Selective Formation of Inter- and Intramolecular A-D-A π-π Stacking: Solid-State Structures of Bis(pyridiniopropyl)benzenes

Take-aki Koizumi,[a] Kanako Tsutsui,[a] and Koji Tanaka*[a]

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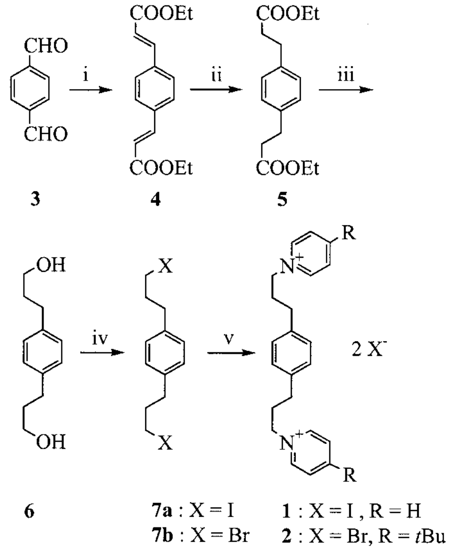
The synthesis and molecular structures of bis(pyridiniopropyl)benzene derivatives, $[1,4\text{-}(4\text{-R-}C_5H_4N^+CH_2CH_2CH_2)_2\text{-}C_6H_4][X^-]_2$ (**1**, R = H, X = I; **2**, R = *t*Bu, X = Br) have been investigated. Compound **1** adopts a linear structure in the solid state and the crystal packing geometry can be defined as isolated triplets formed by the phenylene ring of one molecule and two pyridinium rings of two neighboring molecules. In contrast, compound **2** has an S-shaped arrangement, and an intramolecular acceptor–donor–acceptor triplet is formed among the central phenylene ring and two terminal pyridinium rings in the same molecule. Such a distinct difference in the crystal structures of **1** and **2** can be ascribed to the substituent on the pyridinium unit. The steric repulsion of the bulky *tert*-butyl group hinders intermolecular A-D-A π-π stacking.

Introduction

The π-π stacking of aromatic rings plays a key role in non-covalent intermolecular interactions, and molecular associations utilizing π-π stacking have been well documented in organic,[1] biological,[2] and polymer chemistry.[3] Molecules which have both π-donor and π-acceptor aromatic rings connected by flexible chains are expected to show unique molecular structures and novel physicochemical properties. For example, supramolecules such as (pseudo)-rotaxanes[4] and catenanes[5] have been prepared by taking advantage of π-π interactions between π-electron-deficient and electron-rich aromatic compounds. Furthermore, 7,7,8,8-tetracyanoquinodimethane (TCNQ) bearing two 3-phenylpropyl groups[6] in the 2,5-positions forms intermolecular D-A-D π-π stacking among the central TCNQ unit and terminal phenyl groups of two neighboring molecules, while a similar compound having two benzyl groups[7] in place of the 3-phenylpropyl moiety exhibited no π-π interactions in the solid state. Two neighboring aromatic rings tend to associate through π-π stacking, but the main factor which regulates inter- and intra-molecular π-π stacking still remains unclear. In this study, we have examined the steric influence of bulky substituents on the formation of intra- and inter-molecular π-π stacking. We synthesized two bis(pyridiniopropyl)benzene derivatives, namely 1,1′-(1,4-phenylenedi-3,1-propanediyl)bispyridinium diiodide (**1**) and the *tert*-butyl-substituted compound 4,4′-di-*tert*-butyl-1,1′-(1,4-phenylenedi-3,1-propanediyl)bispyridinium dibromide (**2**) and their crystal structures have been investigated. The selective inter- and intra-molecular A-D-A π-π stacking between phenylene rings and two pyridinium rings was observed.

Results and Discussion

Compounds **1** and **2** were prepared using a five-step procedure shown in Scheme 1. Telephthalaldehyde (**3**) was



Scheme 1. (i) NaH, $(C_2H_5O_2)P(O)CH_2COOEt$, benzene, 60 °C, 72 h; (ii) $NiCl_2 \cdot 6\ H_2O$, $NaBH_4$, EtOH, 6 h; (iii) $LiAlH_4$, THF, 3.5 h; (iv) (**7a**), 55% aq HI, 100 °C, 16 h; (**7b**), 48% HBr, 100 °C, 2 h; (v) (**1**), pyridine, MeCN; (**2**), 4-*tert*-butylpyridine, MeCN

