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On the Structure of Cyclopropylcarbinyl and Cyclobutyl Cations. The 2,8-Dimethyl-8,9-dehydro-2-adamantyl and 4-Phenyl-2,5-dehydro-4-protoadamantyl Cations[1]

Roger K. Murray, Jr.,*[2,3] Thomas M. Ford,[2] G. K. Surya Prakash,[4] and George A. Olah*[4]

Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711, and the Institute of Hydrocarbon Chemistry, University of Southern California, Los Angeles, California 90007.
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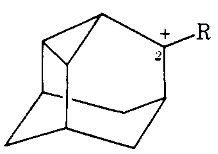
Abstract: The 2,8-dimethyl-8,9-dehydro-2-adamantyl cation (**7**) and the 4-phenyl-2,5-dehydro-4-protoadamantyl cation (**12**) have been prepared under stable ion conditions from the corresponding alcohols. The ^{1}H and ^{13}C NMR spectra of **7** show that, although it is static at −128 °C, upon warming to −26 °C it undergoes a degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement which apparently proceeds either by way of the 3,5-dimethyl-2,5-dehydro-4-protoadamantyl cation (**8**) or via the degenerate 2,3-dimethyl-2,5-dehydro-4-protoadamantyl cation (**9**) and the 8,9-dimethyl-8,9-dehydro-2-adamantyl cation (**10**). The ^{13}C NMR spectra of **12** indicate that, while it is static at −135 °C, upon warming to −40 °C it undergoes a threefold degenerate cyclobutyl–cyclobutyl rearrangement. This process seems to occur via the 1-phenyl-8,9-dehydro-2-adamantyl cation (**13**). From the temperature-dependent NMR behavior of **7** and **12**, an approximate energy barrier of $\Delta G^{\ddagger} = 7.4 \pm 0.5$ kcal/mol can be calculated for **7** → **8** or **9** or **10** and $\Delta G^{\ddagger} = 6.9 \pm 0.5$ kcal/mol for **12** → **13**.

Introduction

The rapid interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in carbocationic reactions has attracted considerable attention.[5] Several reports have appeared concerning the direct observation by NMR spectroscopy of a series of cyclopropylcarbinyl cations under stable ion conditions.[6] This work has also been extended to the study of cyclopropylcarbinyl cations with rigid carbon skeletons.[7] The parent 8,9-dehydro-2-adamantyl cation (**1**, R = H) has been shown by NMR spectroscopy to be a carbenium ion that is undergoing a threefold degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement which is fast on the NMR time scale at −120 °C.[7a] This rearrangement is believed to proceed via the 2,5-dehydro-4-protoadamantyl cation (**2**, R = H). Introduction of an electron-releasing substituent at C-2 in **1** significantly increases the energy barrier for this process. Thus, cations **1**, R = CH_3, C_6H_5, and c-C_3H_5, all have been demonstrated by NMR spectroscopy to be static carbocations with varying degrees of charge delocalization into the rigid cyclopropane ring.[7a] On the other hand, three precursors which potentially could have afforded the 1-methyl-8,9-dehydro-2-adamantyl cation (**3**) were shown by NMR spectroscopy to give under stable ion conditions the 4-methyl-2,5-dehydro-4-protoadamantyl cation (**2**, R = CH_3) which undergoes a threefold degenerate cyclobutyl–cyclobutyl rearrangement that is fast on the NMR time scale even at −120 °C.[7a] It is proposed that this rearrangement occurs via **3**. We now wish to report the preparation and temperature-dependent behavior of suitably substituted derivatives of **1** and **2** which permit an experimental determination of the approximate energy barriers for **1** → **2** and **2** → **1**.



