A RESONANCE RAMAN/IODINE MOESSBAUER INVESTIGATION OF THE STARCH--ETC(U)

R C TEITELBAUM, S L RUBY, T J MARKS

N00014-77-C-0231
A Resonance Raman/Iodine Mössbauer Investigation of the Starch-Iodine Structure:

Aqueous Solution and Iodine Vapor Preparations

by

Robert C. Teitelbaum, Stanley L. Ruby

and

Tobin J. Marks

Prepared for Publication

in

The Journal of the American Chemical Society

Northwestern University
Department of Chemistry
Evanston, Illinois 60201

March 5, 1980

Reproduction in whole or in part is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

*This statement should also appear in Item 10 of Document Control Data - DD Form 1473. Copies of form available from cognizant contract administrator.
**Technical Report No. 11**

**Investigation of the Starch-Iodine Structure: Aqueous Solution and Iodine Vapor Preparations.**

**PERFORMING ORGANIZATION NAME AND ADDRESS**

**C-A**

**PERFORMING ORG. REPORT NUMBER**

**HHP14-77-C-0231**

**CONTRACING OFFICE NAME AND ADDRESS**

**NR-053-640**

**CONTROLLING OFFICE NAME AND ADDRESS**

**Mon**

**NUMBER OF REPORT**

**40**

**MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)**

**12**

**NUMBER OF DISTRIBUTION**

**47**

**DISTRIBUTION STATEMENT (of this Report)**

Approved for public release; distribution unlimited

**DISTRIBUTION STATEMENT (of this Report)**

**TM**

**DISTRIBUTION STATEMENT (of this Report)**

**Inters. rep.**

**KEY WORDS (Continue on reverse side if necessary and identify by block number)**

Resonance Raman spectroscopy

Mössbauer spectroscopy

Starch-iodine

Optical material

1-Dimensional material

**ABSTRACT (Continue on reverse side if necessary and identify by block number)**

The structure of the blue-black iodine complex of amylose (the linear, helical component of starch) prepared either from iodine and iodide in aqueous solution or from crystalline amylose and iodine vapor, has been studied by resonance Raman and iodine -129 Mössbauer spectroscopy. In both cases it is concluded that the identity of the major chromophore is essentially the same: the pentaiodide (I5) anion. For the material prepared from iodine vapor, the iodide required for formation is produced by hydrolysis or alcoholysis of...
Iodine. The other product of this reaction, a hypiodite, has been assigned in the iodine Mössbauer spectrum.
A RESONANCE RAMAN/IODINE MöSSBAUER INVESTIGATION OF THE STARCH-IODINE STRUCTURE: AQUEOUS SOLUTION AND IODINE VAPOR PREPARATIONS.

by Robert C. Teitelbaum, a, c Stanley L. Ruby, b and Tobin J. Marks a, 2

ABSTRACT

The structure of the blue-black iodine complex of amylose (the linear, helical component of starch) prepared either from iodine and iodide in aqueous solution or from crystalline amylose and iodine vapor, has been studied by resonance Raman and iodine 129 Mössbauer spectroscopy. In both cases it is concluded that the identity of the major chromophore is essentially the same: the pentaiodide (I5-) anion. For the material prepared from iodine vapor, the iodide required for I5- formation is produced by hydrolysis or alcoholysis of iodine. The other product of this reaction, a hypoiodite, has been assigned in the iodine Mössbauer spectrum.
Historically, scientific interest in the interaction of the various fractions of starch with iodine has stemmed from the striking color changes which accompany complexation. Amylose, the linear starch fraction, which is comprised of one-dimensional chains of 1,4 linked α-D-glucopyranose units (A), forms an intensely blue-black adduct with aqueous iodine in the presence of iodide: "starch-iodine." In contrast, the branched fraction of starch, amylopectin, does not form such a complex. Although starch-iodine has been known for a great many years, and few chemists indeed are unfamiliar with the use of this intensely colored classic indicator in qualitative
and quantitative analysis, there is surprisingly little unambiguous information on the actual structure of the chromophore with $\lambda_{\text{max}} \approx 600$ nm.

In a series of pioneering optical and X-ray diffraction studies, Rundle and his co-workers established that the iodine component of starch-iodine is present in a unidimensional array within an amyllose helix of diameter $\approx 13\AA$, period $\approx 8\AA$, and with 6 glucose residues per turn. The structure is illustrated in Figure 1. The amyllose employed for the bulk of these investigations was the crystalline "V" form which is an alcohol inclusion complex $3a,4,7$ (amylose is now known to form a great many such complexes, all having the included molecules contained within the helix $3a,4$). Rundle's samples were prepared by staining the solid "V" amyllose with iodine va... The fact that ordinary amyllose will not form the complex under these conditions, and that starch-iodine has been traditionally prepared in aqueous solution, in the presence of iodide, has introduced a significant complication in understanding the structure of starch-iodine.

The actual nature of the iodine chromophore within the amyllose helix has been the subject of considerable speculation and controversy. The earliest proposals were that iodine is present as discrete $I_2$ molecules which are "dissolved" in the relatively hydrophobic interior of the amyllose helix (B).$5b,8$ Several spectrophotometric
and potentiometric investigations in aqueous solution later identified the requirement of $I^-$ for complex formation. Although $I^-$ might have a structure-forming role not related to inclusion, it was also recognized that it might be incorporated within the helix as discrete $I^-$ ions or as $I_5^-$. A model for starch-iodine composed of linear chains of $I_3^-$ (C) as in $(\text{benzamide})_2 H^+ I_3^-$ has also been proposed and widely accepted. The similarity between amylose and the cyclodextrins (cycloamyloses) in structure and in the tendency to form inclusion complexes led to new structural suggestions for starch-iodine based upon the crystal structures of $(\alpha-\text{CD})_2 \cdot \text{Li}_4 \cdot I_2 \cdot 8\text{H}_2\text{O}$ and $(\alpha-\text{CD})_2 \cdot \text{Cd}_{0.5} \cdot I_2 \cdot 26\text{H}_2\text{O}$ (Cyclohexamylose). Either alternating arrays of $I_2$ and $I_5^-$ units (D) or symmetrical, linear $I_5^-$ units (E) were considered to be plausible structures. There is
additional precedent in polyiodide structural chemistry for either
motif. 14, 15

