*Tetrahedron* Vol 41, No. 8, pp. 1579 to 1586, 1985
Printed in Great Britain.

0040–4020/85 $3.00 + .00
Pergamon Press Ltd.

# A MNDO STUDY OF 3-, 5-, 7- AND 9-MEMBERED CARBOCYCLIC, COMPLETELY CONJUGATED, PLANAR CARBENES AND THEIR NONPLANAR ISOMERS

M. Z. KASSAEE, M. R. NIMLOS, K. E. DOWNIE and E. E. WAALI*
Department of Chemistry, University of Montana, Missoula, MT 59812, U.S.A.

(*Received in USA* 11 *April* 1984)

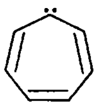
**Abstract**—Molecular orbital calculations have been conducted on a series of planar, cyclic, completely conjugated carbenes and their nonplanar isomers. Energy surfaces have been probed using reaction coordinate diagrams and vibrational force constant calculations. The importance of the *nonplanar* allenic and carbenic isomers is emphasized. In most cases, planar, cyclic, completely conjugated carbenes are not found to be energy minima.

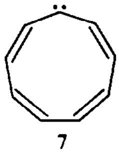
Completely conjugated, carbocyclic carbenes have held a special place in the chemistry of divalent carbon intermediates. The earlier simplicity of a series of carbenes whose properties might be described in terms of the Hückel 4n + 2 rule has recently given way to more complex relationships in which nonplanar isomers must also be considered. We would now like to follow up our preliminary reports,[1,2] with the full results of a theoretical investigation of a series of planar carbenes and the search for their potential valence isomeric nonplanar allene and carbene counterparts using the MNDO molecular orbital (MO) method.[3a]

There have been various MO calculations on carbenes **1**, **3**, **5** and **7** reported in the literature.[4–7] These have used a wide range of sophistication in MO computational techniques. The structural assumptions have also varied and in all cases, some sort of artificial symmetry constraint has been imposed or implied with the structures. Nonplanar structures have been considered in only two cases.[5,6]


1

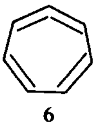

3

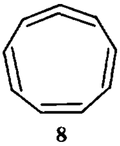

5


7

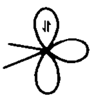

2

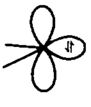

4


6


8

An important aspect of this report which eases comparisons is the fact that a single MO technique has been used in all cases. More importantly, the energy surfaces have been probed by the use of reaction profiles and by the use of vibrational force constant calculations.


$\pi^2$


$\sigma^2$

The pertinent questions for each ring size will be the following. (1) What is the electronic ground state of the carbene if it is constrained to planarity? (2) Is the lowest energy singlet carbene better described as a $\sigma^2$ or a $\pi^2$ carbene?[9a] (3) Is a nonplanar, conjugated allene or another nonplanar form a reasonable alternative to the planar carbene form? (4) Finally, if a nonplanar form is a viable intermediate, does an energy barrier separate it from its planar carbene analog? The results of the calculations will be compared to experimental data whenever possible.

## RESULTS AND DISCUSSION

### *General*

The MNDO program is capable of minimizing the energy of a given species by changing all of the geometric variables in the structure. Since an "optimized" geometry may turn out to be a local minimum, at least two different starting geometries were used to approach each energy minimum. It is sometimes very difficult to recognize the nature of a molecular orbital (symmetric or antisymmetric, $\sigma$ or $\pi$, etc.) if the molecule is not oriented in the coordinate system in a logical way. In this work, dummy atoms and dependent functions which kept the $x$-axis bisecting the carbenic angle or the angle at the central allenic C and kept these carbons and their flanking C atoms in the $x$–$y$ plane were used.

The inappropriate use of symmetry constraints when calculating structural energy minima can lead to erroneous results. This point must be checked. In the cases of the planar singlet carbenes **1**, **3**, **5** and **7**, the geometric optimizations were performed with and without $C_{2v}$ symmetry. There were essentially no differences in the geometries, heats of formation ($\Delta H_f$), orbital energies, and charge distributions. For simplicity in reporting the geometries (Fig. 1), symmetric structures are given.[9b] The allene **6** was treated with and without $C_2$ symmetry constraint. The difference was again negligible. The same held true for nonplanar **7** with $C_s$ symmetry and with those constraints removed. These examples are in contrast with **8** where $C_2$ constraint led to a much different geometry than when this symmetry was relaxed. The half-electron method was used for the triplet states.

An MNDO-based program was used to calculate the vibrational force constant matrices for intermediates and transition states of interest.[11] Structures which had all of their 3N − 6 degrees of geometric freedom optimized (2N − 3 for planar structures) were used for calculating the vibrational force constants. An energy minimum (a stable compound or a reactive intermediate) has *no* negative vibrational force constants.[12] A transition state is a saddle point which has one and only one negative vibrational force constant. A species which has two or more negative force constants indicates a structure which is not a significant point along a reaction pathway. The very recent and profitable use of these criteria has been reported.[13a]

Since the MNDO method is parameterized to give excellent heats of formation and geometries for ordinary organic molecules, one might wonder how closely it predicts the properties of such reactive species as carbenes. Unfortunately, there is not much experimental data on the heats of formation and geometries of carbenes. There is information, though, concerning the parent carbene, methylene ($CH_2$). The MNDO (and experimental) heats of formation for singlet $CH_2$ are 107.4 kcal/mol[3b] (102[13b]) and for triplet $CH_2$ are 77.3 kcal/mol[3b] (93[13b]). MNDO significantly overestimates the stability of triplet $CH_2$. If this difference holds roughly for all carbenes, it could possibly affect our conclusions in this study in the case of carbene **5** (Tables 1 and 2). Since singlet **5** is predicted not to be an energy minimum, though, this possible error in the calculated singlet–triplet energy gap loses some of its significance. The need to experimentally test the predictions of any molecular orbital method is paramount. It is hoped that clever experiments will be designed to test the results of these calculations, determining the level of confidence that can be placed on MNDO calculations for very reactive intermediates.

