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CHARGE TRANSFER COMPLEXES OF BENZOXAZOLE-2(3*H*)-THIONE AND BENZOXAZOLE-2(3*H*)-SELONE WITH DIIODINE: X-RAY CRYSTAL STRUCTURE OF BENZOXAZOLE-2(3*H*)-THIONE BIS(DIIODINE)

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Abstract—Solids of stoichiometry **1**·I_2 ($C_7H_5I_2NOS$; **I**), **1**·$2I_2$ ($C_7H_5I_4NOS$; **II**), **2**·I_2 ($C_7H_5I_2NOSe$; **III**) and **2**·$2I_2$ ($C_7H_5I_4NOSe$; **IV**) have been obtained by reacting respectively benzoxazole-2(3*H*)-thione (**1**) and benzoxazole-2(3*H*)-selone (**2**) with molecular diiodine in a 1 : 1 or 1 : 2 molar ratio in CH_2Cl_2 solution. Crystals suitable for X-ray structure determination have been obtained only for **II** and contain units formed by one diiodine molecule bonded almost linearly [178.44(4)°] to the thionic sulphur atom of **1** and another diiodine molecule weakly interacting with the former. The FT-Raman spectrum in the characteristic ν(I—I) region shows two bands for compound **II** at 176 and 159 cm^{-1}, in accordance with the presence of two differently perturbed diiodine molecules [I(1)—I(2) = 2.769(1) Å, I(3)—I(4) = 2.729(1) Å]. The FT-IR and FT-Raman spectra of compounds **I**, **III** and **IV** are discussed in comparison with the spectrum of **II** and with those reported for similar charge transfer complexes.

In recent years, the great interest in the electrical properties of materials obtained by reacting diiodine with compounds having sulphur or selenium donor atoms[1] has encouraged us to study the interaction of diiodine with different types of substrates in solution and in the solid state. We have observed that the solid compounds are often different from those found in solution, where charge transfer (CT) complexes are normally formed.[2] In fact, when one tries to crystallize solid compounds from solutions containing both the acceptor (I_2) and the donor (D) (in our case D is a ligand having sulphur or selenium donor atoms), several products can be obtained according to at least the following routes: (i) formation of neutral D·I_2 CT complexes, in which the donor atom binds linearly with the diiodine;[3–11] (ii) diiodine concentrations higher than 1 : 1 can produce D·nI_2 CT complexes, in which the other diiodine molecules generally interact with the first bonded I_2[4,7,11–13] (a further example is reported in the present paper); (iii) formation of an I—D—I group by the homolytic break of I—I (see, for example, the hypervalent compounds of sulphur and selenium[6,14–17]); (iv) formation of iodonium salts, in which I^+ binds two donor molecules linearly by heterolytic cleavage of coordinated I—I (counterions are normally polyiodides of varying

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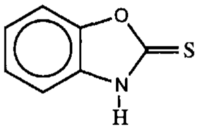
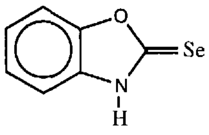
complexity);[18–21] (v) reduction of iodine to polyiodides, by electron transfer from the donor to diiodine. No literature is reported here for the polyiodides, since they are numerous both in variety (I^-, I_3^-, I_5^-, I_7^-, I_8^{2-}, I_{16}^{4-}, etc.) and structural features. The great variability of the products which can be obtained with this type of reaction makes it practically impossible to predict the final compounds and, in most cases, X-ray crystallography has been shown to be essential for their characterization.[18] However, when X-ray determination is not applicable, it is important to be able to ascertain the nature of diiodine through other techniques, such as Raman spectroscopy, widely employed in the field of polyiodides.[22–25] This aspect is of crucial importance in many organic conductors, doped with diiodine or other dihalogens, in order to assess the charge transfer induced on the segregated stacks by the halogen.[23b] For this reason, we have undertaken a program of characterization by X-ray and Raman spectroscopy of a number of crystalline compounds prepared by reacting molecular diiodine with substrates having sulphur or selenium donor atoms, in order to ascertain the ability of Raman spectroscopy to identify the nature of the iodine atoms in the reaction products.[26]


