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Electron Donor-Acceptor Photochemistry of 1-Cyano-Naphthalene with Norbornadiene : Stereospecific Regiorandom [2 + 2] Cycloaddition

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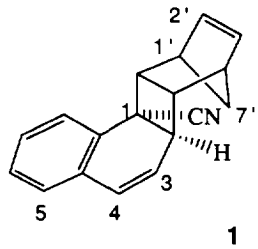
Abstract

The electron donor-acceptor photo-reaction of norbornadiene (**N**) with 1-cyano-naphthalene (**CNN**) in benzene yields four [2+2] cycloadducts, **1** – **4**. The addition occurs exclusively on the exo-face of **N**, on either ring of the acceptor, either at or adjacent to the cyano group, and shows limited preference for anti- vs. syn-addition. In more polar solvents, the reaction becomes more selective, favoring anti-addition to the substituted ring. The formation of the products is rationalized via the "collapse" of short-lived encounter complexes of different geometries.

Light-induced interactions of electron donor acceptor systems have been at the forefront of mechanistic photochemistry for over two decades.[1-3] Depending on the energetics of electron transfer between donor and acceptor, the reaction may proceed via an excited-state complex (exciplex)[1,2,4] or a pair of radical ions.[2-4] Typically, non-polar media favor the formation of exciplexes, whereas polar solvents favor radical ion pairs. The involvement of exciplexes is recognized by characteristic broad, red-shifted (exciplex) emission bands or by stereospecific cycloadditions. Radical ions, on the other hand, can be observed by spectroscopic techniques, such as ESR, CIDNP, ODMR;[3] their involvement has been assigned also from characteristic reactions, such as rearrangements, nucleophilic capture, or deprotonation.[3] Cycloadditions between 1-cyanonaphthalene (**CNN**) or 9-cyanophenanthrene (**CNP**) and olefins are regiospecific at the CN bearing site;[5] symmetric donors (e.g., tetramethylethylene), pose limited problems of regio- or stereochemistry.[5a] The stereospecificity of some [2+2] additions, e.g., between **CNP** and p-methoxystyrene, was rationalized by intermediates utilizing maximum orbital overlap.[6] In this letter, we report the photoinduced [2+2] cycloaddition between norbornadiene (**N**) and **CNN**, which is at once stereospecific and regiorandom and documents significant effects of solvent polarity on regio- and stereochemistry of the cycloaddition.

Irradiation of **CNN** and **N** in benzene (ε = 2.3) generates four [2+2] adducts, **1** – **4**, in comparable yields (19%, 17%, 23%, and 20%, respectively). In more polar solvents (CH_2Cl_2, ε = 9.1), the yields of adducts **1** and **2** (27% and 20%, respectively) increase at the expense of **3** and **4** (15% and 9%, respectively), whereas in acetonitrile (ε = 37.5), **1** (46%) and **2** (29%) are significantly preferred. The structures of the four [2+2] adducts rest on spectral data, particularly on their NMR spectra (^1H, ^{13}C, 2D COSY, NOE).

The mass spectra of all four adducts show molecular ion peaks, M^+ = 245 [$C_{18}H_{15}N = C_{11}H_7N$ (CNN) + C_7H_8 (N)], and prominent peaks at m/z = 153 [$C_{11}H_7N = M^+ - 92$; loss of N]. The ^1H NMR spectra of the four products show features characteristic for the 5,6-disubstituted norbornene unit.[7] Two resonances (d,d; δ ~5.8–6.2 ppm, J ~ 6, 3 Hz), in some cases overlapping, are typical for the olefinic norbornene protons ($H_{2',3'}$). The assignment is confirmed by their correlation with the corresponding bridgehead proton ($H_{1'}$ or $H_{4'}$) in the COSY spectrum. The signals of the bridgehead protons (δ ~3 ppm) are broad because their stereochemical orientation allows simultaneous weak coupling (J < 3 Hz) with several adjacent protons. The bridge protons ($H_{7'}$) appear as AB systems (δ 1.5–2.0 ppm; ^2J = ~9–12 Hz) with only small additional splittings (J ≤ 2 Hz). Finally, the resonances of $H_{5'}$ and $H_{6'}$ show characteristic coupling patterns: $J_{5'n\text{-}6'n}$ = ~8 Hz, $J_{5'n\text{-}4'}$ < 1 Hz, $J_{1'\text{-}6'n}$ = < 1 Hz.