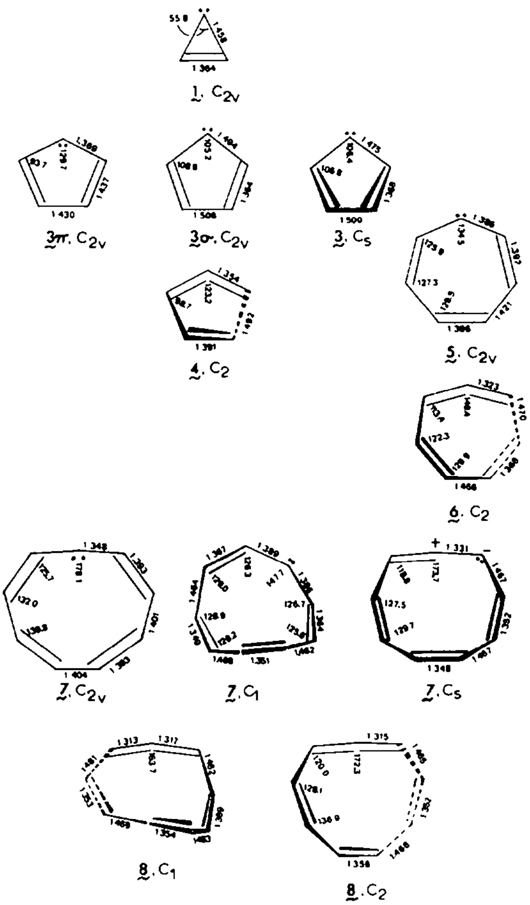


Fig. 1. The geometries of singlet **1**, and **3–8**. The bond lengths are in Angstroms and the angles are in degrees. See ref. 9*b*.

Table 1. Heats of formation and nature of the energy surface for **1**, **3** and **5–8**

| Structure | $\Delta H_f$, kcal/mol | Number of negative vibrational force constants | Nature of structure |
|---|---|---|---|
| **1** (triplet, $C_{2v}$) | 180.4 | — | — |
| **1** (singlet, $C_{2v}$) | 152.3 | zero | an energy minimum |
| **3** (triplet, $C_{2v}$) | 119.5 | — | — |
| **3**π (singlet, $C_{2v}$) | 146.9 | two | not a significant structure |
| **3**σ (singlet, $C_{2v}$) | 141.2 | one | a transition state |
| **3** (singlet, $C_s$) | 140.5 | — | — |
| **4** (singlet, $C_2$) | 145.0 | — | — |
| **5** (triplet, $C_{2v}$) | 97.4 | — | — |
| **5** (singlet, $C_{2v}$) | 114.4 | one | a transition state |
| **6** (singlet, $C_2$) | 91.5 | zero | an energy minimum |
| **6** (triplet, $C_2$) | — | — | neither a transition state nor an energy minimum |
| **7** (triplet, $C_{2v}$) | 126.0 | — | — |
| **7** (triplet, $C_s$) | (119.7)* | — | — |
| **7** (triplet, $C_1$) | (124.6)* | — | — |
| **7** (singlet, $C_{2v}$) | 141.0 | one | a transition state |
| **7** (singlet, $C_1$) | 139.4 | zero | an energy minimum |
| **7** (singlet, $C_s$) | 133.0 | zero | an energy minimum |
| **8** (singlet, $C_1$) | 97.1 | zero | an energy minimum |
| **8** (singlet, $C_2$) | 100.0 | — | — |

* These energies are the results of single calculations for the triplet state at the geometry of the corresponding singlet states. Geometric optimization would lower these energies.

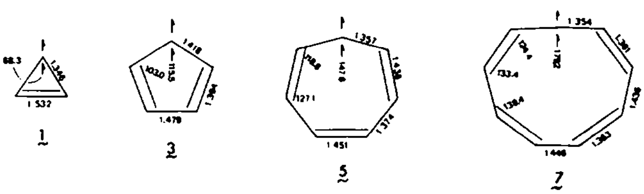


Fig. 2. The geometries of planar ($C_{2v}$), triplet 1, 3, 5 and 7. The bond lengths are in Angstroms and the angles are in degrees.

*Cyclopropenylidene* (1) *and* 1,2-*cyclopropadiene* (2)

The parent cyclopropenylidene (1) has not yet been generated but the diphenyl derivative has been reported.[14] It shows nucleophilic behavior by adding to dimethyl fumarate but not to cyclohexene. This is indicative of the $\sigma^2$ carbene. There is no information concerning the electronic state of the carbene which is responsible for this reaction.

