Photochemistry of Mesoionic Compounds. Photochemical Conversion of 5-Azido-1,3-diaryltetrazolium Salts to Novel Tricyclic Mesoions with a Tetrazolo[1,5-*a*]benzimidazole Skeleton

Shuki Araki*, Hiromi Hattori, Noriyuki Shimizu, Koji Ogawa,
Hatsuo Yamamura and Masao Kawai

Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

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A new type of tetrazolium-5-amide mesoions **2** with a tricyclic tetrazolo[1,5-*a*]benzimidazole skeleton has been synthesized *via* photolysis of 5-azido-1,3-diaryltetrazolium salts **1**.

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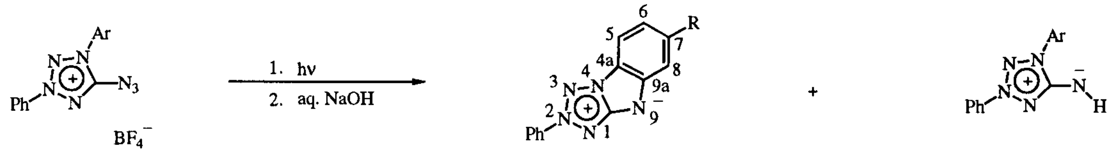
Introduction.

Although extensive studies on the chemistry of mesoionic compounds have been carried out, there are relatively few reports on the photochemistry of mesoions and mesoion-related compounds [1]. We recently reported the synthesis of 5-azido-1,3-diaryltetrazolium salts **1** [2], and this compound is expected to be a good precursor to the unique nitrene possessing a tetrazolium ring *via* photodecomposition [3]. Intramolecular cyclization of *ortho*-substituted arylnitrenes is a well-established procedure for the synthesis of carbazoles and other nitrogen-containing heterocycles [4]. Here we describe the photochemical reaction of **1** which gives, *via* unique 1,3-diaryltetrazolium-bearing nitrenes, novel tricyclic mesoions with a tetrazolo[1,5-*a*]benzimidazole skeleton.

Results and Discussion.

Irradiation of **1a** in methanol with a high-pressure mercury lamp led to a complete consumption of **1a** within 80 minutes. Base treatment and column chromatographic purification of the photolysate gave a new mesoionic compound **2a** as stable yellow crystals in 20% yield, together with known tetrazolium-5-amide **3a** (23%) (Scheme 1). Compound **2a** has the molecular formula $C_{13}H_9N_5$, confirmed by mass and elemental analyses, indicating the loss of nitrogen and tetrafluoroboric acid from **1a**. The coincidence of the longest wave-length absorption of **2a** (λ_{max} 393 nm) with that of **3a** (λ_{max} 396 nm) as well as the reversible protonation/deprotonation nature of **2a** suggest that this compound is also a tetrazolium-5-amide derivative. The two broad doublets at δ 7.90 and 8.05 ppm and the two doublets of doublet with further smaller couplings at δ 7.32 and 7.56 ppm in the ^{1}H nmr spectrum support the presence of the *ortho*-disubstituted benzene ring. The formation of the tricyclic tetrazolo[1,5-*a*]benzimidazole structure of **2a** is rationalized *via* the insertion of the intermediate nitrene to an *ortho*-CH bond of the N^1-phenyl group. Trace amounts of tripolar compound **4** and olate **5** were also isolated from the photolysate mixture. Compound **4** is the condensation product of **1a** and **3a**, and compound **5** is considered to be formed *via* a hydrolysis of **1a** [2]. Results in different solvents with or without additives are summarized in Table 1. In acetonitrile, the yield of **2a** increased to 35%, but compound **3a** did not form in this solvent (entry 2). Interestingly, considerable amount (30% yield) of acetanilide was also isolated from the reaction mixture. In order to investigate the formation of the acetanilide; *i.e.*, whether it originates from the 1-phenyl or 3-phenyl group in **1a**, 5-azido-3-phenyl-1-tolyltetrazolium salt **1b** was subjected to irradiation (entry 3).

