Perhaps the most striking feature of the chemical reaction of an alkali metal with pyridine is the remarkable degree of chemical selectivity which gives almost exclusively the 4,4' isomer. We propose that the unpaired electron density on the pyridine radical anion affects the choice of reaction site and further, that this density on the 4-carbon is great enough to dominate the course of the reaction. Both molecular orbital and valence bond models lend support to these conclusions. An MO model of the pyridine radical is represented most simply as a pyridine molecule with an additional electron added to the lowest lying π^* orbital. The calculations of Mataga and Nishimoto[11] show that, for the lowest π^* orbital of pyridine, the maximum electron density is on the 4-carbon. This result is only indicative, however, since there is substantial electron density on the 2,6- and 3,5-carbons as well. An MO calculation for the pyridine radical would be more useful.

The valence bond model leads substantially to the same conclusions. Of the many canonical structures that are possible for the pyridine radical, the structures
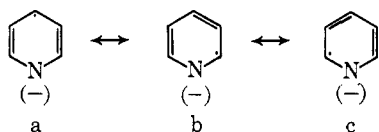
which place the negative charge on the highly electronegative nitrogen atom, should be more important. Of these, structure a provides the greatest separation between the negative charge and the unpaired electron and should, therefore, make the greatest contribution

(11) N. Mataga and K. Nishimoto, Z. Phys. Chem. (Frankfurt am Main), 13, 140 (1957).

to the total structure. It should be noted that no resonance structures may be drawn which place the negative charge on the nitrogen *and* the unpaired electron at a 3- or 5-carbon. Additionally, though it is not required, the valence bond model suggests a change in hybridization of the atom with the greatest unpaired electron density.

Experimental Section

Reagents. Pyridine (Fisher reagent) and γ-picoline (Aldrich, 98%) were purified by distillation from KOH pellets. The center fractions were collected and stored over molecular sieves (Linde 4A). Final dehydration was accomplished by distilling the amines from sodium into a closed dry apparatus on a vacuum line.

Lithium rod (Lithium Corp. of America) was cut in an atmosphere of dry argon and sealed *in vacuo* behind bulb-type break-seals. Sodium (MCB) was distilled *in vacuo* into ampoules fitted with break-seals or directly into the reactions vessels attached to the vacuum line. Cesium was prepared by heating a mixture of cesium chloride (Fisher certified) and calcium turnings *in vacuo*. The cesium metal was distilled directly into the reaction vessel.

General Procedure. Standard high-vacuum line techniques were used. For the hydrogen pressure experiments a clean piece of sodium or lithium was placed in an apparatus of known volume which had been sealed to the vacuum line. The apparatus consisted of a 50-ml flask connected to a mercury manometer that could measure pressure changes as small as 1 mm. Dry pyridine was condensed into the apparatus and the apparatus was sealed from the vacuum line. No pressure change was observed for a period of 2 months.

Spectral Measurements. Visible–ultraviolet spectra were recorded on a Beckman DK-1A spectrometer. At no time were the solutions open to the atmosphere.

The epr spectra were obtained with a Varian V4502-15 epr spectrometer.

Analysis. The concentrations of the metal ions were determined by Galbraith Laboratories, Knoxville, Tenn., by atomic absorption spectrometry.

The Crystal Structure of the Tetrachloroaluminate Salt of the Heptamethylbenzene Cation[1a]

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Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa. Received April 27, 1968

Abstract: The crystal structure of the tetrachloroaluminate salt of heptamethylbenzene, $[(CH_3)_7C_6]^+[AlCl_4]^-$, was determined from single-crystal X-ray diffraction data (film method, visual estimates, 1900 reflections). The monoclinic unit cell data are $a = 8.641 \pm 3$, $b = 12.581 \pm 3$, $c = 16.51 \pm 1$ Å, $\beta = 94.35 \pm 7°$, P2$_1$/n, $D_x = 1.26$ g/cm². The structure was refined by least-squares methods to $R_1 = 0.090$. The AlCl$_4^-$ anion exists as a nearly perfect tetrahedron with an average Al–Cl bond length of 2.120 ± 0.004 Å and an average Cl–Cl length of 3.462 ± 0.004 Å. The cation consists of a seventh methyl group σ-bonded to hexamethylbenzene forming a *gem*-dimethyl group. The cation has idealized point group symmetry C$_{2v}$ with two nearly perpendicular planes containing all of the carbon atoms. A simple (HMO) calculation was performed on the five sp²-bonded ring carbon atoms, and the calculated bond orders are in agreement with the observed bond distances.

