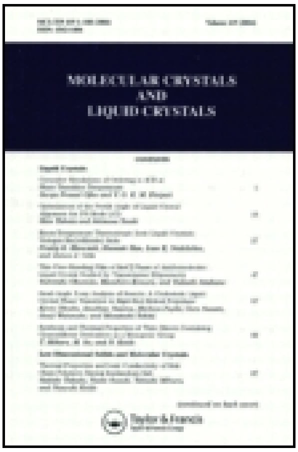

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Structure and Properties of the 4:4′-Bl (2,6-Diphenyl-1-Selenopyranylidene)-Polyiodide Salt (2-$I_{2.03}$)

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Version of record first published: 24 Sep 2006.

To cite this article: A. Leclaire, H. Leligny, C. Regnault Du Mottier, G. Le Coustumer, Y. Mollier & C. Sourisseau (1995): Structure and Properties of the 4:4′-Bl (2,6-Diphenyl-1-Selenopyranylidene)-Polyiodide Salt (2-$I_{2.03}$), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 268:1, 143-151

To link to this article: http://dx.doi.org/10.1080/10587259508031002

Mol. Cryst. Liq. Cryst., 1995, Vol. 268, pp. 143–151
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Structure and Properties of the 4:4′-BI(2,6-Diphenyl-1-Selenopyranylidene)-Polyiodide Salt ($2\text{-}I_{2.03}$)

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(Received June 15, 1994; in final form September 21, 1994)

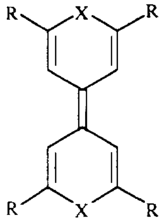
The oxidation of 4:4′-bi(2,6-diphenyl-1-selenopyranylidene) **2** with iodine leads to a radical cation iodide salt of stoichiometry ≈ 1:2. The structure was established by X-ray crystallography and compared to that of the corresponding sulfur compound. In addition to the Bragg reflections, diffuse streak on rotation photographs indicate disordered lattices incommensurate along $\vec{c}$ with a repeat of $c' = 10.95$ Å. The Raman spectra of this radical cation iodide salt shows two kinds of iodide species I_3^- and I_5^- with a relative concentration of 3.4, corresponding to a stoichiometry of $\mathbf{2}\text{-}I_{2.03}$. The *IR* and Raman spectra [1000–1700 cm^{-1} range] of some 4:4′-bi(chalcogenopyranylidenes) are described and compared with the $\mathbf{2}\text{-}I_{2.03}$ spectra.

Keywords: bi(chalcogenopyranylidenes), RX structures, IR and Raman spectra, organic conductors

INTRODUCTION

Some charge transfer complexes and radical ion salts of 4:4′-bi (thiopyranylidene) are reported in the review[1] and the references;[2,3] among their characteristics, crystallographic structures are described.[4-7] Some of them show a metallic state with a relatively high electrical conductivity along the main stacking axis. For the iodide salts, the lower is the iodine content the higher is the electrical conductivity;[2,3] for example the 4:4′-bi (2,6-diphenyl-l-thiopyranylidene)-iodide $\mathbf{1}\text{-}I_{2.28}$ shows a metallic state ($\sigma_{RT} = 250\,\text{Scm}^{-1}$) with a maximum of conductivity at 220 K.[2-3,8] Moreover, the substitution of the sulfur atoms by selenium ones in the tetrathiafulvalene series allows a higher conductivity due to the larger spatial extension of the selenium orbitals which increases the conduction bandwidth. In addition, some iodide salts from bi (ethylenedithio) tetrathiafulvalene are superconducting below 8 K.[9]

So, in the 4:4′-bi (selenopyranylidene) series, radical cation iodide salts were synthetized.[10] The crystallographic structure of the salt of lowest iodine stoichiometry with the 4:4′-bi (2, 6-diphenyl-1-selenopyranylidene) **2** is reported here and linked to its electrical and optical properties.



X = S R = C_6H_5 **1**

X = Se R = C_6H_5 **2**

X = Se R = CH_3 **3**

SYNTHESIS AND STRUCTURE

The oxidation of 4:4′-bi(2, 6-diphenyl-1-selenopyranylidene) **2** with iodine in methylene chloride solution leads to various iodide salts[10] the lowest iodine stoichiometry obtained is **2** – $I_{\approx 2}$.

