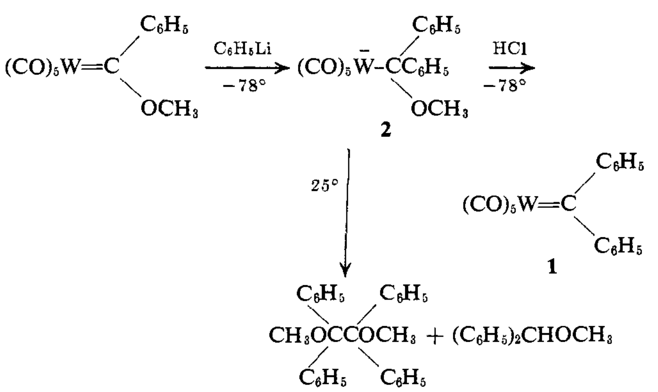
of the preparation of diphenylcarbene complexes since we felt that these complexes would be less stable and potentially more reactive in methylene transfer reactions than heteroatom substituted carbene complexes. Here we report the synthesis, isolation, and surprising thermal stability of (diphenylcarbene)pentacarbonyltungsten(0) (**1**).

The reaction of phenyllithium with a phenylmethoxycarbene complex provides a straightforward route to a diphenylcarbene complex. Fischer and Riedmuller[9] have reported that reaction of phenyllithium with (phenylmethoxycarbene)pentacarbonylchromium(0) in ether at 0° gives 1,2-dimethoxy-1,1,2,2-tetraphenylethane in addition to other products. Similarly we have found that addition of phenyllithium to a red solution of (phenylmethoxycarbene)pentacarbonyltungsten(0) in ether at −78° produces a homogeneous brown solution which, on warming to room temperature, undergoes decomposition to give 1,2-dimethoxy-1,1,2,2-tetraphenylethane (19%) and benzhydryl methyl ether (20%). The formation of these products can be rationalized in terms of the decomposition of the tetrahedral adduct **2**.



To convert the presumed adduct **2** to the diphenylcarbene complex **1**, 1 equiv of HCl in ether was added to the brown solution of **2** at −78°. An immediate dramatic color change to dark red indicated that a reaction had occurred. Column chromatography (silica gel–pentane) followed by recrystallization of a fast moving band from pentane at −78° gave a 50% yield of (diphenylcarbene)pentacarbonyltungsten(0) (**1**) as a black solid, mp 65–66°. The structure of **1** was assigned on the basis of spectral data: ir (heptane) 2077 (s), 1965 (sh), 1959 (s) cm^{-1}; nmr (CS_2) δ 7.10, multiplet; uv (hexane) 232 mμ (46,500), 485 (10,400). A small parent ion was observed at *m/e* 490 in the mass spectrum; the exact mass of the larger M–CO peak was observed at *m/e* 462.0058, in good agreement with *m/e* of 462.0088 expected for $C_{17}H_{10}O_4W$.

Anal. Calcd for $C_{18}H_{10}O_5W$: C, 44.11; H, 2.05; W, 37.51. Found: C, 43.94; H, 2.11; W, 37.69.

The diphenylcarbene complex **1** was further characterized by chemical reactions. Ceric ammonium nitrate, a reagent known to convert metal–carbene complexes to the corresponding carbonyl compounds,[10] reacted with **1** in ether at room temperature to give benzophenone (58%). Methylenetriphenylphosphorane, a reagent which reacts with metal–carbene complexes to produce the corresponding methylene compound,[10] reacted with **1** in ether at room temperature to give 1,1-diphenylethylene in high yield.

The diphenylcarbene complex **1** is more thermally labile than (phenylmethoxycarbene)pentacarbonyltungsten. Thermal decomposition of **1** in heptane was complete in less than 2 hours at 100° and gave $W(CO)_6$ (19%), tetraphenylethylene (35%), and diphenylmethane (10%). Decomposition of **1** in cyclohexene gave increased amounts of diphenylmethane (30%) and decreased amounts of tetraphenylethylene (13%); no 1,1-diphenylnorcarane was detected under these conditions.