A large battery of physicochemical techniques has been directed
at identifying the form(s) of iodine present in starch-iodine. These
methods have included optical, 7a,b,9,10 infrared, 16 electron para-
magnetic resonance, 17 ORD/CD, 18 iodine Mössbauer, 19 and
resonance Raman spectroscopy, 20 as well as x-ray powder diffrac-
tion, 7a,c,d,g spectrophotometric and potentiometric titrations, 9
and intrinsic viscosity studies. Many of these investigations have
unfortunately suffered from the intrinsic deficiencies of the particu-
lar method when applied to such a problem, and/or from the lack of
realistic model compounds and modern data analysis procedures. Thus,
in early (but important) iodine Mössbauer studies, 19 only structural pos-
sibilities B and C were considered, and no attempt was made to determine
relative iodine site populations. Structure C was chosen over B because non-
equivalent iodine sites were observed and because spectral parameters were
reminiscent of (benzamide)2H+2I3-. An early resonance Raman
investigation of starch-iodine 20 also only considered possibilities B and C;
structure C was assigned with limited reference to appropriate model
compounds and the symmetries of internal coordinate changes most likely
to be resonant enhanced. The degree to which the aqueous and "V" amylose preparations of starch-iodine might or might not be the same has been an additional complication. The net result of these efforts is that it has not been possible to unambiguously differentiate among the various proposed structures, and there has been no definitive information on the identity of the iodine species in starch-iodine.

We recently reported resonance Raman and iodine-$^{129}$ Mössbauer spectroscopic results on the structure of starch-iodine prepared in aqueous solution. A full range of model compounds was utilized, and Mössbauer spectral analysis was carried out by iterative computer simulation. It was concluded in that preliminary report that the predominant iodine-containing species present was $I_5^-$, as in structure E. This polyiodide species formally requires the presence of both $I_2$ and $I^-$ for formation, in agreement with experimental observations. An important and unanswered question in developing a complete and coherent description of starch-iodine is whether or not the chromophore in the material prepared from "V" amylose and $I_2$ vapor is really the same, and if so, how this comes about. In this contribution we present a full discussion of our spectral studies of starch-iodine, prepared by both aqueous and $I_2$ vapor methods.
EXPERIMENTAL

Synthesis of Starch-Iodine. Aqueous Solution Method. Granular potato amylose was purchased from Aldrich Chemical Company. A typical preparation involved the reaction with stirring of 1.8 g of amylose, 0.88 g (3.5 mmole) triply sublimed L₂, and 0.53 g (3.5 mmole) NaI in 50 ml of deionized water. The resulting blue-black complex, which is formed immediately, was collected by centrifugation, and washed with deionized water. Washing was then repeated until no I⁻ could be detected in the water washings, when treated with AgNO₃ solution. The product was then freeze-dried.

Synthesis of Starch-Iodine. Iodine Vapor Method. Granular potato amylose was crystallized from H₂O and n-butanol according to the procedure of Schoch. In a typical crystallization, 0.50 g of granular amylose was dissolved in 150 ml. of boiling deionized water, with constant stirring. To the boiling solution, 10.5 ml of n-butanol was slowly added, and the solution allowed to cool to room temperature over a period of about 6 hours. The "wet" crystalline "V" amylose was collected by suction filtration and washed repeatedly with analytical reagent grade methanol. The remaining methanol was removed by drying in a vacuum dessicator. Iodination was accomplished by placing a vial of the crystalline "V" amylose in a closed vessel in contact with iodine vapor. The characteristic color of the starch-iodine complex developed immediately. A sample prepared
in this manner typically contained 5-10% iodine by weight.

**Synthesis of Starch-Iodine-129. Aqueous Solution Method.** The reagent $^{129}\text{I}_2$ was prepared by oxidation of an acidified Na $^{129}\text{I}$ solution (obtained from Oak Ridge National Laboratory) and subsequent extraction with pentane. The pentane was then evaporated in a stream of prepurified nitrogen to yield solid $^{129}\text{I}_2$. For a source of I$^-$, the basic Na$^{129}\text{I}$ solution from Oak Ridge was neutralized with $\text{H}_2\text{SO}_4$ and used without dilution. The Mössbauer spectroscopy sample of the amylose-iodine complex was prepared by combining 0.71 g of amylose with 35 mg $^{129}\text{I}_2$ and 0.80 ml of the neutralized Na$^{129}\text{I}$ solution in 30 ml of deionized water. The product was collected by centrifugation, washed with water, and the same freeze-drying procedure as described above was employed for drying.

**Synthesis of Starch-Iodine-129. Iodine Vapor Method.** The Mössbauer spectroscopy sample of the "V" amylose-iodine complex was prepared using the same procedure as for the unenriched sample (*vide supra*), except that $^{129}\text{I}_2$ was used. The reagent $^{129}\text{I}_2$ was prepared as described above.

**Raman Measurements.** Laser Raman spectra were recorded with Kr$^+$ (6471 Å) or Ar$^+$ (4579 Å, 4880 Å, 4965 Å, 5145 Å) excitation using a Spex 1401 monochromator and photon counting detection. The solid samples were studied in 5 or 12 mm Pyrex sample tubes spinning at 1200 rpm. A 180$^\circ$ back-scattering geometry was employed. A number of scans
were made of each sample (the initial at lowest laser power) to check for possible sample decomposition. Spectra were calibrated with the exciting line ($\nu_0$) or laser plasma lines.