There have been more calculations reported for 1 than for 3, 5 or 7 due, in part, to the economy of theoretical work with small rings. In each case, a singlet ground state carbene is predicted with the carbenic electrons occupying the $\sigma$ system ($\sigma^2$).[4] Not surprisingly, MNDO also predicts a singlet ground state with a $\sigma^2$ carbene configuration. Singlet 1 is predicted to be more stable than triplet 1 by 28 kcal/mol. Other values reported for this separation are 80.9 (INDO[4c]) and 52 kcal/mol (MCSCF[4e]). The triplet 1 reported in Fig. 2 has a shorter C1—C2 bond than the C2—C3 bond. We also find a local minimum at 16 kcal/mol higher energy with a shorter C2—C3 bond.

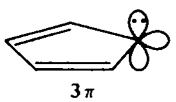
Since the three carbons of 2 must reside in a plane, any nonplanarity in 2 is most simply described as out-of-plane C—H bond bending. This could skew the $\pi$ system and might allow some overlap with the previously orthogonal $\sigma$ orbital. Starting geometries that had the hydrogens on the same or opposite sides of the ring resulted in final structures that were essentially identical with planar 1. In addition, the vibrational force constants for planar singlet 1 were *all positive*. The evidence that planar 1 is an energy minimum is indeed strong.

Note added in proof: a report of the matrix isolation of 1 appeared subsequent to the submission of this paper. H. P. Reisenauer, G. Maier, A. Riemann and R. W. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **23**, 641 (1984).

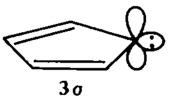
*Cyclopentadienylidene* (3) *and* 1,2,4-*cyclopentatriene* (4)

The chemistry of 3 appears to be well established. It is a ground state triplet[15] but its solution chemistry results from the singlet state.[16] Extended Hückel (EH) calculations predict 3 to be a ground state triplet.[4a]

*Two* MNDO energy minima are found for *planar* singlet 3 and are shown in Fig. 1. The eigenvectors show that these correspond to $\sigma^2$ and $\pi^2$ carbenes, with $3\sigma$ being more stable than $3\pi$ by *ca* 6 kcal/mol (probably within the error of the calculation method). It is possible to find both only because widely different starting geometries were used for the optimizations. All reports to date have been concerned with the $\pi^2$ carbene ($3\pi$).[17] The structural differences between $3\sigma$ and $3\pi$ are exactly what one would expect for the $\sigma^2$ and $\pi^2$ carbenes. The antiaromatic $3\sigma$ is expected to show bond localization. Since $3\pi$ has six $\pi$ electrons, we expect some $\pi$ bond delocalization, which is indeed found. The angle at the carbene carbon in $3\pi$ (129.7°) is larger than the corresponding angle in $3\sigma$ (105.2°). We would expect that a $\pi^2$ carbene would have a larger carbenic angle to allow for more p character in the LUMO which is a $\sigma$ orbital, highly localized on the carbene carbon.



$3\pi$



$3\sigma$

Although $3\sigma$ and $3\pi$ both have positively charged carbene carbons (+0.073 and +0.219, respectively), it is the frontier MO considerations that are important in determining the cycloaddition tendencies.[18] The HOMO–LUMO separations in $3\sigma$ and $3\pi$ are very similar and would make their cycloaddition electronic tendencies very similar. In other words, the antiaromatic component of $3\sigma$ gives it electrophilic properties which would also be consistent with previously reported experimental results.[19] Figure 3 shows slices of the energy surface as a function of the carbenic angle and illustrates the need to try quite different starting geometries in these structural optimizations. If a normal pentagon is used for the starting carbon framework (carbene angle = 108°) $3\sigma$ will finally result. If a carbene angle greater than about 119° is used, $3\pi$ will result. The conversion of $3\pi$ to $3\sigma$ is forbidden for the *planar* structures but their interconversion could occur through a nonplanar intermediate or transition state.

The force constant calculations for planar $3\sigma$ and $3\pi$ are extremely informative and makes much of the

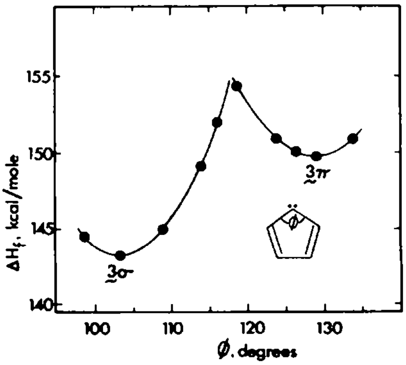
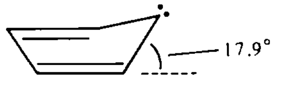


Fig. 3. The heat of formation of planar cyclopentadienylidene (3) as a function of carbenic angle. The C—H bond distances were maintained at 1.1 Angstroms and the C—H bonds were forced to bisect the C—C—C angle to whose central carbon the hydrogen in question was attached. Therefore, the energies of the minima differ somewhat from those reported in Table 1.

above discussion moot. The planar $3\sigma$ has *one negative vibrational force constant*. The vibrational mode which corresponds to this force constant ("frequency" = 171 $i\text{cm}^{-1}$) would transform the intermediate to a structure of $C_s$ symmetry (mirror plane). In other words, the planar $C_{2v}$ $3\sigma$ carbene is a transition state and not an energy minimum. It would transform into the $C_s$ version of 3 which is shown below and in Fig. 1. This