Scheme 1



1a Ar = Ph
b *p*-Tol
c Mes

2a R = H
b Me

3a Ar = Ph
b *p*-Tol
c Mes

Table 1

Photochemical Reaction of 5-Azidotetrazolium Salt [a]

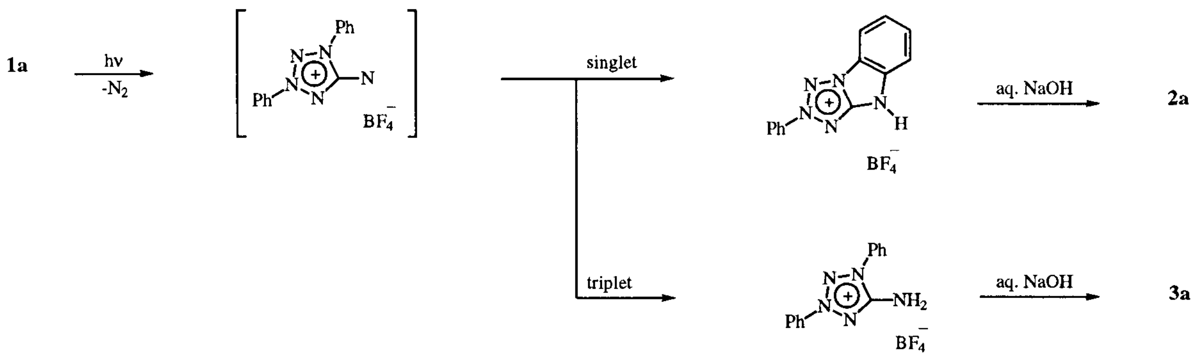
Entry	1	Additive	Products (Yield/%)
1	**1a**	—	**2a** (20), **3a** (23), **4** (1), **5** (2)
2 [b]	**1a**	—	**2a** (35), acetanilide (30)
3 [b]	**1b**	—	**2b** (22), acetanilide (12), *p*-acetotoluide (12)
4	**1a**	acetophenone	**3a** (72)
5	**1a**	pyrene	**2a** (8), **3a** (15), **4** (16), **5** (2), **6** (7)
6	**1a**	anthracene	**2a** (3), **3a** (26), **7** (13)
7	**1c**	—	**3c** (56)

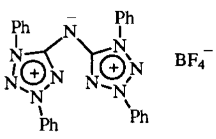
[a] All reactions were carried out in methanol, unless otherwise stated; [b] In acetonitrile.

Almost equimolar amounts of acetanilide and *p*-acetotoluide were obtained (total 23%), together with the tricyclic mesoion **2b** (22% yield). At present the reaction mechanism for the formation of these amides is not clear, but their formation must involve the fragmentation of the tetrazolium ring and the coupling with the solvent acetonitrile.

When the photolysis of **1a** in methanol was carried out in the presence of the triplet sensitizer acetophenone, the formation of **2a** was completely suppressed and **3a** was obtained exclusively in good yield (72%) (entry 4). This fact supports that **2a** is a singlet nitrene-derived product, whereas **3a** is formed *via* the triplet state [3] (Scheme 2). Pyrene and anthracene are known as triplet quenchers and singlet promoters [5]. The reactions with these additives, however, gave increased amounts of **3a** (entries 5 and 6). Hence, these polycyclic aromatics do not act as effective triplet quenchers in this reaction. Small amounts of tetrazolium amides **6** and **7** were isolated and these compounds are considered to be insertion products of the singlet nitrene to the polycyclic hydrocarbons. The structure of **6** was confirmed by direct comparison with an authentic sample alternatively prepared from 1-aminopyrene and 5-chloro-1,3-diphenyltetrazolium salt. The azidotetrazolium salt **1c** bearing a mesityl group at the 1-position was expected to give **8** *via* benzylic hydrogen abstraction from an *ortho*-methyl group by the triplet nitrene [6]. However, only amide **3c** was isolated in 56% yield and no trace of **8** was obtained from this reaction (entry 7). Pyrolysis of azide **1a** was undertaken in connection with the photolysis. Compound **1a** was heated at 200° for 30 min-

