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Photoreactions of 1,2,4,5-benzenetetracarbonitrile with arylethenes—photo- olefin dimerization–aromatic substitution reactions

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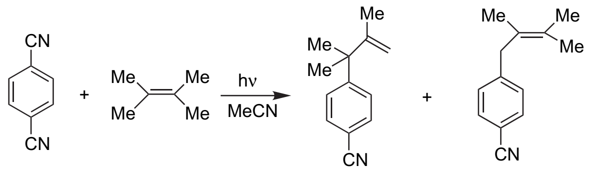
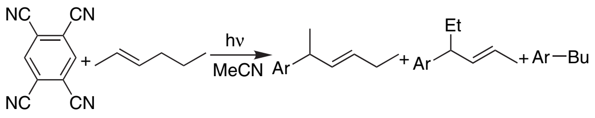
Abstract—Irradiation of 1,2,4,5-tetracyanobenzene (TCNB) with styrene derivatives **1**–**4**, respectively, leads to a photochemical olefin dimerization–aromatic substitution reaction to give the corresponding (2,4,5-tricyanophenyl)tetralin derivative (**8**, **12**, **16**, **17**, and **20**) as the main product. Further irradiation of the primary product with alkene results in substitution of the *meta*-CN group by another phenyltetralinyl to give the corresponding 4:1 (alkene–TCNB) product. According to the effect of the codonor (biphenyl) and salt (magnesium perchlorate) on reaction rate, the result of photoinduced reactions of TCNB with tetralin (**6**) and 1-phenyltetralin (**7**) and analysis of the known kinetic data for relevant processes in the cyanoarene–alkene reactions, the mechanism for the formation of the olefin dimerization–aromatic substitution products (such as **8**) is proposed to involve radical pair combination of the alkene cyclodimer radical (the corresponding 4-phenyl-1-tetralinyl radical) with TCNB$^{-\bullet}$ followed by expulsion of a CN^{-}. Photoreactions of TCNB with the alkene photocyclodimer (1-phenyltetralin) may also make minor contributions. Photoinduced reaction of TCNB with 1-phenylcyclohexene (**5**) takes a different pathway from **1**–**4** to afford the 1:1 (**5**–TCNB) primary product **21** by deprotonation of **5**$^{+\bullet}$ and radical pair combination with TCNB$^{-\bullet}$ followed by elimination of HCN.

1. Introduction

Photoinduced electron transfer (PET) reactions of cyanoarenes with alkenes have been the subject of active research.[1] They have contributed a wealth of knowledge to the structures and reactivities of the cation radicals of various alkenes, and have been a source of new chemical reactions of synthetic and mechanistic value. Several typical reaction modes in this area have been studied, which depend on the structures of the cyanoarene and the alkene, as well as on reaction conditions such as solvent polarity, the presence of added nucleophile, cosensitizer (codonor), base, etc. In the photoreactions of aliphatic alkenes with cyanoarenes in the absence of ambient nucleophile, the strongly acidic cation radical of the alkene deprotonates to give an allylic type radical, which combines with the cyanoarene anion radical followed by extrusion of a cyanide anion to give an alkene–cyanoarene 1:1 *ipso* substitution product as exemplified by reactions 1 and 2.[2]



(1)



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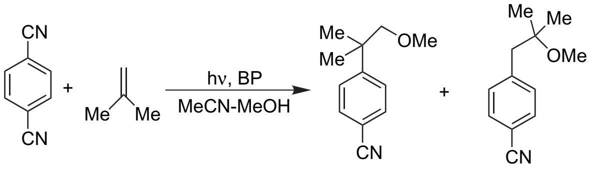
In the presence of added nucleophile such as methanol or anions (cyanide, fluoride), the aliphatic alkene cation radical is first attacked by the nucleophile regioselectively, giving a β-methoxyalkyl, β-cyano, or β-fluoroalkyl radical, which subsequently adds to the cyanoarene anion radical followed by extrusion of a cyanide anion to afford a nucleophile–olefin combination, aromatic substitution (photo-NOCAS) product (reactions 3[2c] and 4[2g]).[1h,2–5]



(3)

Keywords: Photochemistry; 1,2,4,5-Tetracyanobenzene; Arylethene.

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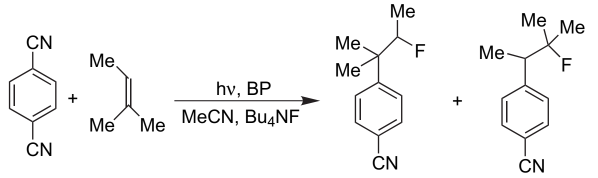
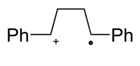


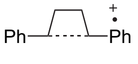
(4)

The cation radicals of arylethenes behave quite differently from their aliphatic counterparts. In PET reactions with cyanoarenes in the presence of added high concentration nucleophile, such as an alcohol as cosolvent, the arylethene cation radical is trapped by the nucleophile regioselectively and the resulting alkene–nucleophile addition radical is then reduced by the cyanoarene anion radical to a carbanion, which is protonated. The net result is an *anti*-Markovnikov addition of the nucleophile to the arylethene.[1b,6a]

In the absence of added nucleophile, the arylethene cation radical tends to attack a neutral arylalkene molecule, which is a stronger nucleophile than aliphatic alkenes, to give the dimeric cation radical as an open chain 1,4-distonic cation radical[7] or a long bond cyclobutane cation radical.[8] Transformation of **A** and **B** to the cyclobutane and hexatriene cation radicals followed by reduction by the acceptor anion radical or by the starting neutral alkene affords the cyclobutane and tetralin products.[6] This is caused by the higher electron acceptor ability of the arylalkene's dimer cation radical than the aliphatic alkene cation radical. Radical pair combination between the arylethene's dimer cation radical and the cyanoarene's anion radical is therefore largely averted. In these reactions, the cyanoarene more often serves as a sensitizer without taking part in net reactions, and alkene dimer–cyanoarene *ipso* substitution reactions are seldom reported.[9] To our knowledge, there are only two reports on such reactions, all for 1,4-dicyanobenzene (DCNB). In photoreactions of DCNB with phenylcyclopentene in MeCN, the alkene dimer–DCNB coupling product **I** was formed as a minor product together with the alkene dimer products.[9a,b] In photoreaction of DCNB with *p*-methylstyrene, the coupling product **II** was formed in low yield (30%).[9c]



A



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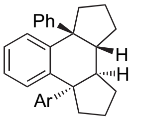
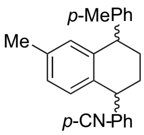
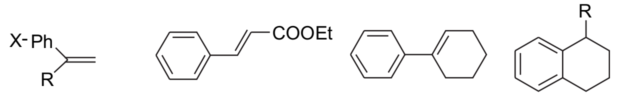


I



II

Tetracyanobenzene (TCNB) has a half wave reduction potential of −0.65 V (SCE, MeCN) and a singlet excited state (S_1) energy of 3.83 eV, and with an excited state reduction potential of 3.18 V, it is the strongest electron acceptor of all cyanoarenes.[1b,10] With the singlet excited TCNB as an electron acceptor, even saturated aliphatic alkanes with high oxidation potential may serve as σ-donor to take part in PET reactions to give alkane cation radicals in which the C–H σ bond is activated for ready deprotonation leading to the alkyl radicals.[11] Because of the much higher oxidation potential of TCNB anion radical (−0.65 V) than that of other cyanoarenes such as DCNB, back SET from TCNB$^{-\bullet}$ to the arylethene dimer cation radical is inhibited, it is therefore anticipated that this would open the way for efficient TCNB$^{-\bullet}$–arylalkene dimer cation radical combination, leading to an olefin dimerization–aromatic substitution reaction. However, this type of reaction has not been reported before for TCNB.[12] We report here our investigation on photoinduced reactions of TCNB with the arylalkenes **1**–**5**. In these reactions, the olefin dimerization–aromatic substitution products were formed in high yield for **1**–**4**, while **5** gave 1:1 substitution product. Photoinduced reactions of TCNB with tetralin **6** and 1-phenyltetralin **7** were also investigated to provide insight to the mechanism of the photoreactions of TCNB with **1**–**4**.



1 X=R=H
2 X=*p*-Me, R=H
3 X=H, R=Me
4
5
6 R=H
7 R=Ph

Chart 1.

