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## Charge Transfer and Partial Oxidation in the Conductive Hydrocarbon–Iodine Complex "2Perylene·3I<sub>2</sub>"

Robert C. Teitelbaum,<sup>1a,b</sup> Stanley L. Ruby,<sup>1c</sup> and Tobin J. Marks\*<sup>1a,</sup>

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 February 2, 1979

**Abstract:** It has long been thought that the highly conductive complexes formed between elemental iodine and various polycyclic aromatic hydrocarbons are molecular complexes; i.e., they contain iodine as I<sub>2</sub>. In this contribution we report resonance Raman and iodine-129 Mössbauer spectroscopic characterization of the form of the iodine in the most highly conductive of these materials: "2perylene·3I<sub>2</sub>". We find that "2perylene·3I<sub>2</sub>" is not a molecular complex, but rather a partially oxidized, mixed-valence compound, the charge distribution of which can be approximately formulated on the basis of the spectral data as (perylene)<sup>+0.4</sup>(I<sub>3</sub><sup>-</sup>·2I<sub>2</sub>)<sub>0.4</sub>.

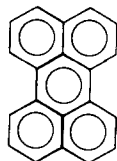
### Introduction

A question of great current interest in the field of electrically conductive, low-dimensional materials composed of molecular stacks<sup>3</sup> concerns the importance of incomplete charge transfer or "partial oxidation" in facilitating charge transport.<sup>3,4</sup> Considerable experimental and theoretical evidence points to the prerequisite of bringing the arrayed molecules (usually planar, conjugated organics or metal-organics) into formal fractional oxidation states (mixed valency) to help overcome band-filling, bandwidth, and Coulombic impediments to charge conduction along the molecular stack.<sup>3,4</sup> This ionic, mixed valent state is usually brought about via the addition of electron acceptors (or donors) to the system. In apparent contradiction to the above viewpoint stands a large class of highly conductive solids formed by the addition of elemental iodine to various polycyclic aromatic hydrocarbons.<sup>5</sup> In several cases, iodination increases the electrical conductivity of the

hydrocarbon by as much as 10<sup>12</sup>–10<sup>14</sup>.<sup>5</sup> These materials have long been formulated as covalently bonded molecular complexes, i.e., unoxidized with iodine present as I<sub>2</sub>.

In contrast to the conventional structural model for conductive hydrocarbon–iodine complexes, recent investigations in several laboratories, including our own, have shown that halogenation is an exceedingly effective method for introducing partial oxidation in a number of planar organic and metallo-macrocyclic systems.<sup>6–8</sup> The structures of such materials generally consist of arrays of partially oxidized donor molecules and reduced halogen acceptor counterions.<sup>6–8</sup> In the case of iodine dopants we have also shown that the powerful combination of resonance Raman and iodine-129 Mössbauer spectroscopy can be used to deduce the form of the iodine present in such materials (i.e., I<sub>2</sub>, I<sup>-</sup>, I<sub>3</sub><sup>-</sup>, I<sub>5</sub><sup>-</sup>, or mixtures thereof), and thus the degree of partial oxidation.<sup>6a-c,9</sup> This technique is especially informative in instances where disorder<sup>6b</sup> or (as in

the present case)<sup>10a</sup> the extreme complexity of the structure hinders diffraction studies. With these considerations in mind, we have now applied the Raman-Mössbauer technique to the most highly conductive [ $\sigma(300\text{ K}) \approx 0.1\text{ (ohm cm)}^{-1}$  for compressed, polycrystalline samples<sup>10g</sup> and  $5\text{--}20\text{ (ohm cm)}^{-1}$  for single crystals<sup>11</sup>] and most thoroughly studied of the hydrocarbon-iodine complexes, that of perylene (A):



A

"2perylene-3I<sub>2</sub>".<sup>10</sup> Our goal was to determine whether or not this is a molecular complex. We report here that "2perylene-3I<sub>2</sub>" is not a molecular complex, but is a partially oxidized, mixed valence compound.

### Experimental Section

**Synthesis of Perylene-I<sub>2</sub>.<sup>92</sup>** Lustrous, silver-black crystals of "2perylene-3I<sub>2</sub>" were grown from hot benzene solutions of perylene and I<sub>2</sub> by using the procedure of Kommandeur and Hall.<sup>10h</sup> The product was quickly washed with benzene and was briefly dried under a stream of prepurified nitrogen. Since noticeable discoloration (due to iodine loss) of this compound occurs within 10–15 min at room temperature in an open vessel, samples were stored in closed containers under nitrogen at  $-35\text{ }^\circ\text{C}$  in the dark. The sample for elemental analysis was maintained at  $0\text{ }^\circ\text{C}$  until immediately prior to analysis. The stoichiometry determined corresponds to perylene-I<sub>2</sub>.<sup>92</sup>

Anal. Calcd for C<sub>20</sub>H<sub>12</sub>I<sub>2</sub>.<sup>92</sup>: C, 38.56; H, 1.94; I, 59.49. Found: C, 38.28; H, 1.80; I, 59.04.