Scheme 2





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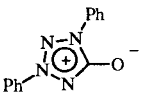

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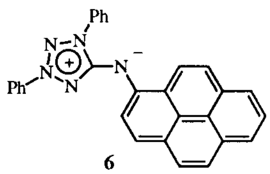

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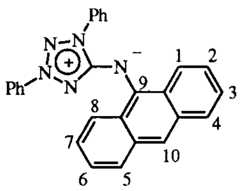

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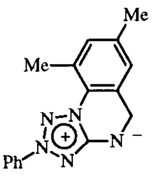

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utes *in vacuo*. The decomposition occurred gently with evolution of nitrogen. However, a large amount of resinous substance was formed and only modest yield (<10%) of **2a** was isolated from the pyrolysate.

In summary, photolytic behavior of 5-azido-1,3-diaryltetrazolium salts have been examined, and the unique tricyclic mesoions with a tetrazolo[1,5-*a*]benzimidazole skeleton have been synthesized. These compounds can be classified as heteropentalene mesomeric betaines [7] and have never been prepared thus far. The present results demonstrate that photochemical conversion of mesoions and mesoion-related compounds provides a useful tool for the construction of new heterocyclic systems which are difficult to synthesize by other conventional methods. Further studies on photochemical reactions of a series of tetrazolium mesoions are now in progress.

EXPERIMENTAL

The melting points were determined with a hot-stage apparatus and are uncorrected. The ir spectra were taken with potassium bromide discs with a JASCO A-102 instrument. The ^1H and ^{13}C nmr spectra were run with a Varian Gemini 200 (200 MHz and 50 MHz, respectively) and referenced using either the residual non-deuterated solvent or tetramethylsilane. The J values are given in Hz. Electronic spectra were measured on a Hitachi U-3500 spectrophotometer. Mass spectra were measured with a Hitachi M-2000 instrument. Elemental analyses were performed at Elemental Analysis Centre of Kyoto University. Column chromatography was carried out on 3-aminopropylsilane-modified silica gel (Fuji Silysia Chemical, NH-DM 1020). For photochemical reactions, a Riko Kagaku Sangyo UVL-100HA-100P apparatus was used.

1-Mesityl-4-phenylthiosemicarbazide.

A mixture of mesitylisothiocyanate [8] (1.2 g, 7.0 mmoles) and phenylhydrazine (0.69 ml, 7.0 mmoles) in ethanol (25 ml) was heated at reflux for 2 hours. The reaction mixture was cooled to room temperature, and the resulting precipitate was filtered to give a crude product (1.6 g). Recrystallization from ethanol gave pure 1-mesityl-4-phenylthiosemicarbazide (1.5 g, 74%), colorless crystals, mp 163-164° (ethanol); ir 3350, 3300, 3160, 2970, 1600, 1530, 1490, 1372, 1338, 1300, 1262, 1230, 1210, 1154, 1110, 1024, 908, 882, 858, 750, 766, 720 and 692 cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.08 (6H, s, *o*-Me), 2.21 (3H, s, *p*-Me), 6.78-6.82 (5H, m, *o*- and *p*-H of Ph and *m*-H of Mes), 7.23 (2H, t, J = 7.9, *m*-H of Ph), 8.06 (1H, br s, NH), 9.31 (1H, br s, NH) and 9.51 (1H, br s, NH).

Anal. Calcd. for $C_{16}H_{19}N_3S$ (285.41): C, 67.33; H, 6.71; N, 14.72. Found: C, 67.42; H, 6.75; N, 14.55.

1-Mesityl-3-phenyltetrazolium-5-olate.

