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Stereospecific nucleophilic trapping of encounter complexes between photoexcited 1-cyanonaphthalene and norbornadiene

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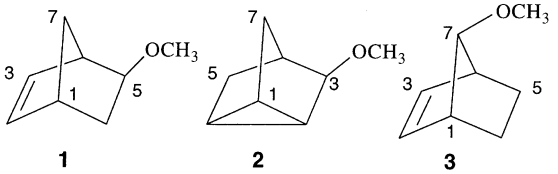
ABSTRACT: Photo-induced electron donor–acceptor reactions between 1-cyanonaphthalene (**CNN**) and norbornadiene (**N**) generate products of several structure types. Methanol adducts (1–3) formed in polar solvents are rationalized via the radical cation, $\mathbf{N}^{+\cdot}$, and stereospecific (*exo*-) nucleophilic attack by methanol. In less polar solvents, **CNN** and **N** form [2 + 2]-cycloadducts, exclusively on the *exo*-face of **N.** In non-polar solvents containing methanol, **CNN, N** and methanol combine to form 1:1:1 adducts, containing the sensitizer on the *endo*- and the methoxy groups on the *exo*-face. The formation of these products is rationalized via the trapping of encounter complexes of different geometries. Any rearrangement of the norbornenyl system can be eliminated, since neither tricyclyl nor 7-methoxynorbornenyl structures are formed. Apparently, the alcohol captures an *endo*-encounter complex of **CNN** and **N** by attack from the *exo*-face, similar to the attack of methanol on $\mathbf{N}^{+\cdot}$. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: encounter complexes; 1-cyanonaphthalene; norbornadiene; stereospecific; nucleophilic trapping

INTRODUCTION

Light-induced interactions of electron donor–acceptor systems have been at the forefront of mechanistic photochemistry for over two decades.[1–3] The nature or structure of the reaction intermediates has been the focus of particular attention; depending on the energetics of electron transfer between donor and acceptor, the reaction may proceed via an excited-state complex (exciplex)[1,2] or a pair of radical ions.[2,3] Typically, non-polar media favor the formation of exciplexes, whereas radical ion pairs are generated preferentially in polar solvents. The involvement of exciplexes is typically recognized by the observation of characteristic broad, red-shifted (exciplex) emission or by highly stereospecific cycloadditions. Radical ions, on the other hand, can be observed and characterized by a variety of spectroscopic techniques (viz. ESR,[4] CIDNP[5] and ODMR)[6]; alternatively, their involvement can be inferred from characteristic reactions, such as rearrangements, nucleophilic capture or deprotonation.

The valence isomers norbornadiene (**N**) and quadricyclane (**Q**) have been the target of considerable attention for the past two decades. Both systems contain two identical groups, either ethene units or cyclopropane moieties, held rigidly in orientations allowing the study of through-space or through-bond interactions, respectively.[7] The valence isomers have also received attention because of their potential for the storage of solar energy[8] or as the basis of an optical memory system.[9] The interconversion may proceed via radical cations or via an exciplex. Recently, we reported results of the electron donor–acceptor photochemistry of **N** and **Q** with 1,4-dicyanobenzene (**DCB**) in polar media. The reaction products were compatible with the intermediacy of radical cations, $\mathbf{N}^{+\cdot}$ and $\mathbf{Q}^{+\cdot}$, nucleophilic capture from the *exo*-face and rearrangements of and hydrogen abstraction by the resulting free radicals.[10] Our study showed substantial disagreement with an earlier report describing the donor–acceptor photochemistry of 1-cyanonaphthalene (**CNN**) with **N** or **Q** in methanol.[11] We observed much lower yields of methanol adducts, **1**–**3**, and isolated a different product type, containing both methoxy and cyanophenyl substituents. The obvious discrepancy led us to reinvestigate the donor–acceptor photochemistry of **CNN** with **N** in alcoholic solvents.



1 **2** **3**

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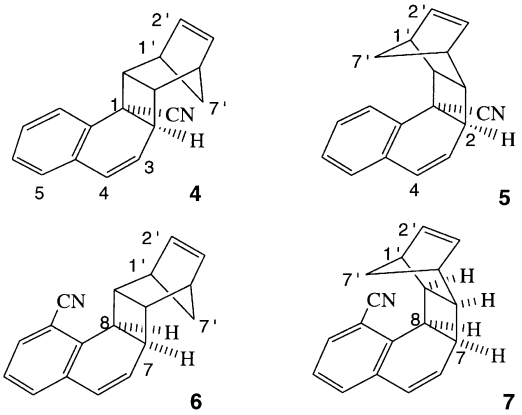
The product distribution with **CNN** is substantially different from that obtained with **DCB**;[10] **CNN** and **N** were depleted and formed (at least) four [2 + 2]-cycloadducts, **4**–**7**, in substantially higher yields than obtained for the methanol adducts.[12] The discrepancies with earlier results[11] are ascribed to advances in separation techniques during the intervening years.



