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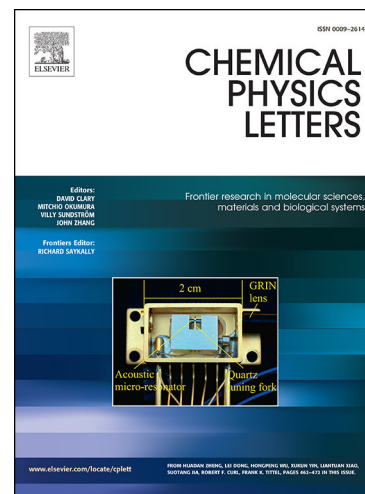
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Ionic reaction products of iodine with pyridine, 4-methylpyridine, and 4-*tert*-butylpyridine in a polyethylene matrix. A FTIR polarization spectroscopic investigation.

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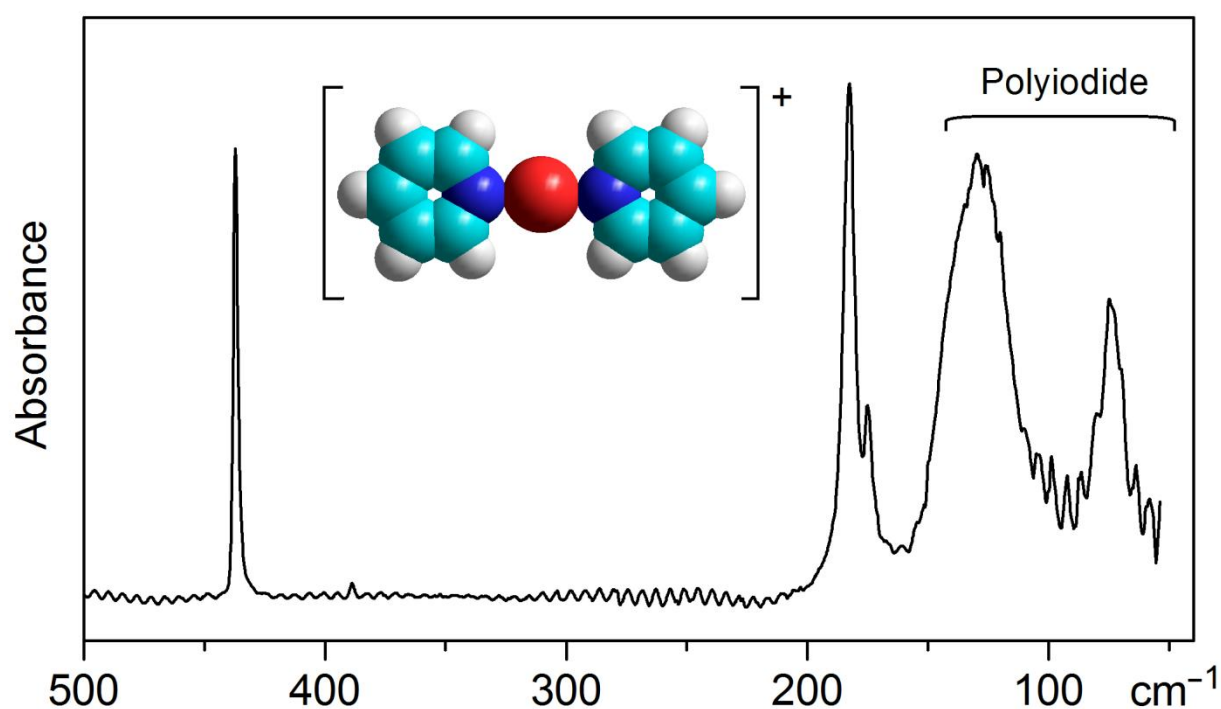
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KEYWORDS

bis(pyridine)iodine(I) cation; bis(4-methylpyridine)iodine(I) cation; bis(*t*-butylpyridine)iodine(I) cation; 4-methylpyridinium cation; polyiodide; IR polarization spectroscopy; stretched low-density polyethylene; micro-crystalline aggregates.

ABSTRACT

The ionic reaction products of the title pyridines with iodine in low-density polyethylene are identified by comparison of their IR spectra with literature data. The bis(pyridine)iodine(I), bis(4-methylpyridine)iodine(I), and bis(*tert*-butylpyridine)iodine(I) cations are spontaneously formed in the polymer medium. At elevated temperature, the 4-methylpyridinium cation is identified as a product of the reaction between 4-methylpyridine and iodine. In spite of their elongated molecular shape, the bis(pyridine)iodine(I) and bis(4-methylpyridine)iodine(I) cations are randomly aligned in stretched polyethylene; they probably form micro-crystalline polyiodide aggregates in the amorphous regions of the polymer. In contrast, the bis(*tert*-butylpyridine)iodine(I) cation is efficiently aligned in stretched polyethylene.



(Graphical abstract)

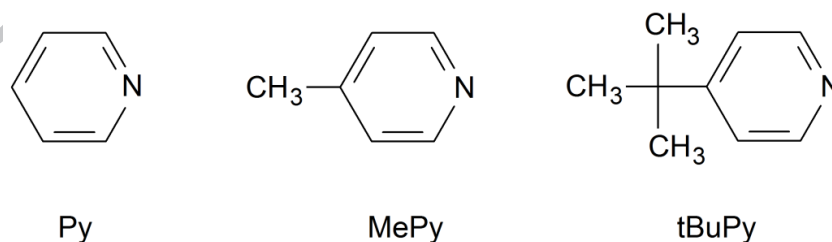
Highlights:

- Spontaneous formation of polyiodide salts in low-density polyethylene
- Vibrational fundamentals of the bis(pyridine)iodine(I) cation
- Bis(4-methylpyridine)iodine(I) and bis(*t*-butylpyridine)iodine(I) cations
- Formation of the 4-methylpyridinium cation at elevated temperature
- Possible formation of micro-crystalline polyiodide aggregates in polyethylene

1. Introduction

It is well known that pyridine and other aza-aromatics may react with diiodine to form so-called charge transfer (CT) complexes [1]. This is a classic example of the non-covalent interaction designated as halogen bonding [2,3]. In general, the 1:1 pyridine-diiodine CT complex is stable in ‘inert’ media, while ionic compounds are formed in ionizing media [4,5]. But some years ago it was discovered that the reaction between pyridine and diiodine dissolved in low-density polyethylene (PE) leads to ionic species as the main products, corresponding to a polyiodide salt [6]. The spontaneous and efficient formation of charged solute species in an alkane medium like PE was surprising. Ionic reaction products of pyridine with diiodine had not previously been observed in an alkane environment [4]. Evidently, the conditions prevailing in the reaction cavities of a PE host somehow catalyze the formation of ionic products.

The ionic product of the reaction between pyridine and diiodine in PE was first assigned to *N*-iodopyridinium polyiodide [6]. In the present communication we reconsider the reaction, arriving at a different assignment of the ionic product. We furthermore extend the investigation to the corresponding systems involving 4-methylpyridine (γ -picoline) and 4-*tert*-butylpyridine (Scheme 1). The 4-*tert*-butylpyridine/iodine system is of particular interest because of its possible importance in dye-sensitized solar cells [7-11]. The reaction between the pyridines and diiodine, confined to the cavities of a stretched PE host, is investigated by Fourier Transform Infrared (FTIR) Linear Dichroism (LD) spectroscopy [12-16]. The observed LD contains information on the vibrational transition moment directions [12-16] of the product species, thereby providing a clue to their structural assignment. The study is supported by the results of quantum chemical calculations. Additional information is provided as supplementary data, referred to as S1–S10 in the ensuing text.



Scheme 1. Pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy).

2. Calculations

Quantum chemical calculations on the parent bis(pyridine)iodine(I) cation, Py_2I^+ , were performed with the GAUSSIAN09 software package [17] by using B3LYP [18,19] density functional

theory (DFT) and the LanL2DZ [20,21] basis set. Vibrational transitions were computed within the harmonic approximation and by using the anharmonic second order perturbation (VPT2) procedure by Barone and coworkers (freq=anharm) [22-24]. The predicted nuclear equilibrium coordinates and fundamental vibrational transitions are provided as S1. The computed anharmonic wavenumbers are essentially proportional to the harmonic values ($\nu_{\text{anharm}} = 0.96629 \times \nu_{\text{harm}}$; $R = 0.9999$, $SD = 17.9 \text{ cm}^{-1}$). The suggested assignment of the observed transitions to the calculated ones is given in Table 1.

