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A criterion to demarcate the dual Diels–Alder and σ-complex behaviour of aromatic and heteroaromatic superelectrophiles

R. Goumont,[a,*] F. Terrier,[a,*] D. Vichard,[a] S. Lakhdar,[a] Julian M. Dust[b] and E. Buncel[c,*]

[a]*Laboratoire SIRCOB, Institut Lavoisier-Franklin, UMR CNRS 8086, Université de Versailles, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France*
[b]*Department of Chemistry, Sir Wilfred Grenfell College, Memorial University of NewFoundland, Corner Brook, Canada NF A2H 6P9*
[c]*Department of Chemistry, Queen's University, Kingston, Canada ON K7L 3N6*

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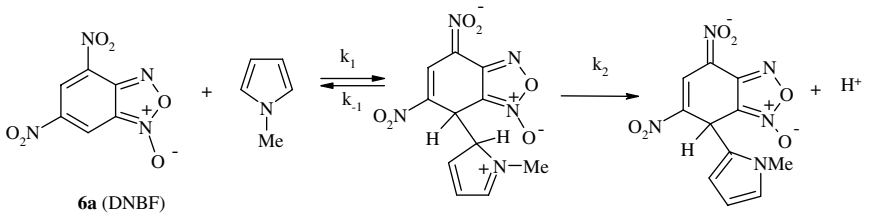
Abstract—A frontier demarcating superelectrophilic compounds that undergo both Diels–Alder reactivity and σ-complexation reactions, from traditional electrophiles, is afforded through the thermodynamic tendency for σ-complexation as defined by the pK_a values for H_2O addition to electron-deficient aromatic and heteroaromatic substrates.

The virtual complete lack of reactivity of unactivated or electron-rich aromatics with nucleophilic reagents is one of the tenets of synthetic and mechanistic chemistry. In contradistinction, is the facile reactivity towards nucleophiles observed with electron-deficient aromatics, as taken advantage in S_NAr chemistry or, in the absence of a good leaving group, in the isolation of σ-adducts such as the methoxide adduct of 1,3,5-trinitrobenzene (TNB), first isolated by Meisenheimer in 1902.[1]

A major new development in the area of electron-deficient aromatics in the last two decades is the discovery of much more strongly electrophilic heteroaromatic structures such as 4,6-dinitrobenzofuroxan (DNBF).[2–11] The latter undergoes σ-complex formation with extremely weak carbon nucleophiles such as polyhydroxybenzenes, anilines or π-excessive heterocycles, for example, pyrroles, indoles, thiophenes, furans,[4c,d,5,6,8,12] Eq. 1. Quantitative evaluation of thermodynamic reactivity is afforded from a comparison of pK_a values for



6a (DNBF)

(1)

Keywords: Nitrobenzofuroxan; Heterocycles; σ-Complexation; Diels–Alder cycloadditions; Superelectrophiles.
* Corresponding authors. Tel.: +33 1 3925 4450; fax: +33 1 3925 4452; e-mail addresses: goumont@chimie.uvsq.fr; terrier@chimie.uvsq.fr; buncele@chem.queensu.ca

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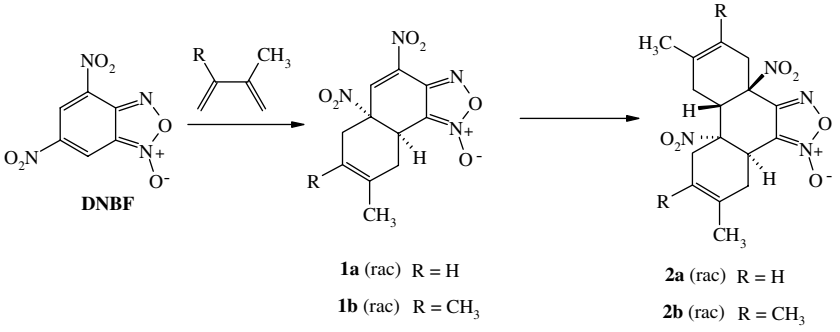
H_2O addition: $pK_a^{DNBF} = 3.75$;[4a,13] $pK_a^{TNB} = 13.43$.[14] On this basis, DNBF and some related molecules have been termed superelectrophiles.[13]