The different product types require the existence of divergent mechanisms, featuring radical ions giving rise to methanol adducts, and loose encounter 'aggregates' collapsing to the [2 + 2]-cycloadducts. In order to elucidate this intriguing mechanistic duality in more detail, we further varied the reaction conditions. We used solvents of different polarities, from acetonitrile to benzene, in the presence and absence of methanol. In order to obtain optimal mechanistic insight, we carried out a complete analysis of all products formed in yields >2%. The advent of routine analysis by GC–MS techniques and separation by column chromatography allowed us to perform a detailed examination of the entire reaction mixture.

EXPERIMENTAL

Materials and solvents. Norbornadiene (Aldrich; 99%) was distilled after passing it through a short silica gel column to remove the stabilizing inhibitor (0.05% BHT). Quadricyclane (Aldrich; 99%) was used as received. 1-Cyanonaphthalene (Aldrich; 98%) was purified by column chromatography and recrystallized from *n*-hexane. Acetonitrile and methylene chloride (Fischer, ACS) were distilled from calcium hydride. Methanol (Fischer, Spectranalyzed) was refluxed over *ca* 2 gl^{-1} of sodium and distilled. The solvents so dried were stored over 4 Å molecular sieve in brown bottles under an argon atmosphere.

Photo-reactions. Solutions of 0.1 M donor and 0.1 M acceptor were purged with argon for 15 min before irradiation. They were irradiated in a Rayonet photoreactor with 16 RPR-3000 lamps, with analytical runs in 5 mm NMR tubes and preparative runs in water-cooled 30 mm i.d. tubes. The reactions were monitored by gas chromatography on a GC–MS system (HP 5890 Series II Plus GC with a HP 5972 mass-selective detector) on a 30 m × 0.25 mm i.d. × 0.25 μm film thickness HP-5 capillary column (cross-linked methylsilicone on fused silica).

Isolation of products. Products were isolated by preparative GLC and column chromatography, preparative GLC on a 6 ft column packed with 10% CP-5 on Chromosorb W HP, liquid chromatography on columns with i.d. ranging from 1 to 5 cm, packed with *ca* 15 cm of TLC standard grade silica gel (Aldrich; without binder) and eluted with solvent gradients, usually from light petroleum ether (b.p. < 65 °C) to mixtures with either methylene chloride or ethyl acetate. Typically, several passes were required to isolate the products.

Characterization of products. Structure assignments of isolated products are based on MS and NMR data. Proton NMR spectra were recorded on either a Varian XL-400 or a Varian VXR-200 spectrometer. ^{13}C and HETCOR spectra were recorded on a Varian VXR-200 spectrometer operating at 50.3 MHz. The structural assignments are based on 1D ^{1}H, 2D COSY and ^{13}C–^{1}H HETCOR, where appropriate. Extensive NOE difference spectra were recorded to elucidate the structure and to probe substituent stereochemistry and the spatial relationship between the different functional groups.

RESULTS

Reactions in the presence of methanol

Reaction A. Irradiation of **CNN** in the presence of **N** in methanol produced methanol adducts **1, 2** and **3** in yields of 4, 3 and 3%, respectively.[10] The sensitizer, **CNN**, was consumed and two types of molecular adducts were formed. Adducts containing **N** and **CNN** in a ratio of 1:1 were formed in *ca* 55% combined yield, (*exo*-[2 + 2]-adducts **4**–**7** 50%; a *meta*-addition adduct **8**, *ca* 6%). Adducts composed of **N, CNN** and CH_3OH in a ratio of 1:1:1 were formed in *ca* 25% combined yield. The gas chromatogram in the region of 1:1:1 adducts is not well resolved. The ^{1}H NMR spectrum of the mixture of 1:1:1 adducts shows six distinct OCH_3 singlets (δ 3.2–3.5 ppm) and an abnormal OCH_3 signal at δ 2.7 ppm in a ratio of 1:4:2:2:2:1:2; five products, **9a**–**11**, were isolated and identified.