This compound was prepared according to the literature method [9]. 1-Mesityl-4-phenylthiosemicarbazide (1.2 g, 4.1 mmoles) was suspended in ethanol (60 ml) and concentrated hydrochloric acid (1.5 ml) was added. The mixture was cooled and aqueous sodium nitrite (0.42 g) in water (3 ml) was added slowly below 5°. The mixture was stirred for 1 hour and then filtered. The filtrate was made alkali with aqueous sodium hydroxide (10 *N*, 2.3 ml), heated at reflux for 1 hour, and then cooled to room temperature. The mixture was poured into water (400 ml) and the resulting precipitate was filtered, washed with water, and dried to yield the olate (0.96 g, 83%), colorless crystals, mp 163-164° (acetonitrile); ir: 1700, 1480, 1462, 1348, 1330, 1300, 1280, 1234, 1080, 940, 856, 762, 744 and 678 cm^{-1}; ^1H nmr (chloroform-d): δ 2.19 (6H, s, *o*-Me), 2.36 (3H, s, *p*-Me), 7.03 (2H, s, *m*-H of Mes), 7.55-7.60 (3H, m, *m*- and *p*-H of Ph) and 8.11-8.16 (2H, m, *o*-H of Ph).

Anal. Calcd. for $C_{16}H_{16}N_4O$ (280.33): C, 68.55; H, 5.75; N, 19.99. Found: C, 68.85; H, 5.85; N, 20.13.

5-Chloro-1-mesityl-3-phenyltetrazolium Tetrafluoroborate.

The olate (1.2 g, 4.2 mmoles) was allowed to react with phosphorus oxychloride (2.2 ml, 24 mmoles) according to the literature [2] to give the product (1.3 g, 82%), colorless crystals, mp 186-188° (acetonitrile-ether); ir: 1600, 1470, 1442, 1264, 1124, 1082, 1036, 860, 760 and 680 cm^{-1}; ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.23 (6H, s, *o*-Me), 2.41 (3H, s, *p*-Me), 7.34 (2H, s, *m*-H of Mes), 7.80-7.93 (3H, m, *m*- and *p*-H of Ph) and 8.34-8.37 (2H, m, *o*-H of Ph).

Anal. Calcd. for $C_{16}H_{16}N_4BClF_4 \cdot 1/2(H_2O)$ (395.60): C, 48.58; H, 4.33; N, 14.16. Found: C, 48.04; H, 4.12; N, 14.10.

5-Azido-1-mesityl-3-phenyltetrazolium Tetrafluoroborate (1c).

5-Chloro-1-mesityl-3-phenyltetrazolium tetrafluoroborate (0.77 g, 2.0 mmoles) was treated with sodium azide (0.12 g, 2.0 mmoles) in *N,N*-dimethylformamide (2.0 ml) according to the literature [2]. The crude product (0.86 g) was recrystallized from ethanol to give **1c** (0.38 g, 48%), colorless crystals, mp 186-187° dec (ethanol); ir: 2200 (N_3), 1600, 1546, 1482, 1470, 1364, 1338, 1286, 1266, 1224, 1080, 1050, 998, 850, 758, 718 and 674 cm^{-1}; ^1H nmr (chloroform-d): δ 2.20 (6H, s, *o*-Me), 2.40 (3H, s, *p*-Me), 7.10 (2H, s, *m*-H of Mes), 7.62-7.78 (3H, m, *m*- and *p*-H of Ph) and 8.22-8.26 (2H, m, *o*-H of Ph).

Anal. Calcd. for $C_{16}H_{16}N_7BF_4$ (393.15): C, 48.88; H, 4.10; N, 24.94. Found: C, 48.70; H, 4.14; N, 25.21.

Photochemical Reactions.

All photochemical reactions were carried out under an argon atmosphere using a 100W high pressure mercury lamp with a Pyrex filter.

