propyl cation.[14] Furthermore, the positive charge is more evently distributed to all five carbons in nonplanar **3** than in planar **1** and **2**; this may account for the stability of **3**.

We conclude from these calculations that there should be two minima on the $(CH)_5^+$ energy hyperplane, with a significant barrier between them. One is pyramidal C_{4v} structure **6** of Stohrer and Hoffmann;[1] alternatives for the second are **1**, **2**, or **3**. Neither **4** nor **5** should be stable species. As expected from its antiaromatic character, the singlet cyclopentadienyl cation does not possess D_{5h} symmetry.[15]

Acknowledgment. This work was supported at Princeton by grants from the National Science Foundation and Hoffmann-La Roche, Nutley, N. J.

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[14] This is akin to the "half-opened" cyclopropyl cation suggested by U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Lett.*, 3639 (1967).

[15] These qualitative conclusions agree with those derived from the accompanying MINDO/3 (M. J. S. Dewar and R. C. Haddon, *J. Amer. Chem. Soc.*, **95**, 5836 (1973)) and *ab initio* (W. J. Hehre and P. v. R. Schleyer, *ibid.*, **95**, 5837 (1973)) calculations. The three theoretical methods give different *quantitative* results, however. In particular, **6** is found to be less stable than **1–3** in the other studies.

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MINDO/3 Study of $(CH)_5^+$ and $(CH)_5^-$

Sir:

The polymethines, $(CH)_n$, are a group of compounds formed by arbitrary linkage of CH units. It is an interesting problem to determine the stable species for each value of *n*. Here we report calculations for $(CH)_5^+$ and $(CH)_5^-$, using an improved version (MINDO/3[1]) of the MINDO method.[2,3] MINDO/3 avoids most of the systematic errors of MINDO/2.[3] In particular it is the first semiempirical treatment to give satisfactory heats of formation for hydrocarbons containing small rings.

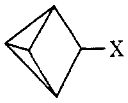
Various structures might exist as stable species in the $(CH)_5^+$ system, *i.e.*, **1–6**, the bishomoallylic ion **8**, the triplet form (**9**) of **4**, and the bicyclopentenyl cation **10**. The most interesting of these is the "nonclassical" ion **3** which, as Stohrer and Hoffmann[4] have pointed out, is essentially isoelectronic with pentaborane.[5] Since pentaborane is the only known stable B_5H_9 species, it is interesting to see if **3** will likewise be the only stable form of $(CH)_5^+$. Stohrer and Hoffmann[4] indeed concluded that this should be the case on the basis of EH calculations.

Since the application of MINDO to triplet states involves the use of the "half-electron" approximation[6] and since this modification of MINDO/3 has yet to be thoroughly tested, we confined our calculations to **1–8**, and **10** using our SIMPLEX[7] procedure for the optimization of geometries. We found only two true minima on the $(CH)_5^+$ potential surface, *i.e.*, **3** and a distorted form (**7**) of **6**. The rearrangements of **1** to **2**, of **2** to **3**, of **8** to **3**, and of **10** to **7** are predicted to take place without activation while the symmetrical planar cation **4** should not only undergo Jahn–Teller distortion (to **5** or **6**) but also a deformation from coplanarity (to **7**), again without activation. Figure 1 shows the calculated geometries and energies of **1–7**, those of the unstable species **1**, **2**, **4**, **5**, and **6** being found by imposing suitable symmetry restraints to stop them rearranging. No unique solution can be found in this way for **10** since its geometry cannot be defined in terms of a symmetry restraint.

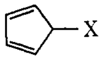
8

10

11



12



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14

15

According to our calculations, the most stable $(CH)_5^+$ species is **7** rather than **3**. This is a distorted form of the antiaromatic cyclopentadienate cation **4**,[8–10] the distortions being such as to reduce the unfavorable cyclic conjugation by leading to a semilocalized structure with weakly interacting C=C and C=C=C$^+$ units.