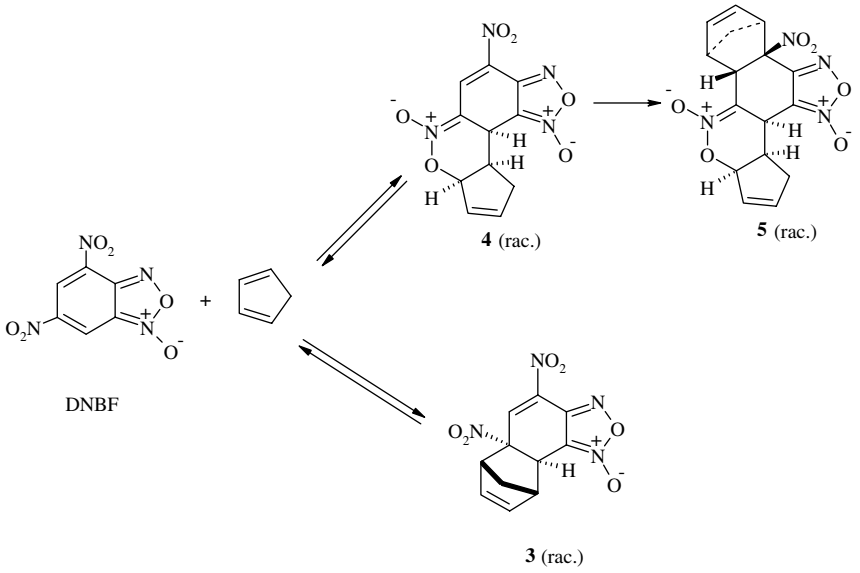
Of equal interest, however, is that DNBF has also been found to undergo a variety of Diels–Alder type reactions.[15,16] This is exemplified in Eq. 2 and Scheme 1, which shows that DNBF can formally act as a dienophile in normal electron-demand (NED) Diels–Alder processes as well as a heterodiene in inverse electron-demand (IED) Diels–Alder processes. In Eq. 2, the NED monoadducts **1a**, **1b** are first formed with high stereoselectivity and high regioselectivity; while in Scheme 1 the reaction affords initially a mixture of the two stereoselective NED and IED adducts **3** and **4**.[15a,16a] Because the remaining nitroolefinic fragment of these monoadducts is also very reactive, diadduct formation subsequently occurs, proceeding with high stereoselectivity to give the highly functionalized structures **2a**, **2b** and **5** as the thermodynamically stable products of the reactions. Interestingly, the exclusive formation of the NED monoadduct **8a** (in its racemic form) is observed in the DNBF–cyclohexadiene system (Eq. 3a).[15c,17]

Besides the potentiality of the versatile behaviour of DNBF in terms of new synthetic approaches to heterocyclic chemistry, the results obtained are in themselves evidence that the carbocyclic ring of this superelectrophilic heterocycle has a poor aromatic character relative to TNB. This suggests the existence of a significant relationship between aromaticity on the one hand, electrophilicity in σ-complex formation and pericyclic reactivity on the other hand, thereby raising the question of whether one could predict that a given electron-deficient aromatic will be suitable for the above two domains of reactivity or not. Should this be possible, this will be of considerable importance to anticipate synthetic applications. In this letter, we report that the $pK_a^{H_2O}$ values for water addition to electron-deficient substrates with the formation of the corresponding σ-adducts, as exemplified for the prototype DNBF system in Eq. 4, can be used as a reliable thermodynamic index for this purpose.