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[a] Institute for Molecular Science, CREST, Japan Science and Technology Corporation (JST),
38 Nishigonaka, Myodaiji, Okazaki, Aichi 444-8585, Japan
Fax: (internat.) + 81-564-55-5245
E-mail: ktanaka@ims.ac.jp

transformed into the α,β-unsaturated ester **4** by the Horner−Emmons reaction with $(EtO)_2P(O)CH_2CO_2Et$ and NaH.[8] The unsaturated bond of **4** was reduced with $NiCl_6\cdot 6H_2O/NaBH_4$ in ethanol to give the diester **5** in high yield.[9] Reduction of **5** with $LiAlH_4$ produced the diol **6**, which was then converted into the corresponding dihalide **7** by reaction with 55% hydroiodic acid (for dihalide **7a**) or 48% hydrobromic acid (for dihalide **7b**)[10]. Figure 1 shows the molecular structure of **7a** determined from an X-ray crystallographic study, and selected bond lengths and angles are summarized in Table 1. Treatment of **7** with excess pyridine in acetonitrile afforded bis(pyridinium) **1** and **2** in moderate yields.

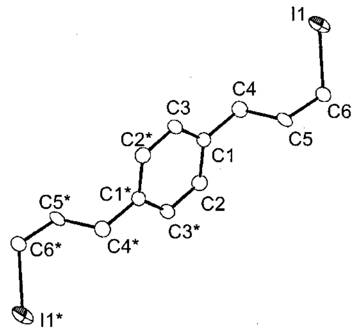


Figure 1. ORTEP diagram of **7a** with 50% thermal ellipsoids. Hydrogen atoms omitted for clarity

Table 1. Selected bond lengths [Å] and angles [deg] in 1, 2, and 7a

	1	**2**	**7a**
C1−C2	1.391(6)	1.385(4)	1.407(7)
C1−C3	1.393(7)	1.400(4)	1.389(8)
C2−C3*	1.387(7)	1.388(5)	1.398(8)
C1−C4	1.518(7)	1.570(4)	1.522(8)
C4−C5	1.512(7)	1.538(4)	1.522(7)
C5−C6	1.527(7)	1.522(4)	1.513(8)
N1−C7	1.349(6)	1.348(4)	
N1−C11	1.359(6)	1.352(4)	
C7−C8	1.367(8)	1.381(4)	
C8−C9	1.378(8)	1.392(4)	
C9−C10	1.383(8)	1.405(4)	
C10−C11	1.362(8)	1.374(4)	
C9−C12		1.523(4)	
I1−C6			2.161(6)
C1−C4−C5	115.7(4)	115.6(3)	114.4(4)
C4−C5−C6	108.0(4)	114.7(3)	114.7(5)
N1−C6−C5	111.5(4)	112.8(2)	

Single crystals of **1** and **2** suitable for X-ray crystallography were grown from methanol solutions into which diethyl ether vapor was allowed to slowly diffuse. Figure 2 depicts the molecular structures of **1** and **2** determined from the X-ray diffraction studies and selected bond lengths and angles are summarized in Table 1.[11] In **1**, two alkyl chains linked to the *para*-position of the phenylene group are in a linear fashion. The dihedral angle between the central phenylene ring and a pyridine ring is approximately perpendicular [104.0(1)°], and two pyridine rings are situated in a *trans* conformation with respect to the central phenyl ring. The crystal packing geometry of **1** shows intermolecular π-π stacking between the central phenylene ring and two neighboring pyridine rings with formation of A-D-A triplets (Figure 3). The centroid-centroid π-stacking distance is 3.695(7) Å, which is typical of aromatic-aromatic face-to-face π-π stackings.[1g] This crystal packing is similar to that of 2,5-bis(3-phenylpropyl)TCNQ,[7] but different from that of the bis(pyridinium) compound, 1,1′′-[1,4-phenylenebis(oxy-2,1-ethanediyl)]bis(4,4′-bipyridinium), which has a similar molecular framework to **1**.[12]