3, $C_s$

structure was then optimized. It was the lowest energy cyclopentadienylidene found in this study. Even though the energy difference between $3\sigma(C_{2v})$ and $3(C_s)$ is very small, we would expect that the carbene C of $3\sigma(C_{2v})$ would lift out of the plane of the other carbon atoms due to its antiaromaticity. The $C_s$ isomer has also been found in the theoretical search for a molecule which contains a pyramidal tetracoordinated carbon atom.[5]

The planar $\pi^2$ carbene $3\pi$ has *two* negative vibrational force constants (503 and 796 $i\text{cm}^{-1}$). It is neither an energy minimum nor a transition state, according to MNDO. The two "normal modes" for these negative force constants correspond to atomic movements which would yield $C_s$ and $C_2$ structures, respectively. Optimization of the $C_5H_4$ structure was then done with $C_2$ constraint. A slightly twisted structure showing the bond length alternation of the allene **4** was found at an energy slightly lower than that for $3\pi$ (Fig. 1 and Table 1).

*Cycloheptatrienylidene* (**5**) *and* 1,2,4,6-*cyclohepta-tetraene* (**6**)

Our preliminary report concerning the MNDO study of the **5**–**6** system has appeared.[1] The partial geometries for planar **5** and nonplanar **6** are given in Fig. 1. An important point is that several computational methods all predict **6** to be more stable than the $\sigma^2$ **5**.[1,6] STO-3G calculations for the much higher energy $\pi^2$ version of **5** have been reported.[6b] The $\Delta H_f$ for **6** can also be estimated using the group values of Benson[20] (74.9 kcal/mol). The difference between this and the MNDO value (91.5 kcal/mol) represents a strain enthalpy of about 17 kcal/mol. As was pointed out,[1] the crucial question no longer involves the order of stability of **5** and **6**, but does a barrier exist for a **5** → **6** conversion?

We can look at the process using a forceful reaction coordinate method. The reaction profiles in Fig. 4 are generated by changing all of the dihedral angles and the central carbene angle a certain percentage of the total changes necessary to convert the planar carbene to the nonplanar allene form. At each point, the bond distances and remaining angles are reoptimized.[21] The process was also repeated in the allene → carbene direction. The use of less forceful reaction coordinates shows discontinuities which sometimes plague the reaction coordinate method.[22] While the reaction path for the **5**–**6** interconversion in Fig. 4 is not necessarily the actual path, the true path must be *at least this favorable*. The conclusion is that **5** is *not an energy minimum*, according to MNDO.

The vibrational force constant matrix has been calculated for **5** and shows a *single negative force constant*. Inspection of this "normal mode" of vibration ("frequency" = 428 $i\text{cm}^{-1}$) shows precisely the atom movement necessary to convert **5** into **6**. Thus, according to MNDO, planar **5** is a *transition state* for the interconversion of chiral **6** and its enantiomer. $\Delta H_f$ for racemization would be about 23 kcal/mol in the gas phase.[23] The vibrational force constant calculation for **6** shows no negative force constants. The infrared spectral frequencies which can be obtained from this calculation will be reported shortly along with the calculated infrared spectral features of other reactive intermediates.

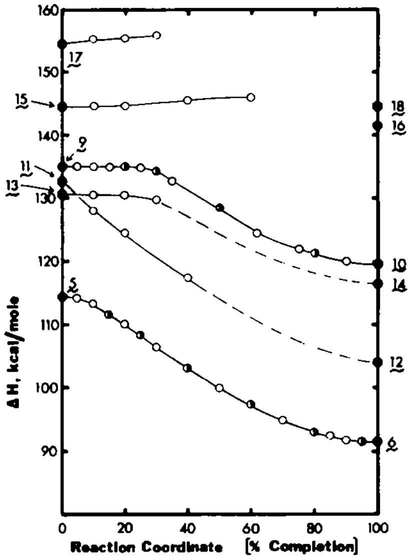
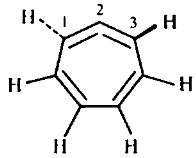
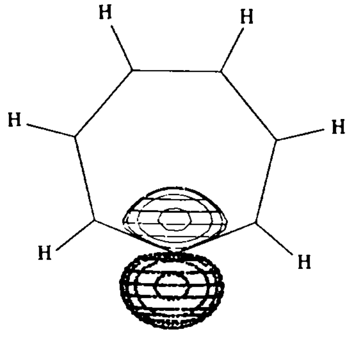


Fig. 4. Reaction profiles for the interconversion of **5** and **6** and the interconversion of their benzo derivatives. See the text for the definition of the reaction coordinate. ●, optimized geometries for **5**, **6**, **9**–**18**; ○, reaction path from left to right; ◑, reaction path from right to left.

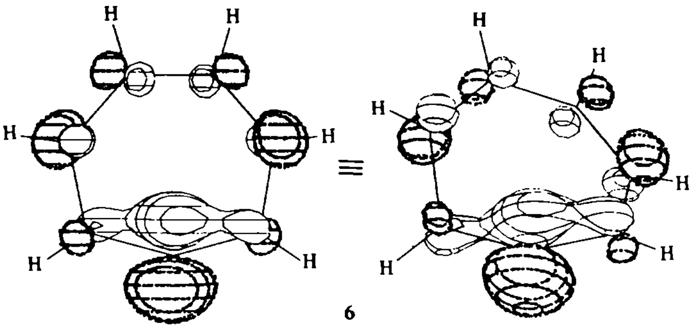
The very strong tendency for planar **5** to seek a nonplanar $C_2$ geometry is illustrated by the following calculation. Even if the entire carbon framework and H4—H7 are constrained to the same plane; H1 and H3, given complete geometric freedom, resist joining the plane. A $C_2$ structure with C1—C2—C3—H3 and C3—C2—C1—H1 dihedral angles of 200.5° results, due to what must be very significant repulsions between H1 and H3 and the $\sigma$ carbene electron pair.



