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The Diels–Alder reactivity of nitrobenzofuroxans: mono- and di-adducts of isoprene and 2,3-dimethylbutadiene. New convenient precursors to naphtho- and phenanthreno-furoxanic and -furazanic structures

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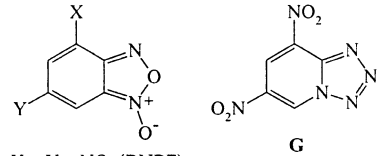
Abstract—The reactions of a series of differently substituted nitrobenzofuroxans with isoprene and 2,3-dimethylbutadiene have been investigated. A variety of mono- and di-adducts resulting from normal electron demand Diels–Alder condensations involving the activated C_6C_7 and/or C_4C_5 double bonds of the carbocyclic ring as the dienophile contributors have been identified and structurally characterized. The regioselectivity of the reactions is found to be strongly dependent on the substitution pattern of this ring. In the 4-nitro-6-X-series, the diene molecule first adds to the C_6C_7 double bond if X is a strong electron-withdrawing substituent (X=NO_2, SO_2CF_3) but to the nitroactivated C_4C_5 double bond if X is a moderately activating substituent (X=CN, CF_3). Subsequent addition of a second molecule of diene occurs to give highly stereoselective diadducts in the 6-cyano, 6-trifluoromethyl and 6-nitro systems. Contrasting with this behavior, only monoadducts corresponding to the addition of diene to the nitroactivated C_6C_7 double bond were obtained in the 4-X-6-nitro-series (X=CN, CF_3). 4,6-Dinitrotetrazolo[1,5-*a*]pyridine reacts similarly to 4,6-dinitrobenzofuroxan, i.e. highly stereoselective diadducts are formed on the reaction with isoprene and 2,3-dimethylbutadiene. A most significant finding is that the treatment of some of the isolated mono- and di-adducts by a strong base like *t*-BuOK results in a facile β-elimination of nitrous acid. Concomitant oxidative rearomatization of the resulting cyclohexadiene moieties then occurs spontaneously to afford otherwise difficultly available naphtho- or phenanthreno furoxanic or furazanic structures as well as azaphenanthrenotetrazoles. © 2002 Published by Elsevier Science Ltd.

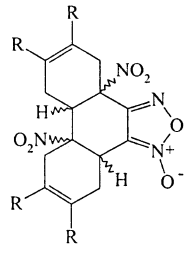
1. Introduction

The high susceptibility of nitro-substituted 2,1,3-benzoxadiazoles and related 1-oxides, commonly referred to as nitrobenzofurazans and nitrobenzofuroxans, to undergo covalent nucleophilic addition or substitution processes has attracted considerable attention in the last few years, leading to numerous synthetic, analytical and biological applications.[1–11] In 1973, Kresze and Bathelt reported that treatment of 4,6-dinitrobenzofuroxan **A** (DNBF) with butadiene and 2,3-dimethylbutadiene afforded, after several weeks, the diadducts **1** and **2**, respectively.[12] Although, the formation of these two compounds was accounted for in terms of normal electron demand Diels–Alder (NEDDA)-type processes, this promising discovery did not lead to further investigation and neither the stereochemistry nor the mechanistic sequence leading to **1** and **2** was elucidated.



A X = Y = NO_2 (DNBF)
B X = NO_2, Y = CF_3
C X = NO_2, Y = CN
D X = NO_2, Y = SO_2CF_3
E X = CF_3, Y = NO_2
F X = CN, Y = NO_2

G



1 R = H
2 R = CH_3

Recently we have shown that the carbocyclic ring of nitrobenzofuroxans can in fact be involved in a variety of Diels–Alder type reactions which proceed with a high stereoselectivity.[13–16] An illustrative example is the reaction of DNBF with 1-trimethylsilyloxybuta-1,3-diene **3** which gives rise nearly quantitatively to the monoadduct **4** in its racemic form (Eq. (1)).[14] Interestingly, this adduct was inert to further reaction with **3** but not with vinyl ethyl ether. In

Keywords: Diels–Alder adducts; nitrobenzofuroxans; rearomatization; phenanthrenofuroxanic structures; precursor; stereoselectivity.

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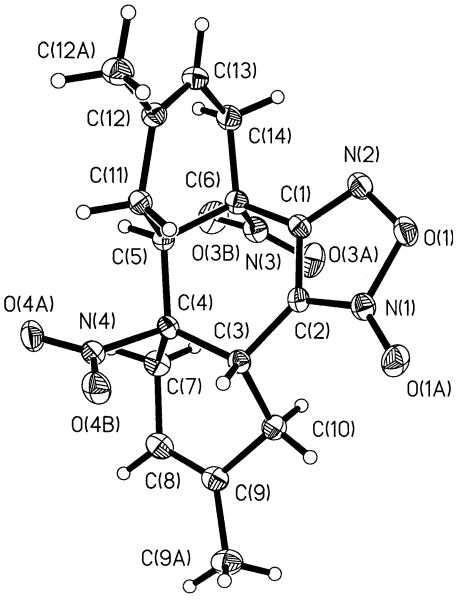
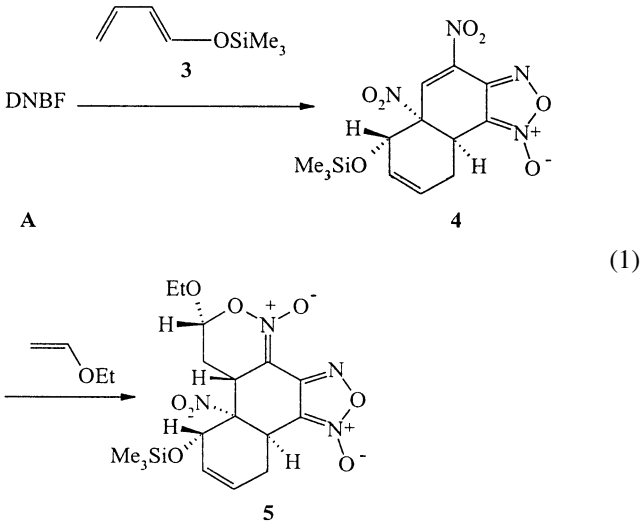


Figure 1. ORTEP view of **A**–**II**$_2$.



(1)

this instance, the dihydrooxazine *N*-oxide **5** was obtained in 92% yield, resulting from a highly diastereoselective inverse electron demand Diels–Alder (IEDDA)-condensation involving the $O_4N_4C_4C_5$ fragment of **4** as the heterodiene contributor. The stereochemistry of **5** was firmly attributed by X-ray crystallography.[14]

The potential importance of the above reactions for synthetic purposes called for further exploration of the various facets of the pericyclic reactivity of nitrobenzofuroxans in general. In this paper, we report on the reactions not only of the series of differently substituted benzofuroxans **A**–**F** but also of 4,6-dinitrotetrazolo[1,5-*a*]pyridine **G**–an interesting related substrate–[8] with 2,3-dimethylbutadiene **I** and/or isoprene **II**. As will be seen, this work has led to the characterization and isolation of a number of mono- and di-adducts, which are all the result of NEDDA processes. Most importantly, we have found that these adducts are suitable precursors for a simple and efficient access to naphtho- and phenanthrenofuroxanic structures as well as azaphenanthrenotetrazoles.

2. Results

2.1. The reactivity of DNBF (A)

The ORTEP view in Fig. 1 shows that the product obtained in the case of the DNBF–isoprene system is a diadduct which is only formed as the diastereomer **A**–**II**$_2$ in its racemic form. The stereochemistry of **A**–**II**$_2$ in the crystal agrees well with the structural information provided by a detailed analysis of the ^{1}H and ^{13}C NMR spectra recorded in $CDCl_3$ solution via COSY, SDEPT-1D and HETCOR, as well as J-modulation experiments.[17] Among other notable diagnostic features for **A**–**II**$_2$, there is the observation that the disappearance of the low field proton and carbon resonances associated with the $C_4C_5C_6C_7$ fragment of the DNBF structure goes along with a strong deshielding of the two sp^3 carbons C_4 and C_6. Both benefit from the strong electron-withdrawing inductive effect exerted by a NO_2 group.[18] Tables 1 and 2 show that the various ^{1}H and ^{13}C NMR parameters collected for the product obtained in the DNBF–2,3-dimethylbutadiene system are closely similar to those for **A**–**II**$_2$. This leaves little doubt that this product is the diadduct **A**–**I**$_2$.

Table 1. ^{1}H and ^{19}F NMR data ($CDCl_3$)

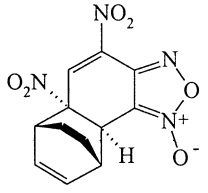
Compounds	H_5	H_7	CH_3	CF_3	Coupling constants (Hz)
A–**I**$_1$	7.54	4.15	1.75; 1.70	–	$^3J_{5/N4}$=3.0 Hz
A–**II**$_1$	7.57	4.22	1.76	–	$^3J_{5/N4}$=3.0 Hz
B–**I**$_1$	3.52	7.34	1.73; 1.69	−74.32	–
A–**I**$_2$	3.78	4.19	1.67;1.65; 1.60; 1.56	–	–
A–**II**$_2$	3.90	4.19	1.71 (11); 1.66 (16)	–	–
B–**I**$_2$	3.71	3.36	1.72; 1.70	−67.29	–
C–**I**$_2$	3.59	3.42	1.78; 1.72	–	–
C–**II**$_2$	3.62	3.50	1.78; 1.77	–	–
D–**I**$_1$	7.29	3.99	1.78 (12); 1.70 (11)	−69.94	–
D–**II**$_1$	7.30	4.05	1.76	−69.96	–
E–**I**$_1$	6.87	4.14	1.69; 1.72	−65.92	–
E–**II**$_1$	6.91	4.21	1.75	−66.03	–
F–**I**$_1$	7.03	4.15	1.69; 1.73	–	–
F–**II**$_1$	7.08	4.21	1.74	–	–
G–**I**$_2$	3.90	5.48	1.69; 1.66; 1.65; 1.61	–	–
G–**II**$_2$	3.98	5.58	1.72 (11); 1.66 (16)	–	–

Table 2. ^{13}C NMR data ($CDCl_3$)

Compounds	C_4	C_5	C_6	C_7	C_8	C_9	CH_3	CF_3	CN
A–I$_1$	141.06	137.29	88.25	33.17	109.88	143.39	18.33 (11); 18.84 (12)	–	–
A–II$_1$	141.13	137.64	87.32	33.08	109.72	143.50	22.56	–	–
B–I$_1$	86.88	29.67		139.25		144.35	18.92; 18.50		–
A–I$_2$	86.80	43.49	93.95	30.37	112.40	149.50	18.59 (12); 18.27 (16,11); 18.12 (15)	–	–
A–II$_2$	86.26	42.23	92.56	30.64	112.33	149.65	22.27 (11); 22.62 (16)	–	–
B–I$_2$	90.12	37.77	47.94	29.64	112.61	152.27	18.90; 18.77; 18.42; 18.21	127.80	–
C–I$_2$	88.85	37.31	40.65	33.01	112.20	151.34	18.73; 18.69; 18.43; 18.19	–	120.82
C–II$_2$	88.12	36.91	39.64	33.21	112.25	151.52	22.92; 22.63	–	121.00
D–I$_1$	142.96	134.05	70.82	29.62	110.58	143.66	19.06; 18.61	120.02	–
D–II$_1$	143.57	134.40	69.96	29.11	110.74	143.74	22.66	119.95	
E–I$_1$	124.54	137.34	87.82	33.00	109.12	145.74	18.76; 18.29	120.08	–
E–II$_1$	124.73	137.72	86.92	32.89	108.97	145.71	22.56	120.05	–
F–I$_1$	108.72	147.09	88.38	32.91	108.50	146.51	18.80; 18.29	–	110.94
F–II$_1$	108.80	147.50	87.50	32.74	108.43	146.51	22.46	–	110.92
G–I$_2$	85.54	41.82	91.19	54.86	–	148.28	18.66; 18.45; 18.39; 18.11	–	–
G–II$_2$	84.98	39.67	89.93	55.25	–	148.44	21.96 (11); 22.58 (16)	–	–