(1)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In this paper we report the studies carried out on the solid compounds, **1**·I_2 (**I**), **1**·$2I_2$ (**II**), **2**·I_2 (**III**) and **2**·$2I_2$ (**IV**), obtained by reacting benzoxazole-2(3*H*)-thione (**1**) and benzoxazole-2(3*H*)-selone (**2**) with molecular diiodine in CH_2Cl_2 solution.

EXPERIMENTAL

Preparation of compounds I *and* II

These two compounds were obtained respectively as a powder with a green metallic lustre and as black crystals with a violet metallic lustre, by standing dichloromethane solutions containing **1** and diiodine in 1 : 1 and 1 : 2 molar ratios respectively in air and at room temperature for several days. Found (Calc. for $C_7H_5I_2NOS$; **I**): C, 21.0 (20.7); H, 1.3 (1.2); N, 3.7 (3.5); S, 8.2 (8.0). Found (Calc. for $C_7H_5I_4NOS$; **II**): C, 13.0 (12.8); H, 0.8 (0.8); N, 2.4 (2.1); S, 5.0 (4.9)%.

Preparation of compounds III *and* IV

Compounds **III** and **IV** were obtained as black micro-needles with a violet metallic lustre, by standing dichloromethane solutions containing **2** and diiodine in 1 : 1 and 1 : 2 molar ratios respectively in air and at room temperature for several days. Found (Calc. for $C_7H_5I_2NOSe$; **III**): C, 18.8 (18.6); H, 1.1 (1.1); N, 3.4 (3.1). Found (Calc. for $C_7H_5I_4NOSe$; **IV**): C, 12.0 (11.9); H, 0.6 (0.7); N, 2.2 (2.0)%.

X-ray data collection and structure determination of II

Crystal data and other experimental details are summarized in Table 1. The crystal used was coated with cyanoacrylate glue in order to prevent loss of diiodine during data collection. The diffraction measurement was carried out on an Enraf–Nonius CAD4 diffractometer at room temperature, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A least-squares fit of 25 randomly oriented intense reflections having $8.9 < \theta < 16.0°$ provided the unit-cell parameters and an orientation matrix. The diffracted intensities were col-

Table 1. Crystallographic data

Compound	$C_7H_5NOS \cdot 2I_2$ (**II**)
Formula weight (amu)	658.80
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	4.500(1)
b (Å)	18.803(7)
c (Å)	16.609(6)
β (°)	96.54(2)
U (Å^3)	1396(1)
Z	4
$F(000)$	1160
D_{calc} (g cm^{-3})	3.134
Crystal dimensions (mm)	0.10 × 0.13 × 0.12
μ (Mo-K_α) (cm^{-1})	89.54
Transmission factors	
Psi-scan	0.77–1.00
DIFABS	0.87–1.36
Scan mode	ω
ω-scan width (°)	$1.00 + 0.35 \tan\theta$
θ range (°)	3–21
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	1512
Unique reflections with $I > 3\sigma(I)$	1337
Final R and R_w indices[a]	0.030, 0.047
No. of variables	132
GOF[b]	2.035

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$.

[b] $GOF = [\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$.

lected using a variable scan speed. Three standard reflections were measured at regular intervals and showed a constant decay of the scattering power of the crystal, which was evaluated at about 33% on F_o at the end of the data collection. The set of data was therefore corrected for decay as well as for Lorentz and polarization effects. An absorption correction was applied according to the procedure described in Demartin *et al.*,[27] i.e. by performing a psi-scan correction[28] followed by a DIFABS correction.[29] Secondary extinction correction was in the form $|F_c|/1+gI_c$ with $g = 3.1 \times 10^{-7}$. Scattering factors for all the atomic species and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from ref. 30. The structure was solved by direct methods (MULTAN)[31] and refined by full-matrix least-squares, minimizing the function $\Sigma w(|F_o|-k|F_c|)^2$.

