The Crystal Structure of the σ-Complex of 4,6-Dinitrobenzofuroxan and Potassium 2-Nitropropenide

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A crystalline σ-complex (**4d**) of 4,6-dinitrobenzofuroxan and potassium 2-nitropropenide has been prepared and characterized by single-crystal X-ray analysis. There are two K^+ and two independent anionic 2-nitropropane DNBF moieties per asymmetric unit. A cis-configuration of the hydrogen and NO_2 substituents is observed. This structure determination suggests a syn-elimination process for the loss of nitrous acid from **4d** which readily occurs in Me_2SO solution to give the carbanion (**6d**) of 4,6-dinitro-7-methylbenzofuroxan.

There is currently much interest in the extremely high electrophilic character of 4,6-dinitro-2,1,3-benzoxadiazole N-oxide, more commonly known as 4,6-dinitrobenzofuroxan (DNBF).[1-8] This behaviour is best illustrated by the exceptional ability of DNBF to react with very weak carbon nucleophiles such as enols or π-excessive aromatic or heteroaromatic derivatives, e.g. 1,3,5-trimethoxybenzene, indole and pyrrole, to afford very stable carbon-bonded σ-complexes of the type 1–3.[5-7]

DNBF

1

$R^1 = CH_3$ $R^2 = H$
$R^1 = CH_3$ $R^2 = COCH_3$
$R --- R^1 = —(CH_2)_3—$
$R --- R^1 = —(CH_2)_4—$

2   **3**
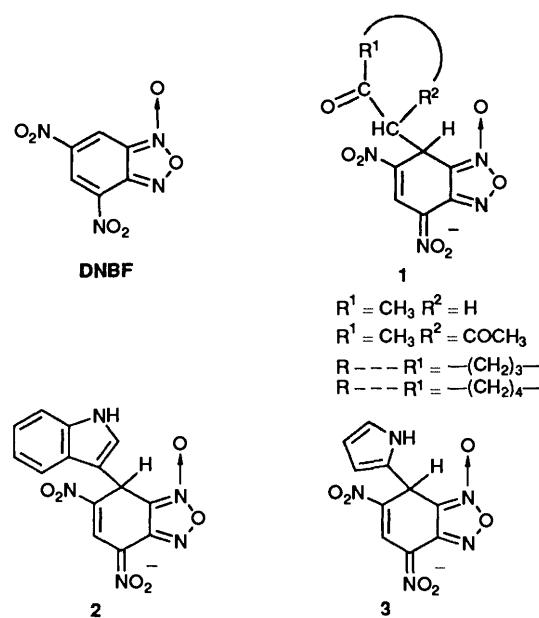
In an effort to obtain a quantitative measure of the reactivity of DNBF towards nucleophilic carbons, we have recently carried out a kinetic and thermodynamic analysis of the reaction of this compound with a number of nitroalkane anions in aqueous solution, eqn. (1).[9] In the course of this study we succeeded in isolating the resulting σ-adducts **4a–d** as crystalline potassium salts and we looked at the possibility of a further ionization of the nitroalkane moiety of **4a–c** to give the dianions **5a–c** in basic solution, eqn. (2). We thus discovered that **4a–c** are very susceptible to a base-catalysed elimination of nitrous acid in DMSO to afford the carbanions **6a–c** according to eqn. (3). This process also occurs, and is especially clean, with

the non-ionizable 2-nitropropane adduct **4d** which gives the carbanion **6d** of 4,6-dinitro-7-methylbenzofuroxan.

DNBF   **4a–d**

a $R^1 = R^2 = H$
b $R^1 = CH_3$, $R^2 = H$
c $R^1 = C_2H_5$, $R^2 = H$
d $R^1 = R^2 = CH_3$

5a–c

4a–d

6a–d
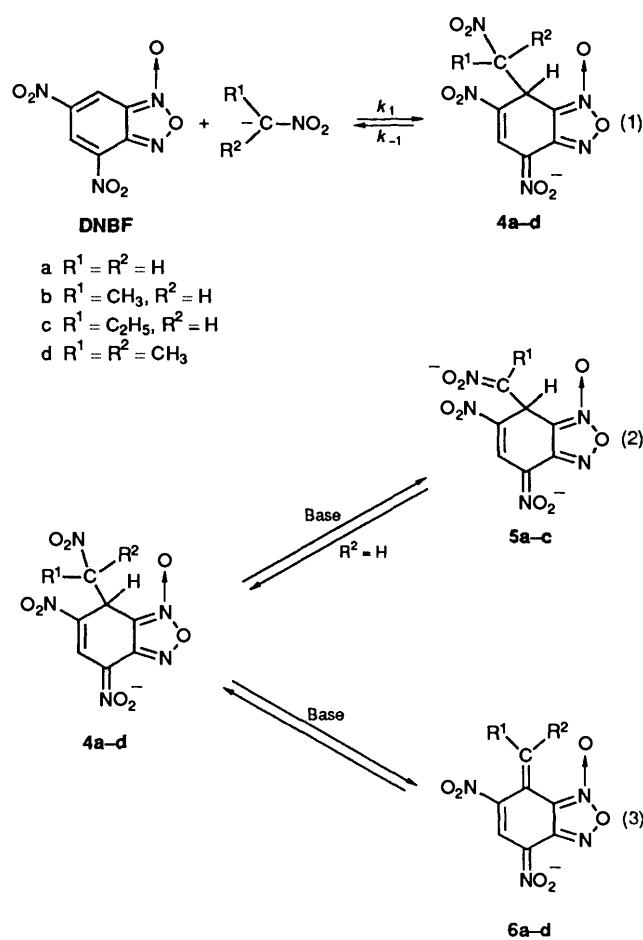
While several examples of a relatively facile elimination of nitrous acid from compounds that contain an electron-withdrawing substituent β to the NO_2 group have been described,[10-18] only in a few cases has a mechanistic analysis of the reactions been made.[13] As part of a general study undertaken to understand the mechanism of the conversion of

