1810–1880 cm^{-1} and 1510–1550 cm^{-1}. Although a detailed analysis has not yet been performed, it has been suggested that these absorptions originate from strong coupling of the double bonds. The infrared spectrum of methylenecyclopropene itself was obtained by slowly introducing the hydrocarbon and argon onto a polished copper surface cooled to 15 K with a closed-cycle helium refrigerator. The spectrum (Figure 2) was recorded on an IBM Model 98 FT IR spectrometer. Although several impurity peaks including those of isobutylene[6] could be subtracted, we are still unable to associate the weak absorptions with methylenecyclopropene. Concentration studies did, however, show that the five strongest peaks of the spectrum arise from methylenecyclopropene.[7] It is interesting that the high-energy transition of methylenecyclopropene is shifted to 1770.3 cm^{-1}, which is also consistent with the dipolar structure (enhanced single-bond character) **1a**.

The mass spectrum of methylenecyclopropene (20 eV) shows a parent molecular ion (also base peak) at m/e 52; high-resolution mass spectrum, m/e calculated for C_4H_4 52.0313, found 52.0312.

Finally, quantities of this heretofore inaccessible hydrocarbon are now available for additional studies of its properties, many of which have already been anticipated by theoreticians.[2] These studies will be reported later.

Acknowledgment. We gratefully acknowledge The Robert A. Welch Foundation (Grant C-490) for support of this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge many stimulating discussions with Professor S. Staley who has independently synthesized methylenecyclopropene.

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[7] We thank Drs. Robert Hauge, Zakya Kafafi, and Judy Chu for assistance in securing this spectrum.

Synthesis and Direct Observation of Methylenecyclopropene

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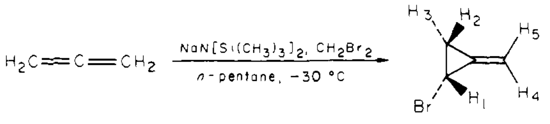
Methylenecyclopropene (**1**) occupies a central position in organic structural chemistry as the simplest member of a family of cross-conjugated nonalternant hydrocarbons known as the fulvenes.[1] Both the exceptional polarity of the π system expected from this structural arrangement (**1** ↔ **1a**) as well as the high strain imparted by the three-membered ring, which raises the energies of the σ orbitals and lowers those of the σ* orbitals, are expected to have unusual chemical and spectroscopic consequences. We now report the synthesis and direct observation of this molecule, which had previously only been trapped in situ.[2]

1 **1a**

The immediate precursor for **1** was 2-bromomethylenecyclopropane (**2**), prepared by the addition of bromocarbene[3] to allene.



2

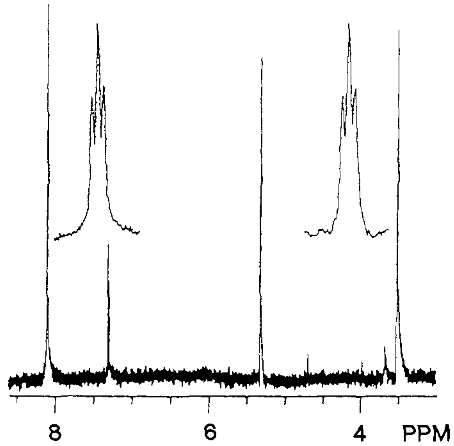


Figure 1. 360-MHz ^1H NMR spectrum of methylenecyclopropene in CD_2Cl_2 at −90 °C. The apparent triplets shown at the top are expansions of the peaks at δ 3.60 and 8.18. The peak at δ 5.41 is the solvent ($CHDCl_2$); the smaller signal at δ 7.4 is unidentified.

