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A novel application of the Diels–Alder reaction: nitronaphthalenes as normal electron demand dienophiles

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Abstract—Thermal reactions between nitronaphthalenes and butadienes were studied. It was demonstrated that these reactions are capable of undergoing the normal electron demand Diels–Alder reaction, with a variety of dienes affording the phenanthrene derivatives. The influence of the extension and type of substitution was also discussed. When the electron-withdrawing activation of the naphthalenic nucleus or the donor properties of the dienes were not enough, *N*-naphthylpyrroles were detected as main product, suggesting that a competitive reaction would probably take place. The results clearly confirmed the dienophilic nature of nitronaphthalenic double bonds and provided an alternative procedure for phenanthrene derivatives and *N*-naphthylpyrroles' synthesis. The relative reactivity of the reactants and the viability of the reactions were discussed from a theoretical point of view.

1. Introduction

The Diels–Alder (DA) reaction is one of the most significant and useful tools available in synthetic chemistry. It allows the simple construction of a six-membered ring from a diene and a dienophile bearing an almost unlimited number of variants. It is worth noting that these variants exist not only in the substitution of the reaction components but also in the electronic nature of these dienes and dienophiles.

In the 1980s, studies of aromatic heterocycles such as indoles, benzofurans, pyrroles, furans, and thiophenes in Diels–Alder reactions demonstrated the viability of these systems as dienophiles.[1] Further studies focused on the dienophilic character of indoles since their adducts seemed to be appealing for the total synthesis of carbazole and *Aspidosperma* alkaloids.[2] Attention has been recently turned to the investigation of the dienophilicity of substituted naphthalenes. While the use of these substrates as dienes in thermal and high-pressure Diels–Alder reactions has been widely studied,[3,4] the employment of such compounds as dienophiles has received relatively little attention in the literature.

Herein we report our findings on the dienophilic behavior of naphthalenes properly mono and disubstituted with an electron-withdrawing group such as nitro, cyano, acetyl, and chloro. These dienophiles were exposed to a series of dienes under thermal conditions.

In the last few years, the density functional theory (DFT) has been successful in explaining the reactivity and regioselectivity of cycloaddition reactions.[5] Current studies, based on DFT and applied to DA reactions, have shown that the classification of the diene/dienophile pair within a unique scale of electrophilicity is a powerful tool to predict the feasibility of the process and the type of reaction mechanism involved.[6] Accordingly, experimental studies were combined with computational ones in order to explain the observed reactivity.

Therefore, part of this work is specifically concerned with the evaluation of the frontier molecular orbitals (FMO), which provide qualitative information about the feasibility of the DA reaction.[5,7a] Besides, the global electrophilicity index (ω) is employed to estimate the electrophilic character of the dienophiles used in the cycloaddition reactions.

2. Computational details

According to recent studies, the B3LYP method, even with a 6-31G(d) basis set, is adequate to model DA reactions concerning medium-sized molecules. This method was applied to different diene/dienophile combinations yielding satisfactory results.[5a,8] Accordingly, in the present work the equilibrium geometries were obtained by full optimization at the ground states of the molecules using the B3LYP/6-31G(d) level of theory. The global electrophilicity index (Eq. 1) was calculated employing the electronic chemical potential (μ) and the chemical hardness (η). These two latter parameters can be approximated in terms of the one-electron energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as in

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Eqs. 2 and 3, respectively. All the calculations were performed with the Gaussian 98 program.[9]

$$\omega = \frac{\mu^2}{2\eta} \quad (1)$$

$$\mu = \frac{\in_{\mathrm{HOMO}} + \in_{\mathrm{LUMO}}}{2} \quad (2)$$

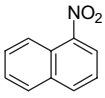
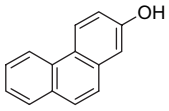
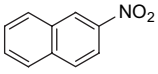
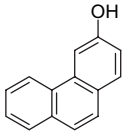
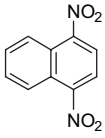
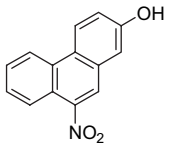
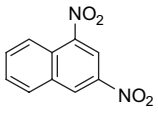
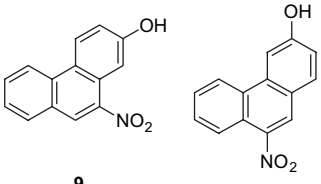
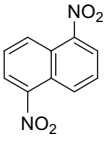
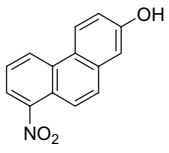
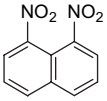
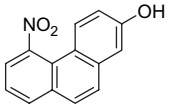
$$\eta = \in_{\mathrm{LUMO}} - \in_{\mathrm{HOMO}} \quad (3)$$

3. Results and discussion

To explore the normal electron demand DA dienophilicity of nitronaphthalenes **1a**–**1f** (Table 1), we choose 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky's diene) (**2**), 1-methoxy-1,3-butadiene (**3**), 1-(*N*-acetyl-*N*-propylamine)-1,3-butadiene (**4**), and isoprene (**5**) as dienes (Fig. 1).

