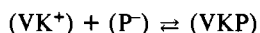


complex. However, this complex is neutral and therefore electrically silent, and of itself does not explain the many observations concerning the effects of picrate on valinomycin transport. It may, however, be one of a number of different transport mechanisms operating simultaneously.

The structure seen here with the weak bond and reasonably compact fit between the valinomycin potassium complex and the picrate ion is probably a good model for the ion pair that would be found in a medium of low polarity such as organic solvents or lipid bilayer membranes. The contribution to the electrical conductance would depend on the extent of dissociation



and would be very dependent on the nature of the anion. As an example, it is easy to observe that a solution of valinomycin in chloroform will readily dissolve solid potassium picrate but will not dissolve potassium chloride. Another example would be the experiments of Ashton and Steinrauf,²⁶ who followed the valinomycin-catalyzed transport of potassium picrate from one water phase through a 1-cm thick barrier of chloroform into another water phase under the influences of different concentrations of potassium picrate and nontransportable ions. They showed that each potassium ion had to be transported with one picrate ion and that no transport took place if the picrate was entirely replaced by chloride. Further evidence for the neutral ion pair was found by Ginsburg et al.,¹⁵ who followed the electrical conductance and cation fluxes of valinomycin facilitated transport through lipid

bilayer membranes. Their proposed mechanism involved TNC^- as the principal charge-carrying species and the cation transport was considered due to the movement of neutral ion pairs.

Certainly the observation by Levitt et al.²⁵ that four water molecules are coupled to the potassium valinomycin complex during transport, a situation that does not hold for the uncomplicated valinomycin on its return through the membrane, can be interpreted as the pockets of the valinomycin-cation complex, providing a means of weakly binding the water molecules. This may be a better mechanism to explain the data of Levitt et al.²⁵ than having the water molecules in the interstices between the complex and the disordered lipid of the artificial membrane.

The weak association of the picrate does not produce any asymmetry in the coordination distances around the potassium ion. These results agree with previous nuclear magnetic resonance studies in solution for the valinomycin potassium complex in the presence of picrate.

Acknowledgment. X-RAY 76 is a system of crystallographic computer programs created by Dr. James Stewart, Computer Science Center, University of Maryland. The research described was supported by a National Institutes of Health Grant PHS ROI GM 24623 and by a National Science Foundation Grant PCM 7422992. Computer time on the CDC-6600 was provided, in part, by the Computing Center, Indiana University-Purdue University at Indianapolis. The crystallographic facilities were supported by a Heart Research Center Grant HE 06307.

Supplementary Material Available: A table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

(26) Ashton, R.; Steinrauf, L. K. *J. Mol. Biol.* 1970, 49, 547-556.

Tetraphenylarsonium 1,2,3,4,5-Pentakis(methylmercapto)cyclopentadienide

F. Wudl,* D Nalewajek, F. J. Rotella, and E. Gebert

Contribution from the Bell Laboratories, Murray Hill, New Jersey 07974, and the Solid State Science and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

Received July 28, 1980. Revised Manuscript Received May 11, 1981

Abstract: The title compound was prepared by reaction of stoichiometric amounts of sodium hydride, cyclopentadiene, and methyl disulfide in tetrahydrofuran. The title compound was characterized by NMR, IR, and cyclic voltammetry measurements. A three-dimensional crystal and molecular structure of $[(\text{C}_6\text{H}_5)_4\text{As}][\text{C}_5(\text{SCH}_3)_5]$ has been determined by an X-ray diffraction study. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5 , No. 14] with $a = 12.568$ (2) Å, $b = 15.948$ (3) Å, $c = 17.523$ (3) Å, $\beta = 106.98$ (1)°, $V = 3359.21$ (10) Å³, and $\rho_{\text{calcd}} = 1.342$ g cm⁻³ for $Z = 4$. The structure was solved via the tangent formula and standard Fourier techniques and was refined by using full-matrix least-squares refinement to conventional discrepancy indices of $R_F = 8.65\%$ and $R_{wF} = 15.76\%$ for the 2652 independent data with $\Delta F/\sigma(F_o) \leq 10.0$ and $F_o \geq \sigma(F_o)$. All atoms with the exception of methyl hydrogens were located. The crystal consists of formula units of $[(\text{C}_6\text{H}_5)_4\text{As}^+][\text{C}_5\text{SCH}_3)_5^-]$, cations and anions being separated by normal van der Waals distances, as are formula units from each other. All distances and angles within the tetraphenylarsonium cation are normal. The methylmercapto groups of the 1,2,3,4,5-pentakis(methylmercapto)cyclopentadienide anion have their configurations relative to the cyclopentadienyl ring fixed by packing forces within the crystal. Distances and angles within the cyclopentadienyl ring are normal. The S-C distances within the anion are reduced from the sum of the covalent radii for sulfur and sp²-hybridized carbon which may indicate the possibility of multiple bonding.