Reaction B. Irradiation in acetonitrile–methanol (3:1, v/v) led to increased yields of methanol adducts (**1**, 3%; **2**, 12%; **3**, 12%) but decreased yields of the *exo*-[2 + 2]-cycloadducts (**4**–**7**, 36% combined yield). Again, the 1:1:1 adducts were formed in significant yields (*ca* 20% combined yield). In addition, minor amounts of acetoni-

Table 1. Product distribution (%) of the donor– acceptor photoreactions between norbornadiene and 1-cyanonaphthalene[a]

	CH_3OH Adducts				**N**/**CNN** *exo*-[2 + 2]-Adducts					*meta*-Adducts		1:1:1 Adducts	Additional [2 + 2]-Adducts[b]
Solvent	**1**	**2**	**3**	σ^c	**4**	**5**	**6**	**7**	σ^c	**8**	σ^c	σ^c	σ^c
CH_3OH	4	3	3	10	19	15	10	7	51	6	~10	~25	—
CH_3CN/CH_3OH	3	12	12	27	17	12	4	3	36	3	~5	~20	—
CH_2Cl_2/CH_3OH	1	1	1	3	19	17	11	5	52	7	~20	trace	7
t-BuOH	0.5	0.1	0.1	<1	20	17	17	12	66	5	~20	—	7
CH_3CN/*t*-BuOH	1.2	7.6	4.4	13	29	18	6	4	57	9	~15	trace	4
CH_3CN	—	—	—	—	46	29	6	4	85	3	~5	—	4
CH_2Cl_2	—	—	—	—	27	20	15	9	71	5	~15	—	10
C_6H_6	—	—	—	—	19	17	23	20	79	1	~5	—	11

[a] Normalized product distribution according to GC integration.
[b] Four adducts assigned as [2 + 2]-adducts based on their MS patterns but not isolated.
[c] Combined yields of product types of identical composition.

trile adducts and trace amounts of adducts containing **N** and CH_3OH in a ratio of 2:1 were observed.[10] The *meta*-adduct (3% yield) was again detected based on its characteristic GC–MS behavior.

Reaction C. In methylene chloride–methanol (3:1), the *exo*-[2 + 2]-cycloadducts (*ca* 50% combined yield) were prominent, whereas methanol adducts **1**–**3** (*ca* 1% each) and 1:1:1 adducts were formed in very low yields. At least five *meta*-adducts (*ca* 20% combined yield), including **8**, were also formed; their MS patterns are essentially identical with that of **8**. Also, at least four adducts (*ca* 10% combined yield; $M^{+\cdot}$ *m/z* 245, base peak *m/z* 91) with MS fragmentation patterns similar to those of adducts **4**–**7** were detected, but not isolated.

Reactions in the absence of methanol

Reaction D. In acetonitrile, the *exo*-[2 + 2]-adducts were the predominant products (85% combined yield), particularly **4** (46%) and **5** (29%). Minor products include four unidentified [2 + 2]-adducts (*ca* 5% combined yield) and at least one *meta*-adduct (*ca* 3%).

Reaction E. In methylene chloride, the *exo*-[2 + 2]-adducts (**4**–**7**) were formed in high yields (27, 20, 15 and 9%, respectively), with decreased regio-preference but increased yields of the unidentified [2 + 2]-adducts (*ca* 11% combined yield) as well as the *meta*-adducts (*ca* 13% combined yield).

Reaction F. In benzene, the four *exo*-[2 + 2]-adducts were formed in virtually identical yields (**4**–**7**, 19, 17, 23 and 20%, respectively); the unidentified [2 + 2]-adducts (*ca* 15% combined yield) and traces of *meta*-adducts (*ca* 5% combined yield) were also detected.

In all reactions, an apparent dehydrogenation product of (a) **CNN**–**N** adduct(s) was formed in *ca* 3–5% yield (highest detectable MS peak, *m/z* 243; base peak, *m/z* 177), possibly a norbornadiene-substituted cyanonaphthalene. The product distributions obtained under the different reaction conditions are summarized in Table 1.

Reaction of quadricyclane

Reaction G. Irradiation of **CNN** and **Q** in methanol causes rapid isomerization to **N**, as observed by previous investigators.[11] In addition, minor amounts of methanol adducts **1**–**3** are formed in a ratio similar to those obtained from the reaction of **CNN** with **N.** Prolonged irradiation of this solution resulted in formation of [2 + 2]-cycloadducts and 1:1:1 adducts as in the **CNN**–**N** reaction, apparently due to a secondary reaction between **CNN*** and **N.**

STRUCTURE ASSIGNMENTS

Because of the importance of the correct structure assignments for the mechanistic conclusions, the spectral features revealing key elements of the product structures are briefly discussed below. In addition to ^1H and ^{13}C spectra, 2D COSY experiments provided significant structural details. Extensive NOE difference spectra were recorded to elucidate substituent stereochemistry and the spatial relationship between different groups. A detailed compilation of spectral data is available as supplemental material.