We started the study by testing the reactivity of 1-nitronaphthalene (**1a**) with Danishefsky's diene since it is one of the strongest dienes and is appropriate to test these aromatic

Table 1. Reactions of nitronaphthalenes with Danishefsky's diene

Entry	Dienophile	Conditions[a]	Product	Yield (isolated)[b]
1	 **1a**	120 °C	 **6**	51 (24)
2	**1a**	150 °C	**6**	62 (43)
3	 **1b**	120 °C	 **7**	45 (21)
4	**1b**	150 °C	**7**	58 (53)
5	 **1c**	120 °C	 **8**	75 (56)
6	**1c**	150 °C	**8**	70 (70)[c]
7	 **1d**	120 °C	 **9** **10**	**9**, 14 (12); **10**, 65 (57)
8	**1d**	150 °C	**9**, **10**	**9**, 5 (5); **10**, 83 (80)
9	 **1e**	120 °C	 **11**	48 (31)
10	**1e**	150 °C	**11**	66 (48)
11	 **1f**	120 °C	 **12**	35 (20)
12	**1f**	150 °C	**12**	50 (43)

[a] Reactions were carried out for 72 h, in ampoules using 2 equiv of Danishefsky's diene and benzene as solvent.
[b] Yield in percentage based on consumed nitronaphthalene, and isolated yield. Optimal conditions involved high temperatures for all substrates **1a**–**1f**, except for **1c**, which showed a significant decomposition.
[c] Significant decomposition of substrate **1c** was observed at the highest temperatures.

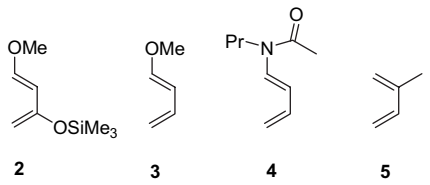
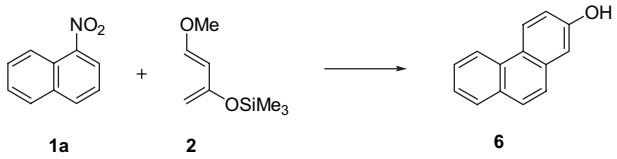


Figure 1.

substrates.[10] Thus, when **1a** and **2** were heated in a sealed tube at 150 °C for 72 h using benzene as solvent, 62% of 2-hydroxy-phenanthrene (**6**) was regioselectively produced (Scheme 1, Table 1, entry 2).



Scheme 1. Diels–Alder reaction of 1-nitronaphthalene with Danishefsky's diene.

The thermal extrusion of the nitro group as nitrous acid along with the loss of the methoxy group as methanol from the initial DA adduct led to the final aromatized product.

This fact was well known for adducts obtained by the reaction of nitroolefins[11] with **2** and was also observed in our previous work with nitroindoles.[2b] It should be remarked that the isolation of the primary adduct was never achieved under the experimental conditions used in this work.

In an analogous fashion to **1a**, 2-nitronaphthalene (**1b**) reacted to give 45% of hydroxyphenanthrene **7** (Table 1, entry 3). The regioselectivity of both reactions was controlled by both the nitro group of the dienophile and the methoxyl group of Danishefsky's diene. This type of total regioselectivity had already been observed when working with nitroindoles,[2b] nitrosubstituted thiophenes[12] and furans.[13]

The dienophilicity of dinitronaphthalenes (**1c**–**1f**) was then investigated with Danishefsky's diene. The influence of the disubstitution was first considered in the same ring of naphthalene and then in the other ring.

In the case of 1,4-dinitronaphthalene (**1c**), due to the enhanced reactivity of this dienophile, the DA reaction at 120 °C proceeded to furnish 75% of the single regioisomer 2-hydroxy-9-nitrophenanthrene **8** (Table 1, entry 5).

On the other hand, the reaction of 1,3-dinitronaphthalene (**1d**) produced the two isomers resulting from the cycloaddition to C1–C2 and C3–C4 bonds (1:4.6 ratio, respectively), with a total yield of 88% (Table 1, entry 8). In order to explain the addition mode observed, we analyzed the size of the LUMO orbital coefficients at the two possible reacting centers because the size of these coefficients is a key factor in orienting the direction of the cycloaddition on the atoms that will form the new bonds.[7] The atoms with the largest coefficients will interact most strongly; therefore, the preferable addition is to the C3–C4 bond because the LUMO coefficient at C4 is larger than at C1.[14]

The reactions of 1,5-dinitronaphthalene (**1e**) and 1,8-dinitronaphthalene (**1f**) yielded the corresponding phenanthrene derivatives in both cases (Table 1, entries 9–12). With **1e** the yield is similar to mononitronaphthalenes (Table 1, entries 9 and 10). In the case of **1f**, the low yields obtained could be explained by steric effects derived from the proximity of the nitro groups, which caused considerable overcrowding in the molecule.[15]

Again, in all these reactions the regioselectivity is controlled by the nitro and methoxyl groups (*ortho–para* relationship).[7a]

Taking into account that the reactivity of a DA reaction depends on the HOMO–LUMO energy separation of the reactants, and that in a normal electron demand DA reaction the strongest interaction takes place between the HOMO of the diene and the LUMO of the dienophile,[7a] we compared the corresponding energies of the reacting partners in order to explain the experimental tendency observed (Table 2).

When the FMO of the reacting pairs are closer in energies, the interaction is higher. Therefore, we expected higher reactivities for **1c** and **1d**, which is consistent with the experimental results (Table 1, entries 5–8).

The DA behavior of nitronaphthalenes substituted in the *para*-position by other electron-withdrawing groups such as cyano (**1g**), acetyl (**1h**), and chloro (**1i**) was also studied under similar conditions (Table 3). Reactions of substrates **1g** and **1h** with Danishefsky's diene clearly produced the expected phenanthrenes **13** and **14**, showing a dienophilic behavior, which did not differ substantially from 1-nitronaphthalene (Table 3, entries 1–4). However, we observed a notable reduction in the reaction yield when using **1i** even though theoretical calculations predicted a higher reactivity for this reactant (lower HOMO–LUMO energy difference compared to **1a**).[16] This reduction in the yield could be attributed to a major effect of the dative conjugation from chloro to the reacting double bond (Table 3, entries 5–6). Nitro site selectivity was observed in all these cases, a fact, which could be ascribed to the stronger electron-withdrawing effect of the nitro group.