3. Experimental

Pyridine (Py), 4-methylpyridine (MePy), and diiodine (I_2) were purchased from Aldrich (+99%), 4-*tert*-butylpyridine (tBuPy) from Fluka (98%), solvents CCl_4 , CS_2 , and methanol from Merck (Uvasol). Polyethylene (PE) material was obtained from laboratory bottles of low-density PE (Kartell Art. 1616).

Ca. $2.5 \times 5 \text{ cm}$ PE pieces cut from the bottles were heated between aluminum plates at 140°C for 30 minutes, quenched in cold water, and uniaxially stretched by approximately 500%. Before stretching, the thickness of the PE was 1.2 mm, after stretching 0.45 mm. According to Differential Scanning Calorimetry (DSC) analyses, the stretching increased the crystallinity of the polymer from ca. 23% to ca. 37% (S2).

Stretched PE samples saturated with Py, MePy, or tBuPy were obtained by submersion in the liquid substance in a sealed container at 50°C for 24 hours. The surfaces of the doped samples were washed with methanol to remove residual pyridine. No noticeable relaxation of the samples as a result of the doping process was observed. The mass increase of a saturated, dried sample was in the range 2.0 – 2.5% (S3). Each sample was then placed in a sealed reaction container with iodine crystals, allowing iodine to enter the polymer by sublimation; the additional mass-increase due to accumulation of iodine was 8 – 9% (S4). The samples were prepared in air. No effects due to reaction with oxygen were observed. The final samples were “black” and opaque in the UV-vis region (S4). For the use as references, stretched samples without solutes were produced in the same manner.

The reaction experiments were conducted at different temperatures: 0, 22, 30, 40, and 50°C . The progression of the reactions was followed by measuring the IR spectra of the samples at different reaction times, ranging from hours to days. Before each measurement, the surface of the samples was washed with methanol to remove deposits. However, experiments conducted at elevated temperatures for several days frequently affected the properties of the PE polymer, thereby complicating analysis of the recorded spectra. Finally, volatile solutes were allowed to evaporate

from the sample and their IR spectra were recorded. The evaporation rates of Py, MePy, or tBuPy solutes from the stretched PE material at room temperature were determined in an independent series of experiments, see S3.

IR spectra were measured on a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer equipped with a rotatable KRS5 aluminum grid polarizer in the sample beam as previously described [6]. The spectra were recorded with a spectral resolution of 1 cm^{-1} and 10 scans. Because of strong baseline absorption, the region $3000\text{--}2700\text{ cm}^{-1}$ and three narrow regions around 1460 , 1365 , and 720 cm^{-1} could not be measured. Two linearly independent absorbance curves were recorded on the stretched PE samples, one with the polarization of the beam parallel to the stretching direction (U), and another with the polarization perpendicular to it (V). The resulting baseline corrected LD absorbance curves are denoted $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$. The corresponding isotropic absorbance curve for an uniaxial sample is given by $E_{\text{ISO}}(\tilde{\nu}) = (E_U(\tilde{\nu}) + 2 E_V(\tilde{\nu}))/3$ [12-16].

4. Orientation factors.

The directional information that can be extracted from the LD curves is represented by the orientation factors K_i for the observed peaks [13,14]:

$$K_i = \langle \cos^2(\mathbf{M}_i, U) \rangle$$

Here (\mathbf{M}_i, U) is the angle between the moment vector \mathbf{M}_i of the i 'th transition and the stretching direction U of the polymer; the pointed brackets indicate averaging over all molecules in the light path. Large K values correspond to transition moments well aligned with the stretching direction, and vice versa. For an isotropic sample all K values will be equal to $1/3$. The K s may be determined by the graphical TEM stepwise reduction procedure [13,14] which involves the formation of linear combinations of $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$, such as the family of reduced absorbance curves $r_K(\tilde{\nu})$ [25]:

$$r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$$

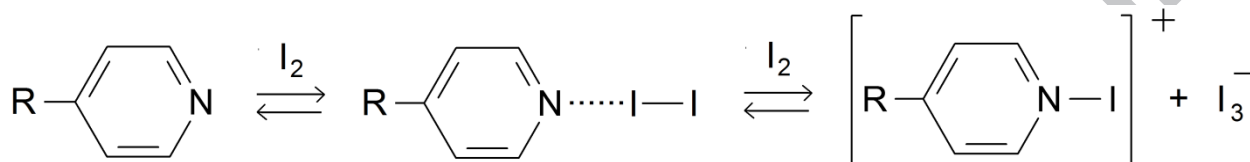
A peak or a shoulder due to transition i will vanish from the linear combination $r_K(\tilde{\nu})$ for $K = K_i$. The orientation factors K_i can thus be determined by visual inspection [25], see f. ex. Fig. 1.

5. Results and discussion

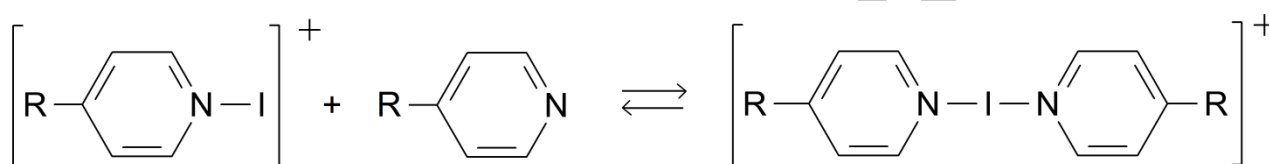
5.1 Pyridine/iodine system

In the previous investigation [6] of the reaction between Py and I_2 in a polyethylene host, stretched as well as unstretched, the observed ionic product was assigned to *N*-iodopyridinium

polyiodide, $\text{PyI}^+, \text{I}_x^-$, assuming the reaction mechanism outlined in Scheme 2 ($\text{R} = \text{H}$). The assignment was based on a comparison of the observed spectrum with a previously published spectrum assigned to the PyI^+ cation [27]. However, we have come to the conclusion that the observed cation product is the bis(pyridine)iodine(I) cation Py_2I^+ , see Scheme 3 ($\text{R} = \text{H}$). As indicated in Table 1, the IR spectrum of the observed ionic product is in excellent agreement with the IR spectrum of the Py_2I^+ cation published by Haque and Wood [26].



Scheme 2



Scheme 3.

The bis(pyridine)iodine(I) cation is an interesting species. The tetrafluoroborate, $\text{Py}_2\text{I}^+, \text{BF}_4^-$, is an iodinating reagent known as Barluenga's reagent [28,29]. Haque and Wood [26] deduced from studies of the IR and Raman spectra of $\text{Py}_2\text{I}^+, \text{BF}_4^-$ and $\text{Py}_2\text{I}^+, \text{PF}_6^-$ in nujol mull and in liquid solutions that the pyridine rings in Py_2I^+ are nearly co-planar, a result which is consistent with those of crystal analyses [30-32]. One of the first theoretical studies of the Py_2I^+ cation was published by Sabin [33], using semiempirical procedures. More recently, the electronic structures of Py_2I^+ and related species were investigated by Georgiou et al. [34], concluding that Py_2I^+ can be considered as a coordination complex of I^+ . The molecular equilibrium structure of Py_2I^+ in the gas phase was found to have D_{2d} symmetry, with mutually perpendicular pyridine rings, but the barrier to rotation around the $\text{N}-\text{I}-\text{N}$ axis was predicted to be small [34]. With B3LYP/LanL2DZ we compute a difference in electronic energy of $0.3 \text{ kcal mol}^{-1}$ between the D_{2d} and the planar D_{2h} conformation in the gas phase.

In Table 1 we list the transitions predicted for Py_2I^+ under the assumption of co-planar rings in the condensed phase (D_{2h} symmetry). It is apparent that the agreement with the observed spectrum is satisfactory. The transitions observed at 637 and 183 cm^{-1} (Fig. 2) can be assigned to the vibrational modes $\nu_{44}(b_{1u})$ and $\nu_{45}(b_{1u})$ which both involve asymmetric stretching motions of the unique $\text{N}-\text{I}-\text{N}$ moiety of Py_2I^+ . The suggested assignments of the main transitions of Py_2I^+ to calculated fundamental transitions are listed in Table 1. The complete spectrum comprising more

than 40 observed peaks is provided as S5, with indication of wavenumbers, absorbances, and integrated intensities.