Cycloaddition products

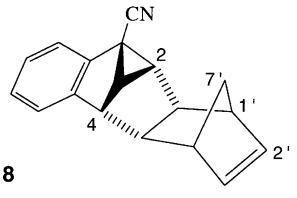
We isolated five products resulting from cycloaddition of **N** to **CNN**, in yields ranging from 19% (**4**) to 6% (**8**). Four [2 + 2]-cycloadducts (**4**–**7**) were described earlier;[12] the minor product (**8**) apparently resulted from

meta-addition. The mass spectra of all five adducts show molecular ion peaks at M^+ *m/z* 245 [$C_{18}H_{15}N = C_{11}H_7N$(**CNN**) + C_7H_8(**N**)]. In contrast to the [2 + 2]-adducts, which have prominent peaks at *m/z* 153 ($M^+ - 92$, $C_{11}H_7N$; loss of norbornadiene by retro-cycloaddition), **8** has a base peak of *m/z* 179 ($M^+ - 66$) corresponding to the loss of cyclopentadiene by retro-Diels–Alder cleavage. The structures are revealed by the 1H NMR spectra.

All cycloaddition products show four features characteristic for the 5,6-disubstituted norbornene unit.[13] First, two resonances (d,d; δ *ca* 5.8–6.2 ppm, $J \approx 6$, 3 Hz), sometimes overlapping, are typical for the olefinic norbornene protons ($H_{2',3'}$). The identification is confirmed by their correlation with the corresponding bridgehead proton ($H_{1'}$ or $H_{4'}$) in the COSY spectrum. The orientation of the bridgehead protons (δ *ca* 3 ppm) causes simultaneous weak coupling ($J < 3$ Hz) with several adjacent protons, resulting in broadened signals. The bridge protons ($H_{7'}$) appear as an AB system (δ 1.5–2.0 ppm; $^2J \approx$ 9–12 Hz) with only small additional splittings ($J \leq 2$ Hz). Finally, the resonances of $H_{5'}$ and $H_{6'}$ show characteristic coupling patterns: $J_{5n-6n} \approx 8$ Hz, $J_{5n-4} < 1$ Hz, $J_{1-6n} < 1$ Hz.

Product **8** has four aromatic and only two olefinic protons, and the familiar norbornene features.[11] The presence of four aromatic protons identifies the CN-substituted aromatic ring as the site of the addition; the absence of olefinic protons (other than those of the norbornene moiety) requires that the two reactants are linked in a way that converts three unsaturated bonds to saturated moieties. This change is typically observed for the *meta*-cycloaddition of alkenes to benzenoid compounds.[14]

The key to the structure of **8** lies in the resonances at 2.31 ppm (d, 6.6 Hz), representing a benzylic proton, and an unresolved multiplet (3.5 ppm; 2H, correlated with the 2.31 ppm proton), which is identified as a cyclopropane resonance. Although unusually high for cyclopropane protons, this chemical shift has precedent in a related *meta*-cycloadduct;[15] in the case discussed here the adjacent cyano group causes a significant downfield shift. The special nature of adduct **8** is also reflected in its MS fragmentation pattern, which features a base peak at *m/z* 179 (M − 66), corresponding to loss of cyclopentadiene.



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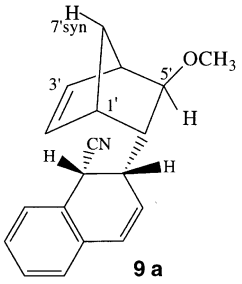
1:1:1 Adducts between N, CNN and methanol

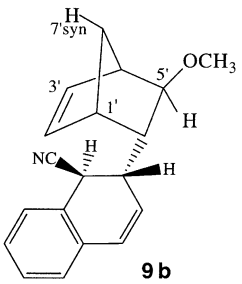
Several adducts showed slightly longer GC retention times than the cyclobutane derivatives. Their molecular ions (M^+ *m/z* 277, $C_{19}H_{19}NO$ = **CNN** + **N** + CH_3OH) indicate that they contain the elements of **N, CNN** and methanol in a ratio of 1:1:1. The ^{1}H NMR spectrum of the mixture shows six distinct OCH_3 singlets (δ 3.2–3.5 ppm) in a ratio of 1:4:2:2:2:1. All six products must contain the (unrearranged) norbornene function, because of prominent MS peaks corresponding to the loss of cyclopentadiene (*m/z* 211, $M^+ - 66$, $C_{14}H_{13}NO$). In addition, the net composition requires that these products contain a (cyano-)dihydronaphthalene function.

We were able to isolate and characterize five products, **9a**–**11**, which were obtained in yields between 5% (**9a**) and 2% (**10**). Similarly to the [2 + 2]-adducts **4**–**7**, their NMR spectra show the general features characteristic for a 5,6-disubstituted norbornene unit.[12] The coupling patterns of the resonances representing $H_{5'}$ and $H_{6'}$ (J_{5n-6x} = 3–6 Hz, $J_{5n-4} < 1$ Hz, $J_{1-6x} \approx 3$ Hz) identify the adducts as 6-*endo*-substituted 5-*exo*-methoxynorbornenes.

