Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Cyanine dyes: Synergistic action of hydrogen, halogen and chalcogen bonds allows discrete I_4^{2-} anions in crystals

Konstantis F. Konidaris,[a] Tullio Pilati,[a] Giancarlo Terraneo,[a] Peter Politzer,[b] Jane S. Murray,[b] Patrick Scilabra[a] and Giuseppe Resnati*[a]

[a] Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milano, Italy. E-mail: giuseppe.resnati@polimi.it.

[b] Department of Chemistry, University of New Orleans, New Orleans, LA 70148 USA.

1. Materials and Methods

1.1. General information

The starting materials 1-ethyl-6-methyl-2-[(*E*)-(3-ethyl-5-methoxy-2(3H)-benzoselenazolylidene)methyl]quinolinium *p*-toluenesulfonate (**1a**) and 1-ethyl-6-methoxy-2-[(*E*)-(3-ethyl-5-methoxy-2(3H)-benzoselenazolylidene)methyl]quinolinium iodide (**1b**) were purchased from Sigma-Aldrich (product codes S137928 and S131105, respectively) and used without further purification. IR spectra were obtained using a Nicolet Nexus FT-IR spectrometer equipped with UATR unit (4000 – 400 cm^{-1} range). ^{1}H-NMR spectra were recorded at ambient temperature on a Bruker AV-400 spectrometer, at 400 MHz.

1.2. 1-*Ethyl-6-methyl-2-[(E)-(3-ethyl-5-methoxy-2(3H)-benzoselenazolylidene)methyl]quinolinium p-toluenesulfonate (**1a**)*

Orange plate-like crystals of **1a** were formed on slow isothermal evaporation at room temperature of a solution of the compound in CH_2Cl_2. FT-IR (ν, cm^{-1}): 2974, 2919, 1614, 1567, 1529, 1391, 1264, 1213, 1164, 1119, 1033, 1011, 798, 680, 563.

1.3. 1-*Ethyl-6-methoxy-2-[(E)-(3-ethyl-5-methoxy-2(3H)-benzoselenazolylidene)methyl]quinolinium iodide (**1b**)*

Red thin needle-like crystals of **1b** were formed on slow isothermal evaporation at room temperature of a solution of the compound in $CHCl_3$/MeOH (4:1). FT-IR (ν, cm^{-1}): 2962, 2934, 1611, 1568, 1515, 1479, 1373, 1257, 1215, 1156, 1030, 787, 698, 442. ^{1}H-NMR (400 MHz, DMSO-d_6, δ (ppm)): 1.38 (t, 3H), 1.49 (t, 3H), 3.88 (s, 3H), 3.93 (s, 3H), 4.48 (q, 2H), 4.71 (q, 2H), 6.23 (s, 1H), 6.95 – 6.97 (m, 1H), 7.20 (s, 1H), 7.56 - 7.61 (m, 2H), 7.88 (d, 1H), 8.03, (d, 1H), 8.13 (d, 1H), 8.47 (d, 1H).

1.4. 1-*Ethyl-6-methoxy-2-[(E)-(3-ethyl-5-methoxy-2(3H)-benzoselenazolylidene)methyl]quinolinium iodide/(diiodine)$_{0.5}$ (**1c**)*

Dark red thin plate-like crystals of **1c** were formed after slow isothermal evaporation at room temperature of a solution of **1b** and I_2 (2:1 molar ratio) in a mixture of $CHCl_3$/MeOH (4:1). FT-IR (ν, cm^{-1}): 2969, 2933, 1611, 1568, 1515, 1481, 1374, 1258, 1213, 1159, 1125, 1056, 1031, 965, 819, 444.

2. Single crystal structure determination

2.1. General information

The single crystal X-ray diffraction measurement of **1a** and **1c** were conducted with a Bruker SMART APEX CCD area detector diffractometer, equipped with a Bruker *KRYOFLEX* low temperature device, graphite monochromator, Mo*K*α radiation (λ = 0.71069 Å). Cell refinement and data reduction were done with Bruker SAINT [1]. Structure solution was performed with SHELXS [2] and refined with SHELX [2]; absorption correction was performed based on multi-scan procedure using *SADABS* [1]. Further crystallographic details of the structures are reported in Table S1.

Table S1. Crystallographic data and structure refinement parameters for **1a**-**c**.