**Synthesis of Perylene-<sup>129</sup>I<sub>2</sub>.<sup>92</sup>** The <sup>129</sup>I-enriched sample was prepared by the above procedure. The reagent <sup>129</sup>I<sub>2</sub> was prepared by hydrogen peroxide oxidation of an acidified solution of Na<sup>129</sup>I (Oak Ridge National Laboratory, 87% <sup>129</sup>I isotopic content). The resulting <sup>129</sup>I<sub>2</sub> was extracted with pentane, and the solution was washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in a nitrogen stream to yield solid <sup>129</sup>I<sub>2</sub>.

**Iodine-129 Mössbauer Studies.** Source, absorber, and detector were employed in the standard transmission geometry. The <sup>66</sup>Zn<sup>129</sup>Te source ( $t_{1/2} = 69\text{ min}$ ) was prepared by irradiation of a <sup>66</sup>Zn<sup>128</sup>Te target (pressed in an aluminum disk) in the Argonne CP-5 reactor for 2 h. The source produced sufficient 27.7 keV  $\gamma$  radiation for 3–4 h of Mössbauer effect data collection. Absorbers were prepared by powdering the iodine-129 enriched sample, mixing it with an inert filler (boron nitride), and loading it into a Lucite sample holder. Both source and absorber were cooled in liquid He during data collection. Three sources were used, in sequence, to collect all of the data. Data collected from each source were checked for reproducibility and then summed to give the final spectrum. The spectrometer velocity was generated with a feedback-controlled vibrator by using sinusoidal acceleration. Velocity calibration was accomplished with <sup>57</sup>Fe foil. Data collection utilized a proportional counter in conjunction with a 400-channel multichannel analyzer, operating in the time mode. Paper tape was used for data storage.

**Mössbauer Data Processing.** Initial Mössbauer effect data processing and analysis employed the computer program, GENFIT,<sup>6b,12</sup> which finds the best values for the parameters of isomer shift ( $\delta$ ), quadrupole coupling constant ( $e^2qQ$ ), line width ( $\Gamma$ ), population ( $p_i$ ) base line, and asymmetry parameter ( $\eta$ ) via nonlinear least-squares minimization of the difference between the observed and calculated spectra. Each unique iodine microenvironment, or site, is described by a set of five parameters and gives rise to an eight-line quadrupole absorption pattern. The observed spectrum is a summation of the absorption patterns of all of the iodine sites.

The goodness of fit is judged by the parameter "Misfit", which has been previously defined by Ruby.<sup>12</sup> Final data processing and analysis were accomplished by using a modified version of GENFIT,<sup>13</sup> which includes corrections for the absorber thickness<sup>13–15</sup> (see Results and Discussion for full explanation), histogram, and cosine errors. Both versions of GENFIT include a broadening parameter,  $\kappa_i$ ,<sup>6b</sup> which allows

one or more sites to have a distribution of quadrupole coupling constants. This occurs when one site can be in several slightly different environments, resulting in a modest spread in the quadrupole coupling constant. This results in a blurring of the spectral peaks from a single octet (for each site  $i$ ) in a way which is larger for those lines at larger velocities. Normally, each site is unique and can be described by five parameters. If one site has a distribution in its quadrupole coupling constant, it could be replaced by several sites with slightly different  $e^2qQ$  values. However, it is more convenient to use the broadening formula by adding one extra parameter for each site. In the present case, it was only necessary to apply this broadening to two of the sites. This nonequivalence was incorporated in the fitting procedure as a velocity-dependent line broadening function (eq 1)

$$\Gamma_n = \sqrt{[\kappa_i(V_n - \delta_i)]^2 + \Gamma_i^2} \quad (1)$$

where  $\Gamma_i$  is the actual line width of the  $i$ th site,  $\kappa_i$  is the broadening parameter applied to the  $i$ th site,<sup>6b</sup>  $V_n$  is the velocity of the  $n$ th line,  $\delta_i$  is the isomer shift of the  $i$ th site, and  $\Gamma_n$  is the observed width of the  $n$ th line. The lines furthest from the center of gravity ( $\delta_i$  isomer shift) are broadened to a greater extent than those lines closer to  $\delta_i$ . This has the same effect as a distribution of quadrupole splittings. Using this value of  $\Gamma_n$ , reasonable line widths are obtained for all sites when compared with the natural line width ( $\Gamma_0$ , vide infra). For a "perfect" sample one expects  $\Gamma_n = \Gamma_0$ , but many effects can cause larger values to be observed.