4a–d to **6a–d**, we report an X-ray determination of the molecular geometry of the potassium salt of the 2-nitropropane σ-adduct **4d**. In as much as **4d** is a carbon-bonded σ-complex, our study is also of relevance to the structure of Meisenheimer complexes.[1,2] So far, only the structures of four oxygen-bonded σ-adducts, namely the adducts **7–10**, have been characterized by X-ray crystallography.[19–22]

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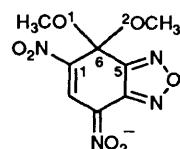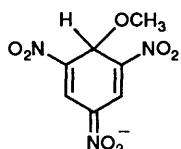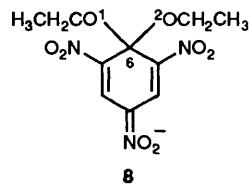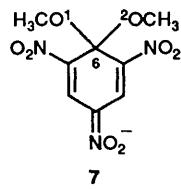
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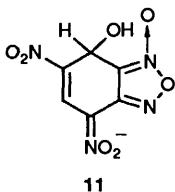
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Results and Discussion

The single crystal X-ray structure consists of two K$^+$ and two independent anionic 2-nitropropane–DNBF moieties per asymmetric unit (denoted **A** and **B**) roughly separated by Van der Waals contacts. The molecular structures, together with the atomic numbering chosen, are shown in Fig. 1. The crystal structure viewed along the *b* axis is shown in Fig. 2. The molecules are piled up, perpendicular to each other, along the *a* axis. Figs. 3 and 4 are stereoscopic views of the packing around, respectively, K(1) and K-(2).* K(1) is linked to three molecules **A** and three molecules **B** while K(2) is linked to three molecules **A** and two molecules **B**. The two molecules have the same conformation, only small differences being observed between chemically equivalent bonds and angles in the two molecules (Table 3).

In agreement with the sp^3 hybridization at C(6) and C(15), the three angles around each carbon average 109.6°. Concomitantly, the C(6)–C(7) and C(15)–C(16) bonds have values typical for C_{sp^3}–C_{sp^3} bonds, e.g. C(6)–C(7) = 1.56(2) Å. In addition, the C(6)–C(1) [1.53(2) Å] and C(6)–C(5) [1.50(2) Å] bonds in the first molecule and the C(15)–C(10) [1.52(2) Å] and C(15)–C(14) [1.51(2) Å] bonds in the second molecule are all similar. While such values compare well with those reported for similar C_{sp^3}–C_{sp^2} bonds in the oxygen-bonded adducts **7–10**, e.g. C(6)–C(1) = 1.50(1) Å, C(6)–C(5) = 1.52(6) Å in **10**, they are much greater than the values found for the analogous bonds in the parent DNBF molecule [C(6)–C(1) = 1.37(2) Å; C(6)–C(5) = 1.39(2) Å].[23] The distances C(1)–C(8) [3.11(2) Å] and C(1)–C(9) [3.10(2) Å] as well as the C(5)–C(8) [2.88(2) Å] and C(5)–N(5) [3.01 (2) Å] bonds are all smaller than the sum of the

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* We would like to thank a referee for helpful suggestions.

