from the literature value[33] of the rotational constant about an axis perpendicular to the symmetry axis.

HCN. All parameters are taken directly from the literature.[33]

CH₃·HCN⁺. The structure[34] is assumed to be $CH_3—C≡N^+·—H$. Vibrational frequencies are taken to be those of $CH_3—C≡CH$,[35] except the C—H and C≡C stretch frequencies are

changed to those expected for N—H and C≡N stretches. The rotational constant is calculated from the structure by using the following bond lengths (in Å) C—H (1.0 for —CH_3 group), C—C (1.6), C≡N (1.16), and N—H (1.01) and assuming the methyl group to be tetrahedral and the sketal chain to be linear.

(34) A. Illies, S. Liu, and M. T. Bowers, *J. Am. Chem. Soc.*, in press.

(35) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Consolidated Vol. I, National Bureau of Standards, Washington, DC, 1972.

Ground States of Molecules. 58.[1] The C4H4 Potential Surface

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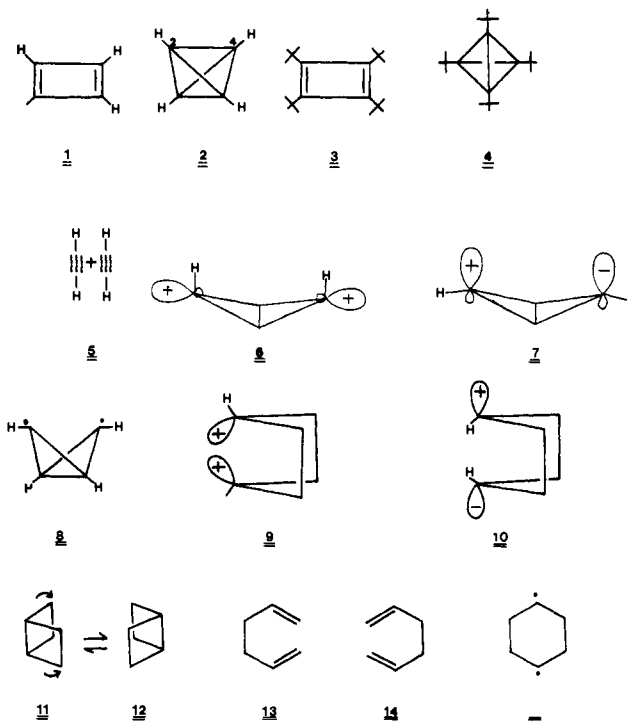*Received October 14, 1980*

Abstract: The singlet potential surface for C_4H_4 species has been extensively explored, using MINDO/3. It is thought that all local minima corresponding to normal closed shell molecules have been located, together with the transition states for their easiest modes of interconversion. Entry to the C_4H_4 system by the dimerization of acetylene can follow two paths, one involving 3-cyclopropenylcarbene as an intermediate. It is suggested that this reaction is responsible for initiation of detonation in acetylene under pressure or as a solid or liquid.

Cyclobutadiene (**1**) and tetrahedrane (**2**) have long been sought by organic chemists, partly because of their chemical significance but perhaps even more so because of their aesthetic appeal. Cyclobutadiene is the simplest cyclic polyene and as such plays a key role in theories of aromaticity. Tetrahedrane, the simplest of the polyhedranes, should exemplify in a very clear manner the effects of extreme angle strain.

After generations of effort, **1** was finally obtained by Pettit et al.[2] as a reaction intermediate. While **1** itself dimerizes immediately, its spectroscopic properties have been studied by several groups of workers in matrices at low temperatures.[3] Derivatives of **1** containing bulky substituents can exist as stable monomeric species[4,5] and one of these (**3**) has been obtained[5] by rearrangement of **4**, the only known[5] derivative of tetrahedrane.

If **1** is aromatic, it should have a symmetrical square structure with equal bond lengths, whereas if it is antiaromatic, the lengths of the bonds in it should alternate. In the latter case, there is the possibility that a square form of the triplet might represent the ground state. Further points of interest are the stabilities of **1** and **2** relative to one another and to two molecules of acetylene (**5**) and the ease of the "forbidden" interconversions of **1**, **2**, and

Chart I

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(2) Watts, L.; Fitzpatrick, J. F.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253; **1966**, *88*, 623.

(3) (a) Krantz, A.; Lin, C. Y.; Newton, M. D. *J. Am. Chem. Soc.* **1973**, *95*, 2744. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *Ibid.* **1973**, *95*, 614. Chapman, O. L.; De LaCruz, D.; Roth, R.; Pacansky, J. *Ibid.* **1973**, *95*, 1337. (c) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *Ibid.* **1978**, *100*, 4879.

(4) (a) Kimling, H.; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 932. (b) Maier, G.; Alzenea, A. *Ibid.* **1973**, *12*, 1015. (c) Masamune, S.; Nakamura, N.; Suda, M.; Ona, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481. Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *Ibid.* **1975**, *97*, 1973.

(5) (a) Maier, G.; Pfriem, S.; Schafer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520. (b) Irngartinger, H.; Riegler, N.; Malsch, K.-D.; Schneider, K.-A.; Maier, G. *Ibid.* **1980**, *19*, 211. (c) The bond alternation in the ring of **3** is less than that in the other stable derivatives of **1** that have been studied, due to the steric repulsions between the *tert*-butyl groups. These distort **3** out of planarity, part way toward **4**. In **4** itself the repulsions between the *tert*-butyl groups should be small.

5. In view of the importance of these problems and the lack until very recently of any experimental data concerning them, numerous attempts have been made to solve them by theoretical calculations, both semiempirical[6] and ab initio.[7] The most reliable ab initio

(6) (a) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3255. (b) Dewar, M. J. S.; Kollmar, H. W. *Ibid.* **1975**, *97*, 2933. (c) Dewar, M. J. S.; Komornicki, A. *Ibid.* **1977**, *99*, 6174. (d) Halevi, E. A.; Matsen, F. A.; Welshar, T. L. *Ibid.* **1976**, *98*, 7088. (e) Schweig, A.; Thiel, W. *Ibid.* **1979**, *101*, 4742. (f) Böhm, M. C.; Gleiter, R. *Tetrahedron Lett.* **1978**, 1179.

calculation, by Kollmar,[7f] predicted the heats of formation of **1** and **2** to be 105 and 134 kcal/mol, respectively, bracketing **5** (108 kcal/mol). The activation energy for **2** → **1** was found to be ca. 30 kcal/mol. Schweig and Thiel,[6e] using MNDO, found the heats of formation of **1** and **2** to be 90.7 and 136.6 kcal/mol, respectively, the activation energy for **2** → **1** being 15.2 kcal/mol. Schweig and Thiel also studied the conversion of **4** to **3** finding it to be less exothermic (ΔH_f: **4**, 81.2; **3**, 74.5 kcal/mol) and to have a higher activation energy (ca. 20 kcal/mol), as would be expected in view of steric effects involving the bulky *tert*-butyl groups.

These theoretical investigations have now been supported by experimental studies of **1** and its derivatives, all of which have proved to have rectangular singlet ground states.[3-5] The conversion of **4** to **3** is moreover exothermic, even though the steric strain due to mutual interactions between the *tert*-butyl groups must be greater in **3**. As yet, however, no quantitative thermochemical data are available for this interconversion or for the relative heats of formation of **3**, **4**, and di-*tert*-butylacetylene (+≡+).

At the time we began the work reported here, a detailed study of the C_4H_4 system by "state of the art" ab initio methods, i.e., SCF-MO treatments, using very large basis sets and including an allowance for electron correlation (e.g., by CI, CEPA, GVB), would have been out of the question. MINDO/3,[8] however, had already been shown to give results at least comparable in accuracy with those of any but the best ab initio methods in the case of hydrocarbons, a conclusion which incidentally has been reinforced by recent detailed tests.[9] We therefore decided to carry out a detailed MINDO/3 study of the C_4H_4 potential surface. This investigation has taken longer than originally anticipated, for various reasons. In the meantime, a new semiempirical method (MNDO[10]) has been developed and shown to be superior to MINDO/3 in most respects. There are, however, some exceptions and two of these are relevant in the present connection, i.e., nonclassical species and four-membered rings. We therefore decided to retain MINDO/3 for the present study.

The C_4H_4 potential surface is of especial interest because, apart from its relevance to small ring chemistry, "state of the art" ab initio techniques have now been developed to a point where systems of this size can be treated, though still at rather heavy cost. In connections such as this, the most profitable course now seems to be to first study the problem with the use of MINDO/3 or MNDO and then use the results as a guide to ab initio calculations for the various stationary points. The semiempirical results are good enough to provide a very good guide to the location of the latter so the computing time required for the ab initio calculations is very greatly reduced. It is important that such calculations be carried out because the accuracy with which they can reproduce activation energies of reactions is still not known, due to their cost, and because *really* accurate calculations for even simple systems would be of major value for testing the semiempirical treatments which alone can usefully be applied at present to the more complex ones. Indeed, one of us has already studied part of the C_4H_4 surface in this way.[7e]

Procedure

The calculations were carried out by using the standard MIN-DO/3 procedure with the standard parameters for carbon and hydrogen.[8] Our study of the $(CH)_4$ surface has extended over several years, using successively more sophisticated techniques. The results reported here were based on rigorous optimization of geometries by an improved version of the DFP (Davidon–Fletcher–Powell) method,[11] no assumptions being made. Cal-

culations were carried out by both spin restricted (RHF) (MIN-DO/3) and unrestricted (UHF) (UMINDO/3) versions of MINDO/3 to identify biradical-like regions of the potential surface. The energies of biradical-like species were in a number of cases recalculated by the "half-electron" method.[12] Transition states were located approximately by the reaction coordinate method and then refined by minimizing the scalar gradient of the energy, following the procedure used by McIver and Komornicki.[13] We also used their procedure,[13] i.e., diagonalization of the Hessian (second derivative or force constant) matrix, to identify stationary points and to check that convergence to them was complete. In the case of transition states we also examined the eigenvector (transition vector) corresponding to the negative eigenvalue. The form of this vector gives an indication of the two structures to whose interconversion the transition state in question refers. This provides additional assurance that a given transition state does in fact correspond to the reaction under study.