Iodine-129 Mössbauer Spectroscopy. These measurements employed the apparatus described previously.\textsuperscript{23,24a} Absorbers were prepared by thoroughly powdering the iodine-129 enriched sample and, where necessary, mixing it with an inert filler (boron nitride) to achieve complete filling of the sample container. The absorbers typically contained ca. 7 mg. $^{129}$I/cm$^2$. Both the source and absorber were cooled to 4.2° K during data collection. Typically, 2-3 sources were used, in sequence, to collect all the data for a given sample. Data collected from each source were summed to give the final spectra. Individual runs were checked for reproducibility. The spectrometer velocity was generated with a feedback-controlled vibrator using sinusoidal acceleration, and the velocity drive was calibrated with $^{57}$Fe foil. Mössbauer effect data processing and analysis employed the computer program, GENFIT,\textsuperscript{23} which finds the best values of the parameters of isomer shift, quadrupole coupling constant, linewidth, populations, baseline and asymmetry parameter via non-linear least-squares minimization of the difference between the observed and calculated spectra. Starting spectral parameters were based on literature data,\textsuperscript{19,24a,33-35} and care was taken to approach optimum fits from several directions so that converging on local minima would be avoided. The goodness of fit is judged by the parameter "Misfit," which has been previously defined by Ruby.\textsuperscript{25}
The end sites in the pentaiodide ion showed somewhat larger line-widths than the other iodine sites. This could be explained if the end sites have a slight distribution of quadrupole coupling constants. That is, not all end sites are exactly equivalent. This nonequivalence was incorporated in the fitting procedure as a velocity-dependent line-broadening function (eq. (1)), where \( \gamma_{\text{true}} \) is the actual linewidth, \( \delta \) is

\[
\gamma_n = \sqrt{\kappa (V_n - \delta)^2 + \gamma_{\text{true}}^2}
\]

the isomer shift, \( V_n \) is the velocity of line \( n \), \( \kappa \) is the broadening parameter, and \( \gamma_n \) is the observed width of the \( n \)th line. This function broadens the lines furthest away from the center of gravity (\( \delta \), isomer shift) to a greater extent than those lines close to \( \delta \). This has the same overall effect as a quadrupole distribution. Using this value of \( \gamma_n \), reasonable linewidths for all sites are obtained.
RESULTS AND DISCUSSION

The reaction of amylose with iodine and iodide in aqueous solution or the reaction of the "V" form of amylose with iodine vapor gives an intensely blue-black adduct, "starch-iodine." In investigating the nature of the iodine chromophore in these materials, by resonance Raman and iodine-129 Mössbauer spectroscopy, we apply the techniques and criteria which we have developed in our solid-state studies of iodine-oxidized mixed valence compounds. In this contribution we restrict our discussion to amylose-iodine stoichiometry ranges which would be considered typical.

Resonance Raman Studies

In Figure 2 are presented resonance Raman spectra of solid starch-iodine samples prepared by the aqueous solution, I⁻ procedure, and by the I₂ vapor procedure. Importantly, the spectra are essentially identical, indicating that the scattering species are essentially identical. The spectra vary only modestly with exciting laser frequency (ν₀ = 5145 - 4579 Å) as illustrated in Figure 3. In an effort to determine whether any structural changes in the samples might have occurred upon drying, freshly prepared solid samples were subjected to high vacuum (10⁻³ torr) for various periods of time. There was no observable change in Raman spectra over the course of several hours. Indeed, even at temperatures as high as 70°C, only slight changes in the spectrum could be discerned in the course of one hour (Figure 4), i.e., a slight relative increase (ca. 15%) in the intensity of the 109 cm⁻¹ scattering. The interpretation of these changes will
be deferred until after spectral assignments have been made. Interestingly, aqueous suspensions of starch-iodine are decolorized by heating to temperatures greater than 60°C.

The resonance Raman spectra of both starch-iodine samples (Figure 2, 3) exhibit strong scattering at 163 cm\(^{-1}\) and considerably weaker transitions at 109 and 56 cm\(^{-1}\). In addition, overtone bands are assigned at 322 (2x163)cm\(^{-1}\) and 215(2x109)cm\(^{-1}\). A combination band which is assigned at 272(163+109)cm\(^{-1}\) is assurance that the 163 and 109 cm\(^{-1}\) fundamental transitions are not in separate lattices (i.e. due to different compounds). In interpreting the starch-iodine spectra, reference is made to model compounds of established structure which are relevant to the differentiation of species B-E, as well as other possibilities. The spectra of most polyiodides can be understood by recognizing that I\(_2\) acts as a Lewis acid and that coordination to electron donors (i.e. I\(^-\)) results in population of molecular orbitals with I-I antibonding character, hence decrease in I-I bondlength, bond order, and stretching force constant.\(^{24, 27}\) The spectra and structures of most complex polyiodides can be understood in terms of aggregates of the simpler subunits I\(_2\), I\(_3\), and I\(^-\).\(^{24, 28}\)

Figure 5 compares the resonance Raman spectrum of starch-iodine to spectra of various model compounds. In a nonpolar environment such as hexane or benzene (Figure 5C), I\(_2\) exhibits a stretching frequency at 210 cm\(^{-1}\) (hexane), 207 cm\(^{-1}\) (benzene); this is clearly
not in accord with the spectrum in Figure 5A. Likewise, the proposal that molecular iodine is coordinated to ethereal (O(1) of A) or alcoholic (O(2), O(3), or O(6) of A) oxygen atoms near the interior of the amylose helix is not supported by the resonance Raman spectrum of I\textsubscript{2} in ether (\(\nu = 204 \text{ cm}^{-1}\)) or n-butanol (\(\nu = 197 \text{ cm}^{-1}\)). The spectrum of the I\textsubscript{5} chain compound (C) (benzamide)\textsubscript{2}H\textsuperscript{+}I\textsubscript{3}\textsuperscript{-9} (Figure 5D) is in excellent accord with the presence of I\textsubscript{5} units (\(\nu_{\text{symmetric}} = 108 \text{ cm}^{-1}\) plus an overtone progression) but bears little resemblance to that of starch-iodine. Structures having combinations of I\textsubscript{2} and I\textsubscript{5} units such as (phenacetin)\textsubscript{2}H\textsuperscript{+}I\textsubscript{3}\textsuperscript{14} (Figure 5E) or (\(\alpha\)-CD)\textsubscript{2}Li\textsuperscript{+}I\textsubscript{3}\textsuperscript{-9}·I\textsubscript{2}·8H\textsubscript{2}O\textsuperscript{12} (Figure 5F) exhibit spectra in good agreement with the presence of I\textsubscript{5} ions (120 and 110 cm\(^{-1}\), respectively) and weakly coordinated I\textsubscript{2} molecules (187 and 173 cm\(^{-1}\), respectively). These spectra also do not agree with that of Figure 5A. On the other hand, the spectrum of (trimesic acid · H\textsubscript{2}O)\textsubscript{10}H\textsuperscript{+}I\textsubscript{5} (Figure 5B), a pentaiodide chain compound (E), exhibits strong scattering at 162 cm\(^{-1}\) and weaker transitions at 104 and 75 cm\(^{-1}\). These as well as the overtone (207 and 325 cm\(^{-1}\)) and combination (ca 260 cm\(^{-1}\)) bands are strikingly similar in energy and relative intensity to the starch-iodine scattering pattern. An I\textsubscript{5} ion of idealized D\textsubscript{sh} symmetry should exhibit two Raman-active stretching modes of \(\Sigma_{g}^{+}\) symmetry and a Raman-active bending mode of \(\Pi_{g}\) symmetry. The relative intensities of these transitions will largely depend on the degree to which the particular normal mode
transforms the molecule into the structurally altered geometry of the resonant excited state. We assign the band at 162 cm\(^{-1}\) to a fundamental normal mode involving primarily the symmetric coupling of the internal expansion of the two "I\(_2\)" units of the pentaiodide ion (E), while the weaker band