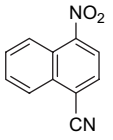
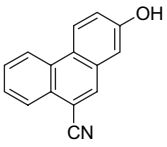
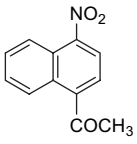
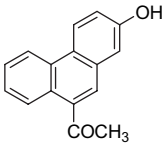
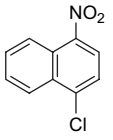
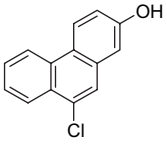
The diene **2** results exhibited so far demonstrate that the incorporation of a second nitro group in a different ring of 1-nitronaphthalenes (**1e** and **1f**), and of either a cyano, acetyl or chloro group in the same ring (**1g**–**1i**) did not produce further activation on the naphthalenic nucleus. However, the insertion of a second nitro group in the same ring of 1-nitronaphthalenes (**1c** and **1d**) generated the desired activation of the nucleus.

Table 2. Calculated LUMO energies for the dinitronaphthalenes and calculated HOMO energy for diene **6**

Molecule	FMO energy[a]
1,4-Dinitronaphthalene (**1c**)	−3.3223
1,3-Dinitronaphthalene (**1d**)	−3.1313
1,5-Dinitronaphthalene (**1e**)	−3.1022
1,8-Dinitronaphthalene (**1f**)	−2.7392
Danishefsky's diene (**2**)	−5.0883

[a] In eV. The LUMO energies were evaluated at the B3LYP/6-31G(d) level of theory for the ground state optimized geometries.

Table 3. Diels–Alder reactions of 1,4-disubstituted naphthalenes with Danishefsky's diene

Entry	Dienophile	Conditions[a]	Product	Yield (isolated)[b]
1	 **1g**	120 °C	 **13**	53 (22)
2	**1g**	150 °C	**13**	66 (49)
3	 **1h**	120 °C	 **14**	50 (28)
4	**1h**	150 °C	**14**	57 (45)
5	 **1i**	120 °C	 **15**	35 (25)
6	**1i**	150 °C	**15**	43 (40)

[a] Reactions were carried out for 72 h, in ampoules using 2 equiv of Danishefsky's diene and benzene as solvent.
[b] Yield in percentage based on consumed nitronaphthalene, and isolated yield.

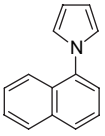
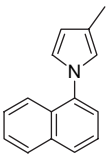
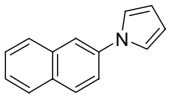
Unexpected results were observed when using nitronaphthalenes with less reactive dienes such as 1-methoxy-1,3-butadiene (**3**), 1-(*N*-acetyl-*N*-propylamine)-1,3-butadiene (**4**), and isoprene (**5**).

Interestingly, when nitronaphthalenes **1a** and **1b** reacted with dienes **3–5**, they produced *N*-naphthylpyrroles **16–18** with yields according to the electron-donor properties of the diene (Table 4, entries 1–7). In order to employ lower temperatures and verify the obtention of the corresponding *N*-naphthylpyrrole, we performed the reactions using 1-nitronaphthalene and 1-methoxy-1,3-butadiene in toluene at refluxing temperatures for 144 h (anhydrous conditions), thus obtaining pyrrole **16**.

It is important to notice that the reactions with dienes **3** and **4**, which furnished the final *N*-naphthylpyrrole, no longer bear the heterosubstituents initially present in the 1-position of the dienes. These results are consistent with the formation of *N*-phenylpyrroles using nitrosobenzene and dienes oxygenated in 1-position as reported in the literature.[18a]

On the other hand, reactions of 1-alkyl and 1-acyl-1,3-butadienes with nitrosobenzene produced the corresponding alkylated and acylated *N*-phenylpyrroles[18,19] thus showing that the nature of the rearrangement process only causes the extrusion of heterosubstituents at the 1-position of the diene. In previous studies with 2,3-dimethoxy-1,3-butadiene and 1-nitronaphthalene, we have demonstrated that oxygenated substituents were kept in this case.[10c] Within the above-mentioned limitations, and choosing the right substitution pattern in the diene, it might be possible to elaborate the desired *N*-naphthylpyrrole.

Table 4. Thermal reactions of monosubstituted nitronaphthalenes with dienes **3–5**

Entry	Dienophile	Diene	Conditions[a]	Product	Yield (isolated)[b]
1	**1a**	**3**, 3 equiv	120 °C, 72 h	 **16**	94 (82)
2	**1a**	**3**, 3 equiv	150 °C, 72 h	**16**	100 (90)
3	**1a**	**4**, 3 equiv	120 °C, 72 h	**16**	43 (35)
4	**1a**	**4**, 12 equiv	180 °C, 96 h	**16**	23 (15)[c,d]
5	**1a**	**5**, 12 equiv	150 °C, 96 h	 **17**	36 (22)[d]
6	**1a**	**5**, 12 equiv	180 °C, 96 h	**17**	47 (46)[d]
7	**1b**	**3**, 3 equiv	150 °C, 72 h	 **18**	57 (41)

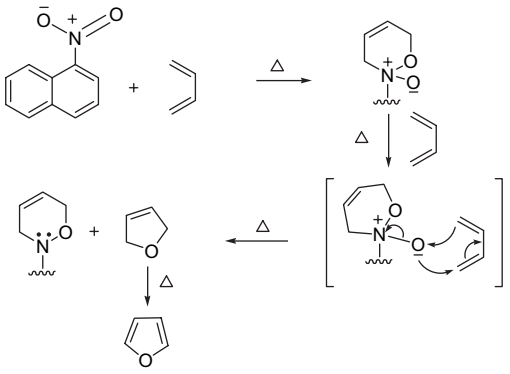
[a] Reactions were carried out in ampoules using benzene as solvent.
[b] Yield in percentage based on consumed nitronaphthalene, and isolated yield.
[c] Thermal instability of diene **4** was already reported over 150 °C.[2b]
[d] Small amounts of the corresponding naphthylamines were also observed.[17]

It should be worth mentioning that heterocycloaddition adducts or any other subsequent rearrangement products from the interaction of nitronaphthalenes with Danishefsky's diene are not feasible in any case.