Results and Discussion

A. Introduction. Since the MINDO/3 potential surface for the C_4H_4 system has proved unexpectedly rich and complex, we will start by presenting the essential features of the whole surface in outline. Figure 1 indicates the minima we have located, together with the transition states for their interconversion. Numbers in rectangles correspond to the numbering of formulas in the text. The other numbers, in parentheses, are the calculated heats of formation (kcal/mol at 25 °C), while the numbers in brackets are the calculated heats of formation of the various transition states. Our discussion will be divided into four sections, the first dealing with the conversion of tetrahedrane (**2**) to cyclobutadiene (**1**), the second with conversions of **1** or **2** to methylenecyclopropene (**26**) or vinylacetylene, and the third with the relationships of these species to acetylene (**28**). The last section will consider the remainder of the C_4H_4 surface.

B. Conversion of Tetrahedrane to Cyclobutadiene. The conversion of **2** to **1** was studied by using the length of one breaking bond (C_2C_4) as the reaction coordinate and imposing a plane of symmetry through C_2 and C_4. The resulting MERP (minimum energy reaction path; Figure 2) had two intervening minima, corresponding to the biradical-like species **6** and **7**. Both these and the three transition states along the reaction path were shown to be minima of the required type by calculating and diagonalizing the corresponding Hessian (force constant) matrices.[13] The relative phases of the relevant AO's of C_2 and C_4 in the HOMO's of **6** and **7** are indicated in the usual way in the formulas. The phases in the LUMO's are opposite to those in the HOMO's. The overall reaction is predicted to be very exothermic (ΔH, −32 kcal/mol), in very good agreement with ab initio calculations,[7] and to have a low activation energy (11 kcal/mol). While this is a little less than the MNDO value (15 kcal/mol[6e]) and much less than the most recent ab initio one (~30 kcal/mol[7e,f]), it still implies that it should be possible to prepare and isolate **2** at low temperatures.

While **2** has not yet been reported, its tetra-*tert*-butyl derivative (**4**) rearranges on heating to tetra-*tert*-butylcyclobutadiene (**3**), implying that the conversion (**4** → **3**) is exothermic.[5a] Since this reaction must lead to an increase in the steric strain due mutual repulsions between the bulky *tert*-butyl groups,[5c] there seems little doubt that (**2** → **1**) must also be exothermic, as predicted. The thermal stability of **4** indicates that the barrier to rearrangement must be considerably greater than that estimated for (**2** → **1**). This, however, would be expected since stretching a bond in the ring of **4** will lead to an increase in the steric strain due to *tert*-butyl repulsions. These intuitions are moreover supported by the MNDO calculations of Schweig and Thiel.[6e] Consequently the ab initio

(7) (a) Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1968**, *48*, 354; *J. Am. Chem. Soc.* **1969**, *91*, 4342. (b) Haddon, R. C.; Williams, G. R. J. *J. Am. Chem. Soc.* **1975**, *97*, 6582. (c) Kollmar, H.; Staemmler, V. *Ibid.* **1977**, *99*, 3583. (d) Borden, W. T.; Davidson, E. R.; Hart, P. *Ibid.* **1978**, *100*, 5012. (e) Kollmar, H. *Theor. Chim. Acta* **1978**, *50*, 235. (f) Kollmar, H. *J. Am. Chem. Ser.* **1980**, *102*, 2617.

(8) Bingham, R.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285, 1294, 1302, 1307.

(9) (a) Dewar, M. J. S. *Science*, **1975**, *187*, 1037. (b) Halgren, T. A.; Klein, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6595. (c) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 5558.

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(13) McIver, J. W., Jr.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303.

(14) Longuet-Higgins, H. D.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045.

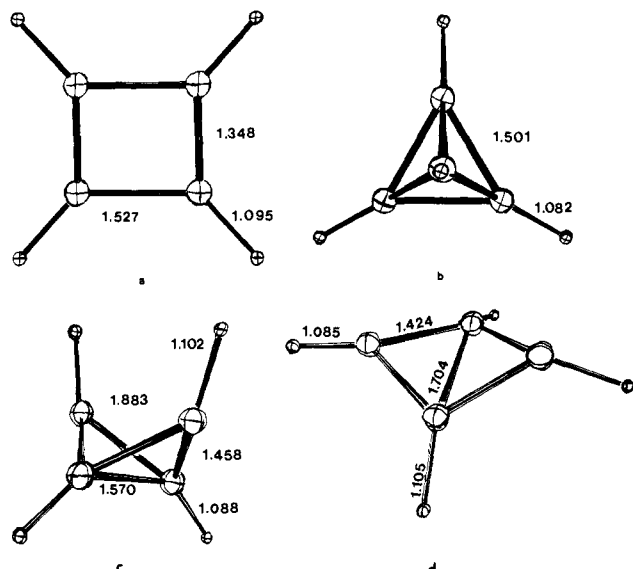(15) Woodward, R. B.; Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

Figure 1. Global representation of the C_4H_4 system. Calculated heats of formation (kcal/mol at 25 °C) of stable species are shown in parentheses under the formulas (reference numbers in rectangular boxes) and of transition states in square brackets above the double-headed arrow linking the species involved.

Figure 2. Schematic representation of the MERP (minimum energy reaction path) for conversion of tetrahedrane (**2**) to cyclobutadiene (**1**).

value for the activation energy for **2** → **1** seems likely to be too large.

Figure 3a–d shows the geometries calculated for **1, 2, 6,** and **7.**

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Figure 3. ORTEP plots and bond lengths (Å) for: (a) **1**; (2) **2**; (c) **6**; and (d) **7**.

Figure 4. Planes of symmetry ($\cdots$) in tetrahedrane.

Use of MINDO/3 in this connection requires justification in view of its tendency to underestimate strain energies in small rings.[8] Much of this error seems, however, to arise from an underestimation of eclipsing interactions between adjacent sp^3 carbon atoms. Thus extrapolation of the errors in the MINDO/3 heats of formation[8] for cyclobutane (−11.9 kcal/mol) and cyclobutene (−4.3 kcal/mol) suggests that the error in the case of cyclobutadiene is probably quite small. Concerning tetrahedrane, MINDO/3 also tends to give heats of formation for crowded molecules that are too positive[8] and in the case of cubane the resulting error seems to cancel that due to underestimation of ring strain, the calculated heat of formation (139.8 kcal/mol) being in quite good agreement with experiment (148.7 kcal/mol).[8] A similar compensation seems to occur in passing from cyclopropane to bicyclobutane, the errors in the MINDO/3 heats of formation being −6.8 and −2.1 kcal/mol, respectively.[8] It therefore seems not unlikely that MINDO/3 may give reasonable heats of formation for both **1** and **2** and hence by implication for the intervening potential surface.

The reaction in Figure 2 corresponds to a mechanism that is not merely not synchronous but not even concerted. It takes place in at least two steps, and in the rate-determining step one of the breaking bonds in **2** is not even weakened (cf. Figure 3b,c). Surveys of the potential surface by two-dimensional grid searches failed to reveal any better route from **2** to **1**. Indeed, the mechanisms reported here for all the reactions studied were shown to be the optimum ones by analogous surveys of the potential surface.

The MERP of Figure 2 corresponds to retention of two planes of symmetry throughout the reaction, one passing through C_2, C_4, and the midpoint of C_1C_3, and the other passing through C_1, C_3, and the midpoint of C_2C_4; see Figure 4. The MO's of the various species can therefore be correlated on the basis of their symmetry with respect to reflection in these two planes. It is easily seen on this basis that a HOMO/LUMO crossing must occur at some point along the MERP and that the overall reaction must consequently be "forbidden".[14-16] Our calculations showed that such a crossing did occur, between **6** and **7**, very close to **6**.

A HOMO/LUMO crossing on a potential surface corresponds to an orbitally degenerate species, i.e., a singlet biradical.[16,17] The correlation energy between the two "unpaired" electrons can then be very large. While MINDO/3 contains a built-in correction for electron correlation via the parameters used in it, it cannot cope with the situation in a typical biradical. It is therefore necessary to make explicit all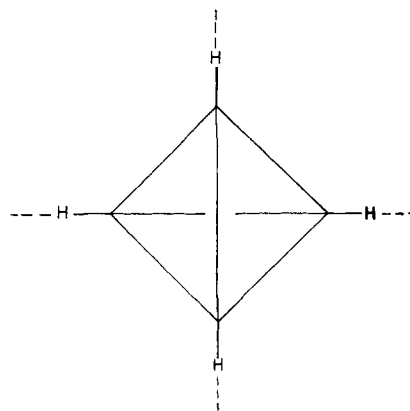owance for this by one of the techniques used in ab initio RH calculations. Four such procedures have been used: (a) inclusion of CI with the lowest singly and doubly excited configurations[17] (3 × 3 CI) (MINDO/3/CI); (b) use of the Pople–Nesbet UHF formalism[18] (UMINDO/3); (c) use of the Roothaan RHF formalism[19,20] for open-shell systems; and (d) the "half-electron" method[12,20] (MINDO/3/HE), which is a convenient approximation to procedure c. These procedures provide complete compensation for correlation between the unpaired electrons in a "real" biradical where the radical centers are widely separated. Complications consequently arise in the case of MINDO where a compensation for "normal" correlation is built in via the parametrization. Use of MINDO/3/CI or MINDO/3/HE for "real" biradicals therefore leads to estimated heats of formation that are systematically too low. Empirically this error amounts to ca. 15 kcal/mol. The error in the case of UMINDO/3 is somewhat larger (20–25 kcal/mol) because here allowance is also made for other kinds of electron correlation. Our experience indicates that MINDO/3/CI and MINDO/3/HE are therefore better for studying systems where biradicals may play a role.

Further problems arise in the case of biradical-like species where the segregation of the unpaired electrons is incomplete. Here inclusion of CI or use of HE should again lead to an overestimation of the correlation energy, but possibly to a lesser extent than in the case of a "real" biradical. Lack of data have prevented us from reaching a definite solution of this problem. At present, for lack of a better alternative, we assume that the error is always the same, except when the corresponding correction would lead to an energy more positive than the RH value. In such cases, the "normal" (RHF) MINDO/3 value is adopted. Any errors so introduced should be no greater than those inherent in MINDO/3, the average error in calculated heats of formation being 5–10 kcal/mol.