Four of the adducts contain four aromatic and two norbornene protons; therefore, the aromatic ring bearing the CN function must be the site of addition. One pair of adducts, **9a** and **9b** (OCH_3 signals at 3.36 and 3.43 ppm, respectively), contain two additional olefinic protons. These adducts must be formed by addition at the ring carbon bearing the cyano group. The similarity of the spectra of **9a** and **9b** suggests that they differ in the stereochemistry of the connection between the norbornene and dihydronaphthalene units. The detailed stereochemistry rests on NOE experiments.



9 a

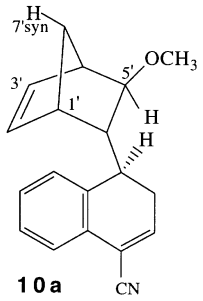


9 b

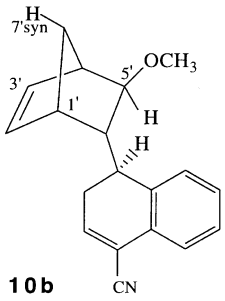
Another pair of adducts, **10a** and **10b** [OCH_3 at 3.39 and 2.72 (!) ppm, respectively], contain one additional olefinic proton, suggesting an olefinic bond between C_1 and C_2 and, accordingly, that the addition occurs in the position *para* to the cyano group. The similarity between the spectra of **10a** and **10b** suggests that the norbornene and dihydronaphthalene moieties are linked in stereochemically different fashion. The detailed stereochemistry was established by NOE experiments.

The fifth adduct, **11**, (OCH_3 at 3.35 ppm) has one strongly deshielded (δ 8.32), seven aromatic (δ 7.8–8.0, 3H; δ 7.5–7.6 ppm, 4H), and two olefinic protons (δ 6.10 ppm). The presence of seven aromatic protons shows that the naphthalene system is retained; the signal at 8.32 ppm is characteristic of the α-^{1}H of an aryl-substituted imine.[16] Therefore, this adduct must be

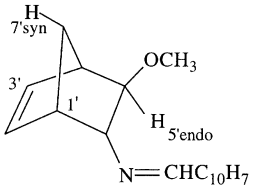
formed by addition of **N** to the C≡N function. This type of addition has precedence.[17]



10a



10b



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DISCUSSION

The product distribution with **CNN** as sensitizer differs greatly from the **DCB**-sensitized reaction[10] and from the results reported for the reaction with **CNN** in methanol.[11] The energetics of key reaction steps rule out electron transfer from **N** to ^{1}**CNN***. We confirmed the reported conversion of **Q** to **N** as a major reaction, possibly in competition with nucleophilic capture. This finding is in striking contrast to the results observed for the photoreaction of **Q** with **DCB**, which clearly proceeds via nucleophilic capture of $\mathbf{Q}^{+\cdot}$ by methanol.[10] Similarly, TR-ESR results have demonstrated that the reaction of $\mathbf{Q}^{+\cdot}$ with methanol is much faster than its valence isomerization to $\mathbf{N}^{+\cdot}$.[18] In view of these results, it is questionable whether $\mathbf{Q}^{+\cdot}$ can be the major intermediate in the quenching of **CNN** fluorescence by **Q.**

The **CNN**-induced photochemistry of **N** reported here is incompatible with the earlier results.[11] The obvious discrepancies are ascribed to advances in separation techniques during the intervening years. The products reported earlier were isolated by distillation and GC. It is unlikely that adducts **4**–**11** would be isolated under these conditions.

The general course of the reaction between **DCB** and **N** was explained via photo-induced electron transfer [Scheme 1, equation (2)], nucleophilic capture of the resulting radical cation [equation (3)] and hydrogen abstraction from acetonitrile [equation (4)] in competition with aromatic substitution [equation (5)].[10] An additional element of complexity lies in the fact that the free radicals generated by nucleophilic capture undergo rapid skeletal rearrangements, $\mathbf{B}^{\cdot}$ to $\mathbf{C}^{\cdot}$ to

Excitation:

$$\mathbf{A} \rightarrow {}^1\mathbf{A}^* \quad (1)$$

Electron transfer:

$${}^1\mathbf{A}^* + \mathbf{D} \rightarrow \mathbf{A}^{-\cdot} + \mathbf{D}^{+\cdot} \quad (2)$$

Nucleophilic capture:

$$\mathbf{D}^{+\cdot} + CH_3OH \rightarrow CH_3O - \mathbf{D}^{\cdot} + H^+ \quad (3)$$

Hydrogen abstraction:

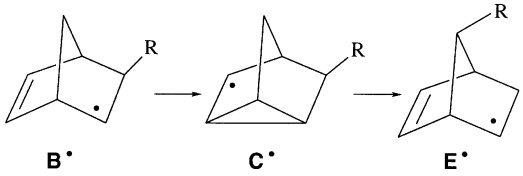
$$CH_3O - \mathbf{D}^{\cdot} + CH_3CN \rightarrow CH_3O - \mathbf{D} - H + {}^{\cdot}CH_2CN \quad (4)$$

Coupling/substitution:

$$CH_3O - \mathbf{D}^{\cdot} + A^{-\cdot} \rightarrow CH_3O - \mathbf{D} - A^- \quad (5)$$

Scheme 1.