Taking into account that the well-known reactions of nitrosobenzene with several butadienes furnish the hetero Diels–Alder adducts, which rearrange into the *N*-phenylpyrroles under thermal[18] and photochemical activation,[19] we expected a similar behavior. Hence, we assumed a probable cycloaddition of the diene to the heterodienophilic fragment of the nitro group forming the oxazine *N*-oxide. This oxide suffers a reduction assisted by the diene to give dihydrofurans and subsequent furans (Scheme 2).[20] As already known of hetero adducts from nitrosobenzene, the thermal cleavage of N–O bond followed by intramolecular nucleophilic addition to aldehyde and final dehydration afford pyrrole derivatives.[21]

Further evidence on the mechanism arose from the production of α-naphthylamine, which is formed in small amounts at temperatures above 150 °C and could be produced through an alternative pathway from the hetero Diels–Alder adduct as reported for reactions of 1,3-butadienes and nitrosobenzene.[17–19]

From the results obtained, we can conclude that there are two competitive reactions that might take place on



Scheme 2. Proposed mechanism for the cycloaddition of the diene to the heterodienophilic fragment of the nitro group.

mononitronaphthalenes: the addition to the nitro group, and the DA reaction on the C1–C2 bond, depending on the strength of the diene partner.

Moreover, when nitronaphthalenes **1c–1f** reacted with dienes **3–5**, they generated *N*-naphthylpyrroles and phenanthrenes with different yield ratios (Table 5, entries 1–9). For 1,4-dinitronaphthalene with a better dienophilic activation on the aromatic nucleus, dienes **3** and **4** were strong enough to produce the corresponding phenanthrene **19** as the major product together with *N*-naphthylpyrrole **20** (Table 5, entries 1 and 2). When the dienophile reacted with diene **5**, it produced *N*-naphthylpyrrole **21** as the major product and phenanthrene **22** (Table 5, entry 3).

In the case of 1,3-dinitronaphthalene, a clear tendency toward the DA cycloaddition to the C3–C4 bond was observed with dienes **3–5** (Table 5, entries 4–6). The reactions with dienes **3** and **4** yielded phenanthrene **19** and traces of *N*-naphthylpyrroles **23a** and **23b**. With diene **5**, **1d** gave the corresponding phenanthrene **24** together with traces of *N*-naphthylpyrroles **25a** [3-methyl-1-(1-nitronaphthalen-3-yl)-pyrrole] and **25b** [3-methyl-1-(2-nitronaphthalen-4-yl)-pyrrole]. In all the cases *N*-naphthylpyrroles were detected by GC–MS. This latter result is not in agreement with the general trend of obtaining *N*-naphthylpyrrole as a major product when using isoprene, what could be attributed to the high dienophilicity exhibited by **1d**.

Since all the reactions involving 1,3-dinitronaphthalene produce only one product in appreciable amounts, we selected this dienophile to explain the difference in reactivity toward the different dienes. Thus, the FMO energies of the reactants were evaluated and calculations of the electrophilicity index were performed. Table 6 shows how Danishefsky's diene leads to the minimum HOMO–LUMO energy difference compared to the other dienes (**3–5**), so that an increase in the reactivity of the system is to be expected. This effect is revealed by an increase in the yield of the DA reaction (Table 1, entries 7 and 8 and Table 5, entries 4–6).

It has been found a good correlation between the difference in the global electrophilicity of the diene/dienophile interacting pair ($\Delta\omega$) and the feasibility of the cycloaddition.[5a,b] Therefore, we present the global electrophilicity index (ω) of the dienes and compare it to that of the dienophile (Table 6).

We also include other global properties such as the values of the electronic chemical potential (μ) and the chemical hardness (η). The molecules are listed in decreasing order of global electrophilicity power. High nucleophilicity and high electrophilicity are opposite ends of this scale. Therefore, it might be expected that the electron-rich dienes will exhibit a small value of ω and so be classified as nucleophiles. The interactions between electrophile/nucleophile pairs showing higher differences in absolute electrophilicity are expected to present high reactivity.[6]

The diene that presents a high global electrophilicity gap with respect to 1,3-dinitronaphthalene ($\Delta\omega=\omega_{\text{dienophile}}-\omega_{\text{diene}}$) corresponds to Danishefsky's diene, which is located at the end of the scale. Therefore, we can predict that this diene/dienophile pair will present the highest reactivity, which is in good agreement with the experimental findings (Table 1, entry 4 and Table 5, entries 4–6).

On the other hand, the reaction of 1,5-dinitronaphthalene with diene **5** gave the corresponding pyrrole **26** as the principal product, whereas the reaction with diene **3** produced phenanthrene **28** (Table 5, entries 7 and 8). In the latter case, traces of naphthylpyrrole **29** [1-(5′-nitro-naphthalen-1′-yl)-pyrrole] were detected by TLC and GC–MS.

In the case of 1,8-dinitronaphthalene, it reacted through the naphthalenic bond to furnish phenanthrene isomers **30a** and **30b** (Table 5, entry 9). The low yield of this reaction and the absence of the corresponding pyrrole product could be attributed to its more hindered structure that probably obstructs the hetero-DA reaction and subsequent rearrangement leading to *N*-naphthylpyrrole.[15]

In the reaction of **1g** with diene **5** we obtained only *N*-naphthylpyrrole **31** (Table 7, entry 1). The higher yield compared to the reaction with **1a** (Table 4, entries 5 and 6) could be attributed to the enhancement of the dienophilic character caused by the cyano group.