**Resonance Raman Studies.** Laser Raman spectra were recorded with Kr<sup>+</sup> (6471 Å) or Ar<sup>+</sup> (4880, 5145 Å) excitation by using a Spex 1401 double monochromator and photon counting detection. Samples were examined in nitrogen-flushed, 5- or 12-mm, spinning (ca. 1200 rpm), Pyrex sample tubes. A 180° back scattering detection geometry was employed. Several scans were made of each sample (the initial at lowest laser power) to check for sample decomposition. This effect was relatively minor and resulted only in gradual diminution of the polyiodide bands with accompanying increase in perylene fluorescence. Spectra were calibrated by using the exciting line ( $\nu_0$ ) or the laser plasma lines.

### Results and Discussion

The goal of this investigation was to identify, via resonance Raman and I-129 Mössbauer spectroscopy, the form(s) of iodine present in "2perylene-3I<sub>2</sub>" and thus to determine whether or not this material is partially oxidized. Further details of the very complex crystal structure are under investigation by diffraction techniques and will be reported in due course.

Crystals of "2perylene-3I<sub>2</sub>" were grown from hot benzene solutions of perylene and I<sub>2</sub> (<sup>127</sup>I<sub>2</sub> or <sup>129</sup>I<sub>2</sub>) by the procedure of Kommandeur and Hall.<sup>10h</sup> Elemental analysis of a freshly prepared sample indicated that the composition is approximately perylene-I<sub>2</sub>.<sup>92</sup>

In Figure 1 are presented resonance Raman scattering spectra (5145-Å excitation; sealed, spinning polycrystalline samples) of perylene-I<sub>2</sub>.<sup>92</sup> along with those of relevant model compounds in which the form of the iodine present has already been unambiguously established by diffraction methods. Since the perylene complex slowly loses iodine on standing in an open container at room temperature, spectra were also recorded of samples which had been deliberately depleted of iodine by using a flow of prepurified nitrogen gas. Except for a progressive diminution of polyiodide scattering intensity and an increase in perylene fluorescence, spectra were identical with that shown in Figure 1A. It was also established that the perylene-I<sub>2</sub>.<sup>92</sup> Raman spectra are essentially independent of exciting wavelength over the range 4880–6471 Å (Figure 2). The spectral scattering pattern exhibited by the perylene complex (175 s, 145 w, 115 m, cm<sup>-1</sup>) is clearly and, most importantly, inconsistent with a simple molecular I<sub>2</sub> charge transfer complex. Interaction with the  $\pi$  cloud of benzene perturbs  $\nu_{1-1}$  of I<sub>2</sub> only slightly (Figure 1B, 209 cm<sup>-1</sup>) from the gas phase value of 215 cm<sup>-1</sup>,<sup>16</sup> while even a stronger donor such as Me<sub>2</sub>SO only displaces  $\nu_{1-1}$  to 189 cm<sup>-1</sup>.<sup>17a,b</sup> This effect can be understood by viewing I<sub>2</sub> as a Lewis acid. Interaction with Lewis bases