A

B
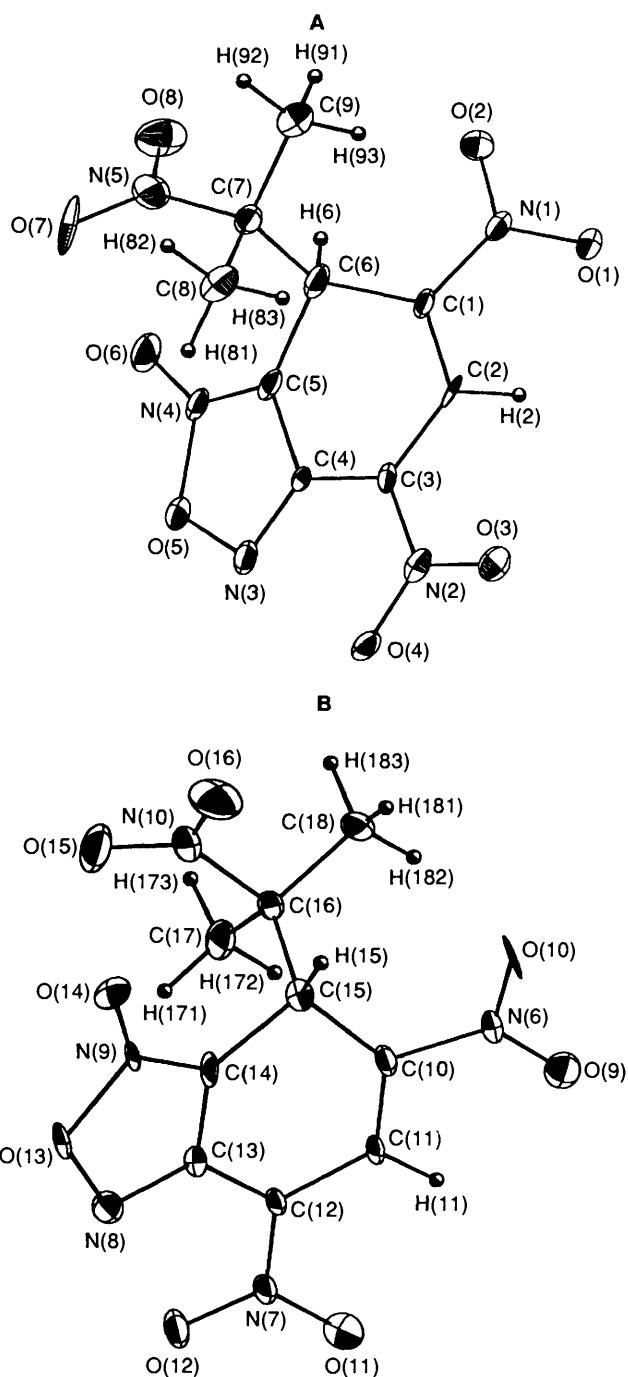
Fig. 1   Molecular geometry and atom labelling scheme for molecules **A** and **B** (C$_9$H$_8$N$_5$O$_8$)$^-$
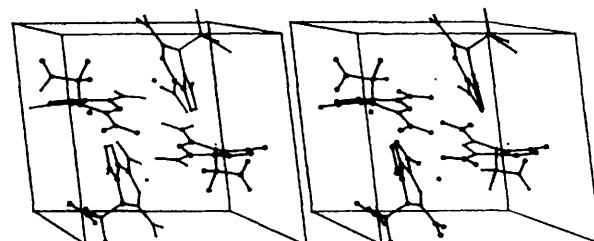
Fig. 2   Stereoscopic view of (C$_9$H$_8$N$_5$O$_8$)$^-$ K$^+$

Table 1　Distances/Å from atoms to the mean plane defined by atoms

Molecule A[a]							
Plane 1		Plane 2		Plane 3		Plane 4	
C(3)	0.00(1)	C(1)	−0.00(1)	C(4)	0.01(1)	C(1)	0.13(1)
N(2)	−0.00(1)	N(1)	0.00(1)	C(5)	−0.02(1)	C(2)	0.03(1)
O(3)	0.00(1)	O(1)	−0.00(1)	N(3)	0.01(1)	C(3)	−0.15(1)
O(4)	0.001(9)	O(2)	−0.00(1)	N(4)	0.02(1)	C(4)	0.07(1)
				O(5)	−0.02(1)	C(5)	0.09(1)
						C(6)	−0.18(1)
Molecule B[b]							
Plane 5		Plane 6		Plane 7		Plane 8	
C(12)	0.00(2)	C(10)	0.00(1)	C(13)	−0.01(1)	C(10)	0.09(2)
N(7)	−0.01(1)	N(6)	−0.01(1)	C(14)	−0.01(1)	C(11)	0.03(2)
O(11)	0.00(1)	O(9)	0.00(1)	N(8)	0.01(1)	C(12)	−0.09(2)
O(12)	0.00(1)	O(10)	0.00(1)	N(9)	0.01(1)	C(13)	−0.01(1)
				O(13)	−0.02(1)	C(14)	0.11(1)
						C(15)	−0.15(1)

[a] Angles between the planes: 1–4, 5.53°; 2–4, 18.24°; 3–4, 14.09°. [b] Angles between the planes: 5–8, 11.80°; 6–8, 16.21°; 7–8, 11.44°.