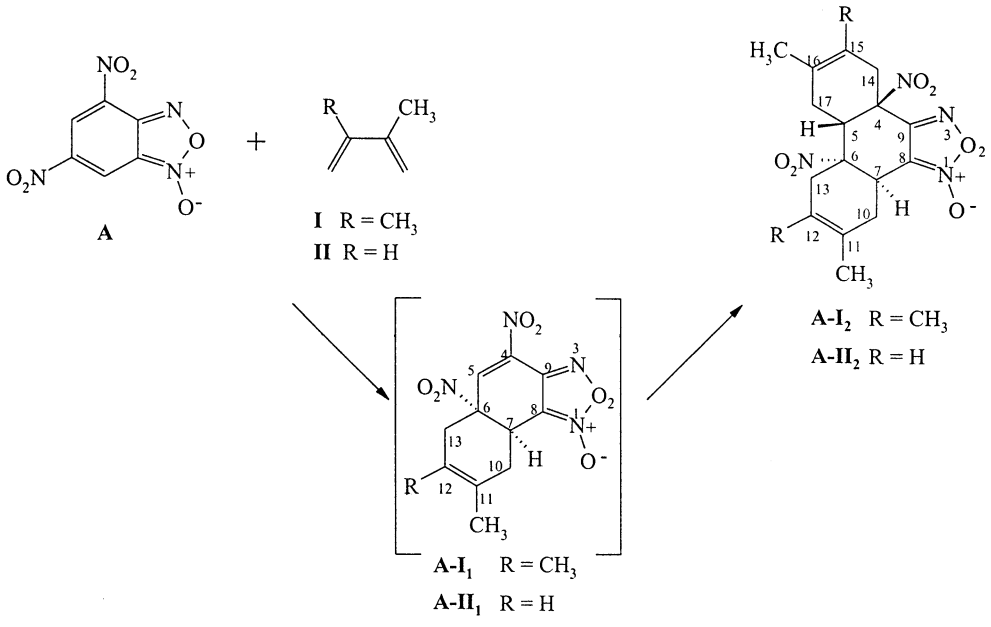
Information on the reaction sequences leading to **A–I$_2$** and **A–II$_2$** was obtained by recording a series of ^1H and ^{13}C spectra within a few hours after mixing equimolar amounts of DNBF and 2,3-dimethylbutadiene or isoprene. At this stage, the spectra showed the partial disappearance of the signals due to the starting materials and the concomitant appearance of a new set of resonances indicating the formation of a new product. The evidence is that this product can be formulated as the monoadduct **A–I$_1$** (or **A–II$_1$**) (in its racemic form), resulting from a regioselective NEDDA process involving the C_6C_7 double bond of the DNBF as the dienophile contributor (Eq. (2)).

The regioselectivity of the addition was demonstrated through ^{15}N labeling of the 4-NO_2 group of DNBF. In this instance, the only low-field proton observed in the ^1H spectra of **A–I$_1$** (and **A–II$_1$**) is coupled with the ^{15}N atom ($^3J_{N4H5}$=3 Hz), confirming that this proton is H_5. In contrast, the *cis* configuration of **A–I$_1$** (and **A–II$_1$**) could not be unambiguously confirmed from the collected NMR data. However it is clear that structure **A–I$_1$** (and **A–II$_1$**) with the 6-NO_2 group and H_7 being on the same side of the two rings is the only one which can be viewed as a precursor of the diadduct **A–I$_2$** (and **A–II$_2$**). Interestingly a X-ray structure has recently shown that such a configuration characterizes the *endo*-monoadduct **A–III** resulting from the reaction of DNBF with cyclohexadiene.[15]



A-III

Structure **A–II$_1$** is also related to that of the *endo* adduct **4** formed in the reaction of DNBF with 1-trimethylsilyloxybuta-1,3-diene (Eq. (1)).[14] The most significant ^1H and ^{13}C NMR parameters for **A–I$_1$**, **A–I$_2$**, **A–II$_1$** and **A–II$_2$** are given in Tables 1 and 2.



A **I** R = CH_3; **II** R = H

A-I$_1$ R = CH_3; **A-II$_1$** R = H

A-I$_2$ R = CH_3; **A-II$_2$** R = H

(2)

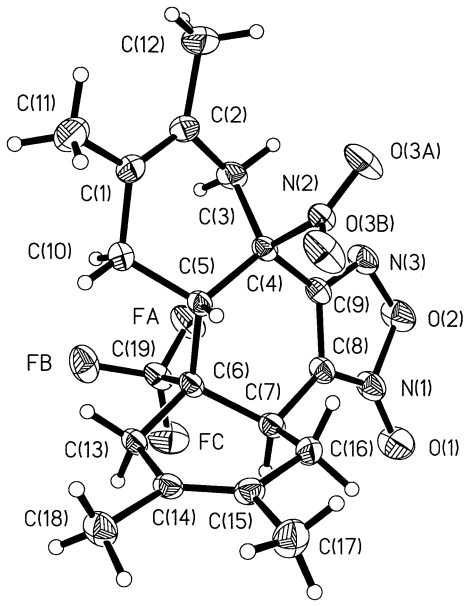
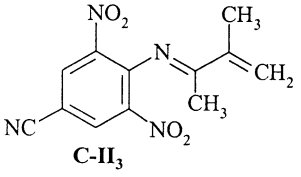


Figure 2. ORTEP view of **B**–$\mathbf{I_2}$.

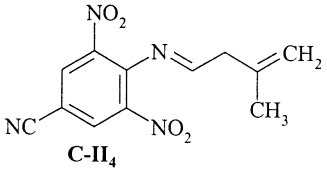
2.2. The reactivity of 4-nitro-6-X-benzofuroxans (B–D)

Analysis of the ^1H and ^{13}C spectra recorded in $CDCl_3$ solution shows that the products obtained in the reactions of the 6-cyano- and 6-trifluoromethyl-4-nitrobenzofuroxans **B** and **C** with isoprene and 2,3-dimethylbutadiene can be formulated as diadducts resulting from two normal electron demand Diels–Alder condensations at the C_4C_5 and C_6C_7 double bonds. The ORTEP view in Fig. 2 reveals that the diadduct formed in the 2,3-dimethylbutadiene–6-CF_3–4-NO_2 system corresponds in fact to the diastereomer **B**–$\mathbf{I_2}$ in its racemic form.

Thus the two condensations proceed via *trans* additions, as found above for the related DNBF system. On grounds of analogy, the same stereochemistry is assigned to the adducts **C**–$\mathbf{I_2}$ and **C**–$\mathbf{II_2}$. To be noted is that this latter diadduct is formed as a minor compound together with two other products that we could identify as the two 2,6-dinitro-4-cyano aryl imines **C**–$\mathbf{II_3}$ and **C**–$\mathbf{II_4}$, arising from an IEDDA addition of the isoprene molecule to the $N_1C_8C_9N_3$ fragment of the annelated furoxan ring of **C**.[19] The NMR parameters for **B**–$\mathbf{I_2}$, **C**–$\mathbf{I_2}$ and **C**–$\mathbf{II_2}$ are summarized in Tables 1 and 2 (see also Section 4).



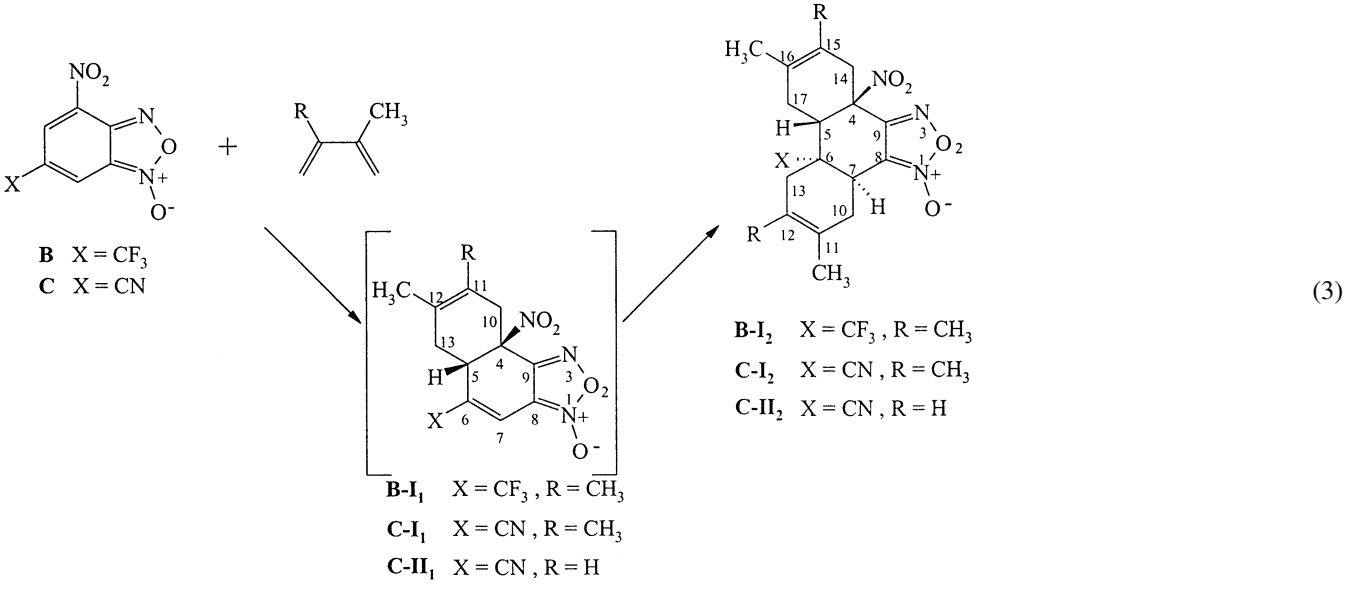
C-II$_3$



C-II$_4$

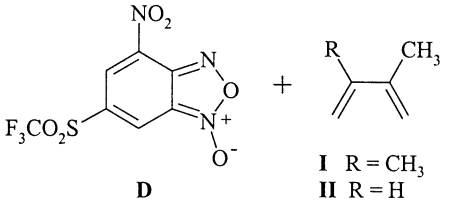
As for the DNBF–isoprene and DNBF–2,3-dimethylbutadiene systems, following in situ in a $CDCl_3$ solution the progress of the reaction of **B** with 2,3-dimethylbutadiene revealed the transient formation of a monoadduct. From the collected NMR data (Tables 1 and 2), there is little doubt that this monoadduct can be identified to **B**–$\mathbf{I_1}$ (in its racemic form) resulting from a regioselective NEDDA process involving the C_4C_5 double bond of the carbocyclic ring of **B** as the dienophile contributor. Consistent with this structural assignment was in particular the finding of a resonance at 86.88 ppm, typical of the nitrosubstituted quaternary sp^3 carbon.[15,18]

