458 (1.423), CH 1.084 (1.090)                                                                                                      | <i>g</i> |
| η <sup>5</sup> -CpBeC≡CH                                                            | <i>C<sub>5v</sub></i> | BeC 1.609 (1.634), BeC 1.993 (1.919), C≡C 1.209 (1.231), CC 1.457 (1.428)                                                                                                     | <i>h</i> |
| (η <sup>5</sup> -Cp) <sub>2</sub> Be                                                | <i>D<sub>5d</sub></i> | BeC 2.071 (2.256, 1.907) CC 1.449 (1.425)                                                                                                                                     | <i>i</i> |
| η <sup>5</sup> -CpBeH <sub>2</sub> BH <sub>2</sub>                                  | <i>C<sub>s</sub></i>  | BH <sub>t</sub> 1.166 (1.170), BH <sub>b</sub> 1.271 (1.29) BeH <sub>b</sub> 1.611 (1.78), BeC 2.019 <sup>k</sup> (1.915),<br>CC 1.456 <sup>k</sup> (1.422), CH 1.084 (1.116) | <i>j</i> |
| η <sup>5</sup> -CpBeH <sub>3</sub> BH                                               | <i>C<sub>s</sub></i>  | BH <sub>t</sub> 1.159 (1.16), BH <sub>b</sub> 1.230 (1.28), BeH <sub>b</sub> 1.818, BeC 2.021 (1.915)<br>CC 1.455 (1.422), CH 1.084 (1.116)                                   | <i>j</i> |
| BeNH ( <sup>1</sup> Σ <sup>+</sup> )                                                | <i>C<sub>∞v</sub></i> | BeN 1.319, NH 0.971                                                                                                                                                           |          |
| BeNH ( <sup>3</sup> Π)                                                              | <i>C<sub>∞v</sub></i> | BeN 1.550, NH 0.972                                                                                                                                                           |          |
| Be(NH <sub>2</sub> ) <sub>2</sub>                                                   | <i>D<sub>2d</sub></i> | BeN 1.556, NH 0.991, BeNH 125.4                                                                                                                                               |          |
| BeO ( <sup>1</sup> Σ <sup>+</sup> )                                                 | <i>C<sub>∞v</sub></i> | BeO 1.335 (1.331)                                                                                                                                                             | <i>c</i> |
| BeO ( <sup>3</sup> Π)                                                               | <i>C<sub>∞v</sub></i> | BeO 1.570                                                                                                                                                                     |          |
| BeO ( <sup>3</sup> Σ <sup>+</sup> )                                                 | <i>C<sub>∞v</sub></i> | BeO 1.462                                                                                                                                                                     |          |
| Be <sub>2</sub> O <sub>2</sub>                                                      | <i>D<sub>2h</sub></i> | BeBe 1.968, BeO 1.606                                                                                                                                                         |          |
| HBeOH                                                                               | <i>C<sub>∞v</sub></i> | BeO 1.459, HO 0.918, HBe 1.271                                                                                                                                                |          |
| Be(OH) <sub>2</sub>                                                                 | <i>C<sub>2h</sub></i> | BeO 1.487, HO 0.920, BeOH 152.4                                                                                                                                               |          |
|  | <i>D<sub>3h</sub></i> | BeO 1.686, BeH 1.300, OH 0.942, BeBe 3.055                                                                                                                                    |          |
|  | <i>C<sub>2v</sub></i> | BeO 1.833, OC <sup>1</sup> 1.389, C <sup>1</sup> C <sup>2</sup> 1.363, C <sup>2</sup> C <sup>3</sup> 1.459, C <sup>3</sup> C <sup>4</sup> 1.360, C <sup>4</sup> Be 1.680      |          |
| BeF                                                                                 | <i>C<sub>∞v</sub></i> | BeF 1.458 (1.361)                                                                                                                                                             | <i>c</i> |
| BeF <sub>2</sub>                                                                    | <i>D<sub>∞h</sub></i> | BeF 1.459                                                                                                                                                                     |          |
| Be <sub>2</sub> F <sub>4</sub>                                                      | <i>D<sub>2h</sub></i> | BeF <sub>t</sub> 1.472, BeF <sub>b</sub> 1.656, BeBe 2.447                                                                                                                    |          |
| BeF <sub>4</sub> <sup>2-</sup>                                                      | <i>T<sub>d</sub></i>  | BeF 1.618                                                                                                                                                                     |          |
| FBeOH                                                                               | <i>C<sub>∞v</sub></i> | BeO 1.457, BeF 1.468                                                                                                                                                          |          |
| HBeOF                                                                               | <i>C<sub>s</sub></i>  | BeO 1.590, HBe 1.265, OF 1.266, BeOF 128.2, HBeO 172.9                                                                                                                        |          |
| FBeOF                                                                               | <i>C<sub>s</sub></i>  | BeO 1.607, FBe 1.452, OF 1.271, BeOF 120.9, FBeO 171.9                                                                                                                        |          |
| FBeOBeF                                                                             | <i>D<sub>∞h</sub></i> | BeF 1.466, BeO 1.489                                                                                                                                                          |          |