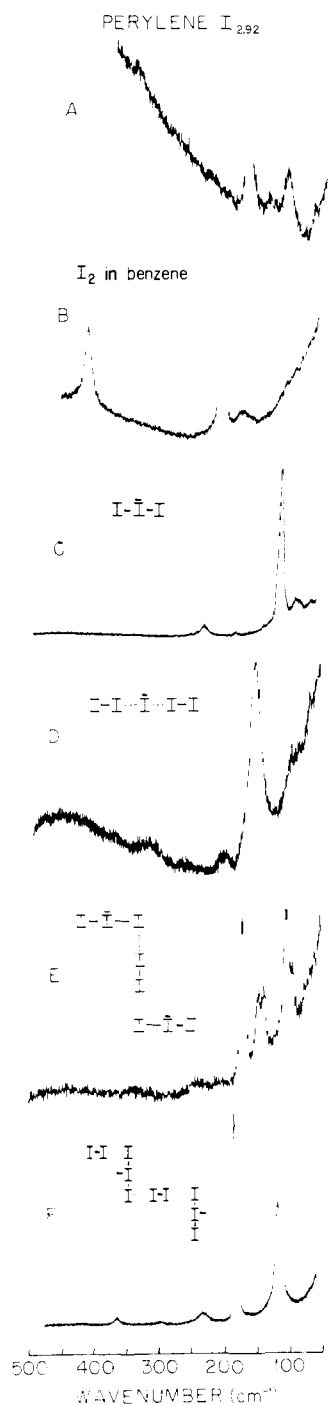


Figure 1. Resonance Raman spectra ( $\nu_0 = 5145 \text{ \AA}$ ) of (A) polycrystalline perylene- $I_{2.92}$ ; (B)  $I_2$  as a solution in benzene; (C) polycrystalline  $As(C_6H_5)_4^+I_3^-$ ; (D) polycrystalline  $(trimesic\ acid \cdot H_2O)_{10}H^+I_5^-$ ; (E) polycrystalline  $Cs_2I_8$ ; (F) polycrystalline  $(phenacetin)_2H^+I_3 \cdot I_2$ .

populates molecular orbitals with l-l antibonding character,<sup>17c,d</sup> thus increasing the l-l bond lengths and decreasing the stretching force constant.<sup>6a-c</sup> It is also possible to reject, in perylene- $I_{2.92}$ , the presence exclusively of symmetrical (i.e.,  $D_{\infty h}$ )  $I_3^-$  units, as exemplified by  $As(C_6H_5)_4^+I_3^-$ <sup>18</sup> (Figure 1C,  $\nu_{I_3^-}$  symm, fundamental =  $113 \text{ cm}^{-1}$ ) and a number of other symmetrical triiodide compounds.<sup>6a,9</sup> Likewise, the Raman scattering energies of an unsymmetrical ( $C_s$ ) triiodide ion (B) as in  $CsI_3$ ,<sup>18</sup>  $146 \text{ s}$  and  $99 \text{ s cm}^{-1}$ ,<sup>9,19</sup> are at considerable variance with the perylene results. The spectral pattern

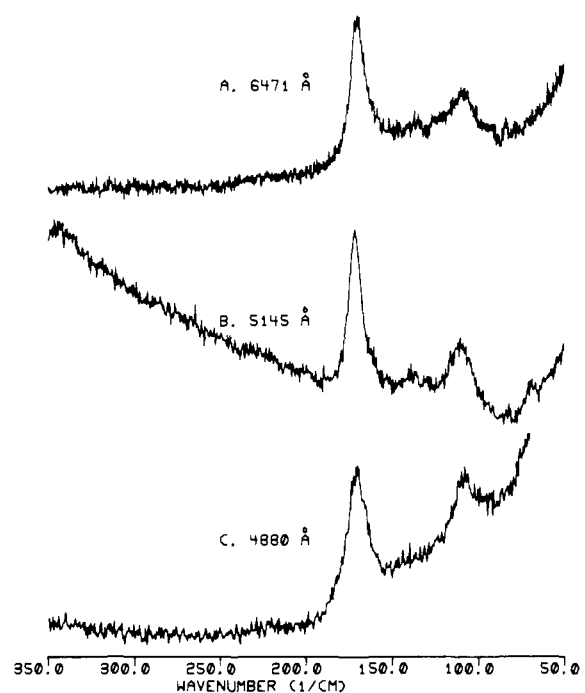
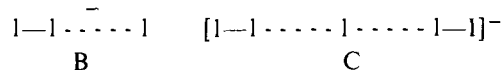


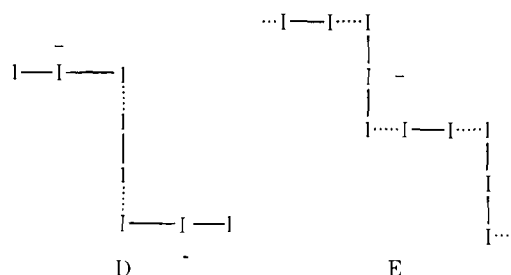
Figure 2. Resonance Raman spectra of perylene- $I_{2.92}$  at various exciting frequencies ( $\nu_0$ ). (A)  $Kr^+$ ,  $6471 \text{ \AA}$ ; (B)  $Ar^+$ ,  $5145 \text{ \AA}$ ; (C)  $Ar^+$ ,  $4880 \text{ \AA}$ .

Table I. Resonance Raman Data and Assignments for Various Polyiodide Containing Compounds<sup>a</sup>

compound	internal coordinate change		
	$\nu_{I_2^-}$	$\nu_{I_3^-}$	other
perylene- $I_{2.92}$	175 s	145 w, 115 m	
$Cs_2I_8$	172 s	150 w, 105 s	
$(phenacetin)_2H^+I_3^- \cdot I_2$	187 m	120 s	
$CsI_3$		146 s, 99 s	
$I_2$ in $Me_2SO$	189 s		
$I_2$ in benzene	209 s		
$I_2$ (gas)	215 s		
$(trimesic\ acid \cdot H_2O)_{10}H^+I_5^-$	162 s		104 w, 75 w

<sup>a</sup> In  $\text{cm}^{-1}$ ; s = strong, m = medium, w = weak.