Compound	**1a**	**1b**	**1c**
Formula	$2(C_{23}H_{25}N_2OSe)\cdot 2(C_7H_7O_3S)\cdot CH_2Cl_2$	$C_{23}H_{25}N_2O_2Se^+\cdot I^-$	$C_{23}H_{25}N_2O_2Se^+\cdot 0.5(I_2)\cdot I^-$
Molecular weight	1276.11	567.31	694.21
Temperature (K)	100	296	296
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	8.008 (7)	8.0417(19)	7.634 (6)
b (Å)	11.380 (9)	14.332(4)	11.179 (11)
c (Å)	17.301 (13)	19.473(5)	15.757 (13)
α (°)	74.32 (3)	90	75.93 (6)
β (°)	86.43 (2)	90.228(11)	79.26 (5)
γ (°)	70.07 (2)	90	70.09 (4)
Volume (Å^3)	1426 (2)	2244.4(10)	1218.4 (19)
Z	1	4	2
Crystal size (mm)	0.1 × 0.08 × 0.02	0.25 × 0.02 × 0.02	0.1 × 0.08 × 0.01
μ (mm^{-1})	1.52	3.07	4.10
F(000)	658	1120	666
No. of measured, independent and observed reflections	12265, 3916, 2468	53785, 2374, 1599	8747, 4221, 2348

$\theta_{min,}$ θ_{max} (°)	3.7, 23.1	2.9, 21.01	3.01, 25.00
wR_{2_obs}, wR_{2_all}	0.143, 0.118	0.153, 0.131	0.098, 0.117
R_{1_obs}, R_{1_all}	0.060, 0.120	0.063, 0.111	0.049, 0.104
GOOF	1.009	1.118	0.908
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	-0.68, 0.59	-0.86, 0.99	-0.95, 0.87
CCDC number	1817362	n.d.[a]	1817361

[a]: The structure **1b** diffracted very poorly and several attempts to improve the quality of the data failed (Data completeness 0.979 with theta max of 21° and Rint of 0.360). For this reason the structure **1b** was not deposited (n.d.) in the CSD. However all heavy atoms were properly located and, for the sake of clarity, the Cartesian coordinate and the ADPs are listed in paragraph 2.2 in shelx res file format.

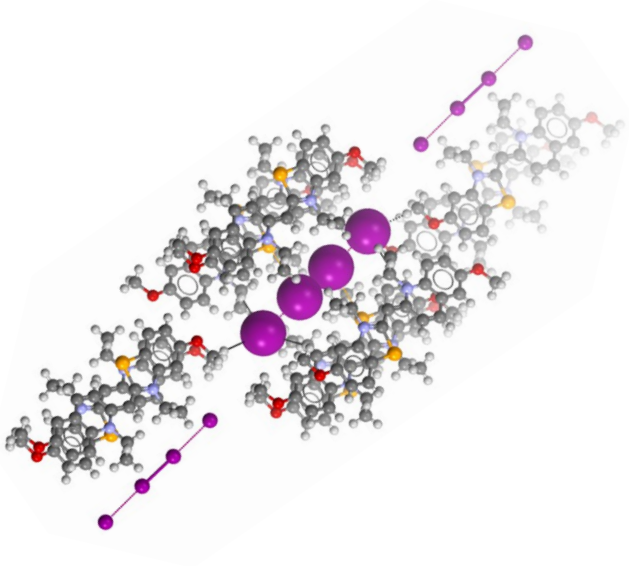


Figure S1

Partial representation (Mercury 3.9) of the crystal packing of **1c** evidencing how I_4^{2-} supramolecular anions are discrete units sitting in a cavity delimited by cations. An orientation different from that adopted in Fig. 4 is used. One I_4^{2-} anion is in space filling style (with reduced atom size representation with respect to standard space filling); the two I_4^{2-} anions closest to the central I_4^{2-} are also reported (in ball and stick). Depth cueing makes atoms at the front darker than those at the back. XBs are purple lines. Colour code for atoms: Grey, carbon; white, hydrogen; sky blue, nitrogen; red, oxygen; ochre, selenium; purple, iodine.

*2.2. Crystal structure of **1b***

The poor quality of diffraction data obtained for **1b** crystals substantially lessens the value of an analyses of the details of the structure. Similar to **1a** and **1c**, the benzoselenazole and quinoline moieties are nearly coplanar (the angle between the mean square planes through the heavy atoms of the two bicyclic systems is 5.86°). The cations adopt a smectic-like organization and form layers which alternate with anionic layers (Fig. S2). Iodide anions are pinned to cations via HBs.