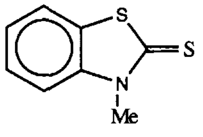
Individual weights were assigned as $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I)+(iI)^2]^{1/2}/Lp$, and i, the "ignorance factor", is equal to 0.04. An anisotropic thermal parameter was assigned to all the non-hydrogen atoms. The hydrogen atoms were introduced in the structure model with an imposed thermal parameter, at calculated positions (C–H 0.95 Å); no refinement was attempted for these atoms, with the exception of the hydrogen attached to N(1). The final difference Fourier synthesis showed maxima residuals of 1.1 e Å^{-3} close to the iodine atoms. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[32]*

FT-Raman and FT-IR spectra

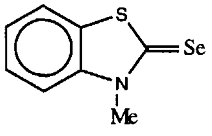
The FT Raman spectra were recorded on a Bruker FRS100 Fourier Transform Raman Spectrometer, operating with a diode-pumped Nd : YAG exciting laser (λ = 1064 nm) and having a power tunable up to 350 mW. The detection of the signal was made with an indium–gallium–arsenide detector operating at room temperature; all spectra were recorded at ±4 cm^{-1} resolution, down to about 50 cm^{-1} Raman shift. The solid samples were packed into a suitable cell and then fitted into the compartment designed for a 180° scattering geometry. The IR spectra were recorded by means of a Bruker IFS66 Fourier Transform IR Spectrometer on polyethylene pellets in the 500–80 cm^{-1} range.

RESULTS AND DISCUSSION

Recently,[4,18] we reported the products obtained by reacting N-methylbenzothiazole-2(3*H*)-thione (**3**) and N-methylbenzothiazole-2(3*H*)-selone (**4**) with molecular diiodine in CH_2Cl_2 solution in both 1 : 1 and 1 : 2 molar ratios.



(**3**)



(**4**)

The reaction of **4** with diiodine in a 1 : 1 molar ratio yields the $[4_2I]^+I_3^-$ iodonium salt; this was the first example of an iodonium salt with a selenium donor atom reported in the literature.[18] Unexpectedly, the reaction carried out in a 1 : 2 molar ratio yields the described neutral adduct of formula $\mathbf{4}\cdot 2I_2$.[4] On the other hand, the reaction of the sulphur isologue compound, **3**, with diiodine in a 1 : 2 molar ratio yielded a $[3_2I]^+I_7^-$ iodonium salt, whose counterion is a heptaiodide describable as $I^-\cdot 3I_2$, having a symmetry very close to C_{3v},[18] whereas in the 1 : 1 molar ratio, the neutral adduct of formula $\mathbf{3}\cdot I_2$ was obtained as a powder together with some crystals of $[3_2I]^+I_7^-$.

On passing from benzothiazole to benzoxazole derivatives, the products obtained on carrying out the reaction in the same conditions as for **3** and **4** are quite different.† In fact, it seems that no ionic compounds were obtained with the present substrates (see the subsequent discussion on the FT-Raman). However, the only compound characterized by X-ray diffraction and obtained by reacting benzoxazole-2(3*H*)-thione with I_2 in a 1 : 2 molar ratio, i.e. $\mathbf{1}\cdot 2I_2$ (**II**), is different from that obtained with **3** and shows a structural analogy with $\mathbf{4}\cdot 2I_2$. Selected interatomic distances and angles for **II** are collected in Table 2. In **II**, a diiodine molecule is linearly bonded to the sulphur donor atom and lies essentially in the plane of the benzoxazole mol-

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*Supplementary material available. Complete listings of fractional atomic coordinates and thermal parameters (1 page), general temperature factor expressions (1 page), interatomic distances (Å) and angles (°) (5 pages), and observed and calculated structure factors (9 pages) have been deposited.