2. Results and discussion

2.1. Results

Although styrene[13a] and α-methylstyrene[13b] form a weak charge transfer complex (CTC) with TCNB in the ground state, they cause no measurable change in the electronic spectrum of TCNB when added to a TCNB acetonitrile solution (1×10^{-3} mol L^{-1}) in concentrations up to 0.5 M. Therefore, in their photoreactions, selective excitation of TCNB without significant CTC excitation involvement can be achieved by irradiation through a glass filter, which cuts off light of $\lambda<300$ nm. Irradiation of an acetonitrile solution of TCNB (0.05 M) and **1** (0.75 M) under nitrogen atmosphere for 13 h resulted in complete consumption of TCNB and gave a single product **8**[14a] in 86% yield. We further found that, irradiation of **8** in MeCN in the presence of **1** resulted in continuous consumption of **8** and the reaction was completed in 22 h, giving two diastereomeric 4:1 products (**1**–TCNB) **10** (66%) and **11** (10%). These two products could also be formed in the photoreactions of TCNB with **1** if the irradiation was continued after the complete consumption of TCNB.

Similar irradiation of TCNB with *p*-methylstyrene **2** for 10 h gave the 4:1 adduct **13** (Fig. 1) as main product (67%) together with a small amount of a 2:1 adduct **12** (2%).

Photoreactions of TCNB with α-methylstyrene **3** in MeCN gave two diastereomeric 2:1 products **16** (36%) and **17** (31%), together with a 4:1 product **18** (18%) and an isocoumarin derivative **19** (11%).

Ethyl cinnamate **4** can also take part in similar reaction with TCNB in MeCN to give the 2:1 product **20** (45%).

In these photoreactions, different amounts of nonpolar products consisting of the alkene dimers were found, which can be eluted out by petroleum ether in column chromatography. However, due to the difficulty in separating them, these were only quantified in the case of reaction of TCNB with **3** (see Section 4).

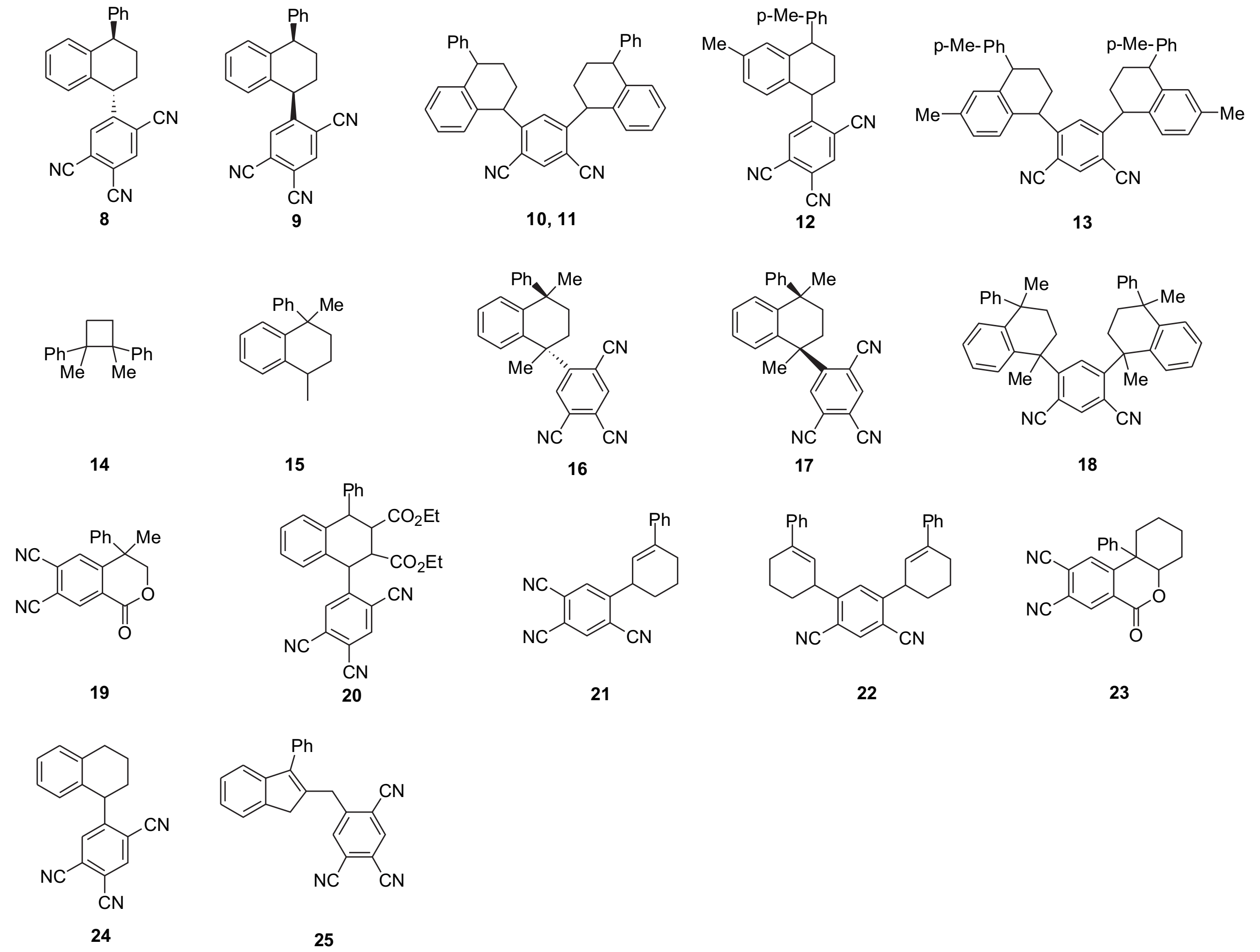


Chart 2.

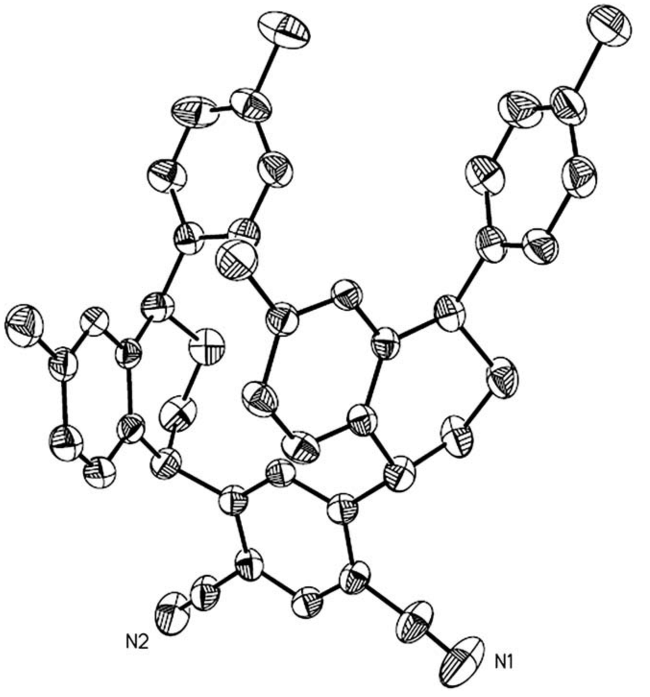


Figure 1. X-ray structure of **13**, showing 30% probability displacement ellipsoids. H-atoms have been omitted for clarity.

To help to clarify the mechanism of these reactions, photoreactions of TCNB with tetralin **6** and 1-phenyltetralin **7** were also investigated. Irradiation of TCNB (0.05 M) with **6** (0.5 M) in MeCN under similar conditions as mentioned above resulted in a sluggish reaction, and the total conversion of TCNB required 48 h irradiation to give the product **24** in 74% yield. Similar photolysis of TCNB (0.05 M) with **7** (0.5 M) in MeCN for 60 h led to the total conversion of TCNB and afforded the same 2:1 product **8** (37%) as obtained in photoreactions of TCNB with **1**, and its diastereomer **9** (21%), along with an indene product **25** (7%) obviously derived from secondary reactions.

