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The crystal and molecular structures of 1-naphthylphenyliodonium tetrafluoroborate and 1-naphthylphenyliodonium tetrakis(pentafluorophenyl)gallate †

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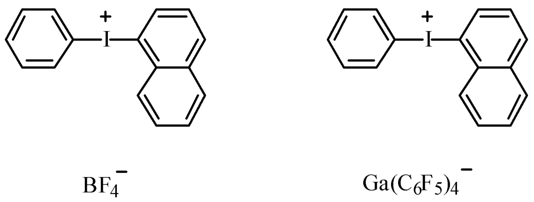
The X-ray structures of 1-naphthylphenyliodonium tetrafluoroborate **1** and 1-naphthylphenyliodonium tetrakis(pentafluorophenyl)gallate **2** are reported. Crystals of **1** are monoclinic, space group $P2(1)/c$, with unit cell dimensions $a = 11.8914(11)$, $b = 8.8699(9)$, $c = 14.4445\ (13)$ Å, $\beta = 90.944(4)°$, $Z = 4$, and $R = 0.0596$ for 8286 unique observed reflections. Crystals of **2** are monoclinic, space group $P2(1)/c$, with unit cell dimensions $a = 15.003(5)$, $b = 18.287(6)$, $c = 14.738(6)$ Å, $\beta = 115.436(13)°$, $Z = 4$, and $R = 0.0222$ for 8063 unique observed reflections. The iodonium cations of **1** exist as π-stacked dimers; however, those of **2** are monomeric.

1 Introduction

Diaryl iodonium salts have been extensively used as cationic photoinitiators in a wide range of applications because of their thermal stability and excellent initiating efficiency.[1] We previously reported and compared the photopolymerization of epoxides using some of these photoinitiators.[2a] We have also reported that iodonium tetrakis(pentafluorophenyl)gallates show the fastest rate of acid release.[3] These gallates are advantageous over other iodonium salts because of their excellent solubility in monomers and high photosensitivity.[4]

Since diphenyliodonium salts were first used as cationic photoinitiators in the 1970's, many studies have focused on the scope of their photochemistry.[5] Most commercial aromatic iodonium salts are phenyl or substituted phenyl, with absorptions concentrated below 300 nm. Upon laser flash photolysis of iodonium salts, several transient species formed, but it was difficult to interpret what they were.[6] The introduction of a naphthyl group will increase the absorption of such iodonium salts at longer wavelengths making it easier to identify transient species formed during photolysis. In this paper, we report the crystal and molecular structures, and packing of the iodonium salts **1** and **2** (Fig. 1). The photophysical studies of these compounds will be reported elsewhere.



1 **2**

Fig. 1 Iodonium salts **1** and **2**.

2 Results and discussion

The reaction of diacetoxyiodoarene with metalloarenes was employed to synthesize these compounds. The X-ray crystal structures of compounds **1** and **2** are shown in Fig. 2. To the best of our knowledge, this is the first report of the X-ray structure of a tetrakis(pentafluorophenyl)gallate iodonium salt photoinitiator.

Alcock[7] *et al.* reported that iodonium salts paired with halide anions invariably existed as dimers in the crystal, with the halide anion as the bridge atom. The packings of **1** and **2** are shown in Fig. 3(a) and (b), respectively. When paired with tetrafluoroborate, the cation of **1** also dimerized; however, the interaction in this case is through the naphthyl π-system, as shown in Fig. 3(c). That was not the case, however, with compound **2**. The absence of dimer aggregation in **2** may explain why iodonium salts paired with this anion have excellent solubility in nonpolar solvents. The two naphthyl rings and the two phenyl rings are parallel to each other in each case. The distance between the centers of the naphthyl planes is 3.63 Å. The distance between the centers of the iodonium cation and the tetrafluoroborate anion (3.576 Å) in **1** is much shorter than that between the centers of the iodonium cation and the tetrakis(pentafluorophenyl)gallate anion (5.57 Å) in **2**. Previously, we reported that the anion has an important effect on the reactivity of iodonium salts.[2] We suggest that it is the distance between the centers of the cation and the anion that is the key factor in this effect.