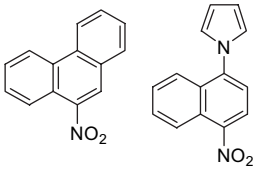
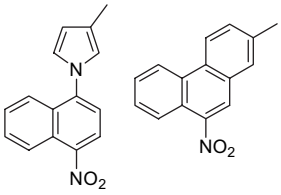
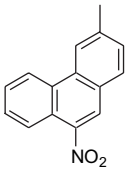
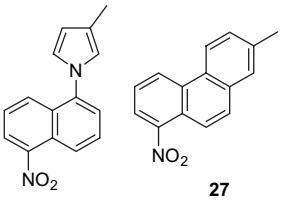
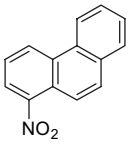
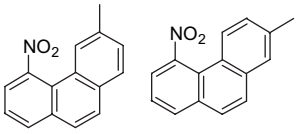
The reaction of **1i** with diene **3** give a 1:1 mixture of *N*-naphthylpyrrole **32** and phenanthrene **33** in moderate yield (Table 7, entry 2).

However, when substrate **1i** reacted with diene **5**, we determined traces of the corresponding *N*-naphthylpyrrole **34** only (Table 7, entry 3). From these latter results, the difference between the electron-withdrawing character of the cyano and chloro groups concerning heterocycloaddition reactions can be appreciated.

When testing the naphthalene **1j**, acetylnaphthalenes **1k**, **1l**, and dicyanonaphthalene **1m** with diene **2** there was no reaction in any case (Fig. 2). This lack of reactivity may be attributed to the highest LUMO energies with respect to the other dienophiles mentioned above as well as to probable steric difficulties as in **1j**.[22] Therefore, the naphthalenic nucleus must be suitably activated to follow the DA reaction.

Quite surprisingly, by employing a cyclic diene like 1,3-cyclohexadiene and a good naphthalenic dienophile like 1,3-dinitronaphthalene, it was possible to accomplish the construction of the bridged product **35** in a single step

Table 5. Thermal reactions of disubstituted nitronaphthalenes with dienes **3**–**5**

Entry	Dienophile	Diene	Conditions[a]	Product	Yield (isolated)[b]
1	**1c**	**3**, 3 equiv	150 °C	 **19** **20**	**19**, 25 (23); **20**, 13 (12)
2	**1c**	**4**, 3 equiv	150 °C	**19**, **20**	**19**, 20 (20); **20**, 8 (8)
3	**1c**	**5**, 10 equiv	150 °C	 **21** **22**	**21**, 15 (13); **22**, 10 (9)
4	**1d**	**3**, 3 equiv	120 °C	**19**, **23a**, **23b**	**19**, 32 (24); **23a**, **23b**, traces[c]
5	**1d**	**4**, 3 equiv	120 °C	**19**, **23a**, **23b**	**19**, 26.3 (18); **23a**, **23b**, traces[c]
6	**1d**	**5**, 5 equiv	120 °C	 **24** **25a**, **25b**	**24**, 23.4 (12); **25a**, **25b**, traces[c]
7	**1e**	**5**, 12 equiv	150 °C	 **26** **27**	**26**, 33 (19); **27**, 5 (3)
8	**1e**	**3**, 3 equiv	150 °C	 **28**	**28**, 29 (24); **29**, traces[c]
9	**1f**	**5**, 12 equiv	150 °C	 **30a** **30b**	**30a**, **30b**, 15 (14) (1.8:1 mixture)

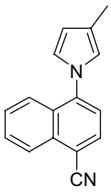
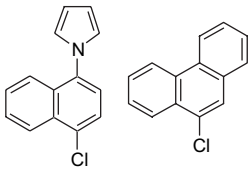
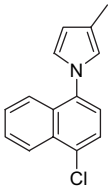
[a] Reactions were carried out for 72 h, in ampoules using benzene as solvent.
[b] Yield in percentage based on consumed nitronaphthalene, and isolated yield.
[c] Detected by GC–MS and TLC. Spraying the TL with a solution of *p*-methoxybenzaldehyde, acetic acid, ethanol, and sulfuric acid (3:1:1:4), naphthylpyrroles were developed as red spots by heating.

Table 6. Global properties values and global electrophilicity scale for reagents of DA reaction. The calculated LUMO energy for **1d** and the calculated HOMO energies for the dienes are also shown

Molecule	Energy[a]	μ[a]	η[a]	ω[a]
1,3-Dinitronaphthalene (**1d**)	−3.1313	−5.11	3.97	3.30
Isoprene (**5**)	−5.9563	−3.29	5.34	1.01
1-(*N*-Acetyl-*N*-propylamine)-1,3-butadiene (**4**)	−5.3250	−2.99	4.67	0.96
1-Methoxy-1,3-butadiene (**3**)	−5.3032	−2.83	4.95	0.81
Danishefsky's diene (**2**)	−5.0883	−2.57	5.03	0.66

[a] In eV. All the quantities were evaluated at the B3LYP/6-31G(d) level of theory for the ground state optimized geometries.

Table 7. Thermal reactions of 1,4-disubstituted nitronaphthalenes with diene **3** and **5**

Entry	Dienophile	Diene	Conditions[a]	Product	Yield (isolated)[b]
1	**1g**	**5**, 12 equiv	150 °C	 **31**	**31**, 55 (27)
2	**1i**	**3**, 3 equiv	120 °C	 **32** **33**	**32**, 16 (11); **33**, 17 (12) (1:1 mixture)
3	**1i**	**5**, 12 equiv	180 °C	 **34**	**34**, traces[c]

[a] Reactions were carried out for 72 h, in ampoules using benzene as solvent.
[b] Yield in percentage based on consumed nitronaphthalene, and isolated yield.
[c] Detected by GC–MS and TLC. Spraying the TL with a solution of *p*-methoxybenzaldehyde, acetic acid, ethanol, and sulfuric acid (3:1:1:4), naphthylpyrroles were developed as red spots by heating.