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Received May 19, 1973

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[9] E. O. Fischer and S. Riedmuller, unpublished results quoted by E. O. Fischer, *Pure Appl. Chem.*, 30, 353 (1972).

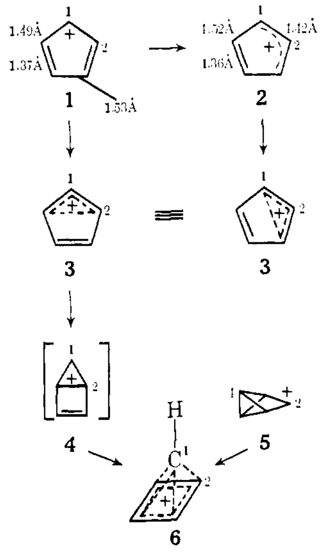
[10] C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **94**, 6543 (1972).

CNDO Calculations on Isomeric $(CH)_5^+$ Cations

Sir:

Stohrer and Hoffmann[1] have posed the intriguing possibility that the most stable structure for the $(CH)_5^+$ cation is not any of the conventional forms, **1–5**, but rather may be a square pyramid, **6**. Furthermore, it was suggested that **6** might be "the unique stable structure in this system," *i.e.*, **1–5** might rearrange without activation to **6** (Scheme I).[1] Experimental interest has quickened,[2-4] but definitive answers are not

Scheme I



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

[2] Reviews: R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970); R. Leone, J. C. Barborak, and P. v. R. Schleyer in "Carbonium Ions," Vol. 4, G. Olah and P. v. R. Schleyer, Wiley-Interscience, New York, N. Y., 1973, Chapter 33, p 1837 ff.

[3] R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972); 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, *ibid.*, **95**, 3017 (1973).

[4] S. Masamune, M. Sakai, and H. Ona, *ibid.*, **94**, 8955 (1972);

yet available. We have investigated these problems in greater depth theoretically, employing a modified[5] CNDO[6] method with full geometry search. Corrections have been applied to the results to minimize inherent errors.

Table I. Calculated Energies of $(CH)_5^+$ Cations (values in kcal/mol)

Cation	Symmetry restriction	Relative energy	Model	Deviation from exp[a]	Corr rel energy
1	C_{2v}	54	**7**	−10	10
2	C_{2v}	54	**7**	−10	10
3	C_s	45	**7** or **8**	Av 3 ± 13	14 ± 13
4	*b*	62	**8**	16	44
5	C_{2v}	27	**9**	37	30
6	C_{4v}	0	**10** + **11**	13 + 21	0

[a] Calculated minus experimental heats of atomization. The experimental values are gained from heats of formation (D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969) and were corrected for zero point energies as in S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [b] **4** is a transition state; the geometry was fully minimized with the exception of the reaction coordinate.


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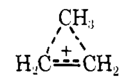

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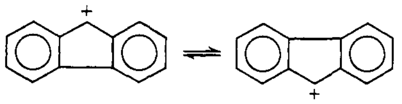
According to our uncorrected calculations (Table I, column 3), pyramidal $(CH)_5^+$ (**6**) is indeed far more stable than any of the alternatives, **1**–**5**. However, **5** is not an energy minimum and rearrangement to **6** proceeds without activation.[4] The planar cyclopentadienyl cations, **1** and **2**, are also not minima but distort to nonplanar **3**. This species, with a long (1.86 Å) C_2–C_5 bond, is found to be an energy minimum lying 45 kcal/mol above **6**. Even though the direct conversion of **1** to **3** is symmetry forbidden, the activation energy is calculated to be quite low, about 19 kcal/mol, owing to the low-lying triplet state in **1**.[7]



If the plane of symmetry common to **1** and **3** is not maintained, a route *via* **2** is possible allowing the formation of **3** without activation. This is the route proposed by Stohrer and Hoffmann.[1] When **3**, already nonplanar, is folded still more, the energy rises. The energy maximum (17 kcal/mol above **3**) corresponds to **4**, approximately the 5-bicyclo[2.1.0]pentenyl cation. The pyramidal structure **6** is achieved from **4** without additional activation energy.

