

## Novel Photocoupling Reaction in Two-Component Crystals of Tetracyanobenzene with Benzyl Cyanide

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We have been studying photoreactions occurring in two-component crystals or in solid mixtures for more than a decade.<sup>1</sup> Here, we report that a crystalline 1:2 adduct of tetracyanobenzene (TCNB) with benzyl cyanide (BzCN) undergoes selectively an unusual photocoupling reaction.

The crystalline adduct TCNB·2BzCN (**1**) was obtained as colorless plates by recrystallization of TCNB from hot BzCN. This crystalline adduct **1** showed no clear melting point; solid TCNB and liquid BzCN separated above 66 °C, and the TCNB part melted at 273–275 °C (TCNB, mp = 270–272 °C). The C,H,N analyses (C, 75.82; H, 3.96; N, 19.68) were consistent with those calculated for (TCNB)(BzCN)<sub>2.2</sub> (i.e., C, 76.05; H, 4.02; N, 19.92). The <sup>1</sup>H NMR spectrum in DMSO-*d*<sub>6</sub> was a simple sum of the spectra for TCNB and BzCN. The IR spectrum in a KBr disk exhibited strong absorptions at 3113, 3033, 2919, 2254, 2243, 1494, 1451, 1406, 1282, 943, 935, 736, and 694 cm<sup>-1</sup>. This is not a simple sum of the spectra of the components. For TCNB, IR (KBr) peaks at 3114, 3048, 2245, 1485, 1277, and 917 cm<sup>-1</sup> were found, and for BzCN, IR (KBr) peaks at 2252, 1497, 1454, 1415, 735, and 696 cm<sup>-1</sup> were observed. The major peaks at 943 and 935 cm<sup>-1</sup> were found neither for TCNB nor BzCN, indicating that **1** is not a simple mechanical mixture of TCNB and BzCN.

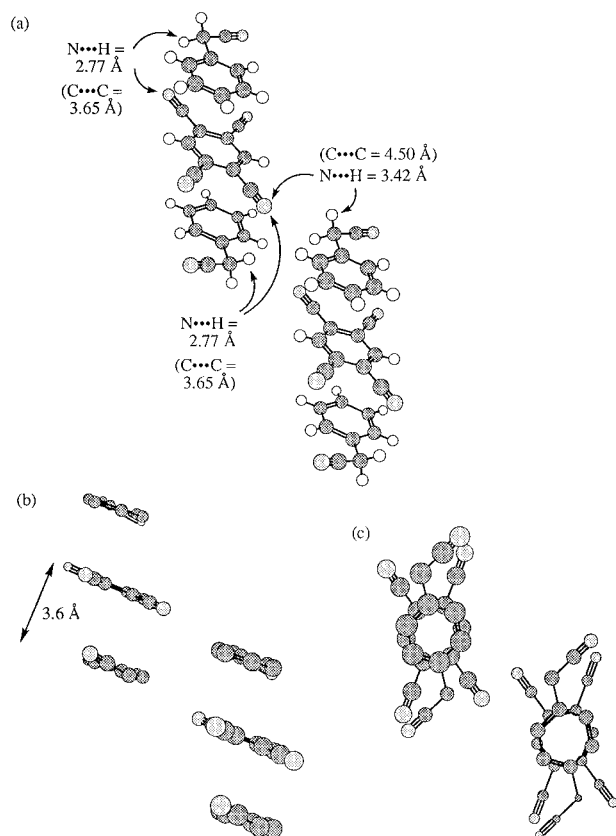
The crystal structure of **1** was determined by X-ray diffraction.<sup>2</sup> Two molecules of BzCN and one molecule of TCNB form a unit cell and are arranged like a BzCN···TCNB···BzCN sandwich in a parallel fashion (Figure 1a–c). There is a center of symmetry at TCNB. The interplane distance is 3.6 Å. This structure suggests that BzCN and TCNB are interacting through weak charge-transfer (CT) forces.<sup>3</sup> In fact, a CT transition was observed around 367 nm in the diffuse reflectance spectrum of the adduct **1** (Figure 2). From absorption spectral studies in acetonitrile, TCNB was also found to form a weak CT complex with BzCN (*K* = 0.07 M<sup>-1</sup>) with a CT transition around 322 nm.