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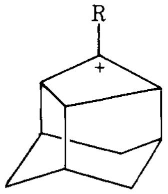

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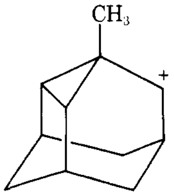

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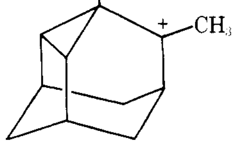
Results and Discussion

The 2,8-Dimethyl-8,9-dehydro-2-adamantyl Cation. Two identical groups can be substituted in the cyclopropylcarbinyl moiety of parent ion **1** in two different ways. Previously we have shown that under stable ion conditions the 1,2-dimethyl-8,9-dehydro-2-adamantyl cation (**4**) is a static carbenium ion from −95 to −10 °C.[7a] No contribution of the 3,4-dimethyl-2,5-dehydro-4-protoadamantyl cation (**5**) to the NMR parameters of **4** was observed. Of course, a degenerate rearrangement in **4** is not possible. However, such behavior could occur in the 2,8-dimethyl-8,9-dehydro-2-adamantyl cation (**7**). In order to explore this possibility, 2,8-dimethyl-8,9-dehydro-2-adamantanol (**6**) was added to a solution of fluorosul-



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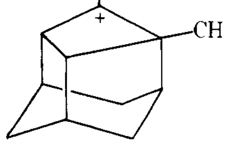

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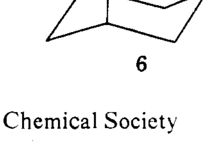

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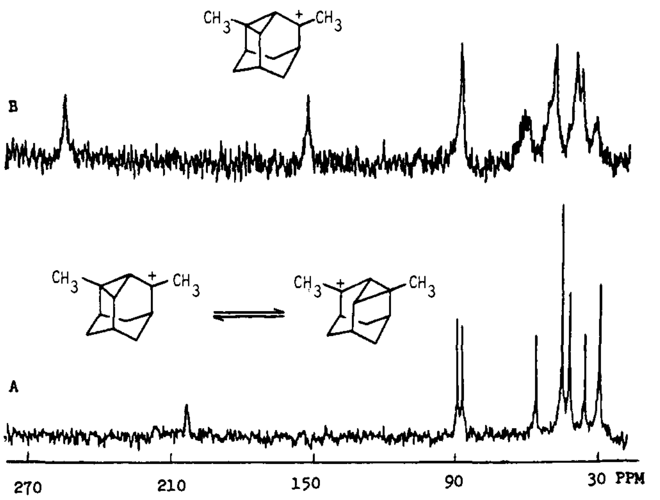
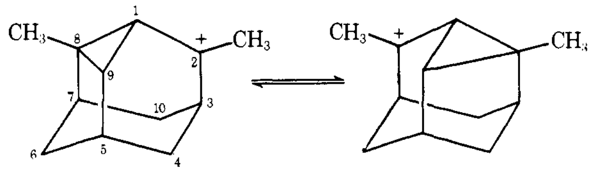


Figure 1. The proton-decoupled 20-MHz ^{13}C NMR spectrum of the 2,8-dimethyl-8,9-dehydro-2-adamantyl cation in FSO_3H-SO_2ClF solution: (A) at −26 °C; (B) at −128 °C.

fonic acid (FSO_3H) in sulfuryl chloride fluoride (SO_2ClF) at −78 °C. The resulting ion shows reversible temperature-dependent behavior between −26 and −128 °C.

At −26 °C the ^1H NMR spectrum of **7** consists of a broad one-proton peak at δ 5.20, a one-proton doublet at δ 4.37, a six-proton singlet at δ 2.78, a broad three-proton multiplet from δ 3.3 to 2.8, and a six-proton peak centered at δ 2.28. These data suggest that ion **7** is the 2,8-dimethyl-8,9-dehydro-2-