The influence of added codonor (cosensitizer)[6d,15–18] and salt[19] on these reactions was also examined by testing the photoreactions of TCNB with **3** in the presence and absence of the added biphenyl (BP) and anhydrous $Mg(ClO_4)_2$, respectively. The results are given in Table 1 (entries 4–6). When the reactants were irradiated for 7.5 h in the absence of BP and salt, it only reached a 95% conversion of TCNB without the formation of secondary 4:1 product **18**. At the same time, parallel runs with added BP and $Mg(ClO_4)_2$, respectively, were 'overirradiated' in view of the complete conversion of TCNB and the formation of the secondary 4:1 product in significant amount by further reactions of **16*** and **17*** with **3**. These results showed that reaction rate was substantially accelerated by the added BP and $Mg(ClO_4)_2$.

Table 1. Photoreactions of TCNB with **1–7**[a]

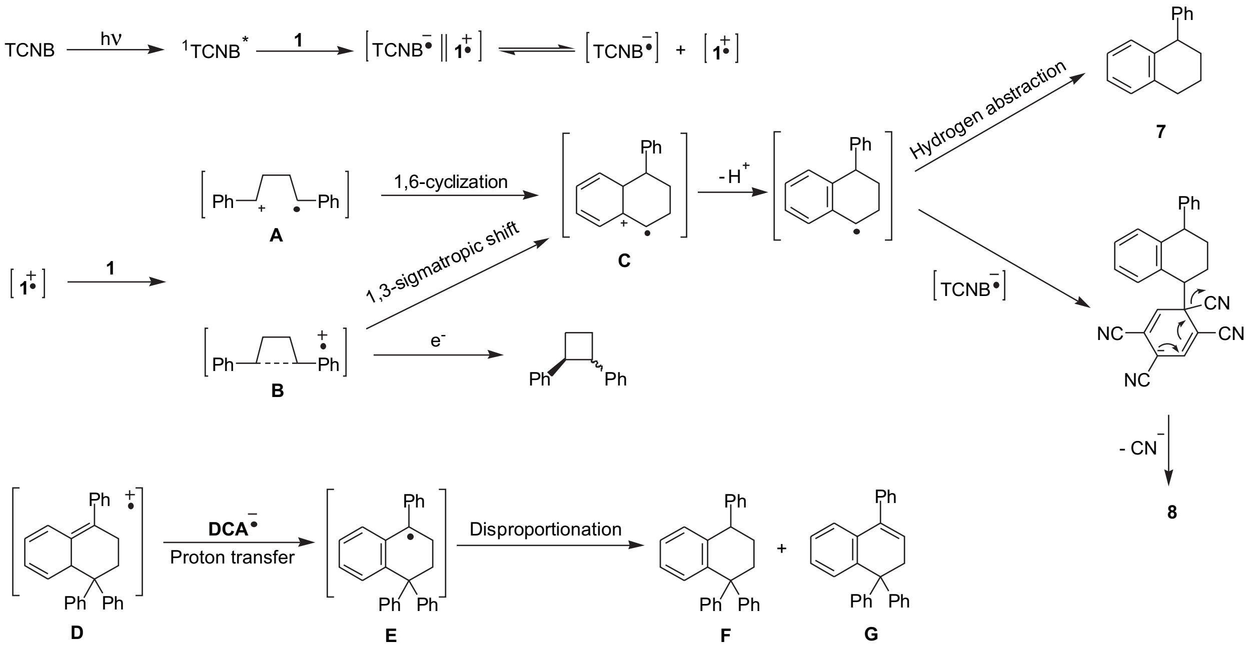
Entry	Donor	$E_{1/2}^{ox}$ [b] (V, SCE)	ΔG_{ET} (kcal mol^{-1})	K_{SV} (M^{-1})	Irrd. time (h)	Conv. (%)	Products and yield (%)
1	**1**	1.93	−30.9	299	13	100	**8** (86)
2	**2**	1.74	−35.3	215	10	100	**12** (2), **13** (66)
3[b]	**3**	1.86	−32.5	248	14	98	**16** (50), **17** (38), **18** (5), **19** (6)
4[c]	**3**				7.5	95	**16** (49), **17** (41), **19** (4)
5[d]	**3**				7.5	100	**16** (47), **17** (33), **18** (14), **19** (4)
6[e]	**3**				7.5	100	**16** (47), **17** (31), **18** (16), **19** (4)
7	**4**	2.16	−25.6	[f]	17	100	**20** (45)
8	**5**	1.61	−38.3	320	48	100	**21** (50), **22** (7), **23** (30)
9	**6**	2.10	−27.0	164	48	100	**24** (74)
10	**7**	2.08	−27.4	233	60	100	**8** (37), **9** (21), **25** (7)

[a] All the reactions were carried out in MeCN solution. For reaction conditions and scale, see Section 4.
[b] Peak potential versus SCE in MeCN.
[c] Entries 4–6 were run parallely under same irradiation conditions. In entry 4, reaction was carried out without any additive.
[d] With added $Mg(ClO_4)_2$ (0.025 M).
[e] With added BP (0.05 M).
[f] Not measured because ethyl cinnamate has absorption at the excitation wavelength.

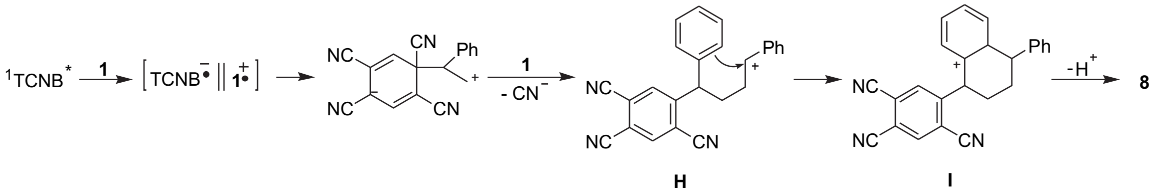
In the photoinduced reaction of TCNB with 1-phenylcyclohexene **5**, the 1:1 product **21** (50%), 2:1 product **22** (7%), and an isocoumarin product **23** (30%) were formed, no tetralin type products were found.

2.2. Mechanism in the photoreactions of TCNB with the arylethenes 1–4

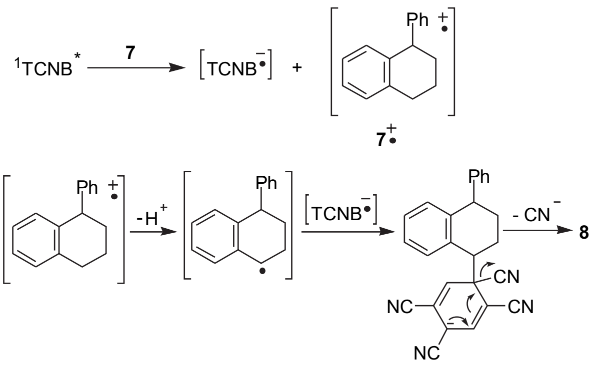
As shown in Table 1, alkenes **1–4** have large negative free energy change (ΔG_{ET}) for single electron transfer (SET) with ^{1}TCNB* and they quench the TCNB fluorescence with a diffusion controlled rate constant (2×10^{10} M^{-1} s^{-1} in MeCN). The photoreactions of TCNB with these alkenes are therefore initiated by SET between ^{1}TCNB* and the alkenes to give solvent separated ion radical pairs (SSIRP) as the primary intermediate in acetonitrile.[20] Three possible pathways for subsequent reactions of the TCNB$^{-\bullet}$–alkene$^{+\bullet}$ ion radical pairs can be envisioned, as shown in Schemes 1–3. In pathway 1 (Scheme 1), following the previously suggested mechanism for the dimerization of arylethene via



Scheme 1.



Scheme 2.



Scheme 3.

