suitable crystals could be prepared, but this has not yet been achieved; the various forms of electronic spectroscopy seem to have the best prospects. It seems unlikely that the various types of kinetic experiments which have been devised will ever really draw such a fine distinction unambiguously. Examination of Figure 3 also suggests that the choice of names, "classical" and "nonclassical", has given the discussion more impetus than its substance would justify.

References and Notes

(1) (a) This work was supported by the National Science Foundation through Grants GP-31360X and CHE76-01181 to the University of Minnesota. (b) A preliminary report of this work has appeared as a communication; M. M. Kreevoy, T. M. Liang, and K.-C. Chang, *J. Am. Chem. Soc.*, **99**, 5207 (1977). (c) M. M. Kreevoy was the guest of the Physical Chemistry Laboratory, Oxford, while much of this work was in progress. He wishes to thank Drs. W. J. Albery and R. K. Thomas, of that laboratory, and Dr. J. C. Speakman of the University of Glasgow for stimulating and helpful discussions of this work.

(2) When A_1 and A_2 are the same, these substances have been called homoconjugates; when they are different, heteroconjugates. I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **66**, 1675 (1962); *J. Am. Chem. Soc.*, **85**, 426 (1963).

(3) I. Olovson and P. G. Jösson in "The Hydrogen Bond—Recent Developments in Theory and Experiment", Vol. II, P. Schuster, G. Zundel, and C. Sandorfy, Eds., North-Holland Publishing Co., Amsterdam, 1976, Chapter 8.

(4) D. Hadži and S. Bratos in ref 3, Chapter 12.

(5) G. Zundel in ref 3, Chapter 15.

(6) J. C. Speakman, *Struct. Bonding* (*Berlin*), **12**, 141 (1972).

(7) (a) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960); (b) A. J. Kresge, *Pure Appl. Chem.*, **8**, 243 (1964).

(8) L is used as a symbol for an atom that may be H, D, or T. The symbol $D(L_2O)$ indicates that the deuterium which enters the equilibrium is taken from liquid water which contains both isomers, preferably in approximately equal amounts; $H(L_2O)$ has the analogous significance for hydrogen.

(9) J. F. Coetzee, *Prog. Phys. Org. Chem.*, **4**, 45 (1967).

(10) A. Martinsen and J. Songstad, *Acta Chem. Scand., Ser. A*, **31**, 645 (1977).

(11) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Am. Chem. Soc.*, **88**, 5430 (1966).

(12) J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **69**, 3193 (1965).

(13) J. C. Evans, *Spectrochim. Acta*, **16**, 994 (1960).

(14) Sadtler Standard Spectra, Standard Grating Spectrum No. 23594.

(15) T. M. Liang, Ph.D. Thesis, University of Minnesota, 1979, pp 146–148.

(16) Reference 15, pp 55–57.

(17) Reference 15, p 14.

(18) M. M. Kreevoy and T. S. Straub, *Anal. Chem.*, **41**, 214 (1969).

(19) S. Nagakura, *J. Chem. Phys.*, **23**, 1141 (1955).

(20) Homoconjugation constants appear to be similar in sulfolane and acetonitrile.[21,22]

(21) J. F. Coetzee and R. J. Bertogzi, *Anal. Chem.*, **45**, 1064 (1973).

(22) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Am. Chem. Soc.*, **90**, 23 (1968).

(23) R. L. Benoit, A. L. Beauchamp, and R. Domain, *Inorg. Nucl. Chem. Lett.*, **7**, 557 (1971).

(24) The pK_{HA} values of benzoic acid, 4-nitrophenol, and acetic acid in acetonitrile are 20.4,[26] 20.9,[11] and 22.3,[21] respectively.

(25) Relative acidities of structurally similar substances appear to be the same in sulfolane as they are in acetonitrile.[21]

(26) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **70**, 856 (1966).

(27) (a) R. L. Schowen, *Prog. Phys. Org. Chem.*, **9**, 275 (1972); (b) J. F. Mata-Segreda, S. Wirt, and R. L. Schowen, *J. Am. Chem. Soc.*, **96**, 5608 (1974).

(28) V. Gold and C. Tomlinson, *J. Chem. Soc. B*, 1707 (1971).

(29) Sadtler Standard Spectra, Standard Grating Spectrum No. 8461.

(30) R. Livingston, "Physico Chemical Experiments", Macmillan, New York, 1957, pp 22–30.

(31) Tetraethylammonium perchlorate has a dissociation constant of 5.6×10^{-2} M in acetonitrile; J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2534 (1965).

(32) R. G. Jones and J. R. Dyer, *J. Am. Chem. Soc.*, **95**, 2465 (1973).

(33) (a) J. L. Wood, *J. Mol. Struct.*, **13**, 141 (1972); (b) R. L. Dean and J. L. Wood, *ibid.*, **26**, 197 (1975).

(34) J. Laane, *Appl. Spectrosc.*, **24**, 73 (1970).

(35) J. L. Wood in "Spectroscopy and Structure of Molecular Complexes", J. Yarwood, Ed., Plenum Press, New York, 1973, pp 336–340. This article also contains references to other papers on this subject.

(36) D. G. Truhlar, *J. Comput. Phys.*, **10**, 123 (1972).

(37) M. M. Kreevoy, "Isotopes in Organic Chemistry", Vol. 2, E. Buncel and C. C. Lee, Eds., Elsevier, Amsterdam, 1976, p 16; however, the harmonic oscillator energy levels have been replaced with those of the indicated potential functions.