The calculated geometries of the various species present some interesting features. In **3**, the CH bonds in the C_4H_4 unit bend upward, toward the apical CH, just as they do in pentaborane.[11] This can be represented in terms of a simple orbital picture in which the basal C_4H_4 unit consists of sp^2 hybridized carbon atoms, their fourth (2p) AO's being used to bond the apical CH group. The calculated geometry corresponds to a tilting of the basal carbon atoms so that their 2p AO's lean inward and so overlap more effectively with the AO's of the apical carbon.

We have also studied the conversion of **3** to **7** *via* **10**, using the angle between the C_4 and C_3 planes (θ in **11**) as a reaction coordinate. For each value of θ the energy was minimized with respect to all the other geometrical variables. Some complications arose due to "flipping" of the apical hydrogen near the transition

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[1] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

[2] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); N. C. Baird, M. J. S. Dewar, and R. Sustmann, *ibid.*, **50**, 1275 (1969); N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969).

[3] M. J. S. Dewar and E. Haselbach, *ibid.*, **92**, 590 (1970); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970).

[4] W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

[5] If the proton in each three-center B–H–B bond in the B_5H_9 unit of pentaborane is absorbed into one of the B nuclei, converting it to C, and if the apical boron is replaced by the isoelectronic ion C$^+$ the result is **3**.

[6] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).

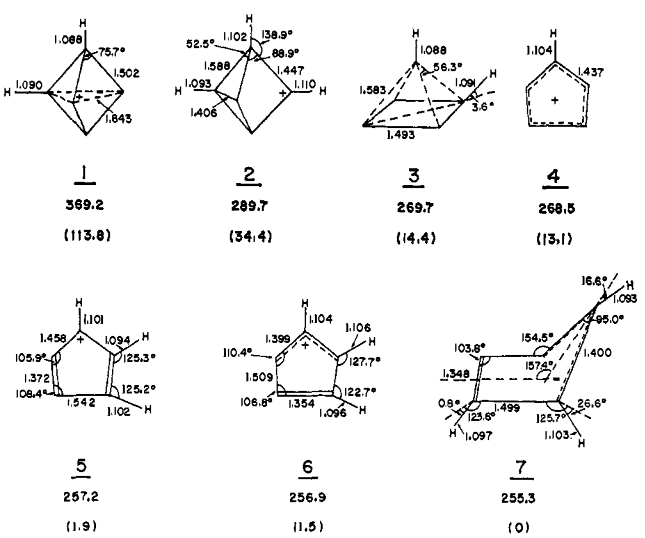
[7] A. Brown, M. J. S. Dewar, and W. Schoeller, *J. Amer. Chem. Soc.*, **92**, 5516 (1970); A. Brown, M. J. S. Dewar, H. Metiu, P. J. Student, and J. Wasson, in course of publication.

[8] The antiaromaticity of **4** follows directly[9] from PMO theory and has recently been demonstrated experimentally.[10]

[9] M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

[10] R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972).

[11] W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954).



1 369.2 (113.8)

2 289.7 (34.4)

3 269.7 (14.4)

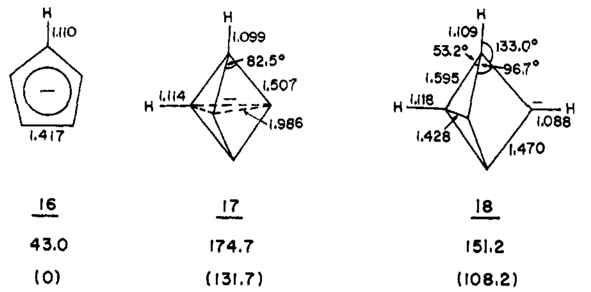
4 268.5 (13.1)

5 257.2 (1.9)

6 256.9 (1.5)

7 255.3 (0)

Figure 1. Geometries (bond lengths in Å), heats of formation (kcal/mol), and (in parentheses) relative energies (kcal/mol) of $(CH)_5^+$ isomers.