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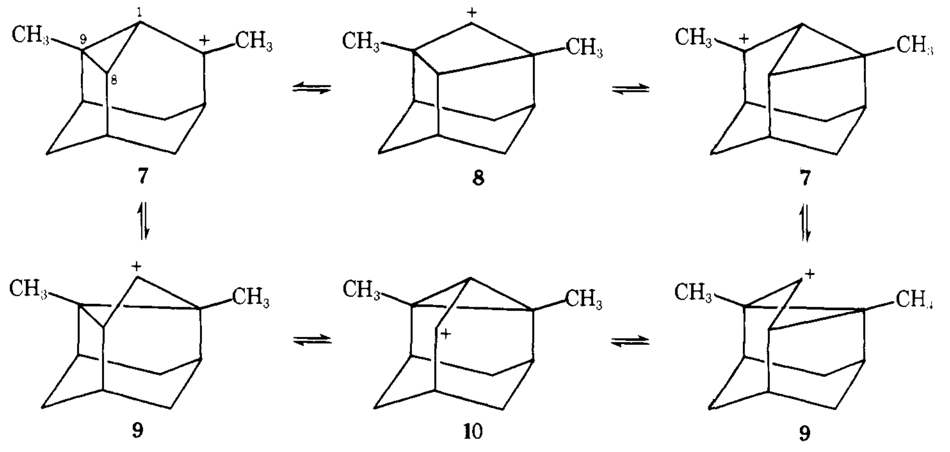
adamantyl cation which is undergoing a degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement which is fast on the NMR time scale at −26 °C. Accordingly, the six-proton singlet at δ 2.78 is assigned to the enantiotopic methyls while the one-proton signals at δ 5.20 and 4.37 are attributed to the protons at C-9 and C-1, respectively. From the relative intensities of the signals at δ 3.3–2.8 and 2.3, the former is assigned to the bridgehead protons at C-3, C-5, and C-7 and the latter to the methylene protons at C-4, C-6, and C-10. Consistent with the proposed structure of ion **7**, the proton noise decoupled natural abundance Fourier tranform (FT) ^{13}C NMR spectrum of **7** at −26 °C (Figure 1) contains only eight carbon resonances. In view of the proton coupled ^{13}C NMR spectrum of **7** and the relative intensities of the signals, the resonances can be assigned as follows: δ 202.7 (C-2 and C-8), 88.4 (C-9), 85.6 (C-1), 55.3 (C-10), 45.1 (C-3 and C-7), 42.2 (C-4 and C-6), 35.8 (C-5), and 29.7 (CH_3).

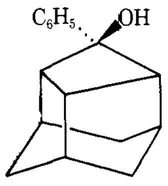
As the temperature is lowered, it is apparent from the NMR spectra of the ion obtained from **6** that the degenerate rearrangement observed at −26 °C is becoming slow on the NMR time scale. The proton noise decoupled ^{13}C NMR spectrum of this ion at −128 °C (Figure 1) indicates that the species present is the static 2,8-dimethyl-8,9-dehydro-2-adamantyl cation. The carbons which were enantiotopic at −26 °C are now constitutionally heterotopic. Thus, the resonances for C-2 and C-8 appear at δ 253.9 and 151.0, respectively, and the methyl carbons attached to C-2 and C-8 occur at δ 32.8 and 26.5, respectively. While it is apparent that the resonances for C-1 and C-9 both occur at ca. δ 85.9, the other signals are not sufficiently sharp to permit a complete assignment. In the ^1H NMR spectra significant broadening of the methyl singlet was observed by −94 °C. However, it was not possible to obtain the ^1H NMR spectrum of this ion with reasonable resolution below −100 °C.

An examination of molecular models of the 8,9-dehydro-2-adamantyl cation suggests that the C-8 to C-9 bond in this ion is situated in an unfavorable alignment for a direct Wagner–Meerwein-type migration. The degenerate equilibration of ion **7** may be accounted for either by an initial shift of the C-1 to C-9 bond in **7** to give as an intermediate the 3,5-dimethyl-2,5-dehydro-4-protoadamantyl cation (**8**) or by migration of the C-1 to C-8 bond in **7** to provide the degenerate 2,3-dimethyl-2,5-dehydro-4-protoadamantyl cation (**9**) which rearranges to **7** via the 8,9-dimethyl-8,9-dehydro-2-adamantyl cation (**10**). At present it is not possible to distinguish between these alternative pathways as the intermediate ions do not seem to contribute to the observed NMR parameters. Since the coalescence temperature of the methyl carbon signals in the ^{13}C NMR spectrum of **7** occurs at −112 °C, an approximate energy barrier[8] of $\Delta G^{\ddagger} = 7.4 \pm 0.5$ kcal/mol can be calculated for **7** → **8** or **9** or **10**.