<sup>a</sup> Bond length *A<sup>i</sup>B<sup>j</sup>* (in angstroms) and bond angle *A<sup>i</sup>B<sup>j</sup>C<sup>k</sup>* (in degrees). <sup>b</sup>*a* and *c* are the unit cell dimensions; cf. K. J. H. Mackay and N. A. Hill, *J. Nucl. Mater.*, **8**, 263 (1963). <sup>c</sup>G. Herzberg, "Molecular Spectra and Molecular Structure. Infrared Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, Princeton, N.J., 1960. <sup>d</sup>G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973). <sup>e</sup>A. Almenningen, A. Haaland, and G. L. Morgan, *Acta Chem. Scand.*, **23**, 2921 (1969). <sup>f</sup>Calculated using the Gaussian 70 program with a 3G basis set: J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976). <sup>g</sup>Reference *f*, Table II. <sup>h</sup>A. Haaland and D. P. Novak, *Acta Chem. Scand.*, **28**, 153 (1974). <sup>i</sup>A. Almenningen, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434 (1964); A. Haaland, *Acta Chem. Scand.*, **22**, 3031 (1968). <sup>j</sup>D. A. Drew, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, **26**, 2147 (1972). <sup>k</sup>Average values.

**10****11**

workers<sup>24</sup> have suggested on the basis of vibrational studies that the molecule contains double beryllium boron hydrogen bridges. We do indeed calculate this form to be favored over the triply bridging form by 0.5 kcal/mol, although the difference is too small to be definitive.

The dicyclopentadienyl derivative **11** is probably the most enigmatic of this class. Almenningen et al.<sup>25</sup> deduced on the basis of electron diffraction studies a structure of *C<sub>5v</sub>* symmetry, with the two rings coplanar. The metal atom is displaced from the center by about 0.2 Å. It should be noted that the vibrational amplitudes are fairly large (0.1 Å for the beryllium atom) and that a strong correlation was found between one BeC distance and a nonbonding CH distance. The gas-phase structure is to be contrasted with the crystal structure,<sup>26</sup> where one ring can be described as pentahapto and the other perhaps monohapto, although the two rings remain coplanar.

The MNDO calculations give no evidence for a double minimum potential, the molecular having *D<sub>5d</sub>* symmetry, with