†The benzothiazole and benzoxazole derivatives give different stability constants with diiodine. In fact, the K values obtained in CH_2Cl_2 solution ($K = 5.91 \times 10^1$ and 6.26×10^2 dm^3 mol^{-1} for **1** and **3** respectively; 25°C) show that the donor ability of **3** is about 10 times that of **1**.[2a] The same trend is found between **2** and **4**, whose K values are 8.12×10^3 and 1.02×10^5 dm^3 mol^{-1} respectively (CH_2Cl_2 solution; T = 17°C).[2a] The latter values are reported at 17°C, since a valuable rate of $\mathbf{2}\cdot I_2$ decomposition prevented us from obtaining reliable stability constants for this adduct at higher temperatures.[2a]

Table 2. Selected interatomic distances (Å) and angles (°) for $C_7H_5NOS \cdot 2I_2$ (**II**)^a

I(1)—I(2)	2.769(1)	I(2)—I(1)—S(1)	178.44(4)
I(1)—S(1)	2.874(2)	I(1)—I(2)—I(3)	88.39(2)
I(2)···I(3)	3.453(1)	I(2)—I(3)—I(4)	178.44(2)
I(3)—I(4)	2.729(1)	I(1)—S(1)—C(7)	101.4(3)
S(1)—C(7)	1.689(7)	C(6)—O(1)—C(7)	106.7(5)
O(1)—C(6)	1.366(8)	C(1)—N(1)—C(7)	110.3(5)
O(1)—C(7)	1.334(8)	N(1)—C(1)—C(2)	134.8(7)
N(1)—C(1)	1.382(8)	N(1)—C(1)—C(6)	104.1(6)
N(1)—C(7)	1.301(8)	C(2)—C(1)—C(6)	121.1(7)
C(1)—C(2)	1.374(9)	C(1)—C(2)—C(3)	116.9(7)
C(1)—C(6)	1.354(10)	C(2)—C(3)—C(4)	122.0(7)
C(2)—C(3)	1.355(10)	C(3)—C(4)—C(5)	121.9(7)
C(3)—C(4)	1.373(11)	C(4)—C(5)—C(6)	115.9(7)
C(4)—C(5)	1.352(11)	O(1)—C(6)—C(1)	109.6(6)
C(5)—C(6)	1.392(10)	O(1)—C(6)—C(5)	128.2(7)
		C(1)—C(6)—C(5)	122.2(7)
		S(1)—C(7)—O(1)	121.9(5)
		S(1)—C(7)—N(1)	128.8(5)
		O(1)—C(7)—N(1)	109.3(5)
I(1)···I(3)	4.365(1)	I(2)···I(3)$^{\text{I}}$	4.424(1)
I(1)···I(3)$^{\text{I}}$	4.371(1)	I(2)···I(3)$^{\text{IV}}$	3.972(1)
I(1)···I(4)$^{\text{II}}$	4.439(1)	I(3)···I(4)$^{\text{I}}$	4.284(1)
I(2)···I(2)$^{\text{III}}$	4.066(1)		

^{a}Symmetry codes: (I) $1+x, y, z$; (II) $1/2+x, 1/2-y, 1/2+z$; (III) $-x, 1-y, 1-z$; (IV) $-x-1, 1-y, 1-z$.

ecule, and the other diiodine molecule interacts with the former [I(2)···I(3) = 3.453(1) Å] and is almost perpendicular [88.39(2)°] to the S—I—I fragment (see Fig. 1). Although the I(1)—I(2) distance is perturbed by the I(2)···I(3) interaction, the *d*[I(1)—I(2)] and *d*[S(1)—I(1)] distances fall fairly well on the previously reported *d*(I—I)/*d*(S—I) hyperbola.[6] A view of the packing of the adduct **II** (Fig. 2) shows that the $\mathbf{1} \cdot I_2$ moieties are stacked in