Inspection of the molecular orbitals of **5** and **6** is instructive. The highest occupied molecular orbitals (HOMO) of **5** and **6** are shown below. The protonation of the HOMO of **5** would result in the formation of the tropylium ion. The HOMO of **6** is similar to that of **5** having a large contribution of an atomic orbital which lies along the $C_2$ axis of symmetry. The symmetries of the frontier orbitals for protonation (LUMO = 1 s on hydrogen + HOMO for **6**) are proper to yield a



5



6

tropylium $\sigma$MO and a $\pi$MO (one of the degenerate tropylium LUMOs). The nature of the HOMO of **6** is consistent with the observed chemistry of the intermediate.[24]

There is experimental evidence based on the chirality of **6** that shows it is the intermediate in a cycloaddition to diphenylisobenzofuran.[25a] The matrix isolation IR spectrum of **6** has been reported.[25b] These reports, coupled with the fact that MNDO predicts **5** to be a transition state, incapable of intermolecular reactions, gives the best picture to date of the **5**–**6** system.

A very interesting feature of the HOMO of **6** is the Möbius relationship of the AO basis set. Eight electrons in a Möbius system such as **6** possesses would constitute an aromatic system. Heilbronner pointed out this possibility for cyclic allenes.[26] Unfortunately, ring strain prevents strong overlap for this Möbius arrangement and, thus, **6** is not *strongly* stabilized.

The chemistry of various benzo substituted derivatives of **5** and **6** has been reported.[27] The results of INDO calculations for these derivatives have also been reported.[6a,c] Our calculations can give the benzo derivatives as much geometric freedom as possible. For instance, the 35 geometric variables of planar **9** and **11** were optimized for the vibrational force constant calculations.

To summarize our results, all of the planar carbenes were found to be of *higher* energy than their analogous allene forms. Even the dibenzo and naphtho allenes were found to be more stable but the energy differences were much less in these cases, possibly within the error of the method.

Table 2. Singlet–triplet energies of **5** and its benzo derivatives

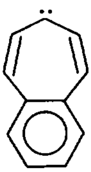
| Structure | Heat of formation Singlet | Triplet |
|---|---|---|
| **5** | 114.4 (116, 115.5)* | 97.4 |
| **9** | 130.5 (118)* | (117.4)† |
| **11** | 132.4 (133)* | (115.9)† |
| **13** | 134.8 (116)* | (120.1)† |
| **15** | 144.7 | (134.2)† |
| **17** | 154.9 | (139.2)† |

* Thermochemical estimates by Wentrup (ref. 28).

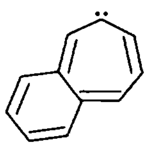
† A single triplet calculation was conducted at the optimized geometry of the singlet version. While the heat of formation of the triplet would be less than this value, this puts an upper limit on the heat of formation and shows that the triplets are all more stable than the singlets.

Wentrup's thermochemical estimates of the heats of formation of the **5** and its benzo derivatives[28] are compared with the MNDO heats of formation in Table 2.

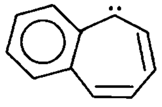
The energy surfaces around these benzo substituted carbenes were also very interesting. The reaction coordinate analysis which was done for the **5**–**6** system was also done for the benzo derivatives (Fig. 4). For **9**, **11**



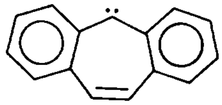
9



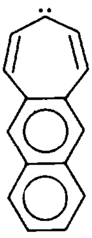
11



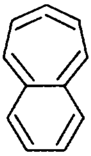
13



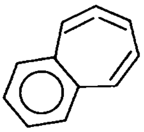
15



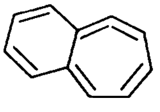
17



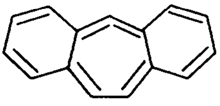
10



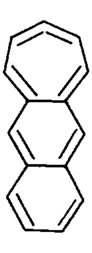
12



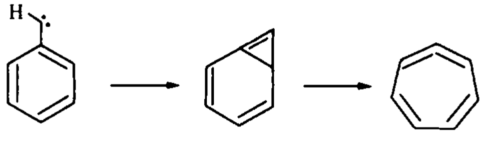
14



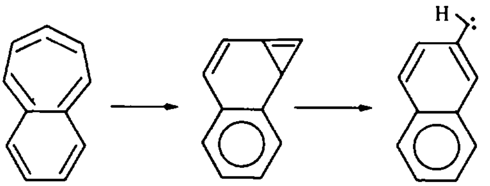
16



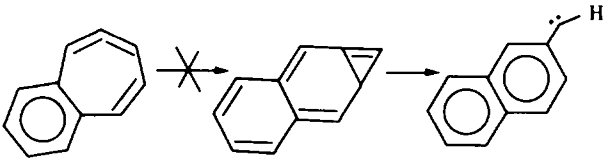
18



6



10



12

and **13**, no energy barrier was found on the reaction path to the allene forms. For the naphtho and dibenzo derivatives **15** and **17**, very small barriers were found. Since there are 69 degrees of geometric freedom for **15** and **17**, it is not surprising that these heavy-handed reaction profiles might not correspond to the actual minimum energy reaction path (MERP). If indeed **15** and **17** are less stable than **16** and **18**, respectively, it is quite possible that they exist on a plateau and are more accessible than the monobenzosubstituted derivatives. In this way intersystem crossing to their corresponding triplet states could occur giving rise to their observed triplet properties.[27b,c,d]