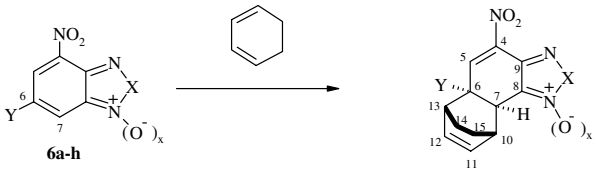
As an approach to answer the above question, we have explored in a systematic manner the Diels–Alder reactivity of the large series of electrophiles listed in Eqs. 3a



(2)



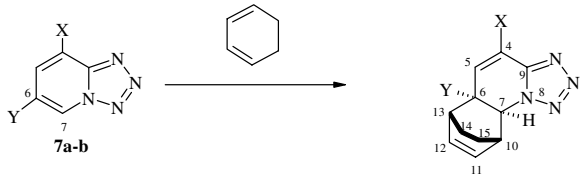
Scheme 1.



6a-h **8a-e** (rac)

6 : (a) x = 1, X = O, Y = NO_2 (DNBF); (b) x = 0, X = O, Y = NO_2 (DNBZ)
(c) x = 1, X = N-picryl, Y = NO_2 (Pi-DNBT); (d) x = 0, X = Se, Y = NO_2 (DNBSe)
(e) x = 0, X = S, Y = NO_2 (DNBS); (f) x = 1, X = N-(4-nitrophenyl), Y = NO_2;
(g) x = 0, X = O, Y = H (NBZ); (h) x = 1, X = O, Y = H (NBF)

(3a)

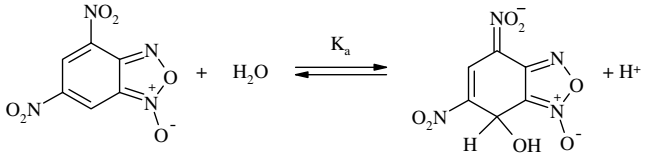


7a-b **9a-b** (rac)

7 : (a) X = Y = NO_2 (DNTP); (b) X = H, Y = NO_2 (6-NTP)

(3b)

and 3b, that is, **6a**–**h** and **7a**–**b**. Importantly, all these compounds, with the exception of **6f**–**h**, behaved as DNBF (**6a**), undergoing addition of only one mole of cyclohexadiene to produce the monoadducts **8a**–**e**[18] and **9a**–**b**[19] in their racemic forms. The general procedure for the preparation of these species, which all result from highly regioselective and stereoselective NED processes involving the nitroactivated C_6–C_7 double bonds of the parent heterocycles as the dienophile contributors is given below.[18] In Table 1 is presented a summary of the observed ease of the various reactions, as deduced by mixing equimolar amounts of the two reagents at room temperature in acetonitrile and monitoring by NMR the appearance of the adducts **8a**–**e** and **9a**–**b** as a function of time. Not only that but the available thermodynamic (pK_a) data pertaining to the formation of the relevant hydroxy σ-adducts of **6a**–**h** and **7a**–**b** according to Eq. 4 in aqueous solution are also listed in Table 1.[13,20–22]



6a (DNBF)

(4)

From the data in Table 1, it is clear that the order of Diels–Alder reactivity of the 4,6-dinitro structures, that is, **6a**–**e** and **7a**, follow the order of electrophilicity, as measured by the $pK_a^{H_2O}$ values for water addition: DNTP > DNBF, DNBZ ≫ Pi-DNBT > DNBSe[23] > DNBS.[24] As the most electrophilic substrate, 4,6-dinitrotetrazolo[1,5*a*]pyridine **7a** ($pK_a^{H_2O} = 0.4$) is the most reactive heterocycle undergoing addition of cyclohexadiene (87% conversion in 2 h) but the process is also very facile with DNBF ($pK_a^{H_2O} = 3.75$) and DNBZ ($pK_a^{H_2O} = 3.92$), with the related adducts **8a** and **8b** being quantitatively formed in ~8 h. Contrasting to this situation, 2 days are needed to achieve complete conversion of 2-picryl-4,6-dinitrobenzotriazole 1-oxide **6c** ($pK_a^{H_2O} = 6.70$) into **8c**. Despite a rather similar pK_a, 4,6-dinitro-2,1,3-benzoselenadiazole **6d** ($pK_a^{H_2O} = 6.34$) reacts somewhat more slowly than **6c**, undergoing 30% conversion into the adduct **8d** in 2 days, but proceeding to 4,6-dinitro-2,1,3-benzothiadiazole **6e** ($pK_a^{H_2O} = 7.86$) results in a more significant decrease in reactivity: 40% conversion into the adduct **8e** after a week. On the other hand, 2-(4-nitrophenyl)-4,6-dinitrobenzotriazole 1-oxide **6f** ($pK_a^{H_2O} = 9.0$) is found to be inert to DA reactivity. Among mononitroactivated substrates 4-nitrobenzofuroxan **6h** ($pK_a^{H_2O} = 10.27$) and 4-nitrobenzofurazan **6g** ($pK_a^{H_2O} = 10.57$), which are less electrophilic than **6f**,[21] do not react at all with