In contrast with the situation for **B** and **C**, treatment of 4-nitro-6-trifluoromethanesulfonylbenzofuroxan **D** with isoprene and 2,3-dimethylbutadiene afforded two monoadducts, **D**–$\mathbf{I_1}$ and **D**–$\mathbf{II_1}$ in their racemic form, as the stable products of the reactions (Eq. (4)). As major diagnostic features for the occurrence of monocondensation processes were the presence in the ^1H NMR spectra of a singlet (δ=7.29 ppm for **D**–$\mathbf{I_1}$, δ=7.30 ppm for **D**–$\mathbf{II_1}$) and a pseudotriplet (δ=3.99 ppm for **D**–$\mathbf{I_1}$, δ=4.05 ppm for **D**–$\mathbf{II_1}$) assignable, respectively, to an olefinic-type proton and a proton bonded to a deshielded sp^3 carbon. That the addition of the diene molecule occurred at the C_6C_7 rather than at the C_4C_5 double bond was unambiguously



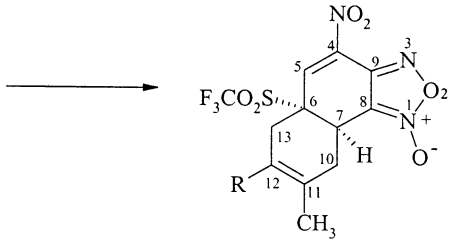
(3)

demonstrated by the following features of the ^{13}C spectra: (1) the absence of a resonance assignable to a nitro-substituted quaternary carbon (δ=90±5 ppm);[18,20] (2) the presence in turn of a resonance at δ=142.96 ppm for **D**–**I$_1$** and δ=143.57 ppm for **D**–**II$_1$** consistent with a sp^2 character of a nitro bearing C_4 carbon in nitrobenzofuroxan structures;[2,3,10,21] (3) the appearance of a resonance at δ=70.82 ppm for **D**–**I$_1$** and δ=69.96 ppm for **D**–**II$_1$**, that is typical of a sp^3 carbon bearing a SO_2CF_3 group.[23] This latter conclusion also agreed with the finding of resonances at δ=−69.94 ppm for **D**–**I$_1$** and δ=−69.96 ppm for **D**–**II$_1$** in the ^{19}F NMR spectra.[23] (Tables 1 and 2).

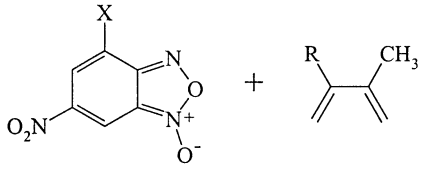


D **I** R = CH_3; **II** R = H

(4)

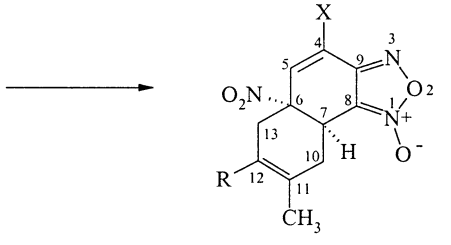


D-I$_1$ R = CH_3
D-II$_1$ R = H



E X = CF_3
F X = CN

(5)



E-I$_1$ X = CF_3, R = CH_3
E-II$_1$ X = CF_3, R = H
F-I$_1$ X = CN, R = CH_3
F-II$_1$ X = CN, R = H

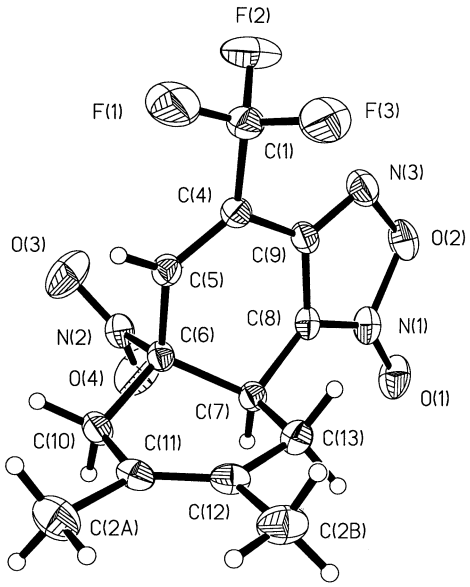


Figure 3. ORTPE view of **E**–**I$_1$**.

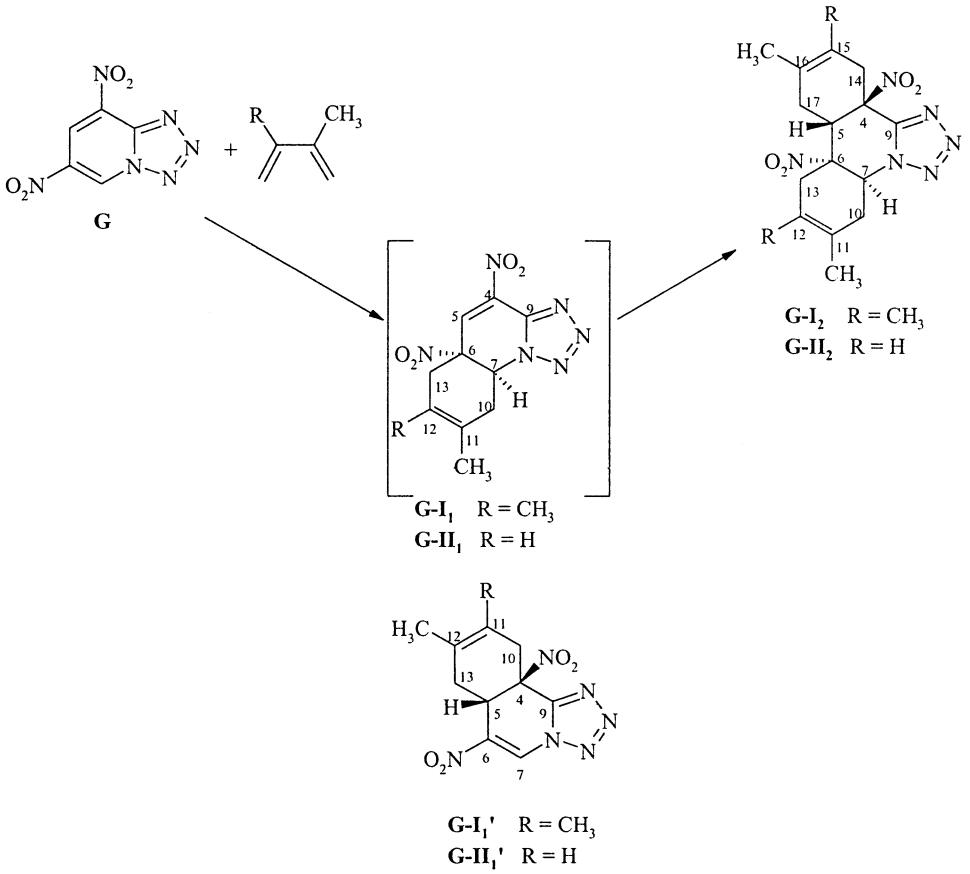
2.3. The reactivity of 4-X-6-nitro-benzofuroxans (E and F)

The ORTEP view in Fig. 3 shows that the single product formed in the reaction of 4-trifluoromethyl-6-nitrobenzofuroxan **E** with 2,3-dimethylbutadiene is the monoadduct **E**–**I$_1$** resulting from a regioselective NEDDA condensation at the C_6C_7 double bond (Eq. (5)). By analogy, the same structure, i.e. **E**–**II$_1$**, is assigned to the related isoprene monoadduct. In fact, structures **E**–**I$_1$** and **E**–**II$_1$** agree well with the NMR information obtained in $CDCl_3$ solution. In particular, the ^1H spectra show a low-field quadruplet (δ=6.87 ppm for **E**–**I$_1$**; δ=6.91 ppm for **E**–**II$_1$**) as expected from the coupling of the strongly deshielded olefinic-type H_5 proton with the fluorine atoms of the CF_3 group ($^4J_{H5F}$=1.3 Hz). Also diagnostic of the addition of the diene molecule at C_6C_7 is the presence in the ^{13}C spectra of a signal (δ=87.82 ppm for **E**–**I$_1$**; δ=86.92 ppm for **E**–**II$_1$**) assignable to the nitro-substituted quaternary sp^3 carbon C_6.[15]

A similar reasoning shows that the monoadducts **F**–**I$_1$** and **F**–**II$_1$** are formed in the reactions involving the 4-cyano-6-nitro- compound **F**. The NMR parameters for **E**–**I$_1$**, **E**–**II$_1$**, **F**–**I$_1$** and **F**–**II$_1$** are summarized in Tables 1 and 2 (see also Section 4).

2.4. The reactivity of 4,6-dinitrotetrazolo[1,5-*a*]pyridine (G)

Each of the reactions of **G** with excess isoprene or 2,3-dimethylbutadiene led, after several days and addition of pentane, to the isolation of a single product. The structural evidence provided by NMR and mass spectrometry data as well as elemental analysis data supports the formation of these products as diadducts resulting from two *trans* NEDDA condensations at the C_4C_5 and C_6C_7 double bonds of **G**. On grounds of analogy with the related DNBF reactions, we suggest that the stereo-



(6)

chemistry shown in **G–I$_2$** and **G–II$_2$** is favored in these systems.

In situ investigations of the isoprene system have allowed us to identify the formation of a small amount of the monoadduct **G–II$_1$** (in its racemic form) in the early stages of the reaction (Eq. (6)). A major diagnostic feature supporting the formation of **G–II$_1$** rather than its regioisomer **G–II$_1$′** was the presence of a rather low-field triplet (δ=5.58 ppm) consistent with a H_7 proton deshielded by the electron withdrawing effect of the polyaza annelated ring (Table 1). As expected, the presence of this triplet goes along with that of a singlet (δ=7.52 ppm) assignable to the H_5 proton of **G–II$_1$**. No detection of the corresponding monoadduct **G–I$_1$** could be made in the 2,3-dimethylbutadiene system.

2.5. Oxidative rearomatization of adducts A–I$_2$, E–I$_1$ and G–I$_2$

In view of the strong activation brought about by the annelated furoxan or tetrazole rings, base-catalyzed elimination of HNO_2 could be envisioned in the afore-described Diels–Alder products.[18,24] Thus, the dinitrobenzofuroxan diadduct **A–I$_2$** and the dinitrotetrazolopyridine diadduct **G–I$_2$** were treated directly with excess *t*-BuOK (3 equiv.) in DMF. After 2 or 3 days at room temperature and addition of water, both systems afforded a pale yellow solid in good yield (73 and 82%, respectively). The ORTEP view in Fig. 4 reveals that the product obtained in the DNBF system is the phenanthrenofurazan **A–I$_3$** (Eq. (7)).

All collected ^{1}H and ^{13}C NMR data as well as mass spectroscopic and elemental analysis data and X-ray crystallographic data agree with structure **A–I$_3$**. Of particular significance is the presence in the ^{13}C spectra of a C_8C_9 pattern characteristic of a furazan moiety (δ_{C8}=149.51; δ_{C9}=148.32).[8,25,26] Although we failed to obtain a X-ray structure of the resulting product, the structural evidence collected in the dinitrotetrazolopyridine system is also consistent with the formation of the completely rearomatized compound **G–I$_3$** (Eq. (8)).

