The Photochemistry of Benzotriazole Derivatives. Part 2: Photolysis of 1-Substituted Benzotriazole Arylhydrazones: New Route to Phenanthridin-6-yl-2-phenyldiazines

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Abstract: Irradiation of 1-substituted benzotriazole arylhydrazones 3a–c, 4a,b and 5a,b with a 16 W low pressure mercury arc-lamp (254 nm) for 24 h gave phenanthridin-6-yl-2-phenyldiazines 9a–c, phenanthridin-6(5H)-ones 10a–c, 1-anilinobenzimidazoles 11a–c, 2-aryl-1H-benzimidazoles 12a–c, 1-arylamino-1H-benzimidazol-2-carboxylic acid ethyl esters 14a,b, 1-aryl-1H, 9H-benzo [4,5][1,2,3] triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl esters 16a,b, 1-arylamino-2-benzoylbenzimidazoles 18a,b and 2-benzoylbenzoxazole 21.

Keywords: 1,2,3-benzotriazole; phenanthridin-6-yl-2-phenyldiazine; phenanthridin-6(5H)-one; 1-anilinobenzimidazole; 1H-benzimidazole; 2-benzoyl-1H-benzoazole; photolysis

1. Introduction

The behavior of benzotriazole and its derivatives under pyrolytic and photolytic conditions has already received considerable attention. In particular, 1-substituted-1H-benzotriazoles pyrolyze via elimination of N₂ to give a 1,3-diradical intermediate which can interact with aromatic or unsaturated substituents to give cyclic and rearranged products [1-10]. In the earlier paper in this series, we have reported the photolysis of N1-vinylsubstituted benzotriazole derivatives 1 into 2-acyl-3-dimethylaminoindoles 2 [11].
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**Scheme 1.** Photolysis of *N*-vinylsubstituted benzotriazoles 1 into 2-acylindoles 2.

![Scheme 1](image)

This investigation is now extended to include seven 1-substituted benzotriazole arylhydrazones 3a–c, 4a,b and 5a,b (Figure 1).

![Figure 1](image)

**2. Results and Discussion**

Compounds 3a–c and 5a,b were obtained by the procedures described earlier and were fully characterized [12-14]. The UV spectra of these compounds display two absorption maxima in the region 243–392 nm wavelength regions.

Irradiation of compounds 3a–c in a quartz tube with a 16 W low pressure mercury arc-lamp (254 nm) in acetonitrile for 24 hours at room temperature produced phenanthridin-6-yl-2-phenyldiazines 9a–c (48–51%), phenanthridin-6(5H)-ones 10a–c (15–18%), 1-anilino-2-arylbenzimidazoles 11a–c (10–14%) and 2-aryl-1H-benzimidazoles 12a–c (8–10%). The formation of these products can be explained by a mechanistic pathway presented in Scheme 2, involving initial photo-extrusion of N₂ to form the corresponding diradical intermediate 6, which cyclizes to diradical 7 and is then converted to 8, and the latter is photooxidized to 9a–c. Partial hydrolysis of 9a–c in the reaction media produces 10a–c. Concurrently, cyclization of the tautomer of diradical intermediate 6 affords compounds 11a–c which are further converted to 12a–c. To confirm that 9a–c and 11a–c are the likely precursors of 10a–c and 12a–c respectively, 9a and 11a were isolated and then subjected to irradiation for 24 hours. In each case the corresponding reaction products 10a and 12a were obtained in quantitative yield. The structures of all isolated products were confirmed based on their full 1H-NMR, 13C-NMR, and mass spectral data. Moreover, an X-ray crystal structure of compound 9a was obtained (Figure 2 and Table 1).
Scheme 2. Mechanism of photolysis of N-(benzotriazol-1-yl-phenylmethylene)-N'-arylhydrazines 3a–c.

\[ \text{hv / 24 h} \quad 3a-c \rightarrow 6 \rightarrow 7 \rightarrow 8 \rightarrow 9a-c \rightarrow 10a-c \]

- a, X = H; b, X = CH₃; c, x = Cl

Figure 2. X-ray structure of compound 9a (thermal ellipsoids).
Table 1. Selected bond lengths and bond angles for compound 9a.