(38) In the case of V_1 the lowest two eigenvalues are separated by a tunneling frequency of 21 cm^{-1}. Since this is only a fraction of thermal energy at room temperature these levels would be very nearly equally populated. Their average energy is shown in Figure 3 and used in the calculation of ϕ_1. None of the other potential functions shown has closely spaced energy values.

(39) (a) A. L. MacDonald, J. C. Speakman, and D. Hadži, *J. Chem. Soc., Perkin Trans. 2*, 825 (1972); (b) G. E. Bacon, C. R. Walker, and J. C. Speakman, *ibid.*, 979 (1977).

(40) R. Attig and J. M. Williams, *J. Chem. Phys.*, **66**, 1389 (1977). This paper actually deals with $D_5O_2^+$, but the oxygen–oxygen distance and IR spectrum are similar to those found in Speakman's "type A" bicarboxylates.

(41) L. J. Altman, D. Laungani, G. Gunnarsson, H. Wennerström, and S. Forsén, *J. Am. Chem. Soc.*, **100**, 8269 (1978).

(42) G. E. Walrafen in "Hydrogen-Bonded Solvent Systems", A. K. Covington and P. Jones, Eds., Taylor and Francis, London, 1968, p 16.

(43) B. S. Ault, *J. Phys. Chem.*, **82**, 844 (1978).

(44) Reference 34, pp 360–363.

(45) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, pp 221–223.

(46) M. C. Flanigan and J. R. de la Vega, *Chem. Phys. Lett.*, **21**, 521 (1973).

(47) A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Am. Chem. Soc.*, **93**, 1148 (1971).

(48) M. M. Kreevoy and B. Ridl, unpublished results.

(49) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, 1972, p 107.

(50) J. C. Speakman, *Spec. Period. Rep.: Mol. Struct. Diffr. Methods*, **3**, 87–91 (1975).

A Resonance Raman/Iodine Mössbauer Investigation of the Starch–Iodine Structure. Aqueous Solution and Iodine Vapor Preparations

Robert C. Teitelbaum,[1a,c,d] **Stanley L. Ruby,**[1b] **and Tobin J. Marks***[1a,2]

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201, and the Physics Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received August 2, 1979*

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 (I_5^-) anion. For the material prepared from iodine vapor, the iodide required for I_5^- formation is produced by hydrolysis or alcoholysis of iodine. The other product of this reaction, a hypoiodite, has been assigned in the iodine Mossbauer 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.[3] Amylose, the linear starch fraction, which is comprised of

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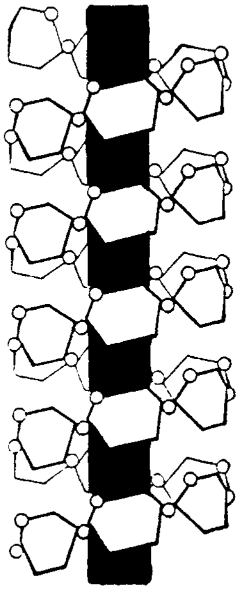
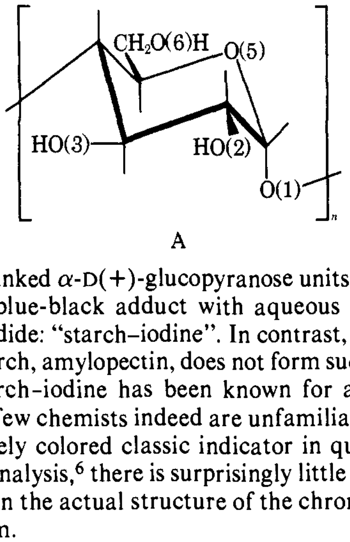


Figure 1. Schematic view of the starch-iodine structure. Shown is the amylose helix with the iodine chain in the center.



A

chains of 1,4 linked α-D(+)-glucopyranose units (A),[3,4] 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,[3,5] and few chemists indeed are unfamiliar with the use of this intensely colored classic indicator in qualitative and quantitative analysis,[6] there is surprisingly little unambiguous information on the actual structure of the chromophore with $\lambda_{max} \approx 600$ nm.

In a series of pioneering optical and X-ray diffraction studies,[7] Rundle and his co-workers established that the iodine component of starch–iodine is present in a unidimensional array within an amylose helix of diameter ~13 Å, period ~8 Å, and with six glucose residues per turn. The structure is illustrated in Figure 1. The amylose 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" amylose with iodine vapor. The fact that ordinary amylose 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 amylose 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 amylose helix (B).[5b,8]

$$\cdots\mathrm{I}-\mathrm{I}\cdots\cdots\mathrm{I}-\mathrm{I}\cdots\cdots\mathrm{I}-\mathrm{I}\cdots$$

