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Solid-State and Solution Photolyses of Tetracyanobenzene with Benzyl Cyanides or Benzyl Alcohols

Yoshikatsu Ito,[a,*] Hironari Nakabayashi,[a] Shigeru Ohba[b] and Hiroyuki Hosomi[b]

[a]*Department of Synthetic Chemistry & Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*
[b]*Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan*

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Abstract—Intermolecular photoreactions of tetracyanobenzene (TCNB) with benzyl cyanide (BzCN), benzyl alcohol (BzOH) and various others were investigated in the solid state (cocrystal) and in solution. The new solid-state photocoupling reaction found for the cocrystal TCNB·BzCN, giving a stilbene derivative followed by the solution isomerization into an isoindole derivative, is a very limited reaction. On the other hand, its solution photocondensation to give products of the diphenylmethane type occurred quite generally, probably under acidic conditions. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

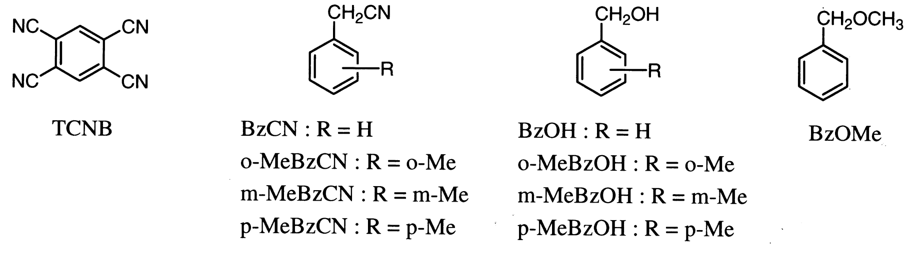
Studies on photochemical reactions occurring in two-component crystals or in solid mixtures are one of the current topics.[1,2] In our recent paper,[3–5] we have described briefly that a crystalline 1:2 complex between tetracyanobenzene (TCNB) and benzyl cyanide (BzCN), which is represented here by TCNB·BzCN, undergoes selectively a photoreductive coupling reaction at the cyano group of TCNB, resulting in production of a *trans*-stilbene derivative **1** in the solid state. By contrast, the photoreaction of TCNB in BzCN solution was very different from that of TCNB·BzCN, giving condensation products **3a**, **4a** and **5**.[3] In order to investigate the generality of these solid-state and solution-state photoreactions, we subsequently studied bimolecular photoreactions of TCNB with various partners that are analogous or homologous to BzCN. In this paper, we summarize the details of the results obtained so far. Scheme 1 lists main compounds that we employed and Scheme 2 shows the structures for various solid-state and solution-state photoproducts isolated in the present work.

Incidentally, we found that the colored charge-transfer crystals between TCNB and anthracene (1:1 complex),[6] *trans*-stilbene (2:1 complex),[7] durene (1:1 complex),[8] biphenyl (1:1 complex),[9] dimethylaniline (1:1 complex),[6] and others[2] were photostable in the solid state.[10]

Results and Discussion

Preparation of cocrystals

The main compounds that were tested to prepare the two-component crystals of tetracyanobenzene (TCNB) are shown in Scheme 1. Thus, TCNB was cocrystallized with the second component such as benzyl cyanides (BzCNs), benzyl alcohols (BzOHs) and benzyl methyl ether (BzOMe). When these second components are liquid at ordinary temperatures, the cocrystallization solvent was the second component itself. Since both *o*-methylbenzyl alcohol (*o*-MeBzOH) and *p*-methylbenzyl alcohol (*p*-MeBzOH) are solid, acetonitrile was used in these



Scheme 1. Main compounds studied.

Keywords: cyano compounds; electron transfer; crystalline complexes; photochemistry.

* Corresponding author. Tel.: +81-075-753-5670; fax: +81-075-753-5670; e-mail: yito@sbchem.kyoto-u.ac.jp

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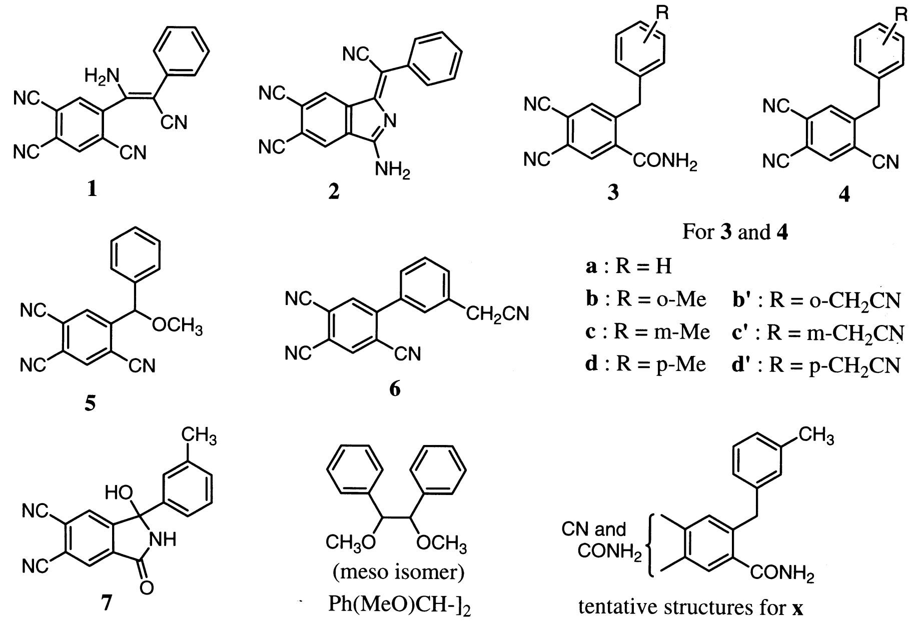


Scheme 2. Photoproducts.

cases as the cocrystallization solvent. Crystalline adducts were formed as colorless crystals in four combinations: TCNB·BzCN, TCNB·*o*-MeBzCN, TCNB·BzOH, TCNB·*m*-MeBzOH. The former two were 1:2 complexes, while the latter two were 1:1 complexes. These were characterized by IR, ^{1}H NMR, and elemental analyses. Their crystal structures were determined by single crystal X-ray diffraction (Figs. 1–4).

The crystal structure of TCNB·BzCN was already published.[3,4] Two molecules of BzCN and one molecule of TCNB form a unit cell and are arranged like a BzCN···TCNB···BzCN sandwich (Fig. 1). There is a center of symmetry at TCNB. The interplane distance is ca. 3.6 Å.

The crystal structure of TCNB·*o*-MeBzCN[5] was very similar to that of TCNB·BzCN. As displayed in Fig. 2, there is a center of symmetry at TCNB and *o*-MeBzCN···TCNB··*o*-MeBzCN are sandwiched with the interplane distance of ca. 3.7 Å.

Fig. 3 shows the crystal structure of TCNB·BzOH. Any molecules of TCNB and BzOH lie at the crystallographic inversion center. In other words, the position and orientation of BzOH is disordered. TCNB and BzOH are stacked alternately along the *a* axis. The interplane distance is ca. 3.8 Å.

The crystal structure of TCNB·*m*-MeBzOH is shown in Fig. 4. There is a positional disorder at the alcohol oxygen atom and the occupancy factors of the O1 and O2 atoms were assumed to be 50% each. Like TCNB·BzOH, TCNB and *m*-MeBzOH are stacked alternately along the *a* axis. The interplane distance is ca. 3.8 Å.

Solid-state photolyses of cocrystals

Crystals of TCNB·BzCN were crushed and were irradiated for 20 h with a high-pressure mercury lamp through Pyrex glass. A novel coupling product **1** was selectively formed (Table 1: 65% yield, ~100% based on reacted TCNB). Other products were not detectable by ^{1}H NMR. While **1** was nearly stable either as a solid or in a DMSO solution, it was unstable in solvents like MeOH, EtOH, acetone and MeCN or in the presence of BzCN, rearranging into an isoindole derivative **2** readily or in the course of several days at room temperature. It was sparingly soluble in ether or insoluble in CHCl$_3$. The structures of **1** and **2** were determined by single crystal X-ray diffraction.[3,4]

A probable reaction mechanism is presented in Scheme 3. Since irradiation through either a Pyrex filter (>280 nm) or a solution filter (7 g/L of BiCl$_3$ in 10% HCl, >355 nm) produced **1** with comparable efficiencies, the initial step must be CT excitation of TCNB·BzCN. The diffuse reflectance spectrum of TCNB·BzCN[4] is redrawn in Fig. 5. The CT excitation accompanied by a proton transfer will result in a hydrogen abstraction by the cyano group of TCNB. Coupling of the photogenerated radical pair and a subsequent 1,3-proton shift will give rise to **1**. Although similar CT excitation and concomitant proton transfer processes were proposed to occur upon irradiation (at 254 nm) of TCNB in an acetonitrile or isobutyronitrile solution,[11] the present reaction is the first example of the photoreductive coupling reaction of the cyano group. The observed high stability of **1** in the solid state is understandable, because the amino group and the relevant *ortho* 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 **1** will be able to change from *anti* to *syn*, where cyclization to **2** may well occur.[13] The proton transfer seems to be a rate-determining step, since the irradiation of cocrystal TCNB·BzCN-d$_2$ (BzCN-d$_2$=PhCD$_2$CN) under similar conditions afforded only a small yield of **1** (Table 1: 3% yield). From the X-ray analysis, the crystal structures of TCNB·BzCN and TCNB·BzCN-d$_2$ were found to be isomorphous.