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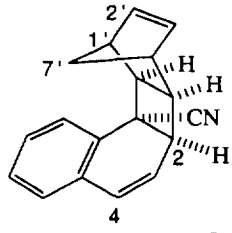

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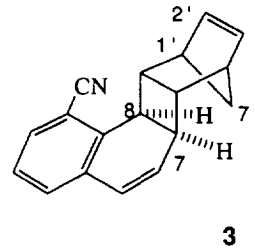

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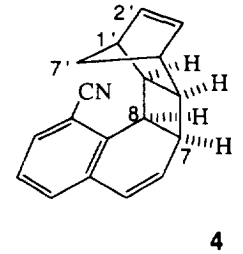
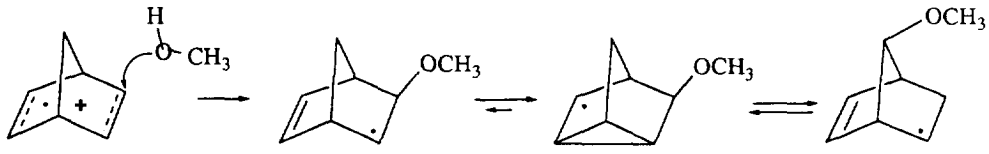


4

Products **1** and **2** have 4 aromatic and 4 olefinic protons. The presence of 4 aromatic protons identify the aromatic ring bearing the CN group as the site of the addition; 4 olefinic protons indicate that the site of addition includes the CN bearing carbon. The stereochemistry was established by NOE experiments; products **1** and **2** differ only in the stereochemistry of their linking. Irradiation of the (more strongly deshielded) *anti*-$H_{7'}$ resonance of **1** caused enhancement of the (shielded) *syn*-$H_{7'}$ and of the allylic cyclobutane resonance (2.9 ppm; H_2), but did not affect any other signals of the dihydronaphthalene moiety. This identifies **1** as the *anti,exo*-isomer. For product **2**, NOE effects between H_4 and an aromatic signal (6.99 ppm; H_5) establish a peri-relationship, confirming $C_{1,2}$ as the site of addition. Irradiation of anti-$H_{7'}$ (1.52 ppm) caused weak enhancement of H_3 and H_4. This identifies **2** as the *syn,exo*-isomer.

The NMR spectra of products **3** and **4** show 3 aromatic and 4 olefinic protons, supporting addition to the unsubstituted benzene ring. NOE effects between an aromatic (H_4, overlapping with H_2) and an olefinic signal (6.26 ppm; dd, J = 9.8, 1.5 Hz; H_5) establish a peri-relationship; therefore, the $C_{7,8}$ bond must be the site of addition for both **3** and **4**. Adduct **3** is assigned the *anti,exo*-structure because of strong NOE effects between two cyclobutane resonances (H_7 and H_8) and the less shielded norbornene bridge proton ($H_{7'anti}$, 1.80 ppm, dbr, J = 9.5 Hz). Since the spectral differences between **3** and **4** show the same trends as those between **1** and **2**, adduct **4** is identified as the *syn,exo*-isomer.

The results reported here are significantly different from previous results obtained in the donor acceptor photochemistry of **CNN** with **N** in methanol,[8] or of 1,4-dicyanobenzene (**DCB**) with **N** in acetonitrile.[9] The earlier results are compatible with the radical cation, **N**•+, as key intermediate; nucleophilic capture of **N**•+ by methanol from the exo-face forms the free radical, **5**•, which rapidly rearranges to (equilibrates with) **6**• and **7**•. In contrast, the reaction between ^{1}**CNN*** and **N** in non-polar solvents is unlikely to proceed via **N**•+.