*Cartesian coordinate and ADPs of **1b** in shelx res file format:*

```
TITL T3 in P2(1)/n 1B.res
CELL 0.71073   8.0417  14.3324  19.4732  90.000  90.228  90.000
ZERR    4.00   0.0019   0.0036   0.0049   0.000   0.011   0.000
LATT 1
SYMM 0.5-X, 0.5+Y, 0.5-Z
MOLE 1
I1    6    0.641955    0.762300    0.276361    11.00000    0.07473    0.07934 =
       0.05361    0.00238   -0.00752   -0.00615
Se1   5    0.384009    0.133882    0.546477    11.00000    0.04328    0.04359 =
       0.04962   -0.00241   -0.00205   -0.00807
C1    1    0.473243    0.242441    0.508344    11.00000    0.04366    0.03864 =
       0.03975   -0.00703    0.00225    0.00837
C2    1    0.551231    0.317474    0.541178    11.00000    0.04672    0.05409 =
       0.05550   -0.01802    0.00268   -0.00770
C3    1    0.607620    0.390511    0.502791    11.00000    0.03862    0.04157 =
       0.06640   -0.01495    0.00820   -0.02300
C4    1    0.588813    0.391160    0.432152    11.00000    0.04581    0.04110 =
       0.06523   -0.00032    0.00432   -0.01167
C5    1    0.510634    0.320360    0.399717    11.00000    0.04907    0.04493 =
       0.05694    0.01784   -0.00490   -0.01683
C6    1    0.455987    0.247143    0.438761    11.00000    0.03398    0.02912 =
       0.06495   -0.00975    0.00675   -0.00364
C7    1    0.322391    0.097225    0.456236    11.00000    0.04805    0.05338 =
       0.03488    0.01420    0.01513    0.01515
N1    3    0.367119    0.167060    0.412215    11.00000    0.07322    0.06626 =
       0.02645   -0.00197   -0.00723   -0.00555
C8    1    0.241522    0.018148    0.434542    11.00000    0.05080    0.03463 =
       0.05168   -0.01683   -0.00824   -0.00783
```

```
C9    1    0.184051   -0.058130    0.473384    11.00000    0.03137    0.03806 =
      0.04632    0.00407    0.00199   -0.00131
C10   1    0.214272   -0.071350    0.543710    11.00000    0.03638    0.04512 =
      0.04285   -0.00389   -0.00028   -0.01240
C11   1    0.162985   -0.145599    0.578967    11.00000    0.05590    0.04022 =
      0.03779   -0.00300   -0.01158   -0.01257
C12   1    0.073755   -0.218108    0.544165    11.00000    0.01699    0.04443 =
      0.05355   -0.00784    0.00447   -0.00038
C13   1    0.023730   -0.298479    0.578178    11.00000    0.05366    0.03932 =
      0.04553    0.00406    0.00077   -0.01172
C14   1   -0.062273   -0.366747    0.542213    11.00000    0.03683    0.03830 =
      0.06210    0.00328    0.00280   -0.00122
C15   1   -0.091093   -0.355831    0.472484    11.00000    0.03027    0.03593 =
      0.07295   -0.00697   -0.01094   -0.00053
C16   1   -0.040574   -0.278314    0.437583    11.00000    0.05636    0.03023 =
      0.05786   -0.00005   -0.01171   -0.00533
C17   1    0.040692   -0.207181    0.473257    11.00000    0.03315    0.02585 =
      0.04608   -0.00159   -0.00182   -0.00210
N2    3    0.092938   -0.126421    0.440693    11.00000    0.05310    0.03233 =
      0.04076   -0.00385   -0.00282   -0.00338
O1    4    0.652420    0.468173    0.401188    11.00000    0.07285    0.04834 =
      0.07243   -0.00254   -0.00087   -0.01498
C18   1    0.608732    0.482286    0.331298    11.00000    0.11046    0.04803 =
      0.09165    0.02446    0.00003   -0.02211
C19   1    0.307221    0.168196    0.337463    11.00000    0.13011    0.04089 =
      0.10813    0.00831    0.02868   -0.02038
C20   1    0.428408    0.118416    0.297883    11.00000    0.13418    0.11730 =
      0.10580    0.00400    0.00482   -0.02665
C21   1    0.041988   -0.111797    0.367875    11.00000    0.05797    0.04524 =
      0.05656   -0.00633   -0.00239   -0.01306
O2    4   -0.120270   -0.447041    0.571259    11.00000    0.06668    0.04551 =
      0.06901    0.01038   -0.00723   -0.02010
C22   1    0.164485   -0.148951    0.319070    11.00000    0.08644    0.07689 =
      0.06375   -0.01101    0.01139   -0.00222
C23   1   -0.094472   -0.462192    0.640795    11.00000    0.09057    0.07584 =
      0.06037    0.01642    0.00992   -0.02364
HKLF 4
END
```