PET reactions with 1,4-dicyanobenzene (DCNB)[6a,b,9a] or 9,10-dicyanoanthracene (DCA),[7] interception of the cation radical $\mathbf{1}^{+\bullet}$ by a neutral **1** gives dimeric cation radical as an open chain distonic 1,4-cation radical **A**[6a,b,7] or as a long bond cyclobutane cation radical **B**.[8] A 1,6-cyclization in the former or a 1,3-sigmatropic shift in the later leads to the substituted hexatriene cation radical **C**. However, the fate of this cation radical is different here than that in the DCNB or DCA sensitized reactions. In DCNB sensitized reactions, the main reaction pathway for the substituted hexatriene cation radical such as **C** is to be reduced by the sensitizer anion radical (DCNB$^{-\bullet}$) to give the tetralin product **7**. In DCA sensitized reactions, beside this back SET, another pathway is also available. DCA$^{-\bullet}$ is a better proton acceptor than DCNB$^{-\bullet}$ because its protonation in would result in less loss of aromatization stabilization than in a monocyclic cyanoarene anion radical as DCNB$^{-\bullet}$. As a result, proton transfer from the hexatriene cation radical (**D** when the alkene is 1,1-diphenylethene, Scheme 1) to DCA$^{-\bullet}$ takes place, giving the tetralin radical **E**, which on disproportionation gives the tetralin **F** and the dihydronaphthalene derivative **G**. In contrast to these DCNB and DCA sensitized reactions, in the photoreactions of TCNB with the alkenes **1**–**4**, the highly stabilized TCNB$^{-\bullet}$ formed is neither a good electron donor nor a strong base. As a result, these reaction pathways might be suppressed by deprotonation of **C** to the solvent to give the tetralin radical. Combination of this radical with TCNB anion radical at the *ipso* position, which has the largest spin density in TCNB$^{-\bullet}$[21] followed by extrusion of a cyanide anion gives the product **8**.

Another possible route to product **8** (Scheme 2) invokes a prior in cage radical pair coupling of the alkene cation radical and TCNB$^{-\bullet}$ to give a zwitterionic intermediate followed by departure of a CN$^-$ and the capture of the cationic center by a neutral alkene, yielding the carbocation **H**. A 1,6-cyclization in **H** followed by deprotonation would give product **8**. However, this reaction sequence is disfavored by consideration of known kinetic data in the cyanoarene–alkene photoreactions. The trapping of the arylethene cation radical by a neutral alkene has been identified as a fast process, taking place with a nearly diffusion controlled rate constant of 10^9–10^{10} M^{-1} s^{-1},[7,8e] and competing favorably with back electron transfer (k_{BET}~10^8 M^{-1} s^{-1})[7] and ion radical pair dissociation (k_{dis}~5.5×10^8 M^{-1} s^{-1}),[7] while in cage ion radical pair coupling to a zwitterionic intermediate is believed to be an inherently slow process, which is not able to be competent with the former processes.[2b] Furthermore, our results using the biphenyl (BP) as a codonor in the reactions of TCNB with **1** also regards pathway 2 as unlikely. In many cases, the use of a codonor (usually an aromatic hydrocarbon) is known to enhance the PET reaction efficiency by avoiding the generation of the acceptor anion radical and the donor cation radical in a geminate pair, and therefore circumventing facile back electron transfer and possible in cage ion radical pair recombination.[15–18] In the photoreactions of TCNB with **3**, significant rate acceleration was found when the codonor BP ($E_{1/2}^{ox}=1.85$ V, SCE, MeCN) was added to the reaction mixture. In this case, BP as a relay intervenes the SET between ^{1}TCNB* and **3**, so that TCNB$^{-\bullet}$ and $\mathbf{D}^{+\bullet}$ were not generated geminately. This would have caused a retardation of the reaction if pathway 2 (Scheme 1) was followed because in cage recombination of the ion radical pairs should be suppressed. The profound rate acceleration effect of BP on the reaction clearly discards the mechanism in Scheme 2 but favors pathway 1 in Scheme 1. Since styrene (**1**) has an oxidation potential (1.93 V) higher than BP, this rate enhancement may be caused by taking advantage of the longer lifetime of BP$^{+\bullet}$ than ^{1}TCNB* and the continuous move of the equilibrium to the right side in the SET between BP$^{+\bullet}$ and alkene owing to the irreversible consumption of alkene$^{+\bullet}$ in subsequent reactions.

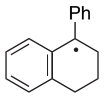
In PET reaction of cyanoarene with electron donor compounds, the addition of a salt with anion of low nucleophilicity, e.g., $Mg(ClO_4)_2$, often leads to a rate acceleration by promoting ion radical pair dissociation.[19] This is similar to the special salt effect in carbocation chemistry where the added $LiClO_4$ suppresses the external return from solvent separated ion pair (SSIP) by anion exchange in the ion pair.[22] We also observed a reaction rate enhancement in the photoreactions of TCNB with **3** by adding an equimolar amount of anhydrous magnesium perchlorate (Table 1, entry 5). This result, together with the cosensitizer effect using biphenyl, renders additional support to the out of cage mechanism in Scheme 1 and disregards a reaction pathway involving an in cage TCNB$^{-\bullet}$–$\mathbf{3}^{+\bullet}$ recombination.

A third mechanistic possibility is that the product **8** may be formed by secondary photoreaction between TCNB and the tetralin product formed in primary reactions of TCNB with the alkenes **1**–**4** (Scheme 3).

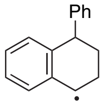
The dimer cation radical **C** formed in photoreaction of TCNB with the arylethene (Scheme 1) was deprotonated (with MeCN as proton acceptor) to give the tetralin radical, which yielded the tetralin product **7** by hydrogen abstraction. In photoreactions of TCNB with the alkenes, the neutral alkene dimers were indeed found in the reaction mixture (vide supra). In this case, the TCNB anion radicals would be accumulated in the solution. However, neutral TCNB may be regenerated by oxidation of TCNB$^{-\bullet}$ by the trace amount of oxygen remained in the solution or by disproportionation of TCNB$^{-\bullet}$.[23] Ground state oxygen has a reduction potential of −0.75 V (SCE).[24] SET between O_2 and TCNB$^{-\bullet}$ ($E_{1/2}^{ox}=-0.65$ V) is a slightly endergonic process. Since we have not found any products that may be derived from the reduced TCNB ($TCNBH_2$) such as 1,2,4-tricyanobenzene in the reaction mixture, we envisage that the main regeneration pathway might be the oxidation by oxygen.

Further photoreaction of TCNB with the tetralin product **7** gives product **8** (Scheme 3). SET of ^{1}TCNB* with **6** and **7** are heavily exergonic (Table 1) and **6** and **7** quenched the TCNB fluorescence with diffusion controlled rate constant. The tetralin cation radical ($\mathbf{7}^{+\bullet}$) generated in the SET event is strongly acidic. Although the pK_a value for this species is not known, it would not be much different from the pK_a of toluene (pK_a∼−17),[25] therefore, deprotonation to the acetonitrile solvent (pK_a∼−11) should be feasible. The formed tetralin radical is then added to the $\text{TCNB}^{-\bullet}$ to give the addition anion radical, which on extrusion of a cyanide anion afforded product **8**.

We examined this mechanism by carrying out the photoreactions of TCNB with tetralin **6** and the independently synthesized 1-phenyltetralin **7**. In contrast to the prompted reactions between TCNB and **1–4** (Table 1), irradiation of TCNB with **6** and **7**, respectively, in MeCN under same conditions resulted in rather sluggish reactions. Therefore, while photoreaction of TCNB with **1** took 13 h to reach a complete conversion of TCNB, a lengthy photolysis of 48 h was needed for the complete conversion of TCNB in reaction with **6**. This gave product **24** in 74% yield. The photoreaction of TCNB with **7** required a 60 h irradiation for complete conversion of TCNB and furnished two diastereomeric addition–substitution products **8** (37%) and **9** (21%), and an indene product **25** (7%).



J



K

In the reaction of TCNB with **7**, we only found coupling products with the tricyanophenyl group attached to the 4-position of **7** (products **8** and **9**) without any products that might be derived from the coupling of the $\text{TCNB}^{-\bullet}$ with the tertiary radical **J**. The diphenylmethylene radical **J** is expected to be thermodynamically more stable than the benzylic radical **K** by better spin delocalization. Also, bond dissociation energy (BDE) in the cation radical $\mathbf{7}^{+\bullet}$ for the C(1)–H should be lower than C(4)–H as estimated by Eq. 5 derived from a thermodynamic cycle.[25]

$$\mathrm{BDE(RH^{+\bullet}) = BDE(R-H) - E^{ox}_{1/2}(RH) + E^{ox}_{1/2}(H^{\bullet})} \qquad (5)$$

The difference in the BDEs of the relevant C–H bonds in the neutral hydrocarbon is manifested in the BDEs of the same bonds in the hydrocarbon cation radical. However, this difference in the BDE of C(1)–H (∼81.8 kcal mol^{-1}, taken as the C–H BDE in Ph$_2$CH–H)[26a] and C(4)–H (∼85 kcal mol^{-1})[26b,c] bonds in 1-phenyltetralin is quite small (∼3 kcal mol^{-1}). Considering that the deprotonation of $\mathbf{7}^{+\bullet}$ is an exergonic process with an early transition state, the breaking of the C(1)–H and C(4)–H bonds would have no significant difference in activation energies. Furthermore, kinetic stability of radicals, and therefore the activity in radical coupling reactions are largely controlled by steric shielding to the radical center. Therefore, coupling of $\text{TCNB}^{-\bullet}$ with the radical **K** is much more favored and it is the predominant reaction pathway.