| Bond                  | Bond lengths (Å) | Bond                  | Bond angles (Å) |
|-----------------------|------------------|-----------------------|-----------------|
| N1-N2                 | 1.2462 (13)      | N1-N2-C5              | 112.58 (9)      |
| N2-C5                 | 1.4368 (14)      | N3-C5-N2              | 117.90 (10)     |
| N3-C6                 | 1.3857 (15)      | N2-C5-N17             | 116.62 (10)     |
| N3-C5                 | 1.2949 (15)      | C5-N3-C6              | 117.99 (10)     |
| C5-C17                | 1.4400 (16)      | C6-C11-C12            | 118.27 (11)     |
| N1-C4                 | 1.4286 (14)      | C10-C11-C12           | 124.11 (11)     |
| C11-C12               | 1.4450 (18)      | N3-C6-C11             | 122.68 (11)     |

Benzotriazol-1-yl-(2-arylhydrazono) acetic acid ethyl esters 4a,b were prepared in 75–77% yield by stirring 1,2,3-benzotriazole with ethyl 2-chloro-2-(2-arylhydrazono)acetate in DCM/TEA for 24 hours at room temperature. Irradiation of 4a,b in acetonitrile for 24 hour afforded 1-aryl amino-1H-benzimidazol-2-carboxylic acid ethyl esters 14a,b (45–48% yield) and 1-aryl-1H,9H-benzo[4,5][1,2,3]triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl esters 16a,b (35–36% yield). It is assumed that initial N₂ extrusion affords the biradical intermediate 13 which then cyclized into 14a,b. On the other hand, formation of photoproducts 16a,b may be explained by assuming a intramolecular 1,6-H shift (Scheme 3). Single crystal X-ray structure analysis (Figures 3 and 4, Table 2) confirmed the structures of new compounds 4b and 14b.

Scheme 3. Mechanism of photolysis of benzotriazol-1-yl-(2-arylhydrazono)-acetic acid ethyl esters 4a,b.
Table 2. Selected bond lengths and bond angles for compounds 4b and 14b.

| Bond   | Bond lengths (Å) | Bond angles (°) | Bond   | Bond lengths (Å) | Bond angles (°) |
|--------|------------------|-----------------|--------|------------------|-----------------|
| N1-C6  | 1.375 (6)        | N1-C6-C1        | 104.8 (4) | N1-C1            | 1.380 (10)      |
| N1-C7  | 1.409 (6)        | N1-C7-C14       | 117.1 (4) | N1-C7            | 1.318 (10)      |
| N4-C7  | 1.301 (6)        | N1-C7-N4        | 125.3 (4) | N2-C7            | 1.375 (9)       |
| C7-C14 | 1.477 (7)        | N1-N2-N3        | 108.5 (4) | N2-N3            | 1.372 (9)       |
| N5-C8  | 1.408 (6)        | N2-N1-C7        | 120.3 (4) | N2-C6            | 1.405 (10)      |
| N4-N5  | 1.328 (6)        | N5-C8-C13       | 118.2 (5) | C7-C14           | 1.495 (11)      |
| N3-C1  | 1.386 (7)        | N3-C1-C6        | 109.2 (4) | N3-C8            | 1.409 (10)      |

Finally, irradiation of 2-arylhydrazono-2-(benzotriazol-1-yl)-1-phenylethanones 5a,b afforded 1-arylamino-2-benzoylbenzimidazoles 18a,b (25–30%), 2-benzoylbenzoxazole 21 (24–27%) and phenantheridin-6(5H)-one 10a (15–17%). The suggested mechanism proposed for this photoreaction is shown in Scheme 4. Initial photo-extrusion of N₂ forms the corresponding diradical intermediate 17,
followed by cyclization to yield $18_{a,b}$. On the other hand, photooxidation of $5_{a,b}$ afforded 1-benzotriazole-2-phenylethan-1,2-dione $19$, which upon elimination of $N_2$ formed diradical $20$, which either cyclizes to yield 2-benzoylbenzoxazole $21$ in (24–27%) or cyclizes to $22$, which spontaneously loses CO through intermediate $23$ to produce phenanthradin-6(5$\text{H}$)-one $10_a$ in 15–17% yield.

**Scheme 4.** Mechanism of photolysis of 2-arylhydrazono-2-(benzotriazol-1-y)-1-phenylethanones $5_{a,b}$.

The structure of all new compounds were assigned by spectroscopic and analytical methods. The structure of $21$ is readily assigned based on 2D-NMR results. The $^1H$- and $^{13}C$-NMR signal assignments and the H-C correlation from the HMBC 2-D experiments are displayed in Figure 5. Table 3 summarizes the absorption maxima ($\lambda_{\text{max}}$) and the photoproducts of substrates $3_a–c$, $4_{a,b}$ and $5_{a,b}$. The fact that the substituents R affected the nature of the products much more than the substituted Ar may be attributed to the strong influence of the substituents on the formed biradicals.