The planar carbene **9** gave one negative force constant with a "normal mode" ("frequency" = 161 icm$^{-1}$) that shows the conversion of **9** to the allene **10**. One negative vibrational force constant was also found for the planar constrained **11** ("frequency" = 1350 icm$^{-1}$). Due to software limitations, it was not possible to conduct the force constant calculations for the rather large **15**–**18**.

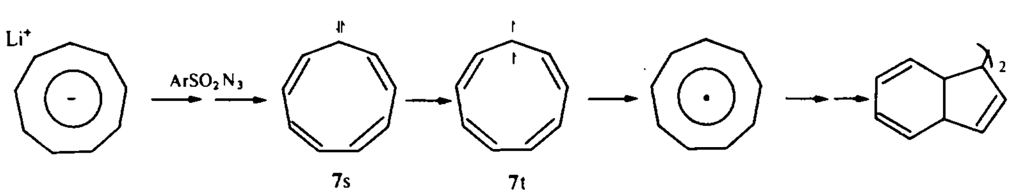
At one time, rearrangements were thought to take place between aryl carbenes and cycloheptatrienylidenes, such as **5** and **9**.[27a] In light of the fact that cycloheptatrienylidenes are unlikely intermediates in any chemical reaction, it is best to explain these rearrangements in terms of allene structures. In fact, when Dewar and Landman computed (MINDO/3) the reaction profile for phenyl carbene itself, no evidence for a planar **5** was found.[29] Instead, the direct formation of **6** was indicated. A driving force for the rearrangement of **10** to 2-naphthyl carbene appears to be the aromatization of the benzo substituent in the cyclic carbene. Allene **10** undergoes this rearrangement at rather low temperature.[27a] On the other hand, no rearrangement products have been observed from allene **12**.[30] In every case, the planar constrained carbene triplets are of lower energy than the planar singlet carbenes. Triplet allene **6** is not an energy minimum and transforms into planar triplet **5** upon optimization with no activation energy. It appears that any authentic carbene chemistry derived from **5** or its derivatives must occur through the triplet state. Experiments designed to constrain the seven membered ring of **5** to planarity and maximize the chance of observing triplet carbene chemistry are in progress.

### *Cyclononatetraenylidene* (**7**) *and cyclononapentaene* (**8**)

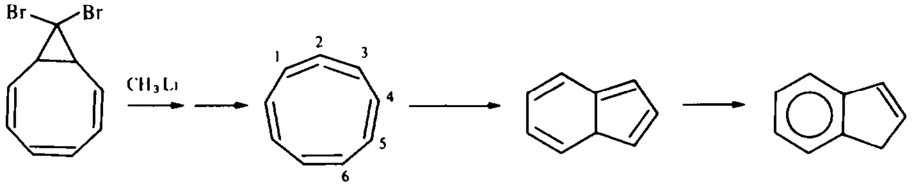
It is in the more flexible **7**–**8** system that there is a very good chance of having two distinct intermediates capable of detection. In fact, there are reports of the intermediacies of **7** and **8** when they are generated from their classical precursers. The carbene **7** gives a dimer via its triplet state[31] while **8** apparently undergoes electrocyclic ring closure and hydrogen migration to give indene.[32]

The construction of a Dreiding model of **8** using standard allene and olefin components is possible and results in a structure with no elements of symmetry. The MNDO optimized structure is shown in Fig. 1. In this structure, C2 and C6 are rather close to one another with their portions of the $\pi$ molecular orbital pointing almost directly at one another. It is not surprising that the electrocyclic ring closure is so facile. The dibenzo analog of **8**[32] has been trapped, though, by diphenylisobenzofuran.[33]

A planar, $C_{2v}$ constrained version of singlet **7** (a $\pi^2$ carbene[34]) is much less stable than **8**. The vibrational force constant calculation for $C_{2v}$ singlet **7** shows one negative force constant. It, according to MNDO, is *not* an intermediate. It would transform to a lower energy $C_2$ structure (an allene) with no activation energy. If a version of **7** which can give the reported hydrogen abstraction reaction is possible, it must not be planar. The potential flexibility of **7** and the possibility of nonplanar isomers has been recognized.[7]

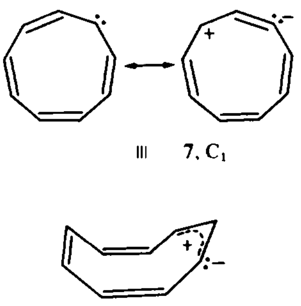


7s 7t

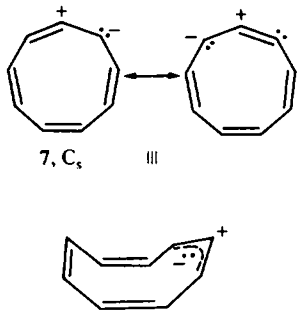


8

There are at least two nonplanar versions of 7, both being more stable than the planar constrained $C_{2v}$ 7. The lowest energy version of 7 which we have found contains a mirror plane of symmetry ($C_s$ symmetry). There is another version of nonplanar 7 which contains no element of symmetry. Analysis of their bond lengths and their orbital configurations (eigenvectors) indicate that the following resonance structures are rather accurate descriptions of their electronic configurations. The triplet states of both of these intermediates are more stable than the corresponding singlet states.