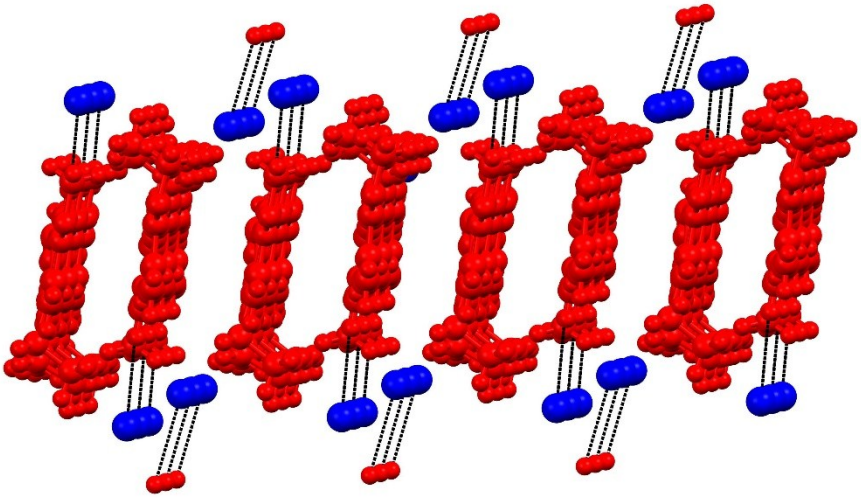


Figure S2

Ball and stick partial representation (Mercury 3.9) of the crystal packing of **1b** evidencing the segregation and layers formation. Cations are in red; iodide anions are in blue. HBs are black dotted lines.

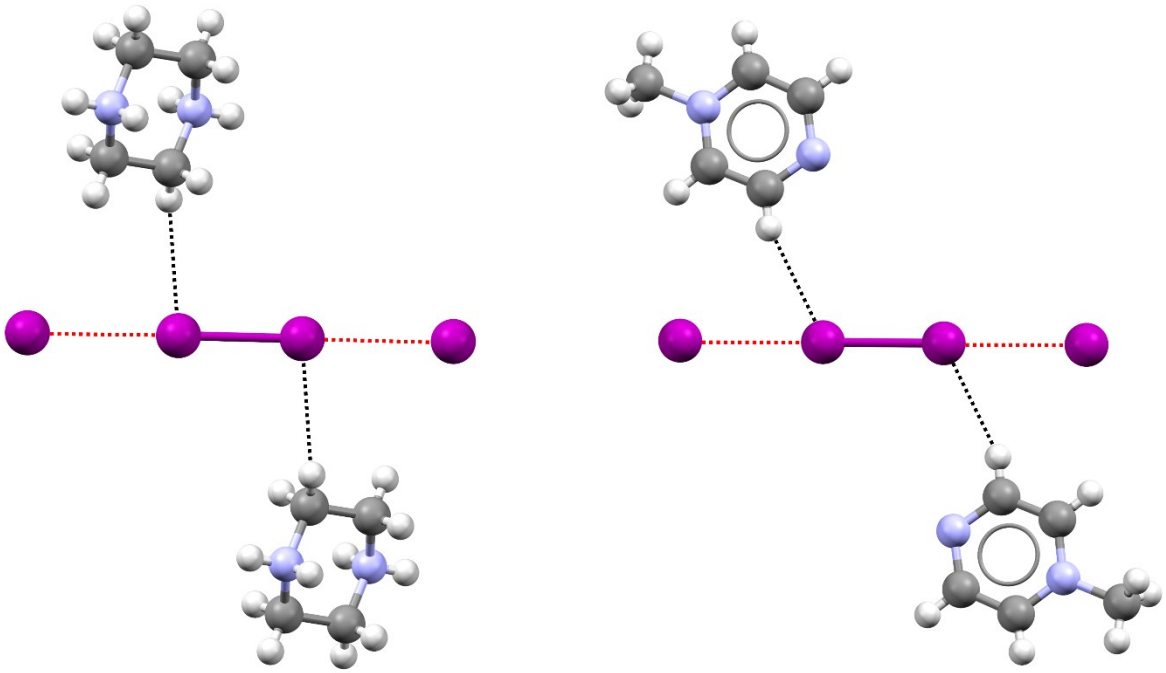
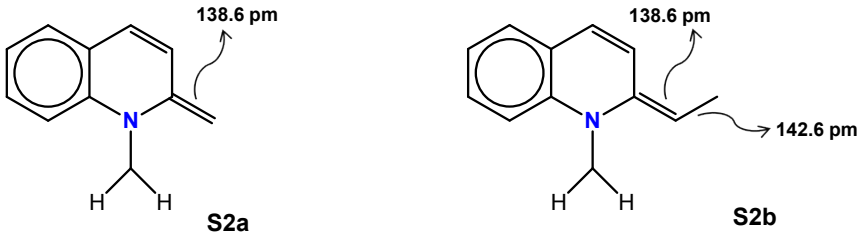