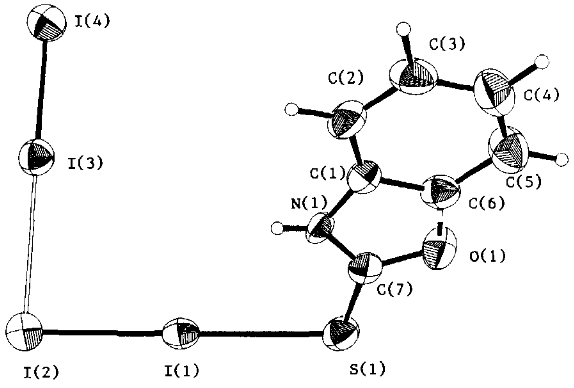

Fig. 1. ORTEP drawing of $\mathbf{1} \cdot 2I_2$.

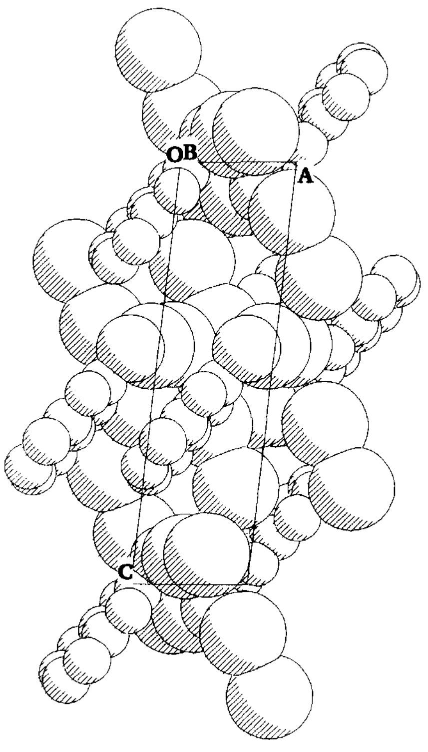

Fig. 2. Crystal packing of $\mathbf{1} \cdot 2I_2$ obtained with PLUTO.

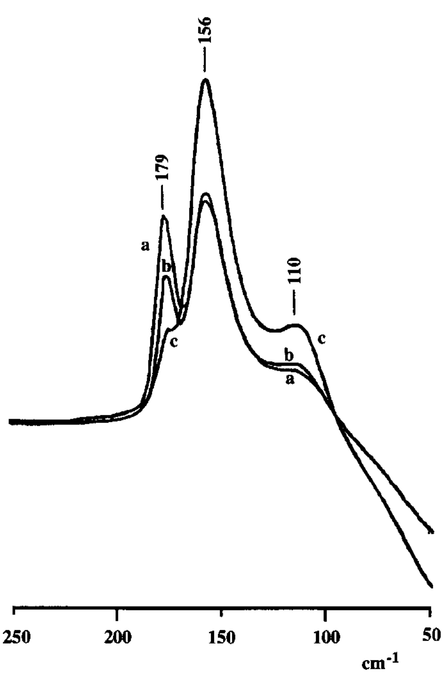

Fig. 3. (a) FT-Raman spectrum of powdered crystals of **1**·$2I_2$. (b, c) Spectra taken respectively after 10 and 20 min of irradiation with a 33 mW laser.

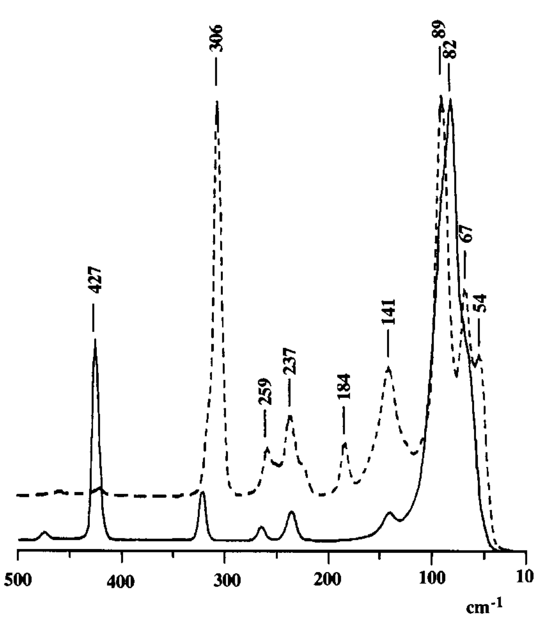

Fig. 4. Superimposed FT-Raman spectra of **1** (full line) and **2** (dotted lines).