The catalyst in reactions of the Friedel–Crafts type often become inactive after a relatively short time. In the methylation of benzene and its methyl homologs with methyl chloride and aluminum trichloride at 80°, deactivation sets in rapidly with the consumption of

relatively large quantities of catalyst.[1b] The nmr[1b] spectrum of the heptamethylbenzene cation is con-

(1) (a) This work was supported by National Science Foundation Grant GP-6855. (b) W. von E. Doering, M. Saunders, *et al., Tetrahedron*, 4, 178 (1958).

sistent with either a seventh methyl group σ-bonded to one of the ring carbon atoms (forming a *gem*-dimethyl group) or an asymmetric π-bonded complex of the methyl group and hexamethylbenzene. A third model, the π complex of hexagonal symmetry (inconsistent with the nmr data), can be ruled out from theoretical considerations.[2] In an attempt to determine the structure of the heptamethylbenzene cation, a complete three-dimensional structural determination was carried out using film data obtained from a single crystal at room temperature.

Experimental Section

The heptamethylbenzene tetrachloroaluminate, $[(CH_3)_7C_6]^+$-$[AlCl_4]^-$ (abbreviated as HMBAlCl$_4$), complex was prepared by the method of von Doering and Saunders.[1b] Bright yellow needle crystals were obtained after two recrystallizations from dry ethyl acetate and washing with dry pentane. These crystals are very hygroscopic but could be stored at $-60°$ under a nitrogen atmosphere. The identity of the product was confirmed by infrared and ultraviolet spectra and elemental analysis. *Anal.* Calcd: C, 45.1; H, 6.1; Cl, 41.0; Al, 7.8. Found: C, 44.9; H, 5.9; Cl, 40.0; Al, 7.9.

The cell constants were obtained from two different types of measurements. The a^*, b^*, and c^* cell dimensions were obtained from back-reflection Weissenberg single-crystal diagrams using a least-squares extrapolation method. The a^* and c^* reciprocal cell dimensions were then used to calibrate the $(h0l)$ precession film in order to determine β: a = 8.641 ± 0.003 Å, b = 12.581 ± 0.003 Å, c = 16.51 ± 0.01 Å; β = 94° 21' ± 4' (Cu Kα_1 = 1.54051 Å, α_2 = 1.54433 Å).

The crystal (0.5 mm × 0.3 mm × 0.2 mm) was mounted in a thin-walled glass capillary and was sealed off in the presence of a N_2 atmosphere. The [$10\bar{1}$] axis extended in the direction of the needle axis of the crystal. Intensity data were obtained from equi-inclination Weissenberg diagrams, zero to ten layers along [$10\bar{1}$], taken with Cu Kα radiation, and Buerger precession camera diagrams $(0kl)$ to $(5kl)$ and $(h0l)$ to $(h6l)$ with Mo Kα radiation. Sufficient repeated visual estimates of the intensities were made so that a standard deviation in the mean intensity was calculated for each reflection. These standard deviations were later used to calculate weights for least-squares refinement of structure factors. The intensities were corrected for Lorentz and polarization factors. The intensity data taken with the Weissenberg camera (Cu Kα radiation) were corrected for absorption (μ = 62.2 cm^{-1}, $\mu R \simeq$ 0.60) assuming a cylindrical rod-shaped specimen. The data obtained from the Mo Kα radiation were not corrected for absorption (μ = 6.78 cm^{-1}, $\mu R \simeq$ 0.070). Approximately 3600 reflections were observed about the three axes of data representing 2450 independent reflections of which approximately 1900 were considered to be present. From the extinctions, (hkl) present in all orders, $(h0l)$ present with $h + l = 2n$ and $(0k0)$ present with $k = 2n$, the space group is P2$_1$/a. The density calculated from X-ray data $(Z = 4)$ is 1.26 g/cm^3. The extreme hygroscopic nature of the crystals prevented an experimental measurement of the density.

The neutral atom scattering factors used in the structure factor calculations were taken from the "International Tables for Crystallography."[3] Both real and imaginary dispersion corrections were applied for Cl and Al in the final stages of refinement. Full-matrix least-squares refinements were carried out using a locally written program for the IBM 7044 computer. Several types of discrepancy factors were calculated: $R_1 = \Sigma |\Delta F| / \Sigma |F_o|$; $R_{1w} = \Sigma w |\Delta F| / \Sigma w |F_o|$; $R_H = [\Sigma w (\Delta F)^2 / \Sigma w F_o^2]^{1/2}$.[4] The function minimized was $\Sigma w \Delta F^2$. The weighting function used was $w = 1/S^2$, where S is the standard deviation in the mean F value determined for each reflection. Those reflections which were less than three times the minimum observable on the intensity scale were arbitrarily assigned a 40% standard deviation. Reflections below the minimum observable were given zero weight unless $|F_c|$ was greater than $|F_o|$ in which case they were assigned a weight of 0.25.