Table 2　X-Ray data

Formula	[C$_9$H$_8$N$_5$O$_8$]$^-$ K$^+$
M_r	353.288
Crystal system	triclinic
a/Å	11.983(4)
b/Å	12.079(5)
c/Å	10.517(3)
α/°	113.02(2)
β/°	78.78(2)
γ/°	96.22(2)
V/Å^3	1373(4)
Space group	$P\bar{1}$
D_c/g cm^{-3}	1.709
Z	4
$F(000)$	360
Radiation	Cu-Kα, 1.5418 Å
μ/cm^{-1}	39.54
θ min./max.	1.5–60
h	$-12 \leqslant h \leqslant 13$
k	$-13 \leqslant k \leqslant 12$
l	$0 \leqslant l \leqslant 11$
T/K	293
Total data measured	4361
Total data unique	3969
Total data observed	1630, $I \geqslant 3\sigma(I)$
Absorption correction	DIFABS[32]
Weighting scheme	$w = 1/\sigma^2(F_o)$
Final $R = \Sigma|\Delta F|/\Sigma|F_o|$	0.0704
Final $R_w = [\Sigma_w(\Delta F)^2/\Sigma_w|F_o^2|]^{\frac{1}{2}}$	0.0763
S	2.7
$(\Delta/\sigma)_{max}$	0.08
Last Fourrier difference	
ρ_{max}/e Å^{-3}	0.2
ρ_{min}/e Å^{-3}	−0.4

Fig. 3　Stereoscopic view of K(1) environment

Van der Waals radii of two carbon or one carbon and one nitrogen atoms.

The planes of the NO$_2$ groups *para* to the tetrahedral carbons C(6) and C(15) are much closer to coplanarity with the carbocyclic rings than those of the *ortho* NO$_2$ groups. This indicates the existence of an appreciable steric repulsion between the latter substituents and the adjacent nitropropane moieties. Concomitantly it is found that the C–N bonds are much shorter at the *para* than at the *ortho* positions and that the C(1)–C(2) and C(10)–C(11) bonds [1.36(2) and 1.37(2) Å] are much shorter than the C(2)–C(3) and C(11)–C(12) bonds [1.41(2) and 1.44(2) Å]. These results suggest that the best structure of the adduct **4d** is the one shown in eqn. (1), in which the carbon *para* to the sp^3 carbon bears a formal nitronate function. A similar conclusion was formulated not only for the dinitrobenzo-furazan adduct **10** but also for the three trinitrobenzene adducts **7–9**.[19–22] The predominance of the paraquinonic structure implies that the annelated furoxan and furazan systems do not markedly contribute to the delocalisation of the negative charge of the σ-adducts **4d** and **10**, and suggests that the strong electron-withdrawing effect exerted by these rings is mainly of inductive nature. In this respect, it is to be noted that the five atoms of the furazan ring are very nearly coplanar in the two molecules of **4d** (Table 1). However, the plane of this heterocyclic ring makes a significant angle with the carbocyclic ring (14.1° in molecule **A**, 11.1° in molecule **B**), so that the whole benzofuroxan entity cannot be regarded as planar. This situation contrasts with that found in the benzofurazan adduct **10** where the two corresponding rings were coplanar.[22] Coplanarity of the benzene and furoxan rings is also achieved in the parent DNBF molecule.[23]

Fig. 5 shows that the hydrogen and NO$_2$ substituents at C(6) and C(7), respectively, in the molecule **A** are in a *cis*-configuration. The corresponding H(6)–C(6)–C(7)–N(5) torsion angle is 51.12°. A similar configuration prevails in molecule **B** (54.28°). Assuming that the crystal structure determination gives a correct picture of the stereochemistry of the elimination of nitrous acid from **4d** in solution, Fig. 5 suggests that the conversion of **4d** to **6d** is a *syn*-elimination process.

In general, the nitro group is not a good leaving group in base-induced β-eliminations, being only capable of departing when there is a strong electron-withdrawing group in the β-position.[10　18] In this respect, the formation of the olefinic carbanion **6d** is noteworthy since it implies that the negatively-charged moiety of the DNBF σ-adducts acts as a powerful electron-withdrawing functionality. A similar conclusion was previously formulated from the observation that the OH group
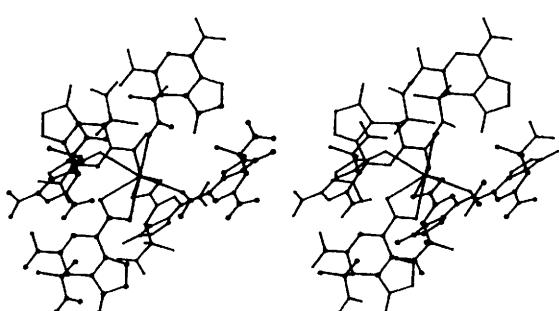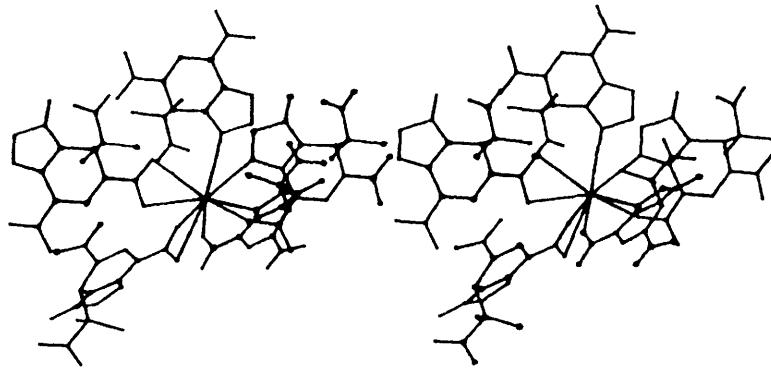
Fig. 4 Stereoscopic view of K(2) environment