B

Several spectrophotometric and potentiometric investigations in aqueous solution later identified the requirement of I^- for complex formation.[9] 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_3^-. A model for starch–iodine composed of linear chains of I_3^- (C) as in $(\text{benzamide})_2\text{H}^+\text{I}_3^-$ [10] has also been proposed[10] and widely accepted. The similarity between amylose and the cyclodextrins[11] (cycloamyloses) in structure and in the tendency to form inclusion complexes[11-13] led to new structural suggestions for starch–iodine based upon the crystal structures of $(\alpha\text{-CD})_2\cdot\text{LiI}_3\cdot\text{I}_2\cdot8\text{H}_2\text{O}$ and $(\alpha\text{-CD})_2\cdot\text{Cd}_{0.5}\cdot\text{I}\cdot2\text{I}_2\cdot26\text{H}_2\text{O}$ (α-CD = cyclohexaamylose).[12] Either alternating arrays of I_2 and I_3^- units (D) or symmetrical, linear I_5^- units (E) were considered to be plausible structures.[12a] There is additional precedent in polyiodide structural chemistry for either motif.[14,15]

$$\cdots\mathrm{I}\cdot\overset{-}{\mathrm{I}}\cdot\mathrm{I}\cdots\cdots\mathrm{I}\cdot\overset{-}{\mathrm{I}}\cdot\mathrm{I}\cdots\cdots\mathrm{I}\cdot\overset{-}{\mathrm{I}}\cdot\mathrm{I}\cdots$$

C

$$---\mathrm{I}\cdot\mathrm{I}---\mathrm{I}\cdot\overset{-}{\mathrm{I}}\cdot\mathrm{I}---\mathrm{I}\cdot\mathrm{I}---\mathrm{I}\cdot\overset{-}{\mathrm{I}}\cdot\mathrm{I}---$$

D

$$[\mathrm{I}\cdot\mathrm{I}\cdots\mathrm{I}\cdots\mathrm{I}\cdot\mathrm{I}]^-\cdots\cdots\cdots[\mathrm{I}\cdot\mathrm{I}\cdots\mathrm{I}\cdots\mathrm{I}\cdot\mathrm{I}]^-$$

E

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,9,10b] infrared,[16] electron paramagnetic resonance,[17] ORD/CD,[18] iodine Mössbauer,[19] and resonance Raman spectroscopy,[20] as well as X-ray powder diffraction,[7a,c,d,g] spectrophotometric and potentiometric titrations,[9] and intrinsic viscosity studies.[8] Many of these investigations have unfortunately suffered from the intrinsic deficiencies of the particular 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 possibilities B and C were considered, and no attempt was made to determine relative iodine site populations. Structure C was chosen over B because nonequivalent iodine sites were observed and because spectral parameters were reminiscent of $(\text{benzamide})_2\text{H}^{+129}\text{I}_3^-$. 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.[21] A full range of model compounds was utilized,[21] 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.[9] 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[7] by *both* aqueous and I_2 vapor methods.

Experimental Section

Synthesis of Starch–Iodine. Aqueous Solution Method.[7a] Granular potato amylose was purchased from Aldrich Chemical Co. A typical preparation involved the reaction with stirring of 1.8 g of amylose, 0.88 g (3.5 mmol) of triply sublimed I_2, and 0.53 g (3.5 mmol) of 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 $AgNO_3$ solution. The product was then freeze-dried.

Synthesis of Starch–Iodine. Iodine Vapor Method.[7] Granular potato amylose was crystallized from H_2O and 1-butanol according to the procedure of Schoch.[22] 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 1-butanol was slowly added, and the solution allowed to cool to room temperature over a period of about 6 h. 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 desiccator. 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 $^{129}I_2$ was prepared by oxidation of an acidified $Na^{129}I$ 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 $^{129}I_2$. For a source of I^-, the basic $Na^{129}I$ solution from Oak Ridge was neutralized with H_2SO_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 of $^{129}I_2$ and 0.80 mL of the neutralized $Na^{129}I$ solution in 30 mL of deionized water. The product was collected by centrifugation and 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 $^{129}I_2$ was used. The reagent $^{129}I_2$ was prepared as described above.

Raman Measurements. Laser Raman spectra were recorded with Kr^+ (6471 Å) or Ar^+ (4579, 4880, 4965, 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° backscattering 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 (ν_0) or laser plasma lines.

Iodine-129 Mössbauer Spectroscopy. These measurements employed the apparatus described previously.[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, two to three 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,[23] which finds the best values of the parameters of isomer shift, quadrupole coupling constant, line width, populations, base line, and asymmetry parameter via nonlinear least-squares minimization of the difference between the observed and calculated spectra. Starting spectral parameters were based on literature data,[19,24a,34-36] 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.[25]

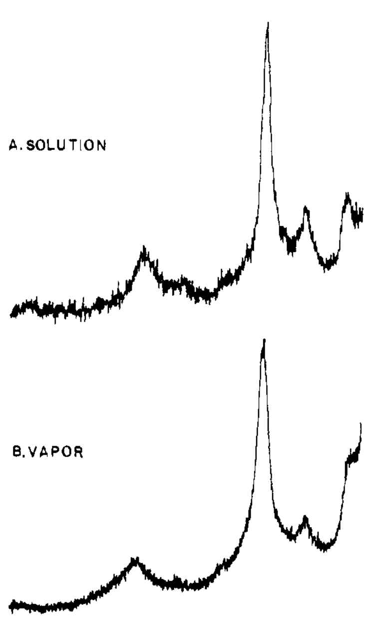


Figure 2. Resonance Raman spectra (ν_0 5145 Å) of (A) starch-iodine prepared in aqueous solution; (B) starch-iodine prepared with iodine vapor.