3 Experimental

3.1 X-Ray crystallography

Preliminary examination and data collection were carried out with Ag-Kα radiation in the case of **1** and Mo-Kα in the case of **2**, using a Bruker AXS SMART platform diffractometer.[8] Intensity data were collected using three different ϕ settings and 0.3° increment ω scans, $2\theta < 60.68°$ for **1** and $2\theta < 55.46°$ for **2**, which corresponds to more than a hemisphere of data. Data integration was carried out with SAINT,[9] and corrections for

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† Contribution no. 456 from the Center for Photochemical Sciences. Electronic supplementary information (ESI) available: colour version of Fig. 3. See http://www.rsc.org/suppdata/dt/b2/b202805k/

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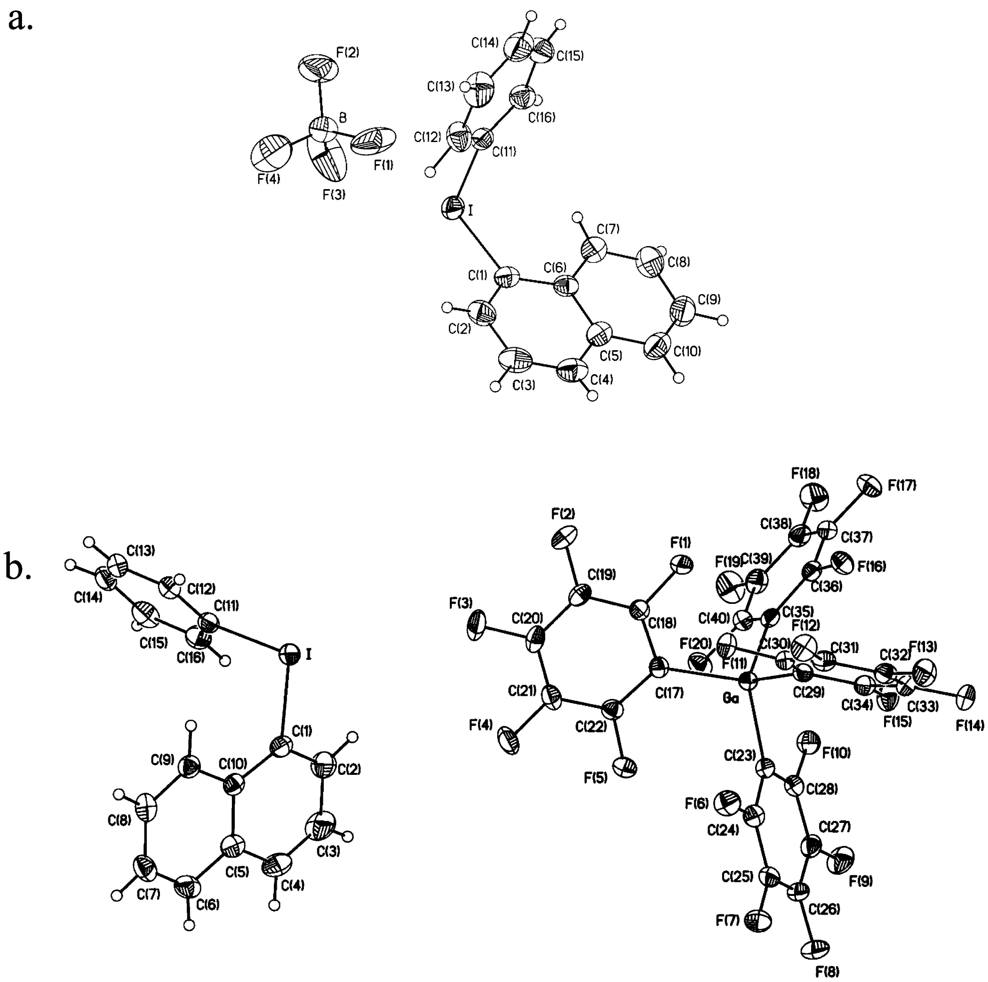