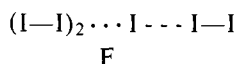
exhibited by symmetrical  $I_5^-$  species (C) as found in  $(trimesic\ acid \cdot H_2O)_{10}H^+I_5^-$ <sup>20</sup> (Figure 1D,  $\nu_{I_5^-} = 162 \text{ s cm}^{-1}$ ; other transitions at  $104 \text{ w}$  and  $75 \text{ w cm}^{-1}$ ) are also not evident. Rather, the resonance Raman spectrum of perylene- $I_{2.92}$  can be assigned to a structural model with both  $I_3^-$  and  $I_2$  units, probably weakly interacting. An example of this type of compound is  $Cs_2I_8$  (Figure 1E,  $\nu_{I_2^-} = 172 \text{ s cm}^{-1}$ ,  $\nu_{I_3^-} = 150 \text{ m}$  and  $105 \text{ s cm}^{-1}$ ) which is known to possess " $I_8^{2-}$ " units<sup>21</sup> (D) (i.e.,  $I_2$  and distorted  $I_3^-$ , weakly interacting), and



$(phenacetin)_2H^+I_3^- \cdot I_2$  (Figure 1F,  $\nu_{I_2^-} = 187 \text{ m}$ ,  $\nu_{I_3^-} = 120 \text{ s cm}^{-1}$ ) which possesses chains of alternating  $I_3^-$  and  $I_2$  units (E).<sup>22</sup> The Raman transition at  $145 \text{ cm}^{-1}$  in perylene- $I_{2.92}$  is most reasonably ascribed to the same origin as the  $150\text{-cm}^{-1}$  transition in  $Cs_2I_8$ : slight distortion of the  $I_3^-$  units (i.e., unequal l-l bond distances). This vibrational mode is also ob-

served in the resonance Raman spectrum of CsI<sub>3</sub><sup>9,19,23</sup> and is formally derived from the Raman-inactive antisymmetric stretching transition under  $D_{\infty h}$  symmetry. Resonance Raman data and spectral assignments for the above compounds are compiled in Table I.

Iodine-129 Mössbauer studies of perylene·I<sub>2</sub><sup>92</sup> were undertaken to obtain additional, quantitative information on the polyiodide species present as well as to investigate the possible presence of Raman-inactive I<sup>-</sup> or other iodine containing species. The experimental spectrum is represented by the data points in both Figures 3A and 3B. It is possible to immediately reject the presence of significant amounts of isolated I<sup>-</sup> ( $\delta = -0.51$  mm/s,  $e^2q^{129}Q = 0.00$  MHz<sup>24</sup>). The presence of isolated I<sub>2</sub> molecules (for I<sub>2</sub> in benzene,  $\delta = +0.76$  mm/s,  $e^2q^{129}Q = -1692$  MHz<sup>24</sup>; for I<sub>2</sub> in hexane,  $\delta = +0.98$  mm/s,  $e^2q^{129}Q = -1587$  MHz<sup>24</sup>) as the sole iodine containing species could also be rejected. Rather, the spectrum is more complex, and considerable effort was put into deriving an optimized polyiodide structural model for perylene·I<sub>2</sub><sup>92</sup>. Initial attempts were made to fit the data to two sites with relative populations of either 1:1 or 1:2 (symmetrical I<sub>3</sub><sup>-</sup>). In neither case was acceptable agreement found between experimental and calculated spectra. Similarly, attempting to fit the data to three sites with relative populations 1:1:1 (distorted I<sub>3</sub><sup>-</sup>) or 2:2:1 (symmetric I<sub>5</sub><sup>-</sup>) did not result in a good agreement. Even attempting to fit the data to four sites resulted in poor agreement between experimental and calculated line shapes. However, with five sites, a satisfactory fit was obtained by using either of two different refinement procedures (vide infra). It will be seen that such a fit can be reasonably interpreted in terms interacting I<sub>2</sub> units and I<sub>3</sub><sup>-</sup> ions. Derived relative populations suggest that two I<sub>2</sub> units weakly coordinate to each distorted I<sub>3</sub><sup>-</sup> ion, as exemplified by F. Such a structure is in good agreement with the Raman data.