$\mathbf{E}^{\cdot}$ (e.g. R = CH_3O), resulting in a variety of products.[10,12,19]



$\mathbf{B}^{\cdot}$ $\mathbf{C}^{\cdot}$ $\mathbf{E}^{\cdot}$

The driving force for electron transfer [equation (2)] from **N** to ^{1}**CNN*** is different from that to ^{1}**DCB***. The free energy of radical ion pair formation is given by the excited state energy, $E_{(0,0)}$, the reduction and oxidation potentials of the reagents, $E_{(A-/A)}$ and $E_{(D/D+)}$, and a term accounting for ion pairing which, in polar solvents, has a value of *ca* 0.06 eV:[20]

$$-\Delta G = E_{(0,0)} - E_{(D/D^+)} + E_{(A^-/A)} - e^2/\varepsilon a \quad (7)$$

With **DCB** as sensitizer, electron transfer is exergonic (**DCB**, $E_{0,0}$ = 4.29 eV, $E_{(A-/A)}$ = −1.60 V;[21] **N**, $E_{(D/D^{+\cdot})}$ = 1.54 V;[22] ΔG = −1.0 eV), allowing efficient generation of radical ions. The **CNN**-sensitized reaction is only marginally exergonic ($E_{(0,0)}$ = 3.75 eV,[23] $E_{(A-/A)}$ = −1.98 V;[21] $\Delta G \approx -0.2$ eV); under these conditions radical ion generation is inefficient. The relatively low yields of the methanol adducts **1**–**3** observed in our hands is fully compatible with these considerations. The significantly higher yields reported earlier[11] are hard to reconcile with the energetics of electron transfer from **N** to ^{1}**CNN***.

On the other hand, the reducing power of $\mathbf{CNN}^{-\cdot}$ is greater by *ca* 0.4 eV than that of $\mathbf{DCB}^{-\cdot}$; it is sufficient to reduce the free radical, CH_3—O—$\mathbf{B}^{\cdot}$, formed by nucleophilic capture of $\mathbf{N}^{+\cdot}$, and the rearranged free radicals, CH_3O—$\mathbf{C}^{\cdot}$ and CH_3O—$\mathbf{E}^{\cdot}$. The incorporation of deuterium into the methanol adducts suggests the protonation of anions, CH_3O—$\mathbf{B}^-$, CH_3O—$\mathbf{C}^-$ and CH_3O—$\mathbf{E}^-$.[10] The mechanism invoked for these intermediates implies the radical cation $\mathbf{N}^{+\cdot}$ as a key

intermediate in their formation, even if formed with low efficiency.

One group of 1:1 adducts between **CNN** and **N**, viz. **8**, clearly belongs to a different structure type than the [2 + 2]-cycloadducts or the 1:1:1 adducts. The shortage of olefinic resonances suggests the presence of an additional (cyclopropane) ring; the assigned structure identifies it as a *meta*-cycloadduct, a product type often formed between an aromatic singlet state and alkenes, and formulated via exciplex intermediates.[24] *Meta*-cycloadducts may be formed as major products from aggregates with limited charge-transfer character; the present system clearly has considerable charge-transfer character, compatible with the formation of **8** and its isomers as minor products. The predominant products formed from **CNN** and **N** are [2 + 2]-cycloaddition products (**4**–**7**), suggesting exciplex formation as the key mechanism.

[2 + 2]-Cycloaddition of CNN to N

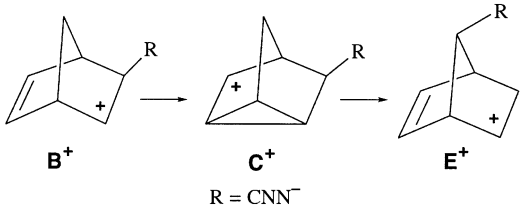
The involvement of (an) exciplex(es) in the deactivation of ^{1}**CNN*** by **N** was considered for several reasons. The photo-reactions of **CNN** with donor olefins (**D**) lead to [2 + 2]-cycloadducts[25] and show exciplex emission;[23,26] these results support ^{1}(**CNN**–**D**)* exciplexes. The reaction between ^{1}**CNN*** and **N** shows no such emission; this rules out exciplexes as well defined intermediates. Still, the [2 + 2]-adducts are compatible with short-lived encounter complexes of various geometries. The structures of the adducts provide insight into the stereochemistry of addition to **N** (*endo* or *exo*), the regiochemistry of addition to **CNN** and the relative orientation of the two fragments (*syn* or *anti*). The addition occurs exclusively on the *exo*-face of **N**, on either ring of the acceptor, with limited preference for *anti*- vs *syn*-addition. In polar solvents, the reaction is more selective, favoring *anti*-addition to the substituted ring.[12]