Fig. 2 ORTEP drawings (50% probability ellipsoids) of **1** (a) and **2** (b). Selected bond lengths (Å) and angles (°): I–C(1) 2.109(3), I–C(11) 2.106(2), C(11)–I–C(1) 97.36(9) in **1**. I–C(1) 2.107(2), I–C(11) 2.110(2), Ga–C(17) 2.0095(19), Ga–C(23) 2.0115(19), Ga–C(29) 2.0223(19), Ga–C(35) 2.0197(19), C(1)–I–C(11) 96.26(8), C(17)–Ga–C(23) 112.49(8), C(17)–Ga–C(35) 105.86(7), C(23)–Ga–C(35) 113.36(7), C(17)–Ga–C(29) 113.77(8), C(23)–Ga–C(29) 101.30(8), C(35)–Ga–C(29) 110.26(7) in **2**. Selected dihedral angles (°) in **2**: the dihedral angle between the mean plane of the ring containing C(17) [{C(18)C(17)C(22)}] and that including C(23) [{C(24)C(23)C(28)}] is 118.4, {C(18)C(17)C(22)} and {C(30)C(29)C(34)} 67.4, {C(18)C(17)C(22)} and {C(36)C(35)C(40)} 88.1, {C(30)C(29)C(34)} and {C(24)C(23)C(28)} 75.4, {C(30)C(29)C(34)} and {C(36)C(35)C(40)} 115.1, {C(24)C(23)C(28)} and {C(36)C(35)C(40)} 65.6.

absorption and decay were applied using SADABS.[9] The X-ray structures were determined by direct methods[10] and refinement was by full matrix least squares[11] on F^2 using all 8286 (for **1**) and 8063 (for **2**) unique data. The final refinement included anisotropic thermal parameters for non-hydrogen atoms with isotropic thermal parameters for all hydrogen atoms. The refinement converged to $wR_2 = 0.1259$ (for F^2, all data), $R_1 = 0.0454$ [F, 8286 reflections with $I > 2\sigma(I)$] in the case of **1**, and $wR_2 = 0.0561$, $R_1 = 0.0237$ in the case of **2**. The crystal data and experimental details are listed in Table 1. The molecular structures of compounds **1** and **2** are shown in Fig. 2.

CCDC reference numbers 178309 and 178310.

See http://www.rsc.org/suppdata/dt/b2/b202805k/ for crystallographic data in CIF or other electronic format.

3.2 Materials

All chemicals and solvents (Spectrophotometric Grade) were purchased from Aldrich Chemical Co. and used as received, unless otherwise noted. Lithium tetrakis(pentafluorophenyl)gallate was synthesized as previously reported.[11]

1-Diacetoxyiodonaphthlene. The title compound was synthesized from 1-iodonaphthalene and sodium peroxyborate-tetrahydrate ($NaBO_3 \cdot 4H_2O$) following a literature procedure.[12] To a stirred solution of 1-iodonaphthalene (2.54 g, 10 mmol) in 90 ml acetic acid held at 40–45 °C, $NaBO_3 \cdot 4H_2O$ (15.4 g, 0.1 mol) was added portionwise over 20 min. After stirring for 8 h, 100 ml water was added. The crude product was filtered off and washed with diethyl ether. After recrystallization from acetic acid, pure product was obtained (60%), mp 193 °C dec. ^{1}H-NMR (200 MHz, acetone-d_6, δ): 8.70 (d, J = 7.4 Hz, 1H, Ar H), 8.334 (d, J = 8.2 Hz, 1H, Ar H), 8.19 (d, J = 8.0 Hz, 1H, Ar H), 8.107 (d, J = 8.2 Hz, 1H, Ar H), 7.81–7.63 (m, 3H, Ar H), 1.817 [s, 6H, $(CH_3CO_2)_2$].

9-Diacetoxyiodophenanthrene. The title compound was synthesized from 9-iodophenanthrene and $NaBO_3 \cdot 4H_2O$ by the same procedure mentioned above. Yield: 68%; mp 199 °C dec. ^{1}H NMR (200 MHz, acetone-d_6, δ): 8.88 (s, 1H, Ar H), 8.78 (d, J = 7.4 Hz, Ar H), 8.22–8.17 (m, 1H, Ar H), 8.02 (d, J = 7.6 Hz, 1H, Ar H), 7.85–7.69 (m, 4H, Ar H), 1.94 (s, 6H, $(CH_3CO_2)_2$).