Since the conversion of **2** to **1** had been shown to involve a HOMO/LUMO crossing and hence a biradical intermediate, we recalculated the MERP with the use of MINDO/3/CI, with the results shown in Figure 2. It will be seen that the relevant parts of the potential surface, in particular the minima **1**, **2**, **7**, and the main transition states, are predicted to have no significant biradical character, their MINDO/3/CI heats of formation being only a few kcal/mol less than the MINDO/3 values. The changes occur between **6** and **7**, in a portion of the surface that is not kinetically significant. Our conclusions concerning the heats of reaction and of activation for **2** → **1** remain unchanged.

The predicted lack of biradical character in **6** and **7** is somewhat surprising, given that neither can be represented by a normal closed shell valence structure. Both indeed seem to be variants of the 2,4-bicyclobutylene biradical **8**. This anomaly is emphasized by comparison of **6** and **7** with the apparently analogous biradicaloid species **9** and **10**, involved respectively in the ring inversion of bicyclohexane (**11** → **9** → **12**) and the "boat" Cope rearrangement of 1,5-hexadiene (**13** → **10** → **14**). The relationship of **6** or **7** to

(16) (a) Dewar, M. J. S.; Kirshner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 5240. (b) Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W.; Wade, L. E. *Ibid.* **1974**, *96*, 5242.

(17) Salem, L.; Rowland, *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(18) Pople, J. A.; Nesbet, R. K. *Chem. Phys.* **1951**, *23*, 69.

(19) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

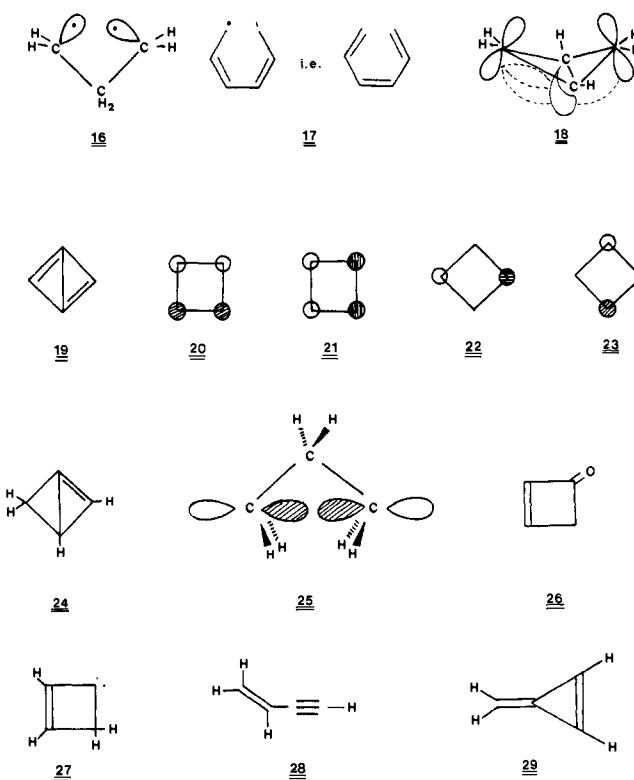(20) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1979**, *101*, 4958.

8 is clearly analogous to that between **9** or **10** to the cyclohexylene biradical (**15**). The geometries calculated[21] by MINDO/3 for **9** and **10** are similar to those for **6** and **7**, the radical carbon atoms showing similar deviations from planarity, and while the HOMO's of **6** and **9** are bonding between the "radical" carbon atoms, those of **7** and **10** are antibonding. Yet MINDO/3 predicts strong biradical character for both **9** and **10**, their energies being lowered very considerably by inclusion of CI, but none for **6** or **7**.

In **15**, the "unpaired" electrons can interact either directly across space or hyperconjugatively through the intervening CC bonds.[16] Any such interaction removes the degeneracy of the singly occupied AO's, ϕ_1 and ϕ_2, leading to MO's, ψ^+ and ψ^-, to each of which ϕ_1 and ϕ_2 both contribute. In ψ^+ the AO's ϕ_1 and ϕ_2 overlap in phase, and in ψ^- out of phase. The direct interaction lowers ψ^+ in energy relative to ψ^- while the indirect interaction has the opposite effect.[16] The relative magnitudes of the two effects can be altered by tilting the hydrogen atoms at the radical centers. Tilting in one direction increases the through-space interaction (see **9**) while tilting in the other direction increases the through-bond one (see **10**). Thus **9** and **10** are lumomers,[16] interconnected via a biradical (**15**) where the two interactions cancel. Both species nevertheless retain significant biradical character because in each case the dominant interaction is countered by a significant residue of the other.

The radical centers in **8** can also interact either directly across space or indirectly via bonds. The latter interaction cannot, however, involve normal hyperconjugation because there is only a single intervening carbon atom. One possible mode of interaction is by σ conjugation,[22] making use of the fact that the resonance integral between two hybrid AO's of a given carbon atom does not vanish, even though the AO's are orthogonal.[23] The resulting σ interaction between two hybrid AO's of a carbon atom in a paraffin will then couple the C–C bond MO's, just as the π interaction between the 2p AO's of two adjacent "singly bound" carbon atoms in a polyene couples two adjacent π bonds. The unit –C– in the former is thus equivalent to =C–C= in the latter.[22] Consequently the C–C–C interactions in cyclopropane lead to cyclic conjugation analogous to that in benzene,[22] while the interactions in the 1,3-trimethylene biradical, with C_1 and C_3 pyramidal, lead to linear conjugation analogous to that in hexatriene;[22] cf. **16** with **17**. The bond order between the terminal AO's in **16** is therefore positive, like that between C_1 and C_6 in **17**.[24] The through-bond σ conjugation between the unpaired electrons in **16** therefore acts in phase with any through-space interaction, both combining to bring about stabilization and leading to a HOMO that is symmetrical with respect to reflection in a plane of symmetry bisecting the line joining the radical centers. Thus **8** can be stabilized by three distinct interactions, two involving σ conjugation (via $C_2C_1C_4$ or $C_2C_3C_4$) and one across space. Here, however, in contrast to **15**, all three interactions act in concert. It is therefore not surprising that the resulting stabilization leads to a closed shell system (**6**) with essentially no biradical character. The geometry of **6** is determined by the through-space interaction, the through-bond ones requiring only that the "singly occupied" AO's be hybridized.

This discussion accounts for the stability of **6** at the expense of apparently leaving **7** in the lurch. The existence of this second "nonclassical" species can be attributed to an alternative mode of interaction between the "singly occupied" AO's in **8**, this time by a π interaction with the central atoms. The bending of the central bond in bicyclobutane (see **18**) makes such a π interaction with the 2p AO's of C_1 and C_3 possible. The resulting system

(21) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 5069.

(22) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957.

(23) The resonance integral between two hybrid AO's of a given atom vanishes only if the components (s, p, d, etc.) have identical valence state ionization potentials. This is not the case. For example, the valence state ionization potential for the 2s AO in sp³ carbon is greater by 9.7 eV than that for 2p: Hinze, J.; Jaffé, H. H. *J. Am. Chem. Soc.* **1962**, *84*, 540.

(24) For two recent examples, see: (a) Meersche, M. V.; Germain, G.; Declerg, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3370. (b) Washburn, W. N.; Zahler, R.; Chen, I. *Ibid.* **1978**, *100*, 5863.
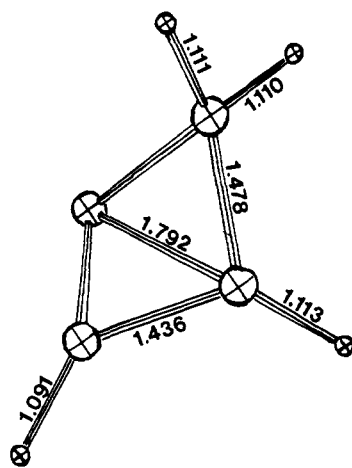
Chart II

is then isoconjugate with bicyclobutadiene (**19**) and can indeed be derived from it by breaking the central (C_1C_3) σ bond and using the corresponding carbon AO's to form CH bonds. Since the HOMO of **19** consists of an antibonding combination $(1/\sqrt{2})(\phi_2 - \phi_4)$ of the 2p AO's of atoms C_2 and C_4, there is clearly a complete parallel between it and **7**. The necessary π interactions will be accentuated by flattening the molecule. The geometry calculated for **7** (Figure 3b) indeed shows it to be almost planar.

This structure can also be regarded as a possible tautomeric form of cyclobutadiene (**1**). Square cyclobutadiene has a degenerate HOMO. The two corresponding π MO's can be represented in a variety of equivalent ways. One of these is indicated in **20** and **21**. A closed shell configuration in which one of these is populated will distort into a rectangle. This is what happens in the ground state of **1**. The degenerate π MO's can, however, be represented equivalently as in **22** (π_1) and **23** (π_2). Population of π_1 will lead to an antibonding interaction between C_2 and C_4. Since the lower filled π MO in **1** is bonding between all pairs of atoms and since π_1 is nonbonding between C_1 and C_3, the net interaction between C_1 and C_3 will be bonding. This configuration of **1** will then adopt a lozenge-shaped geometry, the C_1C_3 distance decreasing and C_2C_4 increasing. Since the C_1C_3 interaction will be favored by hybridization of the 2p AO's of C_1 and C_3, a further distortion into the geometry calculated for **7** would then be expected.

C. Conversion of 1 or 2 to Vinylacetylene (28) and Methylenecyclopropane (29). In our preliminary studies of the section of the C_4H_4 surface considered above, we obtained for **7** a slightly different structure of C_{2v} symmetry with one negative force constant. Later we found that the potential surface around **7** is very flat and that we had simply failed to find the true minimum. However, in our attempts to find the species whose interconversion involved "**7**" as a transition state, we located another minimum on the potential surface, corresponding to 1-bicyclobutene (**24**), whose geometry is shown in Figure 5.