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

$$\Gamma_n = \sqrt{[\kappa(V_n - \delta)]^2 + \Gamma_{\text{true}}^2} \qquad (1)$$

where Γ_{true} is the actual line width, δ is the isomer shift, V_n is the velocity of line n, κ is the broadening parameter, and Γ_n is the observed width of the nth line. This function broadens the lines furthest away from the center of gravity (δ, isomer shift) to a greater extent than those lines close to δ. This has the same overall effect as a quadrupole distribution. Using this value of Γ_n, reasonable line widths 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.[24] In this contribution we restrict our discussion to amylose-iodine stoichiometry ranges and preparative methodologies which would be considered typical.[7]

Resonance Raman Studies. In Figure 2 are presented reso- by the aqueous solution, I^- procedure,[7a] and by the I_2 vapor procedure.[7] Importantly, the spectra are essentially identical, indicating that the scattering species are essentially identical. The spectra vary only modestly with exciting laser frequency (ν_0 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 1 h (Figure 4), i.e., a slight relative

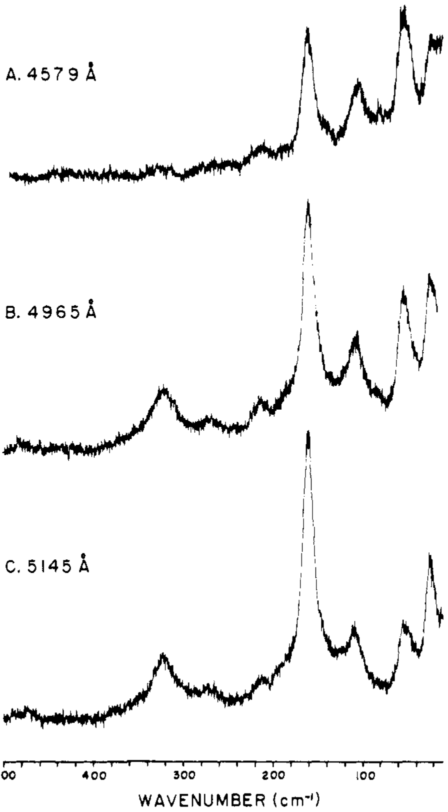


Figure 3. Exciting frequency (ν_0) dependence of the resonance Raman spectrum of the starch–iodine complex: (A) Ar$^+$, 4579 Å; (B) Ar$^+$, 4965 Å; (C) Ar$^+$, 5145 Å.

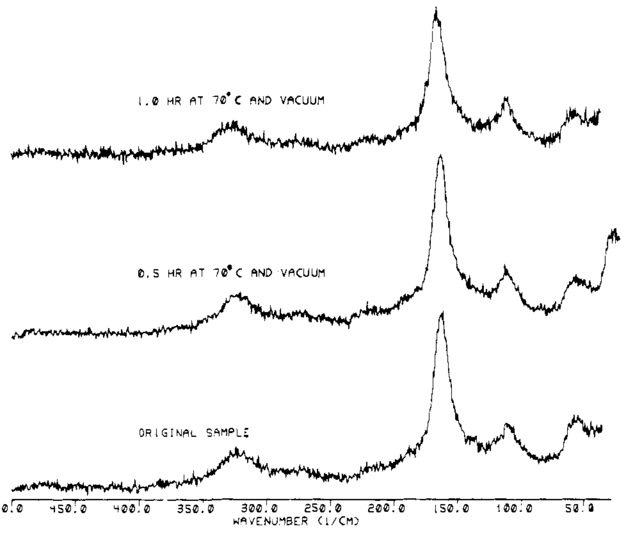


Figure 4. Effects of heating and vacuum on the resonance Raman spectrum of the starch-iodine complex (ν_0 5145 Å).

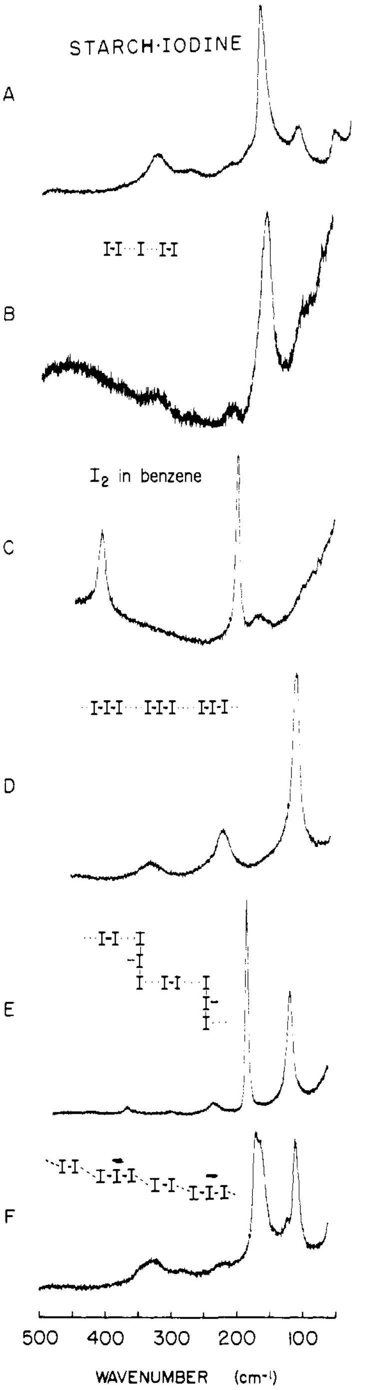


Figure 5. Resonance Raman spectra (5145-Å excitation) of (A) starch (amylose)-iodine; (B) polycrystalline (trimesic acid·$H_2O)_{10}$·$H^+I_5^-$; (C) I_2 dissolved in benzene; (D) polycrystalline (benzamide)$_2H^+I_3^-$; (E) polycrystalline (phenacetin)$_2H^+I_3^-$·I_2; (F) polycrystalline (α-cyclohexaamylose)$_2Li^+I_3^-$·I_2·$8H_2O$.