16 43.0 (0)

17 174.7 (131.7)

18 151.2 (108.2)

Figure 2. Geometries (bond lengths in Å), heats of formation (kcal/mol), and (in parentheses) relative energies (kcal/mol) of $(CH)_5^-$ isomers.

state, *i.e.*, a change in the angle ϕ (in **11**) from $<180°$ (in **3** and **7**) to $>180°$ in the vicinity of $\theta = 95°$. Our final estimate of the activation energy was 43 kcal/mol.

This high value suggests that **3**, once formed, should be quite a stable species. Since we predict **2** to rearrange spontaneously to **3**, **3** should be formed by solvolysis of compounds of the type **12**, but not **13**. Stohrer and Hoffmann[4] also predicted the rearrangement of **2**. However, we differ from them in predicting **7** to be not only stable but more stable than **3**. The available experimental evidence seems to be consistent with these predictions. Thus reaction of 5-iodocyclopentadiene with silver ion led[10] to products derived from **4** or some equivalent structure (*i.e.*, **5**, **6**, or **7**) while solvolysis of a dimethyl derivative of **12** in $SO_2FCl-FSO_3H$ gave a cation whose nmr spectrum suggested that it was a dimethyl derivative of **3**.[12]

MINDO/3 calculations on protonated **14** and **15** (X = F), in which the fluorine leaves as HF, lead to the prediction that the solvolysis of **14** should give rise to **3**, whereas the solvolysis of **15** should lead to **7**. This is consistent with the observations of Schleyer and coworkers[13] on the reactions of analogous saturated systems. In the exo series, corresponding to **14**, concerted ring opening is forbidden. In the case of **14**, however, an alternative (concerted) process is available involving the double bond and is expected to lead to the formation of **3**.

We have also carried out similar calculations for $(CH)_5^-$ (Figure 2). Here, as one would expect, the most stable species by far is the planar aromatic anion **16**. The only other stable species seems to be the analog (**18**) of **2**. In this case the C_{4v} structure **19**, analogous to **3**, is unstable because it contains two electrons in an antibonding MO.

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[12] S. Masamune, M. Sakai, and H. Ona, *J. Amer. Chem. Soc.*, **94**, 8955 (1972); S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972). See also H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

[13] P. R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

Cyclopentadienyl and Related $(CH)_5^+$ Cations

Sir:

The D_{5h} cyclopentadienyl cation (I) is antiaromatic[1] and should possess a triplet ground state. This is apparently true for the parent[2] and certain derivatives[3] but considerable evidence points to the existence of ground singlet states of highly substituted cyclopentadienyl cations.[3b,4,5] A theoretical study by Stohrer and Hoffmann[6] indicates that the singlet surface of $(CH)_5^+$ contains another minimum, of C_{4v} symmetry resembling cyclobutadiene complexed to CH^+ (IV).

The possibility of square pyramidal $(CH)_5^+$ has received experimental support.[7] Masamune and his coworkers[7a] recently recorded the proton and ^{13}C nmr spectra of what they believe is dimethyl (apical base) IV.

Semiempirical molecular orbital calculations[8] have not only provided evidence for IV but also indicate the existence of another (cyclopentadienyl type) singlet minimum. The two theoretical methods (CNDO[8a] and MINDO[8b]) disagree, however, as to which form is of lower energy.

Using *ab initio* molecular orbital theory[9] the lowest minimum on the singlet potential corresponds to planar

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[1] The singlet is a Jahn-Teller molecule and must distort to a lower symmetry.

[2] M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *J. Amer. Chem. Soc.*, **95**, 3017 (1973); (b) R. Breslow, and J. M. Hoffman, Jr., *ibid.*, **94**, 2110 (1972).

[3] (a) R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964); (b) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967).

[4] R. Breslow, H. W. Chang, and W. A. Yager, *ibid.*, **85**, 2033 (1963).

[5] R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

[6] W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 1661 (1972).

[7] (a) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972); (b) H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972).

[8] (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *ibid.*, **95**, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, **95**, 5836 (1973).

[9] The STO-3G basis[10] is used to locate energy minima; single 4-31G[11] calculations are then performed.

[10] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[11] R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, **54**, 724 (1971).