The heat of formation calculated for this seemingly outrageous compound was surprisingly low, 97.1 kcal/mol, only 2.7 kcal/mol higher than that for **1**. However, recent work has shown[24] that equally unlikely-looking species can be much more stable than might have been expected on the basis of conventional ideas

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Figure 5. ORTEP plot and bond lengths (Å) for 1-bicyclobutene (**24**).

Figure 6. (a) Use of major and minor lobes of an sp^n hybrid AO for σ bonding; (b) optimum directions of σ bonds formed by sp^2 AO's of a carbon atom, two via major lobes and one via a minor lobe; (c) representation of the minor lobe/major lobe CC bond in **24**; (d) representation of the minor lobe/minor lobe CC bond in 1(3)-bicyclobutene (**45**).

concerning ring strain and directed valence, following the assumption that bonds formed by hybrid AO's involve only their main lobes. The minor lobes of hybrid AO's are, however, far from negligible and should also be effective for forming bonds.[25] The strength of a σ bond formed by a minor hybrid lobe will be greater in a direction diametrically opposite to that for a "normal" bond formed by the major lobe.

This relationship is indicated diagrammatically in Figure 6a. Here θ is the bond angle between σ bonds formed via the major lobes of two hybrid AO's, e.g., 120° for sp^2 hybrids. The optimum angle between a normal (major lobe) σ bond and a minor lobe σ bond will then be $(180° - \theta)$. Thus the optimum geometry for three σ bonds formed by a given carbon atom via sp^2 hybrid AO's, two via major lobes and one via the minor lobe, will be that indicated in Figure 6b, the minor lobe being indicated by a dotted line. The geometry of **24** is therefore much less unfavorable than it seems at first sight, C_1 being in fact unstrained although of course one of the bonds formed by it will be weaker than usual. The situation in **24** can be conveniently represented by the notation of Figure 6c, the minor lobe component of the C_1C_3 bond being indicated by replacing by dots half the full line representing the bond. On this basis one would expect the isomeric 1(3)-bicyclobutene (Figure 6d) to be *less* stable than **24**, even though its structure seems at first sight much less outrageous, because here the C_1C_3 bond is formed by minor lobes of *both* contributing AO's. As indicated in Figure 6d, this type of bond can be conveniently represented by a continuous line of dots.

This argument suggests that analogues of **24** with one or two four-membered rings may be *more* strained than **24** itself, **24** representing a secondary "island of stability" in the series of 1-bicyclo[$m.n.$0] alkenes. Similar situations may also be expected in other "one-sided" molecules where a carbon atom forms all its bonds in the same direction, i.e., all to one side of a plane passing through the carbon atom. Here again three-membered rings may prove to be unexpectedly favorable.

At this point we realized we had joined a part of the C_4H_4 potential surface studied by Shevlin et al.[26] in connection with an investigation of the reaction between carbon atoms and cyclobutenone (**26**), which, by analogy with other ketones, was expected to lead to cyclobutenylidene (**27**). The only product isolated, apart from carbon monoxide and unreacted **26**, was vinylacetylene (**28**). Shevlin et al. carried out MINDO/3 calculations for **27** and for its conversions to **1**, **28**, and methylenecyclopropene

(**29**), finding the activation energies to be 50.3, 23.6, and 42.9 kcal/mol, respectively, and so apparently accounting for the formation of **28**.

The transition state for conversion of **24** to **1** given by Shevlin et al. is also similar to ours (Figure 7a) but higher in energy by 8 kcal/mol and with a somewhat different geometry. The discrepancy is probably due to the fact that their work was carried out at a time when the McIver–Komornicki[13] procedure was not generally available for MINDO/3 calculations. Such errors can very easily arise in the location of transition states by earlier procedures, as we have ourselves found on several occasions. It cannot be too strongly emphasized that use of the McIver–Komornicki procedure is *essential* if transition states are to be located reliably. As yet no satisfactory alternative has been devised.

In view of this, we checked their calculations for the conversions of **24** to vinylacetylene (**28**) and methylenecyclopropene (**29**). A similar but smaller discrepancy appeared in the case of (**24** → **29**), our activation energy being less by 3 kcal/mol; the calculated structure for our transition state is shown in Figure 7b. In the case of **24** → **28**, the structure and energy of our transition state (Figure 7c) were almost the same as theirs; however, we found an additional minimum along the reaction path (Figure 1), corresponding to a "nonclassical" species that can be regarded as a conjugate base (**30**) of the 3-cyclopropenylmethyl cation (**31**). **31** is best represented as a π complex (Figure 8a) derived from acetylene as donor and vinyl cation as acceptor, with back-coordination,[27,28] analogous to the cyclopropylmethyl cation which is best represented as a similar π complex from ethylene and vinyl cation.[28,29] Analogy suggests that **30** should be represented likewise as a π complex (Figure 8b), a suggestion supported by the geometry and charge distribution calculated for it (Figure 8c).

We also found an alternative route from **24** to **28**, of almost as low energy ($\Delta H^{\ddagger}$, 29 vs. 24 kcal/mol) as that via **30** and

(25) The possibility of weak σ bonds being formed by pairs of atoms with the use of minor lobes of hybrid AO's has been pointed out previously in several connections; e.g., in the "claw" conformer (**25**) of the trimethylene biradical (Jean, Y.; Salem, L.; Wright, J. S.; Horsley, J. A.; Moser, C.; Stevens, R. M. *Pure Appl. Chem. Suppl.* (*23rd Congress*) **1971**, *1*, 197), *m*-benzyne (Dewar, M. J. S.; Li, W.-K. *J. Am. Chem. Soc.* **1974**, *96*, 5569), and bicyclo[1.1.1]pentane (Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773).

(26) Dyer, S. F.; Kammula, S.; Shevlin, P. B. *J. Am. Chem. Soc.* **1977**, *99*, 8104.
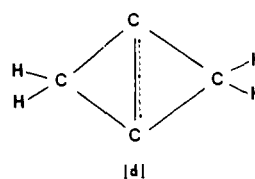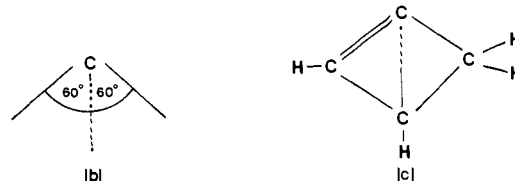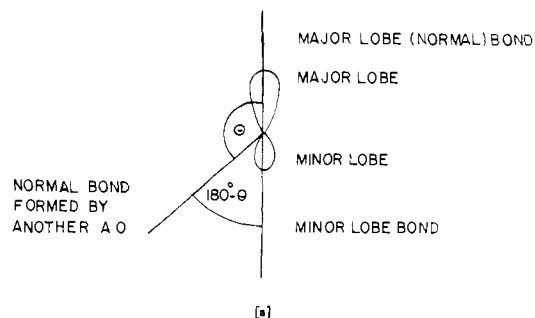
(27) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.

(28) Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321.

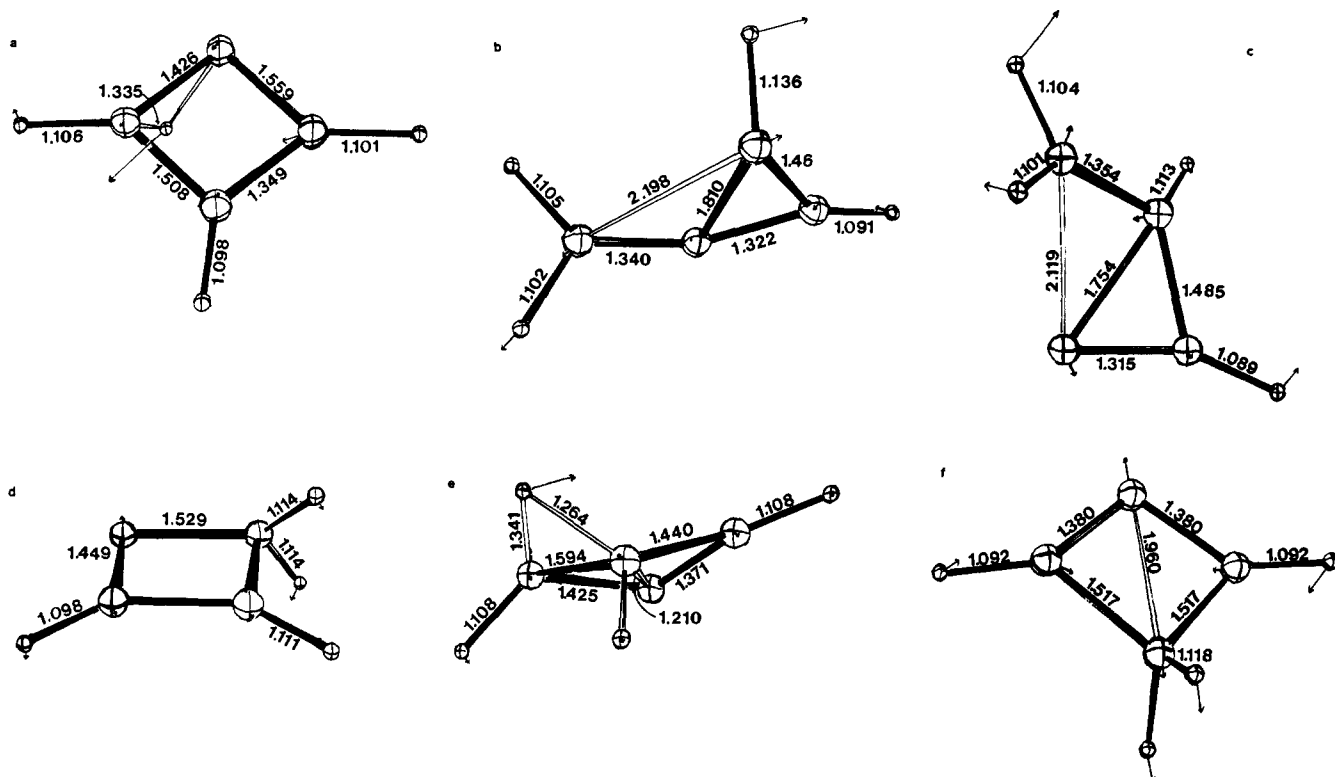(29) Dewar, M. J. S.; Haddon, R. C.; Komornicki, A.; Rzepa, H. S. *J. Am. Chem. Soc.* **1977**, *99*, 1685.