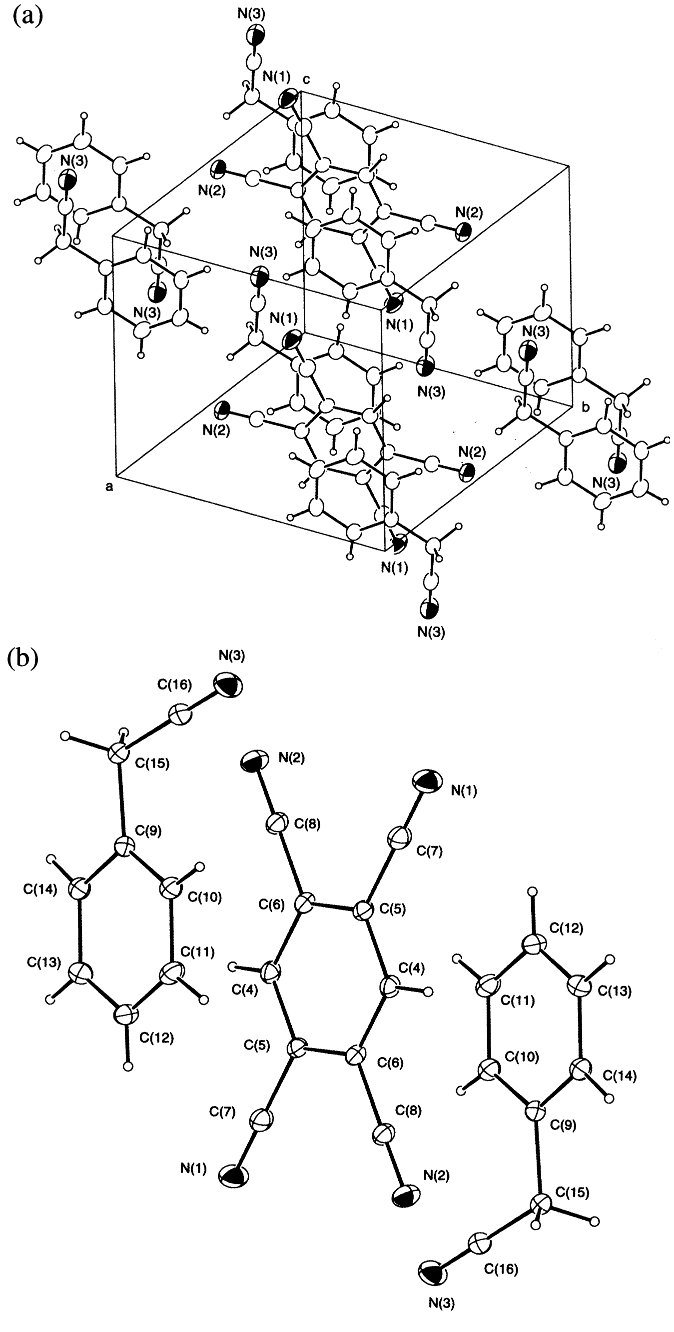


Figure 1. Crystal structure of TCNB·BzCN.[3]

Interatomic distance in crystal is the first measure to evaluate the solid-state reactivity.[2,14,15] The hydrogen abstraction reaction by the carbonyl or nitro group in the solid state has been well studied.[14,15] It was shown from these studies that the optimum value of distance for intramolecular hydrogen atom abstraction by ketone oxygen was around the sum of the van der Waals radii for oxygen and hydrogen (2.72 Å) and the upper limit was 3.1 Å.[14] For the cocrystal TCNB·BzCN, the distance between one of the cyano nitrogens of TCNB and the nearest benzylic hydrogen of BzCN N···H is 2.77 Åand the pertinent C···C distance is 3.65 Å (Fig. 6a). Although the solid-state hydrogen abstraction by the cyano group is unprecedented, these distances 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 van der Waals sum of the N and H atoms is 2.75 Å and that of the C and C atoms 3.4 Å. The crystallographic N···H distance (2.77 Å) is close to the van der Waals sum (2.75 Å).

Unlike TCNB·BzCN, TCNB·*o*-MeBzCN was photoinert under the same reaction conditions (Table 1). Its crystal structure was found to be similar to that of TCNB·BzCN (Figs. 1 and 2), but the distance between the cyano nitrogen of TCNB and the nearest benzylic hydrogen N···H is as long as 3.45 Å (the pertinent C···C, 3.95 Å) (Fig. 6b). Therefore, the absence of the short N···H contact may be responsible for the photoinertness of TCNB·*o*-MeBzCN.

Upon photolysis of pulverized crystals of TCNB·BzOH or

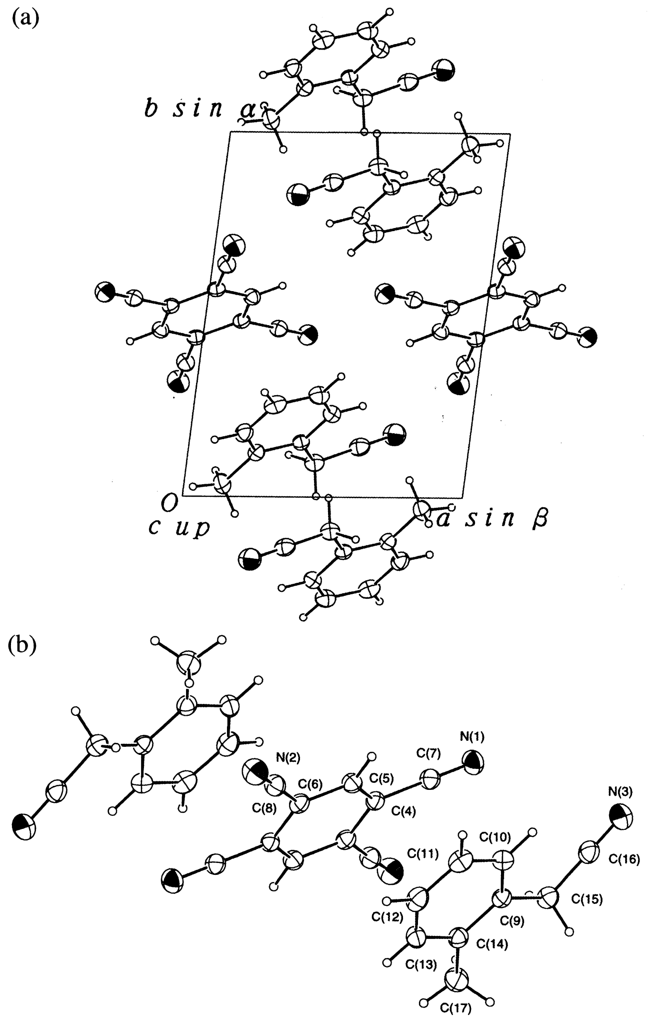


Figure 2. Crystal structure of TCNB·*o*-MeBzCN.[5]

TCNB·*m*-MeBzOH, the surfaces of the sample readily turned into dark brown or fairly brown, respectively. Isolation of the colored substances, however, were unsuccessful due to their so tiny amounts. Only the oxidation of the BzOH component to benzaldehyde or *m*-tolualdehyde, respectively, could be observed (Table 1). Further irradiation did not appreciably increase the product yields, probably due to the internal filter effect by the colored substances

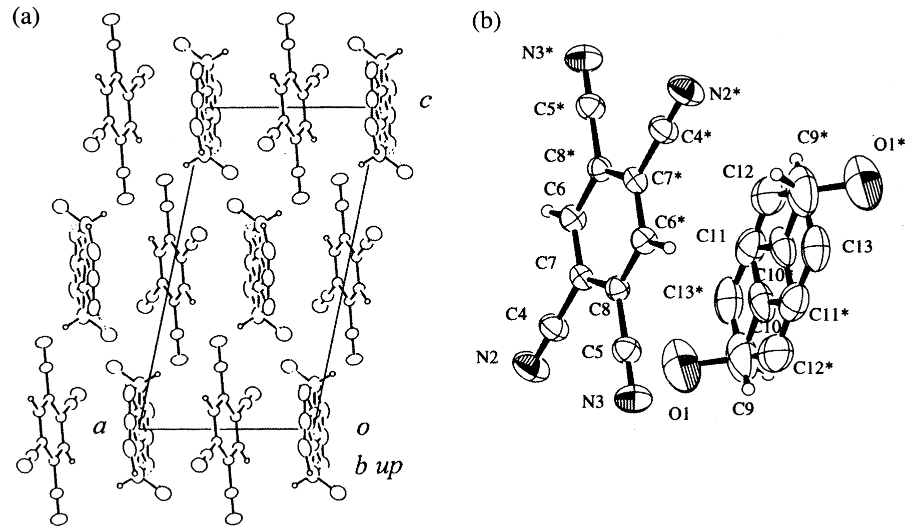


Figure 3. Crystal structure of TCNB·BzOH.