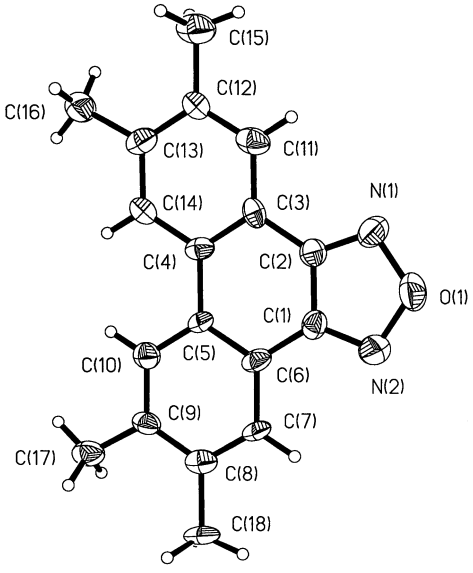
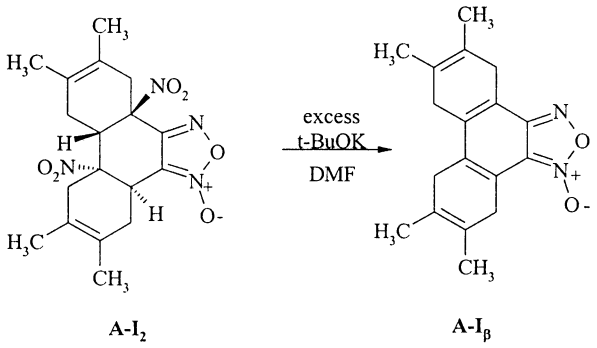
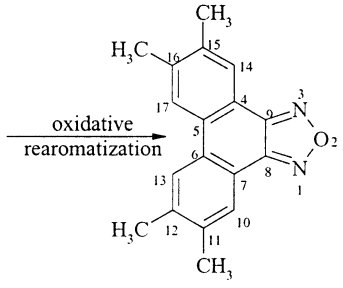


Figure 4. ORTEP view of **A–I$_3$**.

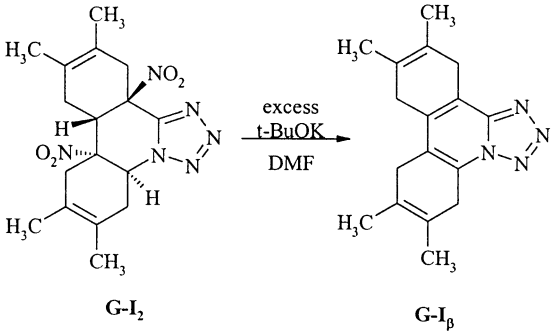


A-I$_2$ **A-I$_\beta$**

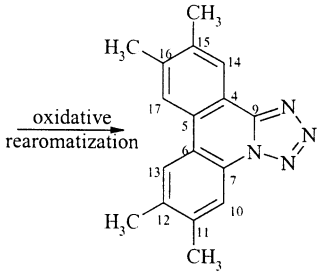


A-I$_3$

(7)



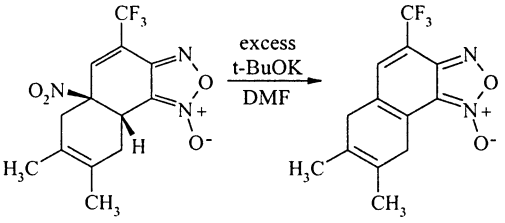
G-I$_2$ **G-I$_\beta$**



G-I$_3$

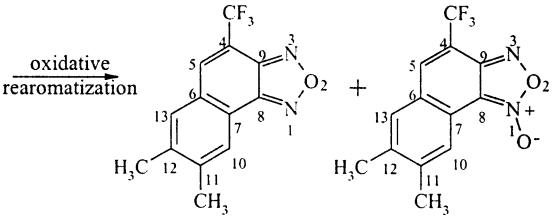
(8)

Contrasting with the two above systems, a similar treatment of the monoadduct **E–I$_1$** with excess *t*-BuOK afforded a mixture of two products in 7:3 ratio. The evidence is that the major species corresponds to the naphthofurazan **E–I$_3$** and the minor species to the naphthofuroxan **E–I$_4$**. In accord with this structural assignment, the ^{1}H spectra of **E–I$_3$** and **E–I$_4$** are very similar, consisting of the signals expected for the three aromatic protons of the carbocyclic rings (δ=8.37, 7.96, 7.68 ppm for **E–I$_3$**; δ=8.38, 7.86, 7.61 ppm for **E–I$_4$**) as well as two resonances at δ=2.5±0.05 ppm supporting the bonding of the methyl groups to aromatic carbons. On



E-I$_1$ **E-I$_\beta$**

(9)



E-I$_3$ **E-I$_4$**

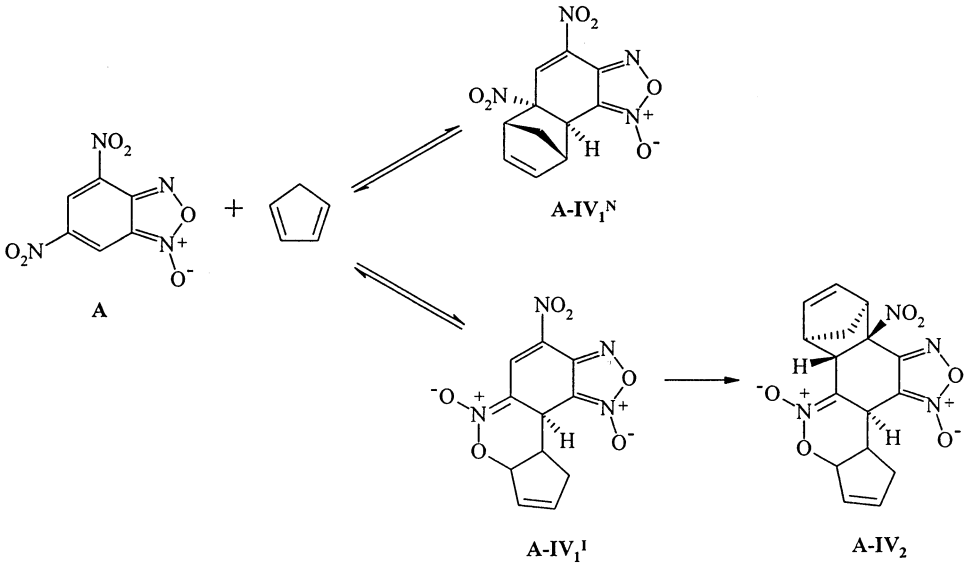
the other hand, the ^{13}C spectra of **E–I$_3$** and **E–I$_4$** are equally very similar with the noteworthy exception of the C_8C_9 pattern which is typical of a furazan ring for **E–I$_3$** (δ_{C8}=148.24; δ_{C9}=144.39) but a furoxan ring for **E–I$_4$** (δ_{C8}=109.81; δ_{C9}=147.54).[8,25,26] Mass spectroscopy and elemental analysis data are also in accord with the proposed structures.

3. Discussion

3.1. NEDDA versus IEDDA condensations

As predicted by theoretical calculations and found in previous studies of the DNBF–1-trimethylsilyloxybuta-1,3-diene (Eq. (1)) and DNBF–cyclopentadiene (Scheme 1) systems, it is the C_6C_7 and not the C_4C_5 double bond of the carbocyclic ring of DNBF which acts as the preferred dienophile contributor for the first addition of isoprene and 2,3-dimethylbutadiene, giving rise to the NEDDA monoadducts **A–II$_1$** and **A–I$_1$**, respectively.[13] Then, a second NEDDA process takes place at the remaining nitroalkene-like C_4C_5 fragment of **A–II$_1$** and **A–I$_1$** to afford the NEDDA–NEDDA diadducts **A–II$_2$** and **A–I$_2$** (Eq. (2)).[27,28] Going from DNBF to the 4,6-dinitrotetrazolopyridine **G** does not change this reactivity pattern with the successive formation of the monoadduct **G–II$_1$** and the diadduct **G–II$_2$** (Eq. (6)).

The NEDDA–NEDDA reactivity sequence of Eq. (2) is a noteworthy feature of the chemistry of DNBF, contrasting in particular with the situation found in the DNBF–cyclopentadiene system.[15] In this instance, the initially formed NEDDA monoadduct **A–IV$_1^N$** disappears rapidly because of a competitive but thermodynamically preferred reaction in which DNBF now acts as a heterodiene through the $O_6N_6C_6C_7$ fragment. Then the resulting IEDDA monoadduct **A–IV$_1^I$** suffers the NEDDA addition of a second molecule of cyclopentadiene at the C_4C_5 double bond to form the 'unsymmetrical' IEDDA–NEDDA diadduct **A–IV$_2$** which is the thermodynamically more stable product of the interaction. On the other hand, we have found that

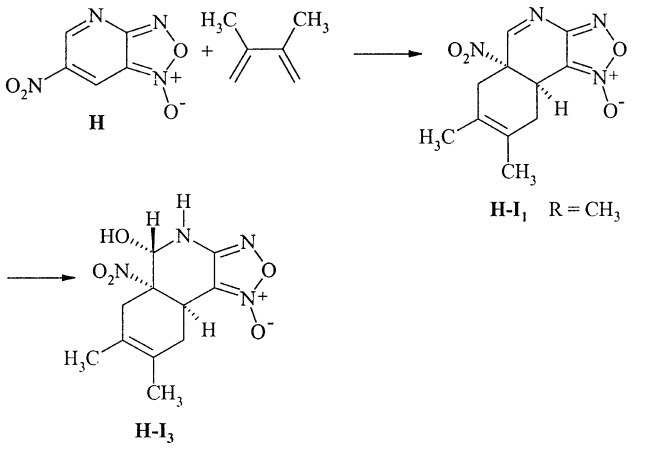


Scheme 1.

IEDDA-type processes are always favored in systems involving vinyl ethyl ether as the electron-rich reagent, e.g. see Eq. (1).[13,14]

3.2. Regioselectivity and stereospecificity

Substituting the 4-NO_2 group of DNBF for a less electron-withdrawing CF_3 or CN group has no effect on the nature and regioselectivity of the monocondensation process. Thus, compounds **E** and **F** give rise to the monoadducts **E**–**I$_1$** (or **E**–**II$_1$**) and **F**–**I$_1$** (or **F**–**II$_1$**), respectively, resulting from the NEDDA addition of the 2,3-dimethylbutadiene (or isoprene) molecule at the nitro-activated C_6C_7 double bond (Eq. (5)). In these systems, however, the activation of the remaining C_4C_5 double bond of the carbocyclic ring appears too low to induce a second addition process. The Diels–Alder behavior of **E** and **F** compares well with that previously observed for the related 4-aza-6-nitrobenzofuroxan **H**.[16] In this instance, the 2,3-dimethylbutadiene monoadduct **H**–**I$_1$** readily formed but it was so sensitive to water addition that only the hydrated structure **H**–**I$_3$** was successfully isolated and characterized by X-ray crystallography (Eq. (10)).[16]



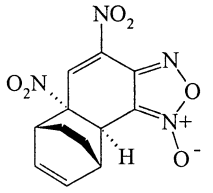
(10)

Replacement of the 6-NO_2 group of DNBF by a CF_3 or CN group results in a complete reversal of the regioselectivity. The dienophilic reactivity of the nitro-activated C_4C_5 double bonds of **B** and **C** is now greater than that of the CF_3- or CN-activated C_6C_7 double bonds. Accordingly, the first formed products are the NEDDA monoadducts **B**–**I$_1$** and **C**–**I$_1$** (or **C**–**II$_1$**). These adducts behave as their DNBF analogues **A**–**I$_1$** (or **A**–**II$_1$**), undergoing addition of a second molecule of the diene reagent to their C_6C_7 double bond to form the isolated diadducts **B**–**I$_2$** and **C**–**I$_2$** (or **C**–**II$_2$**) (Eq. (3)).

