Photochemical Nitration by Tetranitromethane. Part XL.† Regiochemistry of Trinitromethyl Attachment in the Photolysis of Benzofuran with Tetranitromethane

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The photolysis of the charge-transfer (CT) complex of benzofuran (3) and tetranitromethane in dichloromethane by light exciting only the CT complex ($\lambda > 435$ nm) gives the epimeric pairs of adducts, 3-nitro-2-trinitromethyl-2,3-dihydrobenzofurans 10 and 11, 2-nitro-3-trinitromethyl-2,3-dihydrobenzofurans 12 and 13, 3-hydroxy-2-trinitromethyl-2,3-dihydrobenzofurans 15 and 16, 7-nitro-4-trinitromethyl-4,7-dihydrobenzofurans 17 and 18, nitronic ester 14, dinitro dimers 19 and (21), 6-nitro- and 4-nitro-benzofurans 9 and 22, and 4-trinitromethylbenzofuran 21. In acetonitrile solution similar photolysis gives the same group of products and in addition the epimeric pairs, 2,3-dinitro-2,3-dihydrobenzofurans 4 and 5, 3-hydroxy-2-nitro-2,3-dihydrobenzofurans 6 and 7, and 3-nitrobenzofuran (8). Adducts 10, 11, 15 and 16 are formed by attack of trinitromethanide ion at C2 in the benzofuran radical cation 3·⁺, adducts 12, 13 and 14 by similar attack at C3, and adducts 17 and 18, and 4-trinitromethylbenzofuran (21) by attack at C4.

In 1,1,1,3,3,3-hexafluoropropan-2-ol the analogous photolysis of the CT complex of benzofuran (3) and tetranitromethane gives substantially the dinitro dimers 19 and 20, with small amounts of 3-nitro- (8), 6-nitro- (9), and 4-nitro-benzofuran (22).

Reaction of benzofuran (3) with nitrogen dioxide in dichloromethane in the dark gives mainly the 2,3-dinitro adducts 4 and 5, and the 3-hydroxy-2-nitro adducts 6 and 7.

High-level quantum chemical calculations (CASSCF/CASPT2), in combination with the valence bond configuration mixing (VBCM) model of the transition state of the radical cation–nucleophile reaction, were performed in order to obtain reactivity indices expressing the reactivity of the various sites of 3·⁺ toward a nucleophile for comparison with the experimental results.

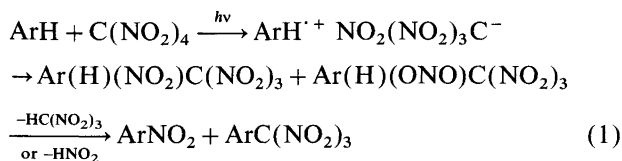X-ray crystal structures are reported for compounds 5, 8, 14 and 21.

The photochemical activation of the charge transfer (CT) complex of tetranitromethane with aromatic compounds ArH by suitably filtered light has been shown to occur predominantly by addition of the elements of tetranitromethane, $-NO_2$ or $-ONO$ (most often ending up as $-OH$ under the conditions employed) and $-C(NO_2)_3$, across the aromatic ring.[2] After the photo-induced electron

transfer (ET) step, the product forming reaction sequence is initiated by attack of trinitromethanide ion upon the radical cation ArH·⁺.[3,4] The nitro- and/or nitrito-trinitromethyl adducts are either stable enough to permit isolation or undergo more or less facile elimination of nitroform and/or nitrous acid to give substitution products $ArNO_2$ and/or $ArC(NO_2)_3$ [eqn. (1)]. The latter are unstable for Ar groups containing electron-donating substituents, being converted into ArCOOH and sometimes $ArNO_2$ under the photolysis conditions.[5]

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† Part XXXIX, see Ref. 1.
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$$ArH + C(NO_2)_4 \xrightarrow{h\nu} ArH^{\cdot +} \; NO_2(NO_2)_3C^-$$

$$\rightarrow Ar(H)(NO_2)C(NO_2)_3 + Ar(H)(ONO)C(NO_2)_3$$

$$\xrightarrow[\text{or } -HNO_2]{-HC(NO_2)_3} ArNO_2 + ArC(NO_2)_3 \qquad (1)$$

A consequence of this mechanism is that the percentages of the trinitromethyl group appearing at the various positions of the final product(s) may provide an index of reactivity for the attack of trinitromethanide ion upon the radical cation, thus adding potentially yet another prototype case of nucleophile–radical cation reactions, otherwise relatively scarce.[6]

High-level quantum chemical calculations (CASSCF/CASPT2), in combination with a simple model of radical cation reactivity [the valence bond configuration mixing (VBCM) model], were recently[7] applied to a number of nonalternant systems[8] and predictions made about the regiochemistry of their radical cations vs. nucleophiles. Only for dibenzofuran radical cation ($1^{\cdot +}$) were enough data available on its reactions with nucleophiles, among them trinitromethanide ion, to test reliably the prediction that nucleophilic attack should predominantly occur at C1 and C3; the experimental results[9] from the photolysis of 1–tetranitromethane were in accord with the calculated regiochemistry. The scarce experimental data available for the regioselectivity of dibenzothiophene radical cation ($2^{\cdot +}$) reactions[10] with nucleophiles were also in line with results of calculations, although here experimental problems still make conclusions less certain.

