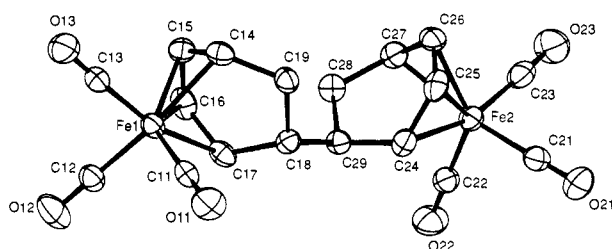**Figure 1.** IR spectral changes accompanying near-UV irradiation of 2 mM (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ in a CO-saturated toluene solution at 298 K. The negative peaks indicate the consumption of starting material, while the positive peaks at 2040, 1971 cm^{-1} correspond to formation of (η^4-C,C'-(cyclohexadiene)$_2$)Fe$_2$(CO)$_6$ (eq 1).

Figure 2. ORTEP diagram of isomer A of eq 1, showing the atom labeling scheme and 40% probability ellipsoids. Selected bond distances (Å): Fe1–C11 = 1.795 (6); Fe1–C12 = 1.786 (6); Fe1–C13 = 1.780 (7); Fe1–C14 = 2.109 (5); Fe1–C15 = 2.033 (6); Fe1–C16 = 2.057 (6); Fe1–C17 = 2.134 (6); C11–O11 = 1.125 (7); C12–O12 = 1.144 (6); C13–O13 = 1.148 (7); C14–C15 = 1.414 (8); C14–C19 = 1.517 (8); C15–C16 = 1.400 (8); C16–C17 = 1.411 (8); C17–C18 = 1.528 (7); C18–C19 = 1.534 (7); C18–C29 = 1.542 (7). The dihedral angle between the C24–C25–C26–C27 plane and the C24–C29–C28–C27 plane is 37.91°.

Scheme I summarizes our current understanding of the chemistry reported here. The ring–ring coupling products signal radical character in the hydrocarbon ligand of the "19e$^-$" (cyclohexadienyl)Fe(CO)$_2$L species. The lack of ring–ring coupled products from other (cyclodienyl)Fe(CO)$_2$L systems studied[1,2] presumably stems from the fact that these species are mainly Fe-centered radicals. Further studies are in progress to establish factors controlling whether 19e$^-$ radicals are metal- or ligand-centered, because it is appreciated that the coupling chemistry does not necessarily characterize the electron distribution of the radicals.[3e,f]

Supplementary Material Available: Listing of experimental details of the X-ray study of Fe$_2$(CO)$_6$(C$_{12}$H$_{14}$), final positional parameters, thermal parameters, interatomic distances, and angles (10 pages). Ordering information is given on any current masthead page.

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The Tetramethyleneethane Radical Cation. An ESR and ENDOR Study[1]

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Tetramethyleneethane (**1**) is an intriguing alternant π-system of eight carbon centers for which a Kekulé formula with less than two unpaired electrons cannot be drawn.[2] The radical anion **1**$^{\cdot-}$
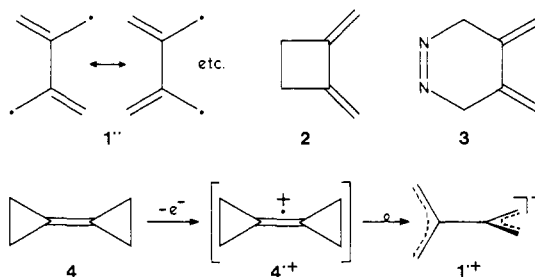
was prepared from 1,2-dimethylenebutane (**2**) in liquid ammonia some time ago.[3] More recently, an ESR study of the neutral **1**, using the azo precursor **3**, has clearly established that this molecule is a ground-state triplet (**1**$^{\cdot\cdot}$).[2] Here, we report on the still missing third member of the series, the radical cation **1**$^{\cdot+}$, which is obtained by opening of the two rings in the radical cation of bicyclopropylidene (**4**).[4]

Upon γ-irradiation of **4** in a CF$_3$CCl$_3$ matrix at 77 K,[5] an ESR spectrum was observed which consisted of nine broad hyperfine components spaced by ca. 0.75 mT ($g = 2.0029 \pm 0.0002$). Figure 1 shows this spectrum taken at a higher temperature, 140 K, required to achieve a better resolution. Additional information was provided by ENDOR spectroscopy, of which the use for radical cations in freon matrices has recently been initiated by the Basel research group.[1] In the present study, the corresponding proton ENDOR spectrum exhibited two essentially isotropic signals at 25.83 and 24.58 MHz, i.e., at positions given by $\nu_H + |a/2|$, where ν_H and $a/2$ stand for the free proton frequency (14.56 MHz) and half the coupling constant (in MHz), respectively.[6] These signals are reproduced at the top of Figure 1; their low-frequency counterparts, positioned at $\nu_H - |a/2|$, were too weak to be detected in our ENDOR experiment.