Table 3 Intramolecular bond distances/Å and angles/°

C(1)–C(2)	1.36(2)	C(10)–C(11)	1.37(2)
C(1)–C(6)	1.53(2)	C(10)–C(15)	1.52(2)
C(1)–N(1)	1.42(2)	C(10)–N(6)	1.44(2)
C(2)–C(3)	1.41(2)	C(11)–C(12)	1.44(2)
C(3)–C(4)	1.43(2)	C(12)–C(13)	1.41(2)
C(3)–N(2)	1.38(2)	C(12)–N(7)	1.37(2)
C(4)–C(5)	1.41(2)	C(13)–C(14)	1.41(2)
C(4)–N(3)	1.33(1)	C(13)–N(8)	1.32(2)
C(5)–C(6)	1.50(2)	C(14)–C(15)	1.51(2)
C(5)–N(4)	1.32(2)	C(14)–N(9)	1.30(1)
C(6)–C(7)	1.56(2)	C(15)–C(16)	1.54(2)
C(7)–C(8)	1.47(2)	C(16)–C(17)	1.52(2)
C(7)–C(9)	1.54(2)	C(16)–C(18)	1.51(2)
C(7)–N(5)	1.51(2)	C(16)–N(10)	1.56(2)
N(1)–O(1)	1.27(1)	N(6)–O(9)	1.24(1)
N(1)–O(2)	1.24(1)	N(6)–O(10)	1.24(1)
N(2)–O(3)	1.23(1)	N(7)–O(11)	1.26(1)
N(2)–O(4)	1.25(1)	N(7)–O(12)	1.26(1)
N(3)–O(5)	1.37(1)	N(8)–O(13)	1.42(1)
N(4)–O(5)	1.44(1)	N(9)–O(13)	1.42(1)
N(4)–O(6)	1.22(1)	N(9)–O(14)	1.22(1)
N(5)–O(7)	1.19(2)	N(10)–O(15)	1.23(2)
N(5)–O(8)	1.18(2)	N(10)–O(16)	1.20(2)
C(6)–C(1)–C(2)	125.1(12)	C(15)–C(10)–C(11)	127.0(11)
N(1)–C(1)–C(2)	118.5(12)	N(6)–C(10)–C(11)	113.5(12)
N(1)–C(1)–C(6)	116.4(11)	N(6)–C(10)–C(15)	119.5(11)
C(3)–C(2)–C(1)	120.9(12)	C(12)–C(11)–C(10)	120.4(12)
C(4)–C(3)–C(2)	117.6(12)	C(13)–C(12)–C(11)	116.7(12)
N(2)–C(3)–C(2)	118.7(12)	N(7)–C(12)–C(11)	119.6(12)
N(2)–C(3)–C(4)	122.4(12)	N(7)–C(12)–C(13)	123.5(12)
C(5)–C(4)–C(3)	118.1(11)	C(14)–C(13)–C(12)	121.2(11)
N(3)–C(4)–C(3)	130.5(12)	N(8)–C(13)–C(12)	127.9(12)
N(3)–C(4)–C(5)	111.2(11)	N(8)–C(13)–C(14)	110.2(10)
C(6)–C(5)–C(4)	126.1(12)	C(15)–C(14)–C(13)	124.9(10)
N(4)–C(5)–C(4)	108.1(11)	N(9)–C(14)–C(13)	110.2(10)
N(4)–C(5)–C(6)	125.7(12)	N(9)–C(14)–C(15)	124.8(11)
C(5)–C(6)–C(1)	104.5(11)	C(14)–C(15)–C(10)	104.7(10)
C(7)–C(6)–C(1)	113.0(11)	C(16)–C(15)–C(10)	110.9(11)
C(7)–C(6)–C(5)	110.7(11)	C(16)–C(15)–C(14)	111.3(11)
C(8)–C(7)–C(6)	111.6(11)	C(17)–C(16)–C(15)	114.5(12)
C(9)–C(7)–C(6)	114.5(11)	C(18)–C(16)–C(15)	114.2(13)
C(9)–C(7)–C(8)	109.2(13)	C(18)–C(16)–C(17)	111.5(13)
N(5)–C(7)–C(6)	106.4(12)	N(10)–C(16)–C(15)	104.2(11)
N(5)–C(7)–C(8)	109.6(13)	N(10)–C(16)–C(17)	106.7(13)
N(5)–C(7)–C(9)	105.3(12)	N(10)–C(16)–C(18)	104.7(11)
O(1)–N(1)–C(1)	117.2(11)	O(9)–N(6)–C(10)	120.5(12)
O(2)–N(1)–C(1)	120.8(12)	O(10)–N(6)–C(10)	118.5(12)
O(2)–N(1)–O(1)	122.0(11)	O(10)–N(6)–O(9)	121.0(12)
O(3)–N(2)–C(3)	121.0(12)	O(11)–N(7)–C(12)	119.9(11)
O(4)–N(2)–C(3)	118.3(11)	O(12)–N(7)–C(12)	119.8(12)
O(4)–N(2)–O(3)	120.7(11)	O(12)–N(7)–O(11)	120.3(11)
O(5)–N(3)–C(4)	105.0(10)	O(13)–N(8)–C(13)	104.9(10)
O(5)–N(4)–C(5)	105.6(10)	O(13)–N(9)–C(14)	105.7(10)
O(6)–N(4)–C(5)	134.9(12)	O(14)–N(9)–C(14)	134.5(11)
O(6)–N(4)–O(5)	119.4(10)	O(14)–N(9)–O(13)	119.7(10)
O(7)–N(5)–C(7)	119.7(17)	O(15)–N(10)–C(16)	117.6(14)
O(8)–N(5)–C(7)	115.8(15)	O(16)–N(10)–C(16)	117.2(14)
O(8)–N(5)–O(7)	124.5(18)	O(16)–N(10)–O(15)	125.1(16)
N(4)–O(5)–N(3)	109.9(9)	N(9)–O(13)–N(8)	108.9(9)