In order to probe further the use of tetranitromethane–ArH photolysis as a tool for acquiring information on the regioselectivity of $ArH^{\cdot +}$–nucleophile reactions, a study of benzofuran (3) has been performed. Electrophilic reactions of 3 are well documented,[11] the 2-position being the main position of attack by electrophiles. In addition, the 2,3-bond has considerable double-bond character, being formally part of an enol ether system, and and is therefore susceptible to addition by certain electrophiles, such as halogens. Finally, benzofuran is a non-alternant system and therefore different substitution patterns are expected for the $3^{\cdot +}$–nucleophile and the 3–electrophile reactions, respectively. This difference might be synthetically useful.

Results

Thermal addition of NO_2 to 3, a possible complication. At the outset we realized that nitrogen dioxide in the reaction mixture, known in for example the case of naphthalene to build up to a significant concentration during the photolysis period,[12] might add to the enol ether system

of the heterocyclic ring. In a control experiment of benzofuran (3) with a saturated solution of nitrogen dioxide in dichloromethane in the dark addition reactions did occur, yielding the 2,3-adducts 4–7 together with the nitrobenzofurans 8 and 9 (see below). In the event (see below) the 2,3-adducts 4–7 were not formed in the photolysis of the benzofuran–tetranitromethane charge transfer (CT) complex in dichloromethane, but did arise in the analogous reactions in acetonitrile solution.

Reaction of benzofuran (3) with nitrogen dioxide in dichloromethane in the dark at 20 °C and identification of adducts 4–7 and 3-nitrobenzofuran (8). A solution of 3 in dichloromethane saturated with nitrogen dioxide was stored in the dark at 20 °C. The composition of the mixture was monitored by withdrawing small samples for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and removal of nitrogen dioxide, was conducted at a temperature $\leqslant 0$ °C. The crude product mixtures were stored at -78 °C and were analysed (Table 1) by ^{1}H NMR spectroscopy as soon as possible. The final solution (after 6 h) contained a mixture of adducts 4 (11%), 5 (24%), 6 (24%) and 7 (12%), and nitrobenzofurans 8 (12%) and 9 (2%). The components of the mixture were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents.

The structure of the first material eluted was determined by single-crystal X-ray analysis. A perspective drawing of 3-nitrobenzofuran (8), $C_8H_5NO_3$, is presented in Fig. 1, and the corresponding atomic coordinates are given in Table 2. In itself this structure is unremarkable, but compound 8 was formed also during the crystallization of *t*-3-nitro-*r*-2-trinitromethyl-2,3-dihydrobenzofuran (10) (see below), and it was thus important to confirm unequivocally the position of the nitro substituent.

The epimeric 2,3-dinitro adducts 4 and 5 were the next compounds eluted, and in that order. The structure of *r*-2,*t*-3-dinitro-2,3-dihydrobenzofuran (5), $C_8H_6N_2O_5$, was determined by single-crystal X-ray analysis. A perspective drawing is presented in Fig. 2, and corresponding atomic coordinates are given in Table 3. In the solid state the heterocyclic ring is slightly buckled [torsional angles: C(2)–C(3)–C(3A)–C(7A) 3.7(2)°; C(2)–O(1)–C(7A)–C(3A) $-8.5(2)°$] with the two nitro groups at a torsional angle: N(2)–C(2)–C(3)–N(3) $-129.6°$. The spectroscopic data for the *trans*-dinitro adduct 5 were consistent with the established structure, and the appearance of the ^{1}H NMR signals for H2 and H3 as broad singlets were in accord with the torsional angle H(2)–C(2)–C(3)–H(3) 113.5(1)°.
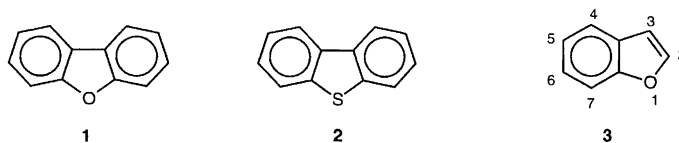
1

2

3

Table 1 Overview of yields of products from the reaction of benzofuran (0.53 mol dm⁻³) in dichloromethane saturated with nitrogen dioxide in the dark at 20 °C.