Figure 7. ORTEP plots and bond lengths (Å) for the following transition states: (a) **24 → 1**; (b) **24 → 29**; (c) **24 → 28 (30)**; (d) ring inversion in **24**; (e) **24 → 34**; (f) **34 → 33**. Arrows in the ORTEP plots indicate by direction and length the transition vector ("transition coordinate").

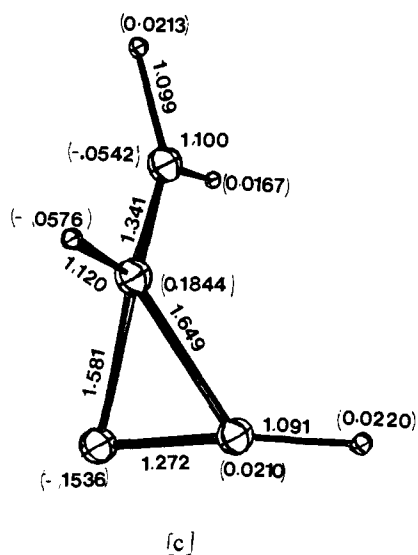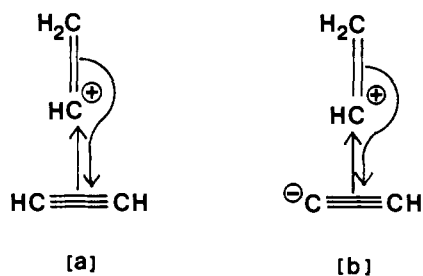**[a]**   **[b]**

[c]

Figure 8. (a,b) π-Complex representations of **31** and **30**, respectively; (c) ORTEP plot and bond lengths (Å) for **30**.

involving another C₄H₄ species (1-cyclopropenylcarbene, **32**) as a stable intermediate (Figure 1).

During our explorations of the potential surface around **24**, we encountered reaction paths for two further rearrangements.
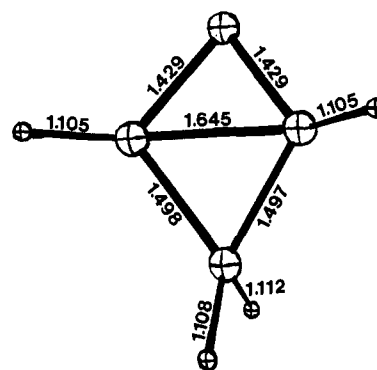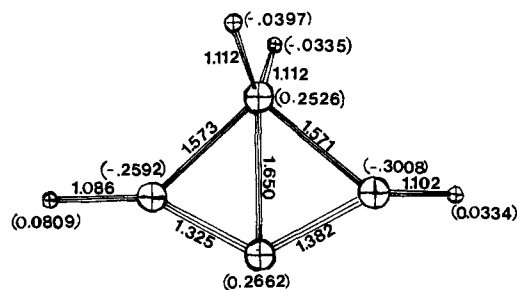

Figure 9. ORTEP plot and bond lengths (Å) for **24**.

Figure 10. ORTEP plot, bond lengths (Å), and net atomic charges for **34**.

The first involves ring inversion of **24** via a planar transition state which could be regarded as being, in effect, the carbene **27**. However, a 1,3 π interaction between the empty carbenoid 2p AO and the double bond distorts it into a lozenge shape, leading simultaneously to a negative charge on the carbenoid carbon and positive charges on the methine carbons; see Figure 7d. The calculated barrier to inversion is 16.6 kcal/mol (Figure 1).

The second rearrangement of **24** leads to bicyclobutylidene (**33**) via another "nonclassical" intermediate (**34**), the conversion of **24** to the latter being rate determining. The structures of **24** and **34** are shown in Figures 9 and 10, respectively, while Figures 7e

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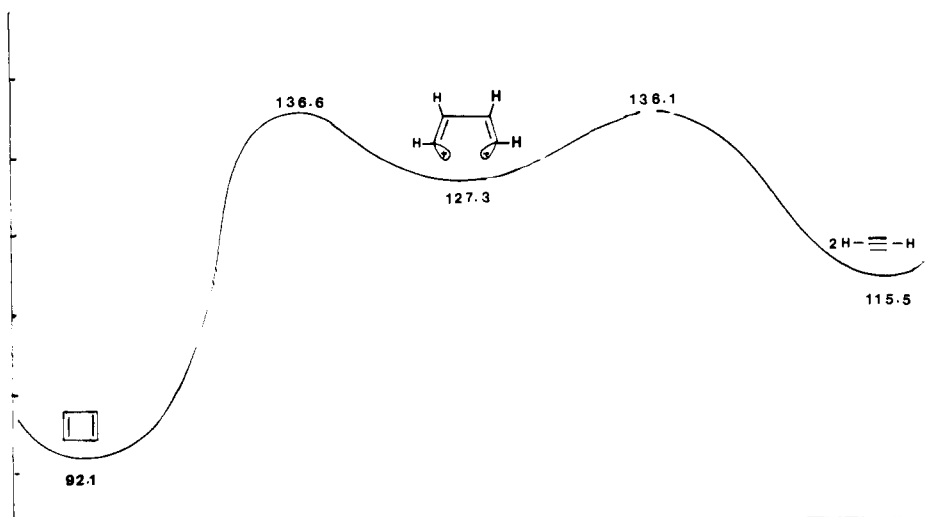*J. Am. Chem. Soc., Vol. 103, No. 18, 1981* 5299

Figure 11. Schematic representation of the MERP for conversion of cyclobutadiene (1) to acetylene (5).

and 7f show those of the two transition states.

Since the methylene carbon (C_1) in **34** is bonded to all three other carbon atoms (Figure 10), two of the CC bonds must evidently correspond to parts of a single CCC three-center bond. The observed geometry (Figure 10) is consistent with this, two of the CC bonds (C_1C_2, C_1C_4) being very long (1.57 Å). C_1 thus has sp^2 hybridization, two of the hybrid AO's being used to form bonds to hydrogen and one to C_3. The latter bond is also long, being formed by a minor lobe of an sp^2 AO of C_3. $C_2C_3C_4$ must form an allyl system, C_2 and C_4 thus having sp^2 hybridization. Two of the sp^2 hybrid AO's are used to form normal σ bonds to hydrogen and C_3 while the third takes part in the $C_2C_1C_4$ three-center bond. The resulting structure is indicated in **35**, derived from **36**. A head count of electrons indicates that there are four in the allylic π system; C_2 and C_4 should share the resulting negative charge. The three-center $C_2C_1C_6$ bond contains only two electrons; the corresponding positive charge should be shared between the three atoms. Thus C_2 and C_4 in **34** should have quite large negative formal charges and C_1 quite a large negative one, the charges on C_3 being small and positive.[29] The calculated formal charges show this pattern (Figure 10). We would also expect **34** to be planar and to have a plane of symmetry bisecting the line joining C_2 and C_4 (D_2 symmetry); this is also the case (Figure 10).

The activation energies for the four structural rearrangements of **24** to **1**, **28**, **29**, and **33** are then 42.6, 42.1, 23.9, and 41.6 kcal/mol, respectively. Shevlin et al.[26] indeed obtained **28** as the sole identifiable product from the reaction of carbon atoms with **26**.

We made a careful search of the potential surface for other rearrangements of **24** or **33** that did not involve excessively high activation energies. We found only two direct paths, leading from **33** to **6** and from **24** to **1**. The energies of the two transition states were, however, very high (Figure 1). Rearrangement of either **24** or **33** should therefore give **28**, not **1**. It therefore seems unlikely that cyclobutadiene or its derivatives will be obtained via cyclobutylidenes such as **33**. This is unfortunate, since carbenes of this type might be made in a number of possible ways, e.g., by reacting carbon atoms with cyclopropenes.

Finally, it should be noted that no biradical-like species are involved in this part of the C_4H_4 potential surface. The energies of the various species discussed above were virtually unchanged by inclusion of CI.

D. Conversion of Acetylene to Cyclobutadiene. Cyclobutane decomposes to ethylene with an activation energy of 62.5 kcal/mol.[30] From the heat of reaction (18.2 kcal/mol) one can estimate an activation energy of 44.3 kcal/mol for the reverse reaction,

Chart III
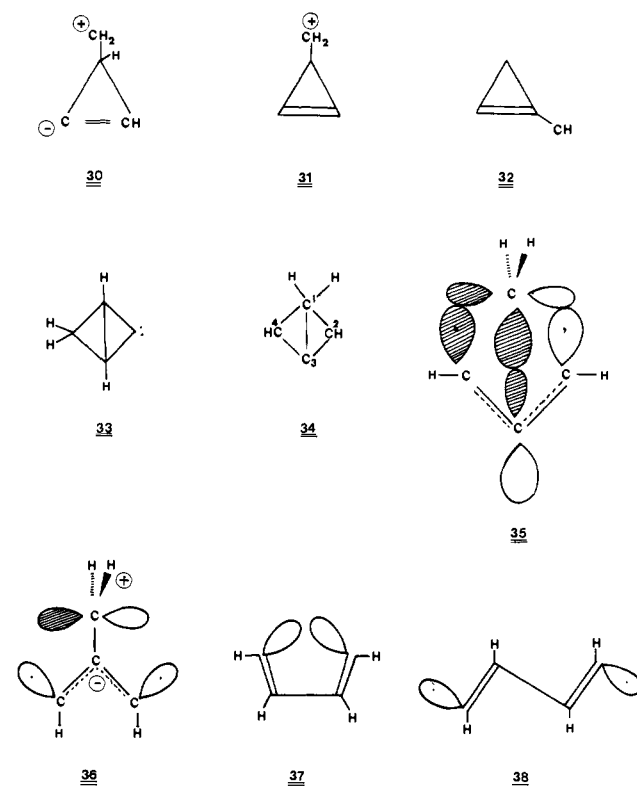
i.e., the thermal dimerization of ethylene. Since the MINDO/3 value for the activation energy for the dissociation of cyclobutane (62.0 kcal/mol[31]) agreed well with experiment and since the calculated heat of dimerization of acetylene to **1** (−21 kcal/mol; Figure 1) is close to that observed for dimerization of ethylene to cyclobutane (−18 kcal/mol[31]), it seemed likely that acetylene should dimerize to **1** with a comparable activation energy and that this could be estimated satisfactorily with the use of MINDO/3.