The identification of the cation product as Py_2I^+ raises a question: Why is this fairly elongated species not efficiently aligned in stretched PE? The observed orientation factors K_i for 30 vibrational transitions of Py_2I^+ all fall in the range 0.3 – 0.4 [6], corresponding to nearly random alignment. We suggest that the lack of alignment can be explained by the formation of micro-crystalline polyiodide aggregates, probably imbedded in the amorphous regions in the polymer. The suggestion is supported by the following observations:

(1) The results of detailed experimental investigations [36-40] show that solutes in PE are either located in the amorphous regions of the polymer or residing on the surfaces of the PE crystallites; only the latter fraction becomes oriented by stretching of the polymer. The formation of crystalline aggregates in the amorphous regions thus explains why no alignment is observed on stretching. Even interaction of the aggregates with the crystallite surfaces would not necessarily lead to appreciable alignment of the individual Py_2I^+ cations. As discussed in the following Section 5.2, similar lack of alignment is observed for $(\text{MePy})_2\text{I}^+$, most likely for a similar reason.

(2) As shown in S5, all the observed IR peaks for Py_2I^+ in PE are very sharp, much sharper than typical peaks due to Py and $\text{Py} \cdot \text{I}_2$ (e.g., Fig. 1), indicating minimal inhomogeneous line broadening. Hence, all Py_2I^+ species in the PE sample must have very similar environments. Crystalline aggregates provide a well-defined homogenous micro-environment for the Py_2I^+ cations, thereby explaining the remarkable sharpness of the bands.

(3) Finally: Analyses of crystalline bis(pyridine)iodine(I) polyiodide characterize the salt as a hepta-iodide, involving the anion I_7^- (or $2\text{I}_2 \cdot \text{I}_3^-$) [30,32]. This is consistent with the result of an approximate stoichiometric analysis of the product formed in PE, see S4 for details.

The assumption that pyridine and iodine in PE react to form micro-crystalline $\text{PyI}^+, \text{I}_x^-$ aggregates is thus supported by a number of observations. But the present spectroscopic evidence does not provide an indication of the size and detailed nature of the possible aggregates. The subject requires further and more advanced investigations, for example like the one published by Wirtz et al. [40].

5.2. 4-Methylpyridine/iodine system

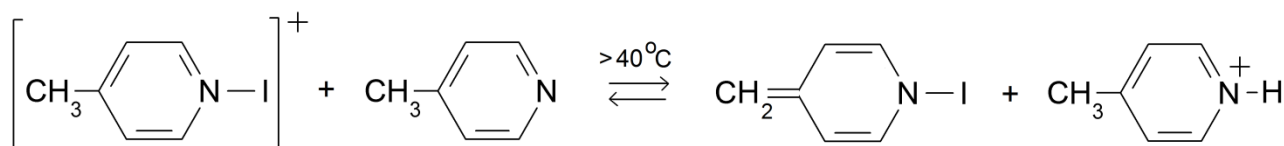
The reaction between MePy and I_2 has been investigated by several workers [26,41-45]. The charge transfer complex $\text{MePy} \cdot \text{I}_2$ is readily observed in solvents like CCl_4 and CS_2 . The IR bands of MePy and $\text{MePy} \cdot \text{I}_2$ tend to overlap, but transitions observed close to 1212, 1067, 1009, and 530 cm^{-1} in CCl_4 and CS_2 solutions can be assigned to $\text{MePy} \cdot \text{I}_2$ (S6). In ionizing solvents the situation is

more complicated, leading to a variety of products, particularly at elevated temperature (see below) [44,45].

The spectral development of the MePy/iodine system in stretched PE at 22 °C is provided as S7, comprising a series of spectra recorded at different intervals of time. Bands due to MePy·I₂ are not easily observed in these spectra, indicating fast further reactions. After one day, the spectrum indicates a mixture of primarily MePy and the bis(4-methylpyridine)iodine(I) cation, (MePy)₂I⁺ (S7, S8). The reaction may proceed according to Schemes 2 and 3 (R = CH₃), but also other reaction mechanisms have been suggested [44,45]. In Fig. 3, the contributions due to MePy have been subtracted from the spectrum. The prominent peaks in the resulting curve are consistent with the spectrum of the (MePy)₂I⁺ cation derived by Haque and Wood [44] from the spectra of the BF₄⁻ and PF₆⁻ salts. After prolonged reaction time the spectrum is changed (S7), indicating the possible formation of additional reaction products.

The LD absorption curves corresponding to the isotropic spectrum in Fig. 3 are shown in S8 (without subtraction of contributions from MePy). The peaks assigned to (MePy)₂I⁺ have orientation factors *K* between 0.3 and 0.4, corresponding to essentially random orientation. This is not what one would normally expect for an elongated species like (MePy)₂I⁺ in stretched PE. A possible explanation would be the formation of polyiodide aggregates, similar to the situation discussed for Py₂I⁺ (Section 5.1).

According to Bora, Hass and Haque [45] the kinetics of the reaction between MePy and I₂ in a polar solvent changes at elevated temperatures. Above 38 °C and with excess MePy, the reaction proceeds to a variety of products, including the methylpyridinium cation (MePyH⁺) and cations like MePy-CH₂-Py⁺, MePy-CH₂-Py-CH₂-Py²⁺, etc. [44,45]. Fig. 4 shows the spectrum observed after one day in stretched PE at 50 °C. The strong, broad band system with maxima at 3250, 3167, and 3083 cm⁻¹ (and Evans windows at 3195 and 3123 cm⁻¹) may be due to the N-H stretching vibration of MePyH⁺. In fact, the spectrum in Fig. 4 is consistent with the spectrum of 4-methylpyridinium perchlorate (MePyH⁺, ClO₄⁻) in acetonitrile solution published by Brzezinski and Zundel [46]. The peaks close to 3250, 3167, 3083, 1637, 1599, 1505, 1311, and 1244 cm⁻¹ are thus found in both spectra. At lower wavenumbers, the spectrum published by Brzezinski and Zundel [46] shows strong bands due to the perchlorate ion. The proton in MePyH⁺ may be donated from the methyl group in MePyI⁺, as indicated in Scheme 4, or perhaps more likely from (MePy)₂I⁺ as suggested by Haque and coworkers [44,45].



Scheme 4. Possible proton transfer from 4-methyl-*N*-iodopyridinium (MePyI⁺) to 4-methylpyridine (MePy) to yield 4-methylidene-*N*-iodopyridine and 4-methylpyridinium (MePyH⁺).

5.3. 4-*tert*-Butylpyridine/iodine system

The spectroscopic properties of this system were recently investigated in some detail by Hansen et al. [11]. The IR spectrum of the solid, red substance isolated from a solution of tBuPy and I₂ in methanol showed that the product was a mixture of the CT complex tBuPy·I₂ and bis(4-*tert*-butylpyridine)iodine(I) triiodide, (tBuPy)₂I⁺,I₃⁻. Analysis of the observed spectrum in terms of contributions from the two components was complicated by near-coincidence of bands, but the results of quantum chemical calculations enabled assignment of all significant transitions in the 1600 – 400 cm⁻¹ region [11].

The formation of tBuPy·I₂ is observed in CCl₄ and CS₂ solutions, but the IR bands of tBuPy and tBuPy·I₂ overlap strongly, and only a well-resolved peak at 1011 cm⁻¹ is easily assigned to tBuPy·I₂ (S9). In the solid state this transition is observed at 1013 cm⁻¹ and additional peaks at 1548, 1415, 1216, 1069, 828, and 723 cm⁻¹ were assigned to tBuPy·I₂ [11]. The transition at 1011 cm⁻¹ is observed after a few minutes in stretched PE at 22 °C (S8), and it remains as a weak feature in the spectra recorded after longer reaction times.

After one day (S10), the observed spectrum indicate a mixture of tBuPy, tBuPy·I₂, and the (tBuPy)₂I⁺ cation. Fig. 5 shows a portion of the corresponding LD absorption curves. The (tBuPy)₂I⁺ cation appears to be well-aligned in stretched PE. Very large orientation factors are determined for the peaks at 1217, 1061, 1021, and 543 cm⁻¹, amounting to *K* = 0.9. These transitions must be assigned to long-axis polarized transitions in the (tBuPy)₂I⁺ cation. The corresponding peaks in the solid state spectrum of (tBuPy)₂I⁺,I₃⁻ are observed at 1216, 1061, 1021, and 543 cm⁻¹ [11]. A small *K* value around 0.1 is observed for the peak at 843 cm⁻¹, indicating a short-axis polarized transition in (tBuPy)₂I⁺; this peak is observed at 833 cm⁻¹ in the solid state [11]. The orientation factors for the transitions assigned to unreacted tBuPy all fall in the approximate range *K* = 0.3 – 0.4, corresponding to nearly random orientation in stretched PE. The peak at 1011 cm⁻¹ has *K* between 0.6 and 0.7, consistent with assignment to a long-axis polarized transition in the complex tBuPy·I₂.