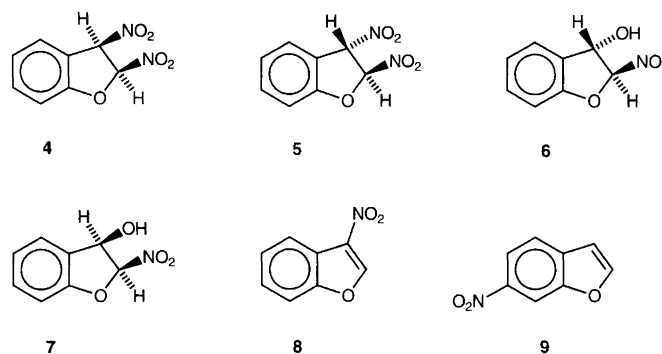Table 1 Overview of yields of products from the reaction of benzofuran $(0.53 \text{ mol dm}^{-3})$ in dichloromethane saturated with nitrogen dioxide in the dark at 20 °C.

	Yield (%)						
t/h	4	5	6	7	8	9	Unidentified products
2	11.8	25.2	23.0	11.8	9.6	2.2	16.3
4	11.2	24.2	23.9	11.8	10.6	1.8	16.5
6	11.3	23.6	23.6	11.8	11.8	1.8	16.1

Table 2. Fractional coordinates for atoms in 3-nitrobenzofuran (8).[a].

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/Å^2$
O(1)	2895(2)	1753(2)	747(1)	28(1)
O(11)	−2668(2)	1900(2)	4619(1)	40(1)
O(12)	−4519(2)	2888(2)	2760(1)	38(1)
N(1)	−2770(2)	2351(2)	3176(2)	27(1)
C(2)	1285(2)	1770(2)	2176(2)	26(1)
C(3)	−749(2)	2254(2)	1896(2)	22(1)
C(3A)	−468(2)	2586(2)	153(2)	21(1)
C(4)	−1823(2)	3101(2)	−915(2)	25(1)
C(5)	−787(3)	3246(2)	−2584(2)	30(1)
C(6)	1528(3)	2892(2)	−3191(2)	31(1)
C(7)	2892(3)	2383(2)	−2152(2)	29(1)
C(7A)	1834(2)	2247(2)	−493(2)	23(1)

[a]The equivalent isotropic temperature factor in Tables 2, 3, 5 and 6 is defined as one-third of the orthogonalized U_{ij} tensor $(Å^2)$.

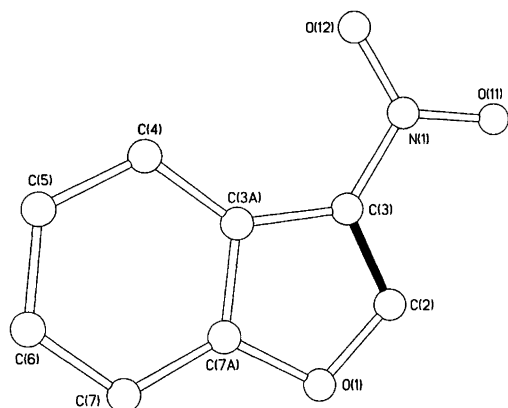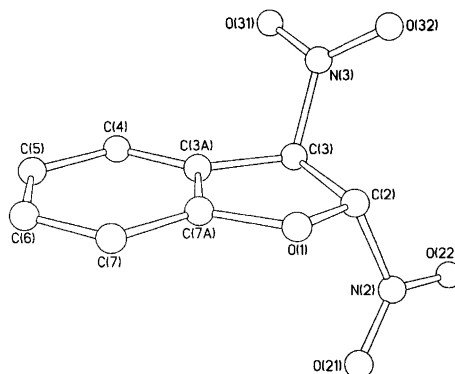
Fig. 1. Perspective drawing of compound 8. The double bond is shown in black in this and subsequent figures.

Fig. 2. Perspective drawing of compound 5.

The spectroscopic data for the 2,3-dinitro adducts 4 and 5 were consistent with their assignment as epimers, and in particular their ¹³C NMR spectra were closely similar (Experimental section). There were significant differences in the ¹H NMR chemical shifts for the CH–NO₂ protons; for the cis-dinitro adduct 4 δ (H2) 6.23, δ (H3) 6.58, and for the trans-dinitro adduct 6 δ (H2) 6.82, δ (H3) 6.23. These differences in ¹H NMR chemical shift for the epimers are undoubtedly due to differences in the orientations of the nitro groups in the two adducts.[13] For example, if the reasonable assumption is made that the conformation of 5 is maintained in solution, the deshielding of H2 can be seen as being due to the proximate O(32) atom, while the shielding of H3 arises because H3 is close to perpendicular to the planes of the C3-nitro group.

The epimeric 3-hydroxy-2-nitro adducts 6 and 7 were the final compounds eluted from the HPLC column, and in that order. All crystals of adduct 7 were twinned but the structure of this adduct was indicated by the preliminary results of a single-crystal X-ray analysis.* A perspective drawing of c-3-hydroxy-r-2-nitro-2,3-dihydrobenzofuran (7) is presented in Fig. 3. The spectroscopic data for adducts 6 and 7 were consistent with their

* Crystal data for a twinned crystal of c-3-hydroxy-r-2-nitro-2,3-dihydrobenzofuran (7), $C_8H_7NO_4$, m.p. 114–116 °C, $a = 4.850(1)$, $b = 9.542(2)$, $c = 17.120(3)$, $V = 792(1)$ $Å^3$.