In our current attempts to prepare organic conductors based on neutral radicals,¹ we proposed that solids based on the theoretically relatively stable² cyclopentadienyl radical embedded in a chalcogen milieu may give rise to high conductivity. This hypothesis was based on the following facts: (a) pentaphenylcyclopentadienyl (A, Scheme I) is stable at room temperature in the solid state, (b) chalcogens (certainly sulfur³) tend to delocalize

spin from a carbon framework to the chalcogen, and (c) chalcogens are free radical stabilizing substituents.^{1,4}

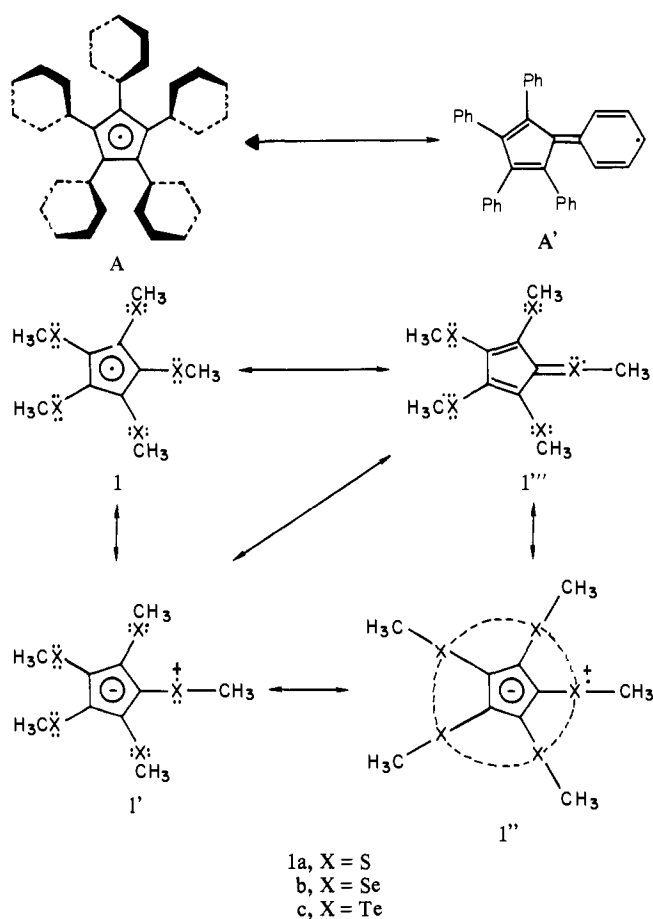
(1) Wudl, F. In "Physics and Chemistry of Low Dimensional Solids"; Alcaicer, L., Ed.; Plenum Press: New York, 1980. Wudl, F. "Physics and Chemistry of One Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; p 248.

(2) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1979, 101, 3771.

(3) Bramwell, F. B.; Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *J. Am. Chem. Soc.* 1978, 100, 4612.

* To whom correspondence should be addressed at Bell Laboratories.

Scheme I



The stability of pentaphenylcyclopentadienyl is most likely due to steric factors, i.e., the phenyls are rotated out of the plane of the cyclopentadienyl, preventing dimerization and at the same time obstructing delocalization of the unpaired spin to the para position, thus hindering the usual dimerization of phenyl-substituted radicals; e.g., triphenylmethyl.⁵ It is precisely this kind of steric effect which is undesirable for the intermolecular spin delocalization in the solid state (band formation) so crucial to the evolution of high conductivity.⁶ Making use of point b (above) would circumvent this problem (Scheme I).

While the methyls would be prohibitively large for enhanced intermolecular solid-state interactions in the case of **1a**, they would be relatively small in the case of **1c**. The latter may be also ideal for attainment of the intriguing, dipolar resonance contributor **1c'**, because of the known Hückel driving force for formation of cyclopentadienide anion, and the tellurium atoms' size (1.35-Å covalent radius, 0.02 Å larger than iodine) and low electronegativity.⁷

Since the organic chemistry of tellurium is still in rudimentary state,⁸ we decided to prepare **2a**, as a model system, for if we could prepare it, we could study (a) its electrochemistry and ascertain the solution stability of **1a** from the half-cell potential of the one-electron oxidation, (b) its ability to form metallocenes, particularly cobaltocene which would in itself be a neutral free radical, and (c) its general organometallic chemistry which may be different than that of the parent cyclopentadienide particularly in

(4) Haddon, R. C.; Wudl, F.; Kaplan, M. L.; Marshall, J. H. *J. Chem. Soc., Chem. Commun.* **1978**, 429.