**Figure 5.** H-C Correlations in the HMBC 2-D experimental of compound $21$. 
### Table 3. Photoproducts formed by irradiation of compounds 3a–c, 4a,b and 5a,b and yield.

| Comp | R          | Ar          | \(\lambda_{\text{max}}\)  | Photo-products and yields (%) |
|------|------------|-------------|----------------------------|--------------------------------|
|      |            |             |                            |                                |
| 3a   | C\(_6\)H\(_5\) | C\(_6\)H\(_5\) | 244, 338                  | 51 16 12 10 - - - -            |
| 3b   | CH\(_3\)C\(_6\)H\(_4\)(p) | C\(_6\)H\(_5\) | 247, 347                  | 48 18 14 8 - - - -            |
| 3c   | ClC\(_6\)H\(_4\)(p) | C\(_6\)H\(_5\) | 243, 392                  | 50 15 10 9 - - - -            |
| 4a   | CO\(_2\)C\(_2\)H\(_5\) | C\(_6\)H\(_5\) | 244, 370                  | - - - 48 36 - - - -          |
| 4b   | CO\(_2\)C\(_2\)H\(_5\) | ClC\(_6\)H\(_4\)(p) | 245, 355                  | - - - 45 35 - - - -          |
| 5a   | COC\(_6\)H\(_5\) | C\(_6\)H\(_5\) | 253, 345                  | - 15 - - - - - - -           |
| 5b   | COC\(_6\)H\(_5\) | CH\(_3\)C\(_6\)H\(_4\)(p) | 256, 379                  | - 17 - - - - - - -           |

### 3. Experimental

#### 3.1. General

All melting points were recorded on a Gallenkamp apparatus. IR spectra were recorded using KBr pellets on a Perkin-Elmer System 2000 FT-IR spectrophotometer. \(^1\)H- and \(^{13}\)C-NMR spectra were recorded on Bruker DPX 400 MHz or Avance\(^{\text{II}}\) 600 MHz super-conducting NMR spectrometers with proton spectra measured at 400, 600 MHz and carbon spectra at 100 and 150 MHz, respectively. Mass spectra were measured on a VG Auto-spec-Q (high resolution, high performance, tri-sector GC/MS/MS) and with LCMS using Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode. Microanalyses were performed on LECO CH NS-932 Elemental Analyzer. The UV/VIS absorption spectra were recorded using a Varian Cary 5 instrument in the wave length range 200–450 nm using dry clean quartz cuvette of 1.0 cm path length. X-Ray analysis were performed using a Rigaku Rapid II diffractometer.

#### 3.2. Synthesis of Starting Compounds 4a,b

To a solution of 1,2,3-benzotriazole (3.57 g, 30 mmol), in DCM (50 mL), TEA (5 drops) and ethyl 2-chloro-2-(2-arylhydrazono)acetate (30 mmol) were added [15]. The mixture was stirred at room temperature for 24 hours, and then diluted with CH\(_2\)Cl\(_2\) (150 mL), washed successively with dil. HCl (6 M, 20 mL), satd. aq. NaHCO\(_3\) (150 mL), and water and then dried over anhydrous Na\(_2\)SO\(_4\). The solvent was then evaporated \textit{in vacuo}, and the residue was crystallized from ethanol to give 4a,b.