Table IV. Net Atomic Charges  $q_x$ 

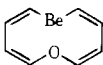
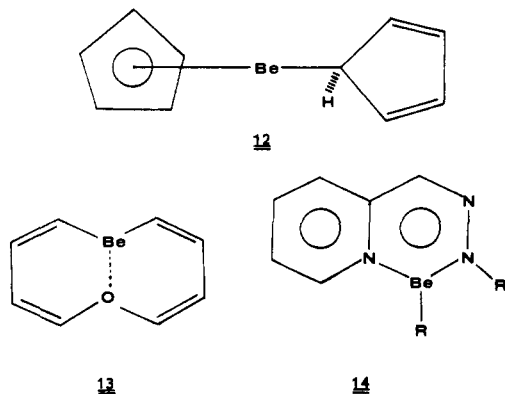
| Molecule                                                                          | Atom ( $q_x/ e $ )                                                                                               |
|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| BeH <sub>2</sub>                                                                  | H (-0.254)                                                                                                       |
| Be <sub>2</sub> H <sub>4</sub>                                                    | H <sub>t</sub> (-0.238) H <sub>b</sub> (-0.194) Be (0.432)                                                       |
| BeB <sub>2</sub> H <sub>8</sub> (D <sub>3d</sub> )                                | Be (0.662) B (-0.234) H <sub>t</sub> (0.030)<br>H <sub>b</sub> (-0.042)                                          |
| Me <sub>2</sub> Be                                                                | C (-0.217) Be (0.446) H (0.003)                                                                                  |
| CpBeH                                                                             | Be (0.251), C (-0.111), H (0.101)<br>H <sub>t</sub> (-0.200)                                                     |
| Cp <sub>2</sub> Be (D <sub>5d</sub> )                                             | Be (0.385) C (-0.129) H (0.090)                                                                                  |
| MeBeH <sub>3</sub> BH                                                             | Be (0.480) C (0.188) H <sub>c</sub> (0.003)<br>H <sub>b</sub> (-0.041) H <sub>t</sub> (0.022)                    |
| (MeBeH <sub>2</sub> BH <sub>2</sub> ) <sub>2</sub>                                | Be (0.469) C (-0.279) H <sub>c</sub> (0.076, 0.041)<br>B (-0.119) H <sub>b</sub> (0.072) H <sub>t</sub> (-0.043) |
| Be(NH <sub>2</sub> ) <sub>2</sub>                                                 | Be (0.445) N (-0.482) H (0.130)                                                                                  |
| HBeOH                                                                             | Be (0.451) O (-0.512) H <sub>o</sub> (0.245)<br>H <sub>Be</sub> (-0.184)                                         |
| HBeOF                                                                             | Be (0.655) O (-0.534) F (-0.374)<br>H (0.253)                                                                    |
| FBeOF                                                                             | Be (0.737) O (-0.320) F <sub>o</sub> (-0.069)<br>F <sub>Be</sub> (-0.348)                                        |
|  | Be (0.280) O (-0.125)                                                                                            |
| BeF <sub>2</sub>                                                                  | Be (0.6378)                                                                                                      |

Table V. Experimental and Calculated Vibrational Assignments for Triply Bridging Beryllium Borohydride (D<sub>3d</sub>)

| Description                                             | $\nu_{\text{obsd}},^a$<br>cm <sup>-1</sup> | $\nu_{\text{calcd}},^b$<br>cm <sup>-1</sup> |
|---------------------------------------------------------|--------------------------------------------|---------------------------------------------|
| A <sub>1g</sub> $\nu$ BH <sub>t</sub> sym               | 2643                                       | 2988                                        |
| $\nu$ BH <sub>b</sub> sym, in phase                     | 2255                                       | 2606                                        |
| $\delta$ BH <sub>b</sub> sym, in phase                  | 1150?                                      | 1228                                        |
| $\nu$ BBeB sym                                          | 540                                        | 583                                         |
| E <sub>g</sub> $\nu$ BH <sub>b</sub> asym, in phase     | 2238                                       | 2557                                        |
| $\delta$ BH <sub>t</sub> sym                            | 1284                                       | 1375                                        |
| $\delta$ BH <sub>b</sub> asym, in phase                 | 1184                                       | 1268                                        |
| Bridge bend, sym                                        | 388                                        | 373                                         |
| A <sub>1u</sub> Torsion                                 |                                            | 114                                         |
| A <sub>2u</sub> $\nu$ BH <sub>t</sub> asym              | 2645                                       | 2989                                        |
| $\nu$ BH <sub>b</sub> sym, out of phase                 | 2175                                       | 2610                                        |
| $\nu$ BBeB asym                                         | 1051                                       | 1026                                        |
| E <sub>u</sub> $\nu$ BH <sub>b</sub> asym, out of phase | 2202                                       | 2575                                        |
| $\delta$ BH <sub>t</sub> asym                           | 1298                                       | 1377                                        |
| $\delta$ BH <sub>b</sub> asym, out of phase             | 1245                                       | 1277                                        |
| Bridge bend, asym                                       | 368                                        | 394                                         |
| BBeB bend                                               | 285                                        | 212                                         |

<sup>a</sup> Reference 11. <sup>b</sup> Calculated for <sup>11</sup>B. See ref 14.