It is evident that although photoreactions of TCNB with **7** afford the same addition–substitution product **8** as in the photoreactions of TCNB with **1**, the reaction rate is at least four times slower than in the TCNB–**1** reaction, taking into account that the concentration of **7** formed in the TCNB–**1** reaction should be much lower than in the TCNB–**7** reaction where **7** is in a large excess amount (10 equiv vs TCNB). The low (TCNB–**7**) reaction rate is also the reason why significant amount of the cyclodimers such as **15** was accumulated in the reaction products in these TCNB–**1** photoreactions. Within the short reaction time and with the small concentration of the formed **7** in the reaction mixture, secondary (TCNB–**7**) photoreaction would not make a significant contribution for the formation of **8** in the TCNB–**1** photoreaction.

We therefore come to the conclusion that the photoreactions of TCNB with the arylethene **1–4** proceed predominately by the reaction pathway 1 in Scheme 1 via the tetralinyl radical–radical anion ($\text{TCNB}^{-\bullet}$) combination, although the secondary photoreaction of TCNB–**7** as shown in Scheme 3 might make a minor contribution.

2.3. Formation of the 4:1 (1:TCNB) product

A control experiment showed that products **10** and **11** was formed by secondary PET reactions of the primary product **8** with styrene **1**. This follows a mechanism similar to Scheme 1. The anion radical $\mathbf{8}^{-\bullet}$ combines with the styrene dimer radical at the *meta*-carbon atom bearing a CN group, and this is followed by loss of a cyanide anion to give **10** (**11**). Again, the coupling of the styrene dimer radical with $\mathbf{8}^{-\bullet}$ takes place at the site with the highest spin density in $\mathbf{8}^{-\bullet}$ as indicated by the result of a DFT UB3LYP/6-31G* calculation[27] on its spin and charge density distribution (Fig. 2).

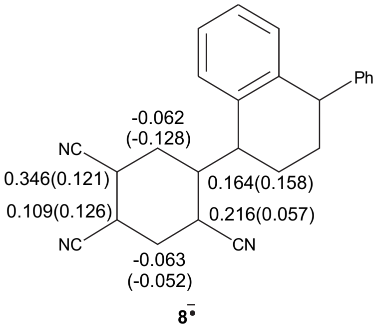
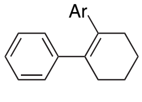
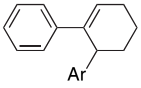


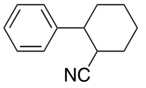
Figure 2. Spin and charge (in parentheses, with the charge density at hydrogen atom summed up to their attached C atom) density in $\mathbf{8}^{-\bullet}$.

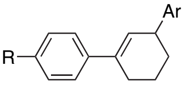
2.4. Mechanism of photoreaction of TCNB with 1-phenylcyclohexene 5

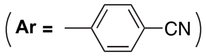
In this reaction, only the 1:1 (**5**–TCNB) product **21** was formed as the primary product. Secondary reaction of excited **21** with **5** resulted in the 2:1 product **22**. No alkene dimerization–aromatic substitution products were formed. This difference in the reactivity of $\mathbf{5}^{+\bullet}$ and the cation radicals of **1–4** is attributed to the special structure of $\mathbf{5}^{+\bullet}$. It was reported that according to a semiempirical PM3 calculation, the optimized $\mathbf{5}^{+\bullet}$ has a nonplanar structure and the cyclohexene ring has a chair-like conformation, which causes a large static hindrance toward its trapping by a neutral **5**. This is supported by a laser flash photolysis (LFP) study of the (DCNB–**5**) system in MeCN, in which only transient absorption bands attributable to the monomer cation radical ($\mathbf{5}^{+\bullet}$) were detected.[9a] In accordance with this, photoinduced reactions of DCNB with **5** in MeCN gave two 1:1 adducts **26** and **27** in 34% total yield together with **28** (17%).[9a] In the photoreactions of TCNB with **5**, we found a 1:1 adduct **21** (50%), along with a 2:1 adduct **22** (7%) and an isocoumarin product **23** (30%).


26

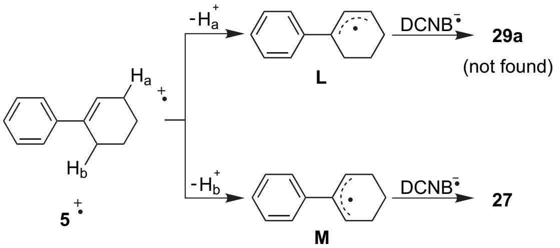

27


28


29a R = H
29b R = Meo



As pointed out based on a PM3 computation,[9a] the deprotonation of $\mathbf{5}^{+\bullet}$ would give radicals **L** and **M**, with the former being thermodynamically more stable. Our own calculation by UB3LYP/6-31G* supports this conclusion by indicating that **L** is 5.27 kcal mol^{-1} more stable than **M**. Although product derived from coupling of **L** with DCNB$^{-\bullet}$ was not found in photoreaction of DCNB with **5** (reaction 6),[9a] in our reaction of TCNB with **5**, we obtained product **21** (which is similar to **29a**) as the only 1:1 coupling product between TCNB and **5**.



(6)

As a matter of fact, in the photoreactions of DCNB with 1-(4-methoxyphenyl)cyclohexene,[28] it was found that by adding collidine as a base, product **29b** derived from the combination of the deprotonated allyl radical similar to **L** with DCNB$^{-\bullet}$ was indeed formed. In this case, the deprotonation of 1-(4-methoxyphenyl)cyclohexene cation radical, which is less acidic than $\mathbf{5}^{+\bullet}$, was promoted by adding a base. The formation of **29b** further supports the mechanism in Scheme 4 for the formation of **21**.

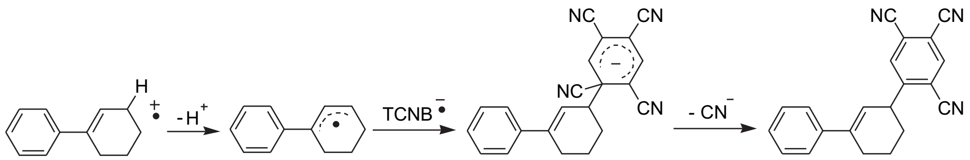
3. Conclusions

In summary, we have described the olefin dimerization–aromatic substitution reactions between singlet excited TCNB with a series of arylethenes that lead to the *ipso* substitution of one or two of the CN groups in TCNB by 1-tetralinyl as the alkene cyclodimer. These reactions gave high yield of products. Based on the codonor and salt effect on the reactions, the result of photoinduced reactions of TCNB with tetralin and 1-phenyltetralin, argument based on the analysis of known kinetic data for relevant processes and computational results on the structures of the alkene cation radicals, these reactions are proposed to follow a mechanism involving out of cage interception of the alkene cation radical by a neutral alkene, deprotonation of the cyclodimer cation radical to the solvent and coupling of the cyclodimer radical with TCNB$^{-\bullet}$. These described reaction modes serve to extend the reaction diversity and help to further clarify several delicate mechanistic issues in the cyanoarene–alkenes PET reactions depending on the structures of the alkene cation radical and cyanoarene anion radical.

4. Experimental

4.1. General

Melting points were measured on a Yanaco microscopic melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz) spectra were recorded on a Bruker DPX 300 spectrometer with CDCl$_3$ as internal standard and solvent. Other NMR spectra were recorded on a Bruker Avance 400 spectrometer with CDCl$_3$ as internal standard and solvent. IR spectra were taken with a Shimadzu IR 440 spectrometer for samples in KBr pellets. Mass spectra were recorded with a VG ZAB-HS spectrometer. Elemental analyses were obtained using a Perkin–Elmer 240 C analyzer. Oxidation potentials were measured by a CHI 600 electrochemical workstation (CH Instruments, USA). Quenching experiments of the fluorescence were performed on an AMINCO Bowman Series 2 fluorescence spectrophotometer. For X-ray crystallographic analysis, the X-ray diffraction intensities and the unit cell parameters were determined on an Enraf-Nonius CAD-4 diffractometer employing graphite-monochromated (MoKα) radiation (λ=0.71073 Å) and operating in the $\omega/2\theta$ scan mode. Data collection and cell refinement were performed with CAD-4 Software. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL. Nonhydrogen atoms were refined by anisotropic displacement parameters, and the positions of all H-atoms were fixed geometrically and included in estimated positions using a riding model.