\textit{Benzotriazol-1-yl-phenylhydrazono-acetic acid ethyl ester (4a).} Colorless crystals, yield 7.2 g (77%), m.p. 183–184 °C. MS: m/z (%) = 309 (M\(^+\), 15), 281 (35), 208 (80). IR (KBr, cm\(^{-1}\)): 3060, 2982, 1683, 1598, 1540, 1501, 1414, 1312, 1235, 1187, 1019, 759. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.69 (br, 1H, NH), 8.01 (d, 1H, \(J = 8.4\) Hz), 7.59 (t, 1H, \(J = 8.0\) Hz), 7.49 (d, 1H, \(J = 8.4\) Hz), 7.43 (t, 1H, \(J = 8.0\) Hz), 7.38–7.32 (m, 4H), 7.09 (t, 1H, \(J = 8.4\) Hz), 4.41 (q, 2H, \(J = 7.0\) Hz), 1.40 ppm (t, 3H, \(J = 7.0\) Hz).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.3, 144.9, 141.6, 132.5, 129.4, 128.9, 125.0, 123.8, 119.9, 118.5, 115.0, 111.2, 62.3, 14.3 ppm. Anal. Calcd. for C\(_{16}\)H\(_{15}\)N\(_3\)O\(_2\) (309.3): C, 62.13; H, 4.89; N, 22.64. Found: C, 62.10; H, 4.80; N, 22.55.
Benzotriazol-1-yl-p-chlorophenylhydrazono-acetic acid ethyl ester (4b). Pale yellow crystals, yield 7.80 g (75%), m.p. 156–158 °C. MS: m/z (%) = 343 (M⁺, 10), 315 (30), 286 (35). IR (KBr, cm⁻¹): 3094, 2986, 1686, 1571, 1489, 1401, 1282, 1235, 1172, 1148, 1092, 1061, 832. ¹H-NMR (400 MHz, CDCl₃): δ 9.77 (br, 1H, NH), 8.03 (d, 1H, J = 8.4 Hz), 7.60 (dt, 1H, J = 7.8, 1.2 Hz), 7.49 (d, 1H, J = 8.4 Hz), 7.44 (dt, 1H, J = 7.8, 1.2 Hz), 7.32 (d, 2H, J = 8.4 Hz), 7.24 (d, 2H, J = 8.4 Hz), 4.40 (q, 2H, J = 6.8 Hz), 1.24 ppm (t, 3H, J = 6.8 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 160.1, 145.0, 140.4, 132.4, 129.5, 129.1, 128.7, 125.2, 120.0, 119.1, 116.2, 111.3, 62.4, 14.3 ppm. (HRMS = 343.0831, requires C₁₆H₁₄ClN₅O₂ 343.0830).

3.3. Irradiation Using a Low Pressure Mercury Arc-Lamp

Each of the substrates 3a–c, 4a, b and 5a, b (10.0 mmol) was dissolved in acetonitrile (250 mL) in a number of quartz tubes (10 × 25 mL) and introduced to irradiate for 24 hours at room temperature (RT). The progress of each reaction was monitored by using TLC. The solvent was removed in vacuo and the resulting residue was subjected to column chromatography on silica gel using ethyl acetate/petroleum ether (b.p. 60–80 °C) as the eluent to give the corresponding products.

Phenanthridin-6-yl-2-phenyldiazine (9a). Red crystals from ethanol, m.p. 158–160 °C. MS: m/z (%) = 283 (M⁺, 10), 254 (100), 178 (70). IR (KBr, cm⁻¹): 3061, 3004, 2957, 1611, 1562, 1527, 1484, 1349, 1193, 925, 763. ¹H-NMR (600 MHz, DMSO-d₆): δ 8.98 (d, 1H, J = 7.8 Hz), 8.88 (d, 1H, J = 8.4 Hz), 8.55 (d, 1H, J = 8.0 Hz), 8.18 (d, 1H, J = 8.0 Hz), 8.07 (t, 1H, J = 7.6 Hz), 7.88 (t, 1H, J = 7.6 Hz), 7.84 (t, 1H, J = 7.6 Hz), 7.81 ppm (m, 3H). ¹³C-NMR (150 MHz, DMSO-d₆): δ 159.6, 152.5, 142.4, 133.8, 133.0, 131.9, 130.5, 129.7, 129.6, 128.3, 127.9, 125.7, 124.5, 123.4, 123.0, 122.9 122.1 ppm. Anal. Calc. for C₁₉H₁₃N₃ (283.3): C, 80.54; H, 4.62; N, 14.83. Found: C, 80.50; H, 4.60; N, 14.79.

9-Methylphenanthridin-6-yl-2-phenyldiazine (9b). Red crystals from ethanol, m.p. 140–142 °C. MS: m/z (%) = 297 (M⁺, 10), 268 (100), 192 (40). IR (KBr, cm⁻¹): 3056, 2918, 1617, 1509, 1483, 1373, 1308, 1189, 1022, 822, 760. ¹H-NMR (400 MHz, CDCl₃): δ 8.62 (dd, 2H, J = 8.4, 2.0 Hz), 8.50 (s, 1H), 8.31 (d, 1H, J = 8.0 Hz), 8.21 (dd, 2H, J = 8.4, 2.0 Hz), 7.76 (t, 1H, J = 7.8 Hz), 7.70 (t, 1H, J = 7.6 Hz), 7.63–7.58 ppm (m, 3H). ¹³C-NMR (150 MHz, DMSO-d₆): δ 159.5, 153.3, 143.3, 141.9, 134.9, 132.4, 131.6, 129.4, 129.2, 129.1, 127.4, 126.3, 125.0, 124.0, 122.1, 121.9, 121.7, 22.5 ppm. Anal. Calc. for C₂₀H₁₅N₃ (297.4): C, 80.78; H, 5.08; N, 14.13. Found: C, 80.70; H, 5.00; N, 14.10.