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.[26]

The resonance Raman spectra of both starch-iodine samples (Figures 2 and 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 (2 × 163) and 215 (2 × 109) 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 an increase in I–I bond length and a decrease in bond order and stretching force constant are observed.[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

Table I. Iodine-129 Mössbauer Parameters

	amylose-iodine		
	aqueous solution[a]	vapor[b]	(trimesic acid·$H_2O)_{10}$-H^+I_5
Site 1			
δ, mm/s[c]	1.22(1)	1.08(2)	1.15(3)
$e^2q^{129}Q$, MHz	−1743(15)	−1795(15)	−1777(5)
Γ, mm/s[d]	1.14(1)	1.67(9)	1.15(5)
rel intensity	1.9(2)	2.0	2.0(1)
Site 2			
δ, mm/s	0.53(3)	0.64(2)	0.53(5)
$e^2q^{129}Q$, MHz	−1187(20)	−1473(20)	−1404(8)
Γ, mm/s	2.13(6)	1.20(5)	1.75(5)
κ[e]	0.15(1)	0.19(5)	0.14(1)
rel intensity	1.8(3)	2.0(4)	1.0(1)
Site 3			
δ, mm/s	0.14(1)	0.31(10)	0.13(5)
$e^2q^{129}Q$, MHz	−842(25)	−909(25)	−965(5)
Γ, mm/s	1.08(3)	1.12(9)	1.04(4)
rel intensity	1.0	0.5(2)	1.0
Site 4			
δ, mm/s		1.29(4)	
$e^2q^{129}Q$, MHz		−1967(15)	
Γ, mm/s		1.38(5)	
rel intensity		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.

nonpolar environment such as hexane or benzene (Figure 5C), I_2 exhibits a stretching frequency at 210 (hexane) and 207 cm^{-1} (benzene); this is clearly not in accord with the spectrum in Figure 5A. Likewise, the proposal[16,29] that molecular iodine is coordinated to ethereal (O(1) or O(5) 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_2 in ether (ν 204 cm^{-1}) or 1-butanol (ν 197 cm^{-1}). The spectrum of the I_3^- chain compound (C) (benzamide)$_2$-$H^+I_3^{-9}$ (Figure 5D) is in excellent accord with the presence of I_3^- units[23] ($\nu_{\text{symmetric}}$ 108 cm^{-1} plus an overtone progression) but bears little resemblance to that of starch-iodine. Structures having discrete combinations of I_2 and I_3^- units such as (phenacetin)$_2H^+I_3^-\cdot I_2$[14] (Figure 5E) or (α-CD)$_2Li^+I_3^-\cdot I_2\cdot 8H_2O$[12] (Figure 5F) exhibit spectra in good agreement with the presence of I_3^- ions (120 and 110 cm^{-1}, respectively) and weakly coordinated I_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·$H_2O)_{10}H^+I_5^-$ (Figure 5B), a pentaiodide chain compound[15] (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_5^- ion of idealized $D_{\infty h}$ symmetry should exhibit two Raman-active stretching modes of Σ_g^+ symmetry and a Raman-active bending mode of π_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.[24,30] 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 (F), while the weaker band at 109 cm^{-1} is reasonably ascribed to symmetrically coupled motion of the two "I_2" units (G).[31] There is likely to be some mixing of the two Σ_g^+ modes.[24,32] Other examples of I_5^- resonance Raman spectra that closely resemble that of starch-iodine are those of Ni(dpg)$_2$I and Pd(dpg)$_2$I (dpg = diphenylglyoximato).[24a] 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).

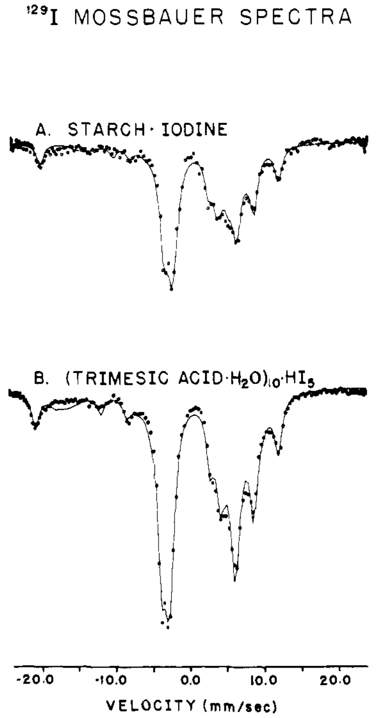


Figure 6. Iodine-129 Mössbauer spectra of the indicated compounds at 4 K. The solid lines represent the best computer fit to the experimental data. The vertical direction represents percent effect, the maximum of which is 16% for (A) and 13% for (B).

$$[\mathrm{I} \longleftrightarrow \mathrm{I} \cdots\cdots \mathrm{I} \cdots\cdots \mathrm{I} \longleftrightarrow \mathrm{I}]^-$$

F

$$[\mathrm{I}-\mathrm{I} \longleftarrow\!\!-\!\!-\!\!-\, \mathrm{I} \,-\!\!-\!\!-\!\!\longrightarrow \mathrm{I}-\mathrm{I}]^-$$

G

It was observed (vide supra) 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:

$$I_5^- \xrightarrow[\Delta]{} I_3^- + I_2 \qquad (2)$$

Iodine Mössbauer Studies. Further efforts to quantitatively investigate the I_5^- 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_5^- formation might be obtained.