Table 4 Distances/Å around K(1) and K(2)

K(1)–O(1)	2.82(1)	K(1)–O(3)	2.86(1)
K(1)–O(4)	2.797(9)	K(1)–O(8)	2.68(1)
K(1)–O(9)	2.88(1)	K(1)–O(10)	2.98(1)
K(1)–O(12)	2.99(1)	K(1)–O(14)	2.86(1)
K(2)–N(3)	2.98(1)	K(2)–N(8)	2.91(1)
K(2)–O(1)	2.826(9)	K(2)–O(2)	2.95(1)
K(2)–O(4)	2.654(9)	K(2)–O(6)	2.80(1)
K(2)–O(11)	2.96(1)	K(2)–O(12)	2.74(1)
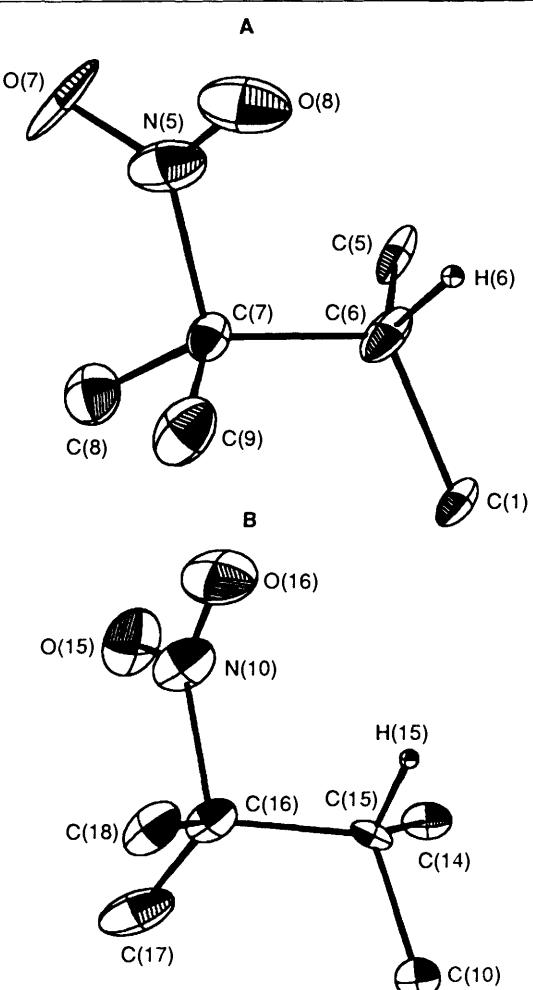
Fig. 5 Partial molecular structure showing the *cis*-configuration of H and NO₂ groups in molecules **A** and **B**

of the hydroxy adduct **11** undergoes ionization in dilute aqueous hydroxide solutions ($pK_a = 11.30$).[3]

Because of the strong acidifying effect of the DNBF moiety on the departing hydrogen in **4d**, one can reasonably postulate that the elimination process of eqn. (3) occurs either *via* a carb-