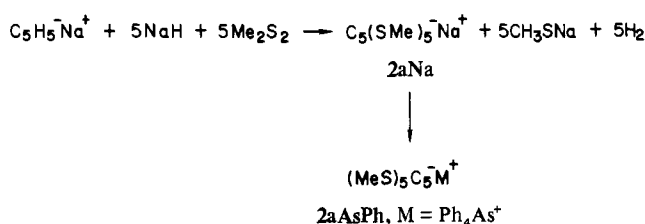
(5) McBride, J. M. *Tetrahedron* **1974**, 30, 2009.

(6) Schultz, T. D.; Craven, R. A. In "Highly Conducting One-Dimensional Solids"; Devreese, J. T.; Evrard, R. P.; van Doren, V. E.; Eds.; Plenum Press: New York, 1979; pp 147 ff.

(7) Cooper, W. C. "Tellurium"; Van Nostrand-Reinhold Co.: New York, 1971.

(8) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974.

Scheme II



regard to catalysis (e.g., pentamethylcyclopentadienide derivatives⁹).

Here we report on the preparation of the title compound and its sodium salt and the crystal structure determination of the former.

Results and Discussion

While one may envision multistep syntheses of **2**, a "one-pot" preparation based on the approach used for cyanation of cyclopentadienide¹⁰ was found to be successful¹¹ (Scheme II).

Since the resulting sodium salt was unstable in air, metathesis in deoxygenated water with tetraphenylarsonium chloride hydrate produced material which exhibited ¹H NMR aromatic and S-CH₃ resonances at 7.77 and 2.20 ppm vs. Me₄Si respectively in a ratio of 4:3.

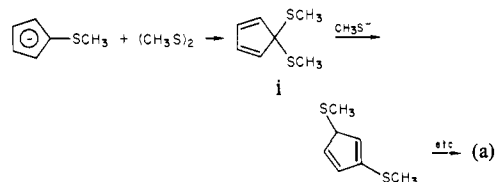
As expected, **2aAsPh** has an extremely low oxidation potential in solution [*E*^{1/2} = -0.03 and 0.83 V (both irreversible) vs. SCE, CH₃CN, (Bu)₄N⁺BF₄⁻ supporting electrolyte] and must consequently be protected from oxygen and other mild oxidizing agents. This oxidative lability, while desirable for the preparation of **1** from the anion, appears to be a liability when other reactions of this anion are attempted. Thus, when either sodium or tetraphenylarsonium pentakis(methylmercapto)cyclopentadienide is allowed to react with ferrous chloride, no characterizable product can be isolated. The same result was obtained with cobaltous chloride. It is possible that the thiomethyl groups hinder formation of a metallocene either sterically or by binding with the transition metal. Evidence for the latter stems from the observation that Fe(CO)₅ decomposes the title cyclopentadienide producing (as only characterizable product) the cis and trans isomers of (CO)₃Fe(SCH₃)₂Fe(CO)₃.¹²

Because the tetraphenylarsonium salt was stable and reactions with transition-metal salts were apparently leading to Cp-sulfur

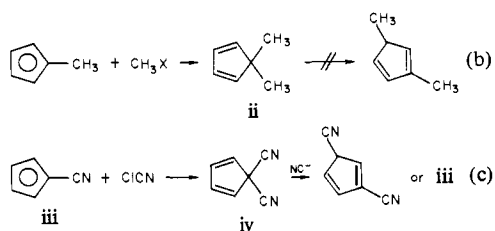
(9) Maitlis, P. M. *Acc. Chem. Res.* **1978**, 11, 301 and references therein.

(10) Webster, O. W. *J. Am. Chem. Soc.* **1966**, 88, 3046.

(11) Attempts to generate the much coveted (CH₃)₅C₅⁻ via "one-pot" multiple methylation using methyl iodide or dimethyl sulfate failed probably



because of



While intermediates i and iv (if iv is formed at all) can easily be degraded to multiply substituted cyclopentadienides, ii cannot under the conditions of the reaction.

(12) Seyterth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, 101, 508.