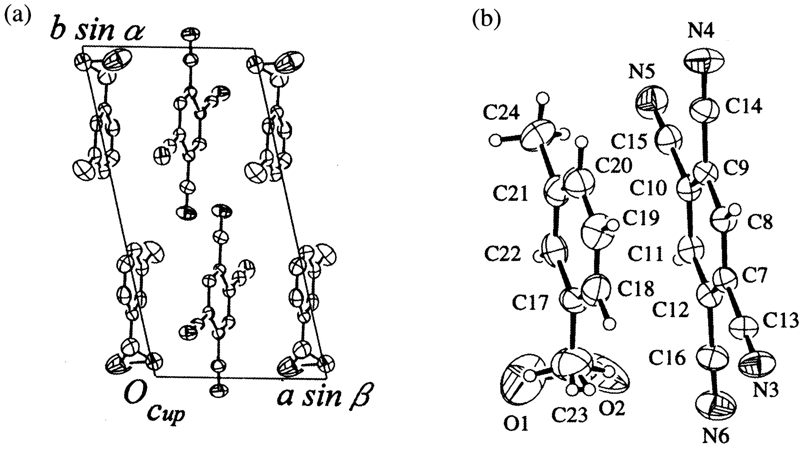


Figure 4. Crystal structure of TCNB·*m*-MeBzOH.

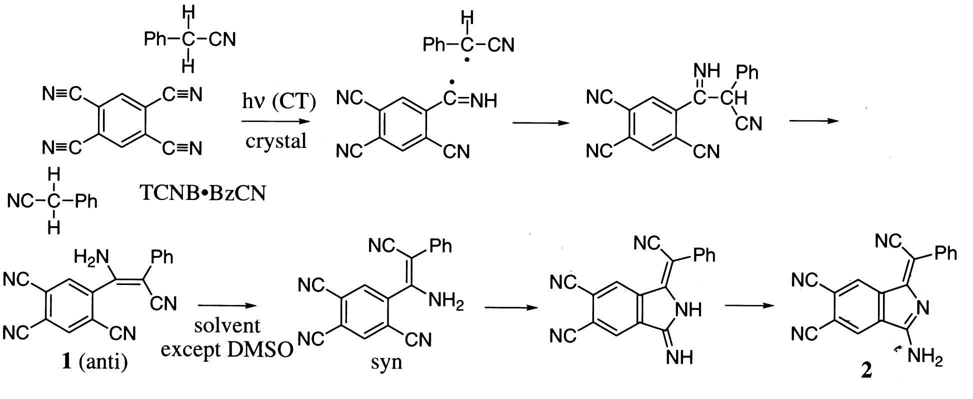
Table 1. Photolyses of two-component crystals involving TCNB in the solid state: irradiation time, 20 h

Reactants	Products (%)[a]				Recovered (%)	
	1	3–7	PhCHO	*m*-Me-PhCHO	TCNB	BzCNs or BzOHS
TCNB·BzCN (1:2 complex)	65	0	0	0	35	66
TCNB·BzCN-d$_2$ (1:2 complex)	3	0	0	0	97	99
TCNB·*o*-MeBzCN (1:2 complex)	No reaction				100	100
TCNB·BzOH (1:1 complex)	0	0	1	0	~100	99
TCNB·*m*-MeBzOH (1:1 complex)	0	0	0	15	95	85

[a] Yields were estimated by NMR or HPLC and are based on TCNB initially employed.

formed over the crystal surface. Irradiation under an argon (Table 1) or oxygen stream did not affect results. Inspection of the crystal structures for TCNB·BzOH and TCNB·*m*-MeBzOH showed that the distance between the cyano nitrogen of TCNB and the nearest benzylic hydrogen N···H was 3.01 and 2.93 Å, respectively (Fig. 6c and d). Although these distances are rough estimation because of their disordered crystal structures, they appear to be short enough for the hydrogen transfer to occur (vide supra). The resultant $ArCH(OH)^{\cdot}$ radical ($Ar{=}C_6H_5$ or *m*-MeC_6H_4) will possibly decay to generate the observed product $ArCH{=}O$. Because we were unable to identify the colored products, we can not tell more about the reaction mechanism.

In the hope that other unusual photoreactions such as TCNB·BzCN→**1** may be found, considerable efforts were made to prepare cocrystals of TCNB. Besides those compounds listed in Scheme 1, *p*-hydroxybenzyl cyanide, *p*-methoxybenzyl cyanide, *p*-xylylene dicyanide, *p*-chlorobenzyl cyanide, *p*-nitrobenzyl cyanide, benzylamine, benzyl chloride, ethylbenzene, propylbenzene, cumene, allylbenzene, phenylacetylene, 2-phenylethylamine, 2-phenylpropionitrile, 3-phenylpropionitrile, 1-phenylethanol, 2-phenylethanol, (2-chloroethyl)benzene, phenylacetaldehyde, *o*-, *m*-, *p*-pyridylacetonitrile, and *o*-, *m*-, *p*-pyridylcarbinol were tested. As mentioned above, when these compounds are liquid at ordinary temperatures, they were



Scheme 3. Solid-state photolysis of TCNB·BzCN.

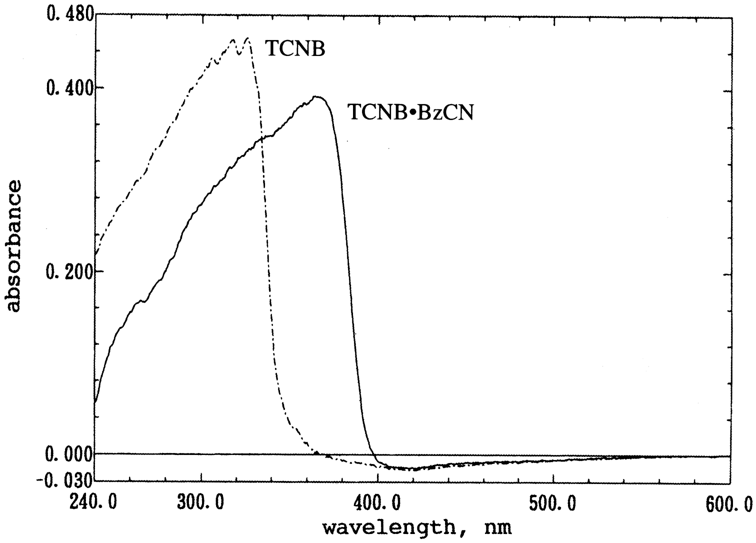


Figure 5. Diffuse reflectance spectra of TCNB and TCNB·BzCN.[4]

used as the recrystallization solvent. When these are solid, acetonitrile was used as the recrystallization solvent. In all cases, however, we failed to obtain crystalline adducts.

Solution photolyses

As summarized in Table 2, photolyses of TCNB in solution by using BzCNs, BzOHs, or BzOMe as the solvent afforded various condensation products **3**–**7**. The results are very different from those of the solid-state photolyses (Table 1). The structures of **3a**[4] and **7** (Fig. 7) were established by the X-ray analysis. Despite that the products **3**–**7** appear to have been formed via complicated steps, material balances were good in all cases. By contrast, irradiation of an acetonitrile solution containing TCNB and BzCN (molar ratio 1:2), TCNB and *o*-MeBzCN (1:2), TCNB and *m*-MeBzCN (1:2), TCNB and *p*-MeBzCN (1:2), TCNB and BzOH (1:1), TCNB and *m*-MeBzOH (1:1), or TCNB and BzOMe (1:1) (0.1–1 M in each reactants) afforded no or little reaction products. In the course of these studies, we found that the photochemistry of TCNB in BzCN was strongly dependent on acid or amine impurities in BzCN.

Upon dissolving TCNB in BzCN which was purchased from several commercial sources (Wako, Nakarai, Tokyo Kasei, and Aldrich), the solution became dark orange-red in a few hours. This coloring is probably due to amine impurities in BzCN.[†,‡] In fact, after a sulfuric acid-treatment of commercial BzCN, the solution of TCNB remained colorless for days and was pale yellow even after weeks.

Irradiation of a solution of TCNB (0.042 M) in acid-treated BzCN afforded **3a** (45%), **5** (18%), and **4a** (4%). Only a trace of TCNB was recovered (the first entry in Table 2). On the other hand, irradiation of a solution of TCNB (0.039 M) in non-acid-treated BzCN furnished **6** (31%) and **4a** (9%) along with a quantitative recovery of TCNB (60%) (the second entry in Table 2).[§] Scheme 4 describes a tentative mechanism for the solution-state photolysis of TCNB in acid-treated BzCN and the discussion follows.

Long multistep pathways are considered in Scheme 4. The first part of the mechanism (TCNB+BzCN→→A) is essentially the same as the one previously presented.[11] The initial event, i.e. the photochemical hydrogen transfer to TCNB from BzCN, is probably a common process in view of the fact that the TCNB excited state is a strong oxidant.[11,12,16] Although it seems that intermediates A and B might be isolable, no evidence was obtained by ^{1}H NMR analysis for the presence of these primary products. Final products **3a**, **4a**, and **5** were formed from early stages of irradiation. Before the product analysis, however, the resultant photolysate was directly evaporated under reduced pressure at high temperatures (~100°C) to remove the solvent BzCN. Therefore, transformations of some intermediates such as **A→B** and **B→C** may have proceeded thermally in the presence of acid impurities. In fact, albeit a low yield (12%), a compound analogous to **A** was previously isolated as a final product from the photolysis of TCNB in acetonitrile or isobutyronitrile.[11] The final part of the mechanism (**C→→3a**+**4a**+**5**) is highly speculative. However, irradiation of TCNB (0.03 M) in acid-treated BzCN containing CD_3OD or D_2O (BzCN/CD_3OD or D_2O=10:1 v/v) led to production of **3a**–**d** and **4a**–**d** (quantitative incorporation of one deuterium from ^{1}H NMR analyses) as expected from this final part of the mechanism. Since the deuterium incorporation into **5** was not observed, the formation mechanism for **5** and even the source of its methoxy group are still unclear.