Scheme 4.

Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 293776. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.2. Materials

1-Phenylcyclohexene (**5**) was synthesized according to a procedure described for the synthesis of 1-phenylcyclopentene.[29] Tetracyanobenzene and 1-phenyltetralin (**7**) were prepared by literature procedures.[30,31] Acetonitrile (AR grade) was first refluxed with phosphorus pentoxide and distilled and then refluxed with anhydrous potassium carbonate and redistilled. Other reagents were CP or AR grade and were used as received without further purification. Petroleum ether refers to the fraction with boiling point in the range 60–90 °C.

4.3. Cyclic voltammetric measurements

Oxidation potentials of the alkenes were measured at 298 K by cyclic voltammetry in dry acetonitrile with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Platinum electrodes were used as working electrode and auxiliary electrode, and the reference electrode was a saturated calomel electrode (SCE). The scan speed was 100 mV s^{-1}. The solutions were 0.5–1 mM in the substrate and were purged with dry nitrogen for 10 min before measurements to remove dissolved oxygen.

4.4. Fluorescence quenching

Excitation was at 313 nm. The monitoring wavelength was 333 nm. The solutions were deoxygenated by argon purging for 10 min prior to the measurements. Relative emission intensities were measured for MeCN solution containing TCNB (2.5×10^{-5} M) with electron donors at various concentrations ($0–1.0\times10^{-1}$ M) at 298 K. There was no change in the shape but there was a change in the intensity of the fluorescence spectrum by the addition of an electron donor. The Stern–Volmer relationship

$$I_0/I = 1 + K_{SV}[D]$$

was obtained from the ratio of the emission intensities in absence and presence of electron donors (I_0/I) and the concentrations of quenchers [D].

4.5. Procedures for the preparative photolysis of TCNB with alkynes

The light source was a medium-pressure mercury lamp (500 W) in a glass cooling water jacket to cut off light of wavelength shorter than 300 nm. If it was further surrounded by a layer of filter solution (10% aqueous sodium nitrate, 1 cm thick), it gave light of wavelength longer than 330 nm. The solution of tetracyanobenzene (TCNB) and an excess amount of alkene in MeCN was purged with dry argon for 15 min and then irradiated under continuous argon purging. The reaction course was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure and the residue was separated by flash chromatography on a silica gel column with petroleum ether–ethyl acetate as eluent.

4.5.1. Photolysis of TCNB with 1. A solution of TCNB (713 mg, 4 mmol) and **1** (6.25 g, 60 mmol) in MeCN (80 mL) was photolyzed (λ>300 nm) for 13 h to reach a complete conversion of TCNB. The solvent was removed under reduced pressure and the residue was separated by flash chromatography on a silica gel column with petroleum ether–ethyl acetate as eluent to give **8** (1.23 g, 86%).

4.5.1.1. 4-Phenyl-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (8). Colorless crystals from petroleum ether–acetone, mp 221–222 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79–1.90 (1H, m), 1.93–2.04 (1H, m), 2.14–2.24 (1H, m), 2.39–2.49 (1H, m), 4.32 (1H, t, J=6.6 Hz), 4.87 (1H, t, J=6.7 Hz), 6.71 (1H, dd, J=6.9 and 1.6 Hz), 7.11–7.14 (2H, m), 7.17 (1H, dd, J=6.8 and 1.6 Hz), 7.21–7.25 (2H, m), 7.26–7.29 (1H, m), 7.34–7.38 (2H, m), 7.49 (1H, s), 8.13 (1H, s) ppm; IR (KBr): 3024, 2939, 2920, 2861, 2240, 1596, 1488, 1447, 1384, 1236, 1029, 1002, 912, 814, 765, 751, 705, 662 cm^{-1}; MS (EI): *m/z* (% base) 359 (M^+, 85), 358 (100), 341 (34), 330 (25), 302 (6), 280 (72), 226 (4), 202 (2), 180 (59), 165 (29), 152 (6), 104 (24), 91 (19), 77 (16), 63 (5), 51 (12). Anal. Calcd for $C_{25}H_{17}N_3$: C, 83.54; H, 4.77; N, 11.69. Found: C, 83.35; H, 4.53; N, 11.52.

4.5.2. Photolysis of 8 with 1. A solution of **8** (209 mg, 0.6 mmol) and **1** (0.94 g, 9 mmol) in MeCN (12 mL) was photolyzed (λ>300 nm) for 22 h to reach a complete conversion of TCNB. Workup as described above gave **10** (31 mg, 10%) and **11** (213 mg, 66%).

4.5.2.1. 2,4-Di(4-phenyl-1,2,3,4-tetrahydro-1-naphthyl)-1,5-benzenedicarbonitrile (10). Colorless crystals from petroleum ether–acetone, mp 105–107 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.70–1.92 (5H, m), 1.99–2.14 (1H, m), 2.26–2.40 (2H, m), 3.94–4.01 (1H, m), 4.11–4.22 (1H, m), 4.68 (2H, dd, J=5.9 and 9.3 Hz), 6.57–6.70 (1H, m), 6.74–6.77 (2H, m), 6.86–6.89 (3H, m), 7.03–7.25 (10H, m), 7.29–7.33 (4H, m) ppm; IR (KBr): 3059, 3023, 2934, 2860, 2228, 1599, 1490, 1448, 1238, 748, 701, 521 cm^{-1}; MS (EI): *m/z* (% base) 540 (M^+, 100), 180 (38), 179 (13), 165 (15), 91 (19), 70 (24). Anal. Calcd for $C_{40}H_{32}N_2$: C, 88.85; H, 5.96; N, 5.18. Found: C, 88.83; H, 5.98; N, 5.09.

4.5.2.2. 2,4-Di(4-phenyl-1,2,3,4-tetrahydro-1-naphthyl)-1,5-benzenedicarbonitrile (11). Colorless crystals from petroleum ether–acetone, mp 109–110 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83–2.02 (4H, m), 2.20–2.24 (2H, m), 2.35–2.43 (2H, m), 4.10–4.32 (2H, m), 4.75 (2H, t, J=6.6 Hz), 6.80–6.83 (1H, m), 6.97–7.00 (2H, m), 7.13–7.19 (7H, m), 7.24–7.41 (9H, m), 7.49 (1H, d, J=6.3 Hz) ppm; IR (KBr): 3024, 2932, 2859, 2229, 1599, 1491, 1448, 1389, 908, 748, 701, 528 cm^{-1}; MS (EI): *m/z* (% base) 540 (M^+, 26), 539 (26), 281 (7), 255 (6), 179 (34), 180 (100), 181 (12), 191 (19), 178 (17), 165 (45). Anal. Calcd for $C_{40}H_{32}N_2$: C, 88.85; H, 5.96; N, 5.18. Found: C, 88.81; H, 6.01; N, 5.13.

4.5.3. Photolysis of TCNB with 2. A solution of TCNB (713 mg, 4 mmol) and **2** (4.72 g, 40 mmol) in MeCN

(80 mL) was photolyzed (λ>300 nm) for 10 h to reach a complete conversion of TCNB. Workup as described above gave **12** (28 mg, 2%) and **13** (1.58 g, 66%).

4.5.3.1. 6-Methyl-4-(4-methylphenyl)-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (12). Colorless crystals from petroleum ether–acetone, mp 181–182 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.81–1.90 (2H, m), 2.12–2.19 (2H, m), 2.23 (3H, s), 2.37 (3H, s), 4.23 (1H, t, J=6.7 Hz), 4.68 (1H, t, J=6.6 Hz), 6.69 (1H, d, J=7.8 Hz), 6.80 (1H, s), 6.94–7.16 (7H, m) ppm; IR (KBr): 3018, 2921, 2860, 2229, 1612, 1513, 1495, 1447, 1387, 894, 813, 518 cm^{-1}; MS (EI): *m*/*z* (% base) 295 (2), 283 (2), 234 (4), 208 (31), 193 (11), 105 (19), 104 (46), 77 (4), 64 (16), 57 (15), 55 (12), 44 (100), 43 (23). Anal. Calcd for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.61; H, 5.55; N, 10.76.