(2) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
(3) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1959.
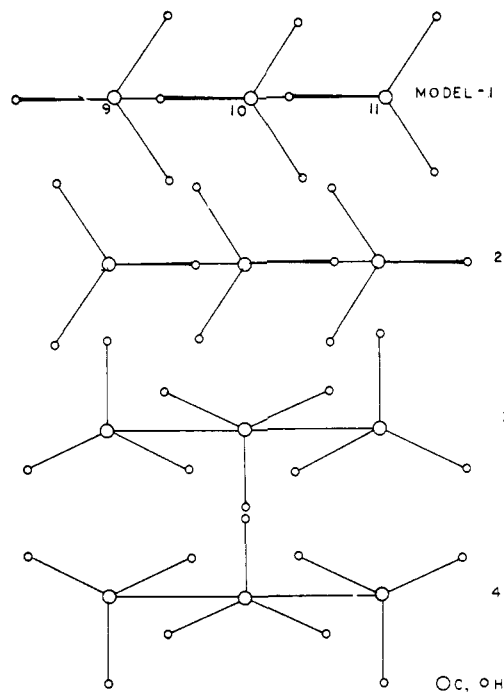(4) W. C. Hamilton, *Trans. Am. Cryst. Assoc.*, **1**, 17 (1965).

Figure 1. Schematic view of the four arrangements of H atoms in the methyl groups of the heptamethylbenzene cation. Each model is an edge view of the benzene ring showing the relative configuration of three methyl groups with respect to the plane of the benzene ring.

Structure Determination

The coordinates of the AlCl$_4^-$ group were obtained from a three-dimensional Patterson map (R_1 = 0.39). A set of phases based on the AlCl$_4^-$ coordinates revealed the coordinates of the five ring atoms and four methyl groups in addition to AlCl$_4^-$. A subsequent electron density map revealed all carbon atoms in the cation. Introduction of these atoms with individual isotropic temperature factors in the least-squares structure factor calculations dropped R_1 to 0.20, R_{1w} = 0.21, and R_H = 0.225. When the AlCl$_4^-$ group was allowed to refine on anisotropic temperature factors, R_1 became 0.16, R_{1w} = 0.083, and R_H = 0.121. At this stage all equivalent reflections taken with the same radiation were averaged and interlayer scale factors fixed. When all carbon atoms were allowed to refine anisotropically, R_1 became 0.130, R_{1w} = 0.069, and R_H = 0.0995. The difference electron density map showed no peaks which were higher than 0.1 e/Å^3 (while carbon atoms in an electron density map are about 6 e/Å^3). Both the complete data set and a data set consisting of sin $\theta/\lambda \leq$ 0.025 Å^{-1} were used for the difference map calculations. No meaningful hydrogen atom coordinates could be found in the difference maps.

Hydrogen atom positions were calculated for each of the four models (see Figure 1) which appeared to be reasonable from space-filling molecular models of the cation, and all the hydrogen atoms were added to the calculation of the structure factor. These hydrogen positions were not varied in the least-squares refinements which then were carried out for each of the four models. After two cycles of full-matrix refinement, each calculation resulted in slightly higher R_{1w} (*ca.* 7.4%) but lower R_H. An approximation to a random configuration of hydrogen atoms was tested in which

Table I

Model	R_H	$0.0995/R_H$	$R_H/0.0905$
1	0.0972	1.024	1.074
2	0.0948	1.048	1.049
3	0.0966	1.030	1.067
4	0.0950	1.047	1.050
Random	0.0905	1.099	...

data of Huffman, Parks, and Daniels[6] for hexamethylbenzene has been interpreted by Pauling[7] to be evidence for the onset of rotation of the methyl groups at 151°K. Thus, it would be reasonable to expect rotation of the methyl groups in the heptamethylbenzene cation, and the X-ray data are compatible with this model. Table II lists the final positional and thermal parameters of the nonhydrogen atoms for HMBAlCl₄. A list of

Table II. Atomic Parameters[a] for Heptamethylbenzene Tetrachloroaluminate ($\times 10^4$)