The iodine-129 Mössbauer spectrum of the starch-iodine complex prepared by the aqueous method[7a] 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 (δ), quadrupole coupling constant

($e^2q^{129}Q$), line width (Γ), broadening parameter (κ), and relative site populations. No asymmetry (η) 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 $(\text{benzamide})_2{\cdot}\mathrm{H^+I_3^-}$ [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[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/s, $e^2q^{129}Q = -1692$ MHz;[34] for I_2 in hexane, $\delta = +0.98$ mm/s, $e^2q^{129}Q = -1587$ MHz[34]) or I^- ($\delta = -0.51$ mm/s, $e^2q^{129}Q = 0$[34]) in the spectrum. It is estimated that these species, although undetected, could be present in no greater than 5 mol % each. For comparison with the starch–iodine spectrum, the Mössbauer spectrum of $(\text{trimesic acid}{\cdot}\mathrm{H_2O})_{10}\mathrm{H^+I_5^-}$, which is known to contain linear chains of symmetrical I_5^- ions (E),[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 $(\text{trimesic acid}{\cdot}\mathrm{H_2O})_{10}\mathrm{H^+I_5^-}$ 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.[24a] Thus, the iodine-129 Mössbauer spectrum of starch-iodine prepared in aqueous solution is in good agreement with pentaiodide model E.

$$\begin{array}{lccccccccc} & [\mathrm{I} & - & \mathrm{I} & \cdots & \mathrm{I} & \cdots & \mathrm{I} & - & \mathrm{I}]^- \\ \text{site} & 2 & & 1 & & 3 & & 1 & & 2 \end{array}$$

H

The Mössbauer spectrum of starch-iodine prepared from "V" amylose and iodine vapor[7] 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 δ (mm/s) and $e^2q^{129}Q$ (MHz) values of 1.08 (2) and −1795 (15); 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/s 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_3^-, I_5^-, or any other polyiodide in any known chemical environment.[21,24a,b,34,36] Organic iodides also exhibit considerably different spectral parameters as exemplified by $CH_3{}^{129}I$ ($\delta = +0.20$ mm/s, $e^2q^{129}Q = -1219$ MHz)[34] or $C^{129}I_4$ ($\delta = +0.65$ mm/s, $e^2q^{129}Q = -1474$ MHz).[34] The observed quadrupole splitting in the fourth site also rules out IO_3^-; typical iodate parameters[34,35] are +699 ($K^{129}IO_3$), +706 ($NH_4{}^{129}IO_3$), and +722 MHz ($Ba({}^{129}IO_3)_2$). 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 ${}^{129}IBr$ ($\delta = 1.77$ mm/s, $e^2q^{129}Q = -2028$ MHz[36]), ${}^{129}ICl$ ($\delta = 2.27$ mm/s, $e^2q^{129}Q = -2195$ MHz[36]), and ${}^{129}ICN$ ($\delta = 1.73$ mm/s, $e^2q^{129}Q = -1851$ MHz[36]).

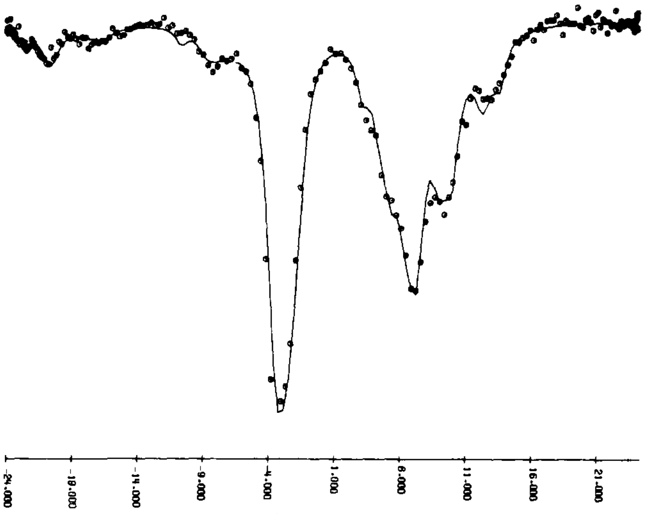


Figure 7. Iodine-129 Mössbauer spectrum of the starch-iodine complex prepared by the vapor method. The solid line represents the best computer fit to the experimental data. The vertical direction is percent effect, the maximum of which is 5.2%.

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:

$$n\mathrm{H_2O} + \text{amylose} + 3n\mathrm{I_2} \rightleftarrows \text{amylose}(\mathrm{I_5^-})_n + n\mathrm{H^+} + n\mathrm{HOI} \quad (3)$$

$$n\mathrm{ROH} + \text{amylose} + 3n\mathrm{I_2} \rightleftarrows \text{amylose}(\mathrm{I_5^-})_n + n\mathrm{H^+} + n\mathrm{ROI} \quad (4)$$