9-Chlorophenanthridin-6-yl-2-phenyldiazine (9c). Red crystals from ethanol, m.p. 136–138 °C. MS: m/z (%) = 319 (M⁺, 10), 317 (M⁺, 20), 268 (100). IR (KBr, cm⁻¹): 3062, 2907, 2957, 1605, 1512, 1486, 1380, 1309, 1143, 1015, 910, 761. ¹H-NMR (400 MHz, CDCl₃): δ 8.70 (d, 1H, J = 8.4 Hz), 8.66 (s, 1H), 8.53 (d, 1H, J = 8.0 Hz), 8.33 (d, 1H, J = 7.8 Hz), 8.19 (dd, 2H, J = 7.8, 1.2 Hz), 7.81 (t, 1H, J = 7.8 Hz), 7.73 (t, 1H, J = 8.0 Hz), 7.70 (dd, 1H, J = 8.0, 1.2 Hz), 7.62–7.58 ppm (m, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ 158.9, 153.3, 143.6, 138.0, 135.9, 132.7, 131.7, 129.9, 129.2, 128.3, 128.2, 127.9, 127.3, 124.1, 124.0, 122.2, 122.0 ppm. Anal. Calc. for C₁₉H₁₂ClN₃ (317.8): C, 71.81; H, 3.81; N, 13.22. Found: C, 71.75; H, 3.80; N, 13.17.
Phenanthridin-6(5H)-one (10a). White crystals, mp. 289–290 °C (lit. [13] m.p. 290–292 °C). MS: \( m/z \) (%) = 195 (M⁺, 100), 167 (20), 139 (15). \(^1\)H-NMR (400 MHz, DMSO-d₆): \( \delta \) 11.70 (br, 1H, NH), 8.52 (d, 1H, J = 8.0 Hz), 8.40 (d, 1H, J = 8.0 Hz), 8.33 (dd, 1H, J = 8.0, 1.2 Hz), 7.82 (dt, 1H, J = 8.0, 1.2 Hz), 7.65 (t, 1H, J = 8.0 Hz), 7.49 (dt, 1H, J = 8.0, 1.4 Hz), 7.36 (dd, 1H, J = 8.0, 1.4 Hz), 7.27 ppm (dt, 1H, J = 8.0, 1.4 Hz). \(^13\)C-NMR (100 MHz, DMSO-d₆): \( \delta \) 160.9, 136.6, 134.3, 132.9, 129.6, 128.0, 127.5, 125.7, 123.3, 122.7, 122.3, 117.6, 116.1 ppm.

9-Methylphenanthridin-6(5H)-one (10b). Colorless crystals, m.p. 251–253 °C (lit. [16] m.p. 250–251 °C). MS: \( m/z \) (%) = 209 (M⁺, 100), 180 (25). \(^1\)H-NMR (600 MHz, DMSO-d₆): \( \delta \) 11.58 (br, 1H, NH), 8.36 (d, 1H, J = 7.8 Hz), 8.32 (s, 1H), 8.19 (d, 1H, J = 8.0 Hz), 7.46 (dt, 2H, J = 8.4, 1.6 Hz), 7.34 (dd, 1H, J = 8.0, 1.4 Hz), 7.25 (dt, 1H, J = 8.4, 1.2 Hz), 2.51 ppm (s, 3H, CH₃). \(^13\)C-NMR (150 MHz, DMSO-d₆): \( \delta \) 160.8, 143.0, 136.7, 134.2, 129.4, 129.1, 127.5, 123.4, 123.2, 122.5, 122.1, 117.5, 116.1, 21.5 ppm.

9-Chlorophenanthridin-6(5H)-one (10c). Colorless crystals, m.p. 268–270 °C. LCMS: \( m/z \) = 232 (M + 3), 230 (M + 1). \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 11.53 (br, 1H, NH), 8.43 (d, 1H, J = 8.0 Hz), 8.25 (d, 1H, J = 8.0 Hz), 8.14 (d, 1H, J = 8.4 Hz), 7.80 (t, 1H, J = 7.8 Hz), 7.64 (t, 1H, J = 7.8 Hz), 7.45 (d, 1H, J = 8.0 Hz), 7.38 ppm (t, 1H, J = 7.8 Hz) [13].