	X	Y	Z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Al	-4051 (2)	2350 (2)	1585 (2)	124 (4)	70 (2)	60 (2)	18 (4)	-32 (4)	-25 (3)
Cl₁	-3264 (3)	3902 (1)	1905 (2)	243 (4)	115 (2)	67 (2)	-46 (5)	20 (5)	-43 (3)
Cl₂	-4688 (3)	1537 (2)	2640 (2)	246 (4)	65 (1)	116 (2)	18 (4)	-116 (5)	-32 (3)
Cl₃	-2267 (2)	1482 (2)	1089 (2)	185 (4)	99 (2)	71 (2)	81 (4)	62 (4)	4 (3)
Cl₄	-6004 (2)	2464 (2)	726 (2)	164 (4)	157 (2)	78 (2)	45 (5)	94 (5)	42 (3)
C₁	1410 (7)	3393 (6)	3403 (5)	104 (11)	81 (6)	26 (5)	20 (12)	10 (12)	-9 (9)
C₂	3003 (8)	3803 (5)	3619 (5)	128 (10)	61 (5)	57 (5)	33 (11)	46 (13)	18 (9)
C₃	4044 (8)	3234 (5)	4099 (5)	124 (11)	64 (5)	47 (5)	12 (11)	-48 (13)	00 (8)
C₄	3672 (8)	2215 (5)	4353 (5)	117 (11)	71 (6)	58 (6)	63 (12)	5 (14)	2 (9)
C₅	2208 (8)	1734 (5)	4148 (6)	121 (11)	65 (5)	69 (6)	16 (12)	21 (15)	5 (9)
C₆	1116 (7)	2284 (5)	3668 (5)	84 (10)	65 (5)	48 (6)	7 (11)	41 (12)	19 (9)
C₇	262 (9)	4129 (6)	3798 (6)	168 (14)	75 (6)	83 (7)	68 (14)	53 (16)	34 (10)
C₈	3360 (9)	4898 (6)	3330 (6)	206 (14)	81 (6)	76 (6)	-14 (16)	24 (17)	16 (10)
C₉	5668 (8)	3677 (6)	4317 (6)	105 (11)	118 (7)	60 (6)	-68 (14)	-18 (14)	-1 (11)
C₁₀	4841 (9)	1605 (6)	4887 (7)	165 (13)	80 (6)	100 (7)	74 (14)	-42 (17)	39 (11)
C₁₁	1891 (10)	609 (6)	4438 (7)	243 (16)	65 (6)	104 (8)	5 (16)	00 (19)	27 (11)
C₁₂	-449 (9)	1834 (6)	3462 (7)	170 (14)	92 (6)	80 (6)	-68 (15)	-67 (16)	-9 (10)
C₁₃	1174 (9)	3422 (7)	2441 (7)	168 (14)	123 (8)	60 (7)	5 (17)	-8 (17)	00 (12)

[a] Anisotropic temperature factor, $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$. Estimates of standard deviations in last significant digit are given in parentheses.

hydrogen atoms were allowed to occupy the sites of models 1–4 one-fourth of the time. This model places one-fourth of a hydrogen atom in 12 minima about each methyl carbon atom. The discrepancy factor, R_H, became 0.0905.

The number of parameters in the least-squares refinement was 163. For the models 1–4, 63 additional positional parameters and 7 additional temperature parameters were used, but again, only the 162 heavy atom parameters and one over-all scale parameter were allowed to vary. A conservative application of Hamilton's R ratio test[5] would assume a dimension of 70 and $2450 - (163 + 70) = 2217$ degrees of freedom for comparing models 1–4 with the model in which hydrogen atoms were omitted. From interpolation from F tables, the value of the R ratio should be 1.023 at the 1% level. For comparison of the random hydrogen atom model with the model in which hydrogen atoms were omitted, the dimension is 259, the degrees of freedom are 2028, and the ratio should be 1.078. For a comparison of the random hydrogen model with models 1–4, the dimension is 189, the degrees of freedom are 2028, and the R ratio should be 1.058. The application is conservative, since the additional parameters were not allowed to vary in the least-squares refinement, and, hence, the greatest reduction in R might not have been achieved (see Table I).

Thus, all of the models containing hydrogen show significant improvement over the calculations in which the hydrogen atoms were omitted. The random hydrogen model is significantly better than models 1 and 3 at the 1% level, but it is not as clearly to be preferred over models 2 and 4. The heat capacity

(5) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

calculated and observed structure factors and a table of hydrogen atom coordinates corresponding to the random hydrogen model are available.[8]

Discussion of the Structure

The structure can be described as consisting of an organic cation and a tetrahedral inorganic $AlCl_4^-$ anion. (See Figures 2 and 3 for bond distances and angles.) The average value of 2.120 ± 0.004 Å for the Al–Cl bond distance is in agreement with the reported value of 2.13 ± 0.02 Å by Turner and Amma[9] for the complex of $Ag(I)AlCl_4 \cdot C_6H_6$. It is also in agreement with the 2.13 Å reported by Baenziger[10] for the salt $NaAlCl_4$ and the 2.157 ± 0.018 Å reported by Ibers[11] for $Co(AlCl_4)_2$. The average Cl–Cl distance is 3.462 ± 0.004 Å. The uniformity of the Cl–Cl distances is a consequence of the nearly perfect tetrahedral coordination in the anion, and the Cl–Al–Cl angles listed in Table III further illustrate this feature.