Table 3. Fractional coordinates for atoms in *r*-2-*t*-3-dinitro-2,3-dihydrobenzofuran (5).

| Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/\text{Å}^2$
O(1)	767(1)	−4002(2)	4049(1)	29(1)
O(21)	964(1)	−5312(2)	2511(1)	40(1)
O(22)	2209(1)	−4109(2)	2523(1)	42(1)
O(31)	1804(1)	2109(2)	4002(1)	32(1)
O(32)	2501(1)	−502(2)	4460(1)	35(1)
N(2)	1543(1)	−4354(2)	2827(1)	26(1)
N(3)	1933(1)	300(2)	4037(1)	23(1)
C(2)	1460(1)	−3280(3)	3673(1)	23(1)
C(3)	1340(1)	−1009(2)	3484(1)	20(1)
C(3A)	449(1)	−702(3)	3674(1)	20(1)
C(4)	−71(1)	956(3)	3578(1)	25(1)
C(5)	−885(1)	720(3)	3786(1)	29(1)
C(6)	−1161(1)	−1124(3)	4082(1)	29(1)
C(7)	−641(1)	−2782(3)	4189(1)	28(1)
C(7A)	162(1)	−2506(3)	3977(1)	22(1)
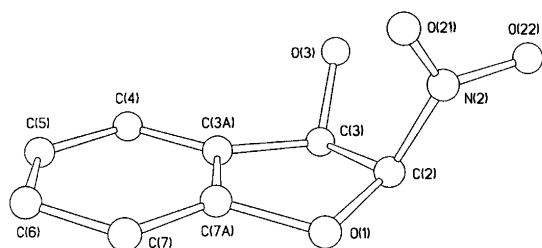
Fig. 3. Perspective drawing of compound **7**.

assignment as epimers (Experimental section). In particular, the ¹³C NMR chemical shifts for C2 and C3 in the two adducts indicated the location of the nitro and hydroxy functions, respectively. Notably, although the ¹H NMR signals for H2 and H3 in the *trans*-adduct **8** appeared as broad singlets, the H2,H3-coupling constant in the *cis*-adduct **9** was 6.8 Hz, in contrast to that found for the *cis*-dinitro adduct **6**.

Photochemistry of benzofuran with tetranitromethane. General. The photochemical experiments were performed with filtered light exciting only the CT band (cut-off at 435 nm, 5 cm water IR filter, with a 300 W incandescent lamp),[12] and small samples were withdrawn for analysis at suitable intervals. The work-up procedure, involving evaporation of solvent and excess tetranitromethane, was conducted at a temperature of ⩽0 °C. The crude product mixtures were stored at −78 °C and were analysed (¹H NMR spectroscopy, see Experimental section) as soon as possible.

Photochemistry in dichloromethane at 20 °C and the identification of adducts 10–19, 4-trinitromethylbenzofuran (21) and 4-nitrobenzofuran (22). A solution of **3** and tetranitromethane in dichloromethane was irradiated at 20 °C. The composition was monitored by withdrawing samples for NMR spectral analysis (Table 4). The final solution (after 6 h) contained a mixture of adducts **10** (13%), **11** (7%), **12** (6%), **13** (11%), **14** (6.5%), **15** (18.5%), **16**

(6%), **17** (9%), **18** (3%), **19** (1%), and **20** (2%), nitrobenzofurans **9** (1%) and **22** (5%), 4-trinitromethylbenzofuran **21** (3%), unidentified adducts (total 7%), and unidentified aromatic compounds (total 2%). The components of this mixture were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as eluting solvents. The order of elution of materials from the HPLC column is given in the Experimental section, but here for simplicity the evidence for structural assignments will be presented for groups of products; the assignment of structure to the dinitro dimer **19** will be deferred until the isolation of its isomer **20** from the photolysis of the CT complex benzofuran–tetranitromethane in 1,1,1,3,3,3-hexafluoropropan-2-ol is described (see below).