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(1) For recent publications, see: (a) Ito, Y.; Asaoka, S.; Saito, I.; Ohba, S. *Tetrahedron Lett.* **1994**, 35, 8193–8196. (b) Ito, Y.; Borecka, B.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1995**, 36, 6083–6086. (c) Ito, Y.; Borecka, B.; Olovsson, G.; Trotter, J.; Scheffer, J. R. *Tetrahedron Lett.* **1995**, 36, 6087–6090. (d) Ito, Y. *Mol. Cryst. Liq. Cryst.* **1996**, 277, 247–253. (e) Ito, Y.; Fujita, H. *J. Org. Chem.* **1996**, 61, 5677–5680. (f) Ito, Y.; Olovsson, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 127–133.

(2) Rigaku four-circle diffractometer. Crystal data for **1**: C<sub>26</sub>H<sub>16</sub>N<sub>6</sub> (*M*<sub>r</sub> = 412.45), triclinic *P*1, *a* = 7.767, *b* = 10.957, and *c* = 7.682 Å, α = 93.80°, β = 117.61°, γ = 103.05°, *V* = 553.2 Å<sup>3</sup>, *Z* = 1, *D*<sub>x</sub> = 1.238 g/cm<sup>3</sup>, λ (Mo Kα) = 0.710 73 Å, μ = 0.077 mm<sup>-1</sup>, *R* = 0.053. Crystal data for **3**: C<sub>18</sub>H<sub>9</sub>N<sub>5</sub> (*M*<sub>r</sub> = 295.30), triclinic *P*1, *a* = 7.721, *b* = 13.393, and *c* = 7.219 Å, α = 103.19°, β = 105.65°, γ = 78.45°, *V* = 692.2 Å<sup>3</sup>, *Z* = 2, *D*<sub>x</sub> = 1.417 g/cm<sup>3</sup>, λ (Mo Kα) = 0.710 73 Å, μ = 0.090 mm<sup>-1</sup>, *R* = 0.053. The details have been deposited at the Cambridge Crystallographic Data Centre.

(3) Dahl, T. *Acta Chem. Scand.* **1994**, 48, 93–106. Kobayashi, T.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1971**, 44, 2603–2610. Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, 46, 4116–4126.



**Figure 1.** (a) Crystal structure of TCNB·2BzCN (**1**). (b) View a is horizontally rotated by  $-34^\circ$ . (c) View a is horizontally rotated by  $64^\circ$ . For b and c, hydrogens are removed for clarity.

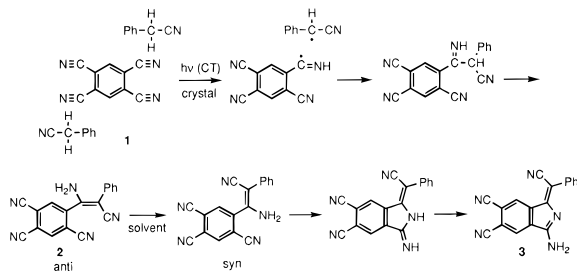
Irradiation of **1** in the solid state led to selective formation of a novel coupling product (**2**). While **2** was nearly stable either as a solid or in a DMSO solution, it was unstable in solvents such as MeOH, EtOH, acetone, and MeCN or in the presence of BzCN, rearranging into an isoindole derivative **3** readily or in the course of several days at room temperature. It was sparingly soluble in ether and insoluble in CHCl<sub>3</sub>.

In a typical experiment, the crystals of **1** (40 mg) were spread between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp for 20 h under argon. During the irradiation, the photolysis vessel<sup>1d</sup> was cooled from the outside by circulation of cold water (4 °C). After the irradiation, the orange photolysate was immediately evaporated in vacuo at 60 °C to remove unreacted BzCN. The residue, where **2** was present as a sole product in a 65% yield on the basis of TCNB (NMR), was fractionally recrystallized with MeCN (0.6 mL) to furnish, fortunately, 3 mg of pure **2** as orange-yellow plates: mp > 300 °C (dec.). The separation of **2** from unreacted TCNB was not easy, because **2** often cyclized into **3** during the workup. Although the crystals of **2** obtained were twin crystals, their X-ray data were collected and the structure could be estimated (*R* = 0.270). The conformation of **2** is shown in Scheme 1 and is called *anti* here. When the spectral data<sup>4</sup> as well as the rearrangement reaction **2** → **3** are considered, the structure of the primary product **2** is doubtless.