The structure of the cation can be discussed from two points of view, which are dependent on the reliability of the bond distances and angles and the degree of

(6) H. M. Huffman, G. S. Parks, and A. C. Daniels, *J. Am. Chem. Soc.*, **52**, 1547 (1930).

(7) L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

(8) A list of calculated and observed structure factors and a table of the hydrogen atom coordinates which correspond to the random hydrogen model have been deposited as Document No. 10039 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(9) R. W. Turner and E. L. Amma, *J. Am. Chem. Soc.*, **88**, 3243 (1966).

(10) N. C. Baenziger, *Acta Cryst.*, **4**, 216 (1951).

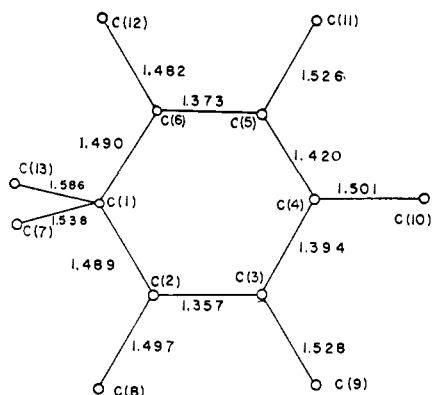(11) J. A. Ibers, *ibid.*, **15**, 967 (1962).

Figure 2. Bond distances in the heptamethylbenzene cation and the AlCl₄⁻ anion.

Figure 3. Bond angles in the heptamethylbenzene cation and the AlCl₄⁻ anion.

uncertainty one is willing to attribute to the atom positions. Adopting the point of view that the errors in the atom positions have been underestimated, one can consider the cation to have the idealized point

from the planes are small; the average deviation from plane 1 is 0.022 Å and from plane 2 it is 0.005 Å. The estimated uncertainty in the position of an individual carbon atom is about 0.008 Å. Five of the ring carbon

Table III. Interatomic Distances^a (Å) and Angles (Degrees) for Heptamethylbenzene Tetrachloroaluminate

Al–Cl₁	2.122 (3)	C₁–C₂	1.489 (9)
Al–Cl₂	2.128 (4)	C₂–C₃	1.357 (9)
Al–Cl₃	2.105 (3)	C₃–C₄	1.394 (10)
Al–Cl₄	2.125 (3)	C₄–C₅	1.420 (9)
		C₅–C₆	1.373 (10)
Cl₁–Cl₂	3.474 (3)	C₁–C₁₃	1.586 (13)
Cl₁–Cl₃	3.465 (3)	C₁–C₇	1.538 (11)
Cl₁–Cl₄	3.460 (3)	C₂–C₈	1.497 (11)
Cl₂–Cl₃	3.427 (4)	C₃–C₉	1.528 (9)
Cl₂–Cl₄	3.479 (4)	C₄–C₁₀	1.501 (10)
Cl₃–Cl₄	3.467 (2)	C₅–C₁₁	1.526 (11)
		C₆–C₁₂	1.482 (9)
		C₇–C₁₃	2.588 (15)
Cl₂–Al–Cl₁	109.7 (3)	C₂–C₃–C₉	120.1 (7)
Cl₂–Al–Cl₄	109.7 (2)	C₄–C₃–C₉	119.6 (8)
Cl₂–Al–Cl₃	108.2 (2)	C₃–C₄–C₁₀	119.1 (10)
Cl₁–Al–Cl₄	109.1 (1)	C₅–C₄–C₁₀	118.0 (7)
Cl₁–Al–Cl₃	110.1 (2)	C₄–C₅–C₁₁	119.9 (7)
Cl₄–Al–Cl₃	110.1 (2)	C₆–C₅–C₁₁	121.1 (12)
		C₅–C₆–C₁₂	121.0 (8)
C₁–C₂–C₃	121.1 (7)	C₁–C₆–C₁₂	117.6 (8)
C₂–C₃–C₄	120.2 (12)	C₆–C₁–C₁₃	107.7 (7)
C₃–C₄–C₅	122.8 (9)	C₆–C₁–C₇	108.0 (7)
C₄–C₅–C₆	118.9 (7)	C₂–C₁–C₁₃	106.1 (4)
C₅–C₆–C₁	121.1 (12)	C₂–C₁–C₇	107.7 (6)
C₆–C₁–C₂	115.4 (8)	C₇–C₁–C₁₃	111.9 (6)
C₁–C₂–C₈	116.8 (7)		
C₃–C₂–C₈	121.9 (12)		

^{a} Estimated standard deviation of last significant digit is given in parentheses.