Such a process would involve iodine reaction with either water, butanol, or a glucose hydroxyl moiety and yields one hypoiodite species per I_5^- formed. Equation 3 is analogous to the known hydrolysis reaction of iodine[37,38]

$$\mathrm{I_2} + \mathrm{H_2O} \rightleftarrows \mathrm{H^+} + \mathrm{I^-} + \mathrm{HOI} \quad (5)$$

except that I_5^- complexation by amylose would presumably shift the equilibrium far to the right. Equation 5 responds similarly to the addition of alkali or mercuric oxide.[37] Neither HOI[37,38] nor ROI[39] species appear to have appreciable long-term stability, although both have been generated in solution (but have not been isolated in a pure state); immobilization within the amylose helix may introduce significant stabilization.[40] Although iodine Mössbauer parameters are not known for HOI or ROI compounds, a plausible estimate of the nuclear quadrupole coupling constant for HOI should be accessible by multiplying $e^2q^{129}Q$ of ·OI (−1326 MHz)[41] by the ratio of the $HO^{35}Cl$ and $\cdot O^{35}Cl$ nuclear quadrupole coupling constants (−121.9/−86.6 MHz).[41,42] The resulting estimation, −1866 MHz, is in reasonable agreement with $e^2q^{129}Q$ determined for the fourth site. Judging from the similarity of the CH_3OCl nuclear quadrupole coupling constant (−117.1 MHz)[44] to that of HOCl (−121.0 MHz),[42] the $e^2q^{129}Q$ parameters 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 pentaiodide formation is produced by hydrolysis (or alcoholysis) of iodine. A hypoiodite 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.[14,15,28] In the present case there may well be a connection between the commensurability of the pentaiodide repeat distance (15.5 Å)[15] and twice the helix repeat dimension (ca. 16 Å).

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References and Notes

(1) (a) Northwestern University. (b) Argonne National Laboratory. (c) Thesis Parts Appointee, Argonne National Laboratory. (d) Research Laboratories, Eastman Kodak Co., Kodak Park, Rochester, N.Y. 14650.

(2) Camille and Henry Dreyfus Teacher–Scholar.

(3) (a) Banks, W.; Greenwood, C. T., Eds. "Starch and Its Compounds"; Edinburgh University Press: Edinburgh, 1975. (b) Thomas, J. A.; Stewart, L. In "Starch: Chemistry and Technology", Whistler, R. L., Pascall, E. F., Eds.; Academic Press: New York, 1965; Vol. I, Chapter IX. (c) Foster, J. F. In ref 3b, Chapter XV.

(4) (a) Rees, D. A. "Polysaccharide Shapes"; Chapman and Hall: London, 1977; pp 31–32, 56–58. (b) Murphy, V. G.; Zaslow, B.; French, A. D. *Biopolymers* **1975,** *14*, 1487–1501. (c) Zaslow, B.; Murphy, V. G.; French, A. D. *Ibid.* **1974,** *13*, 779–790. (d) Winter, W. T.; Sarko, A. *Ibid.* **1974,** *13*, 1461–1482. (e) *Ibid.* **1974, 13,** 1447–1460. (f) French, A. D.; Zaslow, B. *J. Chem. Soc., Chem. Commun.* **1972,** 41–42.

(5) (a) Colin, H.; Gaultier de Claubry. *Ann. Chim.* (*Paris*) **1814,** *90*, 87. (b) Freudenberg, K.; Schaaf, E.; Dumpert, G.; Ploetz, T. *Naturwissenschaften* **1939,** *22*, 850–853. (c) Greenwood, T. C. *Adv. Carbohydr. Chem.* **1956,** *11*, 335–393. (d) Kennedy, J. F. *Adv. Carbohydr. Chem. Biochem.* **1974,** *29*, 305–405.

(6) (a) Reference 4a, p 56. (b) Skoog, D. A.; West, D. M. "Fundamentals of Analytical Chemistry"; Holt, Rinehart and Winston: New York, 1963; pp 461–464.

(7) (a) Rundle, R. E.; Baldwin, R. *J. Am. Chem. Soc.* **1943,** *65*, 544–557. (b) Rundle, R. E.; French, D. *Ibid.* **1943,** *65*, 558–561. (c) *Ibid.* **1943,** *65*, 1707–1710. (d) Rundle, R. E.; Edwards, F. C. *Ibid.* **1943,** *65*, 2200–2203. (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*, 1769–1772. (h) Stein, R. S.; Rundle, R. E. *J. Chem. Phys.* **1947,** *16*, 195–207.

(8) Liang, J.-N.; Knauss, C. J.; Meyers, R. R. *Rheol. Acta* **1974,** *13*, 740–744.

(9) (a) Thoma, J. A.; French, D. *J. Am. Chem. Soc.* **1960,** *82*, 4144–4147. (b) Schneider, F. W.; Cronan, C. L.; Podder, S. *J. Phys. Chem.* **1968,** *72*, 4563–4568, and references cited therein. (c) Cronan, C. L.; Schneider, F. W. *Ibid.* **1969,** *73*, 3990–4004, and references cited therein.

(10) (a) Reddy, J. M.; Knox, K.; Robin, M. B. *J. Chem. Phys.* **1964,** *40*, 1082–1089. (b) Robin, M. B. *Ibid.* **1964,** *40*, 3369–3377.

(11) (a) Bender, M. L.; Komiyama, M. "Cyclodextrin Chemistry"; Springer-Verlag: West Berlin, 1978. (b) Saenger, W. In "Environmental Effects on Molecular Structure and Properties", Pullman, B., Ed.; Reidel Publishing Co.: Dordrecht, Holland, 1976; pp 265–305.

(12) (a) Noltemeyer, M.; Saenger, W. *Nature* (*London*) **1976,** *259*, 629–632. (b) Cramer, F.; Bergmann, U.; Manor, P. C.; Noltemeyer, M.; Saenger, W. *Justus Liebigs Ann. Chem.* **1976,** 1169–1179.