Unfortunately, the reparameterized CNDO method employed here does not give reliable energies for small ring systems.[5] Thus, the relative energies listed in the third column of Table I cannot be taken literally. Since the CNDO errors for hydrocarbons related to **1**–**6** can be obtained, it is possible to correct the CNDO relative energies to provide more realistic but still approximate comparisons.

As the structure of **3** is intermediate between **1** and **4**, the correction energy average between **7** and **8** was employed as a rough estimate. The best model for **5** would be tricyclo[2.1.0.0^{2,5}]pentane, but no experimental data are available; bicyclobutane (**9**) was used instead. **6** is the most difficult to approximate. Cyclobutene (10 kcal/mol) and cyclobutane (7 kcal/mol)[5] have similar reparameterized CNDO errors; an extrapolated value (13 kcal/mol) can be taken for the cyclobutadienoid portion of **6**. The bridging CH^+ in **6** utilizes the same orbitals as does the CH^+ in C_{4v} CH_5^+.[8,9] Reparametrized CNDO relative energies for C_s, C_{4v}, and D_{3h} forms of CH_5^+[8] are in excellent agreement with near Hartree–Fock *ab initio* results.[9,10] Thus, the errors due to bridging carbon in C_{4v} and C_s forms of CH_5^+ are comparable. Like small rings, bridged carbocations tend to be too stable by CNDO.[11,12] The difference relative to the *ab initio* 4-31G energies is 21 kcal/mol for the corner protonated cyclopropane (methyl-bridged ethylene) *vs.* the 1-propyl cation.[13] Hence, the maximum total estimated error for **6** is 34 kcal/mol.

The model compounds, estimated energy corrections and corrected relative energies for **1**–**6** are presented in columns 4–6 of Table I. Although the difference between **1** and **6** is now greatly compressed, pyramidal $(CH)_5^+$ (**6**) remains substantially more stable than the remaining isomers. Since the magnitude of the correction for **3** is uncertain, either **1** or **3** may represent the second energy minimum in the $(CH)_5^+$ series. The estimated barrier for conversion of **1** to **6** is quite large, about 34 kcal/mol. It would thus appear that **12** and **13**[4] rather than **14** would be better starting materials for attempted preparation of **6**.

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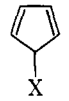

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Some of the calculated structural features of **1**–**6** are of interest. The two planar forms of the singlet cyclopentadienyl cation, although practically isoenergetic, have quite different bond lengths (shown in **1** and **2**). As no energy barrier separates these forms, the resultant structure is problematical; it is not even unlikely that the minimum energy structure might have five different C–C bond lengths! The structure and charge distribution in **3** is intermediate between an allyl and a cyclo-

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S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8956 (1972); also see H. Hart and M. Kuzuya, *ibid.*, **94**, 8958 (1972). For an analogous $(CCH_3)_6^{2+}$ dication, see H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); H. T. Jonkman and W. C. Nieuwpoort, *ibid.*, 1671 (1973).

(5) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

(6) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).

(7) This path may be followed in a (hypothetical) degenerate 9-fluorenyl cation rearrangement

(8) H. Kollmar and H. O. Smith, *Chem. Phys. Lett.*, **5**, 7 (1970).

(9) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *ibid.*, **5**, 361 (1970).

(10) P. C. Hariharan, W. A. Lathan and J. A. Pople, *ibid.*, **14**, 38 (1972).

(11) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(12) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 7529 (1970).

(13) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972); at the 6-31G* level, the energy difference is 13 kcal/mo (J. A. Pople, private communication).

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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Received June 29, 1972

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.

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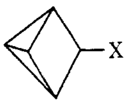

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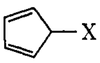

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According to our calculations, the most stable $(CH)_5^+$ species is **7** rather than **3**. This is a distorted form of the antiaromatic cyclopentadienate cation **4**,[8–10] the distortions being such as to reduce the unfavorable cyclic conjugation 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_8 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).