To ensure maximum reliability, two approaches were employed in the Mössbauer data analysis. The optimized computer fit shown in Figure 3A employs the standard "thin" absorber approximation. That is, the quadrupole pattern is assumed to be the sum of Lorentzians, the positions, intensities, and widths of which have the ideal values calculated from the ground and excited state quadrupole Hamiltonians.<sup>13,15</sup> Parameters obtained in this fit are compiled in Table II. When individual lines of the spectrum are well resolved or when the absorber thickness,  $T$ , approaches zero, as is often found, the "thin" approximation is valid.  $T$  is given by eq 2

$$T = \sigma_0 f_{\Lambda} n \quad (2)$$

where  $\sigma_0$  is the resonance cross section per nucleus,  $f_{\Lambda}$  is the recoilless fraction of the absorber at the measurement temperature, and  $n$  is the number of resonant nuclei per unit area. Appreciable absorber thickness (significant  $T$ ) results in saturation of the most intense lines and a resultant relative increase in the intensities of other lines. Also observed are saturation of poorly resolved lines as well as minor changes in the quadrupole line positions. It was noted in the "thin" absorber fit (Figure 3A) that slight disparities occurred in the intensities of central lines relative to the outermost lines. This situation plausibly arises from neglect of absorber thickness, so corrections were introduced as outlined below, employing a modified version of the fitting routine.<sup>13</sup>

The theory and computational techniques employed for the inclusion of thickness effects have been explained in detail elsewhere:<sup>13-15</sup> only the pertinent and important points will be summarized here. The calculated counting rate or transmitted flux as a function of the relative velocity ( $v$ ) of source

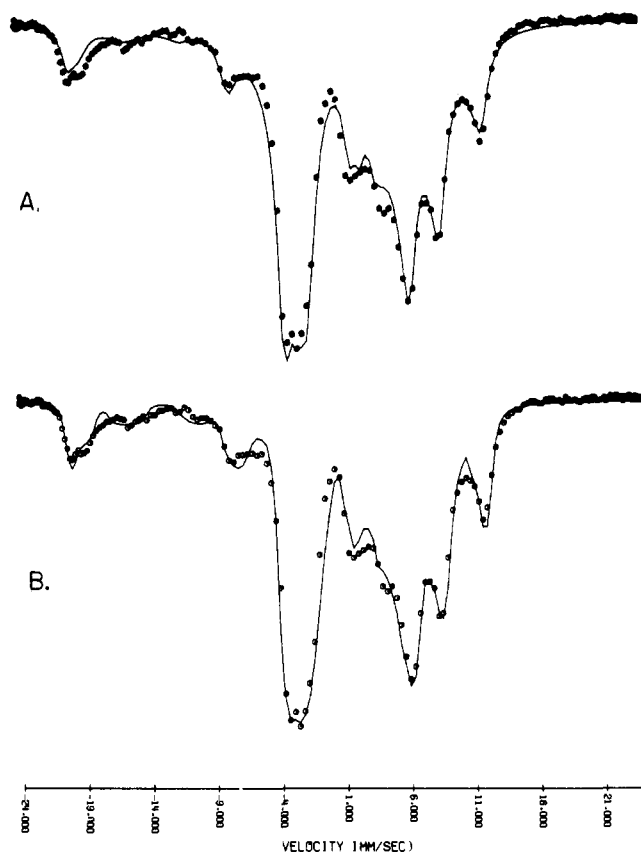


Figure 3. Iodine-129 Mössbauer spectrum of poly-crystalline perylene·I<sub>2</sub> at 4 K. (A) The solid line represents the optimized computer fit to the experimental data points, using the "thin" approximation. (B) The solid line represents the optimized computer fit using absorber thickness corrections.

and absorber is given by eq 3<sup>15</sup>

$$\text{rate}(v) = \int \text{FLUX}(E,v) * \text{TRANS}(E) dE \quad (3)$$

where the flux distribution (FLUX) and transmission (TRANS) are defined in eq 4<sup>15</sup> and 5<sup>15</sup>

$$\text{FLUX}(E,v) = B + S(1 - f_s) + \frac{2f_s S}{\pi \Gamma_s} \left[ 1 + \left( \frac{E - E_0 - E(v/c)}{\Gamma_s/2} \right)^2 \right]^{-1} \quad (4)$$

$$\text{TRANS}(E) = \exp[-T * A(E)] \quad (5)$$

where  $E_0$  is the nominal  $\gamma$ -ray energy,  $E$  is the actual energy of the  $\gamma$ -ray,  $B$  is the background counting rate,  $S$  is the integrated signal rate,  $f_s$  is the source recoilless fraction,  $A(E)$  is the normalized absorption shape,  $\Gamma_s$  is the source line width, and  $c$  is the speed of light. This is the flux that is used for a nonsplit single-site source, e.g., ZnTe. FLUX, in general, is not this simple. It is instructive to look at the form of the normalized absorption shape (eq 6):<sup>15</sup>

$$A(E) = \sum_{i=\text{sites}} \sum_{l=\text{lines}} \alpha_l p_i * \left[ 1 + \left( \frac{E - E_0 - \delta_l - E(v/c) - e^2 q Q \epsilon_l}{\Gamma_s/2} \right)^2 \right]^{-1} \quad (6)$$