Crystallographic Structure

The projection along $\vec{c}$ of the structure of the radical ion salt **2** – $I_{\approx 2}$ (Figure 1) shows its similarity with **1** – $I_{2.15}$.[7] In the unit cell one observes for the iodine atoms, tubes of continuous electronic densities waving along $\vec{c}$ instead of well resolved peaks. This shows a disorder of the iodine atoms consistent with the existence of I_3^- ions and some I_5^- ions. A X-ray diffraction film of the crystal rotating around the *c* axis shows, in addition to the Bragg reflections, a diffuse streak incommensurable with the *c* axis. This diffuse line is the intersection of the film with a (001) diffusion plane produced by the fact that the iodine atoms in the columns do not respect the crystal translation. It corresponds to the diffuse streak named A observed by D. Chasseau *et al.*[6] for the sulfur compound **1**-$I_{2.28}$ similar to the **1**-$I_{2.15}$[7] but we do not observe the other diffuse lines they noticed which correspond to a stacking period of 9.8 Å attributed by these authors to the I_3^- ions.

The iodine repartition deduced from the structure refinement and the results obtained from the diffuse streak with the method of Comès *et al.*[11] indicate that most of the iodine atoms are I_3^- species with a stacking period of 10.95 Å, the eventual diffuse lines of I_5^- being too weak to be observed. Columns filled only with I_3^- lead to a $I_{2.04}$ stoichiometry, columns filled only with I_5^- having the geometry reported by Luss *et al.*[7] lead to $I_{2.016}$. The Raman spectrum is consistent with a ratio $(I_3^-)/(I_5^-) = 3.4$ giving a stoichiometry of **2**-$I_{2.03}$. From elemental analysis of iodine, the stoichiometry of this same radical ion salt is **2**-I_2.[10] The radical ion

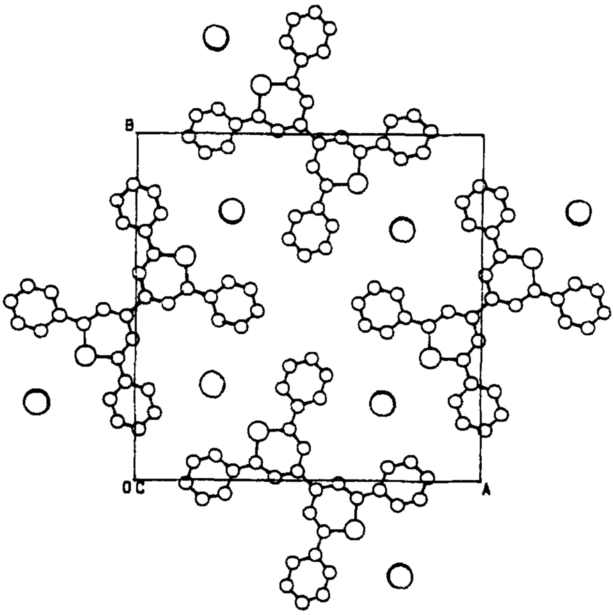


FIGURE 1 Projection of 2-$I_{2.03}$ along c axis. ○ I ○ Se.

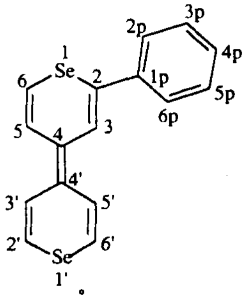
salt 2-$I_{2.03}$ has a segregated stack structure; the distance between Se atoms (3.73 Å) is lower than the sum of the Se Van der Waals radii (3.8–4.0 Å);[12,13] this implies a real interaction between the atoms of the conductive stackings[14] that translates a metallic state of this salt at room temperature. This Se...Se distance stands between the ones observed with "Organic Metals" including heterocycles such as $(TSeT)_2I$ (3.45 Å) [14] and $(TMTSeF)_2$ X with X = PF_6, ClO_4, ReO_4 (≈ 3.9 Å).[15] For 1-$I_{2.15}$, similar to 2-$I_{2.03}$, the thiopyranylidene rings are stacked with a regular interplanar spacing of 3.68 Å (ΣVRs = 3.6–3.7 Å).[12] This value of 3.68 Å close to the Van der Waals radii of sulfur atoms points out the fact that there is any specific interaction

TABLE 1

Crystallographic data of 2-$I_{2.03}$

Formula	$C_{34}H_{24}Se_2I_{2.03}$
Formula weight	844.30 g
Space group	P4b2
Z	2
Unit cell	
a = b	19.838 (2) Å
c	3.731 (1) Å
V	1468.5 $Å^3$
Calc. density	1.91 g/cm^3
μ (CuKα)	20.6 mm^{-1}
μl	0.25
R	0.056
Rw	0.057