Table 1. Electrophilic versus Diels–Alder reactivity of nitrobenzofuroxans and related heterocyclces

Parent electrophile		Electrophilic reactivity[a]	Pericyclic reactivity adduct formation, %[b]				
		$pK_a^{H_2O}$	2 h	8 h	24 h	48 h	7 days
6a	DNBF	3.75	70	100	100	100	100
6b	DNBZ	3.92	65	100	100	100	100
6c	Pi-DNBT	6.70	—	38[c]	62	100	100
6d	DNBSe	6.34	—	—	~10	30	60
6e	DNBS	7.86	—	~3	—	~17	40
6f	NP-DNBT	9.00	—	—	—	—	—
6g	4-NBZ	10.57	—	—	—	—	—
6h	4-NBF	10.27	—	—	—	—	—
7a	DNTP	0.4	87	100	100	100	100
7b	6-NTP	7.55	—	—	—	~5	~15

[a] As measured by the pK_a value for formation of the related hydroxy σ-adducts in aqueous solution (Eq. 4); Refs. 4a and 20a for **6a** and **7a**; Ref. 20b for **6b**, **6d** and **6e**; Ref. 13 for **6c** and **6f**; Refs. 21 and 22 for **6g** and **6h** in this instance, data refer to σ-complexation at carbon C_5; Ref. 20b for **7b**.
[b] As measured with reference to mixing of equimolar amounts of the electrophile and cyclohexadiene and NMR monitoring of the conversion into the DA adducts at room temperature in acetonitrile, see text.
[c] Four hours after mixing.

cyclohexadiene. In contrast, 6-nitrotetrazolo[1,5*a*]pyridine **7b**, whose $pK_a^{H_2O} = 7.55$ is comparable to that of **6e**, reacts with cyclohexadiene at a comparable rate.

On the above ground, it is apparent that a $pK_a^{H_2O}$ value of 8–8.5 is a benchmark for demarcating the capability of the above electrophilic structures to contribute to pericyclic processes with cyclohexadiene. Even though the related interactions can involve diadduct formation and/or competition between NED and IED processes, the experimental evidence is that the above frontier also fits well the behaviour of the electrophiles **6a**–**h** and **7a**–**b** towards other similarly reactive dienes such as isoprene, 2,3-dimethylbutadiene (Eq. 2) or cyclopentadiene (Scheme 1). As found for the cyclohexadiene systems, these three dienes do not react at all with the 4-mononitro compounds **6f**–**h** under similar conditions. It is only on treatment with highly reactive dienes like the Danishefsky diene that such mononitroactivated structures can exhibit some pericyclic reactivity.[25]

Altogether, the above results suggest that $pK_a^{H_2O} \sim 8$–8.5 for σ-complex formation can be used as a key and readily accessible thermodynamic index to demarcate those electrophiles that can exhibit dual pericyclic and electrophilic behaviour from those which do not. In as much as it is also a clear reflection of an effective water contribution to the σ-complexation process in aqueous solution (Eq. 4),[4a,13] this $pK_a^{H_2O}$ value can also be viewed as defining the frontier between superelectrophilicity and electrophilicity of common neutral electron-deficient aromatics.