III 7, $C_1$



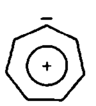
7, $C_s$ III

## SUMMARY

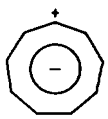
It was once thought that the planar, singlet carbenes 1, 3, 5 and 7 could achieve very stable "aromatic" structures by the inclusion of the carbenic electron pair in the $\sigma$ or $\pi$ system in order to give $4n+2$ $\pi$ electrons. While the following structures may have some importance, it should now be understood that such *complete* resonance delocalization would result in extensive charge separation in 3, 5 and 7. The result is that these singlet "aromatic" carbenes are not actually as stable as was once thought. Because of its small ring size, the carbene 1 can take good advantage of this aromatic stabilization without extensive separation of charge. Only 1 is likely to be a planar, ground state singlet carbene. Planar 3, 5 and 7 are not energy minima, according to MNDO. More stable nonplanar, singlet carbene or allene analogs would be formed from these with no activation energy.

1′

3′



5′



7′

While these semiempirical MO calculations may suffer from a limited basis set and the lack of consideration of electron correlation which may be important in carbenes, they do point out the importance of nonplanar isomers of the carbenes of interest. Any future higher level calculations must take into account the many nonplanar options available to the cyclic, completely conjugated carbenes.

*Acknowledgement*—This work was supported in part by the MONTS-NSF program ISP-8011449, by the Research Corporation (M. J. Murdock Charitable Trust Grant), and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank the University of Montana for a University Research Grant. Stimulating discussions with Professors W. M. Jones and J. D. Scott and Dr. J. O. Jarvie have been especially enjoyable. The assistance of Professor R. J. Field and the University of Montana Computer Center in installing the computer programs is greatly appreciated.

## REFERENCES

[1] E. E. Waali, *J. Am. Chem. Soc.* **103**, 3604 (1981).

[2] Partial accounts of this work were presented at the Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, U.S.A., August, 1980 and the 28th Congress of IUPAC, Vancouver, British Columbia, August, 1981.

[3a] M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 and 4907 (1977). Program 353, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, IN 47405. [b] Dewar and Rzepa [*J. Am. Chem. Soc.* **100**, 784 (1978)] report the MNDO heat of formation of singlet $CH_2$ (102.6 kcal/mol) using a 3 × 3 configuration interaction (CI) and of

triplet $CH_2$ (77.3 kcal/mol). The heat of formation of singlet $CH_2$ reported in the text is calculated without CI.

[4] [a]R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.* **90**, 5457 (1968); [b]W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman and Z. R. Wasserman, *Ibid.* **98**, 4378 (1976); [c]C.-K. Lee and W.-K. Li, *J. Molec. Structure* **38**, 253 (1977); [d]H. Kollmar, *J. Am. Chem. Soc.* **100**, 2660 (1978); [e]R. Shepard, A. Banerjee and J. Simons, *Ibid.* **101**, 6174 (1979).

[5] V. I. Minkin and R. M. Minyaev, *Zh. Org. Khim.* **15**, 225 (1979).

[6] [a]R. L. Tyner, W. M. Jones, Y. Ohrn and J. R. Sabin, *J. Am. Chem. Soc.* **96**, 3765 (1974); [b]L. Radom, H. F. Schaefer III and M. A. Vincent, *Nouv. J. Chim.* **4**, 411 (1980); [c]M. Balci, W. R. Winchester and W. M. Jones, *J. Org. Chem.* **47**, 5180 (1982).

[7] M. Kausch and H. Dürr, *J. Chem. Res.* (*S*) 2 (1982).

[8] Subsequent to our initial reports, there appeared very brief theoretical descriptions of some of the intermediates which are discussed in this paper (ref. 10). These aspects will be discussed later.

[9] [a]Only the closed shell singlet states are treated in the present work. [b]The dihedral angles for the nonplanar isomers are available from one of the authors (E.E.W.).

[10] C. Glidewell and D. Lloyd, *J. Chem. Res.* (*S*) 178 and 180 (1983).

[11] [a]M. J. S. Dewar, G. P. Ford, M. L. McKee, H. S. Rzepa, W. Thiel and Y. Yamaguchi, *J. Molec. Structure* **43**, 135 (1978). We thank Professor Dewar for making this program available and Dr. J. Ritchie for discussions on its use. [b]The semiempirical MNDO program is rather time efficient but considering the large size of some of the molecules of interest to this work, some of the computations required a large amount of time. For instance, complete geometric optimization of nonplanar **7** (no symmetry, 45 geometric variables) took 10 hr of CPU time on a DEC 2060 computer. The vibrational force constant calculation for **11** took 16 hr of CPU time.

[12] J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.* **64**, 371 (1968).

[13] [a]J. Breulet and H. F. Schaefer III, *J. Am. Chem. Soc.* **106**, 1221 (1984). [b]R. K. Lengel and R. M. Zare, *Ibid.* **100**, 7495 (1978).