[†] An acetonitrile solution containing TCNB and amine such as benzylamine, 2-phenylethylamine, aniline, and *N*,*N*-dimethylaniline, readily became dark colored.

[‡] In the previous report,[3] we used long-shelved BzCN (Nakarai), which had been left in an old bottle. This BzCN gave results similar to those of acid-treated BzCN.

[§] Two-component crystal TCNB·BzCN was obtained from either acid-treated BzCN or non-acid-treated BzCN. Solid-state photolyses of these samples, however, gave indistinguishable results.

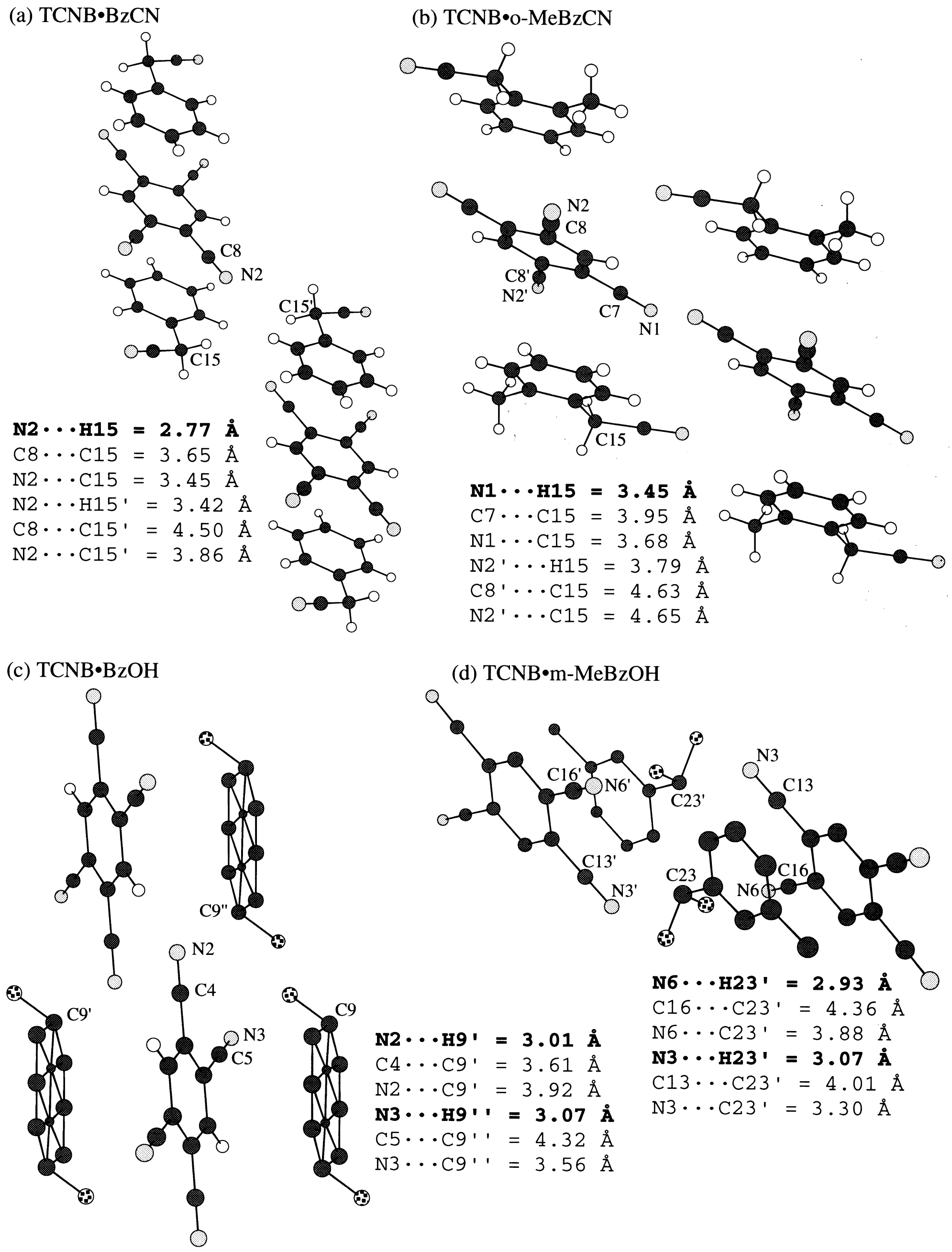


Figure 6. The distances between the TCNB nitrogen and the benzylic hydrogens nearby (N···H) as well as the relevant distances (C···C, N···C): (a) TCNB·BzCN; (b) TCNB·*o*-MeBzCN; (c) TCNB·BzOH; (d) TCNB·*m*-MeBzOH.

Table 2. Solution photolyses of TCNB in BzCNs, BzOHs and BzOMe: irradiation time, 15–20 h

Solvent ([TCNB])	Products (%)[a]					Recovered TCNB (%)
	1	**3**	**4**	**5**	Others	
BzCN (0.042 M)[b]	0	**3a**, 45	**4a**, 4	18	–	Trace
BzCN (0.041 M)[c]	0	0	**4a**, 9	0	**6**, 31	60
BzCN-d$_2$ (0.034 M)	0	0	Trace	0	–	~100
o-MeBzCN (0.035 M)	–	0	**4b**, 9; **4b′**, 23	0	–	68
m-MeBzCN (0.058 M)	–	0	**4c′**, 19	0	**x**, 3	76
p-MeBzCN (0.034 M)	–	**3d**, 10	**4d′**, 40	0	–	50
BzOH (0.015 M)	–	**3a**, 70	0	0	PhCHO, 21	3
m-MeBzOH (0.05 M)	–	**3c**, 33	0	0	**7**, 22; *m*-MePhCHO, 30	15
BzOMe (0.045 M)	–	0	0	64	Ph(OMe)CH–]$_2$, 21	0

[a] Yields were estimated by NMR or HPLC and are based on TCNB initially employed.

[b] Acid-treated BzCN was used.

[c] Non-acid-treated BzCN was used.

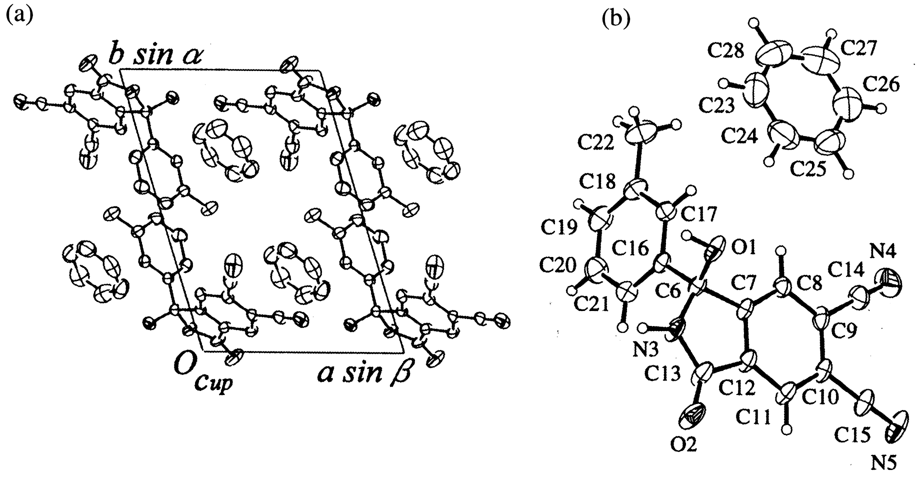
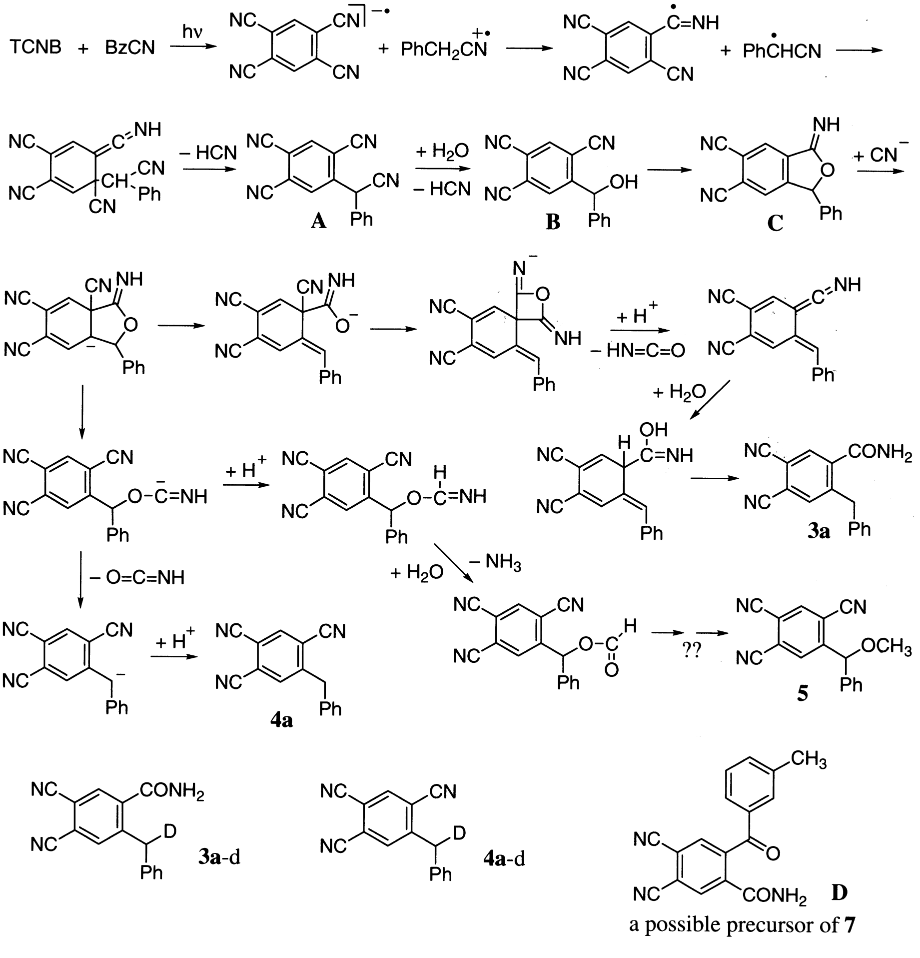


Figure 7. Crystal and molecular structures of compound **7**.