The ESR and ENDOR spectra are readily analyzed in terms of two isotropic coupling constants of 0.805 ± 0.010 and 0.716 ± 0.010 mT, each due to a set of four equivalent protons. These hyperfine data cannot be attributed to the primary radical cation **4**$^{\cdot+}$ which represents a tetraalkyl-substituted ethene that is ionized by an electron removal from the π-system of the double bond.[7]

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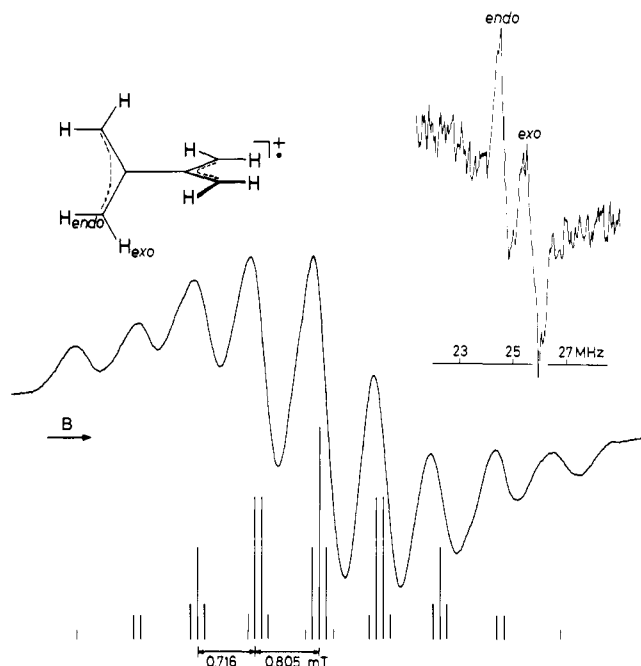
Figure 1. Center: ESR spectrum of **1**[•+] in a CF_3CCl_3 matrix at 140 K. Top, right: proton ENDOR signals observed above the free proton frequency under the same conditions. Bottom: stick diagram of the ESR spectrum.

Considering the coupling constant of 1.72 mT for the 12 equivalent β-protons in the radical cation of tetramethylethene[8] and taking into account the $\cos^2 \theta$ dependence of such values,[9] a hyperfine splitting as large as 2.5–3.0 mT is expected for the eight β-protons in **4**[•+]. On the other hand, the observed hyperfine data compare well with the halved coupling constants of the two exo (1.481 mT/2 = 0.741 mT) and the two endo protons (1.390 mT/2 = 0.695 mT) in the allyl radical.[10] This similarity strongly suggests that the ESR and ENDOR spectra in Figure 1 should be ascribed to the radical cation of tetramethyleneethane (**1**) which is a positively charged 2,2′-biallyl. We therefore assign the coupling constant of 0.805 mT to the four equivalent exo protons and that of 0.716 mT to the four likewise equivalent endo protons in **1**[•+]; both values are undoubtedly negative. The increase in the hyperfine splittings on going from a "neutral double allyl" (average 0.713 mT) to **1**[•+] (average 0.761 mT) is in line with the charge dependence of the α-proton coupling constants.[11] It is noteworthy that the difference between the coupling constants of the exo and the endo protons could not be determined for the anion **1**[•−] and the neutral **1**[••], as no use was made of the ENDOR technique in those studies.[2,3]

The arguments presented above in favor of **1**[•+] are corroborated by INDO calculations.[12] As anticipated, the singly occupied orbital of **1**[•+] is a linear combination of two nonbonding allyl MO's, and it thus exhibits squared LCAO coefficients of 0.25 at the four methylene carbon atoms. The calculated coupling constants are −0.793 and −0.735 mT for the four exo and the four endo protons, respectively.

The conversion of the initially formed **4**[•+] into **1**[•+] implies opening of both cyclopropylidene rings which is likely to occur stepwise. According to recent ab initio calculations,[13] ring opening in the radical cation of methylenecyclopropane is exothermic and

requires an activation energy of only 8 kJ/mol. This reaction, which yields the radical cation of trimethylenemethane, is fully analogous to that converting one ring in **4**[•+] to an allyl moiety in **1**[•+]. However, a simultaneous opening of the two rings in **4**[•+] cannot be excluded without further experimental and/or theoretical evidence.

In the formulas drawn in this paper and in the INDO calculations of the coupling constants, we have assumed that the two allyl moieties in **1**[•+] are rotated by an angle ϕ of 90° about the essential single bond linking them. For the ground-state triplet **1**[••], such a geometry is indicated by the absence of splitting between the *x* and *y* components in the ESR spectrum.[2] Moreover, in both INDO and AM1-UHF[14] approximations, a planar radical cation **1**[•+] ($\phi = 0°$) has higher energy than that with $\phi = 90°$. Whereas for ϕ of either 0° or 90° the unpaired electron should be delocalized over both allyl moieties, localization on one moiety is predicted for an intermediate angle ϕ (ca. 45°). In this context, we note that the intensities and shape of some hyperfine components in the ESR spectrum of **1**[•+] deviate significantly from those expected for an interaction with two sets of four equivalent protons (c.f. stick diagram in Figure 1). These deviations will be considered in a paper on structurally related radical cations.[15]

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p-Quinone Methide Initiated Cyclization Reactions

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Quinone methides are believed to play an important role in biosynthesis[1] and in the biological activity of many quinonoid antitumor compounds.[2,3] In spite of the major role these compounds are proposed to play in nature, the synthetic applications of quinone methides have been limited primarily to the use of in situ generated *o*-quinone methides as heterodienes in Diels–Alder reactions.[4,5] The use of *p*-quinone methides as synthetic inter-

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