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17. Compound **8a** was prepared as previously described and its structure fully confirmed by X-ray crystallography.[15c]
18. Typical experimental procedure: Excess cyclohexadiene (10 equiv) was added to a suspension of 0.2 g (0.84 mmol) of **6b**–**e** and **7a**–**b** in $CHCl_3$ or dichloromethane (10 ml) at room temperature and the reaction mixture stirred at this temperature for a period depending of the structure of the electrophile (2 h to 20 days). The resulting white precipitate was collected by filtration, washed with pentane and dried under vacuum. *Selected data for* **8b**: Yield: 57; mp 122 °C (dec); *m*/*z* (EI) 290 $(M)^{+\cdot}$, 244 $(M-NO_2)^{+\cdot}$; ^1H NMR (300 MHz, $CDCl_3$): δ 1.16, 1.46, 1.87 (m, 4H, H-14, H-15), 3.35 (dd, $J = 8.2$ Hz, $J = 2.7$ Hz, 1H, H-10), 3.82 (d, $J = 7.5$ Hz, 1H, H-13), 4.46 (d, 1H, $J = 2.7$ Hz, H-7), 6.35 (dd, 1H, $J = 7.8$ Hz, $J = 6.7$ Hz, H-12), 6.72 (dd, 1H, $J = 7.8$ Hz, $J = 6.7$ Hz, H-11), 8.00 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2, C-15; 21.5, C-14; 36.7 C-10; 40.4, C-13; 59.3 C-7; 92.3 C-6; 130.9, C-12; 136.9, C-11; 137.1, C-5; 137.7 C-4; 143.6, C-9; 153.5, C-8. Anal. Found: C, 49.72; H, 3.37; N, 19.10. Calcd for $C_{12}H_{10}N_4O_5$: C, 49.66; H, 3.45; N, 19.31. *Selected data for* **8c**: Yield: 82%; mp 154 °C (dec); ^1H NMR (300 MHz, $CDCl_3$): δ 0.86, 1.36, 1.77 (m, 4H, H-14, H-15), 3.65 (m, 2H, H-10, H-13), 4.36 (d, 1H, $J = 2.8$ Hz, H-7), 6.59 (t, 1H, $J = 7.9$ Hz, H-12), 6.72 (t, 1H, $J = 7.9$ Hz, H-11), 7.56 (s, 1H, H-5), 9.26 (s, 2H, Picryl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, C-15; 20.6, C-14; 29.2, C-10; 36.3, C-7; 39.7, C-13; 93.7, C-6; 122.8, C-8; 124.5, C-3′, C-5′; 124.7, C-1′; 130.2, C-12; 133.8, C-11; 136.1, C-9; 136.4, C-5; 141.1, C-4; 146.5, C-2′, C-6′ (broad signal); 148.7, C-4′. Anal. Found: C, 41.51; H, 2.35; N, 21.92. Calcd for $C_{18}H_{12}N_8O_{11}$: C, 41.86; H, 2.32; N, 21.70. *Selected data for* **8d**: Yield: 78%; mp 146 °C (dec); *m*/*z* (EI) 354 $[M]^{+\cdot}$, 308 $[M-NO_2]^{+\cdot}$; ^1H NMR (300 MHz, $CDCl_3$): δ 1.16, 1.45, 1.63 (m, 4H, H-14, H-15), 3.50 (m, 1H, H-10), 3.63 (m, 1H, H-13), 4.37 (d, 1H, $J = 1.9$ Hz, H-7), 6.28 (dd, 1H, $J = 7.6$ Hz, $J = 6.0$ Hz, H-12), 6.65 (dd, 1H, $J = 7.6$ Hz,