Entry 1: A solution of **1a** (0.10 g, 0.28 mmole) in methanol (80 ml) was irradiated at room temperature. Gas evolution started immediately. After 80 minutes the solvent was removed and the residue was dissolved in dichloromethane and shaken with aqueous sodium hydroxide (1 *N*). The organic layer was separated, dried over anhydrous sodium sulfate and the solvent was evaporated. The residue was column chromatographed (dichloromethane) to give crude **2a** (18 mg), **3a** (15 mg, 23%), and **4** (1 mg, 1%). Recrystallization of the crude **2a** from acetonitrile gave pure **2a** (14 mg, 20%) and **5** (2 mg, 2%).

Entry 2: In a similar manner, **1a** (0.10 g, 0.28 mmole) was photolysated in acetonitrile (80 ml) for 30 minutes. Column chromatography (dichloromethane) gave **2a** (23 mg, 35%) and acetanilide (23 mg, 30%).

Entry 3: A solution of **1b** (0.10 g, 0.27 mmole) in acetonitrile (80 ml) was irradiated for 30 minutes. Column chromatography (dichloromethane) gave **2b** (15 mg, 22%) and a mixture of acetanilide and *p*-acetotoluide (1:1 by ^1H nmr) (18 mg, 23%).

Entry 4: A solution of **1a** (0.10 g, 0.28 mmole) and acetophenone (4 ml) in methanol (80 ml) was irradiated for 45 minutes. Column chromatography (dichloromethane) gave **3a** (48 mg, 72%).

Entry 5: A solution of **1a** (0.10 g, 0.28 mmole) and pyrene (0.11 g, 0.56 mmole) in methanol (80 ml) was irradiated for 30 minutes. Column chromatography (dichloromethane:hexane = 2:1) gave crude **2a** (11 mg), **3a** (10 mg, 15%), **4** (12 mg, 16%), and **6** (9 mg, 7%). Recrystallization of the crude **2a** from acetonitrile yielded pure **2a** (5 mg, 8%) and 5 (2 mg, 2%).

Entry 6: A solution of **1a** (0.10 g, 0.28 mmole) and anthracene (0.10 g, 0.56 mmole) in methanol (80 ml) was irradiated for 50 minutes. Column chromatography (dichloromethane:hexane = 1:2) gave crude **2a** (2 mg, 3%), **3a** (17 mg, 26%), and **7** (15 mg, 13%).

Entry 7: A solution of **1c** (0.20 g, 0.50 mmole) in methanol (160 ml) was irradiated for 3 hours. Column chromatography (dichloromethane) gave **3c** (78 mg, 56%).

Synthesis of an Authentic Sample of **6**.

A mixture of 5-chloro-1,3-diphenyltetrazolium tetrafluoroborate (50 mg, 0.15 mmole) and 1-aminopyrene (33 mg, 0.15 mmole) in dry acetonitrile (3 ml) was stirred at room temperature for 24 hours. The solvent was removed and the residue was dissolved in dichloromethane. Aqueous sodium hydroxide (1 *N*) was added and the organic layer was separated. After drying over anhydrous sodium sulfate, the solvent was removed and the residue was washed with hexane. Column chromatography (dichloromethane:hexane = 1:2) gave **6** (23 mg, 35%).

2-Phenyl-1*H*-tetrazolo[1,5-*a*]benzimidazolium Hydroxide, Inner Salt (**2a**).

The compound was obtained as yellow crystals, mp 216-217° (acetonitrile); ir: 1640, 1580, 1558, 1500, 1470, 1450, 1338, 1316, 1280, 1240, 1080, 970, 924, 880, 780, 758, 744 and 690 cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.32 (1H, ddd, J = 8.3, 7.2 and 1.1, H^6), 7.56 (1H, ddd, J = 8.4, 7.2 and 1.2, H^7), 7.60-7.72 (3H, m, *m*- and *p*-H of Ph), 7.90 (1H, br d, J = 8.4, H^8), 8.05 (1H, br d, J = 8.3, H^5) and 8.31-8.36 (2H, m, *o*-H of Ph); ^{13}C nmr (chloroform-d): δ 113.0 (C^8), 120.4 (C^5 or C^6), 120.7 (C^5 or C^6), 121.0 (*o*-C of Ph), 122.1 (C^{4a}), 127.6 (C^7), 130.2 (*m*-C of Ph), 131.5 (*p*-C of Ph), 138.0 (*i*-C of Ph), 151.7 (C^{9a}) and 159.5 (C$^+$); uv: λ_{max} (acetonitrile) (log ε)/nm 204 (4.42), 212 (4.46), 254 (4.46), 320 (4.29) and 393 (3.45); ms: m/z (EI, 70 eV) 235 (M$^+$, 73%), 181 (5), 169 (5), 131 (8), 119 (8), 105 (18) and 77 (100, Ph): hrms Calcd. for $C_{13}H_9N_5$: 235.0858. Found: M$^+$, 235.0874.