\[
\begin{align*}
&\text{I} \leftrightarrow \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \\
&\text{E}
\end{align*}
\]

at 109 cm\(^{-1}\) is reasonably ascribed to symmetrically coupled motion of the two "I\(_2\)" units (G). There is likely to be some mixing of the

\[
\begin{align*}
&\text{I} \quad \text{I} \quad \text{I} \quad \text{I} \\
&\text{G}
\end{align*}
\]

two \(\tilde{G}\) modes. Other examples of I\(_2\) resonance Raman spectra that closely resemble that of starch-iodine are those of Ni(dpg)\(_2\)I and Pd(dpg)\(_2\)I (dpg = diphenylglyoximato). In summary, the resonance Raman data reject structures B-D as major components of starch-iodine prepared by either aqueous or iodine vapor procedures and argue strongly in favor of a pentaiodide configuration (E).

It was observed upon heating a solid starch-iodine sample (aqueous preparation) under high vacuum that the 109 cm\(^{-1}\) Raman transition increased slightly in intensity with respect to the 163 cm\(^{-1}\) mode (Figure 4). This can be interpreted in terms of I\(_2\) depletion of pentaiodide to form triiodide (eq. (2)).
Iodine Mössbauer Studies

Further efforts to quantitatively investigate the $I_3^-$ structural model were undertaken by iodine $-129$ Mössbauer spectroscopy. In addition, two other pieces of information were sought. For starch-iodine derived from aqueous syntheses, it was of interest to learn whether appreciable quantities of iodine might be retained as bound $I^-$. These would not be detectable by resonance Raman spectroscopy. In the case of starch-iodine prepared from "V" amylose and iodine vapor, information on the origin of the $I^-$ required for $I_3^-$ formation might be obtained.

The iodine $-129$ Mössbauer spectrum of the starch-iodine complex, prepared by the aqueous method is shown in Figure 6A. A model containing three inequivalent iodine sites with approximate relative populations of 2:2:1 gave the best fit to the experimental data. In Table I are presented the derived values of isomer shift ($\delta$), quadrupole coupling constant ($e^2q^{2s}Q$), linewidth ($\Gamma$), broadening parameter ($\kappa$), and relative site populations. No asymmetry ($\eta$) was detected, indicating that approximate axial symmetry prevails. This is in accord with the X-ray diffraction results.$^{7a,c,d,g}$ In the course of the spectral analysis, attempts were made to fit the experimental data to a variety of other structural models for the iodine-containing species. Constraining the model to one site or to two inequivalent
sites with relative populations of 1:1 or 2:1 (e.g. symmetric triiodide as in (benzamide)$_2$·H$^+I_3^-$\textsuperscript{10,33}) resulted in precipitous deterioration in the goodness of fit parameter, i.e., an increase of over 50% in Misfit (see Experimental Section) compared to the $I_5^-$ fit. Attempting to fit the data to three inequivalent sites with relative populations 1:1:1 (e.g. distorted triiodide, as in CsI$_3$\textsuperscript{24,33}) also resulted in poor agreement with the experimental spectrum, i.e., an increase of ca. 25% in Misfit. There was no evidence of isolated molecular iodine (for $I_2$ in benzene, $\delta=+0.76$ mm/sec, $e^2gQ=-1692$ MHz; for $I_2$ in hexane, $\delta=+0.98$ mm/sec, $e^2gQ=-1587$ MHz) or $I^-$ ($\delta=-0.51$ mm/sec, $e^2gQ=0$) in the spectrum. It is estimated that these species, although undetected, could be present in no greater than ca. 3 mol % each. For comparison with the starch-iodine spectrum, the Mössbauer spectrum of (trimesic acid · H$_2$O)$_n$H$^+I_5^-$, which is known to contain linear chains of symmetrical $I_5^-$ ions (E),\textsuperscript{15} is presented in Figure 6B. The values of the parameters for the best fit to this spectrum are set out in Table I. They are in close agreement with the data for starch-iodine prepared in aqueous solution. The derived (trimesic acid · H$_2$O)$_n$H$^+I_5^-$ pentaiodide site populations give an indication of the confidence which can be placed in the population analysis. The assignment of the sites to particular pentaiodide atoms in these compounds is shown in H, and the rationale for the assignments is discussed in detail for the trimesic acid complex elsewhere. Thus, the iodine $\nu$-129 Mössbauer spectrum of starch-iodine prepared in aqueous solution is in good agreement with
The Mössbauer spectrum of starch-iodine prepared from "V" amylose and iodine vapor is presented in Figure 7. The spectrum is somewhat more complex than that of the material prepared in aqueous solution. Three inequivalent sites are found with $\delta$ (mm/sec) and $e^2q^{129}Q$(MHz) values of $1.08(2)$ and $-1795(5)$; $0.64(2)$ and $-1473(20)$; $0.31(10)$ and $-909(25)$. These parameters are rather similar to those obtained for the I$_{5}^-$ moiety in starch-iodine prepared in aqueous solution. The slight disparity in the quadrupole splitting for site 2 is reasonably attributed to differences in the I$_{5}^-$ microenvironment and to the likelihood that the terminal iodine atoms of the ion will be most sensitive to these differences. Refined spectral parameters are compiled in Table I; the complexity of the spectrum introduced somewhat greater than usual uncertainty in the refinement of the site populations. In addition to the spectral features which can be attributed to I$_{5}^-$, a fourth site is identified with $\delta = 1.29(4)$ mm/sec and $e^2q^{129}Q=-1967(15)$ MHz. The relative population of this site is approximately one per I$_{5}^-$ ion. The Mössbauer parameters for this site are unusual. A nuclear quadrupole coupling constant of this magnitude has never been observed for I$_{2}$, I$_{4}^-$, I$_{5}^-$ or any other polyiodide in any known chemical environment.$^{21,24a,b}$ Organic iodides also exhibit considerably different spectral parameters as exemplified by CH$_{3}$I$_{29}^-$ ($\delta = +0.20$ mm/sec, $e^2q^{129}Q=-1219$ MHz)$^{34}$ or C$_{29}^-$ ($\delta = +0.65$ mm/sec, $e^2q^{129}Q=-1474$ MHz)$^{34}$. 