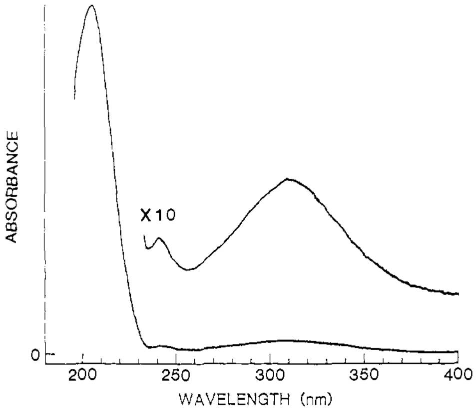
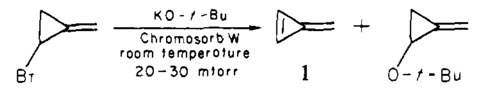


Figure 2. Ultraviolet spectrum of methylenecyclopropene in *n*-pentane at −78 °C.

The 360-MHz NMR of **2** (purified by gas chromatography on a 10% Carbowax 20M on Chromosorb W column at 90 °C) in $CDCl_3$ was reproduced by computer synthesis with the following parameters: δ 3.51 (H_1), 1.84 (H_2), 1.49 (H_3), 5.81 (H_4), 5.64 (H_5), J_{12} = 8.02, J_{13} = 3.81, J_{14} = 0.90, J_{15} = 1.56, J_{23} = 10.85, J_{24} = J_{34} = 2.86, J_{25} = J_{35} = 2.14, J_{45} < 0.6 Hz.

When **2** was passed through a horizontal half-filled 1.0 cm i.d. × 35 cm column of potassium *tert*-butoxide on Chromosorb W at room temperature and 20–30 mtorr,[4] unchanged **2** and 2-*tert*-butyoxymethylenecyclopropane (**3**)[2b] were trapped at −78 °C whereas methylenecyclopropene (**1**) was trapped as a white solid in a second trap cooled with liquid nitrogen. It has proven difficult to perform this reaction so as to produce more than several milligrams of **1**. Treatment of **2**-*2-d* under these conditions afforded **1**, which displayed a ^1H NMR spectrum (see below) that was identical with that of **1** generated from unlabeled **2**. This is consistent with H/D exchange occurring at the ring carbons in **1** under the conditions of this reaction.



2 **1** **3**

The 360-MHz ^1H NMR spectrum of **1** in CD_2Cl_2 at −90 °C (Figure 1) displayed two equivalent apparent triplets (line separation = 2.2 Hz) at δ 3.60 (exocyclic protons) and 8.18 (ring protons). It is clear that this spectrum displays evidence for a significant contribution from resonance form **1a**. We believe that hydrogen bonding is also important, as evidenced by an interesting

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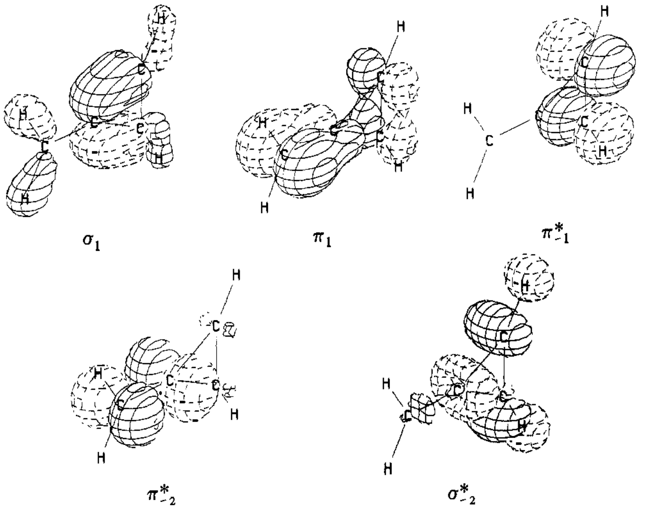
solvent dependence (e.g., δ 3.53 and 8.88 in ammonia-d_3 at −70 °C) which is currently under further investigation.