1-Naphthylphenyliodonium tetrafluoroborate (1). The title compound was synthesized following a literature procedure.[13] To a stirred solution of 0.744 g (2 mmol) 1-diacetoxyiodonaphthalene and 0.854 g (2 mmol) tetraphenyltin in 20 ml dichloromethane under argon, 0.51 ml (4 mmol) trifluoroboron diethyl etherate was added dropwise. The solution was stirred overnight and filtered. The filtrate was washed with 10 ml water, and the organic layer was evaporated to give a white solid. After recrystallization twice from acetone/chloroform, a pure pale yellow crystal was obtained (54%), mp 186–187 °C. ^{1}H-NMR (200 MHz, acetone-d_6, δ): 8.83 (d, J = 7.8 Hz, 1H), 8.32–8.25

Table 1 Crystal data and experimental details

Empirical formula	$C_{16}H_{12}BF_4I$	$C_{40}H_{12}F_{20}GaI$
Formula weight	417.97	1069.12
Temperature/K	150(1)	120(1)
Wavelength/Å	0.56086	0.71073
Crystal system, space group	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/c$
Unit cell dimensions	$a = 11.8914(11)$ Å, $\alpha = 90°$	$a = 15.003(5)$ Å, $\alpha = 90°$
	$b = 8.8699(9)$ Å, $\beta = 90.944(4)°$	$b = 18.287(6)$ Å, $\beta = 115.436(13)°$
	$c = 14.4445(13)$ Å, $\gamma = 90°$	$c = 14.738(6)$ Å, $\gamma = 90°$
Volume/Å^3	1523.3(3)	3651(2)
Z, Calculated density/Mg m^{-3}	4, 1.822	4, 1.945
Absorption coefficient/mm^{-1}	1.138	1.734
$F(000)$	808	2064
Crystal size/mm	0.20 × 0.25 × 0.18	0.48 × 0.45 × 0.25
θ range for data collection/°	1.35 to 30.24	4.07 to 27.73
Limiting indices	$-20 \le h \le 20$, $-15 \le k \le 14$, $-24 \le l \le 15$	$-17 \le h \le 18$, $-22 \le k \le 23$, $-18 \le l \le 18$
Reflections collected/unique	24408/8286 [R(int) = 0.0596]	34816/8063 [R(int) = 0.0222]
Refinement method	Full matrix least squares on F^2	Full matrix least squares on F^2
Data/restraints/parameters	8286/0/231	8063/0/607
Goodness-of-fit on F^2	1.007	1.101
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.1083$	$R_1 = 0.0237$, $wR_2 = 0.0561$
R indices (all data)	$R_1 = 0.1193$, $wR_2 = 0.1259$	$R_1 = 0.0250$, $wR_2 = 0.0568$
Largest diff. peak and hole/e Å^{-3}	2.004 and −1.173	0.350 and −0.682