Reactions of this kind are "forbidden"[14-16,32] processes which take place via biradical-like species. As noted above, calculations for such reactions must be carried out with the use of some procedure to allow for the extreme correlation between the unpaired electrons. We decided to use MINDO/3/CI because this was the method used in studying the dissociation of cyclobutane.[31] Bringing the molecules together in a cis orientation and using MINDO/3 without CI, we found the calculated activation energy,

(30) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968, Section 3.10.

(31) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 5246.
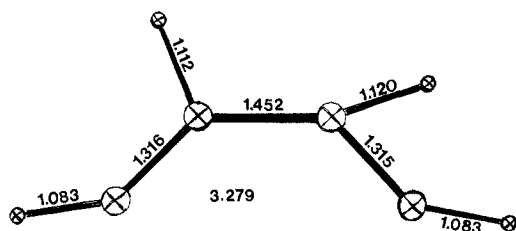(32) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 961.

Figure 12. ORTEP plot and bond lengths (Å) for the transition state for (1 → 5). Arrows indicate the transition vector.
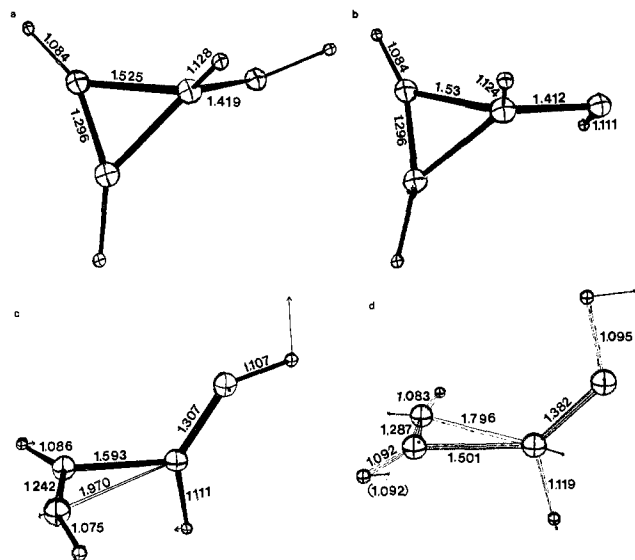

Figure 13. ORTEP plots and bond lengths (Å) for: (a) **39**; (b) **40**; and (c,d) the transition states for (5 → 39) and (5 → 40), respectively. Arrows indicate the transition vectors.

Chart IV

as expected, to be very high (75 kcal/mol). Inclusion of CI lowered this greatly, confirming the biradical nature of the reaction. The corresponding MERP is shown in Figure 11. A shallow minimum was found corresponding to a biradicaloid (**37**) whose geometry is shown in Figure 12. The rate-determining step is the formation of this biradicaloid from acetylene, the calculated heat of formation of the corresponding transition state being 136 kcal/mol. This again is a biradical-like species, the energy calculated without CI being 160 kcal/mol. Applying the rule indicated earlier, we estimate the true heat of formation to be 136 + 15 = 151 kcal/mol, corresponding to an overall activation energy of 36 kcal/mol for the direct dimerization of acetylene to cyclobutadiene.

We also found an alternative route, involving first the dimerization of acetylene to a *trans*-butadienediyl biradical (**38**), followed by cyclization to the syn (**39**) and anti (**40**) isomers of 3-cyclopropenylcarbene. In this case the biradical was not a stable species, representing only an intermediate on the way to the two transition states. The transition states were moreover "normal" species, not biradicals, because the energies calculated for them, with and without CI, were nearly the same. Therefore no corrections are needed, their heats of formation being the values calculated without CI, shown in Figure 1. The corresponding activation energies for formation of **39** and **40** were 47.1 and 34.3 kcal/mol, respectively. The geometries calculated for them are shown in Figure 13a,b and those for the transition states leading to them in Figure 13c,d.

Both **39** and **40** are easily converted to methylenecyclopropene (**29**) by 1,2-hydrogen shifts, with activation energies of 4 kcal/mol. However, **40** can also rearrange to **7**, by internal addition of the carbene center to one end of the double bond. This process is even easier than the rearrangement to **29**, the activation energy being only 2.8 kcal/mol. There is therefore an indirect path from acetylene to **1**, via **40** and **7**, formation of **40** being rate determining (Figure 1). The overall activation energy for this route is, however,
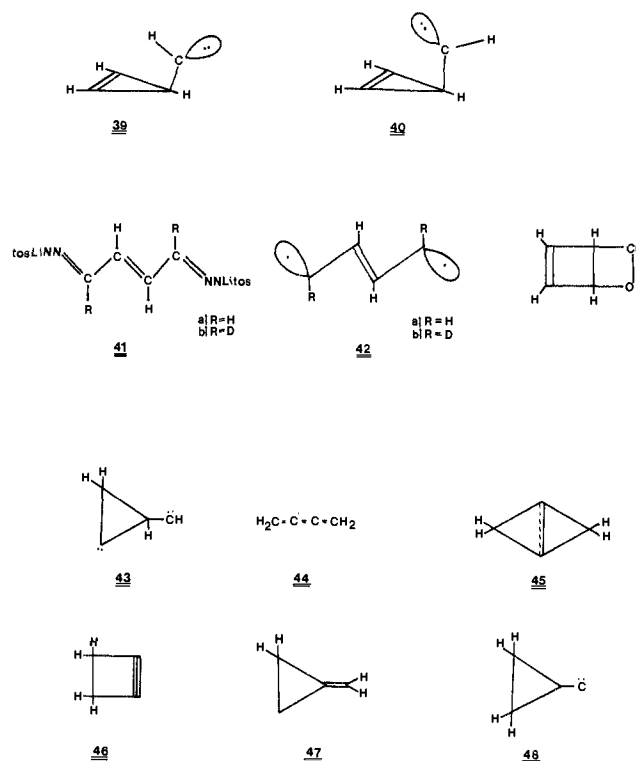
47.1 kcal/mol, much greater than that for the direct one.

We tried to find additional low-energy paths relating **39** or **40** to **1**, but without success. There is a route connecting **40** to **6**, but the activation energy was considerably greater than that for **40** → **7** (Figure 1). Furthermore, any attempt to convert **39** into **40** led to collapse into **29**. Dimerization of acetylene to **1** by this alternative route is therefore unlikely to compete with the direct one, except at low pressures where a "hot molecule" reaction could conceivably take place via **39**, **29**, and **24**.
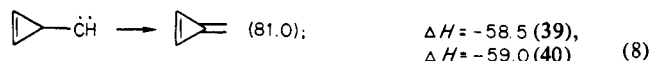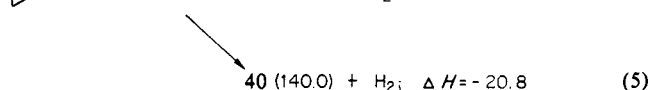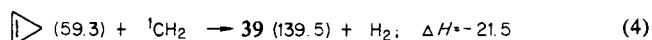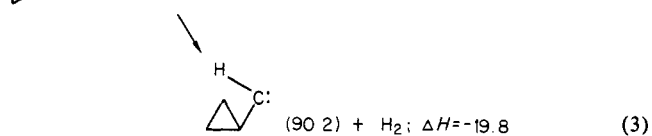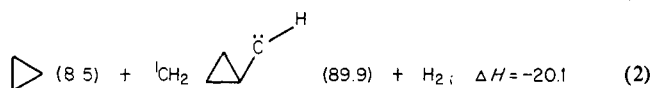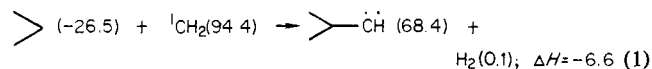
Rodewald and Lee[33] tried to synthesize **1** by pyrolysis of the dilithium derivative **41a** of fumaraldehyde bis(tosylhydrazone). They anticipated that the biscarbene **42a** would be formed and that this might be converted to **1** by a double intramolecular carbene addition, via **40**. The only product isolated was acetylene, which could have been formed by dissociation of **42a**. When, however, they repeated the experiment with the dideuterio derivative (**41b**) of **41a**, the acetylene formed contained considerable amounts of DC≡CD and HC≡CH as well as the HC≡CD that would alone be formed by fission of **42b**. Rodewald and Lee suggested that the **42b** might have undergone reversible conversion to **1**, where the hydrogen atoms are of course equivalent.

Their intermediate **42a** bears the same relationship to our trans biradical **38** that a singlet carbene bears to a triplet carbene. In **42a**, both the carbene centers are of singlet type. If they were both triplets, the electrons in the singly occupied 2p AO's of the terminal (carbene) carbon atoms would interact with the π system, leading to **38**. Since triplet carbene is lower in energy than singlet carbene and since the π interaction in the bis triplet should be strongly bonding, it is clear that **38** must be much lower in energy than **42a**. Furthermore, both species are singlets. Thus **42a** is a singlet excited form of **38** and as such should undergo conversion to **37** in <10^{-9} s. Since our calculations indicate that **38** dissociates without activation to acetylene, it is extremely unlikely that it could have been an intermediate in the system studied by Rodewald and Lee. Presumably the decomposition of **41** takes place stepwise, via a monocarbene monotosylhydrazone. Several reasonable schemes can be written for scrambling of the deuterium label by intra- or intermolecular reactions. However, since the yield of acetylene was low and the scrambling far from statistical, further

(33) Rodewald, B. R.; Lee, H. *J. Am. Chem. Soc.* 1973, *75*, 623.

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speculation seems rather pointless.