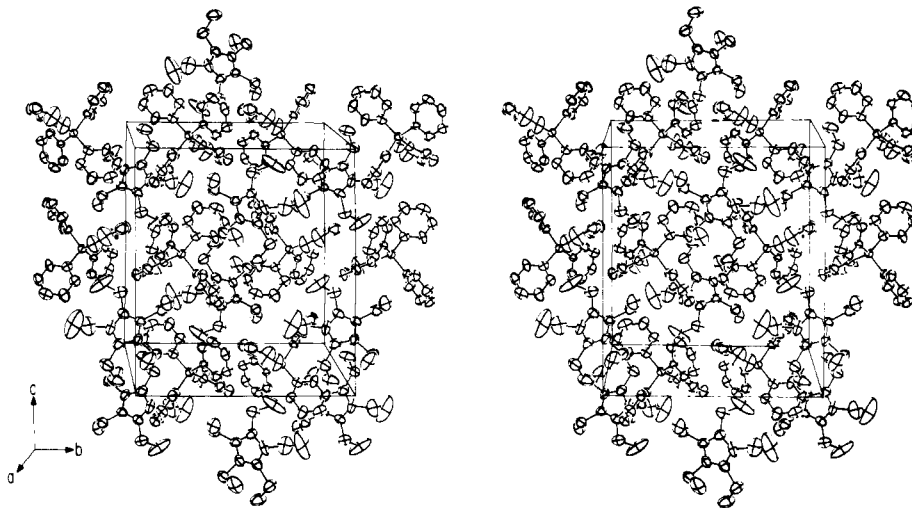


Figure 1. Stereoview of mode of packing of tetraphenylarsonium pentakis(thiomethyl)cyclopentadienide.

Table I. Experimental Data for the X-ray Diffraction Study of $[(C_6H_5)_4As][C_5(SCH_3)_5]$

(A) Crystal Data	
crystal system:	monoclinic
space group:	$P2_1/c$
unit cell parameters ^a	
a	12.568 (2) Å
b	15.948 (3) Å
c	17.523 (3) Å
β	106.98 (1)°
V	3359.2 (10) Å ³
temp	23.5 (5) °C
Z	4
mol wt:	678.90
ρ (calcd)	1.342 g cm ⁻³
(B) Intensity Data	
radiation used:	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
monochromator:	highly oriented graphite
reflectns measd:	$+h, +k, \pm l$
max 2θ measd:	40.0°
min 2θ measd:	4.5°
scan type:	coupled θ (crystal) 2θ (counter)
scan speed:	2.0°/min
scan range:	asymmetrical, from $[2\theta(K\alpha_1) - 0.8]^\circ$ to $[2\theta(K\alpha_2) + 1.1]^\circ$
bkgd measment:	stationary crystal/stationary counter at beginning and end of scan, each for one-third of the time taken for the scan
standard reflections:	3, measured every 47 reflections; percent variances from the mean, 4.41% for 610, 4.06% for 018, and 4.53% for 093
data set information:	3730 reflections collected, of which 166 were systematic absences and 226 were standard reflections
equivalent reflections were averaged, ^{b,c}	yielding 3156 symmetry-independent reflections
(C) Data Treatment Parameters	
"Ignorance factor":	$p = 0.03$, applied to $\sigma(F^2)$ as $[\{\sigma(F^2)\}^2 + \{pF^2\}^2]^{1/2}$
abs coeff: ^c	$\mu = 1.620$ mm ⁻¹

^a Determined by a least-squares fit of the setting angles of the unresolved Mo $K\alpha$ peaks of 24 reflections with $2\theta = 19.7$ – 27.1° .

^b The agreement indices between the averaged, symmetry-equivalent reflections were $R(F) = 3.2\%$ and $R(F^2) = 3.6\%$. ^c No absorption correction was applied to the data (see text).

cleavage, we decided to check via X-ray crystallography whether the Cp-SMe bonds were unusually long (weak) and/or whether there was bond alternation in the Cp itself.

The title compound crystallizes as bright yellow prisms in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^2 , No. 14]. The pertinent unit cell parameters and intensity data are exhibited in Table I. Table III is a collection of bond distances and angles in the structure, and information relating to the planarity of the

Table II. Data for the Structural Solution via MULTAN

(A) Statistical Distribution of Normalized Structure Factor Amplitudes			
function	obsd	theoretical ^a	
		centric	acentric
$\langle E \rangle$	0.810	0.798	0.886
$\langle E ^2 \rangle$	1.000 ^b	1.000	1.000
$\langle E^2 - 1 \rangle$	0.943	0.968	0.736
(B) MULTAN Data			
reflectns input:	285 with $ E \geq 1.70$		
Σ_2 relationships found:	1800		
min "triple-product" value:	8.44		
Σ_1 reflectns determined:	none		
origin fixing			
reflectns:	$h \ k \ l \ E$	phase angle	parity class
	7 3 $\bar{10}$ 2.99	0°	o o e
	4 5 1 2.23	0°	e o o
	2 3 $\bar{6}$ 1.99	0°	e o e
structure solution parameters			
"phasing" reflectns: ^c	$h \ k \ l \ E$	selected phase angle	
	4 4 $\bar{4}$ 2.67	180°	
	7 1 $\bar{14}$ 2.28	180°	
	2 3 0 1.74	0°	
"absolute figure of merit":	1.2126		
"residual":	21.96		
"combined figure of merit":	2.0000		

^a Karle, I. L.; Dragonette, K. S.; Brenner, S. A. *Acta Crystallogr.* 1965, 29, 713. ^b Fixed by an adjustable scale factor.