The 4-Phenyl-2,5-dehydro-4-protoadamantyl Cation. We have also found that the energy barrier for the degenerate rearrangement of the 4-methyl-2,5-dehydro-4-protoadamantyl cation is increased when the methyl substituent is replaced by a phenyl group. Addition of 4-*endo*-hydroxy-4-*exo*-phenyl-2,5-dehydroprotoadamantane (**11**) to a solution of FSO_3H in SO_2ClF at −78 °C gives ion **12**, which shows reversible temperature-dependent behavior between −40 and −135 °C.

At −40 °C the proton noise decoupled FT ^{13}C NMR spectrum of **12** contains only four resonances in the nonaromatic region. As one scans these signals from the resonance that is most deshielded to increasingly more shielded ones, the signals correspond to a single quaternary carbon bearing most of the positive charge, three equivalent tertiary carbons, three other tertiary carbons which are also mutually equivalent, and three





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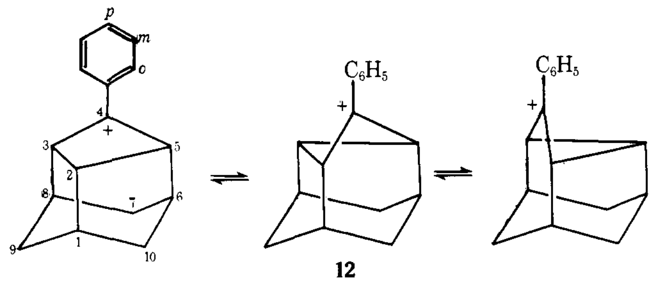

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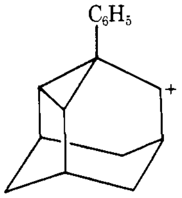
equivalent secondary carbons. These data clearly suggest that on the NMR time scale at −40 °C ion **12** possesses a threefold axis of symmetry. We assign to **12** the structure of the 4-phenyl-2,5-dehydro-4-protoadamantyl cation which is undergoing a facile threefold degenerate cyclobutyl-cyclobutyl rearrangement at −40 °C. Consequently, the resonances in the ^{13}C NMR spectrum of **12** are assigned as follows: δ 222.2 (C-4), 146.8 (C_p), 137.1 (C_o), 132.0 (C_m), 131.5 (C_i), 72.7 (C-2, C-3, and C-5), 58.3 (C-1, C-6, and C-8), and 43.0 (C-7, C-9, and C-10). Consistent with this structure assignment, the ^1H NMR spectrum of **12** at −40 °C consists of a broad five-proton multiplet for the aromatic protons from δ 8.6 to 7.8, a three-proton multiplet at δ 4.6 for the homotopic bridgehead protons at C-2, C-3, and C-5, a three-proton multiplet at δ 3.8 for the equivalent protons at C-1, C-6, and C-8, and a six-proton multiplet at δ 2.2 for the methylene protons at C-7, C-9, and C-10.

The degenerate equilibration of **12** may be rationalized as proceeding via the 1-phenyl-8,9-dehydro-2-adamantyl cation (**13**) as an intermediate. Since the 1-phenylcyclobutyl cation (**14**) is known to be static and to show temperature-independent behavior,[6a,9] we were encouraged that the degenerate rearrangement of **12** might be frozen out. Cooling **12** led to substantive changes in the NMR spectra which show that the rearrangement of **12** observed at −40 °C is becoming slow on the NMR time scale. The proton noise decoupled ^{13}C NMR spectrum of this ion at −135 °C indicates that the species present is the static 4-phenyl-2,5-dehydro-4-protoadamantyl cation. In particular, the homotopic bridgehead carbons of the degenerate cyclobutyl cation moiety at −40 °C are now resolved into resonances at δ 46.8 and 85.2 for C-2 and enantiotopic carbons C-3 and C-5, respectively. While the resonance for C-4 occurs at δ 222.0, the other signals are too complex to assign. Since the coalescence temperature of the resonances for C-2, C-3, and C-5 in **12** occurs at −110 °C, an approximate energy barrier[8] of $\Delta G^{\ddagger} = 6.9 \pm 0.5$ kcal/mol can be calculated for **12** → **13**.