The ultraviolet (UV) spectrum of **1** in *n*-pentane at −78 °C (Figure 2) displays a broad low-intensity band at 309 nm, a more narrow low-intensity band at 242 nm, and a strong band at 206 nm. All bands disappear at the same rate when the sample is warmed. The long-wavelength band is identified with a $^1B_2$ ($\pi_1 \rightarrow \pi^*_{-1}$, internal charge transfer) transition on the basis of its strong solvent dependence (276 nm in methanol −78 °C) and INDO/S-CI calculations.[5] These calculations, along with the relative intensity (ϵ is estimated to be >3000) and the small solvent dependence (210 nm in methanol), identify the 206-nm band as arising from a $^1A_1$ ($\pi_1 \rightarrow \pi^*_{-2}$) transition. Finally, the approximate relative areas (1.5:0.01:0.2) and energies (6.02, 5.12, and 4.01 eV) of the three UV bands in Figure 2 agree reasonably well with those theoretically predicted[5] (0.62:0.01:0.05 and 6.22, 5.59, and 4.54 eV, respectively) if the small middle band (which is centered at 248 nm in methanol) arises from a $^1B_1$ ($\pi_1 \rightarrow \sigma^*_{-2}$) transition. A second $^1B_1$ transition ($\sigma_1 \rightarrow \pi^*_{-1}$) is also theoretically predicted but is probably obscured by the long-wavelength tail of the 206-nm band.



The most stable form of $C_4H_4^{+\cdot}$ has been considered to be the radical cation of **1**.[6] We have determined that the collision-induced dissociation (CID) spectrum (70 eV, EI) of the *m/z* 52 peak from **1** (*m/z* (relative intensity): 39 (15), 38 (77), 37 (100), 36 (31), 27 (27), 26 (99), 25 (31), 24 (7)) is essentially identical with those obtained for the corresponding ions obtained from benzene and pyridine.[7]

As expected, methylenecyclopropene is a highly reactive compound. On warming, solid samples of **1** (trapped at −196 °C) polymerize to a sparsely soluble white or light yellow film which displays ^1H NMR peaks at δ 7.28, 1.10, and 0.05 in 10% acetone-d_6/CS_2. Dilute solutions of **1** in pentane show a half-life of approximately 20 h at −78 °C as determined by monitoring the ultraviolet spectrum.

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Registry No. 2, 90246-24-5; **3**, 23230-90-2; allene, 463-49-0; bromocarbene, 17141-28-5; methylenecyclopropene **1**, 4095-06-1.

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Experimental Evidence for a C_{2v} ($^2B_1$) Ground-State Structure of the Methane Cation Radical: ESR and ab Initio CI Investigations of CH_4^+ and $CD_2H_2^+$ in Neon Matrices at 4 K

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The electronic ground state and structure of the fundamentally important CH_4^+ cation radical has not been previously established by experiment. Neon matrix ESR results combined with ab initio CI spin-density calculations are presented which provide the first direct experimental evidence for a C_{2v} ($^2B_1$) ground-state assignment. Extremely interesting H/D isotope effects were also observed in this preliminary study. The properties of CH_4^+ are important for several reasons. Its potential significance as an interstellar species and its possible involvement in chemical evolution preceeding the origins of life have been discussed.[1] The early planetary atmosphere presumably contained large quantities of methane, and CH_4^+ is known to be a highly reactive and major radiation product of CH_4. Molecular ions in general are difficult to study experimentally and the short lifetime of CH_4^+ has hindered efforts to obtain direct spectroscopic measurements in the gas phase.[1]

Numerous theoretical studies concerning the equilibrium structure and Jahn–Teller distortion have been reported over the last 20 years that have predicted differing ground-state assignments.[1-9] More recent and extensive theoretical calculations indicate a C_{2v} ($^2B_1$) ground state, which conflicts with earlier theoretical conclusions used to interpret details of photoelectron results.[5,7-9] A recent summary of the photoelectron data has questioned the suggested D_{2d} ground-state assignment.[10] Although valuable information for large alkane cations trapped in matrices such as CCl_3F and SF_6 has been obtained by ESR,[11-13] the failure to detect CH_4^+ by such methods has recently been cited by Symons.[14]

The three independent ion generation methods employed in the experiments were open-tube neon discharge photoionization at 17 eV, electron bombardment, and high-energy neutral-atom bombardment of the neon matrix gas doped with approximately 0.1% CH_4. These generation methods and experimental details of trapping small cation radicals in neon matrices at 4 K have been discussed in recent reports on CO^+,[15] H_2O^+,[16] N_2^+,[17] and

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