4.5.3.2. 4,6-Di(6-methyl-4-(4-methylphenyl)-1,2,3,4-tetrahydro-1-naphthyl)-1,3-benzenedicarbonitrile (13). Colorless crystals from petroleum ether–acetone, mp 252–254 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.63–1.81 (4H, m), 1.90–2.24 (4H, m), 2.09 (3H, s), 2.20 (3H, s), 2.33 (3H, s), 2.42 (3H, s), 4.09–4.12 (2H, m), 4.60–4.66 (2H, m), 6.50 (2H, t, J=8.7 Hz), 6.62–6.87 (7H, m), 6.97 (1H, s), 7.00 (1H, s), 7.14 (4H, dd, J=7.5 and 5.6 Hz), 7.97 (1H, s) ppm; IR (KBr): 3020, 2927, 2856, 2230, 1607, 1513, 1501, 1447, 1382, 1111, 897, 815, 560, 537 cm^{-1}; MS (EI): *m*/*z* (% base) 597 (4), 596 (M$^+$, 23), 595 (3), 504 (4), 209 (3), 208 (100), 193 (18), 178 (3), 118 (3), 105 (10), 91 (2), 44 (2). Anal. Calcd for $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.51; H, 6.80; N, 4.61.

4.5.4. Photolysis of TCNB with 3. A solution of TCNB (713 mg, 4 mmol) and **3** (7.08 g, 60 mmol) in MeCN (80 mL) was photolyzed (λ>300 nm) for 14 h to reach a 98% conversion of TCNB. Workup as described above gave **14** (188 mg), **15** (586 mg), **16** (754 mg, 50%), **17** (574 mg, 38%), **18** (112 mg, 5%), and **19** (65 mg, 6%).

4.5.4.1. 1,4-Dimethyl-4-phenyl-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (16). Colorless crystals from petroleum ether–acetone, mp 277–278 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.81–1.83 (1H, m), 1.87 (1H, m), 1.90 (3H, s), 2.00 (3H, s), 2.23–2.33 (1H, m), 2.40–2.49 (1H, m), 6.64 (1H, dd, J=7.7 and 1.4 Hz), 7.01 (1H, dd, J=7.7 and 1.4 Hz), 7.14 (1H, td, J=7.7 and 1.5 Hz), 7.19–7.25 (4H, m), 7.30–7.35 (2H, m), 8.01 (1H, s), 8.08 (1H, s) ppm; IR (KBr): 3052, 3020, 2985, 2931, 2240, 1734, 1598, 1490, 1450, 1383, 1280, 1226, 1028, 914, 770, 700 cm^{-1}; MS (EI): *m*/*z* (% base) 387(M$^+$, 17), 372 (100), 355 (19), 294 (12), 280 (10), 223 (7), 197 (81), 119 (19), 91 (39), 77 (15), 43 (32). Anal. Calcd for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.59; H, 5.54; N, 10.78.

4.5.4.2. 1,4-Dimethyl-4-phenyl-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (17). Colorless crystals from petroleum ether–acetone, mp 232–233 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.78 (3H, s), 1.81–1.86 (1H, m), 1.95–2.03 (1H, m), 2.10 (3H, s), 2.09–2.20 (1H, m), 2.38 (1H, ddd, J=14.0, 8.4, and 2.9 Hz), 7.02–7.05 (1H, m), 7.16–7.22 (4H, m), 7.27–7.36 (4H, m), 7.57 (1H, s), 8.08 (1H, s) ppm; IR (KBr): 3112, 3038, 2948, 2235, 1594, 1492, 1440, 1381, 1216, 1102, 1029, 936, 766, 704 cm^{-1}; MS (EI): *m*/*z* (% base) 387(M$^+$, 15), 372 (100), 355 (18), 294 (11), 280 (7), 219 (2), 192 (6), 105 (4), 91 (25), 43 (4). Anal. Calcd for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.62; H, 5.42; N, 10.88.

4.5.4.3. 4,6-Di(1,4-dimethyl-4-phenyl-1,2,3,4-tetrahydro-1-naphthyl)-1,3-benzenedicarbonitrile (18). Colorless crystals from petroleum ether–acetone, mp>300 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.64 (3H, s), 1.77 (3H, s), 1.68–1.82 (2H, m), 1.87 (3H, s), 1.82–1.89 (2H, m), 2.11 (3H, s), 2.22–2.30 (2H, m), 2.40–2.47 (1H, m), 2.63–2.69 (1H, m), 6.66–6.69 (1H, m), 6.92–6.94 (1H, m), 7.01–7.04 (2H, m), 7.10–7.13 (1H, m), 7.15–7.16 (1H, m), 7.18–7.20 (4H, m), 7.21–7.26 (5H, m), 7.27–7.34 (4H, m), 7.98 (1H, s) ppm; IR (KBr): 3055, 2971, 2939, 2228, 1739, 1593, 1489, 1441, 1378, 1237, 1030, 918, 758, 702, 631 cm^{-1}; MS (EI): *m*/*z* (% base) 596 (M$^+$, 19), 581 (100), 503 (5), 465 (2), 331 (1), 283 (12), 176 (4), 105 (1), 91 (19), 44 (1). Anal. Calcd for $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.50; H, 6.49; N, 4.58.

4.5.4.4. 6,7-Dicyano-4-methyl-4-phenyl-3,4-dihydroisocoumarin (19). Colorless crystals from petroleum ether–acetone, mp 217–218 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.84 (3H, s), 4.39 (1H, d, J=11.6 Hz), 4.83 (1H, d, J=11.6 Hz), 7.19–7.22 (2H, m), 7.41–7.46 (3H, m), 7.55 (1H, s), 8.59 (1H, s) ppm; IR (KBr): 3080, 3048, 2994, 2974, 2236, 1728, 1601, 1495, 1466, 1446, 1412, 1310, 1240, 1195, 1096, 1045, 942, 901, 799, 769, 744, 707 cm^{-1}; MS (EI): *m*/*z* (% base) 288 (M$^+$, 23), 258 (100), 243 (20), 215 (19), 176 (2), 165 (1), 129 (2), 77 (3), 51 (3). Anal. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72. Found: C, 74.82; H, 4.32; N, 9.59.

4.5.5. Photolysis of TCNB with 4. A solution of TCNB (534 mg, 3 mmol) and **4** (5.28 g, 30 mmol) in MeCN (60 mL) was photolyzed (λ>300 nm) for 17 h to reach a complete conversion of TCNB. Workup as described above gave **20** (677 mg, 45%).

4.5.5.1. 2,3-Di(ethoxycarbonyl)-4-phenyl-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (20). Colorless crystals from petroleum ether–acetone, mp 177–179 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.92 (3H, t, J=7.1 Hz), 1.13 (3H, t, J=7.1 Hz), 3.40 (1H, q, J=10.5 Hz), 3.43 (1H, q, J=10.5 Hz), 3.87–3.92 (2H, m), 4.07 (2H, m), 4.53 (1H, d, J=10.3 Hz), 5.13 (1H, d, J=10.4 Hz), 6.47 (1H, d, J=6.9 Hz), 6.85 (1H, d, J=6.8 Hz), 7.09–7.13 (2H, m), 7.18–7.21 (2H, m), 7.29–7.40 (3H, m), 7.76 (1H, s), 8.12 (1H, s) ppm; IR (KBr): 3112, 3045, 2983, 2241, 1736, 1600, 1491, 1449, 1375, 1274, 1248, 1185, 1013, 915, 858, 762, 703 cm^{-1}; MS (EI): *m*/*z* (% base) 356 (0.2), 276 (3), 205 (3), 178 (100), 151 (9), 100 (12), 75 (14), 69 (7), 51 (10), 44 (8). Anal. Calcd for $C_{31}H_{25}N_3O_4$: C, 73.94; H, 5.00; N, 8.34. Found: C, 73.69; H, 4.89; N, 8.41.