The orientation factors observed for the (tBuPy)₂I⁺ cation shows that it is aligned like a “normal” elongated, rod-like molecule in stretched PE. This is in marked contrast to the lack of

alignment observed for the Py_2I^+ and $(\text{MePy})_2\text{I}^+$ cations, an observation which can possibly be explained by aggregation as discussed above (Sections 5.1 and 5.2).

6. Conclusions

The reaction of pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy) with iodine in a low-density polyethylene (PE) matrix at room temperature leads to the formation of Py_2I^+ , $(\text{MePy})_2\text{I}^+$, $(\text{tBuPy})_2\text{I}^+$ cations, respectively. At elevated temperature, the 4-methylpyridinium cation (MePyH^+) was observed in the case of MePy. The identification of the observed cations was based on comparison of their IR spectra with spectra from the literature. In addition, the vibrational transitions observed for Py_2I^+ were consistent with theoretically predicted transitions. In spite of their elongated molecular shape, the Py_2I^+ and $(\text{MePy})_2\text{I}^+$ cations are almost randomly aligned in stretched PE. This is most likely due to formation of micro-crystalline polyiodide aggregates in the amorphous regions of the polymer. In contrast, $(\text{tBuPy})_2\text{I}^+$ is very efficiently aligned, with an orientation factor for the long molecular axis equal to $K = 0.9$; this may indicate that no significant aggregation occurs in this case. The present spectroscopic evidence does not explain the origin of the different behavior of Py_2I^+ and $(\text{MePy})_2\text{I}^+$ relative to that of $(\text{tBuPy})_2\text{I}^+$. Full elucidation of these phenomena requires further investigations.

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Table 1IR transitions for the bis(pyridine)iodine(I) cation, Py_2I^+ .

| $\text{Py}_2\text{I}^{+ a}$ | $\text{Py}_2\text{I}^+, \text{I}_x^{- b}$ | | B3LYP/LanL2DZ (D _{2h} symmetry) ^c | | | | |
|-----------------------------|---|--------------------|---|-----------------|------|-------|-------------------------------|
| $\tilde{\nu}^{d,e}$ | $\tilde{\nu}^d$ | E_{ISO}^f | $\tilde{\nu}^{d,g}$ | | | I^h | App. description ⁱ |
| 1602 s | 1599.0 | 98 | v ₃₈ | b _{1u} | 1586 | 66 | Py skel def + CH b |
| | 1588.2 | 4 | | | | | |
| 1576 w | 1570.4 | 12 | v ₄₈ | b _{2u} | 1560 | 3 | Py skel def |
| 1481 w | | | v ₃₉ | b _{1u} | 1458 | 6 | Py skel def + CH b |
| 1452 s | | | v ₄₉ | b _{2u} | 1437 | 141 | Py skel def + CH b |
| ~1400 w | 1394.0 | 16 | | | | | |
| 1355 m | 1348.0 | 33 | v ₅₀ | b _{2u} | 1350 | 5 | CH b |
| | (1331) | | | | | | |
| 1246 m | 1251.4 | 54 | v ₅₁ | b _{2u} | 1285 | 4 | Py skel def |
| 1210 s | 1202.8 | 47 | v ₄₀ | b _{1u} | 1208 | 56 | CH b |
| | (1190) | | | | | | |
| 1158 s | 1155.2 | 12 | v ₅₂ | b _{2u} | 1171 | 5 | CH b |
| 1090 w | 1089.6 | 8 | | | | | |
| 1062 s | 1058.6 | 100 | v ₄₁ | b _{1u} | 1048 | 100 | Py skel def + CH b |
| 1040 m | 1038.0 | 37 | v ₄₂ | b _{1u} | 1020 | 17 | Py skel def |
| 1009 s | 1008.6 | 102 | v ₄₃ | b _{1u} | 982 | 141 | Py ring breath |
| 1005 w | (1004) | | | | | | |
| | 976.0 | 7 | | | | | |
| 945 w | 944.0 | 8 | v ₅₈ | b _{3u} | 957 | 3 | CH oop b |
| | 871.2 | 4 | | | | | |
| | (777) | | | | | | |
| 760 s | 754.8 | 201 | v ₅₉ | b _{3u} | 771 | 142 | CH oop b |
| 707 m | 699.4 | 25 | | | | | |
| 692 s | 688.2 | 261 | v ₆₀ | b _{3u} | 698 | 182 | CH oop b |
| | 676.6 | 48 | | | | | |
| 637 s | 637.2 | 75 | v ₄₄ | b _{1u} | 629 | 57 | Py skel def, N–I–N |
| 438 s | 437.2 | 40 | v ₆₁ | b _{3u} | 453 | 24 | Py skel oop def |
| | 388.8 | 3 | v ₃₃ ? | a _u | 389 | 0 | Py skel oop def |
| 172 s | 182.6 | 109 | v ₄₅ | b _{1u} | 177 | 107 | N–I–N s (asym) |
| | 175.2 | 39 | v ₁₁ ? | a _g | 159 | 0 | N–I–N s (sym) |
| | 130 ^j | 433 | | | | | |
| | 75 ^j | 157 | | | | | |

 a Derived from spectra of $\text{Py}_2\text{I}^+, \text{BF}_4^-$ and $\text{Py}_2\text{I}^+, \text{PF}_6^-$ in CH_2Cl_2 (1650–400 cm^{-1}) and pyridine (400–150 cm^{-1}) [26]. b $\text{Py}_2\text{I}^+, \text{I}_x^-$ in stretched low-density polyethylene (PE) [6]. Further details are given in S5. c Harmonic fundamentals in the gas phase. Full listing provided as S1. d Wavenumbers in cm^{-1} . e s = strong, m = medium, w = weak. f Integrated intensity $E_{\text{ISO}} = E_U + 2E_V$ relative to $E_{\text{ISO}}(1058.6 \text{ cm}^{-1}) = 100$. g Scaling factor $\alpha = 0.9663$. h Calculated IR intensity relative to $I(\nu_{41}) = 100$. i s = stretching, b = bending, oop = out-of-plane, skel = skeleton, def = deformation. j Polyiodide band.