a rotational barrier of 0.2 kcal/mol. The calculated structure of **11** has a ring-to-ring distance of 3.33 Å, very similar to the electron diffraction result (3.37 Å),<sup>25</sup> and has the BeC distances equal at 2.07 Å, almost exactly the average of the two distances (2.256, 1.907) reported experimentally.<sup>25</sup> However, the  $\eta^1$ - $\eta^5$  species **12** is calculated to be 15.6 kcal/mol lower

Table VI. Calculated Vibrational Assignments for Doubly Bridging Beryllium Borohydride (D<sub>2d</sub>)

| Description                                                  | $\nu_{\text{obsd}},^a$<br>cm <sup>-1</sup> | $\nu_{\text{calcd}},^b$<br>cm <sup>-1</sup> |
|--------------------------------------------------------------|--------------------------------------------|---------------------------------------------|
| A <sub>1</sub> $\nu_1$ $\nu$ BH <sub>t</sub> sym             | 2500                                       | 2922                                        |
| $\nu_2$ $\nu$ BeH <sub>b</sub> sym                           |                                            | 2262                                        |
| $\nu_3$ $\nu$ BeH <sub>b</sub> + $\delta$ BH <sub>b</sub>    | 1615                                       | 1532                                        |
| $\nu_4$ $\delta$ BH <sub>t</sub> + $\nu$ BeH <sub>b</sub>    |                                            | 1237                                        |
| $\nu_5$ $\nu$ BBeB sym                                       | 588                                        | 494                                         |
| A <sub>2</sub> $\nu_6$ Torsion                               |                                            | 1234                                        |
| B <sub>1</sub> $\nu_7$ Torsion                               |                                            | 1249                                        |
| $\nu_8$ Torsion                                              |                                            | 344                                         |
| B <sub>2</sub> $\nu_9$ $\nu$ BH <sub>t</sub> asym            |                                            | 2922                                        |
| $\nu_{10}$ $\nu$ BeH <sub>b</sub> asym                       | 2071                                       | 2283                                        |
| $\nu_{11}$ $\nu$ BeH <sub>b</sub> + $\delta$ BH <sub>b</sub> | 1548                                       | 1564                                        |
| $\nu_{12}$ $\delta$ BH <sub>t</sub>                          |                                            | 1225                                        |
| $\nu_{13}$ $\nu$ BBeB asym                                   | 1000                                       | 893                                         |
| E $\nu_{14}$ $\nu$ BH <sub>t</sub> asym                      | 2550                                       | 2977                                        |
| $\nu_{15}$ $\nu$ BH <sub>b</sub>                             | 2000                                       | 2189                                        |
| $\nu_{16}$ $\nu$ BH <sub>b</sub> + $\delta$ BH <sub>t</sub>  | 1650                                       | 1595                                        |
| $\nu_{17}$ $\delta$ BeH <sub>2</sub>                         |                                            | 1201                                        |
| $\nu_{18}$ $\delta$ BH <sub>2</sub>                          |                                            | 873                                         |
| $\nu_{19}$ BBeB bend                                         |                                            | 370                                         |
| $\nu_{20}$ Bridge bend                                       |                                            | 112                                         |

<sup>a</sup> Assignments based on the data given by Nibler in ref. 11. <sup>b</sup> Calculated for the form of D<sub>2d</sub> symmetry.

than **11** in energy and has a calculated dipole moment (2.5 D) similar to that found in solution<sup>27</sup> (2.46 or 2.24 D). This structure could not be made to fit the reported electron diffraction evidence, but is in close agreement with the crystal structure. A third isomer, containing only  $\eta^1$  rings, is higher in energy than **12** but slightly lower than **11**. This again suggests that the MNDO energies for face-bridging species are too positive. The reported infrared results of McVicker and Morgan,<sup>28</sup> while suggesting D<sub>5h</sub> symmetry for both C<sub>5</sub>H<sub>5</sub> rings, cast no light on the position of the beryllium atom because the BeC stretches were not observed.

The bonding in **11** is of some interest. The first five orbitals are shown in Figure 2. The degenerate HOMO does not involve any metal orbitals. The next three orbitals arise from interaction of the beryllium 2p<sub>x,y,z</sub> orbitals with two e<sub>1u</sub> and one a<sub>2u</sub> orbitals from the cyclopentadienyl rings. Finally, the beryllium 2s orbital interacts with an a<sub>1g</sub> orbital from the carbon rings.