Some features of the adducts between ^{1}**CNN*** and **N** differ from those with other donors. The highly stereospecific *exo*-addition to **N** is reminiscent of the stereospecific attack of methanol on $\mathbf{N}^{+\cdot}$.[10] Of course, the stereochemistry of addition to the donor is not an issue for the commonly used symmetrical substrates (2,3-dimethylbut-2-ene, cyclopentene). Adducts **4**–**7** also show an unusual regiochemistry of addition to **CNN.** The donor typically adds at the site of the CN group, whereas adducts **6** and **7** result from addition to the unsubstituted ring. The relative yields of **6** and **7** depend on solvent polarity; in benzene, **4**–**7** are formed essentially randomly; the ratio (**4** + **5**)/(**6** + **7**) increases to *ca* 2 in methanol or methylene chloride–methanol and to *ca* 7.5 in acetonitrile (Table 1). This trend reflects the selectivity–reactivity principle. In non-polar solvents, 1**CNN*** and **N** form aggregates with little charge separation, which rapidly collapse to products. In polar solvents, the reagents form more polar, more stable and more selective aggregates.[8,9] The adducts show little preference for an orientation of **N** to ^{1}**CNN***. The lower steric hindrance in *anti*-isomers suggests a lower barrier for their formation; this is borne out to some extent by product ratios, **4:5** and **6:7** (Table 1). However, the preference for *anti*-combination is notable only in the most polar solvent (acetonitrile; **4:5** $\approx$ 1.6). The high specificity of *exo*-attack on **N** is the most striking feature of these reactions. One explanation for the absence of *endo*-adducts lies in the formation of 1:1:1 adducts and, possibly, in some unidentified [2 + 2]-cycloadducts.

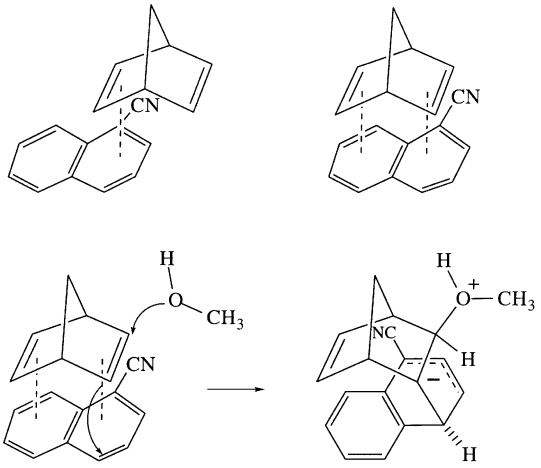
1:1:1 Adducts of cyanonaphthalene, methanol and norbornadiene

Products formed by the combination of a cyano-aromatic acceptor, an olefinic donor and an alcohol have been observed in several systems, including **CNN**, 2,3-dimethylbut-2-ene, methanol[25] or 9-cyanophenanthrene, 2,3-dimethylbut-2-ene, methanol.[2b,27,28] Several mechanistic pathways have been considered, including (a) electron transfer–proton transfer–radical coupling,[28] (b) electron transfer– nucleophilic attack–coupling[29] or (c) electron transfer–coupling–nucleophilic attack;[25] the third mechanism is unique as it invokes a zwitterionic species as the key intermediate.[25] The three-dimensional nature of **N** and the resulting stereochemistry of three adducts, **9**–**11**, provides a rigorous test for the proposed mechanisms. The structures of the 1:1:1 adducts are incompatible with all three mechanisms.

In the system ^{1}**CNN***–**N**–methanol, proton transfer from $\mathbf{N}^{+\cdot}$ to $\mathbf{CNN}^{-\cdot}$ [mechanism (a)] can be eliminated because deprotonation of the bridgehead is unfavorable. Nucleophilic attack by methanol on $\mathbf{N}^{+\cdot}$ [mechanism (b)] is known to generate the methoxy-substituted norbornenyl radical, $\mathbf{B}^{\cdot}$ (R = OCH_3), which undergoes a rapid allylcarbinyl to cyclopropylcarbinyl rearrangement to $\mathbf{C}^{\cdot}$ (R = OCH_3) and and $\mathbf{E}^{\cdot}$ (R = OCH_3).[10] Finally, the



adduct zwitterion, $\mathbf{B}^{+}$ [R = CNN^{-}; mechanism(c)] is expected to undergo an allylcarbinyl to cyclopropylcarbinyl rearrangement to $\mathbf{C}^{+}$ (R = CNN^{-}) followed by a cyclopropylcarbinyl to allylcarbinyl rearrangement to $\mathbf{E}^{+}$ (R = CNN^{-}). The five 1:1:1 adducts, **9**–**11**, unambiguously preclude any rearrangement of the norbornenyl structure (**B**) to either the nortricyclyl (**C**) or the 7-methoxynorbornenyl structure (**E**). All adducts have the