Figures and schemes

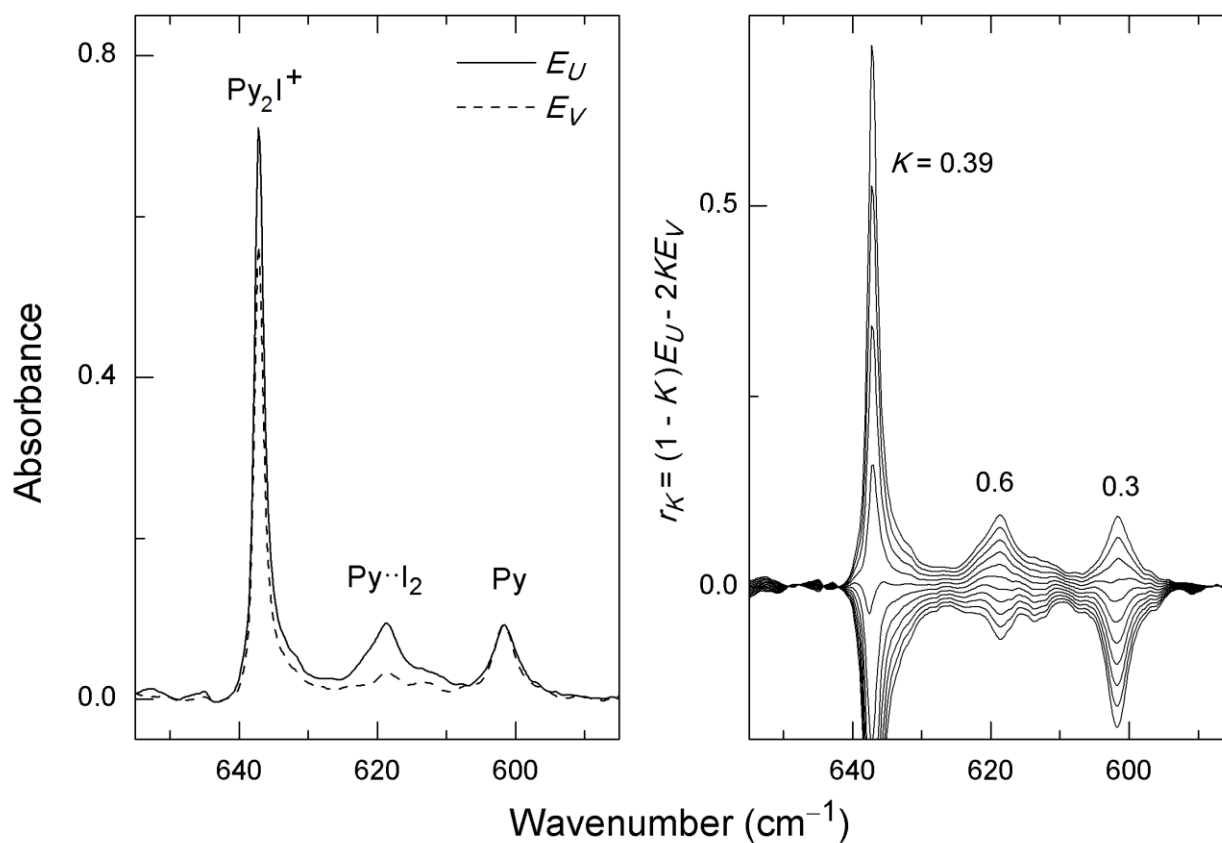


Figure 1. *Left:* Linear dichroic (LD) absorption curves in the 650-590 cm^{-1} region for the pyridine/iodine system in stretched polyethylene at room temperature. $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ designate the absorbance measured with light polarized parallel (U) and perpendicular (V) to the stretching direction. *Right:* Family of reduced absorption curves $r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$ for orientation factors K ranging from 0 to 1. The resulting K values are indicated (see text).

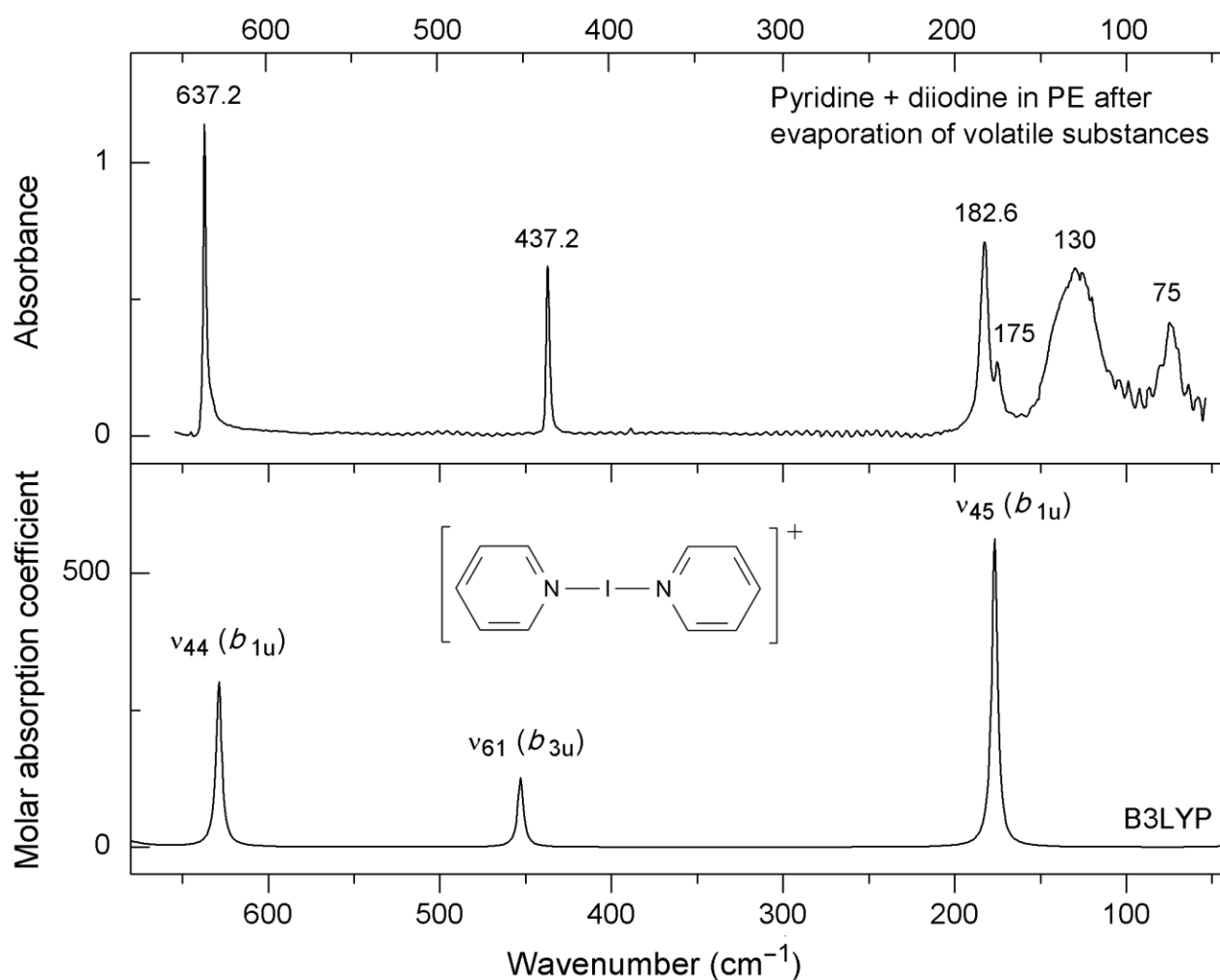


Figure 2. *Top:* Observed isotropic IR spectrum of the pyridine/iodine system in stretched polyethylene after evaporation of volatile substances [6]. *Bottom:* Calculated absorbance spectrum of the bis(pyridine)iodine(I) cation, Py_2I^+ , under the assumption of planar D_{2h} symmetry (Table 1). The molar absorption coefficient was estimated under the assumption of Lorentz band shapes with full width at half maximum (FWHM) equal to 4 cm^{-1} [35].