Production of **3a** in a good yield (70%) from the photolysis of TCNB (0.015 M) in BzOH (Table 2) can be explained with a similar route involving the intermediate **B**, i.e. TCNB+BzOH→→**B**→**C**→→**3a**. Formation of **7** (22%) in addition to **3c** (33%) from irradiation of TCNB in *m*-MeBzOH is also understandable in terms of a similar mechanism. The product **7** may be formed through oxidation/hydrolysis of an intermediate like **B** or **C**, because D seems to be a precursor of **7**. Irradiation of TCNB (0.045 M) in BzOMe produced **5** in 64% yield (Table 2). This reaction can be accommodated by a mechanism similar to the first part of Scheme 4, where **A** should correspond to the final product **5**.

Formation of a biphenyl derivative **6** upon photolysis of a solution of TCNB in non-acid-treated BzCN is somewhat surprising. At present, we are unable to propose a plausible mechanism for this unexpected reaction.



Scheme 4. A possible mechanism for the solution-state photolysis of TCNB in acid-treated BzCN.

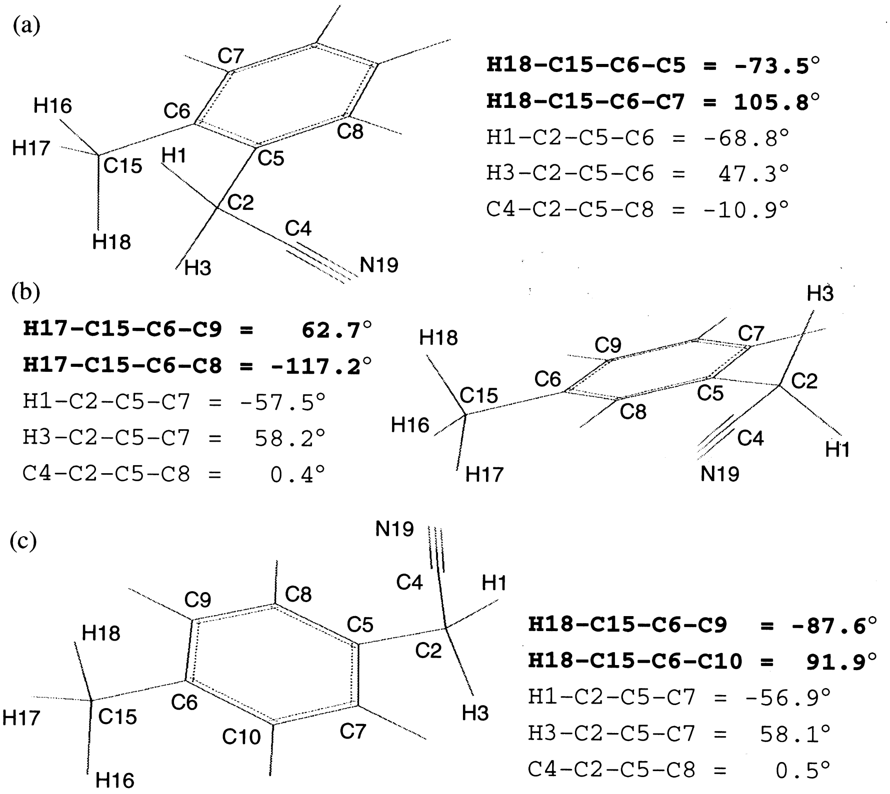


Figure 8. Calculated conformations for the cation radicals of *o*-, *m*-, and *p*-MeBzCN.

Photolyses of TCNB in *o*-, *m*-, and *p*-MeBzCN yielded **4b**′ (23%), **4c**′ (19%), and **4d**′ (40%), respectively, as a predominant product (Table 2). Formation of these products can be understood by a mechanism similar to Scheme 4. It is to be noted, however, that the hydrogen transfer to TCNB occurred from the methyl group rather than the cyanomethyl group of MeBzCN, although this is unexpected from consideration of the radical stability (vide infra). *o*-, *m*-, and *p*-MeBzCN employed here were not treated with acid but the reaction products (**4b**+**4b**′, **x**+**4c**′, **3d**+**4d**′, respectively) were analogous to those (**3a**+**4a**+**5**) obtained from acid-treated BzCN. Biphenyl derivatives corresponding to **6** were not produced, judging from ^{1}H NMR analyses. Furthermore, coloring of a TCNB solution in *o*-, *m*-, or *p*-MeBzCN was far less appreciable than in non-acid-treated BzCN. It seems on the basis of these observations that unlike BzCN, amine impurities in commercial *o*-, *m*-, and *p*-MeBzCN are negligible.

As confirmed by MO calculations,[‖] the cyano(tolyl)methyl radical NC(*o*-, *m*-, or *p*-MeC_6H_4)$CH^{\cdot}$ is more stable than the cyanomethylbenzyl radical *o*-, *m*-, or *p*-$NCCH_2C_6H_4CH_2^{\cdot}$ by 5 kcal/mol. Accordingly, the predominant formation of **4b**′–**4d**′ instead of **3b**–**d** or **4b**–**d** upon photolysis of TCNB in MeBzCN (Table 2) cannot be explained from consideration of the relative stability of radical intermediates. These products may be rationalized by inspection of the optimized geometry for the cation radicals of MeBzCN (Fig. 8a–c).[‖] The cyano group tends to be coplanar with the benzene ring in each case (C4–C2–C5–C8=−10.9, 0.4 and 0.5°, respectively), although more rigorous calculations are required since energy changes from rotation about the C2–C5 bond are small (<1 kcal/mol). With [*p*-$MeC_6H_4CH_2CN$]$^{+\cdot}$ (Fig. 8c), a C–H bond to one of the Me hydrogens (H18) is nearly perpendicular to the benzene ring, while neither of the bonds to the cyanomethyl hydrogens (H1 and H3) is. As a result, H18 may be eliminated more easily than H1 or H3, because an incipient lone-pair orbital being generated from this proton release can better overlap with the benzene π-orbital. Similar consideration based on the orbital overlap may be applicable for [*o*-$MeC_6H_4CH_2CN$]$^{+\cdot}$ and [*m*-$MeC_6H_4CH_2CN$]$^{+\cdot}$. As seen from Fig. 8a and b, the dihedral angle against the benzene plane is nearer to the right angle for one of the Me hydrogens (H18 and H17, respectively) than for the cyanomethyl hydrogens (H1 and H3 for both of the cation radicals). Therefore, as with [*p*-$MeC_6H_4CH_2CN$]$^{+\cdot}$, the methyl proton may be transferred more easily than H1 or H3 in agreement with the experimental data.

In summary, TCNB formed a 1:2 cocrystal with BzCN or *o*-MeBzCN and a 1:1 cocrystal with BzOH or *m*-MeBzOH. Upon photolysis of the cocrystal TCNB·BzCN in the solid state, TCNB and BzCN reacted through reductive coupling of the cyano group of TCNB, leading to a stilbene derivative **1** (65%) as a sole product, which in solution (except in DMSO) isomerized spontaneously to an isoindole derivative **2**. The cocrystals TCNB·*o*-MeBzCN, TCNB·BzOH, and TCNB·*m*-MeBzOH, on the other hand, did not give significant products. Crystal structures of these four cocrystals were determined by single crystal X-ray diffraction

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[‖] Calculations were carried out by using the AM1 semi-empirical model in the MacSpartan Plus molecular modeling program.

and their solid-state photoreactivities were interpreted in terms of the interatomic distances. In contrast with the solid-state photolysis, irradiation of TCNB in BzCN which had been treated with sulfuric acid, produced condensation products **3a** (45%), **4a** (4%), and **5** (18%). Irradiation of TCNB in non-acid-treated BzCN afforded a different product **6** (31%) in addition to **4a** (9%). Irradiations of TCNB in *o*-MeBzCN, *m*-MeBzCN, *p*-MeBzCN, BzOH, *m*-MeBzOH, and BzOMe also produced reasonable yields of condensation products **3**, **4**, **5**, and **7**, i.e. the same type of reactions as in acid-treated BzCN occurred. Probably, commercial BzCN was contaminated with amine impurities, and the above solution reactions seem to be very sensitive to acid or base impurities in the solvent.