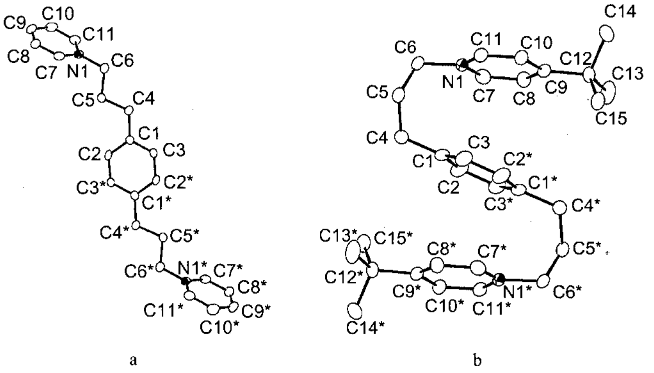


Figure 2. ORTEP diagrams of the cationic parts of **1** and **2** with 50% thermal ellipsoids. Hydrogen atoms omitted for clarity

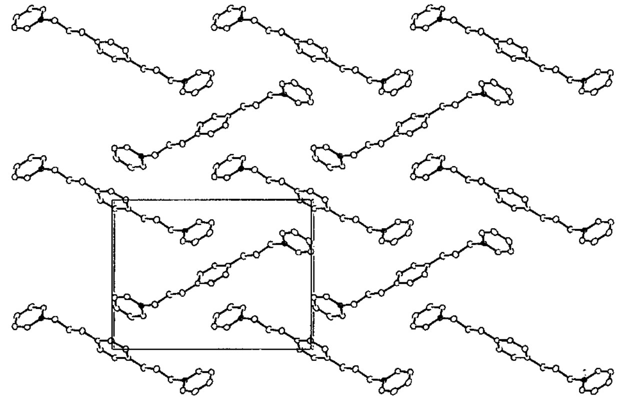


Figure 3. Packing diagram for **1**. Hydrogen and iodine atoms omitted for clarity

A distinct difference was found between the crystal structures of **1** and **2**. The latter has a folded S-shape conformation (Figure 2, b). The terminal pyridine rings are tilted at 21.08(7)° with respect to the central phenylene ring. The bond angle C4−C5−C6 in **2** is 114.7(3)° which is ca. 7° more acute than that of 108.0(4)° in **1**. The centroid-centroid distance between these two aromatic rings of 3.644(5) Å is longer than those observed in [3$_n$]cyclophanes such as [3$_2$]cyclophane (3.29−3.31 Å)[13] and [3$_4$](1,2,4,5)cyclophane (3.054 Å),[14] but close to the intramolecular π-π stacking distances between the pyridine and pyrazine rings in the polymeric Ag^I complexes, $[Ag_3(L)_2](NO_3)_3$ [3.42 and 3.61 Å, L = 2,6-bis(2-pyridylmethylsulfanylmethyl)pyrazine],[15a] $\{[Ag(L')]ClO_4\}_\infty$ [3.49 Å, L′ = 2,5-bis(2-pyridylmethylsulfanylmethyl)pyrazine][15b] and $\{[Ag_2(L')](NO_3)_2\}_\infty$

[3.59 and 3.61 Å, or 3.81 and 3.51 Å (isomers)].[15c] The pyridine and pyrazine rings in the aforementioned Ag^I complexes are accessible to each other due to the coordination of their nitrogen donor atoms to the Ag^I centers.

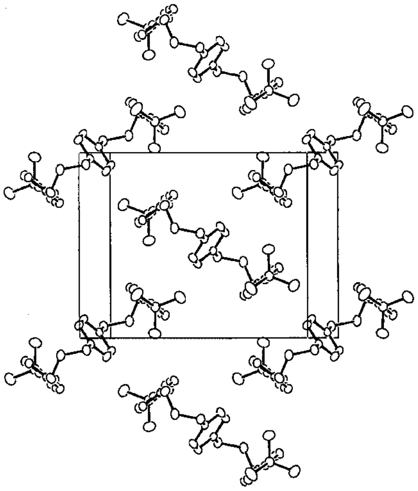


Figure 4. Packing diagram for **2**. Hydrogen and bromine atoms omitted for clarity