Our calculations raise a further relevant point. Alkylcarbenes are usually predicted by MINDO/3 to rearrange to olefins by 1,2-hydrogen shifts without activation. The corresponding rearrangements of **39** or **40** to **29** are, however, predicted to involve the crossing of significant barriers. Furthermore, the barrier to rotation about the C–CH: bond must be still higher because, as noted above, any attempt to interconvert **39** and **40** leads preferentially to conversion to **29**. Thus **39** and **40** must be stabilized, either by ring strain in the rearrangement or by conjugative interactions between the carbene center and the three-membered ring or between it and the double bond. To check these possibilities, we calculated heats of reaction for the following processes, the calculated heats of formation of the various species being given in parentheses (all values in kcal/mol (25 °C)):

$$\ce{>} \; (-26.5) \; + \; {}^1CH_2(94\ 4) \; \longrightarrow \; \ce{>\!-\!\overset{..}{C}H} \; (68.4) \; +$$

$$H_2(0.1); \quad \Delta H = -6.6 \quad (1)$$

Figure 14. ORTEP plot and bond lengths (Å) for **43**.

$$\ce{\triangleright} \; (8\ 5) \; + \; {}^1CH_2 \quad \triangle\!\!\!\diagup^{\ \overset{..}{C}\diagdown H} \quad (89.9) \; + \; H_2; \quad \Delta H = -20.1 \quad (2)$$

$$\triangle\!\!\!\diagup^{H\diagdown \overset{..}{C}:} \quad (90\ 2) \; + \; H_2; \quad \Delta H = -19.8 \quad (3)$$

$$\ce{[\!\!\triangleright} \; (59.3) \; + \; {}^1CH_2 \; \longrightarrow \; \mathbf{39} \; (139.5) \; + \; H_2; \quad \Delta H = -21.5 \quad (4)$$

$$\mathbf{40} \; (140.0) \; + \; H_2; \quad \Delta H = -20.8 \quad (5)$$

$$\ce{>\!-\!\overset{..}{C}H} \; \longrightarrow \; \ce{>\!=} \quad (2.5); \quad \Delta H = -65.9 \quad (6)$$

$$\ce{\triangleright\!-\!\overset{..}{C}H} \; \longrightarrow \; \ce{\triangleright\!=} \quad (33.9); \quad \Delta H = -56.0 \quad (7)$$

$$\ce{[\!\!\triangleright\!-\!\overset{..}{C}H} \; \longrightarrow \; \ce{[\!\!\triangleright\!=} \quad (81.0); \quad \Delta H = -58.5\ (\mathbf{39}), \quad \Delta H = -59.0\ (\mathbf{40}) \quad (8)$$

All four cyclic carbenes are predicted to be stabilized relative to the acyclic one by ca. 14 kcal/mol. Since the stabilization is the same for all four, it must be due to conjugative interaction with the ring. The results for the last three reactions indicate that the rearrangements of the cyclic carbenes are inhibited by ca. 8.0 kcal/mol through ring strain. The main factor in the reduced rate of isomerization of **39** is then the stabilizing interaction between the empty 2p AO of the exocyclic carbon atom and the appropriate Walsh orbital of the ring.

While the thermochemistry of **1** is still unknown, some indication is given by the work of Hedaya et al.[34] on the flash vacuum thermolysis of **1**. At temperatures up to 865 °C, with a contact time of ca. 1 ms, **1** was formed, but accompanied by increasing amounts of acetylene at the higher temperatures. The lifetime of **1** at 865 °C must therefore be somewhat less than 1 ms. If we assume the dissociation of **1** to acetylene to have a frequency factor similar to that for the analogous dissociation of cyclobutane into ethylene[30] our value for the activation energy for dissociation of **1** to acetylene leads to a rate constant of 2.5×10^4 s^{-1} at 865 °C, consistent with the results of Hedaya et al.[34] It is true that MINDO/3 predicts lower activation energies for rearrangement of **1** to **28** or **29** (45 kcal/mol). These reactions should, however, have much lower frequency factors than the dissociation into acetylene and so could well not be competitive. Furthermore, the evidence that these species were not formed was inconclusive, being based solely on measurements of ionization potentials of the effluent from the reactor by electron impact mass spectrometry.

Our calculations also provide an interesting explanation of the tendency of acetylene to detonate, as a liquid or as a gas above ca. 2 atm of pressure. According to MINDO/3, the dimerization
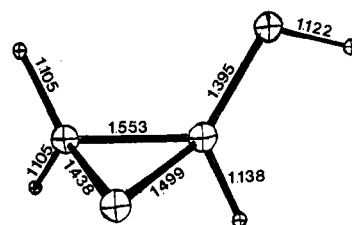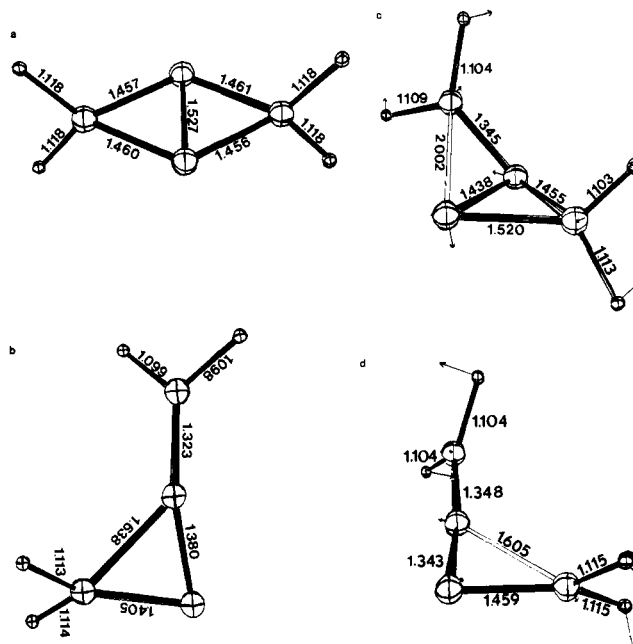

Figure 15. ORTEP plot and bond lengths (Å) for: (a) **45**; (b) **47**; and (c,d) the transition states for (**45** → **47**) and (**47** → **44**), respectively. Arrows indicate the transition vectors.

of acetylene should lead to the cyclopropenylcarbene (**39**) which should be an excellent initiator for polymerization of acetylene. However, **39** can arrange to a stable product (**29**) by a first-order reaction with a low activation energy. Initiation of polymerization involves a bimolecular reaction of **39** with acetylene, a process whose ability to compete with the rearrangement will depend on the concentration of acetylene. Above some critical pressure of acetylene, polymerization should then take over. Being very exothermic, polymerization will lead to a rapid rise in temperature which may result in detonation.

E. Other C_4H_4 Isomers. This study of the C_4H_4 system has revealed an astonishing number of stable isomers with "normal" closed shell structures, i.e., species represented by local minima on the RHF MINDO/3 potential surface. These moreover exhibit a remarkable range of types of bonding. We therefore thought it of interest to try to complete our study, identifying all the C_4H_4 isomers of reasonably low energy.

C_4H_4 isomers can be divided into four groups, depending on the number of hydrogen atoms attached to each carbon atom: (a) $(CH)_4$; (b) $(CH_2)(CH)_2(C)$; and (c) $(CH_2)_2(C)_2$. It seemed fairly certain that the work reported above had included all possible isomers of types a and b. The only additional possibilities involve three-center CHC bonds, which have never been observed or seriously postulated in any stable neutral closed shell hydrocarbon, and some dicarbenes, which are certain to have very high heats of formation. Indeed, one of these (**43**) was located as an intermediate for rearrangement of **24** to **47** (Figure 1). However, its calculated heat of formation was very high (170.0 kcal/mol). Its geometry (Figure 14) gave no indication of any unusual interaction involving, or between, the carbene centers. Type c likewise seemed limited to the well-known compound butatriene (**44**), for which MINDO/3 calculations have already been reported,[8] 1(3)-bicyclobutene (**45**), cyclobutyne (**46**), 2-methylenecyclo-

(34) Hedaya, E.; Miller, R. D.; McNeill, D. W.; D'Angelo, P. F.; Schissel, P. *J. Am. Chem. Soc.* **1969**, *91*, 1875.
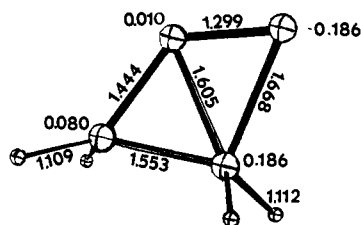
Figure 16. ORTEP plot, bond lengths (Å), and net atomic charges for **50**.

propylidene (**47**), and cyclopropylidenecarbene (**48**).

First we examined **45**. This again had a calculated geometry consistent with the expected structure (Figure 15a). Stretching one C–CH$_2$ bond led to the carbene **47** (Figure 15b) as a marginally stable intermediate which underwent a second ring opening to form **44**. The structures of the two transition states are shown in Figure 15c,d. Butatriene (**44**) is higher in enervy by 3 kcal/mol than vinylacetylene (**28**), which therefore represents the global minimum on the C$_4$H$_4$ surface. As expected, **47** undergoes a facile 1,2-hydrogen shift to form **29**. This provides a connection between **44**, **45**, **47**, and the rest of the C$_4$H$_4$ surface (Figure 1).