4.5.6. Photolysis of TCNB with 5. A solution of TCNB (534 mg, 3 mmol) and **5** (2.84 g, 18 mmol) in MeCN (60 mL) was photolyzed (λ>330 nm) for 48 h to reach a complete conversion of TCNB. Workup as described above gave **21** (457 mg, 50%), **22** (96 mg, 7%), and **23** (297 mg, 30%).

4.5.6.1. 5-(2-Phenyl-2-cyclohexenyl)-1,2,4-benzenetricarbonitrile (21). Colorless crystals from petroleum ether–acetone, mp 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57–1.61 (1H, m), 1.91–1.95 (2H, m), 2.27–2.31 (2H, m), 2.60–2.65 (1H, m), 4.18 (1H, m), 5.96 (1H, s), 7.33–7.38 (1H, m), 7.40–7.42 (2H, m), 7.45–7.48 (2H, m), 7.86 (1H, s), 8.08 (1H, s) ppm; ^{13}C NMR (100.7 MHz, $CDCl_3$): δ 21.13, 27.21, 30.94, 41.24, 113.72, 114.24, 114.53, 117.32, 119.46, 121.67, 125.32, 128.00, 128.59, 133.87, 137.17, 140.88, 142.53, 156.61 ppm; IR (KBr): 3105, 3042, 2934, 2862, 2235, 1644, 1487, 1447, 1381, 1321, 1240, 1184, 920, 792, 744, 698, 509 cm^{-1}; MS (EI): *m/z* (% base) 309 (M^+, 49), 280 (100), 266 (81), 230 (6), 152 (2), 128 (6), 115 (11), 91 (15), 77 (6), 51 (3). Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.32; H, 4.82; N, 13.75.

4.5.6.2. 2,4-Di(2-phenyl-2-cyclohexenyl)-1,5-benzenedicarbonitrile (22). Colorless crystals from petroleum ether–acetone, mp 187–189 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (2H, m), 1.88 (4H, m), 2.23 (2H, m), 2.53 (4H, m), 4.08 (2H, m), 5.94–5.97 (2H, m), 7.15–7.25 (3H, m), 7.27–7.33 (7H, m), 7.48 (1H, s), 7.95 (1H, s) ppm; IR (KBr): 3026, 2932, 2861, 2227, 1602, 1489, 1444, 1390, 1154, 1034, 757, 696 cm^{-1}; MS (EI): *m/z* (% base) 440 (M^+, 100), 439 (97), 422 (2), 414 (17), 383 (2), 255 (3), 227 (1), 205 (2), 191 (1), 157 (5). Anal. Calcd for $C_{32}H_{28}N_2$: C, 87.24; H, 6.41; N, 6.36. Found: C, 87.32; H, 6.62; N, 6.23.

4.5.6.3. 6,7-Dicyano-3,4-cyclohexyl-4-phenyl-3,4-dihydroisocoumarin (23). Colorless crystals from petroleum ether–acetone, mp 183–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.57 (2H, m), 1.69–1.77 (2H, m), 1.93–1.97 (1H, m), 2.24–2.28 (1H, m), 2.39 (1H, ddd, J=23.5, 10.4, and 4.4 Hz), 3.12 (1H, d, J=13.3 Hz), 4.75 (1H, dd, J=4.2 and 2.4 Hz), 7.23–7.28 (1H, m), 7.35 (2H, t, J=7.3 Hz), 7.60 (2H, d, J=7.6 Hz), 7.98 (1H, s), 8.45 (1H, s) ppm; IR (KBr): 3115, 3050, 2952, 2868, 2236, 1731, 1603, 1495, 1453, 1403, 1288, 1256, 1217, 1142, 1044, 788, 726 cm^{-1}; MS (EI): *m/z* (% base) 328 (M^+, 64), 300 (6), 257 (100), 244 (5), 228 (11), 215 (12), 202 (9), 175 (3), 151 (1), 91 (3), 77 (4), 51 (2). Anal. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.92; H, 4.85; N, 8.43.

4.5.7. Photolysis of TCNB with 6. A solution of TCNB (534 mg, 3 mmol) and **6** (3.96 g, 30 mmol) in MeCN (60 mL) was photolyzed (λ>300 nm) for 48 h to reach a complete conversion of TCNB. Workup as described above gave **24** (686 mg, 74%).

4.5.7.1. 1-(2,4,5-Tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (24). Colorless crystals from petroleum ether–acetone, mp 134–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79–1.90 (3H, m), 2.32–2.39 (1H, m), 2.94–2.99 (2H, m), 4.71–4.75 (1H, m), 6.67 (1H, d, J=7.7 Hz), 7.11–7.16 (1H, m), 7.24–7.29 (2H, m), 7.41 (1H, s), 8.10 (1H, s) ppm; IR (KBr): 3109, 3042, 2934, 2862, 2238, 1596, 1543, 1490, 1449, 1384, 1329, 1274, 1246, 1199, 1158, 993, 911, 767, 746 cm^{-1}; MS (EI): *m/z* (% base) 283 (M^+, 87), 282 (100), 265 (81), 254 (21), 240 (10), 228 (135), 200 (6), 188 (2), 175 (3), 154 (2), 128 (6), 115 (10), 104 (86), 91 (8), 84 (47), 77 (5), 49 (39). Anal. Calcd for $C_{19}H_{13}N_3$: C, 80.54; H, 4.62; N, 14.83. Found: C, 80.45; H, 4.52; N, 14.75.

4.5.8. Photolysis of TCNB with 7. A solution of TCNB (713 mg, 4 mmol) and **7** (8.33 g, 40 mmol) in MeCN (80 mL) was photolyzed (λ>300 nm) for 60 h to reach a complete conversion of TCNB. Workup as described above gave **8** (536 mg, 37%), **9** (303 mg, 21%), and **25** (102 mg, 7%).

4.5.8.1. 4-Phenyl-1-(2,4,5-tricyanophenyl)-1,2,3,4-tetrahydronaphthalene (9). Colorless crystals from petroleum ether–acetone, mp 218–219 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62–1.70 (2H, m), 2.75–2.81 (1H, m), 2.93–3.09 (3H, m), 6.51 (1H, d, J=7.7 Hz), 7.10–7.14 (3H, m), 7.25–7.31 (2H, m), 7.35–7.45 (3H, m), 7.46 (1H, d, J=0.4 Hz), 8.05 (1H, d, J=0.4 Hz) ppm; IR (KBr): 3031, 2939, 2873, 2235, 1492, 1483, 1460, 1445, 1424, 1366, 1272, 1206, 927, 914, 785, 752, 742, 702, 532, 512 cm^{-1}; MS (EI): *m/z* (% base) 360 (23), 359 (M^+, 100), 341 (23), 331 (46), 330 (92), 329 (20), 280 (27), 265 (23), 178 (29), 165 (19), 115 (21), 104 (23), 91 (50), 77 (31), 57 (29), 55 (30), 51 (26), 43 (42), 41 (57). Anal. Calcd for $C_{25}H_{17}N_3$: C, 83.54; H, 4.77; N, 11.69. Found: C, 83.47; H, 4.81; N, 11.62.

4.5.8.2. 2-(2,4,5-Tricyanophenylmethyl)-3-phenylindene (25). Colorless crystals from petroleum ether–acetone, mp 219–220 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.49 (2H, s), 4.22 (2H, s), 7.22–7.36 (5H, m), 7.42–7.54 (4H, m), 7.49 (1H, d, J=0.5 Hz), 8.00 (1H, d, J=0.5 Hz) ppm; IR (KBr): 3113, 2235, 1601, 1488, 1459, 1440, 1423, 1394, 1297, 1205, 905, 771, 760, 726, 703, 527, 490 cm^{-1}; MS (EI): *m/z* (% base) 358 (7), 357 (M^+, 26), 192 (23), 191 (100), 190 (13), 189 (33), 166 (12), 165 (23), 139 (11), 51 (6). Anal. Calcd for $C_{25}H_{15}N_3$: C, 84.01; H, 4.23; N, 11.76. Found: C, 84.02; H, 4.16; N, 11.68.

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Supplementary data

Supplementary data, including Stern–Volmer plots for the fluorescence quenching of TCNB, X-ray data and crystallographic structure for compound **13**, NMR spectra of all new compounds (**8**–**13**, **16**–**25**), computational results on $TCNB^{-\bullet}$, $\mathbf{3}^{+\bullet}$, **L**, **M**, and $\mathbf{8}^{-\bullet}$, associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.03.089.

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