Figure S3

Ball and stick representation (Mercury 3.9) of piperazine-1,4-diium bis-iodide-/iodine (Refcode MOYLUJ01, left, [3]) and 1-methylpyrazin-1-ium iodide/iodine$_{0.5}$ (Refcode YUSYUH, right, [4]) evidencing the I···I$^-$ XBs (red dotted lines) and C–H···I HBs (black dotted lines) that hold the iodine molecules in their position.

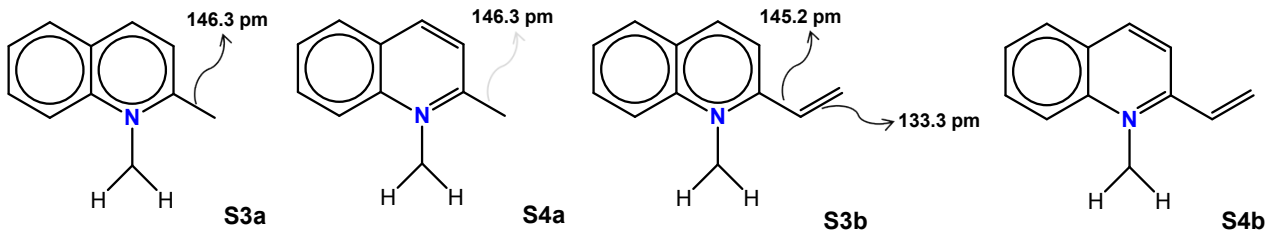
3. Cambridge Structural Database statistics



Scheme S1

A search in the Cambridge Structural Database (CSD) (ConQuest 1.19, CSD version 5.38, updates November 2016, February 2017, May 2017) afforded 17 hits for the bond pattern reported in formula **S2a**. Eight of the hits (Refcodes: DAQYEZ, DECYNI, DEPICY, KEVLED, NABVOB, PEZJUB, PUDMIK, XEVSAU) were not uniquely related to the bond pattern of formula **S2a** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean value of the ylidene bond length (C=C bond) in the remaining nine hits (Refcodes: HOHVUV, LULPUD, LULQAK, MEZFUU, PMTPYQ, SAKHIX, OYEMUC, OYENAJ, OYENEN) is given in formula **S2a**. The respective bond length is 139.2 pm in **1a** and 141.0 pm in **1c**.

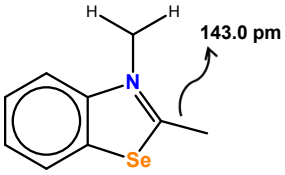
A CSD search afforded a smaller set of hits (16 hits) for the bond pattern reported in formula **S2b**. Seven of them (Refcodes: DAQYEZ, DECYNI, DEPICY, NABVOB, PEZJUB, PUDMIK, XEVSAU) were not uniquely related to the bond pattern of formula **S2b** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean values of the two ylidene bond lengths (C=C and C–C bonds) in the remaining nine hits (Refcodes: HOHVUV, LULPUD, LULQAK, MEZFUU, PMTPYQ, SAKHIX, OYEMUC, OYENAJ, OYENEN) are given in formula **S2b**. The respective bond lengths are 139.2 ($N_{quinoline}$–C–C) and 139.3 (Se-C–C) pm in **1a** and 141.0 ($N_{quinoline}$–C–C) and 134.7 (Se-C–C) pm in **1c**.