$J = 6.3$ Hz, H-11), 7.29 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ18.3, C-15; 20.5, C-14; 33.2, C-10; 36.7, C-13; 45.1, C-7; 94.0, C-6; 130.0, C-12; 130.7, C-5; 136.5, C-11; 149.2, C-4; 150.2, C-9; 163.1, C-8. Anal. Found: C, 40.39; H, 2.83; N, 15.66. Calcd for $C_{12}H_{10}N_4O_4Se$: C, 40.67; H, 2.82; N, 15.81. *Selected data for* **8e**: Yield: 61%; mp 92 °C (dec); *m*/*z* (EI) 260 $[M-NO_2]^{+\cdot}$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16, 1.44, 1.57 (m, 4H, H-14, H-15), 3.47 (m, 1H, H-10), 3.64 (m, 1H, H-13), 4.40 (d, 1H, $J = 2.2$ Hz, H-7), 6.29 (dd, 1H, $J = 7.4$ Hz, $J = 6.2$ Hz, H-12), 6.67 (dd, 1H, $J = 7.4$ Hz, $J = 6.0$ Hz, H-11), 7.38 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.2, C-15; 20.4, C-14; 36.7, C-10; 39.6, C-13; 45.1, C-7; 94.2, C-6; 130.1, C-12; 131.2, C-5; 136.6, C-11; 147.8, C-4; 154.7, C-9; 157.0, C-8. Anal. Found: C, 47.12; H, 3.36; N, 18.00. Calcd for $C_{12}H_{10}N_4O_4S$: C, 47.06; H, 3.27; N, 18.30.

19. *Selected data for* **9a**: Yield: 84%; mp 111 °C (dec); *m*/*z* (EI) 243 $[M-HNO_2]^{+\cdot}$, 215 $[M-HNO_2-N_2]^{+\cdot}$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10, 1.46, 1.50, 1.87 (m, 4H, H-14, H-15), 3.70 (m, 2H, H-10, H-13), 5.71 (d, 1H, $J = 2.7$ Hz, H-7), 6.42 (dd, 1H, $J = 7.8$ Hz, $J = 6.7$ Hz, H-12), 6.66 (dd, 1H, $J = 7.8$ Hz, $J = 6.7$ Hz, H-11), 8.04 (s, 1H, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5, C-15; 21.54, C-14; 36.4, C-10; 40.4, C-13; 59.3, C-7; 92.3, C-6; 131.940, C-12; 133.4, C-11; 134.6, C-5; 144.1, C-4; 143.6, C-9. Anal. Found: C, 45.51; H, 3.38; N, 29.13. Calcd for $C_{11}H_{10}N_6O_4$: C, 45.52; H, 3.47; N, 28.96. *Selected data for* **9b**: Yield: 71%; mp 122 °C (dec); *m*/*z* (EI) 198 $[M-HNO_2]^{+\cdot}$, 170 $[M-HNO_2-N_2]^{+\cdot}$; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85, 1.13, 1.41, 1.72 (m, 4H, H-14, H-15), 3.59 (dd, $J = 7.5$ Hz, $J = 1.6$ Hz, 1H, H-10), 3.66 (d, $J = 7.5$ Hz, 1H, H-13), 5.60 (d, 1H, $J = 1.6$ Hz, H-7), 6.35 (dd, 1H, $J = 7.9$ Hz, $J = 7.5$ Hz, H-12), 6.61 (dd, 1H, $J = 7.9$ Hz, $J = 7.5$ Hz, H-11),6.75 (d, 1H, $J = 10.1$ Hz, H-5), 7.26 (d, 1H, $J = 10.1$ Hz, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0, C-15; 21.4, C-14; 36.4, C-10; 39.3, C-13; 59.6, C-7; 93.5, C-6; 116.7, C-4; 131.5, C-12; 132.2, C-5; 133.4, C-11; 146.9, C-9; Anal. Found: C, 53.88; H, 4.58; N, 28.53. Calcd for $C_{11}H_{11}N_5O_2$:C, 53.87; H, 4.52; N, 28.56.
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