Conclusion

Cocrystals will be intriguing treasury for specific unusual bimolecular reactions which are unlikely to occur in solution. In addition to the present reaction TCNB·BzCN⟶**1** (⟶**2**), we have recently reported: (a) cross photodimerization occurring in the hydrogen-bonded 1:2 cocrystal between fumaric acid and *trans*-cinnamamide[17]; and (b) cross photocycloaddition observed for the crystalline salt of tryptamine with *trans*-3-nitrocinnamic acid.[18] At this stage, however, it is difficult to increase the generality of these reactions, because we do not have enough knowledge to design cocrystals of desired structure.

Experimental

^{1}H NMR spectra were measured on a Varian Gemini-200 or JEOL JNM-A400 spectrometer. IR spectra were recorded in a JASCO FTIR-5M or SHIMADZU FTIR-8100A spectrometer. Mass spectra were obtained in a JEOL JMS-DX 300 or JEOL JMS-SX 102A spectrometer. Diffuse reflectance spectra were gathered with a SHIMADZU UV-2400PC spectrometer equipped with a diffuse-reflectance attachment. HPLC analyses were performed with a SHIMADZU LC-5A chromatograph by using a Cosmosil 5C$_{18}$-AR column (4.6 mm i.d. ×150 mm). Analytical or preparative TLC was carried out on Merck Silica gel 60 F$_{254}$ plastic sheets or 2 mm Merck Silica gel 60 F$_{254}$ PLC plates, respectively. All the irradiation experiments were carried out by using a 400 W high-pressure mercury lamp through Pyrex.

Materials

All reagents were commercially available. BzCNs and BzOH were distilled under reduced pressure prior to use. Since commercial BzCN was found to be contaminated with amines (see text), it was treated with acid. Thus, BzCN (30 mL) was mixed with 10% aqueous sulfuric acid, extracted with 10 mL of ethyl ether twice, dried with Na_2SO_4, and was then distilled under reduced pressure. TCNB was recrystallized from EtOH.

Deuteration of benzyl cyanide

In order to deuterate the benzyl position of BzCN,[19] a mixture of 10.14 g (86.7 mmol) of BzCN and 1.51 g (13.5 mmol) of potassium *tert*-butoxide in 60 mL of D_2O was stirred for 8 h at room temperature. Extraction with ether (60 mL×2), drying with Na_2SO_4 and then evaporation of ether gave α,α-dideuterated benzyl cyanide BzCN-d$_2$ (92% D content from ^{1}H NMR). This was further deuterated by repeating the same procedure and was finally distilled under reduced pressure to give 5.4 g of BzCN-d$_2$ (97% D content).

Preparation of two-component crystals

(a) TCNB·BzCN. TCNB (320 mg) was dissolved in hot BzCN (10 mL).[§] After the solution cooled down, colorless plates soon appeared and were collected by filtration (740 mg, 100% yield). Since the crystals slowly effloresce by loss of BzCN and gradually become pale yellow in the light, they were stored in the dark in a well-capped vial. The crystalline adduct thus obtained showed no clear mp; solid TCNB and liquid BzCN separated above 66°C and the TCNB part melted at 273–275°C (lit.[6] mp of TCNB 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)$_{2.2}$ (i.e. C, 76.05; H, 4.02; N, 19.92). The ^{1}H NMR spectrum in DMSO-d$_6$ was a simple sum of the spectra for TCNB and BzCN (1:2.3). The IR spectrum in a KBr disc exhibited strong absorptions at 3113, 3033, 2919, 2254, 2243, 1494, 1451, 1406, 1282, *943*, *935*, 736, 694 cm^{-1}. The peaks at 943 and 935 cm^{-1} were found neither for TCNB nor BzCN. A CT transition was observed around 367 nm by diffuse reflectance spectroscopy (Fig. 5)[4] and the crystal structure was determined by X-ray diffraction (Fig. 1).[3]

Likewise, TCNB·BzCN-d$_2$ was obtained as colorless plates; mp 65–267°C (not clear); IR (KBr) 3035, 2255, 2242, 1494, 1447, 1283, 1034, 936, 818, 715 cm^{-1}. Its ^{1}H NMR (DMSO-d$_6$, 200 MHz) was in accord with a mixture of TCNB and BzCN-d$_2$ (approximately 1:2). The X-ray analysis demonstrated that it was isomorphous with TCNB·BzCN.

Other two-component crystals were similarly prepared and characterized. Their crystal structures were determined by single crystal X-ray diffraction.

(b) TCNB·*o*-MeBzCN. Colorless plates; mp 57–270°C (not clear); IR (KBr) 3114, 3051, 2242, 1485, 1459, 1278, 912, 760 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 200 MHz) and the C, H, N analyses were in accord with a mixture of TCNB and *o*-MeBzCN (approximately 1:2). The crystal structure was determined by X-ray diffraction (Fig. 2).[5]

(c) TCNB·BzOH. Colorless plates; mp 66–277°C (not clear); IR (KBr) 3460, 3118, 3050, 2247, 1495, 1452, 1282, 1196, 1033, 1021, 923, 750, 702 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 200 MHz) and the C, H, N analyses were in accord with a mixture of TCNB and BzOH (approximately 1:1). The crystal structure was determined by X-ray diffraction (Fig. 3).

(d) TCNB·*m*-MeBzOH. Colorless prisms; mp 62–267°C (not clear); IR (KBr) 3380, 3115, 3049, 2245, 1487, 1279, 1034, 918, 789, 698 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 200 MHz) and the C, H, N analyses were in accord with a mixture of

TCNB and *m*-MeBzOH (approximately 1:1). The crystal structure was determined by X-ray diffraction (Fig. 4).

Solid-state photolysis of TCNB·BzCN

The crystals of TCNB·BzCN (40 mg) were crushed and spread between two Pyrex plates. This sample was placed in a photolysis vessel,[1] and irradiated for 20 h under argon. During the irradiation, the photolysis vessel 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 **1** was present as a sole product judging from ^{1}H NMR measurement in DMSO-d_6 and the conversion of TCNB was 65%, was fractionally recrystallized with MeCN (0.6 mL) to furnish 3 mg of pure **1** as orange-yellow plates: mp>300°C (dec). The separation of **1** from unreacted TCNB was not easy, because **1** often cyclized into **2** during the work-up. In a separate experiment, the orange photolysate was directly subjected to fractional recrystallization with 1 mL of MeCN, followed by further recrystallization from 10 mL of acetone to afford 6 mg of **2** as orange-yellow needles: mp>300°C. The structures of **1** and **2** were unequivocally determined by the X-ray analysis.[3,4]

α-Amino-β,2,4,5-tetracyanostilbene (1). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.29–7.34 (1H, m), 7.38 (2H, s, disappeared on deuteration), 7.45–7.47 (4H, m), 8.72 (1H, s), 8.98 (1H, s);^{13}C NMR (DMSO-d_6, 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, 2241, 2198, 1622, 1583, 1529, 1493, 1446, 1411, 1275, 925, 915, 770, 704 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 295 (92, M$^+$), 294 (100); UV/VIS (DMSO) λ 435 (ϵ 2500), 292 (14200) nm.

1-Amino-3-(α-cyanobenzylidene)-5,6-dicyano-3H-isoindole (2). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.40 (1H, t, J=7.5 Hz), 7.49 (2H, t, J=7.8 Hz), 8.20 (2H, d, J=7.8 Hz), 8.65 (1H, s), 8.81 (1H, s), 8.88 (1H, s, disappeared on deuteration), 9.19 (1H, s, disappeared on deuteration);^{13}C NMR (DMSO-d_6, 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, 1528, 1444, 1392, 1324, 1272, 1194, 772, 697 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 295 (87, M$^+$), 294 (100); HRMS calcd for $C_{18}H_9N_5$ 295.0858, found 295.0845; UV/VIS (MeCN) λ 429 (ϵ 13300), 278 (9800), 239 (25500), 206 (19400) nm; UV/VIS (DMSO) λ 446 (ϵ 24100), 285 (19700) nm.

Incidentally, a solid mixture, which was obtained by grinding 36 mg (0.20 mmol) of TCNB and 47 mg (0.40 mmol) of BzCN in an agate mortar and pestle for 10 min, showed the characteristic IR peaks of TCNB·BzCN at 943 and 935 cm^{-1}. This solid mixture (15 mg) was irradiated for 15 h. The NMR analysis of the resulting orange photolysate indicated that it was a mixture of **2**, TCNB and BzCN and that 33% of TCNB was converted to **2**.

Irradiation of TCNB·BzCN-d_2 under similar conditions for 10 h or 20 h produced **1** in a yield, respectively, only 1/25 or 1/15 that of TCNB·BzCN (from ^{1}H NMR analyses).

Solid-state photolyses of TCNB·*o*-MeBzCN, TCNB·BzOH, and TCNB·*m*-MeBzOH

Solid-state photolyses of TCNB·*o*-MeBzCN, TCNB·BzOH, and TCNB·*m*-MeBzOH were similarly carried out and the products were analyzed by ^{1}H NMR, TLC (1:1 ether–$CHCl_3$), and HPLC (2:3 methanol–water). As summarized in Table 1, no coupling or condensation reactions occurred in these cases.