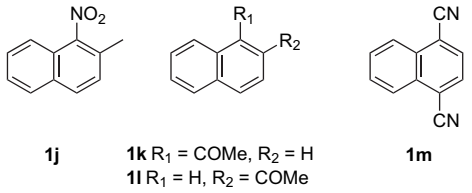
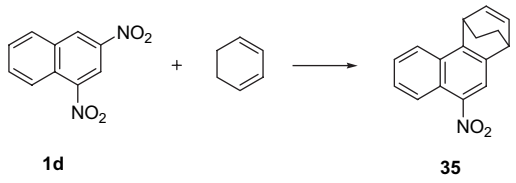


Figure 2.

(38%, 100 °C, 144 h) (Scheme 3). When the reaction was performed at high temperature (120 °C for 72 h), we obtained adduct **35** (25%) and 9-nitrophenanthrene (4%) produced by the thermal extrusion of ethene from **35**.



Scheme 3. Thermal DA reaction of 1,3-dinitrophthalene with 1,3-cyclohexadiene.

4. Conclusions

To our knowledge, the present work is the first formal study on the dienophilicity of naphthalenes in normal electron demand Diels–Alder reactions under standard conditions and it confirms the dienophilic nature of naphthalenic double bonds when properly substituted.

The DA reaction of several substituted 1,3-dienes with nitronaphthalenes yields two types of products, the expected phenanthrene and the unexpected *N*-naphthylpyrrole. The latter reaction seems to be analogous to hetero-DA reactions of nitrosobenzenes previously observed and may proceed through a related reaction pathway. The reaction of mono and dinitronaphthalenes with Danishefsky's diene is an easy way to obtain hydroxyphenanthrenes with total regioselectivity due to the control exercised by nitro and methoxyl groups. On the other hand, when using dienes of lower reactivity like isoprene with mononitronaphthalenes, it is possible to achieve the corresponding *N*-naphthylpyrroles. Moreover, the reaction with disubstituted nitronaphthalenes produces a mixture of the two products.

It has been demonstrated that the introduction of a second nitro group in the same ring of 1-nitronaphthalene produces an extra activation on the naphthalenic nucleus. Instead, when the nitro group is placed in the other ring no additional activation is observed.

It has also been shown that it is possible to carry out the construction of a bridged product in a single step through the reaction of 1,3-cyclohexadiene and a good naphthalenic dienophile such as 1,3-dinitronaphthalene.

Furthermore, DFT calculations concerning the HOMO–LUMO energy difference between the interacting pair diene/dienophile and the global electrophilicity index are useful tools to predict the viability of the cycloaddition reactions.

The results obtained in this work may further contribute to the general reactivity of naphthalene and extend the scope of the Diels–Alder reaction to the application of polycyclic aromatic hydrocarbons as dienophiles.

5. Experimental

5.1. General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on 200 and 50 MHz FT spectrometers, respectively, using TMS as the internal standard; GC–MS analyses were performed in an instrument equipped with a PE-5-type column. IR spectra were recorded from NaCl cells as CCl_4 solutions. Melting points were observed on a Winkle–Zeiss Gottingen microhot stage and were uncorrected. Silica gel of 70–230 mesh was used for chromatography. The following reagents were prepared according to the reported methods: 1,4-dinitronaphthalene (**1c**),[23] 1-acetylnaphthalene (**35a**),[24] 2-acetylnaphthalene (**35b**),[25] and 1-(*N*-acetyl-*N*-propylamine)-1,3-butadiene.[2a] The synthesis of 1,4-dicyanonaphthalene (**36**) was performed from the appropriate amino-naphthalencarbonitrile based on the procedure for **1c** using an alkaline solution of 10 equiv KCN, mp: 210–212 °C (lit.[26] 211 °C). 2-Nitronaphthalene (**1b**, caution: strong cancer suspect agent) was obtained by thermal decomposition (250 °C) of the commercial 2-nitronaphthalene-bis-(hexachlorocyclopentadiene) adduct. Other reagents were obtained from commercial sources and were used as received or purified as required by standard methods. Products **6**,[27] **7**,[28] **8**,[10b] **9**,[10a] **10**,[10a] **13**,[10b] **14**,[10b] **16**,[10a] **17**,[10c] **18**,[29] **19**,[30] **24**,[10c] **25a**,[10c] **25b**,[10c] **26**,[31] and **33**[31] were previously reported.

5.1.1. 1-Cyano-4-nitronaphthalene (1g) and 1-acetyl-4-nitro-naphthalene (1h). Compounds **1g** and **1h** were synthesized from 4-amino-1-cyanonaphthalene and 1-acetyl-4-amino-naphthalene,[32] respectively, by the treatment of diazo-compound with sodium nitrite, similarly to **1c**.[20] Compound **1g**: mp 114–116 °C. ^{1}H NMR δ: 7.80–7.90 (m, 2H), 8.00 (d, 1H, J=7.9 Hz), 8.14 (d, 1H, J=7.9 Hz), 8.40 (dd, 1H, J=7.0, 3.0 Hz), 8.48 (dd, 1H, J=7.9, 3.0 Hz). Compound **1h**: mp 73–74 °C. ^{1}H NMR ($CDCl_3$) δ: 2.76 (s, 3H), 7.67–7.60 (m, 2H), 7.80 (d, 1H, J=7.9 Hz), 8.07 (d, 1H, J=7.9 Hz), 8.43 (m, 1H), 8.49 (m, 1H).

5.1.2. 4-Chloro-1-nitronaphthalene (1i). Compound **1i** was prepared from the corresponding nitronaphthylamine according to the method of Bassilios and Shawky.[33] Mp 85–86 °C. ^{1}H NMR ($CDCl_3$) δ: 7.63 (d, 1H, J=8.4 Hz), 7.69–7.79 (m, 2H), 8.12 (d, 1H, J=8.4 Hz), 8.39 (m, 1H), 8.57 (m, 1H).