The term,  $\alpha_l p_i$ , relates the relative intensity of a given line ( $l$ ) of the eight line quadrupole pattern and the relative number of atoms of each site  $i$  ( $p_i$ ) to the observed absorption spectrum ( $A(E)$ ). The only other new term is  $e^2 q Q \epsilon_l$ , which is the product of  $e^2 q Q$  (the quadrupole coupling constant) and  $\epsilon_l$  (the position of each line in the quadrupole pattern). Thus, it is easy to see that the overall absorption spectrum is the sum of the

**Table II.** Iodine-129 Mössbauer Parameters for Perylene·I<sub>2.92</sub>

	$\delta$ , mm/s <sup>a</sup>	$e^2q^{129}Q$ , MHz	$\Gamma$ , mm/s <sup>b</sup>	$\kappa^c$	$\eta^d$	$p^e$
"thick" absorber corrections						
site 1	1.23 (1)	-1746 (5)	0.51 (3)		0.0 (1)	1.0
site 2	1.27 (2)	-1669 (5)	0.97 (2)		0.0 (1)	2.0 (1)
site 3	1.40 (15)	-958 (10)	1.25 (9)	0.08 (3)	0.0 (1)	0.8 (1)
site 4	-0.07 (2)	-550 (10)	0.77 (8)		0.0 (1)	0.7 (1)
site 5	0.76 (5)	-1341 (10)	1.34 (7)	0.05 (2)	0.0 (1)	1.7 (2)
"thin" absorber approximation						
site 1	1.23 (1)	-1746 (5)	0.97 (3)		0.0 (1)	1.0
site 2	1.18 (2)	-1678 (5)	1.8 (1)		0.0 (1)	2.0 (1)
site 3	1.14 (3)	-1059 (8)	1.6 (5)	0.2 (1)	0.2 (1)	0.8 (1)
site 4	-0.03 (4)	-604 (7)	1.1 (1)		0.0 (1)	0.9 (1)
site 5	0.76 (4)	-1341 (10)	3.5 (3)	0.0 (1)	0.0 (1)	2.2 (2)
Misfit (%)						
"thick" absorber	1.03 (2)					
"thin" absorber	0.87 (2)					
ratio of average population of "I <sub>2":I<sub>3</sub><sup>-</sup></sub>						
"thick" absorber	2.2 (3):1.0					
"thin" absorber	2.1 (3):1.0					

<sup>a</sup> Vs. ZnTe. <sup>b</sup> Line width. <sup>c</sup> Broadening parameter (see text). <sup>d</sup> Asymmetry parameter. <sup>e</sup> Relative population. Numbers in parentheses are estimated standard deviations resulting from the fitting procedure.

eight-line spectra of each of the individual sites. If there is any deviation from axial symmetry at a particular site, then  $\eta$ , the asymmetry parameter, will have a nonzero value. The term  $\epsilon_i$  includes the effects due to  $\eta$ . The rate equation can be rearranged in a more tractable form (eq 7<sup>15</sup>)

$$\text{rate}(v) = R_0 \left[ 1 - f_s \left( \frac{S}{S+B} \right) (1 - TI(v)) \right] \quad (7)$$

where  $TI(v)$  is the transmission integral (eq 8<sup>15</sup>) and  $F(E, v)$  is a function of energy and velocity (eq 9)

$$TI(v) = \int F(E, v) * \text{TRANS}(E) dE \quad (8)$$

$$F(E, v) = \frac{2}{\pi \Gamma_s} \left[ 1 + \left( \frac{E - E_0 - E(v/c)}{\Gamma_s/2} \right)^2 \right]^{-1} \quad (9)$$

The parameter FSB (eq 10<sup>15</sup>) embodies the properties of the source and detector.

$$\text{FSB} = f_s \left( \frac{S}{S+B} \right) \quad (10)$$

Our aim is to find the relative population ( $p_i$ ) of the various iodine sites. We are not concerned whether the total amount of iodine is large or small. To determine the total amount of iodine present (alternately, to measure FSB) would require auxiliary measurements. But, we need merely choose a plausible value for FSB to obtain the proper  $p_i$ . The fitting routine is employed to minimize the difference between the experimental and calculated spectra by using the parameters of isomer shift ( $\delta$ ), quadrupole coupling constant ( $e^2qQ$ ), line width ( $\Gamma$ ), asymmetry parameter ( $\eta$ ), and relative population ( $p_i$ ).