So far our calculations had proceeded according to our expectations. This, however, was not the case for the next isomer, **46**. No local minimum exists on the potential surface with corresponding (C_{2v}) symmetry. A geometry optimization, starting with such a structure, led instead to the completely unexpected "nonclassical" species indicated in Figure 16. This might have been difficult to interpret had we not fortunately already encountered a close analogue, i.e., **35**. As we have already noted, **35** can be represented as arising from the zwitterionic biradical **36** by formation of a three-center bond via two singly occupied sp^2 hybrid AO's of the methine carbon atoms and an empty 2p AO of the methylene group. "**46**" can be derived in a similar way from the zwitterionic biradical **49**, a prototopic tautomer of **36**,
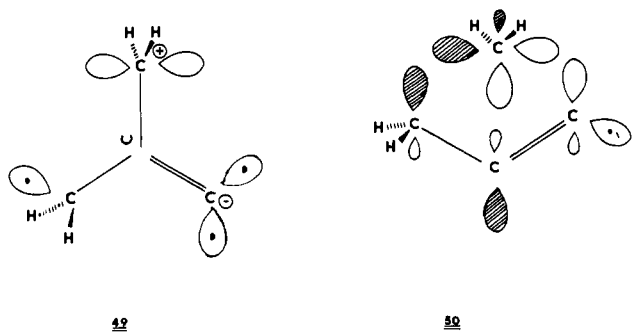
by forming a similar three-center bond, its structure being represented by **50**. On this basis, the carbon atoms should be coplanar, as indeed they are. The bond common to the two rings is long because it is formed from a minor lobe of an sp^2 AO of the bridgehead quaternary carbon atom. In this case the three-center bond is not symmetrical because one of the carbon atoms forming it is neutral, the other anionic. The former should attract more than its share of the corresponding electron pair, so the CH$_2$–CH$_2$ bond should be longer than the CH$_2$–C$^-$ bond. The calculated geometry again corresponds to this prediction. Finally, there should be a large negative charge on the C$^-$ carbon and positive charges on both methylene carbon atoms. The calculated distributions of formal charge (Figure 16) correspond to these expectations.

This curious compound is again predicted to be surprisingly stable, its heat of formation being much more negative than that of **2**. The same is true of the last C$_4$H$_4$ species, **48**, which otherwise presented no unexpected features. Interconversion of **48** and **50** is predicted to be very facile, the activation energy being 5 kcal/mol.

Three paths were found relating **50** (and hence **48**) to the rest of the C$_4$H$_4$ potential surface.

The first involved a concerted double electrocyclic ring opening to form butatriene (**44**), with an activation energy of 19 kcal/mol.

The second involved a migration of hydrogen between the bridgehead positions in **50** to form **33**. This, however, was predicted to be a very high energy process ($\Delta E^* = 69$ kcal/mol).

The third involved an alternative 1,2-hydrogen shift, from the non-bridgehead methylene to the quaternary bridgehead carbon, forming **24** via **27** by a concerted breaking of the transannular bond and formation of the alternative one. This process is also less facile than the rearrangement to **44** ($\Delta E^* = 40$ kcal/mol).

All these reactions are included in Figure 1. Note that this segment of the C$_4$H$_4$ potential surface is also free from biradical-like species. None of the heats of formation calculated for the stationary points was lowered significantly by inclusion of CI.

Cartesian coordinates for all the stationary points reported in this paper are available as Supplementary Material.

Conclusions

The calculations reported here represent the most comprehensive study so far made of the potential surface for a system of this size. We believe that we have located all local minima corresponding to normal closed shell species. While the results may prove useful as a guide in experimental studies of C$_4$H$_4$ species and their derivatives, and while they have thrown a new light on the thermal polymerization of acetylene, the main interest of this work lies in other directions.

First, this work has shown how complex and rich potential surfaces can be, even for a system as simple as C$_4$H$_4$. No less than 19 minima have been located, corresponding to closed shell molecules with no significant biradical character, and the large majority of them are moreover comparable in stability with the typical classical species, tetrahedrane and cyclobutadiene. This is a quite unexpected result, particularly since several quite stable species have very strange-looking structures, involving three-center bonds of a kind not previously encountered in any neutral hydrocarbon, or geometries which look impossibly strained, e.g., bicyclobutene. The former results suggest that an extensive "nonclassical" chemistry of neutral hydrocarbons awaits discovery, analogous to that already familiar in the boron hydrides, carboranes, and carbocations. The latter suggests the possibility of a new kind of σ bonding, involving use of the minor lobes of hybrid AO's ("minor lobe bonds"), the possible importance of which has indeed already been recognized in other connections.[25]

Second, our work emphasizes the magnitude of the task involved in attempts to predict chemical behavior by computation. The present study took a phenomenal amount of computer time. To carry it out using any adequate ab initio procedure would have been astronomically expensive.

Nevertheless, calculations by "state of the art" ab initio methods are now possible for individual molecules of this size, even with complete geometry optimization. It is also possible to trace limited reaction paths; indeed such a study of the conversion of tetrahedrane to cyclobutadiene has recently been reported.[7e,f] While the errors in the absolute energies given by procedures of this kind are still too large for the results to be reliable in any a priori sense and while such methods have as yet been little tested by calculations for other than stable "classical" molecules, there is reason to believe that they may also give good estimates of the energies of "nonclassical" species and transition states. Calculations for the various novel species reported here, and for the transition states for their interconversion, should then provide a valuable check on the accuracy of MINDO/3 in these connections.

It should be emphasized again that ab initio calculations (by the Roothaan–Hall SCF method) can be useful for this purpose *only* if carried out with the use of large basis sets, at least of double-ζ type, and if allowance is made for electron correlation by inclusion of very extensive CI or some comparable procedure (e.g., CEPA). It has now been well-established that ab initio SCF calculations, using small basis sets (e.g., STO-3G, 4-31G), with or without CI, are in general *less* accurate and *less* reliable for the calculation of molecular energies than MINDO/3 or MNDO. Any differences between the results given by such simple ab initio procedures and those given by MINDO/3 or MNDO are therefore more likely to reflect errors in the former than in the latter. These

The Nature of Organosilane to Silica-Surface Bonding

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Abstract: Experimental evidence has been acquired leading to proposals concerning the nature of organosilane to silica-surface bonding. The yellow Schiff's base formed by reacting salicylaldehyde with (aminopropyl)silanes either in solution or on a silica surface has provided a means of measuring the relative stability of these silanes bonded to the surface. Studies of the effect of oven curing on silane-to-surface bonding stability and investigations into the rate of silane removal from the surface in ethanol have provided novel bonding information. Copper(II) ion uptake capacity studies on a series of (aminopropyl)silanes and trimethylsilyl chloride uptake experiments on the series $(CH_3O)_nSi(CH_3)_{4-n}$ ($n = 1-3$) complement the above experiments and suggest the bonding models proposed in this paper.

The numerous applications to chemistry of oxide-immobilized organosilanes are of unquestionable importance. Preconcentration of trace metals using chelating groups immobilized via silylation,[1,2] silica gel as a support for phase-transfer catalysis,[3] chemically modified electrodes,[4] immobilized enzymes,[5] and metal ion chromatography[6] are only some of the applications appearing in the recent literature. The vitality of interest in immobilized organosilanes is further illustrated by a recent symposium on silylated surfaces.[7] The literature on silica and on silane–silica interactions is vast and reflects the versatility that can be obtained by manipulation of the initial nature of the silica and of the silylation reaction conditions. This versatility has led to much confusion but also to many opportunities to create designed silane–silica structures. A number of useful spectroscopic and chemical tools have developed[8-13] to study the silane–silica interface. However, many relevant details remain speculative for thin silane coatings, such as the role of siloxane oligomerization and the number of covalent bonds to the surface. The results and methodology of our experiments is one approach to attempt to clarify important points related to these issues.

Experimental Section

Preparation of Silica-Immobilized (Aminopropyl)silanes. A 3.01-g sample of oven-dried Baker silica gel (60–200 mesh, 300 m²/g) was slurried in 20 mL of 10% (v/v) silane ((3-aminopropyl)triethoxysilane, (3-aminopropyl)methyldiethoxysilane, or (3-aminopropyl)dimethylethoxysilane) in dry toluene. The reaction mixture was stirred frequently at room temperature for 30 min, filtered, and washed exhaustively with toluene. The air-dried solid silica product (**1**, **2** or **3**) turned bright yellow upon treatment with 0.5 mL of ethanol and 1 drop of salicylaldehyde. Percent carbon determination (Huffman Laboratories, Wheatridge, CO): **1** = 3.61%, **2** = 3.91%, **3** = 5.54%, all blank corrected for a blank equal to 0.71%.

The silica–silanes **1**, **2**, and **3** were similarly prepared from 5.00 g of Baker silica gel and 20 mL of 1% (v/v) silane in dry toluene.

Effect of Oven Curing on the Silane-to-Surface Bonding Stability. (Aminopropyl)silanes **1**, **2**, and **3** (from 10% solutions) were each divided into six 0.100-g samples to be oven cured at 80 °C for 0, 1, 3, 6, 12, and 20 h. At the appropriate time, each of these samples, in a test tube, was treated with 5.0 mL of 0.1% salicylaldehyde (excess) in ethanol. After

30 min of occasional stirring, the absorption spectrum (Cary 14) of the supernatant was taken noting the absorbance at λ_{max} 404 nm (salicylaldimine).

(Aminopropyl)silanes **1**, **2**, and **3** (from 1% solutions) were each divided into three 1.01-g samples to be oven cured at 80 °C for 0, 1 and 3. At the appropriate time, each of these samples, in a test tube, was treated with 10.0 mL of 0.1% salicylaldehyde (excess) in ethanol. After 30 min of occasional stirring, the absorption spectrum of the supernatant was taken.

Kinetic Studies. Uncured 2.00-g samples of silica–silanes **1**, **2**, and **3** (from 10% solutions) were slurried in 100.00 mL of absolute ethanol. From slurries **1** and **2**, 3 mL aliquots were removed after 1 h, 4.5 h, 25 h, 3 days, and 6 days. Five drops of 1% salicylaldehyde (excess) was added to the cuvette and after 3–4 min the absorption spectra were recorded, noting the absorbance at λ_{max} = 404 nm. From slurry **3**, 1-mL aliquots were removed at the indicated time, diluted to 3 mL with ethanol, and mixed with 5 drops of 1% salicylaldehyde. After 3–4 min, the absorption spectra were recorded.

Copper(II) Capacity Studies. Approximately 0.2 g (accurately weighed) of silanes **1**, **2**, or **3** were dry packed into a stainless-steel chromatographic column. A microprocessor-controlled ALTEX high-performance liquid chromatograph 110A pump as utilized for cycling studies to determine copper capacity. A switching valve, before the pump, allowed water, acetate buffer at pH 5, 10^{-2} M copper(II) at pH 5, water, and nitric acid at pH 2 to be pumped through the column to

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