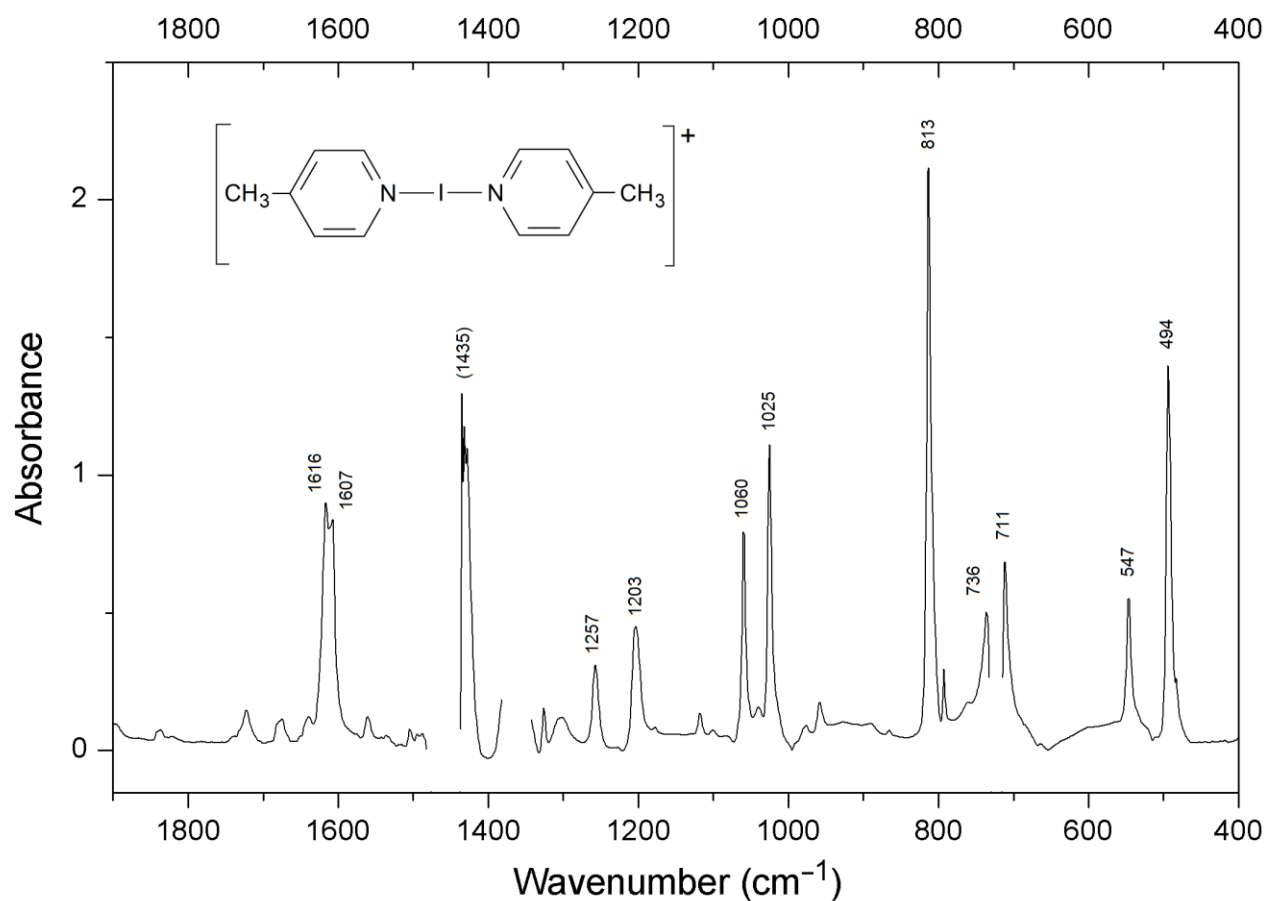


Figure 3. Isotropic absorption spectrum of the reaction products of 4-methylpyridine (MePy) and iodine in stretched polyethylene after one day at 22 °C. The main bands are assigned to the bis(4-methylpyridine)iodine(I) cation, (MePy)₂I⁺. Contributions due to MePy have been removed by subtraction.

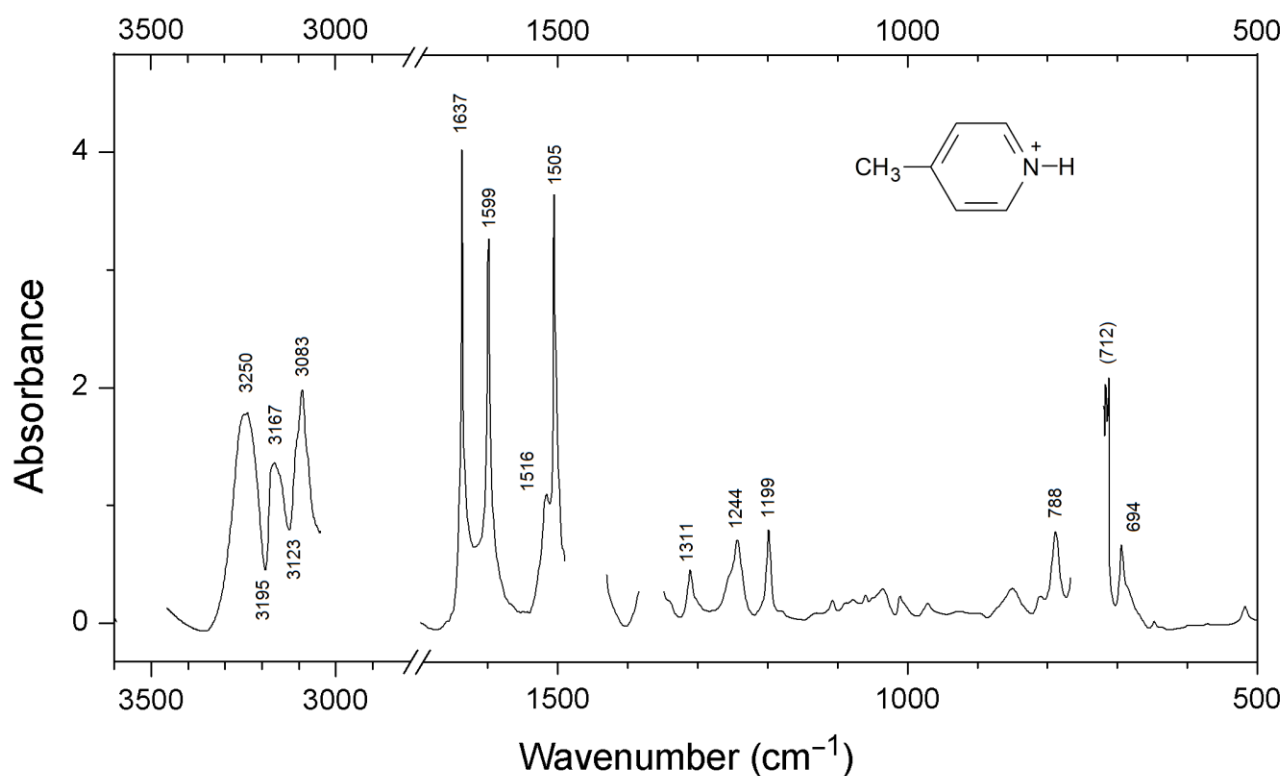


Figure 4. Isotropic absorption spectrum of the reaction products of 4-methylpyridine (MePy) and iodine in stretched polyethylene after one day at 50 °C. The main bands are assigned to the 4-methylpyridinium cation, MePyH⁺.

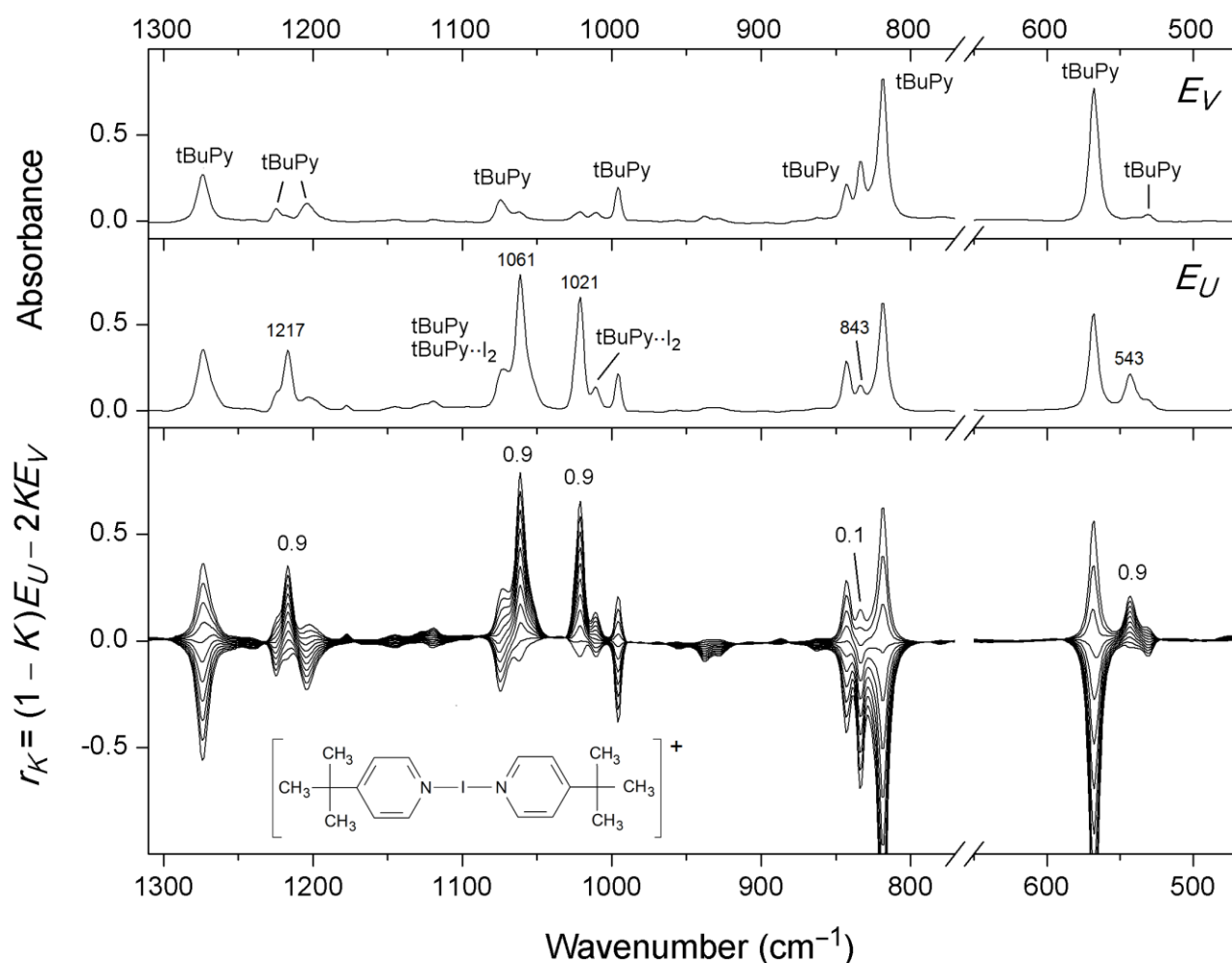
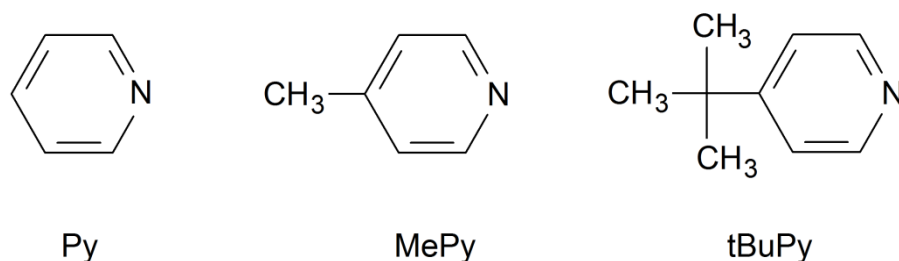
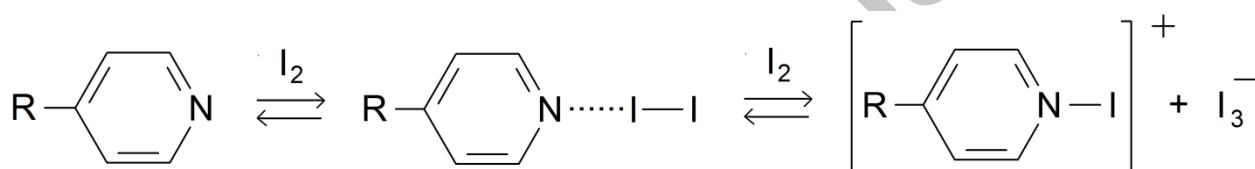