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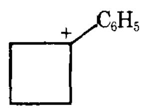

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Experimental Section

2,8-Dimethyl-8,9-dehydro-2-adamantanol (6). A solution of methyllithium (7.45 mmol) in ether was added dropwise to a solution of 8-methyl-8,9-dehydro-2-adamantanone[10] (241 mg, 1.49 mmol) in anhydrous ether (20 mL) which was maintained at 0 °C under nitrogen. The reaction mixture was stirred for 1 h at 0 °C and then for 1 h at room temperature, at which point water was carefully added. The reaction mixture was subsequently saturated with sodium chloride and extracted with ether (2 × 20 mL). The combined extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided a clear oil which was Kugelrohr distilled to give 173 mg (65% yield) of **6** as an oil. Sublimation (100 °C, 0.1 mm) provided pure **6** as a white solid: mp 92-96 °C; ^1H NMR δ ($CDCl_3$) 2.48-0.78 (complex multiplet containing methyl singlets at δ 1.40 and 1.19); IR ν ($CHCl_3$) 3605, 3450 (br), 3005, 2925, 2860, 1460, 1375, 1135, 1115, 1090, 960, and 930 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.02; H, 10.14.

4-*endo*-Hydroxy-4-*exo*-phenyl-2,5-dehydroprotoadamantane (11). A solution of 16.2 mmol of phenyllithium in 8.7 mL of 70:30 benzene-ether was added dropwise at 0 °C to a stirred solution of 2,5-dehydro-4-protoadamantanone[11] (600 mg, 4.05 mmol) in anhydrous ether (20 mL). Stirring was maintained for 1 h at 0 °C and for an additional 1 h at room temperature, at which point water (60 mL) was carefully added. The reaction mixture was saturated with sodium chloride and extracted with ether (3 × 25 mL). The ether extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the solvent at reduced pressure provided an off-white solid which contained biphenyl. This material was column chromatographed on silica gel. The biphenyl was eluted with hexane and alcohol **11** was eluted with 95:5 hexane-ether. Sublimation (85 °C, 0.03 mm) of the fractions containing **11** provided 260 mg (28% yield) of **11** as a white solid: mp 103-104.5 °C; ^1H NMR δ ($CDCl_3$) 7.7-7.0 (br m, 5 H, aromatic protons) and 3.36-1.07 (br m, 13 H); IR ν ($CHCl_3$) 3590, 3420 (br, w), 2940, 2860, 1495, 1465, 1445, 1340, 1315, 1260, 1105, 1080, and 1015 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.67; H, 7.83.

Preparation of Carbocations. The cation precursor was dissolved in SO_2ClF which had been cooled to −78 °C (dry ice-acetone bath temperature). The resulting solution was slowly added with vigorous stirring to a freshly prepared solution of a fourfold excess of FSO_3H in SO_2ClF which was maintained at −78 °C. This procedure afforded an approximately 10-15% solution of the ion. After the addition had been completed, the sample was immediately transferred to a precooled NMR tube.

^1H and ^{13}C nuclear magnetic resonance spectroscopic studies were carried out as previously described.[12] Proton and carbon-13 chemical shifts are in parts per million from external tetramethylsilane (capillary).

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(3) Recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant Award, 1976-1981.
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Picosecond Photophysics of Covalently Linked Pyrochlorophyllide *a* Dimer. Unique Kinetics within the Singlet Manifold

Michael J. Pellin,[1a,b] **Michael R. Wasielewski,***[1b] **and Kenneth J. Kaufmann***[1a,c]

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, and the Department of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received April 25, 1979*

Abstract: The excited state absorption and fluorescence characteristics of the folded configuration of bis(pyrochlorophyllide *a*) ethylene glycol diester were studied on a picosecond time scale. This model for the primary photochemical electron donor in photosystem I of green plants displayed photophysical properties that were found to depend strongly on both solvent and temperature. First, at 290 K the fluorescence lifetime and the lifetime of the excited state absorbance changes following an 8-ps flash at 528 nm varied dramatically with a change in solvent, CH_2Cl_2 vs. CCl_4. At 290 K the absorbance changes of the dimer in CCl_4 showed a large positive optical density change at 660 nm and bleaching at 700 nm. The 660-nm positive optical density change was absent for the folded dimer dissolved in CH_2Cl_2. Second, similar dramatic lifetime variations were observed for folded dimer in CH_2Cl_2 as a function of temperature. Both fluorescence lifetimes and absorption change decay rates were very similar with a lifetime at 290 K of 110 ps increasing to 4.6 ns at 200 K. However, the quantum yield for fluorescence of the dimer remained relatively constant in the 290-200 K temperature range. As the sample of folded pyrochlorophyll *a* dimer in CH_2Cl_2 was cooled from 290 to 270 K the bleaching centered at 700 nm broadened somewhat and a new positive optical density change appeared at 660 nm. This spectrum was completely analogous to that obtained for the folded dimer in CCl_4 at 290 K. These results were interpreted in terms of a dual excited singlet state model with one singlet state fluorescent while the other remains nonfluorescent. Initial excitation of the dimer into the nonfluorescent state followed by a kinetically controlled population distribution between both excited states was shown to account for the data.