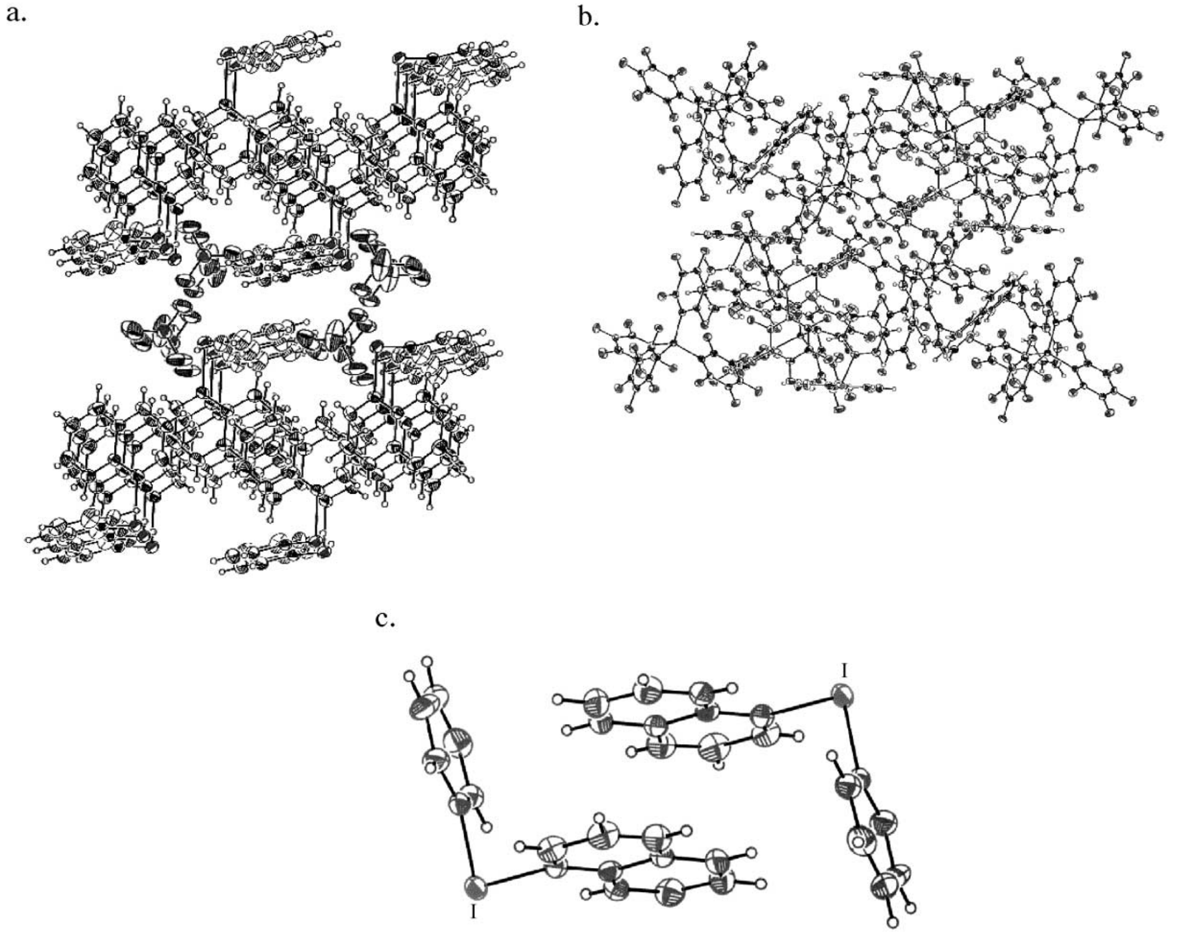

Fig. 3 (a) Packing of **1**; (b) packing of **2**; (c) dimerization of the cation of **1** as revealed by the X-ray measurements.

(m, 3 H), 8.05 (d, J = 8.2 Hz, 1H), 7.85–7.58 (m, 5H), 7.47 (t, J = 7.2 Hz, 1H). ^{13}C-NMR (acetone-d_6 50 MHz, δ): 137.5 (CH), 134.0 (CH), 133.5 (CH), 131.5 (CH), 131.1 (CH), 130.5 (C), 129.2 (CH), 128.7 (CH), 127.5 (CH), 127.2 (CH), 126.7 (CH), 115.4 (C), 112.4 (C). Anal. calcd for $C_{16}H_{12}IBF_4$: C, 45.98; H, 2.89; found: C, 46.04; H, 3.00%.

1-Naphthylphenyliodonium tetrakis(pentafluorophenyl)gallate (2). Compound **1** (0.21 g, 0.5 mmol) was mixed with lithium tetrakis(pentafluorophenyl)gallate (0.46 g, 0.5 mmol) in 10 ml dichloromethane. A white precipitate formed immediately. After stirring for 1 h, the solution was filtered and concentrated to yield crude product. After passage through a short silica gel column and recrystallization from chloroform–hexane, a pale yellow crystal was obtained (60%), mp 117–118 °C. ^{1}H-NMR (200 MHz, acetone-d_6, δ): 8.93 (d, J = 7.8 Hz, 1H), 8.43–8.37 (m, 4H), 8.15 (d, J = 8.2 Hz, 1H), 7.91–7.54 (m, 6H). ^{19}F-NMR (CDCl$_3$, δ): −118.9 (sm, 8F), −155.1(m, 4F), −160.6 (sm, 8F). Anal calcd. for $C_{40}H_{12}IGaF_{20}$ C, 44.94; H, 1.13; found: C, 44.86; H, 1.02%.

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