(A) Nitro–trinitromethyl adducts 10–13 and nitronic ester 14. The connectivity of each of the four nitro–trinitromethyl adducts **10–13** was determined by a consideration of the results of nuclear Overhauser experiments and reverse-detected heteronuclear correlation spectra (HMQC). For the 3-nitro-2-trinitromethyl adducts **10** and **11** the ¹³C NMR resonances for C2 and C3 were **10** (C2, δ 81.1; C3, δ 87.8) and **11** (C2, δ 78.9; C3, δ 85.3); these carbon resonances for C3 lie comfortably in the range of values seen for C3 in the 2,3-dinitro adducts **4** and **5**. For the 2-nitro-3-trinitromethyl adducts **12** and **13** the corresponding carbon resonances were **12** (C2, δ 105.0; C3, δ 52.1) and **13** (C2, δ 100.1; C3, δ 54.4); here the carbon resonances are comparable with those for C2 in the 2,3-dinitro adducts **4** and **5**, and the carbon resonances for C2 indicate clearly the point of attachment of the trinitromethyl function. For the pair of epimers (**10** and **11**) the *trans* epimer exhibits a marked downfield shift in the ¹H NMR chemical shift for the proton *vicinal* to the nitro function, H2 (**10** δ 6.81, **11** δ 6.11), similar to that seen for the *trans*-epimer of the pair of 2,3-dinitro adducts **4** and **5**. Interestingly, for the 2-nitro-3-trinitromethyl adduct epimeric pair, **12** and **13**, a similar downfield shift is seen in the *trans*-epimer **12** for the proton *vicinal* to the nitro function, H3 (**12** δ 5.61, **13** δ 4.86). Within each epimeric pair of adducts, **10** and **11**, and **12** and **13**, the *trans*-epimer was eluted first from the HPLC column.

The structure of the nitronic ester **14**, $C_9H_6N_2O_5$, was determined by single-crystal X-ray analysis. A perspective drawing is presented in Fig. 4, and corresponding atomic coordinates are given in Table 5. In this structure the nitro group and the C(8)–N(2) double bond are close to coplanar [torsional angle: O(11)–N(1)–C(8)–N(2) 7.1(2)°], and the coupling constant, $J_{H2,H3} = 7.8$ Hz, is in accord with the observed torsional angle: H(2)–C(2)–C(3)–H(3) 10.4(1)°.

(B) 3-Hydroxy-2-trinitromethyl adducts 15 and 16. The connectivity in these epimeric adducts was established from a consideration of the results of nuclear Overhauser experiments and reverse-detected heteronuclear correlation spectra (HMQC). The relative stereochemistry of

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Table 4. Yields of products from the photolysis $(\lambda > 435 \, nm)$ in dichloromethane of benzofuran $(0.53 \, mol \, dm^{-3})$ and tetranitromethane $(1.06 \, mol \, dm^{-3})$.

t/h	Yield (%)											Total adducts[a]	9	21	22	Total aromatics[a]
	10	11	12	13	14	15	16	17	18	19	20					
At 20 °C																
2	8.4	6.8	9.1	14.6	7.1	20.2	2.9	8.7	3.4	0.7	1.0	90.2	1.2	2.3	4.3	9.8
4	12.9	5.6	6.5	12.0	6.0	18.3	8.1	9.2	2.8	0.9	1.2	91.2	1.2	2.0	4.2	8.8
6	13.3	6.6	6.0	10.8	6.5	18.5	5.6	9.1	3.3	1.3	1.7	89.3	1.4	2.7	4.9	10.7
At −20 °C																
2	10.7	9.2	11.0	8.6	4.2	15.6	2.4	9.7	4.6	2.4	9.3	93.4	2.5	0.8	1.7	6.6
4	8.8	10.8	10.7	7.8	3.8	14.7	2.8	9.2	5.4	2.9	7.4	89.7	3.7	1.5	2.9	10.3
6	9.1	7.9	8.0	9.4	4.2	17.8	2.8	8.9	4.0	3.5	6.5	89.3	3.6	1.8	3.0	10.7

[a]Including unidentified material.
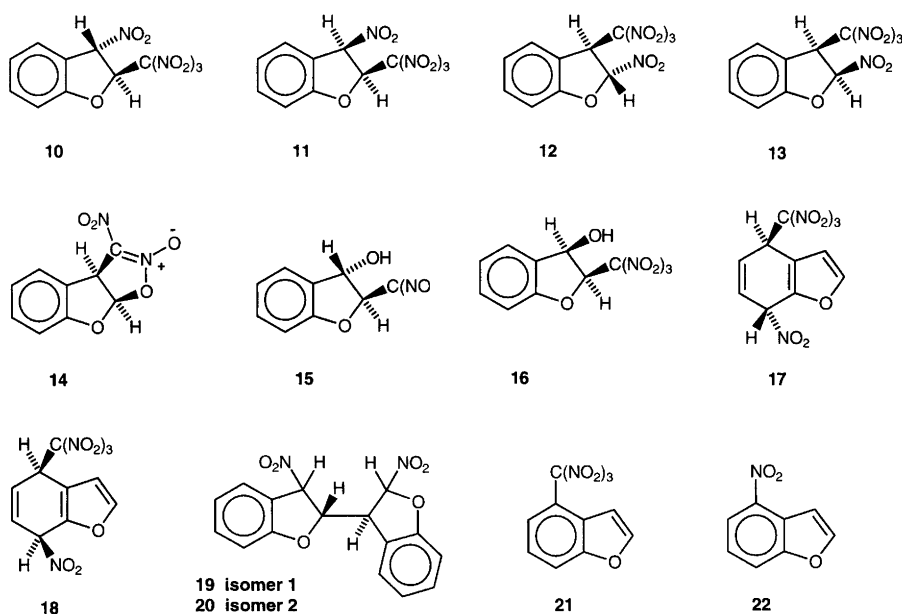
adducts **15** and **16** was assigned tentatively initially on the basis of the elution order from the HPLC column, but confirmed subsequently by nuclear Overhauser