The result of fitting the data using the thickness correction is shown in Figure 3B and the final Mössbauer parameters are set out in Table II, where they can be compared with those obtained from the "thin" absorber data refinement. The fit using the thickness correction did not improve Misfit, but resulted in a significant visual improvement. Also, the values for the line width parameters are now more reasonable; in the "thin" absorber fit, they were found to be several times the natural line width ( $\Gamma_0 = 0.59 \text{ mm/s}^{24a}$ ) a rather unrealistic result. However, only minor changes in isomer shifts, quadrupole coupling constants, and relative populations are observed. Thus, although the final Mössbauer parameters which

will be considered in the discussion of polyiodide structure are those which include the precautionary thickness correction, they differ only slightly from the "thin" absorber parameters.

The isomer shift and quadrupole splitting parameters obtained for the five site polyiodide model (F) compare favorably with values reported for the structurally similar I<sub>5</sub><sup>-</sup> ion ((trimeric acid-H<sub>2</sub>O)<sub>10</sub>H<sup>+</sup>I<sub>5</sub><sup>-</sup>, G) and the distorted I<sub>3</sub><sup>-</sup> ion (Cs<sup>+</sup>I<sub>3</sub><sup>-</sup>, H) as can be seen below.

	site	5	2	4	1	3
$\delta$ (mm/s)		0.76	1.27	-0.07	1.23	1.40
		(1-----)I <sub>2</sub>	.....I	-----I	-----I	-----I
$e^2q^{129}Q$ (MHz)		-1341	-1669	-550	-1746	-958
		F				
		0.53	1.15	0.13	1.15	0.53
		-----I	-----I	-----I	-----I	-----I
		-1404	-1777	-965	-1777	-1404
		G <sup>6b</sup>			H <sup>25</sup>	
					-0.24	1.14
					-----I	-----I
					-616	-1787
						-1036

The parameters obtained for chemically similar sites in the three polyiodides are rather close. For example, the three iodine sites in the distorted triiodide unit of the perylene complex have isomer shift and quadrupole coupling constant values generally similar to those of the distorted triiodide in CsI<sub>3</sub>, and evidencing greater distortion of the I<sub>3</sub><sup>-</sup> than in I<sub>5</sub><sup>-</sup> (G). The "I<sub>2</sub>" site (site 2) closest to the distorted I<sub>3</sub><sup>-</sup> has isomer shift and quadrupole coupling constant values intermediate between those of the "I<sub>2</sub>" unit in CsI<sub>3</sub> and those of free I<sub>2</sub>. They are nearly indistinguishable from those of the "I<sub>2</sub>" unit in I<sub>5</sub><sup>-</sup>. The small but nonzero asymmetry parameter found for site 2 in the "thin" analysis of the perylene complex appears to reflect some deviation from axial symmetry of that particular iodine environment. In summary, the structural model of I<sub>3</sub><sup>-</sup> (very likely distorted) and I<sub>2</sub> deduced from the iodine Mössbauer data is in good accord with the resonance Raman results.

## Conclusions

The results of this resonance Raman/iodine Mössbauer spectral study indicate that "2perylene·3I<sub>2</sub>" (more correctly formulated as perylene·I<sub>2.92</sub>) contains iodine as both I<sub>3</sub><sup>-</sup> and I<sub>2</sub>. On the basis of results for model compounds, these polyiodide units appear to be weakly interacting. Thus, "2perylene·3I<sub>2</sub>" is actually a partially oxidized material with an ap-

proximate charge distribution (perylene)<sup>+0.4</sup>(I<sub>3</sub><sup>-</sup>·2I<sub>2</sub>)<sub>0.4</sub>. Thus, this conductive material is not an exception to the general observations about the importance of mixed valence vis-à-vis charge transport. In this connection, it is interesting to note that the first ionization potential of tetrathiafulvalene,<sup>26</sup> which forms an extensive series of conductive, mixed valence compounds with iodine,<sup>7c,27</sup> is comparable to that of perylene,<sup>28</sup> i.e., 6.83 eV<sup>26</sup> vs. 6.97 eV,<sup>28</sup> respectively. By implication, the present results indicate that other conductive hydrocarbon-iodine complexes are also mixed valent. This question is presently under further investigation.

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