(13) (a) McMullan, R. K.; Saenger, W.; Fayos, J.; Mootz, D. *Carbohydr. Res.* **1973,** *31*, 37–46. (b) *Ibid.* **1973,** *31*, 211–227. (c) James, W. J.; French, D.; Rundle, R. E. *Acta. Crystallogr.* **1959,** *12*, 385–389.

(14) (a) For the $I_3^- \cdots I_2$ motif, see, for example, Herbstein, F. H.; Kapon, M. *Nature* (*London*), *Phys. Sci.* **1972,** *239*, 153–154. (b) Herbstein, F. H.; Kapon, M. *Philos. Trans. R. Soc. London* **1979,** *291*, 199–218.

(15) For the I_5^- motif, see: Herbstein, F. H.; Kapon, M. *Acta Crystallogr., Sect. A* **1972,** *28*, S74. Kapon M. Ph.D. Thesis, Technion, Haifa, Israel, 1975.

(16) Greenwood, C. T.; Rossotti, H. *J. Polym. Sci.* **1958,** *27*, 481–488.

(17) Bersohn, R.; Isenberg, I. *J. Chem. Phys.* **1961,** *35*, 1640–1643.

(18) Pfannenmuller, B.; Bayerhofer, H.; Schulz, R. C. *Biopolymers* **1971,** *10*, 243–261, and references cited therein.

(19) Ehrlich, B. S.; Kaplan, M. *J. Chem. Phys.* **1969,** *51*, 603–606.

(20) Tasumi, M. *Chem. Lett.* **1972,** 75–78.

(21) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1978,** *100*, 3215–3217.

(22) Schoch, T. J. *Adv. Carbohydr. Chem.* **1945,** *1*, 247–277.

(23) Shenoy, G. K.; Freidt, J. M.; Moletta, H.; Ruby, S. L. *Mössbauer Eff. Methodol.* **1974,** *9*, 277–305.

(24) (a) Cowie, M. A.; Gleizes, A.; Grynkewich, G. W.; Kalina, D. W.; McClure, M. S.; Scaringe, R. P.; Teitelbaum, R. C.; Ruby, S. L.; Ibers, J. A.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979,** *101*, 2921–2936. (b) Marks, T. J. *Ann. N. Y. Acad. Sci.* **1978,** *313*, 594–616. (c) Marks, T. J.; Webster, D. F.; Ruby, S. L.; Schultz, S. J. *J. Chem. Soc., Chem. Commun.* **1976,** 444–445. (d) Teitelbaum, R. C.; Ruby, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1979,** *101*, 7568–7573. (e) Kalina, D. W.; McClure, M. S.; Kannewurf, C. R.; Marks, T. J., submitted for publication.

(25) Ruby, S. L. *Mössbauer Eff. Methodol.* **1973,** *8*, 263–276.

(26) Peticolas, W. L. *Nature* (*London*) **1963,** *197*, 898–899.

(27) (a) Gabes, W.; Nijman-Meester, M. A. M. *Inorg. Chem.* **1973,** 12, 589–592. (b) Datta, S. N.; Ewig, C. S.; Van Wazer, J. R. *J. Mol. Struct.* **1978,** *48*, 407–416.

(28) (a) Huheey, J. E. "Inorganic Chemistry. Principles of Structure and Reactivity", 2nd ed.; Harper and Row: New York, 1978; pp 666–669. (b) Popov, A. I. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1972,** *3*.

(29) Murakami, H. *J. Chem. Phys.* **1955,** *23*, 1979; **1954**, *22*, 367–374.

(30) (a) Clark, R. J. H.; Stewart, B. *Struct. Bonding* (*Berlin*) **1979,** *36*, 1–80. (b) Sprio, T. G.; Stein, P. *Annu. Rev. Phys. Chem.* **1977,** *28*, 501–521. (c) Warshel, A. *Annu. Rev. Biophys. Bioeng.* **1977,** *6*, 273–300.

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

(32) (a) The stretch–stretch interaction constants in trihalide ions are relatively large.[32b,c] (b) Maki, A. G.; Forneris, *Spectrochim. Acta, Part A* **1967,** *23*, 867–880. (c) Gabes, W.; Elst, R. *J. Mol. 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.

(34) Gibb, T. C. "Principles of Mössbauer Spectroscopy"; Chapman and Hall: London, 1976; Chapter 4.2.

(35) deWaard, H. "Mössbauer Effect Data Index", 1973; pp 447–494.

(36) Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Chem. Radiochem.* **1972,** *15*, 59–258.

(37) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry: A Comprehensive Text", 3rd ed.; Wiley: New York, 1972; p 477.

(38) Downs, A. J.; Adams, C. J. In "Comprehensive Inorganic Chemistry", Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 2, pp 1188–1192.

(39) (a) Goosen, A.; Lane, H. A. H. *J. Chem. Soc. C* **1969,** 383–385. (b) Reference 38, p 1410.

(40) Iodide is known to catalyze the decomposition of OI^-.[37] Either steric shielding or the scavenging of free I^- to form I_5^- would serve to protect the OI^-.

(41) Saito, S. *J. Mol. Spectrosc.* **1973,** *48*, 530–535.

(42) Mirri, A. M.; Scappini, F.; Cazzoli, G. *J. Mol. Spectrosc.* **1971**, *37*, 218–227.

(43) Amano, T.; Hirota, E.; Morino, Y. *J. Mol. Spectrosc.* **1968,** *27*, 257–265.

(44) Suzuki, M.; Guarnieri, A. *Z. Naturforsch. A* **1976,** *31*, 1242–1258.