Fig. 4. Perspective drawing of compound **14**.

experiments. For the *trans*-epimer **15** irradiation at δ 5.67 (H2) gave no enhancement of the H3-signal (δ 5.77), but a corresponding experiment for the *cis*-epimer **16** resulted in a marked enhancement of the H3-signal (δ 5.96, 5.5%) on irradiation at δ 5.78 (H2).

(C)   7-Nitro-4-trinitromethyl-4,7-dihydrobenzofurans   17 and 18. The connectivity in each of these compounds was established by a consideration of the results of nuclear Overhauser experiments and reverse-detected heteronuclear correlation spectra (HMQC). The assignment of stereochemistry is based on the known order of elution of the analogous epimeric 4-nitro-1-trinitromethyl-1,4-dihydrodibenzofurans **23** and **24** from a cyanopropyl HPLC column using hexane–dichloromethane mixtures as the eluting solvent.[9a]

(D) 4-Trinitromethylbenzofuran (21) and 4-nitrobenzofuran (22). The structure of 4-trinitromethylbenzofuran (**21**), $C_9H_5N_3O_7$, was determined by single-crystal
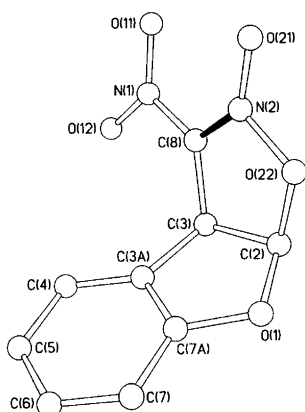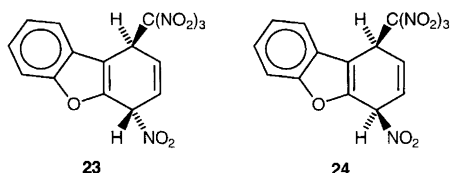
Table 5. Fractional coordinates for atoms in nitronic ester (14).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/Å^2$
O(1)	9011(1)	2339(2)	4446(1)	31(1)
O(11)	4640(1)	−3442(3)	2696(1)	46(1)
O(12)	5622(1)	−4996(2)	3849(1)	43(1)
O(21)	5684(1)	1073(3)	2357(1)	41(1)
O(22)	7731(1)	1866(2)	3161(1)	33(1)
N(1)	5522(1)	−3431(3)	3310(1)	33(1)
N(2)	6505(1)	351(3)	2944(1)	29(1)
C(2)	8652(2)	632(3)	3812(1)	27(1)
C(3)	7793(2)	−1505(3)	4084(1)	25(1)
C(3A)	7560(2)	−532(3)	4880(1)	25(1)
C(4)	6822(2)	−1477(3)	5429(1)	30(1)
C(5)	6883(2)	−190(3)	6139(1)	34(1)
C(6)	7652(2)	1991(4)	6293(1)	35(1)
C(7)	8372(2)	2980(3)	5741(1)	31(1)
C(7A)	8294(2)	1661(3)	5043(1)	26(1)
C(8)	6560(2)	−1527(3)	3434(1)	26(1)

Table 6. Fractional coordinates for atoms in 4-trinitromethyl-benzofuran (21).

Atom	$10^4 X/a$	$10^4 Y/b$	$10^4 Z/c$	$10^3 U/Å^2$
O(1)	3526(2)	4869(2)	3273(2)	42(1)
O(11)	−4398(2)	−1007(2)	3729(2)	51(1)
O(12)	−5578(2)	962(2)	2696(2)	51(1)
O(21)	−422(2)	−603(2)	1415(2)	34(1)
O(22)	−3330(2)	−1957(2)	1200(2)	57(1)
O(31)	−2965(2)	1526(2)	−3(2)	48(1)
O(32)	−2882(2)	3703(2)	1558(2)	43(1)
N(1)	−4346(3)	241(3)	2975(2)	37(1)
N(2)	−2038(3)	−704(3)	1578(2)	33(1)
N(3)	−2815(2)	2180(3)	1185(2)	33(1)
C(2)	3059(3)	4612(3)	1880(3)	42(1)
C(3)	1389(3)	3522(3)	1600(2)	33(1)
C(3A)	659(3)	3008(3)	2912(2)	26(1)
C(4)	−998(3)	1950(3)	3383(2)	25(1)
C(5)	−1189(3)	1878(3)	4805(2)	34(1)
C(6)	221(4)	2803(3)	5748(2)	41(1)
C(7)	1863(4)	3806(3)	5310(3)	40(1)
C(7A)	2027(3)	3880(3)	3907(2)	32(1)
C(8)	−2472(3)	964(3)	2353(2)	27(1)

