

4-Nitrobenzodifuroxan: a highly reactive nitroolefin in Diels–Alder reactions

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Received 23 May 2005; revised 9 June 2005; accepted 13 June 2005

Available online 11 July 2005

Dedicated to Professor Vladimir Minkin on the occasion of his 70th birthday

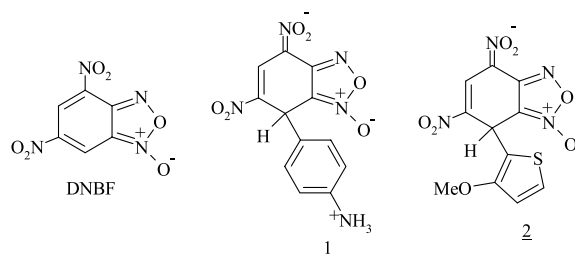
Abstract—The reactions of 4-nitrobenzodifuroxan (NBDF) with a series of common dienes are found to proceed very readily to afford stable cycloadducts, which are the result of highly stereoselective normal electron demand (NED) Diels–Alder reactions. Due to the additional activation provided by the two adjacent furoxan rings, the nitroolefinic double bond of NBDF is also prone to undergo NED reactions with less reactive dienic structures such as the enol form of ethoxymethyleneacetylacetone and the in situ generated 2-ethoxy-4-(2-furfuryl)buta-1,3-diene. A number of X-ray structures could be obtained, which leave no doubt as to the stereochemistry of the resulting cycloadducts. A rationalization of the reactions in terms of the electrophilicity parameter ω defined by Parr suggests that all cycloadditions proceed with a notable polar character.

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1. Introduction

Much evidence has been accumulated that nitro-substituted 2,1,3-benzoxadiazoles and related 1-oxides, commonly referred to as nitrobenzofurazans and nitrobenzofuroxans, respectively, are 10- π electron heteroaromatic substrates, which exhibit an extremely high electrophilic character.^{1–3} As a stronger electrophile than the 4-nitrobenzenediazonium cation, 4,6-dinitrobenzofuroxan (DNBF)—the reference compound in the series—has been used as a probe to assess the reactivity of such weak carbon nucleophiles as benzenoid aromatics (phenols, anilines...) or π -excessive heteroaromatics (indoles, pyrroles, thiophenes, furans...) whose carbon basicities are associated with large negative pK_a values, for example, 1,3-dimethoxybenzene ($pK_a = -9$), aniline ($pK_a = -6$) or 3-methoxythiophene ($pK_a = -6.50$). In all of these reactions, covalent addition of the nucleophile takes place at C-7 of the carbocyclic ring of DNBF to give very stable σ -adducts of type **1** or **2**.^{4–12} Also illustrative of the superselective behaviour of nitrobenzoxadiazole structures is the high tendency of the halogen

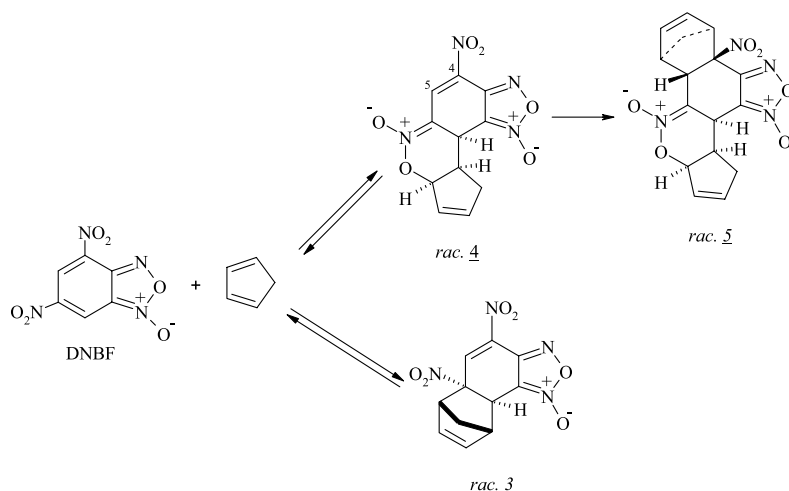
atom of 7-halo-4-nitro- and 7-halo-4,6-dinitro-benzofurazans and -benzofuroxans to depart in nucleophilic aromatic substitutions, leading to numerous synthetic, analytical and biological applications.^{13–15}



It has been recently emphasized that the exceptional electrophilic reactivity of DNBF and related heterocycles is largely the reflection of the low aromatic character of the benzofuroxan and benzofurazan structures.¹⁶ Strong evidence for this relationship has come from the finding that nitrobenzoxadiazoles also behave as very versatile Diels–Alder reagents, contributing to Normal (NED) and Inverse (IED) Electron Demand cycloadditions, which generally proceed with high regio and stereoselectivity.^{17–19} An illustrative example is given in Scheme 1, which shows that the reaction of DNBF with cyclopentadiene affords initially a mixture of the two NED and IED monoadducts **3**

Keywords: Diels–Alder adducts; Nitrobenzodifuroxan; Dinitrobenzofuroxan; Electrophilicity; Nitroolefins.