parallel, whereas the second diiodine molecule fits into the cavities between the sheets. The shortest I···I contact between different adducts is 3.972(1) Å; the I(1)···H(N1) contact of 3.09 Å is not appreciably shorter than the sum of the van der Waals radii. The structure of **II** differs from that of **4**·$2I_2$, since in the latter there are three independent molecular adducts per asymmetric unit, which form a chain of 12 iodine atoms anchored by three selenium atoms.[4]

The FT-Raman spectrum of **1**·$2I_2$ reflects its structural features of a weak or medium-weak adduct; in fact, in this type of adduct, only one peak, due to ν(I—I), dominates all the others. Its shift to lower frequencies is correlated to the lowering of the I—I force constant (or the lengthening of the I—I bond distance) due to interaction with the donor. Two strong peaks at 179 and 156 cm^{-1} are present in the FT-Raman spectrum of **1**·$2I_2$ (Fig. 3). These peaks are not due to **1**, as can be seen from Fig. 4, where the superimposed spectra of **1** and **2** are reported,* but the former, which is practically the same (180 cm^{-1}) as that found in solid I_2,[34] is attributable to the very slightly perturbed diiodine molecule [*d*(I—I) = 2.729(1) Å], while the latter is due to the sulphur bonded I_2 [*d*(I—I) = 2.769(1) Å]. Both values fall in the linear correlation between the ν(I—I) Raman peaks and the *d*(I—I) bond distances found for the weak or medium-weak adducts with diiodine.[26] The FT-IR spectrum of **II** rightly shows the strong absorption at 156 cm^{-1} and a broad absorption around 102 cm^{-1}; the latter may be attributed to the contributions of the ligand band at 82 cm^{-1} and of the deformation of the S···I—I group. The FT-Raman spectrum of **II** changes with time under the laser beam, since the peak at 179 cm^{-1} disappears in accordance with the loss of the weakly bonded diiodine molecule (Fig. 3). The final spectrum is the same as that recorded for **I** (**1**·I_2), thus confirming its 1 : 1 adduct nature. The FT-IR spectrum of **I** again shows an absorption at 159 cm^{-1} and a strong, very broad absorption between 140 and 80 cm^{-1}.

For **III** and **IV**, which are obtained with the selenium donor **2**, no crystals suitable for X-ray crystal structure determination have been obtained, but the FT-Raman spectroscopy can help in hypothesizing their structures. The FT-Raman spectrum of **III** (**2**·I_2) is reported in Fig. 5. As one can see, two strong peaks at 125 and 113 cm^{-1} (125s and 118s cm^{-1} in the FT-IR spectrum) are present, in accordance with the formation of a strong adduct. These values, which are very similar to those at 127 and

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*Comparison of the spectra of **1** and **2** allows us to identify the peaks mainly originated by the C=S (427 cm^{-1}) and C=Se (306 cm^{-1}) group vibrations, since the substitution of selenium for the sulphur atom works as an isotopic substitution.[33]

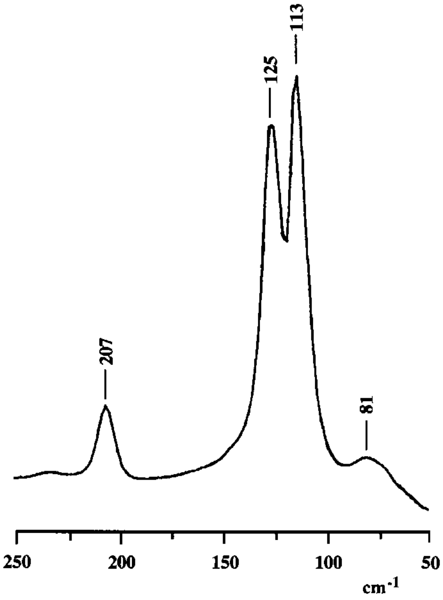

Fig. 5. FT-Raman spectrum of $\mathbf{2}\cdot I_2$.