After this paper was submitted for publication, Marynick<sup>29</sup> reported PRDDO calculations for dicyclopentadienylberyllium. He also concluded that the  $\eta^1$ - $\eta^5$  isomer (**12**) is the most stable and that the  $\eta^5$ - $\eta^5$  isomer (**11**) has D<sub>5d</sub> symmetry with a very low barrier (<0.4 kcal/mol) to rotation. His results differ from ours in predicting a smaller difference in energy between **11** and **12** (6.4 kcal/mol) and a larger difference between **12** and the  $\eta^1$ - $\eta^1$  isomer (44.6 kcal/mol). It should, however, be noted that Marynick made numerous assumptions concerning the geometry of **12** and did not optimize the geometry of the  $\eta^1$ - $\eta^1$  isomer at all. The energies calculated for these isomers, relative to **11**, are therefore likely to be too positive, the error being greater for the  $\eta^1$ - $\eta^1$  isomer.

**6. Compounds Containing Beryllium and Nitrogen, Oxygen, or Fluorine.** BeO is isoelectronic with C<sub>2</sub> and the multiplicity of the ground state is therefore interesting. No triplet states have been detected experimentally, although single-configuration RHF treatments predict the ground state to be <sup>3</sup>Π.<sup>30</sup> Schaefer and co-workers<sup>30</sup> have carried out several calculations on the electronic states of this molecule, with inclusion of extensive CI. They find the ordering and relative energies to be <sup>1</sup>Σ<sup>+</sup> (0), <sup>3</sup>Π (0.73 eV), <sup>3</sup>Σ<sup>+</sup> (1.93 eV), and <sup>3</sup>Σ<sup>-</sup> (repulsive). Configuration interaction should not be necessary in the MNDO method, since allowance for electron correlation is

implicit in the parameters. This is demonstrated by the calculated energies of the electronic states obtained by the half-electron method:  $^1\Sigma^+$  (0),  $^3\Pi$  (0.71 eV),  $^3\Sigma^+$  (1.62 eV),  $^3\Sigma^-$  (2.80 eV). The latter state is not unbound, as Schaefer and co-workers find, but the equilibrium bond length is rather long (1.12 Å).

In the similar molecule BeNH, we calculate the separation between the  $^1\Sigma^+$  ground state and the  $^3\Pi$  triplet state to be 0.24 eV. The geometries of these species are interesting. The singlet, and also the lowest triplet, are linear. In the former, the HOMO is a degenerate  $\pi$  orbital utilizing the  $2p_x$  and  $2p_y$  orbitals of the nitrogen and beryllium. The HOMO-2 in the singlet, of  $\Sigma^+$  symmetry, consists of a combination of an essentially sp-hybridized beryllium orbital and a  $2p_z$  orbital from nitrogen. In the fluorine analogue, BeNF, which is also linear in the ground state, the top four orbitals are of  $\pi$  symmetry, with considerable overlap from the fluorine lone pairs.

BeO and BeN<sub>2</sub> are isoelectronic with C<sub>2</sub> and C<sub>3</sub>, respectively. This analogy leads to a number of interesting substitutions. For example, the amine Be(NH<sub>2</sub>)<sub>2</sub> is calculated to have the orthogonal allene structure, with a barrier to rotation of 4 kcal/mol. The HOMO is a degenerate e type, localized mainly on the nitrogen 2p orbitals.

The acetylene analogue HBeOH is linear, with a HOMO of  $\pi$  symmetry localized extensively on the oxygen. Replacement of the hydrogen adjacent to beryllium by fluorine enhances the acceptor properties of the metal 2p orbitals and so leads to retention of the linear structure (FBeOH). Replacement of the hydroxylic hydrogen by fluorine leads, however, to a bent species (Table III) and an increase in the BeO bond length of 0.14 Å, due presumably to a reduction in the donor properties of oxygen. FBeOF is likewise bent, with a very similar BeO bond length. In both HBeOF and FBeOF the HOMOs are of  $a''$  symmetry, corresponding to the  $\pi$  orbitals in a substituted ethylene. Only the trans isomers are stable. The opposite effect is noticed in HO-BeOH, where the electronic effect of the OH substituent results in a bent molecule, although with a surprisingly large BeOH angle of 151°.