5.2. General procedure for the thermal reactions of naphthalenes 1a–1i

Temperature, length of the reaction and the diene/dienophile ratio were dependent on the starting material and are indicated in Tables 1, 3–5 and 7. An ampoule containing a solution of 1.0 mmol of the dienophile and the required amount of diene in 0.5 mL of dry benzene was cooled in liquid nitrogen, sealed (under nitrogen atmosphere), and then heated in an oil bath. After the reaction time was completed, it was cooled once more in liquid nitrogen and opened. The solution was evaporated and the residue purified by column chromatography.

5.2.1. 1-Hydroxy-7-nitrophenanthrene (11). Elution with 5:1 hexanes–ethyl acetate on silica gel led to the recovery of unreacted dienophile **1e**. Further elution afforded phenanthrene **11**: IR 3250, 1528, 1339 cm^{-1}. ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ: 2.20 (br s, 1H), 7.29 (d, 1H, J=2.4 Hz), 7.31 (dd, 1H, J=9.5, 2.4 Hz), 7.63 (t, 1H, J=8.4 Hz), 7.80 (d, 1H, J=9.5 Hz), 8.06 (dd, 1H, J=8.4, 1.1 Hz), 8.20 (d, 1H, J=9.5 Hz), 8.52 (d, 1H, J=9.5 Hz), 8.82 (d, 1H, J=8.4, 1.1 Hz). ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ: 111.5, 118.4, 119.9, 121.4, 122.4 (2C), 124.3, 124.7, 127.0, 129.7, 131.9, 133.1, 147.6, 156.9. Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.85. Found: C, 70.52; H, 3.85; N, 5.97.

5.2.2. 2-Hydroxy-5-nitrophenanthrene (12). Elution with hexanes–ethyl acetate on silica gel led to the recovery of unreacted dienophile **1f** and further elution afforded **12**: mp 181–183 °C. IR 3247, 1534, 1350 cm^{-1}. ^{1}H NMR ($CDCl_3$/DMSO-d_6) δ: 7.30 (d, 1H, J=1.5 Hz), 7.54 (dd, 1H, J=9.0, 1.5 Hz), 7.81 (d, 1H, J=9.4 Hz), 7.96 (t, 1H, J=8.4 Hz), 8.07 (d, 1H, J=8.4 Hz), 8.18 (d, 1H, J=9.4 Hz), 8.54 (d, 1H, J=9.0 Hz), 8.85 (d, 1H, J=8.4 Hz), 9.45 (br s, 1H). ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ: 111.2, 118.2, 119.6, 124.1, 124.4, 125.7, 126.8, 128.2, 129.5, 130.4, 131.7, 132.8, 147.3, 156.8. Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.85. Found: C, 70.86; H, 3.69; N, 5.98.

5.2.3. 9-Chloro-2-hydroxyphenanthrene (15). Elution with 10:1 hexanes–ethyl acetate on silica gel led to the first fraction containing unreacted substrate **1i** and a second fraction **15**: mp 135–137 °C. IR 3350, 747, 715 cm^{-1}. ^{1}H NMR (acetone-d_6) δ: 2.79 (br s, 1H), 7.26 (s, 1H, J=1.0 Hz), 7.28 (d, 1H, J=8.0, 1.0 Hz), 7.67 (m, 2H), 7.70 (s, 1H), 8.3 (d, 1H, J=8.0 Hz), 8.59 (d, 1H, J=8.8, 1.4 Hz), 8.66 (d, 1H, J=8.1, 1.7 Hz). ^{13}C NMR (acetone-d_6) δ: 111.1, 117.0, 122.2, 123.8, 124.6, 125.3, 125.6, 126.3, 127.5, 128.5, 131.4, 131.5, 133.2, 154.7. Anal. Calcd for $C_{14}H_9OCl$: C, 73.53; H, 3.97. Found: C, 73.83; H, 3.99.

5.2.4. 1-(4′-Nitro-naphthalen-1′-yl)-pyrrole (20). Elution with 10:1 hexanes–methylene chloride on silica gel afforded two consecutive fractions containing products **19**[30] and **20**. Further elution gave the unreacted substrate **1c**. Compound **20**: ^{1}H NMR ($CDCl_3$) δ: 6.46 (t, 2H, J=2.1 Hz), 7.01 (t, 2H, J=2.1 Hz), 7.50 (d, 1H, J=8.2 Hz), 7.63 (ddd, 1H, J=8.3, 7.0, 1.3 Hz), 7.77 (ddd, 1H, J=8.5, 7.0, 1.5 Hz), 7.95 (dd, 1H, J=8.3, 1.5 Hz), 8.25 (d, 1H, J=8.2 Hz), 8.62 (dd, 1H, J=8.5, 1.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 110.3 (2C), 121.2, 123.0 (2C), 123.3, 123.6 (2C), 124.2, 126.2, 128.1, 129.8, 130.1, 143.2. Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.89; H, 4.30; N, 11.98.

5.2.5. 3-Methyl-1-(4′-nitro-naphthalen-1′-yl)-pyrrole (21) and 2-methyl-9-nitrophenanthrene (22). Elution with 10:1 hexanes–methylene chloride on silica gel led to the first fraction containing **21**, a second fraction **22** and further elution led to the recovery of the unreacted **1c**. Selected data for **21**: ^{1}H NMR ($CDCl_3$) δ: 2.22 (s, 3H, Me), 6.28 (dd, 1H, J=2.8, 1.9 Hz), 6.79 (br s, 1H), 6.91 (t, 1H, J=2.4 Hz), 7.41 (d, 1H, J=8.2 Hz), 7.55–7.80 (m, 2H), 8.05 (dd, 1H,

J=7.7, 1.3 Hz), 8.22 (d, 1H, J=8.2 Hz), 8.60 (dd, 1H, J=8.6, 1.5 Hz). Selected data for **22**: ^{1}H NMR ($CDCl_3$) δ: 2.32 (s, 3H), 7.50 (d, 1H, J=7.9 Hz), 7.59–7.80 (m, 3H), 8.24 (d, 1H, J=8.4 Hz), 8.42 (s, 1H), 8.71 (d, 1H, J=7.9 Hz), 9.00 (d, 1H, J=8.8 Hz).