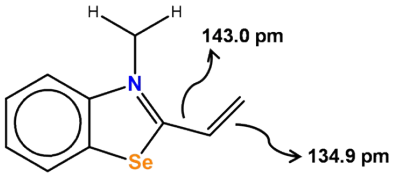
Scheme S2

A CSD search afforded 77 hits for the bond pattern reported in formula **S3a** and 8 hits for the bond pattern reported in formula **S4a**. Thirty one of the hits for formula **S3a** (Refcodes: UTEXAU, UTEXEY, UTEXUO, ABUPEU, DAVLOB, DEPICY, DOKSOM, EJIXIF, EJIXOL, EJIXUR, EJIYAY, ETHIDB, IQIFUL, KAGLUZ, LEFROD, LEFRUJ, LIWCAW, LOFDAN, MUJGAB, OMAHUG, PUDMIK, QINWER, QOHDEX, SAKHET, TURJIB, WINYOJ, WINYUP, WINZAW, WIPBEE, XEVSAU, XIYZUB) and seven of the hits for formula **S4a** (Refcodes: DAQYEZ, DECYNI, MACAZC10, PEZJUB, VAJNOJ, VAJNUP, VAJPAX) were not uniquely related to the bond pattern of formulas **S3a** and **S4a** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean value of the bond length of the quinoline C–C pendant in the remaining forty six hits of formula **S3a** (Refcodes: UTAJOQ, ADAQIG, BUTTER, BUTTIV, BUVXOH, BUZSAR, CERSAU, CIMCOS, GOLDUI, HISHIB, HISHIB01, IFABIB, IKAPER, JAXSAD, JUTBEH, KUTYAA, LEDBOL, LEZRIS, LEZRIS01, LIBXOK, MODQUS, NENMID, NENXOV, NERYUF, NUPTAU, PEMRUU, RIPQOY, RITKUB, RUMGAJ, SAPWIQ, SIFGOE, SIFGOE02, TEJTEH, TIDFOB, VIXMAS, WIBKOJ, WUTPOR, WUTPUX, XICMUS, XICNED, XICWEL, ZAWPOE, ZUGTEC, GOLDUI01, KAMCAF, NAWPOT) and the remaining hit of formula **S4a** (Refcode: KIYYIB) is given in formulas **S3a** and **4a**. The respective bond length is 139.2 pm in **1a** and 141.0 pm in **1c**.

A CSD search afforded 53 hits for the bond pattern reported in formula **S3b** and 7 hits for the bond pattern reported in formula **S4b**. Twenty tree of the hits for formula **S3b** (Refcodes: UTEXAU, UTEXEY, UTEXUO, DEPICY, DOKSOM, EJIXIF, EJIXOL, EJIXUR, EJIYAY, IQIFUL, LIWCAW, LOFDAN, OMAHUG, PUDMIK, QINWER, SAKHET, TURJIB, WINYOJ, WINYUP, WINZAW, WIPBEE, XEVSAU, XIYZUB) and the all seven hits for formula **S4b** (Refcodes: DAQYEZ, DECYNI, MACAZC10, PEZJUB, VAJNOJ, VAJNUP, VAJPAX) were not uniquely related to the bond pattern of formulas **S3b** and **S4b** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean values of the ylidene bond lengths in the remaining thirty hits of formula **S3b** (Refcodes: UTAJOQ, ADAQIG, BUZSAR, CIMCOS, HISHIB, HISHIB01, IFABIB, IKAPER, JAXSAD, JUTBEH, KUTYAA, LEZRIS, LEZRIS01, LIBXOK, MODQUS, NENMID, NERYUF, NUPTAU, RIPQOY, RITKUB, RUMGAJ, SAPWIQ, SIFGOE, SIFGOE02, VIXMAS, XICMUS, XICNED, ZAWPOE, ZUGTEC KAMCAF) are given in formula **S3b**. The respective bond lengths are 139.2 ($N_{quinoline}$–C–C) and 139.3 (Se–C–C) pm in **1a** and 141.0 ($N_{quinoline}$–C–C) and 134.7 (Se–C–C) pm in **1c**.