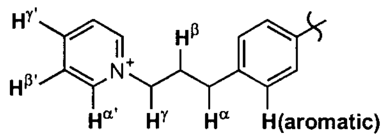
The crystal packing of **2** is shown in Figure 4. The π-π stacking layers between one molecule and its neighbor are mutually perpendicular to each other, indicating a negligibly small intermolecular π-π interaction between neighboring molecules in the solid state. The distance between H2 (attached to C3 carbon) and the pyridinium rings of neighboring molecules is 3.014(3) Å (av.), suggesting the presence of a σ-π interaction between them. The difference in the crystal conformations of **1** and **2**, therefore, can be related to the substituent on the pyridinium ring. Taking into account that **1** and **2** contain two pyridinium units in each molecule, both compounds should prefer linear structures in order to avoid Coulombic repulsions between the two cationic groups. Indeed, **1** has a linear conformation with intermolecular A-D-A π-π stacking between a phenylene ring of one molecule and two pyridinium rings of two neighboring molecules. In contrast, the bulky *tert*-butyl group at the *para*-position of the pyridinium ring apparently blocks the approach of a phenylene group of the neighboring molecule. As a result, two pyridinium and phenylene groups in **2** form intramolecular A-D-A π-π stacking. Flexible sulfonic ester derivatives of 2-(6-iodo-1,3-benzodioxol-5-yl)ethyl-4-nitrobenznenesulfonate have been shown to contain both inter- and intra-molecular π-π stacking in the solid state,[16] while two phenyl groups of *N*,*N*′-dimethyl-*N*,*N*′-diphenylguanidines were selectively situated in a *cis*-position on the rigid CN_3 framework and exhibited intramolecular π-π stacking with a distance of 3.77−3.84 Å.[17] Thus, fixation of neighboring aromatic rings into a relatively rigid framework appears to be a pre-requisite for the design of selective intramolecular π-π stacking in the solid state. It is also worthy of note that the pyridinium and phenylene groups of **1** and **2** are linked through a flexible propylene chain. The inter- and intra-molecular π-π stacking formations in **1** and **2**, respectively, can be simply explained by the blocking of intermolecular associations as a result of the steric hindrance of the *tert*-butyl group on the pyridinium ring.[18]

Conclusion

1,4-Bis(pyridiniopropyl)benzene derivatives **1** and **2** have been prepared and their crystal structures determined. The crystal structures of **1** and **2** exclusively involve inter- and intra-molecular π-π stacking, respectively. Coulombic repulsions between two cationic pyridinium rings in **1** resulted in a "linear" conformation with intermolecular A-D-A π-π stacking between the central phenylene ring and two terminal pyridinium units of two neighboring molecules. Conversely, **2** has a folded S-shape conformation with intra-molecular A-D-A π-π stacking between the central phenylene ring and two terminal pyridinium units in the same molecule. The sterically bulky *tert*-butyl substituents in the pyridinium rings effectively block intermolecular π-stacking with a phenylene group of any neighboring molecules. Thus, careful selection of the substituent on the pyridinium group enabled selective inter- and intra-molecular A-D-A π−π stacking in the solid state.

Experimental Section

Measurements and Materials: ^1H, $^{13}C\{^1H\}$, and ^1H-^1H COSY NMR spectra were recorded on a JEOL GX 500 FT NMR spectrometer. ESI-MS spectra were obtained on a Shimadzu LCMS-2010 spectrometer. Electronic spectra were recorded on a Shimadzu UV/Vis-NIR scanning spectrometer UV-3100PC. Elemental analyses were carried out at the Molecular Scale Nano-Science Center of IMS. $(EtO)_2P(O)CH_2CO_2Et$ was purchased from TCI. Although the preparations of compounds **4**,[19] **5**,[20] **6**[21] and **7a**[22] have been reported previously, we used modified methods or other routes for the syntheses of these compounds (vide infra). The numbering scheme for protons is shown in Scheme 2.



Scheme 2

Diethyl 3,3′-(1,4-Phenylene)bis(2-propenoate) (4): To a suspension of sodium hydride (1.44 g, 36.0 mmol) in anhydrous benzene (120 mL) was added $(EtO)_2P(O)CH_2CO_2Et$ (6.71 g, 30.0 mmol) at 30−35 °C under an N_2 atmosphere. After stirring at 30−35 °C for 1 h, a solution of telephthalaldehyde (2.01 g, 15.0 mmol) in anhydrous benzene (50 mL) was added at 20−30 °C. The reaction mixture was then stirred at 60 °C for 3 days, and filtered. The filtrate was evaporated to dryness in vacuo to yield 2.73 g (67%). ^1H NMR (500 MHz in $CDCl_3$): δ = 7.67 (d, J = 15.9 Hz, 2 H, H^{α}), 7.54 [s, 4 H, H(aromatic)], 6.47 (d, J = 16.1 Hz, 2 H, H^{β}), 4.28 (q, J = 7.1 Hz, 4 H, CH_2CH_3), 1.35 (t, J = 7.1 Hz, 6 H, CH_2CH_3).