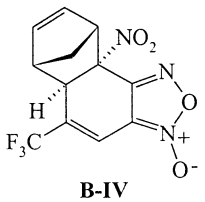
A noteworthy result is the contrasting behavior of 4-nitro-6-trifluoromethanesulfonylbenzo furoxan **D**. This compound gives rise to the NEDDA monoadducts **D**–**I$_1$** and **D**–**II$_1$** that result from the addition of 2,3-dimethylbutadiene or isoprene to the SO_2CF_3-activated C_6C_7 double bond and not to the nitro-activated C_4C_5 double bond. This finding implies that the SO_2CF_3 group behaves here as a powerful activating substituent. This agrees, however, with previous observations made by different authors that the electron-withdrawing influence of a SO_2CF_3 group may be not only considerably larger than that of a carbonyl, a cyano, a trifluoromethyl or a common sulfonyl (SO_2CH_3, SO_2Ph) group but also appreciably larger than that of a NO_2 group in many proton transfer or nucleophilic addition or substitution processes.[22,23,29]

As observed in the few previously studied nitrobenzofuroxan systems, it is a remarkable result that the reactions of **A**–**G** with isoprene and 2,3-dimethylbutadiene all occur with high stereospecificity. Whether the first Diels–Alder condensation takes place at the C_6C_7 or at the C_4C_5 double bond, the accumulated evidence, notably that provided by the three X-ray structures determined in this work, is that the resulting NEDDA adducts have a *cis* junction between the two carbocyclic rings with the hydrogen and the NO_2 (or SO_2CF_3) group being on the same side. While such a diastereospecificity was to be expected in the pericyclic processes at hand, we note that it was also firmly established by X-ray crystallography in the formation of the related

DNBF–cyclohexadiene and 4-nitro-6-CF_3–cyclopentadiene adducts **A–III** and **B–IV**.[15]



A-III



B-IV

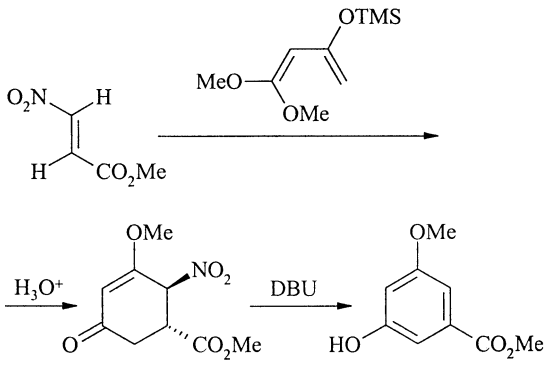
Wherever observed, the addition of a second molecule of diene takes place with a high stereospecificity. The X-ray structures of the diadducts **A–II$_2$** and **B–I$_2$** show conclusively that the two Diels–Alder condensations involved in the overall interactions of Eqs. (2) and (3) proceed via consecutive *trans* additions. By analogy, it is reasonable to assume a similar *trans* arrangement of the two junctions in the other diadducts identified in this work.

3.3. Rearomatization of the adducts

The rearomatization of the carbocyclic rings of the diadducts **A–I$_2$** and **G–I$_2$** and the monoadduct **E–I$_1$** upon treatment of these species with excess *t*-BuOK represents an important transformation which is very promising in terms of access to hitherto difficultly available functionalized heterocycles. Elaborating a possible mechanism for the transformation, it seems reasonable to assume that **A–I$_2$**, **G–I$_2$** and **E–I$_1$** first suffer loss of nitrous acid in base-catalyzed β-elimination reactions.[18,24] Although the NO_2 group is not a very good leaving group in such processes,[30,31] it can readily depart providing that there is a strong activating group in the β-position, a role that the annelated furoxan and tetrazole rings can play in the present system.[18] Also, the *cis* arrangement of the departing H and NO_2 groups, as it is the case in **A–I$_2$**, **G–I$_2$** and **E–I$_1$**, may be a favorable factor since a *syn* stereochemistry is often preferred in eliminations of HNO_2.[32] Going from the resulting compounds **A–I$_\beta$**, **G–I$_\beta$** and **E–I$_\beta$** to the completely rearomatized furazan, furoxan and tetrazole products **G–I$_3$**, and **E–I$_3$** and **E–I$_4$** will then be the result of oxidative processes.

In this regard, the fact that the *N*-oxide group is lost on rearomatization of the diadduct **A–I$_2$** to give **A–I$_3$** and partially lost on rearomatization of the monoadduct **E–I$_1$** to give **E–I$_3$** and **E–I$_4$** suggests that this functionality may act at some stage as an oxidizing agent in the overall process. Despite the absence of a *N*-oxide group, the rearomatization of the tetrazolo diadduct **G–I$_2$** proceeds, however, with a very good yield under the same conditions as those used for the other systems. This implies that other oxidative routes must contribute to the rearomatization. Clearly, further studies are needed to better control and understand the redox processes involved in the transformations.

At present, it is worth noting that the rearomatization of an adduct is somewhat reminiscent of previous work by Danishefsky et al. who reported that a number of Diels–Alder cycloadducts arising from the reactions of *trans*-methyl β-nitroacrylate with various dienes undergo a facile rearomatization in the presence of DBU in THF, as illustrated in Eq. (11).[32]



(11)

4. Experimental

4.1. General

Melting points were determined on a Reichert-type microscope and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported in ppm (*J* values in Hertz) relative to internal Me_4Si. Electronic Impact mass spectra (EI, 70 eV) were obtained using a HEWLETT PACKARD 5989B and a NERMAG R10-10C spectrometer equipped with a quadrupole. Elemental analyses were determined by the Microanalytical laboratory of the University Paris VI, France. IR spectra were recorded on a NICOLET 400D spectrometer. The crystal structures (Figs. 1–4) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-172123 to CCDC-172126.

4.2. Materials

Commercial 2,3-dimethylbutadiene and isoprene were used without further purification.

4.3. Preparation of A–G

A[2–5,10,33] was prepared according to the procedure reported by Drost (mp: 173°C).

Compounds **B** (mp: 126–127°C), **C** (mp: 169–170°C), **D** (mp: 171°C), **E** (mp: 115°C), **F** (mp: 139°C), were prepared from thermal decomposition of the corresponding substituted phenyl azides in toluene.[34]

G was prepared according to the procedure reported by Lowe-Ma (mp: 125°C).[8,35]

4.4. Preparation of the Diels–Alder adducts, general procedure

To a solution of **A–G** (1 g) in CH_2Cl_2 (10 ml) at room temperature was added an excess (10 equiv.) of 2,3-dimethylbutadiene or isoprene. The solution turned rapidly to orange and the reaction mixture was stirred at room temperature for a few days. Addition of pentane resulted

in the immediate formation of a precipitate which was collected by filtration and dried under vacuum and then purified by column chromatography, using pentane–ethylacetate mixtures as eluents.

4.4.1. Compound A–I_1. (Transient species): ^{1}H NMR data (δ ppm, J Hz): 7.54 (H_5, d, $^3J_{5/N4}$=3.0 Hz), 4.15 (H_7, t, $^3J_{7/10}$=7.2 Hz), 2.66 (H_{10a}, dd, $^2J_{10a/10b}$=17.7 Hz, $^3J_{10a/7}$= v7.2 Hz), 2.28 (H_{10b}, dd, $^2J_{10a/10b}$=17.7 Hz, $^3J_{10b/7}$= 7.2 Hz), 3.09 (H_{13a}, d, $^2J_{13a/13b}$=17.4 Hz), 2.71 (H_{13b}, d, $^2J_{13a/13b}$=17.4 Hz), 1.75 (CH_3, s), 1.70 (CH_3, s). ^{13}C NMR data (δ ppm): 141.06 (C_4), 137.29 (C_5), 88.25 (C_6), 33.17 (C_7), 109.88 (C_8), 143.39 (C_9), 30.59 (C_{10}), 126.20 (C_{11}), 121.60 (C_{12}), 40.10 (C_{13}), 18.33 ($CH_{3\ 11}$), 18.84 ($CH_{3\ 12}$).

4.4.2. Compound A–I_2. Yellow solid; yield 89%; mp: 149°C; MS: (CI) 408 $(M+NH_4)^+$, 361 $(M+H-C_2H_6)^+$, 346 $(M+H-C_3H_9)^+$. IR ($CHCl_3$, cm^{-1}): 2914, 2864 (ν_{C-H}), 2435, 2402 ($\nu_{C=N-O}$), 1632 ($\nu_{C=C}$), 1566, 1553 ($\nu_{NO2\ as}$), 1486, 1463, 1449 ($\delta_{CH2,CH3}$), 1357, 1333 ($\nu_{NO2\ s}$), 1133, 1101 ($\nu_{C-C\ ring}$), 876 (ν_{CNO2}). Anal. Calcd for $C_{18}H_{22}N_4O_6$: C, 55.38%; H, 5.68%; N, 14.35%; found: C, 55.32%; H, 5.68%; N, 14.53%. ^{1}H NMR data (δ ppm, J Hz): 3.78 (H_5, dd, $^3J_{5/17a,b}$=8.5 Hz, $^3J_{5/7}$=1.1 Hz), 4.19 (H_7, dd, $^3J_{7/10}$=7.7 Hz, $^3J_{7/5}$=1.1 Hz), 2.73 (H_{10a}, dd, $^2J_{10a/10b}$= 16.5 Hz, $^3J_{10a/7}$=7.7 Hz), 2.34 (H_{10b}, dd, $^2J_{10a/10b}$=16.5 Hz, $^3J_{10b/7}$=7.7 Hz), 2.78 (H_{13a}, d, $^2J_{13a/13b}$=15.6 Hz), 2.27 (H_{13b}, d, $^2J_{13a/13b}$=15.6 Hz), 3.14 ($H_{14a,b}$, s), 2.08 (H_{17a}, dd, $^2J_{17a/17b}$=17.4 Hz, $^3J_{17a,b/5}$=8.5 Hz), 1.85 (H_{17b}, dd, $^2J_{17a/17b}$=17.4 Hz, $^3J_{17a,b/5}$=8.5 Hz), 1.67 (CH_3, s), 1.65 (CH_3, s), 1.60 (CH_3, s), 1.56 (CH_3, s). ^{13}C NMR data (δ ppm): 86.80 (C_4), 43.49 (C_5), 93.95 (C_6), 30.37 (C_7), 112.40 (C_8), 149.50 (C_9), 29.38 (C_{10}), 126.24 (C_{11}), 123.22 (C_{12}), 37.96 (C_{13}), 38.87 (C_{14}), 121.98 (C_{15}), 123.22 (C_{16}), 30.54 (C_{17}), 18.59 ($CH_{3\ 12}$), 18.27 ($2CH_{3\ 11,16}$), 18.12 ($CH_{3\ 15}$).

4.4.3. Compound A–II_1. (Transient species): MS (EI): 248 $(M-HNO_2)^{+\cdot}$. ^{1}H NMR data (δ ppm, J Hz): 7.57 (H_5, t, $^3J_{5/N4}$=3.0 Hz), 4.22 (H_7, t, $^3J_{7/10}$=7.2 Hz), 2.67 (H_{10a}, dd, $^2J_{10a/10b}$=19.0 Hz, $^3J_{10a/7}$=7.2 Hz), 2.32 (H_{10b}, dd, $^2J_{10a/10b}$=19.0 Hz, $^3J_{10b/7}$=7.2 Hz), 5.49 (H_{12}, s), 3.14 (H_{13a}, d, $^2J_{13a/13b}$=19.0 Hz), 2.81 (H_{13b}, d, $^2J_{13a/13b}$= 19.0 Hz), 1.76 ($CH_{3\ 11}$, s). ^{13}C NMR data (δ ppm): 143.13 (C_4), 137.64 (C_5), 87.32 (C_6), 33.08 (C_7), 109.72 (C_8), 143.50 (C_9), 29.06 (C_{10}), 134.39 (C_{11}), 115.50 (C_{12}), 34.64 (C_{13}), 22.56 ($CH_{3\ 11}$).