1-Anilino-2-phenylbenzimidazole (11a). Colorless crystals, m.p. 211–212 °C (lit. [14] m.p. 210–212 °C). LCMS: \( m/z \) = 286 (M + 1). \(^1\)H-NMR (400 MHz, CDCl₃): \( \delta \) 8.07 (m, 2H), 7.86 (d, 1H, J = 8.0 Hz), 7.46–7.43 (m, 3H), 7.34 (t, 1H, J = 7.8 Hz), 7.32–7.24 (m, 3H), 7.21 (t, 1H, J = 8.0 Hz), 7.00 (t, 1H, J = 7.8 Hz), 6.81 (br, 1H, NH), 7.72 ppm (d, 2H, J = 7.8 Hz).

1-Anilino-2-p-tolylbenzimidazole (11b). Colorless crystals, m.p. 233–235 °C (lit. [14] m.p. 234–236 °C). LCMS: \( m/z \) = 300 (M + 1). \(^1\)H-NMR (CDCl₃): \( \delta \) 8.05 (d, 2H, J = 8.0 Hz), 7.82 (d, 1H, J = 8.0 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.33 (t, 1H, J = 7.8 Hz), 7.28 (m, 2H), 7.17 (d, 1H, J = 8.4 Hz), 7.02 (t, 2H, J = 7.8 Hz), 6.81 (br, 1H), 6.67 (d, 2H, J = 8.0 Hz), 2.40 ppm (s, 3H, CH₃).

1-Anilino-2-p-chlorophenylbenzimidazole (11c). Colorless crystals, m.p. 230–233 °C (lit. [14] m.p. 232–234 °C). LCMS: \( m/z \) = 321 (M + 2), 320 (M + 1). \(^1\)H-NMR (400 MHz, CDCl₃): \( \delta \) 8.05 (dd, 2H, J = 8.4, 1.6 Hz), 7.86 (d, 1H, J = 8.4 Hz), 7.43 (dd, 2H, J = 8.4, 1.6 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.30–7.25 (m, 3H), 7.17 (d, 1H, J = 8.0 Hz), 7.02 (t, 1H, J = 7.8 Hz), 6.81 (br, 1H, NH), 6.67 ppm (d, 2H, J = 8.0 Hz).

2-Phenyl-1H-benzimidazole (12a). Colorless crystals, m.p. 290–292 °C (lit. [14] m.p. 289–290 °C). LCMS: \( m/z \) = 195 (M + 1). \(^1\)H-NMR (400 MHz, CDCl₃): \( \delta \) 8.12 (m, 2H), 7.68 (m, 2H), 7.45 (m, 3H), 7.29 ppm (m, 3H, J 7.8 Hz).

2-p-Tolyl-1H-benzimidazole (12b). Colorless crystals, m.p. 271–272 °C (lit. [14] m.p. 269–272 °C). LCMS: \( m/z \) = 209 (M + 1). \(^1\)H-NMR (400 MHz, DMSO-d₆): \( \delta \) 12.78 (br, 1H, NH), 8.06 (d, 2H, J = 8.0 Hz), 7.56 (m, 2H), 7.32 (d, 2H, J = 8.0 Hz), 7.16 (m, 2H), 2.33 ppm (s, 3H, CH₃).
2-p-Chlorophenyl-1H-benzimidazole (12c). Colorless crystals, m.p. 291–292 °C (lit. [14] m.p. 289–291 °C). LCMS: m/z = 231 (M+ + 3), 229 (M + 1). 1H-NMR (400 MHz, DMSO-d6): δ 12.98 (br, 1H, NH), 8.18 (d, 2H, J = 8.4 Hz), 7.58 (d, 2H, J = 8.4 Hz), 7.56 (m, 2H), 7.18 ppm (m, 2H).