Diethyl 3,3′-(1,4-Phenylene)bis(propanoate) (5): To an ethanolic solution of **4** (2.51 g, 9.16 mmol) was added $NiCl_6 \cdot 6H_2O$ (0.88 g, 3.72 mmol) and $NaBH_4$ (2.79 g, 73.8 mmol). After stirring the reaction mixture at room temperature for 6 h, the solvent was removed by evaporation. The residue was dissolved in Et_2O, and the resultant solution was washed with H_2O (3 times), dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated and the residue was dried in vacuo to yield 2.31 g (91%) of **5** as a colorless oil. ^{1}H NMR (500 MHz in $CDCl_3$): $\delta = 7.12$ [s, 4 H, H(aromatic)], 4.12 (q, $J = 7.1$ Hz, 4 H, CH_2CH_3), 2.91 (t, $J = 7.6$ Hz, 4 H, H^{α}), 2.60 (t, $J = 7.6$ Hz, 4 H, H^{β}), 1.23 (t, $J = 7.1$ Hz, 6 H, CH_2CH_3).

3,3′-(1,4-Phenylene)bis(propanol) (6): To a suspension of lithium aluminum hydride (2.46 g, 64.8 mmol) in anhydrous THF (50 mL) was added a THF solution (15 mL) of **5** (2.31 g, 8.31 mmol) at 0 °C under N_2. The reaction mixture was stirred at room temperature for 3.5 h and was then added to water (50 mL) at 0 °C, followed by extraction with Et_2O (3×50 mL). The extracts were washed with water three times, then dried with anhydrous Na_2SO_4, and the solvent was removed by evaporation to yield 1.50 g (81%) of **6** as a colorless solid. ^{1}H NMR (500 MHz in $CDCl_3$): $\delta = 7.13$ [s, 4 H, H(aromatic)], 3.68 (t, $J = 6.4$ Hz, 4 H, H^{γ}), 2.68 (t, $J = 7.6$ Hz, 4 H, H^{α}), 1.88 (m, 4 H, H^{β}), 1.27 (br. s, 2 H, OH).

1,4-Bis(3-iodopropyl)benzene (7a): Diol **6** (0.312 g, 1.23 mmol) was suspended in 55% aqueous HI (10 mL) and the mixture heated to reflux for 16 h under N_2. Although the starting material did not dissolve, the solid gradually turned into a dark purple oil and finally became an emulsion. The emulsion was cooled to room temperature, Et_2O was added, and the acid was extracted with saturated aqueous $NaHCO_3$ (3×40 mL). The organic layer was dried with anhydrous Na_2SO_4 and the solvents evaporated in vacuo to give 0.42 g (76%) of **7a**. ^{1}H NMR (500 MHz in $CDCl_3$): $\delta = 7.12$ [s, 4 H, H(aromatic)], 3.17 (t, $J = 6.8$ Hz, 4 H, H^{γ}), 2.70 (t, $J = 7.1$ Hz, 4 H, H^{α}), 2.12 (tt, $J = 7.1$, 6.8 Hz, 4 H, H^{β}). $C_{12}H_{16}I_2$ (414.07): calcd C 34.81, H 3.89; found C 35.21, H 3.89%.

1,4-Bis(3-bromopropyl)benzene (7b): Diol **6** (0.532 g, 2.74 mmol) was suspended in 48% aqueous HBr (18 mL) and the mixture was heated to reflux for 2 h under N_2. Although the starting material did not dissolve, the solid gradually turned into a dark purple oil which finally became an emulsion. The emulsion was cooled to room temperature, CH_2Cl_2 was added, and the acid was extracted with a saturated aqueous $NaHCO_3$ solution (3×40 mL). The organic layer was dried with anhydrous Na_2SO_4 and the solvents evaporated in vacuo to give 0.71 g (81%) of **7b**. ^{1}H NMR (500 MHz in $CDCl_3$): $\delta = 7.13$ [s, 4 H, H(aromatic)], 3.39 (t, $J = 6.6$ Hz, 4 H, H^{γ}), 2.75 (t, $J = 7.6$ Hz, 4 H, H^{α}), 2.15 (tt, $J = 7.6$, 6.6 Hz, 4 H, H^{β}).