^c "Phasing" reflections are those reflections with large $|E|$ values and large phase reliability indices (α_h), which are allowed to take on variable phase angles, 0° and 180° in this case.

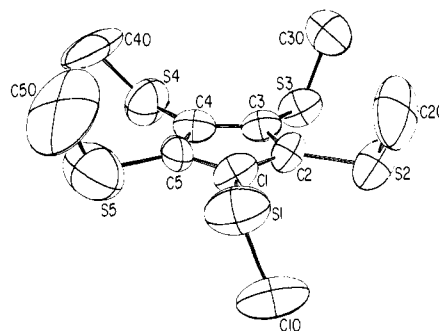


Figure 2. 50% equiprobability ellipsoids of the disposition of the thiomethyl groups in the pentakis(thiomethyl)cyclopentadienide anion.

pentakis(thiomethyl)cyclopentadienide anion is listed in Table IV.

Figure 1 is a stereodiagram of the packing in the unit cell, and Figure 2 shows the arrangement of thiomethyl groups (without

Table IV. Least-Squares Planes (and Esd's)^a and Dihedral Angles

atom ^b	dev, Å	atom ^b	dev, Å
(A) Cyclopentadienyl Plane in the 1,2,3,4,5-Pentakis(methylmercapto)cyclopentadienide Anion			
Plane: $-0.7959X + 0.2355Y - 0.5578Z = -9.3698$			
C1*	0.006 (12)	S4	-0.024 (4)
C2*	-0.010 (12)	S5	0.093 (5)
C3*	0.011 (11)	C10	1.553 (15)
C4*	-0.009 (11)	C20	-1.410 (17)
C5*	0.003 (13)	C30	-1.457 (14)
S1	-0.060 (4)	C40	-1.390 (7)
S2	0.084 (4)	C50	-1.483 (22)
S3	0.186 (3)		
(B) Phenyl Planes in the Tetraphenylarsonium Cation			
Plane I: $0.6165X + 0.7706Y - 0.1615Z = 4.5201$			
C11*	-0.015 (10)	C15*	0.015 (14)
C12*	0.023 (12)	C16*	0.004 (11)
C13*	-0.007 (12)	As	0.087 (1)
C14*	-0.012 (12)		
Plane II: $-0.7215X + 0.1845Y - 0.6673Z = -8.5286$			
C21*	-0.013 (10)	C25*	0.007 (14)
C22*	0.009 (12)	C26*	0.005 (11)
C23*	0.014 (14)	As	-0.157 (1)
C24*	-0.034 (14)		
Plane III: $0.2808X - 0.8098Y - 0.5152Z = -5.8786$			
C31*	0.001 (10)	C35*	0.007 (14)
C32*	-0.000 (11)	C36*	-0.003 (11)
C33*	0.003 (14)	As	-0.069 (1)
C34*	-0.009 (13)		
Plane IV: $0.2436X + 0.4414Y - 0.8636Z = -4.5619$			
C41*	0.007 (9)	C45*	0.008 (17)
C42*	-0.006 (12)	C46*	-0.012 (13)
C43*	0.001 (12)	As	0.068 (1)
C44*	-0.000 (13)		
Dihedral Angles between Phenyl Planes			
plane	plane	angle, deg	
I	II	101.24	
I	III	111.57	
I	IV	50.97	
II	III	90.47	
II	IV	61.18	
III	IV	81.02	

^a Equations of planes are expressed in orthonormal (Å) coordinates (X, Y, Z) which are related to the fractional coordinates (x, y, z) by the transformation:

$$\begin{array}{rcccc} X & a & 0 & c \cos \beta & x \\ Y & =0 & b & 0 & y \\ Z & 0 & 0 & c \sin \beta & z \end{array}$$

^b Those atoms marked with an asterisk were given unit weight in the corresponding plane; those unmarked were given zero weight.

dissolved in a minimum amount of THF (~10 mL) and reprecipitated by slowly adding 400 mL of ether. The resulting white sodium salt was filtered and dried; yield 12.20 g (51%). Further characterization of this salt was difficult due to instability. It was therefore converted to the tetraphenylarsonium derivative.

Tetraphenylarsonium 1,2,3,4,5-Pentakis(methylmercapto)cyclopentadienide. A solution containing 2.2 g (6.9×10^{-3} mol) of the above salt in 100 mL of water was treated dropwise with a solution of 3.0 g (6.9×10^{-3} mol) of tetraphenylarsonium chloride hydrate in 100 mL of water. The yellow precipitate which formed was stirred for 0.5 h, filtered, washed with water (3×10 mL), and dried. Recrystallization from acetonitrile/ether afforded 2.6 g (54%) of bright yellow prisms. mp 184–184.4 °C; NMR (CD_3CN) δ (ppm relative to Me₄Si) 7.77 (20 H), 2.20 (15 H). Anal. Calcd for C₃₄H₃₈S₅As: C, 60.15; H, 5.20; S, 23.62; As, 11.04. Found: C, 60.00; H, 5.28; S, 23.72; As, 11.11.