Photolysis of **TCNB** in **BzCN**:

(a) A solution of TCNB (112 mg, 0.63 mmol) in 15 mL of acid-treated BzCN was irradiated for 15 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C to remove BzCN. The resulted dark-brown viscous residue was analyzed by ^{1}H NMR (DMSO-d_6 and $CDCl_3$). Then it was subjected to repeated preparative TLC (CH_2Cl_2 and 30–50:1 CH_2Cl_2–acetone) to afford 72 mg (44%) of **3a**, 5 mg (3%) of **4a**, 29 mg (17%) of **5**, and a trace of TCNB. Product **3a** was recrystallized from 12 mL of 5:1 CH_2Cl_2–hexane, followed by aqueous MeCN as yellow needles. Product **4a** was recrystallized from ether as colorless plates, while **5** was recrystallized from 2 mL of 1:1 ether–hexane as white crystals. The structure of **3a** was established by single crystal X-ray analysis.[4]

2-Benzyl-4,5-dicyanobenzamide (3a). Mp 182–183°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.28 (2H, s), 5.72 and 5.77 (2H, two br s, NH_2, disappeared on deuteration), 7.14 (2H, finely split d, J=7.2 Hz), 7.27–7.36 (3H, m), 7.61 (1H, finely split (0.4 Hz) s, 7.86 (1H, s);^{13}C NMR ($CDCl_3$, 100 MHz) δ 38.68 (CH_2), 113.90, 114.62, 114.71 and 117.22, 127.41 (CH), 129.11 (CH), 129.19 (CH), 131.90 (CH), 135.77 (CH), 137.41, 139.93, 146.08, 167.41; IR (KBr) 3434, 2235, 1661, 1612, 1406, 742, 701 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 261 (25, M$^+$), 244 (100), 215 (35); HRMS calcd for $C_{16}H_{11}ON_3$ 261.0902, found 261.0877. All the NMR signals were assigned and were confirmed by NOEDF and 2D NMR (NOESY, HMQC and HMBC) measurements.[4]

1-Benzyl-2,4,5-tricyanobenzene (4a). Mp 151–153°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.31 (2H, s), 7.16–7.4 (5H, m), 7.65 (1H, s), 8.06 (1H, s); IR (KBr) 2241, 1600, 1496, 1486, 1458, 1446, 907, 749, 733, 705 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 243 (100, M$^+$), 116 (45); HRMS calcd for $C_{16}H_9N_3$ 243.0796, found 243.0809.

1,2,4-Tricyano-5-(α-methoxybenzyl)benzene (5). Mp 135–137°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.42 (3H, s, H_d), 5.61 (1H, s, H_c), 7.35–7.44 (5H, m, H_e–H_g), 8.00 (1H, d, J=0.6 Hz, H_a), 8.19 (1H, t, J=0.6 Hz, H_b);^{13}C NMR ($CDCl_3$, 100 MHz) δ 57.31 (CH_3), 81.80 (CH), 113.54, 114.18, 114.34, 115.48 and 115.86, 119.73, 127.46 (CH), 129.32 (CH), 129.45 (CH), 132.13 (CH), 136.97 (CH), 137.04, 152.19; IR (film) 2240, 1600, 1486, 1453, 1194, 1098, 913, 736, 701 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 273 (40, M$^+$), 258 (100), 242 (86), 215 (51), 180 (30), 121 (71); HRMS calcd for $C_{17}H_{11}ON_3$ 273.0902, found 273.0914.

The structure was confirmed by NOEDF measurements as well as by gated decoupling and selective decoupling experiments.[4]

(b) A solution of TCNB (234 mg, 1.31 mmol) in 32 mL of non-acid-treated BzCN was irradiated for 18 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d$_6$ and CDCl$_3$) and then separated by preparative TLC (4:1 CHCl$_3$–ether) to afford 19 mg (6%) of **4a**, 63 mg (18%) of **6**, and 122 mg (52%) of TCNB. Product **6** was recrystallized from methanol to afford pale brown needles.

2,4,5-Tricyano-3′-(cyanomethyl)biphenyl (6). Mp 164–167°C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.87 (2H, s), 7.51–7.63 (4H, m), 7.97 (1H, s), 8.18 (1H, s); ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 2.65 (2H, s), 6.38 (1H, finely split s), 6.44 (1H, finely split s), 6.73–6.78 (3H, m or finely split s at δ 6.73 (~0.5H), 6.75 (~1H) and 6.77 (~1.5H)), 6.88 (1H, t, J=7.6 Hz); IR (neat film) 2241, 1597, 1537, 1488, 1431, 1266, 918, 803, 710 cm^{-1}; MS (EI) m/z (rel intensity) 268 (100, M$^+$), 178 (62); HRMS calcd for C$_{17}$H$_8$N$_4$ 268.0749, found 268.0758. 2D NMR (HSQC) was measured to confirm the *meta* substitution.

(c) A solution of TCNB (6 mg, 0.034 mmol) in 1 mL of BzCN-d$_2$ was irradiated for 16 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The ^{1}H NMR analysis of the residue indicated little occurrence of the reaction.

(d) Irradiation of TCNB in BzCN containing CD$_3$OD or D$_2$O. A solution of TCNB (12 mg, 0.069 mmol) in 2 mL of acid-treated BzCN containing 0.2 mL of CD$_3$OD (Aldrich, 99.8% D) was irradiated for 6 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The ^{1}H NMR analysis of the residue (DMSO-d$_6$ and CDCl$_3$) indicated the presence of **3a**–**d**, **4a**–**d**, **5**, and TCNB in molar ratios 0.8:0.3:1:0.2. Approximately one atom of deuterium incorporation was observed for **3a** and **4a** at their benzylic positions, but no deuterium incorporation was observed for **5**. A solution of TCNB (11 mg, 0.062 mmol) in 2 mL of acid-treated BzCN containing 0.2 mL of D$_2$O (Aldrich, 99.9% D) was irradiated for 5 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The ^{1}H NMR analysis of the residue gave similar results.

Photolysis of TCNB in *o*-MeBzCN

A solution of TCNB (190 mg, 1.07 mmol) in 30 mL of *o*-MeBzCN was irradiated for 18 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d$_6$ and CDCl$_3$) and then separated by preparative TLC (CHCl$_3$ and 100:1 CHCl$_3$–acetone) to afford 19 mg (7%) of **4b**, 63 mg (21%) of crude **4b′**, and 101 mg (53%) of TCNB. Because of the instability on silica gel, **4b** could not be purified enough. **4b** was recrystallized from methanol.

1,2,4-Tricyano-5-(*o*-methylbenzyl)benzene (4b). Mp 155–160°C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.17 (3H, s), 4.28 (2H, s), 7.03 (1H, d, J=8 Hz), 7.22–7.33 (3H, m), 7.36 (1H, s), 8.06 (1H, s); IR (film) 2241, 1599, 1493, 1460, 1379, 935, 743 cm^{-1}; MS (EI) m/z (rel intensity) 257 (100, M$^+$), 129 (95), 91 (51); HRMS calcd for C$_{17}$H$_{11}$N$_3$ 257.0953, found 257.0937.

1,2,4-Tricyano-5-[*o*-(cyanomethyl)benzyl]benzene (4b′). ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.67 (2H, s), 4.34 (2H, s), 7.04 (1H, d, J=7 Hz), 7.38–7.48 (3H, m), 7.46 (1H, s), 8.09 (1H, s); MS (EI) m/z (rel intensity) 282 (100, M$^+$), 254 (79), 242 (44), 228 (44), 116 (39); HRMS calcd for C$_{18}$H$_{10}$N$_4$ 282.0905, found 282.0901.

Photolysis of TCNB in *m*-MeBzCN

A solution of TCNB (366 mg, 2.06 mmol) in 35 mL of *m*-MeBzCN was irradiated for 20 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d$_6$ and CDCl$_3$) and then separated by preparative TLC (4:1 CHCl$_3$–ether) to afford 78 mg (14%) of **4c′** and 190 mg (52%) of TCNB along with one uncharacterized product **x** (15 mg) whose tentative structures are shown in Scheme 2. **4c′** was recrystallized from ether–CH$_2$Cl$_2$ (1:1) and **x** was recrystallized from ether–acetone (9:1).

1,2,4-Tricyano-5-[*m*-(cyanomethyl)benzyl]benzene (4c′). Mp 138–139°C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.76 (2H, s), 4.30 (2H, s), 7.17 (1H, d, J=8 Hz), 7.18 (1H, s), 7.31 (1H, d, J=8 Hz), 7.40 (1H, t, J=8 Hz), 7.62 (1H, s), 8.06 (1H, s); IR (film) 2239, 1610, 1489, 1441, 1400, 914, 764 cm^{-1}; MS (EI) m/z (rel intensity) 282 (88, M$^+$), 281 (100), 254 (38), 116 (21); HRMS calcd for C$_{18}$H$_{10}$N$_4$ 282.0905, found 282.0898.

x. Mp 148–150°C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.35 (3H, s), 4.21 (2H, s), 6.93–7.35 (4H, m), 7.62 (1H, s), 8.04 (1H, s); IR (film) 3437, 2239, 1654, 1605, 1487, 1387, 1052, 909, 836, 734 cm^{-1}; MS (EI) m/z (rel intensity) 293 (18, M$^+$), 292 (35), 291 (54), 290 (73), 257 (50), 256 (100); HRMS (for M$^+$−2H$_2$O) calcd for C$_{17}$H$_{11}$N$_3$ 257.0953, found 257.0942.

Photolysis of TCNB in *p*-MeBzCN

A solution of TCNB (60 mg, 0.34 mmol) in 10 mL of *p*-MeBzCN was irradiated for 20 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d$_6$ and CDCl$_3$) and then separated by preparative TLC (4:1 CHCl$_3$–ether) to afford 7 mg (8%) of **3d**, 32 mg (34%) of **4d′**, and 27 mg (45%) of TCNB. **3d** and **4d′** were purified by recrystallization from MeCN–water (3:1) and ether–MeCN (10:1), respectively.