Table IV. Least-Squares Planes of Cation^a

Atom	Deviation, Å
Plane 1	
1	−0.042
2	0.014
3	−0.016
4	−0.005
5	0.005
6	0.026
8	0.009
9	0.031
10	−0.046
11	0.038
12	−0.014

Plane 1: $0.40828X - 0.39082Y - 0.82497Z = -5.92587$

Atom	Deviation, Å
Plane 2	
1	−0.012
4	0.001
7	0.005
10	0.001
13	0.005

Plane 2: $0.64594X + 0.76292Y - 0.02678Z = 3.62869$

Atom	Deviation, Å
Plane 3	
2	0.004
3	−0.007
4	0.006
5	−0.002
6	−0.001

Plane 3: $0.42567X - 0.39701Y - 0.81314Z = -5.910$

^{a} X (Å) $= ax + cz \cos \beta$, Y (Å) $= by$, Z (Å) $= cz \sin \beta$.

group symmetry, C_{2v}. Two mutually perpendicular planes (89.3°) contain all the carbon atoms in the cation (see Table IV). The deviations of the atoms
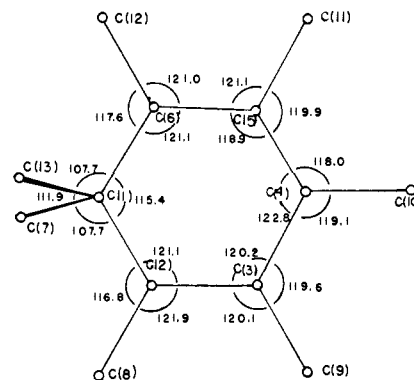
atoms would be expected to have sp²-type bonds and to have four electrons delocalized in π orbitals which would maintain the planarity of the ring. The ring carbon atom, C(1), would not have as great a con-
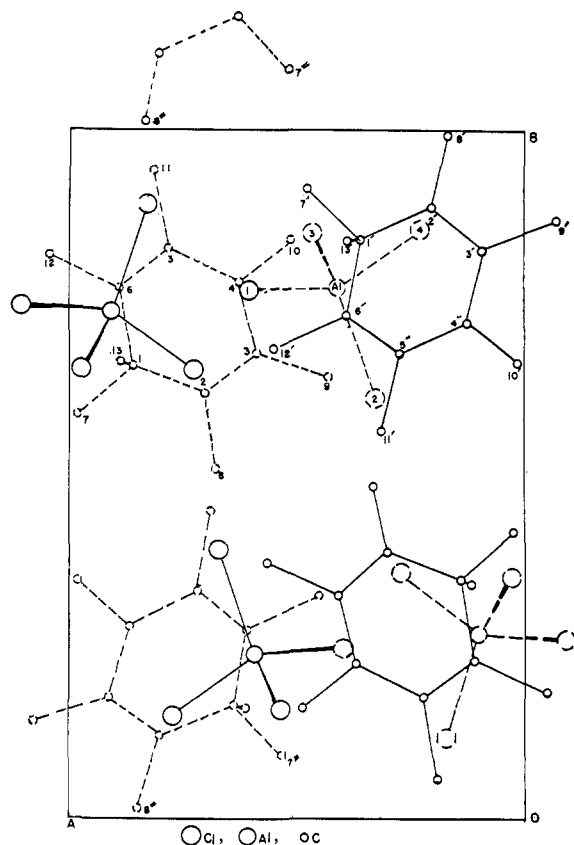
Figure 4. Projection of the structure of the tetrachloroaluminate salt of the heptamethylbenzene cation.

straint for lying in the plane as the remaining ring carbon atoms. Its deviation from the mean plane of all ring carbon atoms and the five methyl groups is 0.042 Å, which could be considered significant. The bond-order calculation from a simple Hückel MO treatment[12] of the five sp^2 carbon atoms gives calculated bond lengths of 1.37 and 1.41 Å for bond 2,3 and 3,4. (The valence-bond method would predict 1.37 and 1.42 Å for the same bonds.) The average of the equivalent bonds assuming the idealized C_{2v} symmetry is 1.365 and 1.407 Å. The average distance of the methyl carbon atoms attached to the ring sp^2-hybridized carbon atoms is 1.507 Å. The radius sum for a sp^2 and a sp^3 carbon atoms is 1.53 Å. The average of the sp^3 *gem*-methyl carbon distances is 1.562 Å.