The primary role of chlorophyll (Chl) in photosynthetic organisms is to convert incident solar radiation into chemical energy. Photons are captured by an extended array of chlorophyll molecules known as the antenna.[2-5] The electronic excitation produced by the light absorption is transmitted via the antenna chlorophyll to a "special pair" of chlorophyll molecules.[6-9] This pair of molecules traps the excitation energy and then rapidly undergoes one-electron oxidation. The resulting charge separation subsequently generates a chemical potential gradient within the organism. The special pair and its associated redox components are contained in a protein matrix and are collectively known as the reaction center.

Although reaction centers of photosystem I (P700) in green plants have not as yet been isolated completely free of antenna chlorophyll, a great deal of information exists regarding their spectroscopic properties.[10] P700 undergoes bleaching upon illumination with 700-nm light. The subsequent appearance of a photoinduced electron spin resonance (ESR) signal of about 7 G line width with $g = 2.0025$ results from the formation of $\mathrm{P700}^{+\cdot}$. A comparison between the signal of monomeric Chl $a^{+\cdot}$ and $\mathrm{P700}^{+\cdot}$ reveals that the line width of the signal due to the in vivo species is narrower by $\sqrt{2}$ than that of in vitro Chl $a^{+\cdot}$.[9] This result agrees with theory regarding delocalization of one electron spin equally over two chlorophyll molecules.[9] Further studies of in vivo systems by electron nuclear double resonance (ENDOR) spectroscopy support the special pair proposal for the structure of reaction center chlorophyll.[11] The delocalization of charge over two chlorophyll molecules in the special pair cation radical is reflected in a lowering of the oxidation potential of the special pair relative to that of monomeric chlorophyll.

Several models have been proposed for the structure of the chlorophyll (Chl_{sp}) special pair. In one model two chlorophyll *a* molecules are linked by coordinating the magnesium atom of one Chl *a* to a nucleophile such as ROH which in turn hydrogen bonds to the keto carbonyl group of the second Chl *a*. Two such interactions result in a structure possessing C_2 symmetry and a 3.6-Å interplanar distance (Figure 1).[12,13] A different model suggests that the structure of the special pair is based on the coordination of a water molecule to the magnesium of one Chl *a* which in turn hydrogen bonds to the carbonyl function of the carbomethoxy group of a second Chl *a*. In this model two such interactions also result in a C_2 symmetric structure with the carbomethoxy groups pointing into the interior of the structure (Figure 2). This results in a larger 5.6-Å interplanar distance.[14]

The finding that two chlorophyll molecules closely interact in vivo to form P700 has stimulated efforts to prepare an in vitro chlorophyll special pair. Chl *a* adducts with ethanol have been prepared that successfully mimic the optical and ESR properties of photosystem I reaction center chlorophyll.[13] These Chl_{sp} systems are assembled from two monomer units by cooling a mixture of Chl *a* and ethanol to temperatures near 100 K. The free energy of association of this in vitro analogue of P700 is greater than zero at room temperature. This is due to a large negative entropy of dimerization as is indicated by the fact that formation of in vitro special pairs requires high Chl *a* concentrations and low temperatures. Solutions of Chl *a* in hydrocarbons containing water also yield species possessing a 700-nm optical absorption.[15] The formation of the desired structure depends not only on the Chl *a* concentration, but also on the mole ratio of Chl *a* to nucleophiles in solution,

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