N·+ 5· 6· 7·

Electron transfer from N to ^{1}CNN* is only marginally exergonic ($E_{0,0}$ = 3.75 eV,[10] $E_{A^-/A}$ = –1.98 V;[11] E_{D/D^+} = 1.54 V;[12] ΔG ~ –0.2 eV). Irradiation of donor-acceptor pairs with such a marginal driving force for electron transfer frequently fail to result in radical ion formation; they show exciplex emission and exciplex derived products instead. The photo-reactions of ^{1}CNN* with various donor olefins (**D**) are known to lead to [2+2] cycloadducts;[5] the observation of exciplex emission in several of these reactions[13] has been interpreted as evidence for the involvement of ^{1}(CNN–D)* exciplexes in the formation of these adducts. By analogy, products **1** – **4** may also be formed via some type of ^{1}(CNN–N)* complex.

The structures of the four products provide some insight into the nature of the aggregates formed between ^{1}CNN* and N. The interactions are characterized by three features: the regiochemistry of addition to the CNN ring; the regiochemistry of addition to the bicyclic substrate; and the relative orientation of the two fragments in the products. The addition to the CNN framework could occur either at the ring bearing the electron-withdrawing cyano group or at the unsubstituted ring; concerning the donor molecule, the topology of the bicyclic substrate allows addition to either the endo- or exo-face; finally, the two substrates may be aligned in syn- or anti-fashion.

The products isolated from the reaction between ^{1}CNN* and N differ from previously reported reactions with other donors (tetramethylethylene) in several respects. First, the addition to the CNN rings appears to be less regiospecific than previously reported for some other systems.[5] The adducts reported earlier apparently were formed exclusively or preferentially by addition at the site of the electron-withdrawing (CN) function; in contrast, we found two adducts, **3** and **4**, resulting from addition to the unsubstituted ring. The relative yields of **3** and **4** depend on the solvent polarity; in solvents of low polarity (benzene), the four adducts are formed essentially randomly; in solvents of intermediate polarity (methanol, methylene chloride/methanol) the ratio of (**1**+**2**)/(**3**+**4**) is ~2; finally, in more highly polar solvents the ratio is significantly higher, viz., ~7.5 in acetonitrile. We see this trend as a result of the selectivity-reactivity principle, causing variations in the pathway of complex or product formation. In non-polar solvents, an encounter between the reactants, ^{1}CNN* and N produces an aggregate with little charge separation, which collapses rapidly and with limited regiospecificity to a product. In polar solvents, on the other hand, the reactants produce (a) more polar aggregate(s),[8,9] whose increased stability leads to a more selective product formation. In more polar solvents, the aggregates (complexes) prefer geometries in which the partial positive charge on the $N^{\delta+}$ fragment is aligned with the partial negative charge density on the $CNN^{\delta-}$ fragment.

Significantly, the addition of CNN is regiospecific with respect to the bicyclic substrate, involving exclusively the exo-face of N; this addition is reminiscent of the regiospecific approach chosen by the nucleophile (methanol) in the capture of N·+.[8,9] On the other hand, the relative (syn- or anti-) orientation of

the two reagents, which is also revealed by the relative yields of the adducts, shows considerably less specificity. The attack on each acceptor ring results in a pair of syn-anti-stereoisomers: products **1** (anti) and **2** (syn) are formed by attack on the substituted ring, whereas isomers **3** (anti) and **4** (syn) result from attack on the unsubstituted ring. The pathway to the anti-isomers appears to be less hindered; however, the product ratios, **1** : **2** and **3** : **4**, show only a subtle preference. The effect is noticeable only in the most polar solvent, acetonitrile, where **1** : **2** ~1.6. The observed effect is ascribed to a more prominent solvation of the partial charges on $N^{\delta+}$ and $CNN^{\delta-}$; this is more easily accommodated in the anti-orientation.

In summary, the four [2+2] cycloadducts resulting from the interaction between ^{1}CNN* and **N** reveal an interesting reactivity pattern for the intervening aggregates: the highly specific exo-attack on **N** stands in contrast to less stringent preferences for the regiochemistry of the attack on **CNN** as well as for the syn- or anti-orientation of the two reagents relative to each other.

Acknowledgement

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