[14] W. M. Jones, M. E. Stowe, E. E. Wells Jr. and E. W. Lester, *J. Am. Chem. Soc.* **90**, 1849 (1968); T. Mitsuhashi and W. M. Jones, *Chem. Commun.* 103 (1974).

[15] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray and W. A. Yager, *J. Am. Chem. Soc.* **86**, 2304 (1964).

[16] R. A. Moss, *J. Org. Chem.* **31**, 3296 (1966); R. A. Moss and J. R. Przybyla, *Ibid.* **33**, 3816 (1968); H. Dürr, B. Ruge and B. Weiss, *Justis Liebigs Ann. Chem.* 1150 (1974).

[17] Although in one report (ref. 10) it was stated that the $3\pi$ was found using MNDO, the dipole moment for the species (2.81 D) and its charge on the carbenic carbon (+0.075) prove that the actual electronic structure for this intermediate was that for $3\sigma$. We find dipole moment and carbenic carbon charges of 2.83 D and +0.073 for $3\sigma$ but 1.46 D and +0.219 for $3\pi$.

[18] [a]I. Fleming, *Frontier Orbitals and Organic Chemical Reaction.* Wiley, New York (1976); [b]W. M. Jones and U. H. Brinker, *Pericyclic Reactions* (Edited by A. Marchand and R. Lehr). Academic Press, New York (1977).

[19] H. Dürr and F. Werndorff, *Angew. Chem. Int. Ed. Engl.* **13**, 483 (1974).

[20] S. W. Benson, *Thermochemical Kinetics* (2nd Edition), p. 272. Wiley, New York (1972).

[21] The C—H bonds were maintained at 1.1 Angstroms for these calculations. We find that giving the C—H bonds the freedom to change improves the energy by only tenths of kcal/mol.

[22] For a review of the reaction coordinate method and other procedures for investigating multidimensional energy surfaces, see: K. Muller, *Angew. Chem. Int. Ed. Engl.* **19**, 1 (1980).

[23] There are some minor factors which could affect the relative stability or possible equilibrium distribution of **5** and **6**. For instance, the calculated dipole moment of **5** (4.03 D) is much larger than that for **6** (0.83 D). In solution, the energy difference between **5** and **6** would be diminished. On the other hand, **6** is a chiral intermediate and would be additionally favored by a small entropy of mixing term (R ln 2) when experimentally as a racemic mixture.

[24] W. Kirmse, K. Loosen and H.-D. Sluma, *J. Am. Chem. Soc.* **103**, 5935 (1981).

[25] [a]J. W. Harris and W. M. Jones, *J. Am. Chem. Soc.* **104**, 7329 (1982); [b]P. R. West, O. L. Chapman and J.-P. LeRoux, *Ibid.* **104**, 1779 (1982).

[26] E. Heilbronner, *Tetrahedron Letters* 1923 (1971).

[27] [a]W. M. Jones, *Acc. Chem. Res.* **10**, 353 (1977) reviews the rearrangement chemistry of these derivatives; [b]S.-I. Murahashi, I. Moritani and M. Nishino, *J. Am. Chem. Soc.* **89**, 1257 (1967); [c]I. Moritani, S.-I. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh and N. Mataga, *Ibid.* **89**, 1259 (1967); [d]A. Hackenberger and H. Dürr, *Tetrahedron Letters* 4541 (1979).

[28] C. Wentrup, *Tetrahedron* **30**, 1301 (1974).

[29] M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.* **99**, 6179 (1977).

[30] E. E. Waali, J. M. Lewis, D. E. Lee, E. W. Allen and A. K. Chappell, *J. Org. Chem.* **42**, 3460 (1977).

[31] E. E. Waali and C. W. Wright, *J. Org. Chem.* **46**, 2201 (1981).

[32] E. E. Waali and N. T. Allison, *Ibid.* **44**, 3266 (1979).

[33] G. R. Peterson, University of Montana, unpublished results.

[34] Glidewell and Lloyd have communicated brief reports of some MNDO calculations on some $C_9H_8$ intermediates (ref. 10). It is difficult to completely assess this work for several reasons. First, it is stated that the structures were completely optimized but the C—C bond lengths and C—C—C angles are reported for only half of each structure implying that symmetry constraints were used. Second, they report a planar structure ($\Delta H_f$ = 127 kcal/mol) which is given the $\sigma^2$ carbene configuration and an octet of electrons with the following bond lengths. When we use these bond lengths and angles in a completely planar structure and then optimize the remaining variables ($C_{2v}$), we find that a $\pi^2$ carbene results ($\Delta H_f$ = 144 kcal/mol). The bond lengths and bond angles in Glidewell and Lloyd's structure are surpsisingly close to those of the $C_2$ version of **8** reported in Fig. 1. It is also stated (ref. 10) that if the allene **8** is more stable than the corresponding carbene isomer **7**, it would be impossible to obtain chemistry *via* the allene. This, of course, assumes thermodynamic control of the isomer distribution and ignores the nature of the energy surface and the possbility of kinetically controlled product distributions. In the present work, we show that **5** and **6** are not separated by an energy barrier but that **7** and **8** are capable of exhibiting their own unique chemistry. We must await the full reports of these preliminary communications (ref. 10) before any more can be said about these apparent discrepancies.

a 125.6°
b 131.4°
c 138.9°
d 144.1°