1-Anilino-1H-benzimidazole-2-carboxylic acid ethyl ester (14a). Colorless crystals from ethanol, m.p. 142–144 °C. MS: m/z (%) = 281 (M+ , 70), 253 (35), 208 (80). IR (KBr, cm⁻¹): 3244, 3054, 2973, 1683, 1600, 1556, 1490, 1392, 1240, 1157, 1053, 734. 1H-NMR (600 MHz, CDCl3): δ 7.95 (d, 1H, J = 8.4 Hz), 7.76 (br, 1H, NH), 7.56 (dd, 1H, J = 8.4, 1.2 Hz), 7.45 (d, 1H, J = 8.4 Hz), 7.36 (dt, 1H, J = 7.8, 1.4 Hz), 7.12 (t, 2H, J = 8.4 Hz), 6.98 (t, 1H, J = 7.8 Hz), 6.54 (d, 2H, J = 8.0 Hz), 4.43 (q, 2H, J = 6.8 Hz), 1.42 ppm (t, 3H, J = 6.8 Hz). 13C-NMR (150 MHz, CDCl3): δ 159.8, 144.7, 141.2, 132.1, 128.9, 128.4, 124.5, 123.3, 119.6, 118.1, 114.5, 110.7, 61.7, 13.7 ppm. Anal. Calcd. for C16H15N3O2 (281.3): C, 68.30; H, 5.37; N, 14.94. Found: C, 68.25; H, 5.35; N, 14.89.

1-p-Chloroanilino-1H-benzimidazole-2-carboxylic acid ethyl ester (14b). Colorless crystals from ethanol, m.p. 146–148 °C. MS: m/z (%) = 315 (M+ , 100), 242 (65), 149 (80). IR (KBr, cm⁻¹): 3224, 3032, 2979, 1723, 1599, 824. 1H-NMR (600 MHz, CDCl3): δ 7.97 (d, 1H, J = 8.4 Hz), 7.76 (br, 1H, NH), 7.56 (dd, 1H, J = 8.4, 1.4 Hz), 7.53 (dt, 1H, J = 8.4, 1.4 Hz), 7.45 (dt, 1H, J = 7.8, 1.4 Hz), 7.18 (d, 2H, J = 8.4 Hz), 6.48 (d, 2H, J = 8.4 Hz), 4.43 (q, 2H, J = 6.8 Hz), 1.42 ppm (t, 3H, J = 6.8 Hz). 13C-NMR (150 MHz, CDCl3): δ 159.2, 145.6, 138.9, 138.8, 135.5, 129.5, 127.6, 126.9, 124.7, 122.1, 115.1, 110.8, 62.7, 14.1 ppm. (HRMS = 315.0769; requires 315.0768).

1-Phenyl-1H,9H-benzo[4,5][1,2,3]triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl ester (16a). Pale yellow crystals from ethanol, m.p. 152–154 °C. MS: m/z (%) = 309 (M+ , 25), 295 (10), 281 (50). IR (KBr, cm⁻¹): 3036, 2982, 1683, 1598, 1540, 1501, 1458, 1312, 1235, 1187, 1063, 1019, 759. 1H-NMR (CDCl3): δ 12.44 (s, 1H, NH), 8.16 (d, 1H, J = 8.4 Hz), 7.60–7.54 (m, 2H), 7.45 (tt, 1H, J = 8.4, 1.6 Hz), 7.37 (t, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 8.4 Hz), 7.12 (t, 1H, J = 7.8 Hz), 4.31 (q, 2H, J = 7.2 Hz), 1.22 ppm (t, 3H, J = 7.2 Hz). 13C-NMR (100 MHz, CDCl3): δ 161.9, 145.8, 142.3, 134.6, 130.1, 130.0, 128.83, 124.80, 124.76, 120.6, 115.5, 110.8, 62.9, 14.5 ppm. Anal. Calcd. for C16H15N3O2 (309.3): C, 62.13; H, 4.89; N, 22.64. Found: C, 62.07; H, 4.82; N, 22.65.

1-p-Chlorophenyl-1H,9H-benzo[4,5][1,2,3]triazolo[1,2-a]tetrazole-3-carboxylic acid ethyl ester (16b). Yellow crystals from ethanol, m.p. 156–158 °C. MS: m/z (%) = 343 (M+ , 15), 315 (30), 126 (100). IR (KBr, cm⁻¹): 3094, 2986, 1680, 1571, 1547, 1489, 1401, 1206, 1285, 1172, 1148, 1062, 832. 1H-NMR (400 MHz, CDCl3): δ 12.43 (s, 1H, NH), 8.15 (d, 1H, J = 8.0 Hz), 7.58–7.55 (m, 2H), 7.48–7.44 (m, 1H), 7.32 (d, 2H, J = 8.4 Hz), 7.22 (d, 2H, J = 8.4 Hz), 4.31 (q, 2H, J = 7.2 Hz), 1.23 ppm (t, 3H, J = 7.2 Hz). 13C-NMR (100 MHz, CDCl3): δ 161.3, 145.2, 140.3, 133.9, 129.6, 129.2, 128.3, 124.2, 120.1, 119.2, 116.1, 110.1, 62.4, 13.9 ppm. (HRMS = 343.0830; requires C16H14ClN3O2 343.0831).