In a separate experiment, fractional recrystallization of the orange photolysate from 1 mL of MeCN, followed by further

(4) For **2**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 7.29–7.34 (1 H, m), 7.38 (2 H, s, disappeared on deuteration), 7.45–7.47 (4 H, m), 8.72 (1 H, s), 8.98 (1 H, s); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ 114.31, 114.55, 114.57, 116.64, 116.66, 118.75, 121.19, 127.12 (CH), 127.77 (CH), 129.16 (CH), 132.67, 135.31 (CH), 138.24 (CH), 144.90, 151.80; IR (KBr) 3460, 3362 (strong), 2241, 2198 (strong), 1622 (strong), 1583, 1529, 1493, 1446, 1411, 1275, 925, 915, 770, 704 cm<sup>-1</sup>; MS (EI) *m/e* (rel intensity) 295 (92, M<sup>+</sup>), 294 (100); UV/vis (DMSO) λ 435 (ε 2500), 292 (14 200) nm.

## Scheme 1



recrystallization from 10 mL of acetone afforded 6 mg of **3** as orange-yellow needles: mp > 300 °C.<sup>5</sup> The structure of **3** was unequivocally determined by X-ray analysis.<sup>2</sup> The X-ray quality crystals were obtained from recrystallization of **3** from MeCN/EtOH (1:1 v/v).

A rational reaction mechanism is presented in Scheme 1. Since irradiation of crystals of **1** through either a Pyrex filter (>280 nm) or a solution filter (7 g/L of BiCl<sub>3</sub> in 10% HCl, >355 nm) produced **2** with comparable efficiencies, the primary step must be CT excitation of **1**. The CT excitation accompanied by a proton transfer will result in a hydrogen abstraction by the cyano group of TCNB. Although a similar process was proposed to occur upon irradiation (at 254 nm) of TCNB in an acetonitrile or isobutyronitrile solution,<sup>6</sup> photochemical hydrogen abstraction reactions by the cyano group are quite rare.<sup>7</sup> Coupling of the photogenerated radical pair and a subsequent 1,3-proton shift will give rise to **2**. The observed high stability of **2** in the solid state is understandable, because the amino group and the relevant *o*-cyano group are fixed in an *anti* relationship in the rigid crystalline environment. In MeOH, EtOH, acetone, MeCN, or BzCN solution, however, the conformation of **2** will be able to change from *anti* to *syn*, where cyclization to **3** may well occur.<sup>8</sup>

Two types of the TCNB/BzCN close contact are indicated in Figure 1a. The distance between one of the cyano nitrogens of TCNB and the nearest benzylic hydrogen of BzCN is 2.77 Å, and the corresponding C...C distance is 3.65 Å. These are probably short enough for the hydrogen abstraction by the cyano group as well as the radical coupling of the resultant radical pair to occur, because the sum of the van der Waals radii for N and H is 2.75 Å and that of C and C is 3.4 Å. Hydrogen abstraction is feasible over distances around the van der Waals sum.

Alternatively, the distance between the cyano nitrogen of TCNB and the second nearest benzylic hydrogen of BzCN is 3.42 Å, and the corresponding C...C distance is 4.50 Å. Although these distances are rather long, we consider that this arrangement cannot be neglected since it requires less molecular rotation through a reaction pathway from **1** to **2**. Recently, we have found several photocycloaddition reactions in multicomponent crystals, where the component olefin molecules are considerably separated or are moving.<sup>9</sup>

As aforementioned, TCNB and BzCN formed a weak CT complex in MeCN. Photochemistry of the TCNB–BzCN

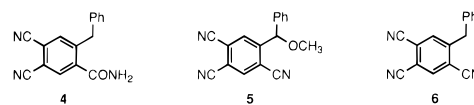
(5) For **3**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 7.40 (1 H, t, J = 7.5 Hz), 7.49 (2 H, t, J = 7.8 Hz), 8.20 (2 H, d, J = 7.8 Hz), 8.65 (1 H, s), 8.81 (1 H, s), 8.88 (1 H, s, disappeared on deuteration), 9.19 (1 H, s, disappeared on deuteration); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ 115.06, 115.82, 116.08, 116.15, 119.55, 126.70 (CH), 127.46 (CH), 128.55 (CH), 128.81 (CH), 129.63 (CH), 133.00, 136.54, 142.85, 155.95, 165.47, 165.56; IR (KBr) 3464, 2235, 2205, 1671 (strong), 1528 (strong), 1444, 1392, 1324, 1272, 1194, 772, 697 cm<sup>-1</sup>; MS (EI) *m/e* (rel intensity) 295 (87, M<sup>+</sup>), 294 (100); HRMS calcd for C<sub>18</sub>H<sub>9</sub>N<sub>5</sub> 295.0858, found 295.0845; UV/vis (MeCN) λ 429 (ε 13 300), 278 (9800), 239 (25 500), 206 (19 400) nm; UV/vis (DMSO) λ 446 (ε 24 100), 285 (19 700) nm.