Scheme 2. Schematic representation of *endo*-**CNN**–**N** encounter complexes and nucleophilic attack of methanol on an *endo-syn*-complex

same C_7H_8 framework; their MS fragmentation patterns show $[M-66]^+$ fragment ions as base peaks, corresponding to loss of cyclopentadiene via retro-Diels–Alder cleavage. This finding is incompatible with all three pathways considered above.

Substitution of an exciplex (or an encounter complex) as the initial intermediate (in place of a radical cation) in the previously postulated mechanisms does not resolve the mechanistic problem. Formation of a single C—C bond in such a complex would generate $\mathbf{B}^+$ ($R = CNN^-$) with structural consequences as discussed; proton transfer is still unfavorable. Clearly, the adducts are formed by a mechanism which is different in principle.

We suggest that the solution to the mechanistic problem lies in the stereochemistry of the 1:1:1 adducts. Products **9**–**11** have an *endo*-1-cyanodihydronaphthyl moiety and an *exo*-methoxy group in common. The stereochemistry of the approach of **CNN** to **N** is opposite to that of the [2 + 2]-adducts, whereas the methoxy groups are introduced analogous to the attack of methanol on $\mathbf{N}^{+\cdot}$.[10] In the light of these results, we explain the formation of the 1:1:1 adducts via several topologically different encounter complexes, with **CNN** on the *endo*-face of **N** (Scheme 2). While *exo*-complexes 'collapse' to cyclobutane-type adducts (**4**–**7**), the *endo*-complexes produce 1:1:1 adducts (**9**–**11**; Scheme 2), by nucleophilic attack from the *exo*-face and formation of an *endo*-C—C (or C—N) bond to the cyanoaromatic. This reaction leads to zwitterionic intermediates which yield the three-component adducts by deprotonation–protonation. The C—C (C—N) bond formation need not be concerted with nucleophilic capture; however, the timing of these steps is important.

The fact that methanol attacks the 'aggregate' and $\mathbf{N}^{+\cdot}$ with the same stereochemistry suggests that the *endo*-complexes have sufficient charge density on the *exo*-face and that their nucleophilicity resembles that of the radical cation. Formally, such an aggregate is a contact radical ion pair (CRIP),[2] in contrast to the solvent-separated radical ion pair (SSRIP) accessible by electron transfer to 1**DCB***. If the free radicals formed by nucleophilic capture of the contact radical ion pair add to the sensitizer anion faster than they rearrange, the difference between the reactions of ^{1}**DCB*** and ^{1}**CNN*** is simply that between a CRIP and a SSRIP.

The variety of 1:1:1 adducts requires several 'loose' complexes with comparable free energies for a range of geometries. A potential energy surface with broad minima, rather than a single, well defined minimum, would allow bonding of the 'developing' methoxynorbornenyl radical ($\mathbf{B}^{\cdot}$, $R = OCH_3$) not only at C-4 or C-2, but also at the CN function of the **CNN** system. Coupling in these positions would give rise to products **9, 10** and **11**, respectively.

The charge-transfer induced coupling of an olefin to the CN function of a cyanoaromatic has precedent in the photo-reactions of benzonitrile with various olefins.[30] The attack of nucleophilic solvents on 'contact ion pairs' has been invoked previously to explain structural features of products resulting from the photoreactions of 2-phenyl-1-pyrrolinium ion with (prop-2-enyl)-cyclopropane or butadiene in methanol.[31]

CONCLUSION

A series of [2 + 2]-cycloadducts and 1:1:1 adducts obtained in the photo-reaction of **CNN** with **N** in the presence or absence of methanol are rationalized via encounter complexes or exciplexes of different geometries. The solvent polarity has a significant role in determining the course of the reaction, ranging from essentially random addition in benzene to somewhat regioselective adduct formation in acetonitrile. The high preference for *exo*-attack on **N** stands in contrast to a less regiospecific attack on **CNN** and little preference for relative orientation of the two reagents in the cycloaddition. The concept of *endo*- and *exo*-exciplexes and their divergent reactivities poses interesting questions; a more detailed investigation of these features is desirable, but goes beyond the scope of the results presented here.

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