TABLE 2



Main distances (Å) and angles (°) of **2**-$I_{2.03}$

I – I	2.842 (8) Å
I – I	2.856 (13) Å
Se – C(2)	1.86 (2) Å
C(2) – C(3)	1.42 (4) Å
C(2) – C(1p)	1.43 (3) Å
C(3) – C(4)	1.40 (3) Å
C(4) – C(4')	1.51 (3) Å
C(1p) – C(2p)	1.40 (4) Å
C(2p) – C(3p)	1.35 (4) Å
C(3p) – C(4p)	1.36 (4) Å
C(4p) – C(5p)	1.40 (4) Å
C(5p) – C(6p)	1.35 (3) Å
C(6p) – C(1p)	1.42 (3) Å
C(2) – Se – C(6)	100 (1)°
Se – C(2) – C(1p)	115 (2)°
Se – C(2) – C(3)	118 (2)°
C(3) – C(2) – C(1p)	125 (2)°
C(2) – C(3) – C(4)	124 (2)°
C(4') – C(4) – C(3)	120 (2)°
C(2) – C(1p) – C(6p)	124 (2)°
C(2) – C(1p) – C(2p)	122 (2)°
C(6p) – C(1p) – C(2p)	97 (1)°
C(1p) – C(6p) – C(5p)	124 (2)°
C(6p) – C(5p) – C(4p)	118 (2)°
C(5p) – C(4p) – C(3p)	120 (3)°
C(4p) – C(3p) – C(2p)	121 (2)°
C(3p) – C(2p) – C(1p)	123 (2)°

between these atoms in the stacks of the donor, however this salt shows a metallic character.[2,8]

OPTICAL PROPERTIES

The Infrared and Raman band wavenumbers of bi(chalcogenopyranylidenes) **1**, **2**, **3** in the 1000–1700 cm^{-1} range are listed in Table 3. Assignments are given from comparison with the IR study of **1**.[16]

TABLE 3

3		2		1		Attributions
(IR)	Raman	(IR)	Raman	IR (16)	Raman	
1635 vs		1610 m		1617 m		$\nu_{c=c}$ interring
	1611 vs		≈ 1610 sh		1600 sh	
		1590 m	1579 vs	1595 m	1581 vs	ν_{8a} phenyls
		1570 m	1570 vs	1572 m	1572 vs	ν_{8b} ,,
	1571 vw			1559 w		
1535 vw	1544 vw	1535	1531 m	1539 m	1534 m	$\nu_{c=c}$ ring
	1496 s		1496 vw	1491 s	1499 sh	
	1489 sh	1485 vs	1470 m		1480 m	$\nu_{c=c}$ ring, ν_{19a}, ν_{19b} phenyls
1425 m	1418 vw	1440 s	≈ 1440 vw	1444 m		δ_{CH}, ring C_5X
			1368 vw		1398 m	
1370 ms	1368 vw					δ_{CH3}
1335 m	1330 w	1330 vw	1329 m	1346 w	1332 m	δ_{CH}, ring C_5X
1315 s	1320 s					
			1282 vw	1279 w	≈ 1290	
				1247 m		
1230 vw	1222 vw	1232 m	1212 m			
		1185 vm	1191 m	1189 w		$\nu_{c-\varphi}$
		1160 vw		1163 w		δ_{CH} phenyls (9a)
1140 s				1150		δ_{CH} phenyls (9b)
1120 sh	1110 m					
1090 m		1100 w		1101		δ_{CH}
		1075 m		1076 w		,,

vs: very strong; s: strong; sh: shoulder; w: weak; vw: very weak

The Raman spectrum of the **2**-$I_{2.03}$ salt (50–500 cm^{-1}) (Figure 2) shows a strong peak at 107 cm^{-1} attributed to ν_S (I_3^-) with its overtones: $2\nu_S$, $3\nu_S$ and $4\nu_S$. A weak band is observed at 155 cm^{-1} due to I_5^- ions.[10,17,18] This vibration is not observed in the **1**-$I_{2.28}$ spectrum (Figure 3). Assuming that under this specific laser excitation, the Raman cross-section of the ν_S (I_3^-) mode is twice that of the ν_1 of I_5^- species according to Zambounis *et al.*,[18] one can easily estimate from the ratio of the intensities of the bands at 107 and 155 cm^{-1} that the relative concentration, of the iodide species is $(I_3^-)/(I_5^-) \approx 3.4$. Previous studies[19] on organic metals showed the existence of strong EMV (Electron-Molecular Vibration) couplings which influence both the Raman and the IR lines. So we notice a decrease of some frequencies between the neutral donor **2** and its iodide salt **2**-$I_{2.03}$:

	2	2-$I_{2.03}$
$\nu_{c=c}$ (interrings)	1610 cm^{-1}	1602 cm^{-1}
ν_{c-c} (ring)	1531 cm^{-1}	1490 cm^{-1}

The ν_{c-c} (ring) mode seems to be more sensitive to the mean electronic charge of the donor **2**. The optical absorption spectrum of **2**-$I_{2.03}$ in the solid state exhibits a band

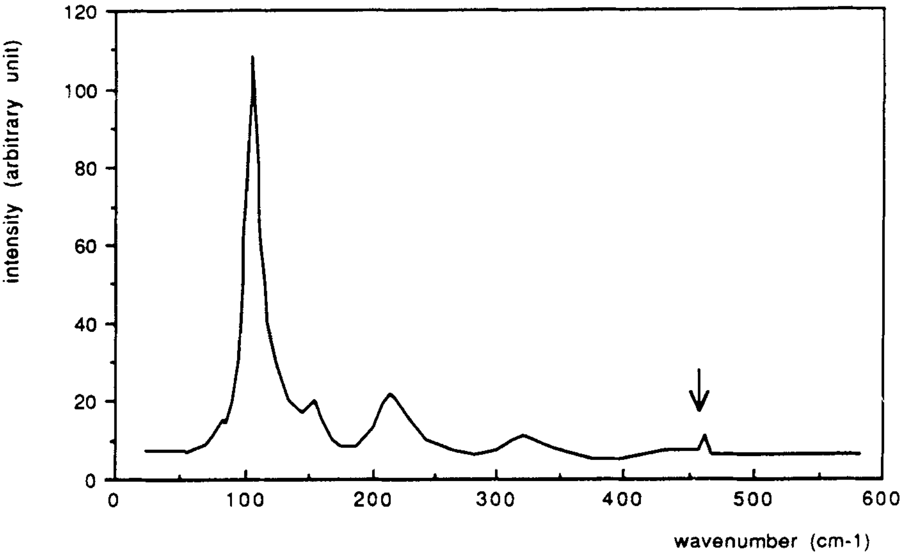


FIGURE 2 Raman spectrum of **2** – $I_{2.03}$ ↓ Band due to the ClO_4^- anion used as internal standard.

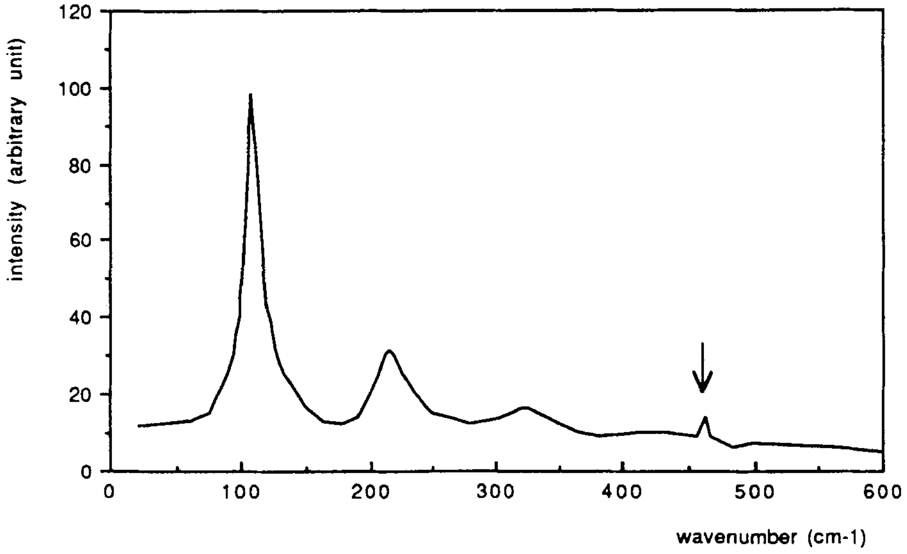


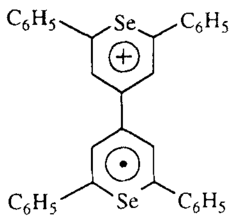
FIGURE 3 Raman spectrum of **1**-$I_{2.28}$ ↓ Band due to the ClO_4^- anion used as internal standard.