The assumption of a mirror plane through carbon atoms 1, 4, 10, 7, and 13 leads to a set of interatomic distances which would be expected to be equivalent, and thus, an independent estimate of the standard deviation in a bond distance can be made which gives 0.012 Å. Now, adopting the second point of view that the estimates of atom position errors are reasonable and the deviations from the idealized C_{2v} model may be real and not artifacts of random or systematic errors in the data produces some interesting conclusions. Fitting a least-squares plane only to carbon atoms C(2), C(3), C(4), C(5), C(6) (plane 3 of Table IV), an excellent fit is attained with the deviations less than the uncertainty in individual atom positions (0.004 Å).

(12) N. C. Baenziger and J. J. Hegenbarth, *J. Am. Chem. Soc.*, **86**, 3250 (1964).

The deviation of ring carbon atom 1 from this plane is −0.073 Å. In addition, the carbon atoms C(7) and C(13) deviate unequal amounts: C(7), −1.420 Å, C(13), +1.185 Å, with the midpoint −0.118 Å from plane 3. Considering that the C(1) atom is tipped out of the plane of the ring, the dihedral angle between plane 3 and the plane defined by C(1), C(2), and C(6) is 5.4°. A second feature is that the ring carbon to methyl distances are shorter for the *o*- and *p*-methyl carbon atoms than for the *m*-carbon atom, which may reflect the concentration of positive charge at these positions. The distance from the *m*-carbon atom to its methyl group is very close to that expected for a sp^3–sp^2 bond, while the *ortho* and *para* distances are shorter. The nmr spectrum[1b] has four peaks with the relative intensities 1:2:2:2 which are displaced 137, 145, 156, and 189 cps from benzene hydrogens. The assignment made by Doering and Saunders is 137 = *para*, 145 = *ortho*, 156 = *meta*, and 189 = *geminal* methyl groups. The correlation of bond distance with nmr shift is not perfect, as the *ortho* and *para* groups are interchanged, but the *ortho* and *para* distances differ by less than two standard deviations.

Figure 4 shows the contents of the cell projected onto the (001) plane while Table V lists those nonbonding Cl–C distances of 4.0 Å or less.

Table V. Nonbonding Cl–C Distances of 4.0 Å or Less

$Cl_3–C_8$	3.90	$Cl_4–C_{13}''$	3.97
$Cl_3–C_9$	3.46	$Cl_1–C_6'$	3.94
$Cl_3–C_{10}$	3.37	$Cl_1–C_{12}'$	3.99
$Cl_3–C_{11}$	3.80	$Cl_1–C_{14}'$	3.84
$Cl_3–C_{14}$	3.86	$Cl_1–C_{15}'$	3.93
$Cl_3–C_{15}$	3.76	$Cl_1–C_{18}'$	3.91
$Cl_2–C_{17}$	3.92	$Cl_4–C_9'$	3.58
$Cl_3–C_{18}$	3.83	$Cl_4–C_{10}'$	3.45
$Cl_3–C_{12}''$	3.86	$Cl_4–C_{11}'$	3.91
$Cl_4–C_{12}''$	3.95	$Cl_4–C_{15}'$	3.69

Table VI. Rigid Group Translational and Librational Tensor Elements[a]

	Translational, Å²		
Anion	0.043 (10)	0.005 (8)	−0.023 (8)
		0.061 (9)	−0.015 (8)
			0.065 (10)
Cation	0.032 (3)	0.008 (2)	−0.006 (3)
		0.047 (3)	−0.007 (3)
			0.050 (3)

	Librational, deg²		
Anion	38 (14)	−6 (9)	−13 (8)
		20 (13)	−2 (9)
			30 (13)
Cation	28 (3)	8 (2)	−3 (2)
		17 (4)	−7 (3)
			18 (3)

[a] Referred to orthogonal cell coordinates. Unit vectors are defined as $i = a/|a|$, $j = b/|b|$, $k = c^*/|c^*|$, where c^* is the reciprocal lattice vector. Estimated standard deviation of last significant digit is given in parentheses.