4,5-Dicyano-2-(*p*-tolylmethyl)benzamide (3d). Mp 150–155°C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.31 (3H, s), 4.21 (2H, s), 5.71 (2H, br s, NH$_2$), 7.00 and 7.12 (4H, AA′BB′ q, J=7.9 Hz), 7.58 (1H, s), 7.84 (1H, s); IR (KBr) 3676 (strong), 2234, 1660 (strong), 1599, 1389, 921, 904, 803 cm^{-1}; MS (EI) m/z (rel intensity) 275 (14, M$^+$), 258

(100), 243 (18), 215 (25); HRMS calcd for $C_{17}H_{13}ON_3$ 275.1059, found 275.1056.

1,2,4-Tricyano-5-[*p*-(cyanomethyl)benzyl]benzene (4d′). Mp 146–147°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.75 (2H, s), 4.29 (2H, s), 7.21 and 7.35 (4H, AA′BB′ q, *J*=8.4 Hz), 7.63 (1H, s), 8.05 (1H, s); IR (KBr) 2240, 1516, 1489, 1425,1384,922 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 282 (100, M$^+$), 255 (44), 240 (19), 116 (43); HRMS calcd for $C_{18}H_{10}N_4$ 282.0905, found 282.0919.

Photolysis of TCNB in BzOH

A solution of TCNB (104 mg, 0.58 mmol) in 40 mL of BzOH was irradiated for 20 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d_6 and $CDCl_3$). Then, 107 mg (70%) of **3a** was isolated with preparative TLC ($CHCl_3$–acetone). The yield of PhCHO was determined by HPLC (2:3 methanol–water) before evaporating the photolysate.

Photolysis of TCNB in *m*-MeBzOH

A solution of TCNB (45 mg, 0.25 mmol) in 5 mL of *m*-MeBzOH was irradiated for 20 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The residue was analyzed by ^{1}H NMR (DMSO-d_6 and $CDCl_3$). Then, by using preparative TLC (10:1 CH_2Cl_2–acetone), 16 mg (23%) of **3c** and 13 mg (18%) of **7** were isolated. Compounds **3c** and **7** were recrystallized from MeCN–water or benzene–acetone–ether, respectively. *m*-MePhCHO was analyzed with HPLC (2:3 methanol–water) before evaporating the photolysate. The structure of **7** was established by the single crystal X-ray analysis. It crystallized with one molecule of benzene included (Fig. 7).

4,5-Dicyano-2-(*m*-tolylmethyl)benzamide (3c). Mp 198–198.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (3H, s), 4.21 (2H, s), 5.68 and 5.76 (2H, two br s, NH_2), 6.90 (1H, d, *J*=8 Hz), 6.92 (1H, s), 7.07 (1H, d, *J*=8 Hz), 7.20 (1H, t, *J*=8 Hz), 7.59 (1H, s), 7.85 (1H, s); IR (film) 3397, 2235, 1667 (strong), 1607, 1590, 1403, 917 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 275 (19, M$^+$), 258 (100), 243 (16), 215 (26); HRMS calcd for $C_{17}H_{13}ON_3$ 275.1059, found 275.1059.

5,6-Dicyano-3-hydroxy-3-(*m*-tolyl)isoindolin-1-one (7). Mp 194–195.5°C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.35 (3H, s), 3.55 (1H, broad s), 6.96 (1H, broad s), 7.20–7.23 (1H, m), 7.27–7.35 (3H, m), 7.77 (1H, s), 8.15 (1H, s); IR (film) 2239, 1717, 1692, 1424, 1303, 1159, 1082, 1067, 759 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 289 (33, M$^+$), 272 (55), 271 (53), 256 (100), 198 (25), 180 (31), 119 (33), 91 (27); HRMS calcd for $C_{17}H_{11}O_2N_3$ 289.0851, found 289.0849.

Photolysis of TCNB in BzOMe

A solution of TCNB (80 mg, 0.45 mmol) in 10 mL of BzOMe was irradiated for 16 h at 20°C under argon bubbling. The mixture was evaporated under reduced pressure at ca. 100°C. The brown residue was analyzed by ^{1}H NMR (DMSO-d_6 and $CDCl_3$) and was then separated by preparative TLC (CH_2Cl_2) to give 56 mg (46%) of **5** and 23 mg (21%) of *meso*-Ph(MeO)CH–$]_2$. The latter product was recrystallized from methanol–water (9:1) as yellow crystals.

(1*R*,2*S*)-1,2-Dimethoxy-1,2-diphenylethane Ph(MeO)CH–]$_2$ (*meso*). Mp 141.5–145°C (lit.[20] mp 144–145°C); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.14 (6H, s), 4.29 (2H, s), 7.12–7.18 (4H, m), 7.23–7.29 (6H, m); IR (neat film) 1177, 1106, 941, 755, 697 cm^{-1}; MS (EI) *m*/*z* (rel intensity) 121 (100, M$^+$/2), 77 (13); HRMS calcd for $C_8H_9O_1$ (=M$^+$/2) 121.0653, found 121.0661.

X-Ray crystal structure determination

X-Ray intensities were measured on Rigaku AFC-5 or AFC-7R diffractometer with graphite monochromatized MoKa radiation (λ=0.71073 Å). The structures were solved by direct methods and were refined using TEXSAN software.[21]

Crystal data. TCNB·BzCN: triclinic $P\bar{1}$, *a*=7.767(1), *b*=10.957(1), *c*=7.682(2) Å, α=93.80(1)°, β=117.61(1)°, γ=103.05(1)°, *V*=553.2(2) Å^3, *Z*=1, D_x=1.238 g/cm^3, *R*=0.053.[3] TCNB·*o*-MeBzCN: triclinic $P\bar{1}$, *a*=8.387(1), *b*=10.780(1), *c*=7.206(1) Å, α=103.40(1)°, β=109.24(1)°, γ=79.12(1)°, *V*=593.9(1) Å^3, *Z*=1, D_x=1.232 g/cm^3, *R*=0.057.[5] TCNB·BzOH: monoclinic $P2_1/_n$, *a*=7.552(1), *b*=7.182(2), *c*=14.356(1) Å, β=101.76(1)°, *V*=762.3(2) Å^3, *Z*=2, D_x=1.247 g/cm^3, *R*=0.066. TCNB·*m*-MeBzOH: triclinic $P\bar{1}$, *a*=7.475(3), *b*=14.930(4), *c*=7.400(2) Å, α=99.24(2)°, β=90.76(2)°, γ=102.72(3)°, *V*=794.1(5) Å^3, *Z*=2, D_x=1.256 g/cm^3, *R*=0.082. **7**: triclinic $P\bar{1}$, *a*=9.605(2), *b*=13.072(3), *c*=9.406(3) Å, α=100.37(2)°, β=114.94(2)°, γ=100.50(2)°, *V*=1008.3(5) Å^3, *Z*=2, D_x=1.210 g/cm^3, *R*=0.066.

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References

1. Ito, Y. *Synthesis* **1998**, 1–32.
2. Ito, Y. *Molecular and Supramolecular Photochemistry* **1999**, *3*, 1–70.
3. Ito, Y.; Endo, S.; Ohba, S. *J. Am. Chem. Soc.* **1997**, *119*, 5974–5975.
4. Supplementary materials in Ref. 3.
5. Hosomi, H.; Ohba, S.; Ito, Y.; Nakabayashi, H. *Acta Crystallogr. C* **1997**, *53*, IUC 9700031.
6. Biley, A. S.; Henn, B. R.; Langdon, J. M. *Tetrahedron* **1963**, *19*, 161–167.
7. Agostini, G.; Corbaja, C.; Giacometti, G.; Pasimeni, L.; Clemente, D. A. *J. Phys. Chem.* **1988**, *92*, 997–1003.
8. Lefebvre, J.; Miniewicz, A.; Kowal, R. *Acta Crystallogr. C* **1989**, *45*, 1372–1376.
9. Pasimeni, L.; Guella, G.; Corvaja, C.; Clemente, D. A.; Vicentini, M. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 25–38.

10. Unpublished results.
11. Tsujimoto, K.; Abe, K.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1983**, 984–985.
12. Tsujimoto, K.; Nakao, N.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1992**, 366–367.
13. Meyers, A. I.; Sircar, J. C. *The Chemistry of the Cyano Group*; Rappoport, Z. Ed.; Wiley-Interscience: New York, 1970; pp 400–404.
14. Ihmels, H.; Scheffer, J. R. *Tetrahedron* **1999**, *55*, 885–907.
15. Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481.
16. Mella, M.; Fagnoni, M.; Freccero, M.; Fasani, E.; Albini, A. *Chem. Soc. Rev.* **1998**, 81–89.
17. Ito, Y.; Hosomi, H.; Ohba, S. *Tetrahedron* **2000**, *36*, 6833–6844.
18. Ito, Y.; Fujita, H. *Chem. Lett.* **2000**, *36*, 6833–6844.
19. Nishiyama, K.; Oda, J.; Inouye, Y. *Bull. Inst. Chem. Res. Kyoto. Univ.* **1974**, *52*, 499–505.
20. Merz, A.; Eichner, M.; Tomahogh, R. *Liebigs Ann Chem.* **1981**, 1774–1784.
21. Molecular Structure Corporation. *TEXSAN*, Single Crystal Structure Analysis Software. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1999.