23   24

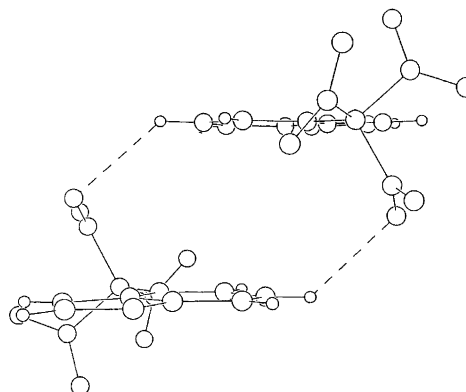Fig. 6. Orientations of two molecules in the unit cell of compound 21.

X-ray analysis. A perspective drawing is presented in Fig. 5, and corresponding atomic coordinates are given in Table 6. In the solid state, the two molecules in the unit cell are orientated as shown in Fig. 6, with a H(6A)···O(21B) distance of 2.54 Å, and a C(6A)–H(6A)–O(21B) angle 137°. The spectroscopic data for compound 21 were in accord with the established structure.

4-Nitrobenzofuran (22) was isolated as an oil, and its structure was established from the observed multiplicity of the ¹H NMR signals and the results of nuclear Overhauser experiments (Experimental section).

Photochemistry in dichloromethane at −20 °C. The photolysis of the 3–tetranitromethane charge-transfer

Fig. 5. Perspective drawing of compound 21.

complex at −20 °C gave similar product mixtures (Table 4) as the reaction at 20 °C above.

Photochemistry in acetonitrile at 20 and at −20 °C. The product compositions for the analogous photochemical reactions in acetonitrile at 20 and −20 °C are given in Table 7. The notable difference between the products from the reactions in dichloromethane and those in acetonitrile is in the formation of 2,3-dinitro adducts 4 and 5, and 3-hydroxy-2-nitro adducts 6 and 7 in the latter solvent.

Photochemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), and the identification of 6-nitrobenzofuran (9) and the dinitro dimers 19 and 20. The photolysis of the 3–tetranitromethane CT complex at 20 °C in HFP gave a mixture of the nitrobenzofurans 8 (2%), 9 (13.5%) and 22 (6%), the dinitro dimers 19 (29%) and 20 (35%), and other compounds (total 15%) not identifiable by ¹H NMR in the mixture, including some 4-trinitro-

Table 7. Yields of products from the photolysis in acetonitrile of benzofuran (0.53 mol dm^{-3}) and tetranitromethane (1.06 mol dm^{-3}).

	Yield (%)																				
t/h	4	5	6	7	10	11	12	13	14	15	16	17	18	19	20	Total adducts[a]	8	9	21	22	Total aromatics[a]
At 20 °C																					
2	3.8	3.3	1.2	2.2	7.1	6.6	2.9	7.1	6.7	16.3	5.4	2.9	3.3	4.4	4.5	85.8	0.7	7.1	1.4	1.4	14.2
4	2.7	2.7	1.4	1.8	8.7	6.9	2.5	5.8	5.7	14.6	3.4	3.6	3.4	5.2	5.5	81.6	1.9	6.8	2.9	2.9	18.4
6	2.2	2.0	1.5	2.2	9.0	7.8	3.1	4.9	5.0	15.2	4.0	4.5	3.9	4.9	4.7	82.0	1.8	6.3	3.6	1.8	18.0
At −20 °C																					
2	2.7	3.0	0.3	—	2.7	1.8	3.9	6.0	6.5	24.4	3.0	1.5	0.9	4.5	3.6	72.3	—	16.0	2.1	2.1	27.7
4	2.4	3.1	0.5	—	4.3	3.3	3.6	5.5	3.8	23.8	2.4	2.4	1.6	4.5	3.1	71.4	—	17.9	2.4	2.4	28.6
6	2.3	3.9	0.7	—	3.9	3.2	4.6	6.9	4.6	22.8	2.3	3.0	1.6	4.3	3.0	74.7	—	15.0	2.3	2.3	25.3

[a]Including unidentified material.

methylbenzofuran (**21**) (Table 8). Chromatography on a silica gel Chromatotron plate allowed the separation of some trinitromethyl compound **21**, 6-nitrobenzofuran (**9**), and the dinitro dimers **19** and **20**. The mass spectrum of 6-nitrobenzofuran (**9**) was identical with that of an authentic sample.