Table 5 Atomic positional parameters

Atom	x/a	y/b	z/c
K(1)	0.7167(3)	0.6338(3)	0.8089(3)
K(2)	0.4561(3)	0.7014(3)	1.1735(3)
C(1)	0.391(1)	0.788(1)	0.811(1)
C(2)	0.384(1)	0.690(1)	0.691(1)
C(3)	0.353(1)	0.700(1)	0.575(1)
C(4)	0.353(1)	0.818(1)	0.574(1)
C(5)	0.353(1)	0.917(1)	0.702(1)
C(6)	0.347(1)	0.912(1)	0.843(2)
C(7)	0.223(1)	0.930(1)	0.925(1)
C(8)	0.140(1)	0.851(2)	0.839(2)
C(9)	0.206(1)	0.912(2)	1.065(2)
C(10)	1.070(1)	0.462(1)	0.736(1)
C(11)	1.124(1)	0.508(1)	0.849(1)
C(12)	1.232(1)	0.462(1)	0.844(1)
C(13)	1.283(1)	0.380(1)	0.713(1)
C(14)	1.2265(9)	0.337(1)	0.596(1)
C(15)	1.102(1)	0.352(1)	0.603(1)
C(16)	1.030(1)	0.240(1)	0.610(2)
C(17)	1.054(2)	0.197(2)	0.719(2)
C(18)	0.903(1)	0.250(1)	0.619(2)
N(1)	0.444(1)	0.777(1)	0.916(1)
N(2)	0.3445(9)	0.597(1)	0.457(1)
N(3)	0.360(1)	0.854(1)	0.467(1)
N(4)	0.3656(9)	1.017(1)	0.675(1)
N(5)	0.198(2)	1.060(1)	0.965(2)
N(6)	0.9732(9)	0.529(1)	0.750(1)
N(7)	1.2828(9)	0.504(1)	0.961(1)
N(8)	1.390(1)	0.347(1)	0.673(1)
N(9)	1.2953(8)	0.277(1)	0.484(1)
N(10)	1.067(1)	0.139(1)	0.464(2)
O(1)	0.4813(8)	0.6749(9)	0.8904(9)
O(2)	0.4515(9)	0.8642(9)	1.026(1)
O(3)	0.353(1)	0.4968(8)	0.458(1)
O(4)	0.3307(8)	0.6084(8)	0.3475(9)
O(5)	0.3650(8)	0.9776(8)	0.527(1)
O(6)	0.3707(9)	1.1238(9)	0.746(1)
O(7)	0.125(1)	1.084(1)	0.919(2)
O(8)	0.257(1)	1.131(1)	1.038(1)
O(9)	0.9368(9)	0.609(1)	0.863(1)
O(10)	0.9298(8)	0.508(1)	0.645(1)
O(11)	1.2427(9)	0.592(1)	1.067(1)
O(12)	1.3711(8)	0.4558(9)	0.961(1)
O(13)	1.4006(7)	0.2779(9)	0.528(1)
O(14)	1.2880(8)	0.2296(8)	0.3592(9)
O(15)	1.124(1)	0.058(1)	0.459(1)
O(16)	1.042(1)	0.149(1)	0.364(1)

anionic stepwise E1cB mechanism or *via* a concerted E2 mechanism involving a transition state of considerable anionic character.[24,25] Interestingly, these two mechanisms are known to be consistent with the occurrence of *syn*-eliminations which are normally less favoured than *anti*-eliminations.[26–28] A detailed kinetic analysis is currently being carried out in order to determine the exact mechanism of eqn. (3).

Experimental

Preparation of the σ-Complex of 4,6-Dinitrobenzofuroxan and Potassium 2-Nitropropenide.—To DNBF (0.226 g) dissolved in nitroethane (5 cm³) was added potassium 2-nitropropenide (1 equiv.) suspended in nitroethane (5 cm³). After being stirred for 5 min, the resulting orange precipitate was filtered, washed with diethyl ether and dried under reduced pressure to give 0.31 g (87%) of the potassium salt of **4d**, which decomposes above 300 C.

Crystal Structure Determination for the σ-Complex of 4,6-Dinitrobenzofuroxan and Potassium 2-Nitropropenide.—Data were collected on a Philips PW 1100 diffractometer with Cu-Kα radiation, using the 'flying stepscans' method.[29] Crystal data

and experimental parameters are summarized in Table 2. Intramolecular bond lengths and angles are given in Table 3. Distances and angles around the K atoms are given in Table 4. Atomic coordinates for all non-hydrogen atoms are given in Table 5. The structure was solved by deconvolution of the Patterson function and developed and refined using standard Fourier and least-squares procedures (CRYSTALS).[30] Non-hydrogen atoms were refined anisotropically, hydrogen atomic positions were calculated and only isotropic equivalent thermal parameters were refined. Figures were drawn using ORTEP.[31] Hydrogen-atom coordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

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* For details, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2,* 1992, in the January issue.