1-Anilino-2-benzoylbenzimidazole (18a). Yellow crystals, m.p. 216–218. °C. MS: m/z (%) = 313 (M+ , 60), 279 (20), 167 (40), 149 (100). 1H-NMR (400 MHz, CDCl3): δ 8.33 (dd, 2H, J = 8.4, 1.6 Hz), 8.12 (br, 1H, NH), 7.96 (d, 1H, J = 8.0 Hz), 7.70 (dt, 1H, J = 8.4, 1.6 Hz), 7.60 (dt, 1H, J = 8.0, 1.4 Hz), 7.53–7.42 (m, 3H), 7.34 (t, 1H, J = 7.8 Hz), 7.16 (t, 2H, J = 8.0 Hz), 6.90 (t, 1H, J = 8.2 Hz), 6.54 ppm
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(d, 2H, J = 7.8 Hz). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 185.7, 147.2, 144.7, 139.1, 135.7, 134.0, 131.2, 129.4, 128.3, 127.6, 126.9, 124.4, 122.4, 122.3, 113.8, 111.1 ppm. (HRMS = 313.1209; requires C$_{20}$H$_{15}$N$_3$O 313.1207).

2-Benzoyl-1-p-toluidinobenzimidazole (18b). Pale yellow crystals, m.p. 226–228 °C. MS: m/z (%) = 327 (M$^+$, 100), 223 (40), 195 (100). IR (KBr, cm$^{-1}$): 3331, 3061, 1648, 730. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.34 (dd, 2H, $J = 8.4$, 1.6 Hz), 8.12 (br, 1H, NH), 7.99 (d, 1H, $J = 8.0$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.64–7.50 (m, 3H), 7.34 (t, 1H, $J = 7.8$ Hz), 7.06 (t, 1H, $J = 8.0$ Hz), 6.99 (d, 2H, $J = 8.8$ Hz), 6.49 (d, 2H, $J = 8.8$ Hz), 2.22 ppm (s, 3H, CH$_3$). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 185.4, 144.5, 137.8, 136.2, 134.6, 132.1, 131.5, 130.0, 129.8, 129.3, 128.9, 127.4, 126.1, 122.3, 114.1, 111.5, 20.6 ppm. (HRMS = 327.1366, requires C$_{21}$H$_{17}$N$_3$O 327.1366).

2-Benzoylbenzoxazole (21). Colorless crystals from ethanol, m.p. 136–138 (lit. [17] m.p. 139 °C). MS: m/z (%) = 223 (M$^+$, 75), 195 (40), 105 (100). $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 8.56 (dd, 2H, $J = 8.4$, 1.6 Hz), 7.97 (d, 1H, $J = 8.4$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.71 (t, 1H, $J = 8.0$ Hz), 7.58 (t, 2H, $J = 7.8$ Hz), 7.56 (t, 1H, $J = 7.8$ Hz), 7.51 ppm (t, 1H, $J = 7.8$ Hz). $^{13}$C-NMR (150 MHz, CDCl$_3$): $\delta$ 180.4 (C), 157.3 (C), 150.5 (C), 140.9 (C), 135.2 (C), 134.1 (CH), 130.9 (2CH), 128.5 (2CH), 128.2 (CH), 125.6 (CH), 122.3 (CH), 111.7 (CH) ppm. Anal. Calcd. for C$_{14}$H$_9$NO$_2$ (223.3): C, 75.33; H, 4.06; N, 6.27. Found: C, 75.23; H, 4.05; N, 6.29.

4. Conclusions

The present study offers a new route for the synthesis of some new heterocyclic phenanthridin-6-yl-2-phenyldiazines. Some of these photoproducts 10a–c have been shown to have efficient complexation properties with transition metals and exhibit interesting photo-emission and fluorescence properties [18,19]. It also shows that 1-substituted benzotriazole arylhydrazones behave photochemically in a different manner than in flash vacuum pyrolysis (FVP) or static pyrolysis (STP) reactions [12-14].

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20. Crystallographic data of (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 852370 (9a), CCDC 852374 (4b) and CCDC 852389 (14b). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

Sample Availability: Samples of the compounds 4, 9, 14, 18 and 21 are available from the authors.

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