$\begin{align*}
\text{site} & : [I - I - I - I - I - I - I - I - I - I^-] \\
\text{H}
\end{align*}$

pentaiodide model $\Omega$. 

The Mössbauer spectrum of starch-iodine prepared from "V" amylose and iodine vapor is presented in Figure 7. The spectrum is somewhat more complex than that of the material prepared in aqueous solution. Three inequivalent sites are found with $\delta$(mm/sec) and $e^2q^{129}Q$(MHz) values of $1.08(2)$ and $-1795(5)$; $0.64(2)$ and $-1473(20)$; $0.31(10)$ and $-909(25)$. These parameters are rather similar to those obtained for the I$_{5}^-$ moiety in starch-iodine prepared in aqueous solution. The slight disparity in the quadrupole splitting for site 2 is reasonably attributed to differences in the I$_{5}^-$ microenvironment and to the likelihood that the terminal iodine atoms of the ion will be most sensitive to these differences. Refined spectral parameters are compiled in Table I; the complexity of the spectrum introduced somewhat greater than usual uncertainty in the refinement of the site populations. In addition to the spectral features which can be attributed to I$_{5}^-$, a fourth site is identified with $\delta = 1.29(4)$ mm/sec and $e^2q^{129}Q=-1967(15)$ MHz. The relative population of this site is approximately one per I$_{5}^-$ ion. The Mössbauer parameters for this site are unusual. A nuclear quadrupole coupling constant of this magnitude has never been observed for I$_{2}$, I$_{4}^-$, I$_{5}^-$ or any other polyiodide in any known chemical environment.$^{21,24a,b}$ Organic iodides also exhibit considerably different spectral parameters as exemplified by CH$_{3}$I$_{29}^-$ ($\delta = +0.20$ mm/sec, $e^2q^{129}Q=-1219$ MHz)$^{34}$ or C$_{29}^-$ ($\delta = +0.65$ mm/sec, $e^2q^{129}Q=-1474$ MHz)$^{34}$. 

$\begin{align*}
\text{site} & : [I - I - I - I - I - I - I - I - I - I - I^-] \\
\text{H}
\end{align*}$

pentaiodide model $\Omega$. 

The Mössbauer spectrum of starch-iodine prepared from "V" amylose and iodine vapor is presented in Figure 7. The spectrum is somewhat more complex than that of the material prepared in aqueous solution. Three inequivalent sites are found with $\delta$(mm/sec) and $e^2q^{129}Q$(MHz) values of $1.08(2)$ and $-1795(5)$; $0.64(2)$ and $-1473(20)$; $0.31(10)$ and $-909(25)$. These parameters are rather similar to those obtained for the I$_{5}^-$ moiety in starch-iodine prepared in aqueous solution. The slight disparity in the quadrupole splitting for site 2 is reasonably attributed to differences in the I$_{5}^-$ microenvironment and to the likelihood that the terminal iodine atoms of the ion will be most sensitive to these differences. Refined spectral parameters are compiled in Table I; the complexity of the spectrum introduced somewhat greater than usual uncertainty in the refinement of the site populations. In addition to the spectral features which can be attributed to I$_{5}^-$, a fourth site is identified with $\delta = 1.29(4)$ mm/sec and $e^2q^{129}Q=-1967(15)$ MHz. The relative population of this site is approximately one per I$_{5}^-$ ion. The Mössbauer parameters for this site are unusual. A nuclear quadrupole coupling constant of this magnitude has never been observed for I$_{2}$, I$_{4}^-$, I$_{5}^-$ or any other polyiodide in any known chemical environment.$^{21,24a,b}$ Organic iodides also exhibit considerably different spectral parameters as exemplified by CH$_{3}$I$_{29}^-$ ($\delta = +0.20$ mm/sec, $e^2q^{129}Q=-1219$ MHz)$^{34}$ or C$_{29}^-$ ($\delta = +0.65$ mm/sec, $e^2q^{129}Q=-1474$ MHz)$^{34}$. 

$\begin{align*}
\text{site} & : [I - I - I - I - I - I - I - I - I - I - I^-] \\
\text{H}
\end{align*}$

pentaiodide model $\Omega$.
The observed quadrupole splitting in the fourth site also rules out \( {\text{IO}}_3^- \); typical iodate parameters \(^{34,35} +699 \text{ MHz}({\text{K}}^{239}\text{IO}_3), +706 \text{ MHz}({\text{NH}}_4^{239}\text{IO}_3), \) and +722 MHz({\text{Ba}}^{239}\text{IO}_3). The iodine Mössbauer parameters for the unique site are closest to those in compounds where iodine is bound to a single, more electronegative atom. Examples of this environment are \(^{129}\text{IBr} (\delta=1.77 \text{ mm/sec, } e^2q^{129}Q=-2028 \text{ MHz }^{36}),\
^{129}\text{ICl} (\delta=2.27 \text{ mm/sec, } e^2q^{129}Q=-2195 \text{ MHz }^{36}), \) and \(^{129}\text{ICN} (\delta=1.73 \text{ mm/sec, } e^2q^{129}Q=-1851 \text{ MHz }^{36}).\)

A plausible explanation both for the identity of the fourth iodine Mössbauer site and for the source of \( I^- \) in the pentaiodide constituent is through hypoiodite formation (eq. (3) or (4)). Such a process would involve iodine reaction with either water, butanol, or a glucose hydroxyl moiety and yields one hypoiodite species per \( I^- \) formed.