4.4.4. Compound A–II_2. White solid; yield 95%; mp: 114–116°C; MS: (EI) 315 $(M-HNO_2)^{+\cdot}$, 285 $(M-HNO_2-2CH_3)^{+\cdot}$, 270 $(M-2NO_2)^{+\cdot}$, 269 $(M-HNO_2-NO_2)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2981, 2920 (ν_{C-H}), 2360 ($\nu_{C=N-O}$), 1632 ($\nu_{C=C}$), 1571 ($\nu_{NO2\ as}$), 1495, 1469, 1449 ($\delta_{C-H\ ring}$), 1388, 1362, 1327 ($\nu_{NO2\ s}$), 1031 ($\nu_{C-C\ ring}$), 863 (ν_{CNO2}). Anal. Calcd for $C_{16}H_{18}N_4O_6$: C, 53.04%; H, 4.97%; N, 15.47%; found: C, 53.05%; H, 4.94%; N, 15.41%.

Crystallographic data: $C_{16}H_{18}N_4O_4$, FW=362.34 g mol^{-1}, monoclinic, $P2_1/c$, a=10.9902 Å, b=9.2632 Å, c= 16.3690 Å, β=100.7730°, V=1637.1 Å^3, D_c=1.470 mg cm^{-3}, Z=4.

^{1}H NMR data (δ ppm, J Hz): 3.90 (H_5, t, $^3J_{5/17a,b}$=8.2 Hz), 4.19 (H_7, t, $^3J_{7/10}$=7.9 Hz), 2.76 (H_{10a}, dd, $^2J_{10a/10b}$=17.7 Hz, $^3J_{10a/7}$=7.9 Hz), 2.45 (H_{10b}, dd, $^2J_{10a/10b}$=17.7 Hz, $^3J_{10b/7}$=7.9 Hz), 5.34 (H_{12}, s), 2.85 (H_{13a}, d, $^2J_{13a/13b}$= 16.6 Hz), 2.41 (H_{13b}, d, $^2J_{13a/13b}$=16.6 Hz), 3.21 ($H_{14a,b}$, s), 5.43 (H_{15}, s), 2.15 (H_{17a}, dd, $^2J_{17a/17b}$=17.9 Hz, $^3J_{17a,b/5}$= 8.2 Hz), 1.93 (H_{17b}, dd, $^2J_{17a/17b}$=17.9 Hz, $^3J_{17a,b/5}$= 8.2 Hz), 1.71 ($CH_{3\ 11}$, s), 1.66 ($CH_{3\ 16}$, s). ^{13}C NMR data (δ ppm): 86.26 (C_4), 42.23 (C_5), 92.56 (C_6), 30.64 (C_7), 112.33 (C_8), 149.65 (C_9), 28.13 (C_{10}), 135.03 (C_{11}), 116.35 (C_{12}), 32.20 (C_{13}), 33.51 (C_{14}), 115.93 (C_{15}), 131.72 (C_{16}), 28.55 (C_{17}), 22.27 ($CH_{3\ 11}$), 22.62 ($CH_{3\ 16}$).

4.4.5. Compound B–I_1. (Transient species): ^{1}H NMR data (δ ppm, J Hz): 3.52 (H_5, t, $^3J_{5/13a,b}$=6.4 Hz), 7.34 (H_7, s), 2.67 (H_{10a}, d, $^2J_{10a/10b}$=17.1 Hz), 2.34 (H_{10b}, d, $^2J_{10a/10b}$= 17.1 Hz), 2.48 (H_{13a}, d, $^2J_{10a/10b}$=16.2 Hz), 2.34 (H_{13b}, d, $^2J_{10a/10b}$=16.2 Hz), 1.73 (CH_3, s), 1.69 (CH_3, s). ^{19}F NMR data (δ ppm): −74.32 (CF_3 group). ^{13}C NMR data (δ ppm): 86.88 (C_4), 29.67 (C_5), 139.25 (C_7), 144.35 (C_9), 35.21 (C_{10}), 29.78 (C_{13}), 18.92 (CH_3), 18.50 (CH_3).

4.4.6. Compound B–I_2. Yellow solid;[†] mp: 131°C; MS: (CI) 431 $(M+NH_4)^+$, 414 $(M+H)^+$, 384 $(M+H-NO)^+$, 368 $(M+H-NO_2)^+$, 367 $(M-NO_2)^+$, 354 $(M+H-N_2O_2)^+$, 353 $(M-N_2O_2)^+$, 352 $(M-HN_2O_2)^+$. IR ($CHCl_3$, cm^{-1}): 2918, 2862 (ν_{C-H}), 2439, 2403 ($\nu_{C=N-O}$), 1639 ($\nu_{C=C}$), 1563 ($\nu_{NO2\ as}$), 1486, 1448 ($\delta_{CH2,CH3}$), 1349 ($\nu_{NO2\ s}$), 1314, 1129 (ν_{CF3}), 1103 ($\nu_{C-C\ ring}$).

Crystallographic data: $C_{19}H_{22}F_3N_3O_4$, FW=413.40 g mol^{-1}, triclinic, P_{-1}, a=7.2206 Å, b=11.1189 Å, c=12.4501 Å, α=98.199°, β=91.932°, γ=107.161°, V=942.25 Å^3, D_c=1.457 g cm^{-3}, Z=2.

^{1}H NMR data (δ ppm, J Hz): 3.71 (H_5, t, $^3J_{5/17a,b}$=7.9 Hz), 3.36 (H_7, dd, $^3J_{7/10a,b}$=9.4, 6.7 Hz), 2.46 (H_{10a}, m), 2.28 (H_{10b}, m), 2.44 (H_{13a}, m), 2.25 (H_{13b}, m), 3.52 (H_{14a}, d, $^2J_{14a/14b}$=16.2 Hz), 2.28 (H_{17a}, H_{17b}, s), 1.72 (CH_3, s), 1.70 (CH_3, s). ^{19}F NMR data (δ ppm): −67.29 (CF_3 group). ^{13}C NMR data (δ ppm): 127.80 (CF_3, q, $^1J_{CF}$=286.3 Hz), 90.12 (C_4), 37.77 (C_5), 47.94 (C_6), 29.64 (C_7), 112.61 (C_8), 152.27 (C_9), 30.89 (C_{10}), 123.29 (C_{11}), 125.91, 123.70 (C_{12}, C_{15}), 33.73 (C_{13}), 38.52 (C_{14}), 121.65 (C_{16}), 28.76 (C_{17}), 18.90 (CH_3), 18.77 (CH_3), 18.42 (CH_3), 18.21 (CH_3). Anal. Calcd for $C_{19}H_{22}F_3N_3O_4$: C, 55.15%; H, 5.32%; N, 10.16%; found: C, 55.45%; H, 5.11%; N, 10.48%.

4.4.7. Compound C–I_2. Green solid; yield 54%; mp: 148°C; MS: (CI) 388 $(M+NH_4)^+$, 371 $(M+H)^+$, 341 $(M+H-NO)^+$, 325 $(M+H-NO_2)^+$, 324 $(M-NO_2)^+$, 310 $(M-N_2O_2)^+$, 309 $(M-HN_2O_2)^+$. IR ($CHCl_3$, cm^{-1}): 2922, 2859 (ν_{C-H}), 2432, 2399 ($\nu_{C=N-O}$), 2234 ($\nu_{C\equiv N}$), 1641, 1632 ($\nu_{C=C}$), 1568 ($\nu_{NO2\ as}$), 1488, 1465, 1453 ($\delta_{CH2,CH3}$), 1382, 1349, 1333 ($\nu_{NO2\ s}$), 1314, 1136, 1101, 1032 ($\nu_{C-C\ ring}$), 863 (ν_{CNO2}). Anal. Calcd for $C_{19}H_{22}N_4O_4$: C, 61.60%; H, 5.98%; N, 15.13%; found: C, 61.38%; H, 6.11%; N, 15.28%. ^{1}H NMR data (δ ppm, J Hz): 3.59 (H_5, t, $^3J_{5/17a,b}$=7.7 Hz), 3.42 (H_7, dd, $^3J_{7/10a,b}$=9.2, 7.2 Hz), 2.57 (H_{10a}, dm, $^2J_{10a/10b}$=17.9 Hz), 2.34 (H_{10b}, dm, $^2J_{10a/10b}$=17.9 Hz), 2.64 (H_{13a}, d, $^2J_{13a/13b}$=17.7 Hz),

[†] Owing to the very low rate of the reaction, several weeks are required to get good yields in this adduct.

2.43 (H_{13b}, d, $^2J_{13a/13b}$=17.7 Hz), 3.52 (H_{14a}, d, $^2J_{14a/14b}$=16.7 Hz), 2.93 (H_{14b}, d, $^2J_{14a/14b}$=16.7 Hz), 2.40 (H_{17a}, dd, $^2J_{17a/17b}$=16.7 Hz, $^3J_{17a,b/5}$=7.7 Hz), 2.22 (H_{17b}, dd, $^2J_{17a/17b}$=16.7 Hz, $^3J_{17a,b/5}$=7.7 Hz), 1.78 ($2CH_3$, s), 1.72 ($2CH_3$, s). ^{13}C NMR data (δ ppm): 120.82 (CN), 88.85 (C_4), 37.31 (C_5), 40.65 (C_6), 33.01 (C_7), 112.20 (C_8), 151.34 (C_9), 30.36 (C_{10}), 123.89 (C_{11}), 120.57 (C_{12}), 36.79 (C_{13}), 38.24 (C_{14}), 124.60, 124.72 (C_{15}, C_{16}), 30.49 (C_{17}), 18.73 (CH_3), 18.69 (CH_3), 18.43 (CH_3), 18.19 (CH_3).

4.4.8. Compound C–II$_2$. The compound was obtained as a minor product together with two arylimines **C–II$_3$** and **C–II$_4$** (see text); MS: (EI) 342 $(M)^{+\cdot}$, 312 $(M-NO)^{+\cdot}$, 296 $(M-NO_2)^{+\cdot}$, 250 $(M-2NO_2)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2920 (ν_{C-H}), 2401 ($\nu_{C\equiv N-O}$), 2243 ($\nu_{C\equiv N}$), 1637 ($\nu_{C=C}$), 1566 ($\nu_{NO2\ as}$), 1490, 1449 ($\delta_{C-H\ ring}$), 1352 ($\nu_{NO2\ s}$), 1154, 1031 ($\nu_{C-C\ ring}$), 914 (ν_{CNO2}). ^{1}H NMR data (δ ppm, J Hz): 3.62 (H_5, t, $^3J_{5/17a,b}$=6.8 Hz), 3.50 (H_7, dd, $^3J_{7/10a,b}$=9.4, 7.2 Hz), 2.58 (H_{10a}, m), 2.34 (H_{10b}, m), 5.41 (H_{12}, s), 2.64 (H_{13a}, m), 2.58 (H_{13b}, m), 3.69 (H_{14a}, d, $^2J_{14a/14b}$=18.7 Hz), 2.96 (H_{14a}, d, $^2J_{14a/14b}$=18.7 Hz), 5.63 (H_{15}, s), 2.43 (H_{17a}, dd, $^2J_{17a/17b}$=17.3 Hz, $^3J_{17a,b/5}$=6.8 Hz), 2.17 (H_{17b}, dd, $^2J_{17a/17b}$=17.3 Hz, $^3J_{17a,b/5}$=6.8 Hz), 1.78 (CH_3, s), 1.77 (CH_3, s). ^{13}C NMR data (δ ppm): 121.00 (CN), 88.12 (C_4), 36.91 (C_5), 39.64 (C_6), 33.21 (C_7), 112.25 (C_8), 151.52 (C_9), 29.34 (C_{10}), 132.82 (C_{11}), 114.92 (C_{12}), 31.31 (C_{13}), 32.35 (C_{14}), 118.02 (C_{15}), 133.06 (C_{16}), 28.57 (C_{17}), 22.92 (CH_3), 22.63 (CH_3).