Anal. Calcd. for $C_{13}H_9N_5$ (235.25): C, 66.37; H, 3.86; N, 29.77. Found: C, 66.55; H, 4.37; N, 28.59.

7-Methyl-2-phenyl-1*H*-tetrazolo[1,5-*a*]benzimidazolium Hydroxide, Inner Salt (**2b**).

This compound was obtained as yellow crystals, mp 219-220° (acetonitrile); ir: 1554, 1490, 1482, 1426, 1334, 1318, 1290, 1262, 1230, 1138, 960, 930, 790, 758, 730 and 680 cm^{-1}; ^{1}H nmr (chloroform-d): δ 2.56 (3H, s, Me), 7.13 (1H, dd, J = 8.5 and 1.1, H^6), 7.58-7.68 (4H, m, *m*- and *p*-H of Ph and H^8), 7.91 (1H, d, J = 8.5, H^5) and 8.29-8.34 (2H, m, *o*-H of Ph); ^{13}C nmr (chloroform-d): δ 22.5 (Me), 112.4 (C^8), 120.2 (C^5 or C^6), 120.8 (*o*-C of Ph), 122.1 (C^5 or C^6), 130.1 (*m*-C of Ph), 131.2 (*p*-C of Ph), 138.0 (*i*-C of Ph), 152.1 (C^{9a}) and 159.6 (C$^+$); uv: λ_{max} (acetonitrile) (log ε)/nm 218 (4.84), 256 (4.84), 329 (4.46) and 395 (3.67); ms: m/z (EI, 70 eV) 249 (M$^+$, 78%), 165 (5), 116 (3), 105 (38, PhN$_2$), 89 (13), 77 (100, Ph), 64 (4) and 51 (21).

Anal. Calcd. for $C_{14}H_{11}N_5$ (249.27): C, 67.46; H, 4.45; N, 28.10. Found: C, 67.69; H, 4.51; N, 28.29.

3-Phenyl-1-*p*-tolyltetrazolium-5-amide (**3b**).

This compound was obtained as yellow crystals, mp 132-134° (hexane); ir: 1618, 1516, 1496, 1468, 1416, 1380, 1338, 1298, 1230, 1244, 1186, 1116, 1070, 958, 816, 758, 714 and 678 cm^{-1}; ^{1}H nmr (chloroform-d): δ 2.42 (3H, s, Me), 3.40 (1H, br s, NH), 7.35 (2H, d, J = 8.2, *m*-H of Tol), 7.56-7.60 (3H, m, *m*- and *p*-H of Ph), 7.98 (2H, d, J = 8.2, *o*-H of Tol) and 8.07-8.12 (2H, m, *o*-H of Ph); uv-vis: λ_{max} (acetonitrile) (log ε)/nm 252 (4.33), 270 (4.24) and 400 (3.74).

Anal. Calcd. for $C_{14}H_{13}N_5$ (251.29): C, 66.91; H, 5.21; N, 27.88. Found: C, 67.09; H, 5.32; N, 28.13.

1-Mesityl-3-phenyltetrazolium-5-amide (**3c**).