(6) Tsujimoto, K.; Abe, K.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1983**, 984–985.

(7) Cantrell, T. S. *J. Chem. Soc., Chem. Commun.* **1975**, 637–638.

(8) Meyers, A. I.; Sircar, J. C. *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Wiley-Interscience: New York, 1970; pp 400–404.

system in solution was very different from that in the solid state. For example, an MeCN solution containing TCNB (0.5 M, solubility limit) and BzCN (1.0 M) was irradiated through Pyrex for 15 h at 20 °C under Ar bubbling. No reaction products were detected by NMR. On the other hand, similar irradiation of a solution of TCNB (0.042 M, solubility limit) in BzCN produced a complex mixture with a trace of recovered TCNB, from which **4** (44%), **5** (17%), and **6** (3%) were isolated by preparative TLC.<sup>11</sup> However, **2** and **3** were undetectable in the reaction mixture. Whether this difference in the reaction course is due to an effect of crystal packing on the primary photochemical hydrogen abstraction step or on the following radical reaction step is not clear at the moment.



Attempts were made to prepare other weak adduct crystals of TCNB by means of recrystallization. For example, a variety of 4-substituted BzCN derivatives such as 4-HOBzCN, 4-MeOBzCN, 4-MeBzCN, 4-NCCH<sub>2</sub>BzCN, 4-ClBzCN, and 4-O<sub>2</sub>NBzCN were tested. In all cases, however, we failed to obtain adduct crystals. It appears that size and shape of the donor molecule is an important factor. As displayed in Figure 1c, the cyanomethyl group of BzCN is just fit for the space between the *o*-cyano groups of TCNB. Therefore, the 4-substituents on BzCN may hamper close packing. So far, other adduct crystals were successfully obtained only with benzyl alcohol (BzOH) to afford colorless plates of a 1:1 adduct TCNB·BzOH. This adduct also underwent photolysis unique to the crystalline state, giving a dark brown photolysate, but product isolation has been unsuccessful yet.<sup>12</sup>

In summary, complex photoproducts **4–6** were produced from irradiation of TCNB in a BzCN solution, while the cocrystal TCNB·2BzCN (**1**) underwent selective photocoupling to give **2**, which subsequently cyclized into **3** in solution. The present results encourage us that though it is still in an embryonic stage,<sup>1,13</sup> the research on two- or multicomponent crystals is an intriguing treasury of novel photoreactions which are completely different from those in solution. Multicomponent crystals to be studied are almost limitless in number, and we believe that this work has opened the door to this promising field of organic photochemistry.

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**Supporting Information Available:** Spectral data and formation mechanism for **4–6**, CT absorption spectra, and X-ray data (for **2** and **4**) (16 pages). See any current masthead page for ordering and Internet access instructions.

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(9) For example, β-type photodimerization of *trans*-*o*-methoxycinnamic acid in the double salt crystals with ethylenediamine (double-bond separation >5.35 Å)<sup>1c</sup> and β-type photodimerization of *trans*-cinnamamide in the 2:1 hydrogen-bonded cocrystals with phthalic acid (double-bond separation 7.52 Å or dynamic disorder).<sup>10</sup>

(10) Ito, Y.; Ohba, S. To be published.

(11) These products suggest that the same type of reaction as the previously reported one<sup>6</sup> occurred initially. See Supporting Information.

(12) Like the TCNB–BzCN system, irradiation of TCNB and BzOH in MeCN yielded essentially no products, while irradiation of TCNB in BzOH gave **4** in a 70% yield.

(13) For intensive investigations on a particular type of two-component crystals, see: Gamlin, J. N.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer, J. R.; Trotter, J. *Acc. Chem. Res.* **1996**, *29*, 203–209 (organic salts). Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480–486 (host–guest crystals). Ito, Y. *Synthesis* To be submitted (review).