4.4.9. Compound D–I$_1$. Yellow solid; yield 60%; mp: 140°C; MS: (CI) 413 $(M+NH_4)^+$, 261 $(M-CO_2HSF_3)^+$, 279 $(M-CNO_2HF_3)^+$, 246 $(M-SO_2CF_3-O)^+$. IR ($CHCl_3$, cm^{-1}): 2919, 2863 (ν_{C-H}), 2436, 2405 ($\nu_{C\equiv N-O}$), 1679, 1607 ($\nu_{C=C}$), 1575 ($\nu_{NO2\ as}$), 1446 ($\delta_{CH2,CH3}$), 1381, 1123 ($\nu_{SO2\ as-s}$), 1367 ($\nu_{NO2\ s}$), 857 (ν_{CNO2}). Anal. Calcd for $C_{13}H_{12}F_3N_3O_6S$: C, 39.49%; H, 3.06%; N, 10.63%; found: C, 39.29%; H, 3.12%; N, 10.71%. ^{1}H NMR data (δ ppm, J Hz): 7.29 (H_5, s), 3.99 (H_7, t, $^3J_{7/10a,b}$=7.2 Hz), 2.64 (H_{10a}, dd, $^2J_{10a/10b}$=16.2 Hz, $^3J_{10a/7}$=7.2 Hz), 2.22 (H_{10b}, dd, $^2J_{10a/10b}$=16.2 Hz, $^3J_{10b/7}$=7.2 Hz), 3.14 (H_{13a}, d, $^2J_{13a/13b}$=16.5 Hz), 2.64 (H_{13b}, d, $^2J_{13a/13b}$=16.5 Hz), 1.78 ($CH_{3\ 12}$, s), 1.70 ($CH_{3\ 12}$, s). ^{19}F NMR data (δ ppm): −69.94 (CF_3 group). ^{13}C NMR data (δ ppm): 120.02 (CF_3, q, $^1J_{CF}$=332.3 Hz), 142.96 (C_4), 134.05 (C_5), 70.82 (C_6), 29.62 (C_7), 110.58 (C_8), 143.66 (C_9), 31.75 (C_{10}), 127.93 (C_{11}), 122.27 (C_{12}), 35.27 (C_{13}), 19.06 (CH_3), 18.61 (CH_3).

4.4.10. Compound D–II$_1$. Pale yellow solid; yield 80%; mp: 89°C; MS: (EI) 248 $(M-SO_2CF_3)^{+\cdot}$, 218 $(M-SO_2CF_3-NO)^{+\cdot}$, 202 $(M-SO_2CF_3-NO_2)^{+\cdot}$, 156 $(M-SO_2CF_3-2NO_2)^{+\cdot}$, 141 $(M-SO_2CF_3-2NO_2-2CH_3)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2982, 2946, 2915 (ν_{C-H}), 2401 ($\nu_{C\equiv N-O}$), 1668, 1632 ($\nu_{C=C}$), 1556 ($\nu_{NO2\ as}$), 1469 ($\delta_{C-H\ ring}$), 1352, 1100 ($\nu_{SO2\ as-s}$), 1332 ($\nu_{NO2\ s}$), 856 (ν_{CNO2}). Anal. Calcd for $C_{11}H_{10}F_3N_3O_6S$: C, 35.79%; H, 2.73%; N, 11.39%; found: C, 35.79%; H, 2.75%; N, 11.47%. ^{1}H NMR data (δ ppm, J Hz): 7.30 (H_5, s), 4.05 (H_7, t, $^3J_{7/10a,b}$=7.5 Hz), 2.68 (H_{10a}, m), 2.15 (H_{10b}, m), 5.56 (H_{12}, t, $^3J_{12/13a,b}$=5.3 Hz), 3.17 (H_{13a}, dd, $^2J_{13a/13b}$=16.8 Hz, $^3J_{12/13a,b}$=5.3 Hz), 2.80 (H_{13b}, dd, $^2J_{13a/13b}$=16.8 Hz, $^3J_{12/13a,b}$=5.3 Hz), 1.76 (CH_3, s). ^{19}F NMR data (δ ppm): −69.96 (CF_3 group). ^{13}C NMR data (δ ppm): 119.95 (CF_3, q, $^1J_{CF}$=332.3 Hz), 143.57 (C_4), 134.40 (C_5), 69.96 (C_6), 29.11 (C_7), 110.74 (C_8), 143.74 (C_9), 29.74 (C_{10}), 135.78 (C_{11}), 115.45 (C_{12}), 29.78 (C_{13}), 22.66 (CH_3).

4.4.11. Compound E–I$_1$. Orange solid; yield 63%; mp: 142°C; MS: (CI) 286 $(M+H-NO_2)^+$, 285 $(M-NO_2)^+$, 272 $(M+H-N_2O_2)^+$, 271 $(M-N_2O_2)^+$, 270 $(M-HN_2O_2)^+$. IR ($CHCl_3$, cm^{-1}): 2920, 2861 (ν_{C-H}), 2436, 2403 ($\nu_{C\equiv N-O}$), 1659, 1639, 1632 ($\nu_{C=C}$), 1567, 1556 ($\nu_{NO2\ as}$), 1466, 1448 ($\delta_{CH2,CH3}$), 1360, 1336, 1333 ($\nu_{NO2\ s}$), 1312, 1148 (ν_{CF3}), 1104, 1065 ($\nu_{C-C\ ring}$), 862 (ν_{CNO2}). Anal. Calcd for $C_{13}H_{12}F_3N_3O_4$: C, 47.13%; H, 3.65%; N, 12.69%; found: C, 46.95%; H, 3.75%; N, 12.52%.

Crystallographic data: $C_{13}H_{12}F_3N_3O_4$, FW=331.26 g mol^{-1}, monoclinic, $P2_1/c$, a=8.2563 Å, b=21.8846 Å, c=8.8347 Å, β=116.299°, V=1431.08 Å^3, D_c=1.537 g cm^{-3}, Z=4.

^{1}H NMR data (δ ppm, J Hz): 6.87 (H_5, q, $^3J_{5/F}$=1.3 Hz), 4.14 (H_7, t, $^3J_{7/10a,b}$=7.2 Hz), 2.61 (H_{10a}, dd, $^2J_{10a/10b}$=17.7 Hz, $^3J_{10a/7}$=7.2 Hz), 2.31 (H_{10b}, dd, $^2J_{10b/10a}$=17.7 Hz, $^3J_{10b/7}$=7.2 Hz), 3.02 (H_{13a}, d, $^2J_{13a/13b}$=18.3 Hz), 2.61 (H_{13b}, d, $^2J_{13a/13b}$=18.3 Hz), 1.69 (CH_3, s), 1.72 (CH_3, s). ^{19}F NMR data (δ ppm): −65.92 (CF_3 group). ^{13}C NMR data (δ ppm): 120.08 (CF_3, q, $^1J_{CF}$=274.8 Hz), 124.54 (C_4), 137.34 (C_5), 87.82 (C_6), 33.00 (C_7), 109.12 (C_8), 145.74 (C_9), 30.08 (C_{10}), 125.73 (C_{11}), 121.69 (C_{12}), 40.13 (C_{13}), 18.76 (CH_3), 18.29 (CH_3).

4.4.12. Compound E–II$_1$. Yellow oil; MS: (EI) 317 $(M)^{+\cdot}$, 271 $(M-NO_2)^{+\cdot}$, 249 $(M-NO_2-CF_3)^{+\cdot}$, 225 $(M-2NO_2)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2919, 2861 (ν_{C-H}), 2406 ($\nu_{C\equiv N-O}$), 1662, 1635 ($\nu_{C=C}$), 1571 ($\nu_{NO2\ as}$), 1475 ($\delta_{C-H\ ring}$), 1362 ($\nu_{NO2\ s}$), 1314, 1160 (ν_{CF3}), 1068 ($\nu_{C-C\ ring}$), 865 (ν_{CNO2}). Anal. Calcd for $C_{12}H_{10}F_3N_3O_4$: C, 45.43%; H, 3.18%; N, 13.25%; found: C, 45.64%; H, 3.30%; N, 13.12%. ^{1}H NMR data (δ ppm, J Hz): 6.91 (H_5, q, $^3J_{5/F}$=1.3 Hz), 4.14 (H_7, t, $^3J_{7/10a,b}$=7.2 Hz), 2.61 (H_{10a}, dd, $^2J_{10a/10b}$=18.0 Hz, $^3J_{10a/7}$=7.2 Hz), 2.35 (H_{10b}, dd, $^2J_{10b/10a}$=18.0 Hz, $^3J_{10b/7}$=7.2 Hz), 5.45 (H_{12}, s), 3.08 (H_{13a}, d, $^2J_{13a/13b}$=17.7 Hz), 2.71 (H_{13b}, d, $^2J_{13a/13b}$=17.7 Hz), 1.75 (CH_3, s). ^{19}F NMR data (δ ppm): −66.03 (CF_3 group). ^{13}C NMR data (δ ppm): 120.05 (CF_3, q, $^1J_{CF}$=274.1 Hz), 124.73 (C_4), 137.72 (C_5), 86.92 (C_6), 32.89 (C_7), 108.97 (C_8), 145.71 (C_9), 28.55 (C_{10}), 133.92 (C_{11}), 115.68 (C_{12}), 34.64 (C_{13}), 22.56 (CH_3).

4.4.13. Compound F–I$_1$. White solid; yield 27%; mp: 116°C; MS: (CI) 262 $(M-CN)^+$, 243 $(M+H-NO_2)^+$, 242 $(M-NO_2)^+$, 229 $(M+H-N_2O_2)^+$. IR ($CHCl_3$, cm^{-1}): 2925, 2864 (ν_{C-H}), 2442, 2399 ($\nu_{C\equiv N-O}$), 2243 ($\nu_{C\equiv N}$), 1659, 1643, 1610 ($\nu_{C=C}$), 1566 ($\nu_{NO2\ as}$), 1486, 1471, 1450 ($\delta_{CH2,CH3}$), 1356, 1332 ($\nu_{NO2\ s}$), 1140, 1100 ($\nu_{C-C\ ring}$), 858 (ν_{CNO2}). Anal. Calcd for $C_{13}H_{12}N_4O_4$: C, 54.16%; H, 4.19%; N, 19.44%; found: C, 54.11%; H, 4.29%; N, 19.28%. ^{1}H NMR data (δ ppm, J Hz): 7.03 (H_5, s), 4.15 (H_7, t, $^3J_{7/10a,b}$=7.2 Hz), 2.63 (H_{10a}, dd, $^2J_{10a/10b}$=17.4 Hz, $^3J_{10a/7}$=7.2 Hz), 2.25 (H_{10b}, dd, $^2J_{10b/10a}$=17.4 Hz, $^3J_{10b/7}$=7.2 Hz), 3.02 (H_{13a}, d, $^2J_{13a/13b}$=17.7 Hz), 2.63 (H_{13b}, d, $^2J_{13a/13b}$=17.7 Hz), 1.69 (CH_3, s), 1.73 (CH_3, s). ^{13}C NMR data (δ ppm): 110.94 (CN), 108.72 (C_4), 147.09 (C_5), 88.38 (C_6),

32.91 (C_7), 108.50 (C_8), 146.51 (C_9), 30.58 (C_{10}), 126.09 (C_{11}), 121.60 (C_{12}), 40.08 (C_{13}), 18.80 (CH_3), 18.29 (CH_3).