around 2000 cm^{-1} due to an intervalence charge transfer in the donor stackings: $D^{+\cdot} + D^0 \leftrightarrows D^0 + D^{+\cdot}$. This charge transfer is characteristic of a conducting state[20] and was also observed in the radical ion salt **1**-$I_{2.28}$.[6] The specular reflectivity spectrum of **2**-$I_{2.03}$ [10] shows a reflectance maximum around 25% from 4000 to 10000 nm which is an another indication of a metallic state of this salt. The parameterization of this spectrum by the Drude's model associated to Lorentz oscillators leads to an optical conductivity of 541 $\mathrm{Scm^{-1}}$. The optical conductivity of **2**-$I_{2.03}$ is higher than for **1**-$I_{2.28}$ ($\sigma_{\mathrm{opt}} = 320\,\mathrm{Scm^{-1}}$; $\sigma_{\mathrm{RT}} = 250\,\mathrm{Scm^{-1}}$).[2,6]

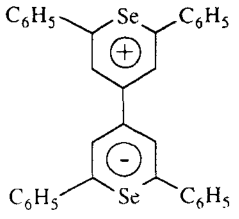
DISCUSSION

From the stoichiometry of **2**-$I_{2.03}$ and if we assume that for the single crystal the ratio $(I_3^-)/(I_5^-)$ is of the same order of magnitude than that determined on microcrystalline powder (3.4), the charge equilibrium would give to the single crystal the following composition: **2**-$(I_3^-)_{0.45}\,(I_5^-)_{0.13}$. The mean charge per molecule of **2** would be about 0.6.

The bond lengths $C_2 - C_3$ and $C_3 - C_4$ correspond to bond orders of 1.40 and 1.52 [21] and are similar to an aromatic bond character; on the other hand the $C_4 - C_{4'}$ bond has a bond order value about 1. So, all these bond lengths and bond orders are quite different of the same bonds of the **1** $- I_{2.28}$ salt [7] whereas these bonds are very similar for the donors **1** et **2**.[22] We also notice that the C – Se (1.86 Å) bond is shorter than the C – Se bond of the neutral donor **2** (1.887);[22] this value is intermediate between a double bond value (C = Se: 1.76 Å)[24] and a single bond value ($\mathrm{Csp^3}$-Se: 1.93 Å)[23] and quite similar to $\mathrm{Csp^2}$-Se ($\approx$ 1.85 Å)[25] for heterocycles with delocalised π electrons. So the structure of **2** in the iodide salt, as for the structure of **1** in **1** $- I_{2.15}$ [7] can be described by the contribution of different schemes: radical ion A, mesoionic B and canonical forms with the charge and lone electron borne by the phenyl rings, since the bond order C(2) – C(1p) [1.43 Å] of 1.49 is between a single and a double bond value. It does not appear that the contribution of a limit form with non delocalised bonds is important owing to the C – C bond order and C-Se bond lengths.



A



B

EXPERIMENTAL

Synthesis

The synthesis of the donor **2** was reported elsewhere.[26] The charge transfer salt **2** $- I_{2.03}$ is obtained when a methylene chloride iodine solution is added around 40 °C to **2** dissolved with the minimum of methylene chloride, with a ratio $(I_2)/(\mathrm{D}) = 1/2$. After cooling and slow evaporation, silver green needles are isolated ($F = 211$ °C).

Crystallographic Study

A crystal needle shaped along $\vec{c}$(0.264 × 0.012 × 0.012 mm) was used for the structure determination. The systematic absences $k = 2n + 1$ for 0kl and $h = 2n + 1$ for h01 are consistent with the P4b2 space group. The data were collected on a CAD 4 Enraf-Nonius diffractometer using the CuKα radiation isolated with a graphit monochromator. 273 reflections with $I > 3\sigma(I)$ were used to solve and refine the structure. The Patterson function is similar to that of **1** – $I_{2.15}$.[7] The refinements of the coordinates and the isotropic thermal factors lead to $R = 0.056$ and $Rw = 0.057$ and to the bond lengths and angles listed on Table 2.

Raman Measurement

The Raman spectrum of a powdered sample, using a large dilution and an homogeneous mixture in $RbClO_4$ (concentration $\approx 2\%$ in weight or 0.023 mmole/g), has been recorded on a Dilor Z 24 triple monochromator using the $\lambda_0 = 528.7$ nm emission line of a Spectra-Physics c.w. Ar^+ laser in conjonction with the rotating disc technique: the sample holder was rotating at about 2000 r.p.m. and a low incident power laser($\leqslant$ 50 mW) was used in order to minimize any local heating or photochemical decomposition effects. Standard photon counting techniques were used for detection and frequency measurements were calibrated using plasma lines.

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