5.2.6. 3-Methyl-1-(5′-nitro-naphthalen-1′-yl)-pyrrole (26) and 2-methyl-8-nitrophenanthrene (27). Elution with 6:1 hexanes–methylene chloride on silica gel afforded consecutively **26** and **27**. Further elution finally led to the unreacted substrate **1e**. Selected data for **26**: ^{1}H NMR ($CDCl_3$) δ: 2.21 (s, 3H), 6.25 (t, 1H, J=2.0 Hz), 6.73 (br s), 6.85 (t, 1H, J=2.4 Hz), 7.46–7.80 (m, 3H), 8.08 (d, 1H, J=8.6 Hz), 8.21 (dd, 1H, J=7.7, 1.3 Hz), 8.51 (d, 1H, J=8.4 Hz). Selected data for **27**: IR 1521, 1330 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.59 (s, 3H), 7.56 (d, 1H, J=8.6, 1.5 Hz), 7.62–7.76 (m, 2H), 7.88 (d, 1H, J=9.3 Hz), 8.17 (dd, 1H, J=9.0, 8.0 Hz), 8.28 (d, 1H, J=9.0 Hz), 8.57 (d, 1H, J=8.6 Hz), 8.93 (d, 1H, J=8.0 Hz).

5.2.7. 3-Methyl-5-nitrophenanthrene (30a) and 2-methyl-5-nitrophenanthrene (30b). Elution with hexanes–ethyl acetate on silica gel led to a first fraction containing a 1.8:1 mixture of the two isomers **30a** and **30b** (which could not be separated). ^{1}H NMR ($CDCl_3$) δ: 2.59 (s, 3H), 2.65 (s, 3H), 7.47–7.59 (m, 2H), 7.63–7.66 (m, 4H), 7.8–7.92 (m, 3H), 8.12–8.31 (m, 3H), 8.48 (d, 1H, J=1.1 Hz), 8.57 (d, 1H, J=8.8 Hz), 8.92 (d, 1H, J=8.1 Hz), 8.96 (d, 1H, J=8.1 Hz). Further elution led to the recovery of the unreacted dienophile **1f**.

5.2.8. 1-(4′-Cyanonaphthalen-1′-yl)-3-methylpyrrole (31). Elution with 15:1 hexanes–ethyl acetate on silica gel led to a first fraction containing **31** and then a second fraction with the unreacted **1g**. Compound **7p**: IR 2222 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.21 (s, 3H), 6.27 (t, 1H, J=2.3 Hz), 6.78 (br s, 1H), 6.90 (t, 1H, J=2.4 Hz), 7.41 (d, 1H, J=7.7 Hz), 7.61 (ddd, 1H, J=8.3, 7.0, 1.3 Hz), 7.71 (ddd, J=8.3, 7.0, 1.3 Hz), 8.05 (dd, 1H, J=8.3, 1.3 Hz), 8.27 (dd, 1H, J=8.3, 1.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 11.5, 108.5, 111.8, 117.3, 120.5, 120.9, 121.3, 122.6, 124.3, 125.3, 128.0, 128.6, 128.8, 132.2, 133.5, 142.5. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 83.15; H, 5.20; N, 12.24.

5.2.9. 1-(4′-Chloro-naphthalen-1′-yl)-pyrrole (32) and 9-chlorophenanthrene (33). Elution with 5:1 hexanes–methylene chloride on silica gel led to a first fraction containing a 1:1 mixture of **32** and **33**, selected data: ^{1}H NMR ($CDCl_3$) δ: 6.40 (t, 2H, J=2.3 Hz), 6.95 (t, 2H, J=2.3 Hz), 7.37 (d, 1H, J=8.0 Hz), 7.51 (dd, 1H, J=8.2, 1.5 Hz), 7.60 (d, 1H, J=8.0 Hz), 7.55–7.76 (m, 6H), 7.80 (dd, 1H, J=7.1, 2.2 Hz), 7.87 (s, 1H), 8.33 (dd, 1H, J=8.0, 1.2 Hz), 8.38 (m, 1H), 8.65 (dd 1H, J=8.0, 1.2 Hz), 8.70 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 109.3 (2C), 122.7, 122.8, 123.2, 123.3, 123.8, 124.8, 125.3 (2C), 125.5, 126.4, 126.9, 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 129.4, 129.5, 131.3, 131.8, 143.2. Further elution led to the recovery of the unreacted naphthalene **1i**.

5.2.10. 9-Nitro-1,4-dihydro-1,4-ethanylphenanthrene (35). Elution with 20:1 hexanes–ethyl acetate led to the first fraction containing **35** and then to a second fraction containing the unreacted dienophile **1d**. Compound **35**: mp 104–107 °C. IR 1316, 1502 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.38–1.75 (m, 4H), 4.22 (ddm, 1H, J=6.0, 1.9 Hz), 4.88 (dm, 1H, J=6.0 Hz), 6.52–6.71 (ddd, 2H, J=13.5, 6.0, 2.0 Hz), 7.58–7.70 (m, 2H), 8.17 (s, 1H), 8.26 (m, 1H), 8.63 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 24.7, 25.7, 35.9, 40.7, 120.5, 122.8, 123.7, 123.9, 126.7, 127.9, 128.8, 129.8, 133.7, 135.8, 140.3, 147.4. Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.93; H, 5.22; N, 5.70.

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