Collection and Treatment of X-ray Diffraction Data

The crystal chosen for the structural analysis was a yellow prism of approximate dimensions 0.28 mm \times 0.33 mm \times 0.25 mm. The crystal was wedged into a 0.3-mm diameter thin-walled glass capillary, which was subsequently flushed with argon, flame-sealed, fixed into an alu-

minum pin with beeswax, and set in an eucentric goniometer head.

The crystal was now placed in the goniostat of a SYNTEX P2₁ four-cycle automated diffractometer controlled by a Data General NOVA 1200 computing system. After accurate centering in a monochromated Mo K α X-ray beam, the crystal's relative orientation and accurate unit cell parameters were determined and intensity data were collected as described previously.¹⁵ The crystal was found to be monoclinic, and perusal of the preliminary data set revealed the systematic absence OkO for $k = 2n + 1$ and hOl for $l = 2n + 1$, which are consistent with the centrosymmetric space group $P2_1/c$ [C_{2h}^2 , No. 14].

Upon completion of intensity data collection, the effects of absorption were assessed by measuring five reflections of varying 2θ values at 10° intervals of ψ (the azimuthal angle, corresponding to rotation of the crystal about its diffraction vector for that reflection) from $\psi = 0^\circ$ to 350°. The worst " ψ scan" was for the 254 reflection ($2\theta = 22.02^\circ$, max/min = 1.202) which showed a variance from the mean of 5.72%. This result coupled with the small absorption coefficient (Table I) and relatively uniform crystal shape indicated that absorption was not a problem in this system.

The primary data set was now transferred to the IBM 370/195 central computing system at Argonne and was converted to a set of squared structure factor amplitudes (F^2). Equivalent reflections were averaged into a final symmetry data set.

Specifics of data collection and treatment are listed in Table I.

Solution and Refinement of the Structure

All calculations were performed on the IBM 370/195 computer. Programs used in the structural analysis were part of the crystallographic programming package available in the chemistry division of Argonne.¹⁶

The atomic scattering factors for all neutral nonhydrogen atoms were taken from the compilation of Cromer and Waber,¹⁷ and Stewart's scattering factors for hydrogen were used;¹⁸ the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms.¹⁹

The function minimized throughout the least-squares refinement was $w(|F_o| - |F_c|)^2$, where $w = \{\sigma(F_o)\}^{-2}$. Discrepancy indices and goodness-of-fit (GOF) are defined as $R_F = [\sum ||F_o| - |F_c|| / \sum |F_o|] \times 100(\%)$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} \times 100(\%)$, and $GOF = [\sum (|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$, where NO is the number of independent observations and NV is the number of variables in the least-squares refinement.

The structure was solved by use of the tangent formula as used in MULTAN.²⁰ The calculation of normalized structure factor amplitudes ($|E|$) and the application of MULTAN to the solution of X-ray structures as used here have been described previously;²¹ the statistical distribution of $|E|$'s and MULTAN data specific to the solution of this structure are collected in Table II. The given solution was used to phase an "E-map" from which the positions of the arsenic atom of the cation, two sulfur atoms of the anion, and eight ring carbon atoms were located. An observed Fourier synthesis based on these positions led to the location of all of the other nonhydrogen atoms in the asymmetric unit. A difference Fourier synthesis revealed a high degree of anisotropy around most of the nonhydrogen atoms; anisotropic thermal parameters were included for all of these atoms and the structural refinement converged to $R_F = 12.0\%$ and $GOF = 4.896$ for the 2749 reflections with $F_o \geq \sigma(F_o)$.

The location of hydrogen atoms was undertaken and a difference Fourier synthesis showed the position of all 24 phenyl hydrogens, but no unambiguous positions could be obtained for the methyl hydrogens of the 1,2,3,4,5-pentakis(methylmercapto)cyclopentadienide anion. The phenyl hydrogens were included in the model by fixing their located positions and holding their thermal parameters at 5.0 Å²; 89 reflections with $\Delta F/\sigma(F_o) \geq 10.0$ were not included in subsequent least-squares cycles. Refinement with 361 parameters converged with $R_F = 10.15\%$, $R_{wF} =$

(15) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265. See also "Fortran Operations Manual: SYNTEX P2₁", SYNTEX Analytical Instruments: Cupertino, CA 1975.