S5a

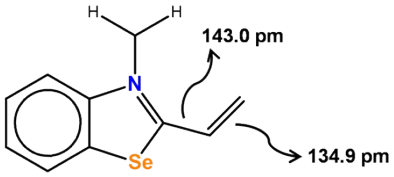


S5b

Scheme S3

A CSD search afforded 13 hits for the bond pattern reported in formula **S5a**. Five of them (Refcodes: ANEQUG, ANERAN, ANERER, ANERIV, MULHIK) were not uniquely related to the bond pattern of formula **S5a** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean value of the bond length of the benzoselenazole pendant (Se–C–C bond) in the remaining eight hits (Refcodes: UTUQIL, UTUQOR, UTUQUX, UTURAE, UTUREI, UTURIM, UTUROS, UTUROS01) is given in formula **S5a**. The respective bond length is 139.3 pm in **1a** and 134.7 pm in **1c**.

A CSD search afforded 12 hits for the bond pattern reported in formula **S5b**. Five of them (Refcodes: ANEQUG, ANERAN, ANERER, ANERIV, MULHIK) were not uniquely related to the bond pattern of formula **S5b** (e.g. they corresponded to one of the likely resonance structures of the compound). The mean values of the ylidene bond lengths in the remaining seven hits (Refcodes: UTUQIL, UTUQOR, UTUQUX, UTURAE, UTUREI, UTUROS, UTUROS01) are given in formula **S5b**. The respective bond lengths are 139.2 ($N_{quinoline}$–C–C) and 139.3 (Se–C–C) pm in **1a** and 141.0 ($N_{quinoline}$–C–C) and 134.7 (S–C–C) pm in **1c**.



S5b

Scheme S4

A CSD search afforded 5 hits for the bond pattern reported in formula **S6** (Refcodes: ANEQUG, ANERAN, ANERER, ANERIV, BUXXUP). Four of them (Refcodes: ANEQUG, ANERAN, ANERER, ANERIV) were not uniquely related to the bond pattern of formula **S6** (e.g. they corresponded to one of the likely resonance structures of the compound). No statistics on bond lengths could be made by using the single remaining hit (Refcode: BUXXUP).

4. Molecular electrostatic potential

3.1. Computational method

Geometry optimizations were carried out using Gaussian 09, with the hybrid meta density functional M06-2X and the 6-311G(d) basis [5]. The WFA-SAS code was used to compute the electrostatic potential on 0.001 au cationic surfaces [6].

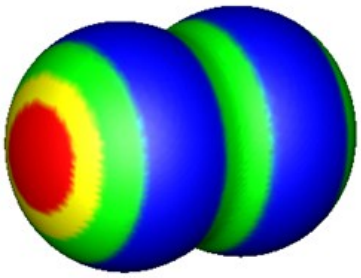


Figure S4

Computed electrostatic potential on the 0.001 au molecular surface of diiodine. Color ranges, in kcal mol^{-1}: red, more positive than 20; yellow, between 20 and 10; green, between 10 and 0; blue, less than 0 (negative). The most positive potentials ($V_{s,max}$) are 32 (red) at the ends of the molecule; the most negative ($V_{s,min}$) are -4 (blue) on the sides.

5. References

[1] Bruker, SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 1999.

[2] G. M. Sheldrick; SHELXL97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany, 1997.

[3] M. A. Flatkenm; M. J. Huber; G. J. Reiss, *Z. Kristallogr. - New Cryst. Struct.* 2014, **229**, 423–424; doi:10.1515/ncrs-2014-9031.

[4] Y. V. Nelyubina; M. Yu. Antipin; D. S. Dunin; V. Yu. Kotov; K. A. Lyssenko, *Chem. Commun.* 2010, **46**, 5325–5327; doi:10.1039/c0cc01094d.

[5] M. J. Frisch; G. W. Trucks; H. B. Schlegel; G. E. Scuseria; M. A. Robb *et al*., Gaussian 09, Revision A.1; Gaussian, Inc., Wallingford, CT, 2009.

[6] F. A. Bulat; A. Toro-Labbé; T. Brinck; J. S. Murray; P. Politzer J. Mol. Model. 2014, **16**, 1679–1691.