\[
\begin{align*}
\text{nH}_2\text{O}+\text{amylose}+3\text{nI}_2 &= \text{amylose} \left( I^- \right)_n + \text{nH}^+ + \text{nHOI} \quad (3) \\
\text{nROH}+\text{amylose}+3\text{nI}_2 &= \text{amylose} \left( I^- \right)_n + \text{nH}^- + \text{nROI} \quad (4)
\end{align*}
\]

Equation (3) is analogous to the known hydrolysis reaction of iodine (eq. \(^{37,39} 5\)), except that \( I^- \) complexation by amylose would presumably shift the equilibrium far to the right. Equation (5) responds similarly to the addition of alkali or mercuric oxide. Neither HOI nor ROI species appear to have appreciable long-term stability, although both have been
generated in solution (but have not been isolated in a pure state); immobi-
larization within the amylose helix may introduce significant
stabilization. Although iodine Mössbauer parameters are not known
for HOI or ROI compounds, a plausible estimate of the nuclear quad-
rupole coupling constant for HOI should be accessible by multiplying
\( e^2 q \frac{129}{Q} \) of \( \cdot \text{OI} (-1326 \text{ MHz}) \) by the ratio of the \( \text{HO}^{35}\text{Cl} \) and \( \cdot \text{O}^{35}\text{Cl} \)
nuclear quadrupole coupling constants \((-121.9 \text{MHz}/-86.6 \text{MHz})\).
The resulting estimation, \(-1866 \text{ MHz}\), is in reasonable agreement
with \( e^2 q \frac{129}{Q} \) determined for the fourth site. Judging from the
similarity of the \( \text{CH}_3\text{OCl} \) nuclear quadrupole coupling constant
\((-117.1 \text{ MHz})\) to that of \( \text{HOCl} (-121.0 \text{ MHz})\), the \( e^2 q \frac{129}{Q} \) para-

ters for HOI and ROI are not expected to differ greatly.
CONCLUSIONS

It is apparent from this study that starch-iodine (amylose-iodine) prepared by standard methods from iodine and iodide in aqueous solution or from crystalline "V" amylose and iodine vapor contains essentially the same major chromophore: the pentaiodide anion. In the case of the iodine vapor preparation, the iodide necessary for penta-iodide formation is produced by hydrolysis (or alcoholysis) of iodine. A hypoiiodite species is the other product of this reaction. Although the remarkable specificity of the amylose helix for $I_5^-$ incorporation appears at first to be highly unusual, it should be remembered that an enormous variety of polyiodides are stabilized by the highly selective (and frequently subtle) environments provided by different organic crystal structures. In the present case there may well be a connection between the commensurability of the pentaiodide repeat distance ($15.5\AA$) and twice the helix repeat dimension (ca. $16\AA$).
ACKNOWLEDGEMENTS

This research was generously supported by the Office of Naval Research (to T.J.M.), the Department of Energy (to S.L.R.), and by the NSF-MRL program through the Materials Research Center of Northwestern University (grant DMR76-80847A01). The assistance of Dr. G.K. Shenoy at Argonne National Laboratory in the acquisition of the starch-iodine-vapor Mössbauer spectrum is greatly appreciated. We also thank Professor F. Herbstein for data in advance of publication.
REFERENCES AND NOTES

1. (a) Department of Chemistry and the Materials Research Center, Northwestern University.
(b) Physics Division, Argonne National Laboratory.
(c) Thesis parts appointee, Argonne National Laboratory.

2. Camille and Henry Dreyfus Teacher-Scholar.

(c) Foster, J.F. ibid., Chapter XV.

(b) Murphy, V.G.; Zaslows, B.; French, A.D. Biopolymers, 1975, 14, 1487-1501.
(c) Zaslows, B.; Murphy, V.G.; French, A.D. Biopolymers, 1974, 13, 779-790.
(e) Winter, W.T.; Sarko, A. Biopolymers, 1974, 13, 1447-1460.

(b) Freudenberg, K.; Schaaf, E.; Dumpter, G.; Ploetz, T. Naturwissenshaften, 1939, 22, 850-853.

6. (a) Rees, D.A. op. cit., p. 56.

(b) Rundle, R.E.; French, D. ibid., 1943, 65, 558-561.
(c) Rundle, R.E.; French, D. ibid., 1943, 65, 1707-1710.
(d) Rundle, R.E.; Edwards, F.C. ibid., 1943, 65, 2200-2203.
22

(e) Baldwin, R.R.; Bear, R.S.; Rundle, R.E.  _ibid._, 1944, 66, 111-115.
(f) Rundle, R.E.; Foster, J.F.; Baldwin, R.R.  _ibid._, 1944, 66, 2116-2120.
(g) Rundle, R.E.  _ibid._, 1947, 69, 1763-1772.


(b) Schneider, F.W.; Cronan, C.L.; Podder, S. J.  _Phys. Chem._, 1968, 72, 4563-4568, and references therein.

(b) Robin, M.B.  _ibid._, 1964, 40, 3369-3377.


(b) Cramer, F.; Bergmann, U.; Manor, P.C.; Noltemeyer, M.; Saenger, W.  _Ann._, 1976, 1162-1175.

(c) James, W.J.; French, D.; Rundle, R.E.  _Acta Crystallogr._ , 1959, 12, 385-389.

14. (a) For the $L_1 \cdots L_1$ motif, see for example, Herbstein, F.H.; Kapon, M.  _Nature, Physical Science._ , 1972, 239, 153-154.


31. One of the low energy bands could also arise from the Raman-active (\(\pi_g\)) bending mode.

32. (a) The stretch-stretch interaction constants in trihalide ions are relatively large.
(c) Gabès, W.; Elst, R. J. Molec. Struct. 1974, 21, 1-5.

33. Although these structures were clearly in disagreement with the Raman data, Mössbauer fits were attempted for the sake of completeness.


(b) Downs, A.J.; Adams, C.J. op. cit., p. 1410.

40. Iodide is known to catalyze the decomposition of \(O^\text{-}\). Either
steric shielding or the scavenging of free I\(^{-}\) to form I\(_{2}\) would serve to protect the OI\(^{-}\).