(16) Structural analysis programs include MULTAN 74 package (phase determination from $|E|$'s via the tangent formula by P. Main, M. M. Woolfson, and G. Germain), LSQR1 (full-matrix least-squares refinement routine, adapted from ORXFLS3 by W. R. Busing and H. A. Levy), Canterbury Fourier Routine (by R. J. Dellaca and W. T. Robinson), ORFFE (distances, angles, and esd's calculation by inclusion of variance-covariance effects of positional parameters by W. R. Busing and H. A. Levy), PLANE (least-squares planes, esd's, and dihedral angles calculations by M. E. Pippy), and ORTEP-II (thermal ellipsoid plotting routine by C. K. Johnson).

(17) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(19) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(20) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

(21) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1978**, *17*, 2614.

15.95%, and GOF = 2.916 for 3067 reflections and $R_F = 8.65\%$, $R_{wF} = 15.76\%$, and GOF = 3.310 for 2652 reflections with $F_o \geq \sigma(F_o)$; the data-to-parameter ratios were 8.50:1 for all included data and 7.35:1 for $F_o \geq \sigma(F_o)$ reflections. The final difference Fourier map showed peaks of approximate density $0.85 \text{ e } \text{Å}^{-3}$ within 1.25 Å of the sulfur atoms in the cyclopentadienide anion. Since no suitable disorder model could be included in the refinement to account for the contribution of the methyl hydrogens, the analysis was declared complete.

Final positional and thermal parameters are given in the supplementary material.

Acknowledgment. F.J.R. and E.G. are grateful to the Division of Basic Energy Research, U.S. Department of Energy, for support of their research. F.W. and D.N. thank J. W. Suggs for helpful discussions.

Supplementary Material Available: A listing of the observed and calculated structure factor amplitudes used in the structure analysis and the positional and thermal parameters (17 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of Methyl Bacteriopheophorbide a. A Model for a Primary Electron Acceptor in Bacterial Photosynthesis

K. M. Barkigia,*^{1a} J. Fajer,^{1a} K. M. Smith,^{1c} and G. J. B. Williams^{1b}

Contribution from the Department of Energy and Environment and the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, and the Department of Chemistry, University of California, Davis, California 95616. Received February 23, 1981

Abstract: Bacteriopheophytin is a key component in the mechanism by which photosynthetic bacteria transduce solar energy into chemical form. The structure of methyl bacteriopheophorbide a, a bacteriopheophytin derivative, has been determined by three-dimensional X-ray diffraction. The compound crystallizes in space group *P1* in a unit cell containing a molecule of methyl bacteriopheophorbide and a benzene molecule of crystallization, with lattice constants $a = 7.2502(8) \text{ Å}$, $b = 8.1070(9) \text{ Å}$, $c = 17.224(5) \text{ Å}$, $\alpha = 90.80(2)^\circ$, $\beta = 94.17(2)^\circ$, and $\gamma = 110.38(1)^\circ$. The structure has been refined with isotropic thermal parameters on *F* by full-matrix least squares to $R_F = 0.110$, based on 860 reflections. The molecules associate in chains via π - π interactions with ring I of one molecule overlapping ring III of its neighbor with a vertical separation of 3.6 Å . The one-dimensional chains form two-dimensional layers without the intervention of the hydrogen bonding by water molecules previously reported for chlorophyllides. This work represents the first crystallographic determination of a bacteriochlorin and confirms the canonical structures and relative orientations of the five chiral centers of bacteriochlorophyll a derivatives.

Photosynthetic bacteria, plants, and algae harvest light via an antenna network comprised of bacteriochlorophylls or chlorophylls and funnel the incident light into reaction centers. In these special environments, an array of (bacterio)chlorophylls transduces the gathered photons into oxidants and reductants that drive the biochemistry of the organisms.²⁻⁴ Reaction centers of purple bacteria⁵ contain four bacteriochlorophylls (BChl), two bacteriopheophytins (BPheo, metal-free BChls) and other components of the electron transport chain. A "special pair" of the BChls^{6,7} acts as electron donor and transfers an electron to BPheo⁷⁻⁹ within

4 ps of excitation,¹⁰ possibly via one or more of the remaining BChls.¹¹ The BPheo anion in turn reduces a quinone in ~ 200 ps.⁹ The rapid translocation of the electron away from the primary donor, via BPheo, thus stabilizes the charge separation and minimizes wasteful back reactions.

Although several crystallographic determinations of chlorophyll derivatives have been reported,¹²⁻¹⁵ no corresponding data exist for bacteriochlorophylls, except for the structure of a BChl protein at 2.8 Å resolution.¹⁶ We report here the crystal and molecular structure of methyl bacteriopheophorbide a (MeBPheo), a bacteriopheophytin in which the esterifying fatty alcohol side chain found in vivo has been replaced by a methyl group (I). Although the precision of this study is limited by the extremely small size of the sole crystal obtained, the results (1) confirm the structures

(1) (a) Department of Energy and Environment. (b) Chemistry Department, BNL. (c) University of California.