In the ethylene analogue, H<sub>2</sub>BeOH<sub>2</sub>, a BeO bond length of 1.78 Å is calculated, with a rotational barrier of 4.0 kcal/mol. The HOMO is essentially BeH bonding, with a  $p_\pi$  orbital next, localized mainly on the oxygen atom.

The naphthalene analogue **13** is intriguing, in view of the reported preparation of the species **14**.<sup>20</sup> The calculated structure of 9,10-berylloxaronaphthalene (Table III) shows a long central bond (1.83 Å) which is slightly longer than that in H<sub>2</sub>BeOH<sub>2</sub>. The five  $\pi$  orbitals show some interesting similarities to naphthalene itself,<sup>3</sup> the two with no density on the central 9,10 atoms being virtually identical in energy (8.56/8.90 and 11.46/11.55 eV). The HOMO has appreciable (~13%) density on the beryllium, and is bonding in the Be-O region, in contrast to naphthalene itself. It should be noted however that there is no  $\sigma$  orbital which is appreciably bonding in the Be-O region, suggesting that the molecule may be homoaromatic.

## Conclusions

We have reported MNDO calculations for beryllium, an element whose gas-phase chemistry has been little studied. The results are in agreement with the available evidence and suggest that MNDO, in conjunction with vibrational spectroscopy, provides a powerful tool for determining structures.

The success of these studies suggests that extension of MNDO to other metallic elements should be profitable, and we have indeed already obtained some preliminary results for aluminum. We are also studying the inclusion of d AOs in MNDO so that it can be extended to transition metals. Such an extension could provide information of major value in or-

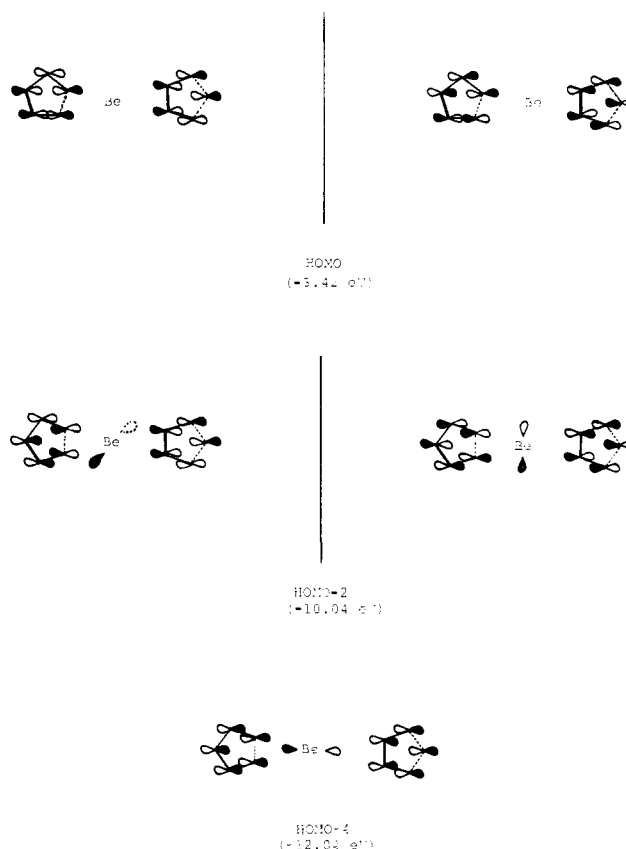


Figure 2. Nodal properties of the highest molecular orbitals in dicyclopentadienylberyllium.

ganometallic chemistry, in particular in the study of catalytic processes.