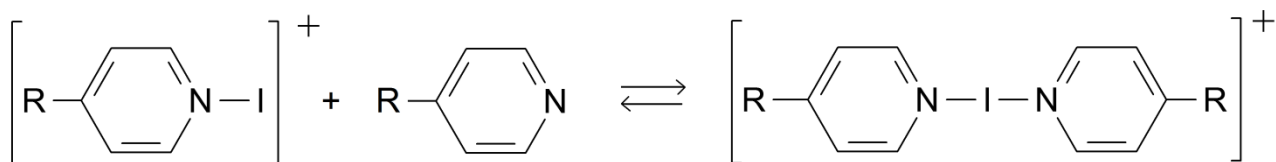
Figure 5. Top: Linear dichroic (LD) absorption curves $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ for the reaction products of 4-*tert*-butylpyridine (tBuPy) and iodine in stretched polyethylene after one day at 22 °C. Wavenumbers indicate prominent peaks assigned to the bis(4-*tert*-butylpyridine)iodine(I) cation, $(\text{tBuPy})_2\text{I}^+$. Bottom: Family of reduced absorption curves $r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$ for K ranging from 0 to 1 (see text). Resulting K values for prominent peaks assigned to $(\text{tBuPy})_2\text{I}^+$ are indicated.



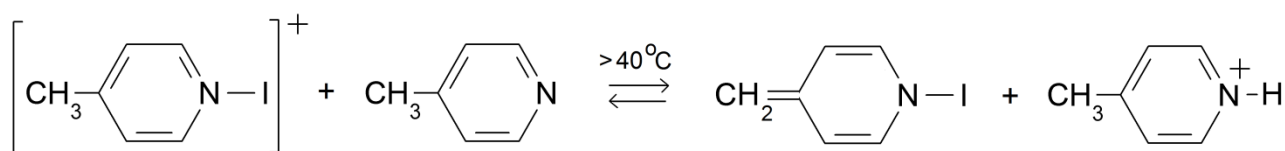
Scheme 1. Pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy).



Scheme 2.



Scheme 3.



Scheme 4. Possible proton transfer from 4-methyl-*N*-iodopyridinium (MePyI⁺) to 4-methylpyridine (MePy) to yield 4-methylidene-*N*-iodopyridine and 4-methylpyridinium (MePyH⁺).