(2) Clayton, R. K.; Sistrom, W. R., Eds. "The Photosynthetic Bacteria"; Plenum Publishing Cor.: New York, 1978.

(3) Govindjee, Ed. "Bioenergetics of Photosynthesis"; Academic Press: New York, 1975.

(4) Olson, J. M.; Hind, G., Eds. *Brookhaven Symp. Biol.* **1976**, *28*.

(5) Straley, S. C.; Parson, W. W.; Mauzerall, D. C.; Clayton, R. R. *Biochim. Biophys. Acta* **1973**, *305*, 597-609. Reed, D. W.; Clayton, R. K. *Biochem. Biophys. Res. Commun.* **1968**, *30*, 471. Gingras, G. in ref 2, pp 119-132. Olson, J. M.; Thornber, J. P. In "Membrane Proteins in Energy Transduction", Capaldi, R. A., Ed.; Marcel Dekker: New York, 1979; pp 279-340. Okamura, M. Y.; Feher, G.; Nelson, N. In "Integrated Approach to Plant and Bacterial Photosynthesis", Govindjee, Ed.; Academic Press: New York, 1981; Chapter 3. Thornber, J. P.; Cogdell, R. J.; Seflor, R. E. B.; Webster, G. D. *Biochim. Biophys. Acta* **1980**, *593*, 60-75.

(6) Katz, J. J.; Norris, J. R.; Shipman, L. L.; Thurnauer, M. C.; Wasielewski, M. R. *Annu. Rev. Biophys. Bioeng.* **1978**, *7*, 393-434. Feher, G.; Hoff, A. J.; Isaacson, R. A.; Ackerson, L. C. *Ann. N.Y. Acad. Sci.* **1975**, *244*, 239-259.

(7) Davis, M. S.; Forman, A.; Hanson, L. K.; Thornber, J. P.; Fajer, J. J. *Phys. Chem.* **1979**, *83*, 3325-3332.

(8) Fajer, J.; Brune, D. C.; Davis, M. S.; Forman, A.; Spaulding, L. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4956-4960. Fajer, J.; Davis, M. S.; Brune, D. C.; Spaulding, L. D.; Borg, D. C.; Forman, A. *Brookhaven Symp. Biol.* **1976**, *28*, 74-104. Parson, W. W.; Monger, T. G. *Ibid.* **1976**, *28*, 195-212. Dutton, P. L.; Prince, R. C.; Tiede, D. M.; Petty, K. M.; Kaufmann, K. J.; Netzel, T. L.; Rentzepis, P. M. *Ibid.* **1976**, *28*, 213-237.

(9) Rockley, M. G.; Windsor, M. W.; Cogdell, R. F.; Parson, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 2251-2255. Kaufmann, K. J.; Dutton, P. L.; Netzel, T. L.; Leigh, J. S.; Rentzepis, P. M. *Science* **1975**, *188*, 1301-1304.

(10) Holten, D.; Hoganson, C.; Windsor, M. W.; Schenk, C. C.; Parson, W. W.; Migus, A.; Fork, R. L.; Shank, C. V. *Biochim. Biophys. Acta* **1980**, *592*, 461-477.

(11) Shuvalov, V. A.; Klevanik, A. V.; Sharkov, A. V.; Matveetz, A.; Krukov, P. G. *FEBS Lett.* **1978**, *91*, 135-139.

(12) Hoppe, W. V.; Will, F.; Gassmann, J.; Weichselgartner, H. Z. *Kristallogr.* **1969**, *128*, 18-35.

(13) Fischer, M. S.; Templeton, D. H.; Zalkin, A.; Calvin, M. J. *Am. Chem. Soc.* **1972**, *94*, 3613-3619.

(14) Strouse, C. E. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 325-328.

(15) Chow, H. C.; Serlin, R.; Strouse, C. E. *J. Am. Chem. Soc.* **1975**, *97*, 7230-7237. Serlin, R.; Chow, H. C.; Strouse, C. E. *Ibid.* **1975**, *97*, 7237-7242.

(16) Kratky, C.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1586-1589; *Ibid.* **1977**, *B33*, 545-547; *J. Mol. Biol.* **1977**, *113*, 431-442.

Kratky, C.; Isenring, H. P.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1977**, *B33*, 547-549.

(16) Mathews, B. W.; Fenna, R. E. *Acc. Chem. Res.* **1980**, *13*, 309-317. Fenna, R. E.; Ten Eyck, L. F.; Matthews, B. W. *Biochem. Biophys. Res. Commun.* **1977**, *75*, 751-756.