Table I. Iodine-129 Mössbauer Parameters

<table>
<thead>
<tr>
<th>Site 1</th>
<th>Aqueous Solution</th>
<th>Vapor</th>
<th>(trimesic acid·H₂O)₁₀H⁺I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ, mm/sec</td>
<td>1.22(1)</td>
<td>1.08(2)</td>
<td>1.15(3)</td>
</tr>
<tr>
<td>ε²δQ, MHz</td>
<td>-1743(15)</td>
<td>-1795(15)</td>
<td>-1777(5)</td>
</tr>
<tr>
<td>τ, mm/sec</td>
<td>1.14(1)</td>
<td>1.67(9)</td>
<td>1.15(5)</td>
</tr>
<tr>
<td>Rel. Int.</td>
<td>1.9 (2)</td>
<td>2.0</td>
<td>2.0 (1)</td>
</tr>
</tbody>
</table>

| Site 2 | | |
|--------| | |
| δ, mm/sec | 0.53(3) | 0.64(2) | 0.53(5) |
| ε²δQ, MHz | -1187(20) | -1473(20) | -1404(8) |
| τ, mm/sec | 2.13(6) | 1.20(5) | 1.75(5) |
| Rel. Int. | 1.8 (3) | 2.0 (4) | 1.0 (1) |

| Site 3 | | |
|--------| | |
| δ, mm/sec | 0.14(1) | 0.31(10) | 0.13(5) |
| ε²δQ, MHz | - 842(25) | - 909(25) | - 965(5) |
| τ, mm/sec | 1.08(3) | 1.12(9) | 1.04(4) |
| Rel. Int. | 1.0 | 0.5 (2) | 1.0 |

| Site 4 | | |
|--------| | |
| δ, mm/sec | - | 1.29(4) | - |
| ε²δQ, MHz | - | -1987(15) | - |
| τ, mm/sec | - | 1.38(5) | - |
| Rel. Int. | - | 1.1 (2) | - |

| Misfit(%) | 1.23(3) | 0.22(7) | 0.70(4) |

a Complex prepared in aqueous solution.
b Complex prepared with iodine vapor.
c Isomer shift (vs ZnTe).
d Line width.
e Broadening parameter.
Figure 1. Schematic view of the starch-iodine structure. Shown is the amylose helix with the iodine chain in the center.
Figure 2. Resonance Raman spectra ($\nu_0=5145\AA$) of
A. Starch-iodine prepared in aqueous solution,
B. Starch-iodine prepared with iodine vapor.
Figure 3. Exciting frequency ($\nu_0$) dependence of the resonance Raman spectrum of the starch-iodine complex: A.\text{Ar}^+, 4579\AA, B.\text{Ar}^+, 4965\AA, C.\text{Ar}^+, 5145\AA.
Figure 4. Effects of heating and vacuum on the resonance Raman spectrum of the starch-iodine complex ($v_0=5145\text{ cm}^{-1}$).
1.0 HR AT 70°C AND VACUUM

0.5 HR AT 70°C AND VACUUM

ORIGINAL SAMPLE

WAVENUMBER (1/cm)
Figure 5. Resonance Raman spectra (5145 Å excitation) of A. Starch (amylose)-iodine, B. Polycrystalline (trimesic acid·H₂O)₂⁺H⁺I₃⁻, C. I₂ dissolved in benzene, D. Polycrystalline (benzamide)₂H⁺I₃⁻, E. Polycrystalline (phenacetin)₂H⁺I₃⁻·I₂, F. Polycrystalline (α-cyclohexaamylose)₃Li⁺I₃⁻·I₂·3H₂O.
RESONANCE RAMAN SPECTRA

STARCH-IODINE

A

I₂ in benzene

B

I₂ in benzene

C

I₂ in benzene

D

I₂ in benzene

E

I₂ in benzene

F

WAVENUMBER (cm⁻¹)
Figure 6. Iodine-129 Mössbauer spectra of the indicated compounds at 4°K. The solid lines represent the best computer fit to the experimental data. The vertical direction represents percent effect, the maximum of which is 16% for A, and 13% for B.
$^{129}$I Mössbauer Spectra

A. STARCH·IODINE

B. (TRIMESIC ACID·$\text{H}_2\text{O})_{10}·\text{HI}_5$
Figure 7. Iodine-129 Mössbauer spectrum of the starch-iodine complex prepared by the vapor method. The solid line represents the best computer fit to the experimental data. The vertical direction is percent effect, the maximum of which is 5.2%.
<table>
<thead>
<tr>
<th>Office of Naval Research</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S. Army Research Office</td>
<td>1</td>
</tr>
<tr>
<td>Office of Naval Research</td>
<td>2</td>
</tr>
<tr>
<td>Naval Ocean Systems Center</td>
<td>1</td>
</tr>
<tr>
<td>Naval Weapons Center</td>
<td>1</td>
</tr>
<tr>
<td>Naval Civil Engineering Laboratory</td>
<td>1</td>
</tr>
<tr>
<td>Department of Physics &amp; Chemistry</td>
<td>1</td>
</tr>
<tr>
<td>Director, Naval Research Laboratory</td>
<td>1</td>
</tr>
<tr>
<td>Naval Ship Research and Development Center</td>
<td>1</td>
</tr>
<tr>
<td>Commander, Naval Air Systems Command</td>
<td>1</td>
</tr>
<tr>
<td>Defense Documentation Center</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Fred Saalfeld</td>
<td>1</td>
</tr>
</tbody>
</table>

**Office of Naval Research**

Attn: Code 472  
800 North Quincy Street  
Arlington, Virginia 22217

Attn: Code 472  
P.O. Box 1211  
Research Triangle Park, N.C. 27709

Attn: Dr. George Sandoz  
536 S. Clark Street  
Chicago, Illinois 60605

Attn: Mr. Joe McCartney  
San Diego, California 92152

Attn: Scientific Dept.  
715 Broadway  
New York, New York 10003

Attn: Dr. A. B. Amster,  
Chemistry Division  
China Lake, California 93555

Attn: Dr. R. W. Drisko  
Port Hueneme, California 93401

Attn: Dr. L. H. Paebles  
Building 114, Section D  
666 Summer Street  
Boston, Massachusetts 02210

Attn: Dr. A. L. Slafkosky  
Scientific Advisor  
Commandant of the Marine Corps (Code RD-I)  
Washington, D.C. 20380