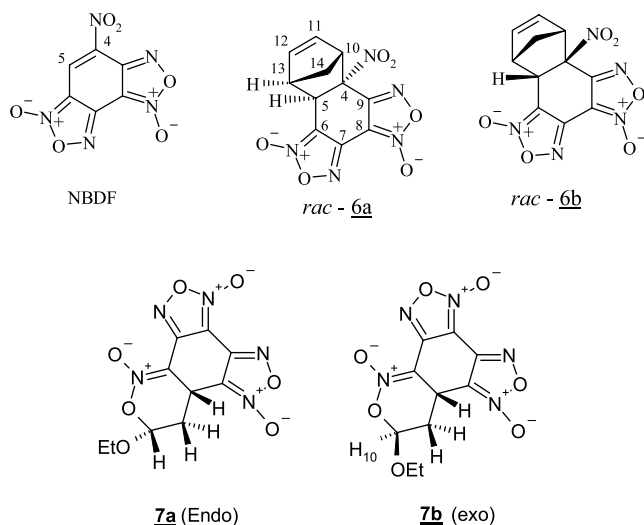
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Scheme 1.

and **4** in their racemic forms. Then, a second and highly stereoselective NED process takes place at the remaining and now purely olefinic nitro-activated C₄–C₅ fragment of **4**, leading to an essentially quantitative formation of the highly functionalized diadduct **5** in its racemic form.^{19a} A theoretical study by Domingo et al. has confirmed the mechanistic and stereochemical features of this interaction.²⁰

The evidence from the above results is that the pericyclic behaviour of DNBF is reminiscent of that of nitroolefins.^{21,22} This encouraged us to look at the potential reactivity of the single nitro-activated C₄–C₅ double bond of the related 4-nitrobenzodifuroxan (NBDF) structure. In fact, we reported recently in a communication that this peculiar nitroolefin behaves as an ambident Diels–Alder reagent, reacting readily with cyclopentadiene to give exclusively the NED monoadduct **6a** (in its racemic form) and with ethyl vinyl ether to afford a 95:5 mixture of the *endo* and *exo* IED adducts **7a** and **7b**.²³ In this paper, we report a detailed investigation of the dienophilic character of NBDF, showing that this compound is so reactive that it undergoes NED reactions with a large variety of dienes, including such poorly reactive structures as the enolic forms of some



β -dicarbonyl compounds, for example, ethoxymethylacetylacetone, and related enol ethers. Also reported are the X-ray structures of NBDF and the cyclopentadiene adduct **6a**, which complement our preliminary report and usefully add to the understanding of the reactions.

2. Results

2.1. The X-ray structure of NBDF

The ORTEP view in Figure 1 shows that the C₄–C₅ double bond of NBDF has a length of 1.339 Å. This is typical of a nitro-olefinic fragment and in contrast with the situation reported for DNBF where values of 1.37 and 1.40 Å have been measured for the two potentially reactive nitro-activated C₆–C₇ and C₄–C₅ double bonds, respectively.²⁴ In accord with these data, the least aromatic C₆–C₇ fragment is the one preferentially involved in Diels–Alder interactions, accounting for the regioselectivity observed in the formation of all DNBF monoadducts so far reported.

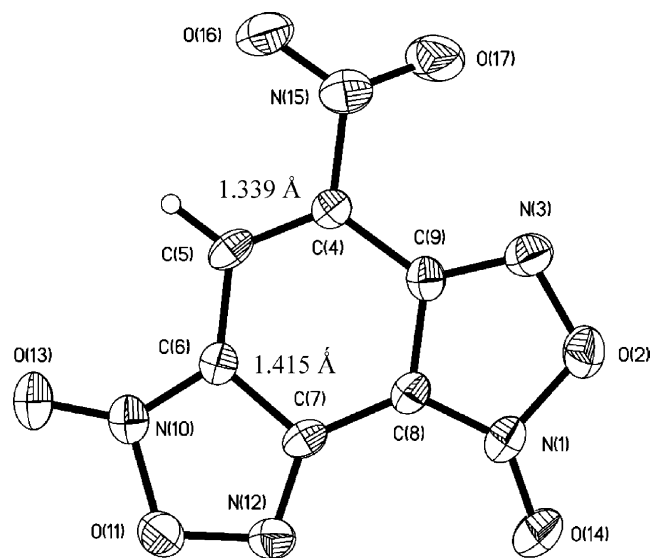


Figure 1. ORTEP view of NBDF.

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