This compound was obtained as yellow crystals, mp 100-101° (hexane); ir: 3300 (NH), 3180, 2350, 1620, 1484, 1464, 1440, 1362, 1348, 1300, 1258, 1204, 1164, 1116, 1076, 1024, 1018, 964, 922, 856, 810, 752, 680 and 660 cm^{-1}; ^{1}H nmr (chloroform-d): δ 2.21 (6H, s, *o*-Me), 2.36 (3H, s, *p*-Me), 3.42 (1H, br s, NH), 7.04 (2H, s, *m*-H of Mes), 7.52-7.60 (3H, m, *m*- and *p*-H of Ph) and 8.06-8.11 (2H, m, *o*-H of Ph); uv: λ_{max} (acetonitrile) (log ε)/nm 245 (4.33) and 380 (3.45).

Anal. Calcd. for $C_{16}H_{17}N_5$ (279.34): C, 68.80; H, 6.13; N, 25.07. Found: C, 68.82; H, 6.30; N, 25.08.

1,3-Diphenyltetrazolium-5-(1-pyrenyl)amide (**6**).

This compound was obtained as reddish brown crystals, mp 246-247° (ethanol); ir: 1628, 1614, 1572, 1538, 1484, 1430, 1364, 1338, 1282, 1210, 1162, 1120, 1070, 970, 842, 736, 720 and 678 cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.47-7.70 (6H, m), 7.87-8.21 (9H, m), 8.50 (3H, d, J = 8.0) and 8.76 (1H, d, J = 9.1); ^{13}C nmr (chloroform-d): δ 120.6 (*o*-C of Ph), 122.8 (*o*-C of Ph), 123.8, 124.0, 124.1, 124.9, 125.2, 125.3, 125.4, 125.7, 125.8, 126.2, 126.5, 126.9, 127.4, 127.5, 131.6, 131.7 (pyrene), 129.6 (*m*-C of Ph), 129.8 (*m*-C of Ph), 129.4 (*p*-C of Ph), 131.8 (*p*-C of Ph), 134.1 (*i*-C of Ph), 135.9 (*i*-C of Ph) and 155.5 (C$^+$); uv-vis: λ_{max} (acetonitrile) (log ε)/nm 237 (4.59), 278 (4.31), 298 (4.29), 388 (4.33) and 409 (4.34); ms: m/z (EI, 70 eV) 437 (M$^+$, 100%), 227 (14), 218 (8), 214 (5), 201 (5), 104 (5) and 77 (Ph, 39).

Anal. Calcd. for $C_{29}H_{19}N_5 \cdot 1/2(H_2O)$ (446.50): C, 78.01; H, 4.51; N, 15.68. Found: C, 78.09; H, 4.33; N, 15.89.

1,3-Diphenyltetrazolium-5-(9-anthracenyl)amide (**7**).

This compound was obtained as orange crystals, mp 195-198°; ir: 1656, 1596, 1558, 1492, 1360, 1334, 1292, 1238, 970, 760, 740 and 698 cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.28-7.48 (8H, m, *m*- and *p*-H of Ph and H^2 and H^7), 7.59 (2H, t, J = 7.6, H^3 and H^6), 7.86-7.99 (4H, m, *o*-H of Ph), 8.13 (1H, s, H^{10}), 8.28 (2H, d, J = 8.5, H^4 and H^5) and 8.56 (2H, d, J = 8.5, H^1 and H^8); ^{13}C nmr (chloroform-d): δ 120.3 (*o*-C of Ph), 125.1 (*o*-C of Ph), 120.9, 121.3, 124.1, 124.9, 128.4 (anthracene), 129.4 (*m*-C of Ph), 129.4 (*m*-C of Ph), 131.5 (*p*-C of Ph), 132.5 (*p*-C of Ph), 135.0 (*i*-C of Ph), 136.1 (*i*-C of Ph) and 154.9 (C$^+$); ms: m/z (EI, 70 eV) 413 (M$^+$, 100%), 206 (13), 203 (20), 190 (6), 176 (5), 168 (5), 104 (10) and 77 (Ph, 79); hrms Calcd. for $C_{27}H_{19}N_5$: 413.1640. Found: M$^+$, 413.1659.

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