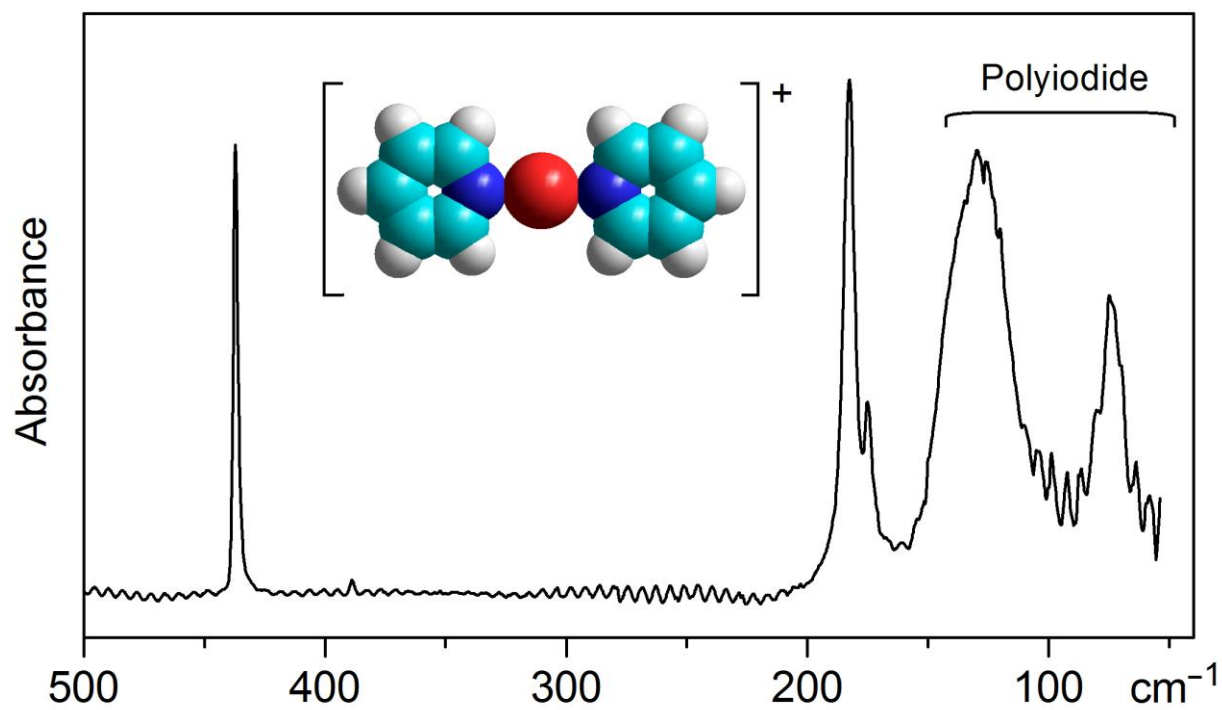
References

- 1 C. Reid, R.S. Mulliken, Molecular Compounds and Their Spectra. IV. The Pyridine-Iodine System. J. Am. Chem. Soc. 15 (1954) 3869-3874.
- 2 P. Metrangolo, G. Resnati (Eds.), Halogen Bonding. Fundamentals and Applications. Series: Structure and Bonding, vol. 126, Springer-Verlag, Berlin, 2008.
- 3 A. Varadwaj, P.R. Varadwaj, H. M. Marques, K. Yamashita, A DFT assessment of some physical properties of iodine-centered halogen bonding and other non-covalent interactions in some experimentally reported crystal geometries. Phys. Chem. Chem. Phys. 20 (2018) 15316-15329.
- 4 T. Tassaing, M. Besnard, J. Yarwood, Far IR vibrational spectroscopic studies of the chemical dynamics of the pyridine/iodine system in solution. Chem. Phys. Letters 267 (1997) 496-500.
- 5 T. Tassaing, M. Besnard, Ionization Reaction in Iodine/Pyridine Solutions: What Can We Learn from Conductivity Measurements, Far-Infrared Spectroscopy, and Raman scattering? J. Phys. Chem. A. 101 (1997) 2803-2808.
- 6 E.M. Karlsen, J. Spanget-Larsen, FTIR investigation of the reaction between pyridine and iodine in a polyethylene host. Formation of *N*-iodopyridinium polyiodide. Chem. Phys. Letters 473 (2009) 227-232.
- 7 B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. Nature 353 (1991) 737-740.
- 8 Z. Kebede, S.E. Lindquist, Donor-acceptor interaction between non-aqueous solvents and I₂ to generate I₃⁻, and its implication in dye sensitized solar cells. Sol. Energy Mater. Sol. Cells 57 (1999) 259-275.
- 9 P.T. Nguyen, A.R. Andersen, E.M. Skou, T. Lund, Dye stability and performances of dye-sensitized solar cells with different nitrogen additives at elevated temperatures - Can sterically hindered pyridines prevent dye degradation? Sol. Energy Mater. Sol. Cells 94 (2010) 1582-1590.
- 10 P.T. Nguyen, B.X.T. Lam, A.R. Andersen, P.E. Hansen, T. Lund, Photovoltaic Performance and Characteristics of Dye-Sensitized Solar Cells Prepared with the N719 Thermal Degradation Products [Ru(LH)₂(NCS)(4-*tert*-butylpyridine)][N(Bu)₄] and [Ru(LH)₂(NCS)(1-methylbenzimidazole)][N(Bu)₄]. Eur. J. Inorg. Chem. (2011) 2533-2539.
- 11 P.E. Hansen, P.T. Nguyen, J. Krake, J. Spanget-Larsen, T. Lund, Dye-sensitized solar cells and complexes between pyridines and iodines. A NMR, IR and DFT study. Spectrochim. Acta A 98 (2012) 247-251.
- 12 J.G. Radziszewski, J. Michl, Fourier Transform Infrared Linear Dichroism. Stretched Polyethylene as a Solvent in IR Spectroscopy, J. Am. Chem. Soc. 108 (1986) 3289-3297.
- 13 J. Michl, E.W. Thulstrup, Spectroscopy with Polarized Light. Solute Alignment by Photoselection, in Liquid Crystals, Polymers and Membranes. VCH-Wiley, Deerfield Beach, FL., 1986/1995.
- 14 E.W. Thulstrup, J. Michl, Elementary Polarization Spectroscopy. Wiley-VCH, New York, Weinheim, 1989.
- 15 A. Rodger, B. Nordén, Circular Dichroism and Linear Dichroism. Oxford University Press, UK, 1997.

- 16 B. Nórdén, A. Rodger, T. Dafforn, Linear Dichroism and Circular Dichroism. A Textbook on Polarized-Light Spectroscopy, RCS Publishing, Cambridge, UK, 2010.
- 17 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, GAUSSIAN 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.
- 18 A.D. Becke, Density functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648-5652.
- 19 C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B. 37 (1988) 785-789.
- 20 W.R. Wadt, P.J. Hay, Ab initio effective core potentials for molecular calculations - potentials for main group elements Na to Bi, J. Chem. Phys., 82 (1985) 284-298.
- 21 P.J. Hay, W.R. Wadt, Ab initio effective core potentials for molecular calculations - potentials for K to Au including the outermost core orbitals, J. Chem. Phys. 82 (1985) 299-310.
- 22 V. Barone, Anharmonic vibrational properties by a fully automated second-order perturbative approach, J. Chem. Phys. 122 (2005) 014108: 1-10.
- 23 P. Carbonniere, T. Lucca, C. Pouchan, N. Rega, V. Barone, V. Vibrational computations beyond the harmonic approximation: performances of the B3LYP density functional for semirigid molecules. J. Comput. Chem. 26 (2005) 384-388.
- 24 V. Barone, M. Biczysko, J. Bloino, Fully anharmonic IR and Raman spectra of medium-size molecular systems: accuracy and interpretation. Phys. Chem. Chem. Phys. 16 (2014) 1759-1787.
- 25 F. Madsen, I. Terpager, K. Olskær, J. Spanget-Larsen, Ultraviolet-Visible and Infrared Linear Dichroism Spectroscopy of 1,8-Dihydroxy-9,10-anthraquinone Aligned in Stretched Polyethylene. Chem. Phys. 165 (1992) 351-360.
- 26 I. Haque, J.L. Wood, The vibrational spectra and structure of the bis(pyridine)iodine(I), bis(pyridine)bromine(I), bis(γ -picoline)iodine(I) and bis(γ -picoline)bromine(I) cations. J. Mol. Struct. 2 (1968) 217-238.
- 27 B. Jones, G.J. Moody, J.R. Thomas, *N*-iodopyridinium dichloroiodate(I). Inorg. Chem. 9 (1970) 114-119.
- 28 J. Barluenga, J.M. Gonzalez, P.J. Campos, G. Asensio, I(py)₂BF₄, a New Reagent in Organic Synthesis: General Method for the 1,2-Iodofunctionalization of Olefins. Angew. Chem., Int. Ed. (1985) 319-320.
- 29 J. Barluenga, Transferring iodine: more than a simple functional group exchange in organic synthesis. Pure Appl. Chem. 71 (1999) 431-436.

- 30 O. Hassel, H. Hope, Structure of the Solid Compound Formed by the Addition of Two Molecules of Iodine to One Molecule of Pyridine. *Acta. Chem. Scand.* 15 (1961) 407-416.
- 31 C. Álvarez-Rúa, S. Garca-Granda, A. Ballesteros, F. González-Bobes, J.M. González, Bis-(pyridine)iodonium(I) tetrafluoroborate. *Acta Crystallogr.* (2002) o1381–o1383.
- 32 Y. Kim, E.J. McKinley, K.E. Christensen, N.H. Rees, A.L. Thompson, Toward the Understanding of Modulation in Molecular Materials: Barluenga's Reagent and its Analogues. *Cryst. Growth Des.* 14 (2014) 6294–6301.
- 33 J.R. Sabin, A Theoretical Study of the Bis(pyridine)iodine(I) Cation. *J. Mol. Struct.* 7 (1971) 407-419.
- 34 D.C. Georgiou, P. Butler, E.C. Browne, D.J.D. Wilson, J.L. Dutton, On the Bonding in Bis-pyridine Iodonium Cations. *Aust. J. Chem.* 66 (2013) 1179-1188.
- 35 D. Vojta, K. Dominković, S. Miljanić, J. Spanget-Larsen, Intramolecular hydrogen bonding in myricetin and myricitrin. Quantum chemical calculations and vibrational spectroscopy. *J. Mol. Struct.* 1131 (2017) 242-249. Appendix A.
- 36 Y.T. Jang, P.J. Phillips, E.W. Thulstrup, Some comments on the mechanism of orientation of organic solutes in stretched polyethylene. *Chem. Phys. Letters* 93 (1982) 66-73.
- 37 P.J. Philips, Mechanism of Orientation of Aromatic Molecules by Stretched Polyethylene. *Chem. Rev.* 90 (1990) 425-436.
- 38 R.G. Weiss, V. Ramamurthy, G.S. Hammond, Photochemistry in organized and confining media: a model. *Acc. Chem. Res.* 26 (1993) 530-536.
- 39 F.R. Steenstrup, K. Christensen, C. Svane, E.W. Thulstrup, Aligned solutes in stretched polyethylene: uniaxiality and temperature effects. *J. Mol. Struct.* 408 (1997) 139-148.
- 40 A.C. Wirtz, C. Hofmann, E. J. J. Groenen. Stretched Polyethylene Films Probed by Single Molecules. *ChemPhysChem* 12 (2011) 1519-1528.
- 41 D.L. Glusker, A. Miller, Reaction Products of γ Picoline and Iodine, *J. Chem. Phys* 26 (1956) 331-337.
- 42 O. Hassel, C. Rømming, T. Tufte, Crystal Structure of the 1:1 Addition Compound Formed by 4-Picoline and Iodine. *Acta Chem. Scand.* 15 (1961) 967-974.
- 43 I. Haque, J.L. Wood, The infra-red spectra of γ -picoline–halogen complexes”, *Spectrochim. Acta A* 23 (1967) 2523-2533.
- 44 I. Haque, J.L. Wood, The Reaction Products of γ -Picoline and Iodine. *J. Phys. Chem.* 72 (1968) 2438-2446.
- 45 T. Bora, N.N. Hass, I. Haque, Kinetics of Reaction between Iodine & γ -Picoline. *Indian J. Chem.* 12 (1973) 70-71.
- 46 B. Brzezinski, G. Zundel, “Symmetrical” and Asymmetrical (NH \cdots N)⁺ Hydrogen Bonds. Infrared Investigations. *J. Chem. Soc. Faraday Trans. II* 72 (1976) 2127-2137.

Graphical abstract



Highlights:

- Spontaneous formation of polyiodide salts in low-density polyethylene
- Vibrational fundamentals of the bis(pyridine)iodine(I) cation
- Bis(4-methylpyridine)iodine(I) and bis(*t*-butylpyridine)iodine(I) cations
- Formation of the 4-methylpyridinium cation at elevated temperature
- Possible formation of micro-crystalline polyiodide aggregates in polyethylene