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**Supplementary Material Available:** Optimized Cartesian coordinates for compounds containing beryllium (14 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) Part 38: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977); M. J. S. Dewar and W. Thiel, *Theor. Chim. Acta*, to be published.
- (2) Part 39: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977).
- (3) Part 40: M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 58 (1978).
- (4) Part 41: M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.*, **99**, 5231 (1977).
- (5) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
- (6) (a) C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.*, **62**, 4815 (1975); (b) R. B. Brewington, C. F. Bender, and H. F. Schaefer, *ibid.*, **64**, 905 (1976). (c) C. E. Dykstra, H. F. Schaefer, and W. Meyer, *ibid.*, **65**, 5141 (1976).
- (7) (a) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and L. Radom, *J. Am. Chem. Soc.*, **98**, 3436 (1976); (b) M. Jungen and R. Ahlrichs, *Mol. Phys.*, **28**, 367 (1974).
- (8) R. Ahlrichs, *Theor. Chim. Acta*, **17**, 348 (1970).
- (9) Experimental investigations: (a) G. Silbiger and S. H. Bauer, *J. Am. Chem. Soc.*, **68**, 312 (1946); (b) S. H. Bauer, *ibid.*, **72**, 622 (1950); (c) A. Almenningen, G. Gundersen, and A. Haaland, *Chem. Commun.*, 557 (1967); (d) A. Almenningen, G. Gundersen, and A. Haaland, *Acta. Chem. Scand.*, **22**, 859 (1968); (e) T. H. Cook and G. L. Morgan, *J. Am. Chem. Soc.*, **91**, 774 (1969); (f) J. W. Nibler and J. McNabb, *Chem. Commun.*, 134 (1969); (g) J. W. Nibler and T. Dyke, *J. Am. Chem. Soc.*, **92**, 2920 (1970); (h) T. H. Cook and G. L. Morgan, *ibid.*, **92**, 6493 (1970); (i) G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **59**, 3777 (1973); (j) K. Brendhaugen, A. Haa-

- land, and D. P. Novak, *Acta Chem. Scand., Ser. A*, **29**, 801 (1975).
- (10) Theoretical investigations: (a) G. Gundersen and A. Haaland, *Acta Chem. Scand.*, **22**, 867 (1968); (b) D. R. Armstrong and P. G. Perkins, *Chem. Commun.*, 352 (1968); (c) R. Alhrichs, *Chem. Phys. Lett.*, **19**, 174 (1973); (d) D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, **95**, 7244 (1973); (e) D. S. Marynick, *J. Chem. Phys.*, **64**, 3080 (1976).
- (11) J. W. Nibler, *J. Am. Chem. Soc.*, **94**, 3349 (1972).
- (12) L. J. Allamandola and J. W. Nibler, *J. Am. Chem. Soc.*, **98**, 2096 (1976).
- (13) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972); *Chem. Phys. Lett.*, **10**, 303 (1971).
- (14) The Cartesian Hessian matrix was obtained from the analytically evaluated Jacobian,<sup>15</sup> using a finite difference method for the second derivatives. Vibrational frequencies were obtained by application of the usual Wilson FG formalism.<sup>13</sup>
- (15) M. J. S. Dewar and Y. Yamaguchi, to be published. These routines were incorporated into our standard force constant program by M. McKee.
- (16) M. L. McKee, Ph.D. Dissertation, University of Texas at Austin, 1977.
- (17) (a) For a general review see A. Haaland, *Top. Curr. Chem.*, **53**, 1 (1975); (b) A. Almenningen, A. Haaland, and G. L. Morgan, *Acta Chem. Scand.*, **23**, 2921 (1969).
- (18) R. A. Kovar and G. L. Morgan, *Inorg. Chem.*, **8**, 1099 (1969).
- (19) D. B. Chambers, G. E. Coates, and F. Glockling, *J. Chem. Soc. A*, 741 (1970).
- (20) G. E. Coates and G. L. Morgan, *Adv. Organomet. Chem.*, **9**, 195 (1970).
- (21) J. B. Collins, J. D. Dill, E. D. Jemmis, T. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976).
- (22) T. Bartke, A. Bjørseth, A. Haaland, K. M. Marstokk, and H. Møllendal, *J. Organomet. Chem.*, **85**, 271 (1975).
- (23) D. A. Drew and A. Haaland, *Acta Chem. Scand.*, **26**, 3074 (1972).
- (24) D. A. Coe, J. W. Nibler, T. H. Cook, D. Drew, and G. L. Morgan, *J. Chem. Phys.*, **63**, 4842 (1975).
- (25) A. Almenningen, O. Bastiansen, and A. Haaland, *J. Chem. Phys.*, **40**, 3434 (1964); A. Haaland, *Acta Chem. Scand.*, **22**, 3030 (1968); D. A. Drew and A. Haaland, *Acta Crystallogr. Sect. B*, **28**, 3671 (1972).
- (26) C.-H. Wong, T.-Y. Lee, K.-J. Chao, and S. Lee, *Acta Crystallogr., Sect. B*, **28**, 1662 (1972).
- (27) E. O. Fischer and S. Scheiner, *Chem. Ber.*, **92**, 938 (1959).
- (28) G. B. McVicker and G. L. Morgan, *Spectrochim. Acta, Part A*, **26**, 23 (1970).
- (29) D. S. Marynick, *J. Am. Chem. Soc.*, **99**, 1436 (1977).
- (30) S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, *Chem. Phys. Lett.*, **10**, 404 (1971); P. K. Pearson, S. V. O'Neil, and H. F. Schaefer, *J. Chem. Phys.*, **56**, 3938 (1972), and references cited therein.