Attn: Code 6100  
Washington, D.C. 20390

Attn: Code 6100  
Washington, D.C. 20390

Attn: Dr. Richard S. Miller  
800 N. Quincy Street  
Arlington, Virginia 22217

Attn: Code 310C (H. Rosenwasser)  
Department of the Navy  
Washington, D.C. 20360

Attn: Dr. G. Bosmajian, Applied Chemistry Division  
Annapolis, Maryland 21401

Attn: Dr. S. Yamamoto, Marine Sciences Division  
San Diego, California 91232

Attn: H. Rosenwasser  
Chemistry Division  
Department of the Navy  
Washington, D.C. 20360

Attn: Mr. John Boyle  
Materials Branch  
Naval Ship Engineering Center  
Philadelphia, Pennsylvania 19112

Attn: Code 472  
800 North Quincy Street  
Arlington, Virginia 22217

Attn: CRD-AA-IP  
P.O. Box 1211  
Research Triangle Park, N.C. 27709

Attn: Mr. Joe McCartney  
San Diego, California 92152

Attn: Dr. A. B. Amster,  
Chemistry Division  
China Lake, California 93555

Attn: Dr. R. W. Drisko  
Port Hueneme, California 93401

Attn: Dr. L. H. Paebles  
Building 114, Section D  
666 Summer Street  
Boston, Massachusetts 02210

Attn: Dr. A. L. Slafkosky  
Scientific Advisor  
Commandant of the Marine Corps (Code RD-I)  
Washington, D.C. 20380

Attn: Code 6100  
Washington, D.C. 20390

Attn: Code 6100  
Washington, D.C. 20390

Attn: Dr. Richard S. Miller  
800 N. Quincy Street  
Arlington, Virginia 22217

Attn: Dr. G. Bosmajian, Applied Chemistry Division  
Annapolis, Maryland 21401

Attn: Dr. S. Yamamoto, Marine Sciences Division  
San Diego, California 91232

Attn: H. Rosenwasser  
Chemistry Division  
Department of the Navy  
Washington, D.C. 20360

Attn: Mr. John Boyle  
Materials Branch  
Naval Ship Engineering Center  
Philadelphia, Pennsylvania 19112
TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco  96503  1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland  21402  1
<table>
<thead>
<tr>
<th>No.</th>
<th>Copies</th>
<th>No.</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dr. R. N. Grimes&lt;br&gt;University of Virginia&lt;br&gt;Department of Chemistry&lt;br&gt;Charlottesville, Virginia 22901</td>
<td>1</td>
<td>Dr. M. H. Chisholm&lt;br&gt;Indiana University&lt;br&gt;Bloomington, Indiana 47401</td>
</tr>
<tr>
<td></td>
<td>Dr. M. Tsutsui&lt;br&gt;Texas A&amp;M University&lt;br&gt;Department of Chemistry&lt;br&gt;College Station, Texas 77843</td>
<td>1</td>
<td>Dr. B. Foxman&lt;br&gt;Brandeis University&lt;br&gt;Department of Chemistry&lt;br&gt;Waltham, Massachusetts 02154</td>
</tr>
<tr>
<td></td>
<td>Dr. M. F. Hawthorne&lt;br&gt;University of California&lt;br&gt;Department of Chemistry&lt;br&gt;Los Angeles, California 90024</td>
<td>1</td>
<td>Dr. T. Marks&lt;br&gt;Northwestern University&lt;br&gt;Department of Chemistry&lt;br&gt;Evanston, Illinois 60201</td>
</tr>
<tr>
<td></td>
<td>Dr. D. B. Brown&lt;br&gt;University of Vermont&lt;br&gt;Department of Chemistry&lt;br&gt;Burlington, Vermont 05401</td>
<td>1</td>
<td>Dr. G. Geoffrey&lt;br&gt;Pennsylvania State University&lt;br&gt;Department of Chemistry&lt;br&gt;University Park, Pennsylvania 16802</td>
</tr>
<tr>
<td></td>
<td>Dr. W. B. Fox&lt;br&gt;Naval Research Laboratory&lt;br&gt;Chemistry Division&lt;br&gt;Code 6130&lt;br&gt;Washington, D.C. 20375</td>
<td>1</td>
<td>Dr. J. Zuckerman&lt;br&gt;University of Oklahoma&lt;br&gt;Department of Chemistry&lt;br&gt;Norman, Oklahoma 73019</td>
</tr>
<tr>
<td></td>
<td>Dr. J. Adcock&lt;br&gt;University of Tennessee&lt;br&gt;Department of Chemistry&lt;br&gt;Knoxville, Tennessee 37916</td>
<td>1</td>
<td>Professor O. T. Beachley&lt;br&gt;State University of New York&lt;br&gt;Buffalo, New York 14214</td>
</tr>
<tr>
<td></td>
<td>Dr. A. Cowley&lt;br&gt;University of Texas&lt;br&gt;Department of Chemistry&lt;br&gt;Austin, Texas 78712</td>
<td>1</td>
<td>Professor P. S. Skell&lt;br&gt;The Pennsylvania State University&lt;br&gt;University Park, Pennsylvania 16802</td>
</tr>
<tr>
<td></td>
<td>Dr. W. Hatfield&lt;br&gt;University of North Carolina&lt;br&gt;Department of Chemistry&lt;br&gt;Chapel Hill, North Carolina 27514</td>
<td>1</td>
<td>Professor K. M. Nicholas&lt;br&gt;Department of Chemistry&lt;br&gt;Boston College&lt;br&gt;Chestnut Hill, Massachusetts 02167</td>
</tr>
<tr>
<td></td>
<td>Dr. D. Seyferth&lt;br&gt;Massachusetts Institute of Technology&lt;br&gt;Department of Chemistry&lt;br&gt;Cambridge, Massachusetts 02139</td>
<td>1</td>
<td>Professor R. Neilson&lt;br&gt;Texas Christian University&lt;br&gt;Fort Worth, Texas 76129</td>
</tr>
<tr>
<td></td>
<td>Professor H. Abrahamson&lt;br&gt;University of Oklahoma&lt;br&gt;Department of Chemistry&lt;br&gt;Norman, Oklahoma 73019</td>
<td>1</td>
<td>Professor H. Newcomb&lt;br&gt;Texas A&amp;M University&lt;br&gt;Department of Chemistry&lt;br&gt;College Station, Texas 77843</td>
</tr>
</tbody>
</table>