118 cm^{-1} found in the structurally characterized N-methylthiazolidine-2(3*H*)-selone$\cdot I_2$ molecular adduct and that have been attributed to the ν_s and ν_{as} vibrations of the Se—I—I three-body system,[18] should support the adduct nature with I_2 also linearly bonded to the selenium atom for **III**. However, recently,[17] by reacting some imidazole-2-selone derivatives with molecular diiodine, we prepared an adduct [1,1′-bis(3-methyl-4-imidazolin-2-selone)methane bis(diiodine)] and the first two examples of I—Se—I hypervalent selenium compounds [i.e. 1,3-dimethyl-4-imidazolin-2-ylium diiodo selenanide and 1,2-bis(3-methyl-4-imidazolin-2-ylium diiodo selenanide)ethane bis(dichloromethane)], all of which were characterized crystallographically. The Raman spectra of the two hypervalent compounds bearing the I—Se—I group are very similar to those of the strong adducts bearing the Se—I—I group. Moreover, they are indistinguishable from the characteristic bands reported for asymmetric triiodides, in which the asymmetric, symmetric stretching and bending modes are all Raman active.[17] Therefore, the presence of the two peaks at 125 and 113 cm^{-1} in the FT-Raman spectrum of **III** could be in agreement with the formation of an adduct or of a hypervalent selenium compound, or it could even indicate the formation of a triiodide. Fortunately, the FT-Raman spectrum of **IV** ($\mathbf{2}\cdot 2I_2$; see Fig. 6), and especially its evolution under the laser beam, allow us to choose among these three hypotheses. In fact, as shown in Fig. 6, the peaks at 159 and 139 cm^{-1} present in **IV** (150s and 140s cm^{-1} in the FT-IR

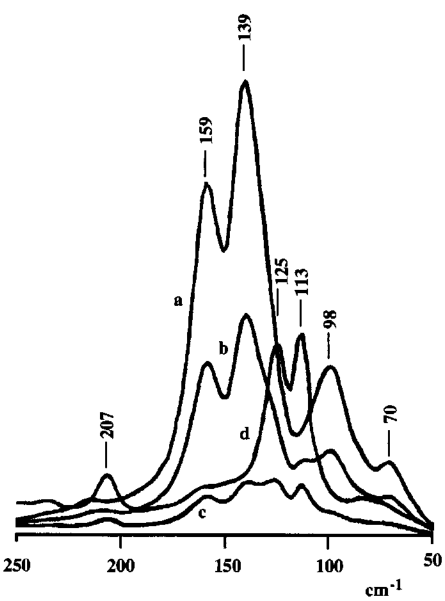

Fig. 6. (a) FT-Raman spectrum of $\mathbf{2}\cdot 2I_2$. (b, c) Spectra taken after 10 and 20 minutes respectively of irradiation with a 33 mW laser. (d) Spectrum recorded on the decomposed sample with a 213 mW laser.

spectrum) disappear with laser beam irradiation and two new peaks corresponding to those found in $\mathbf{2}\cdot I_2$ appear. This fact excludes the formation of a triiodide and strongly supports a structure of $\mathbf{2}\cdot 2I_2$ similar to that found in $\mathbf{1}\cdot 2I_2$ and $\mathbf{4}\cdot 2I_2$ with the D···I—I···I—I sequence (D = donor atom), since hypervalent selenium compounds with iodine are very rare and no examples of hypervalent selenium compounds interacting with another I_2 molecule have so far been found.

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