## Calculations of Electron Affinities Using the MNDO Semiempirical SCF-MO Method

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**Abstract:** MNDO calculations are reported for the energies and geometries of 65 atoms and molecules and their negative ions. The calculated electron affinities of six atoms were too negative by an average of 1.50 eV, and a similar average error of 1.40 eV was found for ten molecules in which the highest occupied molecular orbital (HOMO) of the negative ion is highly localized on one atom. The mean error in the calculated electron affinities of 26 molecules in which the HOMO is delocalized was 0.43 eV. Koopmans' theorem gave reliable estimates for the vertical ionization potential of these molecules. The most stable isomer of NO<sub>3</sub> was calculated to be peroxy nitrite radical, and not nitrate radical, which was calculated to be 1.6 eV higher in energy. This suggests that the previously reported value for the electron affinity of NO<sub>3</sub> may be too low.

Studies of the properties of negative ions have blossomed in the last decade as a result of the introduction of a variety of new instrumental techniques.<sup>1</sup> As a consequence of this renaissance, accurate and reliable values of electron affinities for numerous and widely different molecules are now available. This property, defined as the difference in energy between the lowest rotational-vibrational state of a negative ion and the lowest rotational-vibrational state of the neutral molecule, has been the subject of considerable recent interest.<sup>2</sup> The work of Kebarle and co-workers<sup>3</sup> has shown that knowledge of the electron affinity of a molecule can yield useful thermochemical information about gas-phase ion-molecule reactions. A very wide and related field is the generation of negative ions of organic molecules and their study by negative ion mass spectrometry.<sup>4</sup> A reliable and fast computational method for obtaining electron affinities would obviously be of great aid in such connections.

Current theoretical studies of negative ions have mostly been based on the Hartree-Fock method. Cade<sup>5</sup> was one of the first to show that such calculations cannot lead to reliable estimates of electron affinities. His calculated electron affinity for hydroxyl radical, for example, was -0.1 eV, compared with the experimental value of 1.83 eV.<sup>5</sup> These discrepancies, which can often amount to 2-4 eV, are apparently due to large differences in electron correlation energy between the anions and corresponding radicals.

Cade also demonstrated that the application of Koopmans' theorem could lead to errors in the opposite direction. In the

case of hydroxyl radical, for example, he obtained a value of +2.9 eV from the calculated energy of the highest occupied molecular orbital (HOMO) of OH<sup>-</sup>. This failure of Koopmans' approximation has been noted frequently,<sup>2</sup> both for *ab initio* and  $\pi$  SCF methods.<sup>6</sup> It has been suggested that in the case of the *ab initio* methods, this failure may be partly due to the inadequacy of the basis sets used.<sup>7</sup>

While many significant advances have been made in recent years toward the calculation of electron affinities by *ab initio* methods,<sup>2,8-10</sup> the large amount of computer time required for the calculations limits them to relatively small systems, even if assumed geometries are used. Since the geometries both of the anion and of the neutral species must be *completely* optimized if adiabatic electron affinities are to be reliably calculated, it seems clear that the only hope of obtaining results of practical value for molecules large enough to be of real chemical interest (cf. ref 4) lies in the use of semiempirical procedures.

Recent work here has led to the development of a semiempirical SCF MO procedure (MNDO<sup>11</sup>) which seemed likely to prove especially effective in this connection. The average error in the heats of formation calculated by it for 254 molecules of many different kinds was only 8.7 kcal/mol and the results for a number of positive ions were of similar accuracy.<sup>11a,b</sup> Since the parameters in MNDO were determined<sup>11</sup> by fitting data only for neutral molecules, there seemed good reason to believe that it would be equally successful in the case of negative ions and we therefore decided to test its potential