4.4.14. Compound F–II$_1$. Yellow oil; yield 80%; MS: (CI) 270, 258, 230, 212, 190, 162, 81, 68, 55. Anal. Calcd for $C_{12}H_{10}N_4O_4$: C, 52.55%; H, 3.67%; N, 20.43%; found: C, 52.55%; H, 3.66%; N, 20.67%. ^{1}H NMR data (δ ppm, J Hz): 7.08 (H_5, s), 4.21 (H_7, t, $^3J_{7/10a,b}$=6.4 Hz), 2.70 (H_{10a}, dd, $^2J_{10a/10b}$=17.9 Hz, $^3J_{10a/7}$=6.4 Hz), 2.26 (H_{10b}, dd, $^2J_{10b/10a}$=17.9 Hz, $^3J_{10b/7}$=6.4 Hz), 5.46 (H_{12}, s), 3.06 (H_{13a}, d, $^2J_{13a/13b}$=16.0 Hz), 2.70 (H_{13b}, d, $^2J_{13a/13b}$=16.0 Hz), 1.74 (CH_3, s). ^{13}C NMR data (δ ppm): 110.92 (CN), 108.80 (C_4), 147.50 (C_5), 87.50 (C_6), 32.74 (C_7), 108.43 (C_8), 146.51 (C_9), 29.08 (C_{10}), 134.22 (C_{11}), 115.44 (C_{12}), 34.55 (C_{13}), 22.46 (CH_3).

4.4.15. Compound G–I$_2$. Pale yellow solid; yield 68%; mp: 108°C; MS: (EI) 374 $(M)^{+\cdot}$, 327 $(M-HNO_2)^{+\cdot}$, 299 $(M-HNO_2-N_2)^{+\cdot}$, 282 $(M-HNO_2-3CH_3)^{+\cdot}$, 252 $(M-2HNO_2-N_2)^{+\cdot}$, 237 $(M-2HNO_2-N_2-CH_3)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2920, 2858 (ν_{C-H}), 1601 ($\nu_{C=C}$), 1566 ($\nu_{NO2\ as}$), 1448 ($\nu_{N=N\ ring}$), 1403 ($\delta_{C-H\ ring}$), 1347 ($\nu_{NO2\ s}$), 1118 ($\nu_{C-C\ ring}$).

To be noted is that various attempts to obtain satisfactory elemental analysis have failed, presumably because of some high tendency of such aza compounds to hydration.[16]

^{1}H NMR data (δ ppm, J Hz): 3.90 (H_5, dd, $^3J_{5/17a,b}$=8.2, 6.9 Hz), 5.48 (H_7, t, $^3J_{7/10}$=6.7 Hz), 3.13 (H_{10a}, dd, $^2J_{10a/10b}$=17.3 Hz, $^3J_{10a/7}$=6.7 Hz), 2.80 (H_{10b}, dd, $^2J_{10a/10b}$=17.3 Hz, $^3J_{10b/7}$=6.7 Hz), 2.91 (H_{13a}, d, $^2J_{13a/13b}$=17.0 Hz), 2.50 (H_{13b}, d, $^2J_{13a/13b}$=17.0 Hz), 3.34 (H_{14a}, d, $^2J_{14a/14b}$=16.5 Hz), 3.00 (H_{14b}, d, $^2J_{14b/14a}$=16.5 Hz), 2.29 (H_{17a}, dm, $^2J_{17a/17b}$=17.3 Hz), 2.02 (H_{17b}, dm, $^2J_{17a/17b}$=17.3 Hz), 1.69 (CH_3, s), 1.66 (CH_3, s), 1.65 (CH_3, s), 1.61 (CH_3, s). ^{13}C NMR data (δ ppm): 85.54 (C_4), 41.82 (C_5), 91.19 (C_6), 54.86 (C_7), 148.28 (C_9), 35.33 (C_{10}), 124.20, 124.07, 123.23, 122.37 (C_{11}, C_{12}, C_{15}, C_{16}), 37.40 (C_{13}), 39.69 (C_{14}), 29.58 (C_{17}), 18.66 (CH_3), 18.45 (CH_3), 18.39 (CH_3), 18.11 (CH_3).

4.4.16. Compound G–II$_2$. Pale yellow solid; yield 46%; mp: 186–188°C; MS: (EI) 300 $(M-NO_2)^{+\cdot}$, 254 $(M-2NO_2)^{+\cdot}$. IR ($CHCl_3$, cm^{-1}): 2986, 2946, 2920, 2859 (ν_{C-H}), 1576 ($\nu_{NO2\ as}$), 1448 ($\nu_{N=N\ ring}$), 1326 ($\delta_{C-H\ ring}$), 1362 ($\nu_{NO2\ s}$), 1107, 1051 ($\nu_{C-C\ ring}$).

As for the analogous diadduct **G–I$_2$** attempts to obtain satisfactory elemental analysis have failed.[16]

^{1}H NMR data (δ ppm, J Hz): 3.98 (H_5, dd, $^3J_{5/17a,b}$=8.5, 6.2 Hz), 5.58 (H_7, t, $^3J_{7/10}$=7.1 Hz), 3.12 (H_{10a}, dd, $^2J_{10a/10b}$=17.9 Hz, $^3J_{10a/7}$=7.1 Hz), 2.84 (H_{10b}, dd, $^2J_{10a/10b}$=17.9 Hz, $^3J_{10b/7}$=7.1 Hz), 5.36 (H_{12}, s), 2.84 (H_{13a}, H_{13b}, s), 3.44 (H_{14a}, d, $^2J_{14a/14b}$=17.2 Hz), 2.84 (H_{14b}, d, $^2J_{14b/14a}$=17.2 Hz), 2.32 (H_{17a}, dm, $^2J_{17a/17b}$=17.6 Hz), 2.18 (H_{17b}, dm, $^2J_{17a/17b}$=17.6 Hz), 1.72 (CH_3, s), 1.66 (CH_3, s). ^{13}C NMR data (δ ppm): 84.98 (C_4), 39.67 (C_5), 89.93 (C_6), 55.25 (C_7), 148.44 (C_9), 34.88 (C_{10}), 132.45 (C_{11}), 115.78 (C_{12}), 31.93 (C_{13}), 34.55 (C_{14}), 116.12 (C_{15}), 132.64 (C_{16}), 27.05 (C_{17}), 21.96 ($CH_{3\ 11}$), 22.58 ($CH_{3\ 16}$).

4.5. Oxidative rearomatization, general procedure

To a solution of the cycloadducts **A–I$_2$**, **E–I$_1$** and **G–I$_2$** in DMF (5 ml) were added 3 equiv. of potassium tertiobutoxide at room temperature. The solution turned immediately to dark brown and the reaction mixture was stirred at room temperature for 2 days. Addition of water resulted in the immediate formation of a precipitate, which was collected by filtration.

In the case of the **A–I$_2$** and **G–I$_2$** systems, only one product was obtained which was purified by chromatography to afford pure samples of the phenanthrenofurazan **A–I$_3$** and the tetrazole analogue **G–I$_3$**. In the case of the **E–I$_1$** system, two products, both the naphthofurazan **E–I$_3$** and the naphthofuroxan **E–I$_4$**, were obtained which were separated by column chromatography (eluent: **E–I$_3$**: 6% dichloromethane/94% pentane; **E–I$_4$**: 8% dichloromethane: 92% pentane).

4.5.1. Compound A–I$_3$. Yellow solid; yield 80%; mp: 235°C; MS (EI): 276 $(M)^{+\cdot}$, 261 $(M-CH_3)^{+\cdot}$, 246 $(M-2CH_3)^{+\cdot}$, 231 $(M-3CH_3)^{+\cdot}$, 216 $(M-4CH_3)^{+\cdot}$. Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24%; H, 5.84%; N, 10.13%; found: C, 78.24%; H, 6.08%; N, 9.88%.

Crystallographic data: $C_{18}H_{16}N_2O$, FW=276.33 g mol^{-1}, triclinic, P_{-1}, a=8.7431 Å, b=9.4247 Å, c=10.0659 Å, α=75.862°, β=64.870°, γ=75.131°, V=717.06 Å^3, D_c=1.280 g cm^{-3}, Z=2.

^{1}H NMR: 8.19 (s, 1H), 8.01 (s, 1H), 7.88 (s, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H); ^{13}C NMR: 150.80 (C_8, C_9), 140.76, 139.58, 137.69 (C_{11}, C_{12}, C_{15}, C_{16}), 130.00, 128.45, 118.41, 115.40 (C_4, C_5, C_6, C_7), 124.28, 124.19, 124.06 (2C) (C_{10}, C_{13}, C_{14}, C_{17}), 20.62, 20.57, 19.71, 19.68 ($4CH_3$).

4.5.2. Compound E–I$_3$. White solid; yield 70%; mp: 138°C; m/z (EI): 266 $(M)^{+\cdot}$, 251 $(M-CH_3)^{+\cdot}$, 236 $(M-2CH_3)^{+\cdot}$, 197 $(M-CF_3)^{+\cdot}$. Anal. Calcd for $C_{13}H_9N_2OF_3$: C, 58.65%; H, 3.41%; N, 10.52%; found: C, 58.39%; H, 3.56%; N, 10.32%. ^{1}H NMR: 7.96 (s, 1H, H_5), 8.37 (s, 1H), 7.68 (s, 1H), 2.53 (s, 3H), 2.49 (s, 3H); ^{13}C NMR: 122.22 (q, $^1J_{C-F}$=271.3 Hz, CF_3), 115.36 (C_4), 133.96 (q, C_5, $^3J_{C5-F}$=5.1 Hz), 128.99, 120.03 (C_6, C_7), 141.77, 141.20 (C_{11}, C_{12}), 148.24 (C_8), 144.39 (C_9), 131.13 (C_{10}, C_{13}), 20.31, 20.21 ($2CH_3$).

4.5.3. Compound E–I$_4$. Pale yellow solid; yield 30%; mp: 130°C; m/z (EI): 282 $(M)^{+\cdot}$, 267 $(M-CH_3)^{+\cdot}$, 222 $(M-2NO)^{+\cdot}$. Anal. Calcd for $C_{13}H_9N_2O_2F_3$: C, 55.32%; H, 3.21%; N, 9.93%; found: C, 55.20%; H, 3.32%; N, 10.12%. ^{1}H NMR: 8.38 (s, 1H), 7.86 (s, 1H, H_5), 7.61 (s, 1H); ^{13}C NMR: 121.93 (CF_3, q, $^1J_{C-F}$=275.80 Hz), 116.12 (C_4), 134.57 (q, C_5, $^3J_{C-F}$=5.1 Hz), 127.40, 117.74 (C_6, C_7), 109.81 (C_8), 147.54 (C_9), 131.10, 123.76 (C_{10}, C_{13}), 142.58, 140.62 (C_{11}, C_{12}), 20.38, 20.19 ($2CH_3$).

4.5.4. Compound G–I$_3$. White solid; yield 55%; mp: 208°C; MS (EI) 276 $(M)^{+\cdot}$, 248 $(M-N_2)^{+\cdot}$, 233 $(M-N_2-CH_3)^{+\cdot}$. ^{1}H NMR: 8.40 (s, 1H), 8.31 (s, 1H), 8.08 (s, 2H); ^{13}C NMR: 146.68 (C_9, 1C), 137.06–141.34

(C_{11}, C_{12}, C_{15}, C_{16}), 117.40, 122.93, 123.62, 125.81 (C_{10}, C_{13}, C_{14}, C_{17}), 19.79–20.68 ($4CH_3$). Anal. Calcd for $C_{17}H_{16}N_4$: C, 73.88 %; H, 5.84 %; N, 20.28%; found: C, 73.67%.

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