1,1′-(1,4-Phenylenedi-3,1-propanediyl)bis(pyridinium) Diiodide (1):[23] To an acetonitrile solution of **7a** (0.202 g, 0.49 mmol) was added pyridine (0.5 mL). The reaction mixture was stirred at room temperature for 3 days during which time a white precipitate formed. The resultant solid was collected by filtration and dried in vacuo to give 0.154 g (63%) of **1** as a colorless powder. ^{1}H NMR (500 MHz in CD_3OD): $\delta = 8.99$ (d, $J = 5.5$ Hz, 4 H, $H^{\alpha\prime}$), 8.58 (t, $J = 7.5$ Hz, 2 H, $H^{\gamma\prime}$), 8.09 (t, $J = 7.0$ Hz, 4 H, $H^{\beta\prime}$), 7.16 [s, 4 H, H(aromatic)], 4.68 (t, $J = 7.5$ Hz, 4 H, H^{γ}), 2.72 (t, $J = 7.0$ Hz, 4 H, H^{α}), 2.35 (tt, $J = 7.5$, 7.0 Hz, 4 H, H^{β}). MS [ESI(MeOH)]: $m/z = 159$ $[M - I]^+$. $C_{22}H_{26}I_2N_2$ (572.26): calcd. C 46.17, H 4.58, N 4.90; found C, 45.77, H 4.49, N 4.68%.

4,4′-Di-(*tert*-butyl)-1,1′-(1,4-phenylenedi-3,1-propanediyl)bis-(pyridinium) Dibromide (2): To an acetonitrile solution of **7b** (0.707 g, 2.21 mmol) was added 4-*tert*-butyl pyridine (3.2 mL). The reaction mixture was stirred at room temperature for 3 days during which time a white precipitate formed. The resultant solid was collected by filtration and dried in vacuo to give 1.02 g (78%) of **2** as a colorless powder. ^{1}H NMR (500 MHz in CD_3OD): $\delta = 8.84$ (d, $J = 6.5$ Hz, 4 H, $H^{\alpha\prime}$), 8.08 (d, $J = 6.5$ Hz, 4 H, $H^{\beta\prime}$, 7.15 [s, 4 H, H(aromatic)], 4.61 (t, $J = 7.5$ Hz, 4 H, H^{γ}), 2.72 (t, $J = 7.5$ Hz, 4 H, H^{α}), 2.33 (tt, $J = 7.5$ Hz, 4 H, H^{β}), 1.42 (s, 9 H, *t*Bu). MS [ESI(MeOH)]: $m/z = 215$ $[M - Br]^+$. $C_{30}H_{42}Br_2N_2 \cdot 0.5H_2O$ (599.49): calcd C 60.10, H 7.17, N 4.67; found C 59.68, H 6.98, N 4.66%.

X-ray Crystallographic Studies: Crystals for the X-ray analyses were obtained as described previously. Suitable crystals were mounted on grass fibers or sealed in thin-walled glass capillaries. Data collections for **1**, **2**, and **7a** were performed at −100 °C on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.7107$ Å). All structures were solved using the teXsan software package. Atomic scattering factors were obtained from the literature.[24] Refinements were performed anisotropically for all non-hydrogen atoms using the full-matrix least-squares method. Hydrogen atoms were included from the geometry of the molecules and $\Delta\rho$ maps. During refinement their parameters were fixed in **2** and **7a**, and were refined isotropically in **1**. The residual electron densities were of no chemical significance. Crystal data and processing parameters are summarized in Table 2. CCDC-209594 (**1**), -209595 (**2**), and -209596 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.sc.uk].

Table 2. Crystal data and details of the structure refinements of **1**, **2**, and **7a**

Compound	1	2	7a
Empirical formula	$C_{22}H_{26}N_2I_2$	$C_{30}H_{42}N_2Br_2$	$C_{12}H_{16}I_2$
Molecular mass	572.27	590.48	414.07
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a [Å]	5.704(1)	10.833(5)	22.22(2)
b [Å]	12.031(2)	10.580(5)	6.004(4)
c [Å]	16.243(3)	13.149(6)	10.246(8)
β [deg]	97.989(9)	109.301(5)	97.338(7)
V [Å^3]	1103.8(4)	1422(1)	1355(1)
Z	2	2	4
μ [cm^{-1}]	28.58	28.78	46.07
F(000)	556.00	612.00	776.00
$D_{\text{calcd.}}$ [g cm^{-1}]	1.722	1.379	2.028
Number of unique reflections	2348	3179	1575
Number of reflections measured	2348	3173	1401
Number of variables	157	415	64
R_{int}[a]	0.079	0.065	0.128
R_1	0.053	0.049	0.065
R	0.086	0.087	0.066
R_w	0.133	0.126	0.102

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$ data, $Rw = \Sigma[(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$. Weighting scheme $[\{\sigma(F_o)\}^2]^{1/2}$.

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