References

1 F. Terrier, *Chem. Rev.,* 1982, **82**, 77.
2 E. Buncel, M. R. Crampton, M. J. Strauss and F. Terrier in *Electron-Deficient Aromatic and Heteroaromatic-Base Interactions,* Elsevier, Amsterdam, 1984, ch. 4.
3 F. Terrier, F. Millot and W. P. Norris, *J. Am. Chem. Soc.,* 1976, **98**, 5883.
4 F. Terrier, M. P. Simonnin, M. J. Pouet and M. J. Strauss, *J. Org. Chem.,* 1981, **46**, 3537.
5 (a) F. Terrier, J. C. Hallé, M. P. Simonnin and M. J. Pouet, *J. Org. Chem.,* 1984, **49**, 4363; (b) J. C. Hallé, M. P. Simonnin, M. J. Pouet and F. Terrier, *Tetrahedron Lett.,* 1983, **24**, 2255.
6 (a) E. Buncel, R. A. Renfrow and M. J. Strauss, *J. Org. Chem.,* 1987, **52**, 488; (b) M. J. Strauss, R. A. Renfrow and E. Buncel, *J. Am. Chem. Soc.,* 1983, **105**, 2473.
7 (a) R. J. Spear, W. P. Norris and R. W. Read, *Tetrahedron Lett.,* 1983, **24**, 1555; (b) W. P. Norris, R. J. Spear and R. W. Read, *Aust. J. Chem.,* 1983, **36**, 297.
8 F. Terrier, P. McCormack, J. C. Hallé and M. J. Pouet, *J. Org. Chem.,* 1988, **53**, 4407.
9 F. Terrier, A. P. Chatrousse and T. Boubaker, manuscript in preparation.
10 N. Ono, in *Nitro Compounds. Recent Advances in Synthesis and Chemistry,* H. Feuer and A. T. Nielsen, Editors, VCH Publishers, 1990, ch. 1, pp. 86–110.
11 J. W. Patterson and J. E. McMurry, *J. Chem. Soc., Chem. Commun.,* 1971, 488.
12 D. Seebach, M. S. Hoekstra and G. Protschuk, *Angew. Chem., Int. Ed. Engl.,* 1977, **16**, 321.
13 G. Bartoli, *Acc. Chem. Res.,* 1984, **17**, 109.
14 (a) N. Ono, H. Miyake, R. Tanikaga and A. Kaji, *J. Org. Chem.,* 1982, **47**, 5017; (b) N. Ono, R. Tamura, H. Eto, I. Hamamoto, T. Nakatsuka, J. Hayami and A. Kaji, *J. Org. Chem.,* 1983, **48**, 3678; (c) N. Ono, A. Kanimmura, S. Kawai and A. Kaji, *Nippon Kagaku Kaishi,* 1987, 1338.
15 R. Beugelmans, A. Lechevallier and H. Rousseau, *Tetrahedron Lett.,* 1983, **24**, 1787.
16 D. Seebach, R. Henning and T. Makhopadkyay, *Chem. Ber.,* 1982, **115**, 1705.
17 A. P. Marchand, B. C. Suri, A. D. Earlywine, D. R. Powell and D. Van der Helm, *J. Org. Chem.,* 1984, **49**, 670.
18 C. D. Weis and G. R. Newkome, *J. Org. Chem.,* 1990, **55**, 5801.
19 R. Destro, C. M. Grammacioli and M. Simonetta, *Acta Crystallogr., Sect. B.,* 1968, **24**, 1369.
20 H. Ueda, N. Sakabe, J. Tanaka and A. Furusaki, *Bull. Chem. Soc. Jpn.,* 1968, **41**, 2866.
21 R. Destro, T. Pilati and M. Simonetta, *Acta Crystallogr., Sect. B,* 1979, **35**, 733.
22 (a) G. G. Messmer and G. J. Palenik, *Chem. Comm.,* 1969, 470; (b) *Acta Crystallogr., Sect. B,* 1971, **27**, 324.

23 C. K. Prout, O. J. R. Hodder and D. Viterboo, *Acta Crystallogr.*, *Sect. B*, 1972, **28**, 1523.

24 R. A. Bartsch and J. Zavada, *Chem. Rev.*, 1980, **80**, 453.

25 G. Petrillo, M. Novi, G. Garbarino, C. Dell'Erba and A. Mugnoli, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1291.

26 R. D. Bach, R. C. Radger and T. J. Lang, *J. Am. Chem. Soc.*, 1979, **101**, 2845.

27 E. Bacciocchi, R. Ruzziconi and G. V. Sebastiani, *J. Am. Chem. Soc.*, 1983, **105**, 6114.

28 M. J. S. Dewar and Y. C. Yuan, *J. Am. Chem. Soc.*, 1990, **112**, 2088.

29 A. Cousson, *Acta Crystallogr., Sect. C*, 1985, **41**, 1758.

30 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS*, 1985, Chemical Crystallography Laboratory, University of Oxford, England.

31 C. K. Johnson, *ORTEP*, 1965, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee.

32 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.