Cruickshank's[13] method of rigid group analysis of the anisotropic thermal parameters was carried out individually for the anion and cation. Table VI lists the vibrational and librational tensor elements relative to

(13) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).

the same coordinate axis system as was used for the least-squares planes, with the origin placed on the center of mass. No allowance was made for mixing of libration–vibration motions, since it was felt that this interaction should be small. Examination of the principal diagonal elements of the vibrational tensors of the cation and anion indicates that the principal amplitudes of motion for the anion are larger than those of the cation; this is most likely a result of the cell packing (*i.e.*, the symmetric tetrachloro group "sees" a broader potential well than does the rather asymmetric cation). A comparison of the relative magnitude of the principal librational tensor elements indicates that the more asymmetric cation undergoes a more pronounced anisotropic librational motion than does the anion.

Summary

The heptamethylbenzene–aluminum tetrachloride complex was found to be ionic, with a very nearly symmetric tetrahedral $AlCl_4^-$ group. The cation consists of a seventh methyl group σ-bonded to hexamethylbenzene forming a *gem*-dimethyl group. Two perpendicular planes contain all C atoms of the cation. The ring structure of the cation consists of five sp^2-bonded carbon atoms over which four π electrons are delocalized while the sixth carbon atom possesses somewhat distorted tetrahedral bonding. A simple Hückel MO calculation was performed, and good agreement was obtained between observed and calculated bond distances.
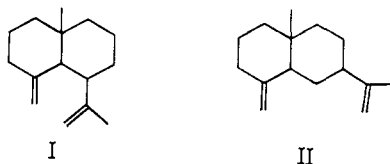
The Crystal Structure of β-Gorgonene–Silver Nitrate[1]

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Abstract: The crystal structure of β-gorgonene–silver nitrate, $C_{15}H_{24} \cdot AgNO_3$, a metal adduct of a new sesquiterpene, has been determined by heavy-atom technique and refined by three-dimensional least-squares methods. The final R index for 1181 reflections (both observed and unobserved) is 0.066, and the standard deviations in the positions of the C, N, and O atoms are in the range of 0.01–0.02 Å. The crystals are orthorhombic, space group $P2_12_12_1$, with $a = 9.036$ Å, $b = 21.786$ Å, and $c = 8.008$ Å, $Z = 4$. The bond distances and angles are normal. The gorgonene molecule does not follow the familiar "isoprene rule" of head-to-tail arrangement, and the isopropyl residue is found to be arranged differently relative to β-selinene. The structure consists of parallel chains of $AgNO_3$ lying along the c axis. The Ag^+ ion is bonded to two neighboring NO_3 groups and two C–C double bonds of a single gorgonene molecule. $Ag^+ \cdots C{=}C$ lengths of 2.44 ± 0.01 and 2.47 ± 0.1 Å, and $Ag^+ \cdots O$ contacts ranging from 2.38 ± 0.01 to 2.80 ± 0.01 Å are observed.

During the investigation of various terpenoids found in some marine organisms, a new bicyclic sesquiterpene skeleton has been encountered in the hydrocarbon β-gorgonene (I), isolated from *Pseudopterogorgia americana*.[3,4] Nmr spectral properties clearly indicated the substitution pattern of β-selinene (II), but its physical properties were not compatible with that compound. Its extreme resistance to dehydrogenation prevented direct determination of the carbon skeleton by nmr.[4] Separation from other hydrocarbons in the

I   II

gorgonians was accomplished by silver nitrate–silicic acid chromatography which converted a portion of the β-gorgonene to the crystalline silver nitrate adduct. The present structure investigation was carried out

with a twofold purpose—to find the correct structure of the gorgonene molecule, and to add some crystallographic data to the studies of the complexes formed between Ag^+ ion and π-bonding systems in the unsaturated compounds. Such studies of complexes between heavy metal ions and π-bonding systems in conjugated and unsaturated compounds have received considerable experimental and theoretical[5–9] attention in recent years.

Experimental Section

Crystals of β-gorgonene–silver nitrate which were grown from hexane–acetone are silvery needles elongated along the c axis. The density was measured by flotation in a mixture of bromobenzene and carbon tetrachloride with some difficulties as the crystals were mildly affected by both liquids. The cell dimensions and space group were obtained from diffraction data collected with the help of a General Electric XRD-5 single crystal diffractometer.

Crystal Data. β-Gorgonene–silver nitrate $(C_{15}H_{24} \cdot AgNO_3)$ exhibited the following characteristics: mol wt, 373; mp 132.5–133.5°; orthorhombic; $a = 9.037 \pm 0.004$ Å, $b = 21.786 \pm 0.007$ Å, $c = 8.008 \pm 0.005$ Å; $V = 1576.6$ Å^3; $d_m = 1.590$ g cm^{-3}, $d_c = 1.571$ g cm^{-3}, $Z = 4$; linear absorption coefficient for

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