The isomeric dinitro dimers were identified tentatively as having structures **19** and **20** from a consideration of the multiplicity of the signals in their ^{1}H NMR spectra, the results of nuclear Overhauser experiments and of reverse-detected heteronuclear correlation spectra (HMQC, HMBC) (Experimental section). Unfortunately neither compound, **19** or **20**, could be induced to crystallize, but it is clear from the above data that they are stereoisomers of the structure 3-(3'-nitro-2',3'-dihydrobenzofuran-2'-yl)-2-nitro-2,3-dihydrobenzofuran. In each compound the ^{13}C NMR resonance for C2 was typical for a 2-nitro-2,3-dihydrobenzofuran (**19**, δ 111.1; **20**, δ 109.5), and that for C3' typical for a 3-nitro-2,3-dihydrobenzofuran (**19**, δ 83.6; **20**, δ 84.8). The ^{13}C NMR resonances for the bridging carbons were for C3: **19**, δ 53.5 and **20**, δ 51.3, and for C2': **19**, δ 91.8 and **20**, δ 84.2.

Reaction of benzofuran (3) with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) in the dark at 20 °C. A solution of **3** in HFP saturated with nitrogen

dioxide was stored in the dark at 20 °C, and the composition of the mixture determined by ^{1}H NMR spectral analysis (Table 9) as for the analogous reaction in dichloromethane. After 6 h the mixture contained the nitrobenzofurans **8** (1%), **9** (38%) and **22** (13%), dinitro dimers **19** (10%) and **20** (17%), and unidentified material (21%).

Theoretical calculations. It was recently[7] shown that the Pross–Shaik VBCM model of the transition state of the reaction between an aromatic radical cation ArH$^{•+}$ and a nucleophile Nu$^-$, the resonance hybrid between the initial state and one in which one electron has been transferred from the nucleophile to the LUMO of ArH$^{•+}$ to give the excited triplet state of ArH [eqn. (2)],[14] can be adapted to high-level quantum chemical calculations of the CASSCF type. In order to make the necessary connection, the LUMO orbital referred to above was denoted the 'transfer orbital' (TO) since it is the orbital which receives the electron. The Pross–Shaik model, its adaptation to the CASSCF method, the methodological problems of the approach and its application to reactions of radical cations of non-alternant systems, were discussed in detail.[7]

$$ArH^{•+} + Nu^- \rightleftharpoons {}^3(^•ArH^-)Nu^• \tag{2}$$
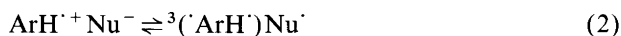
From the model of eqn. (2) the regiochemistry of

Table 8. Yields of products from the photolysis of benzofuran (0.53 mol dm^{-3}) and tetranitromethane (1.06 mol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C.

	Yield (%)					
t/h	19	20	Total adducts[a]	8	9	22	Total aromatics[a]
2	23.8	37.6	69.3	1.0	17.8	5.9	30.7
4	26.8	35.7	71.4	1.8	16.1	5.4	28.6
6	28.9	34.6	73.1	1.9	13.5	5.8	26.9

[a]Including unidentified material.

Table 9. Yields of products from the reaction of benzofuran (0.53 mol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol saturated with nitrogen dioxide in the dark at 20 °C.

	Yield (%)					
t/h	19	20	Total adducts[a]	8	9	22	Total aromatics[a]
2	9.4	16.0	31.9	0.7	37.7	14.5	68.1
4	9.4	18.1	36.9	1.2	35.6	12.5	63.1
6	9.7	17.4	34.2	1.3	38.1	12.9	65.8

[a]Including unidentified material.

nucleophilic attack upon ArH˙⁺ was shown to be controlled by a combination of two indices, namely the spin density of the triplet species and the coefficient of the TO of the radical cation. If both have significant values at a specific site, there should be a high probability of attack by a nucleophile; if either or both of the indices are small, the probability of attack at the corresponding site should be low.

CASPT2 calculations of the total energies of benzofuran, its triplet and radical cation were performed as described before, and the results are shown in Table 10. Table 11 gives the relevant reactivity indices for the triplet and radical cation.
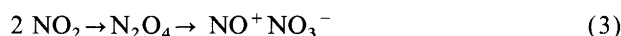
Table 10. CASPT2 total energies, relative energies and dipole moments for the different electronic states of benzofuran (3) and its radical cation (3˙⁺).

State	No. of CCSFs[a]	Total energy/au	Excitation energy/eV	Dipole moment/D
3				
¹A′	1764	−382.500 180	—	1.17[a]
1 ³A′	2352	−382.195 195	3.40[b]	1.51
2 ³A′		−382.182 195	4.12	1.19
3˙⁺				
1 ²A″	2352	−382.375 431	8.24[c]	
2 ²A″		−382.348 951	8.60[d]	

[a]Experimental value 0.79 D;[24] a previous STO-3G calculation gave 0.64 D.[25] [b]Experimental value 3.12 eV in ethanol at 77 K.[26] [c]Vertical $IP = 8.36$ eV;[27,28] adiabatic $IP = 8.27$ eV.[5] [d]Vertical $IP = 8.89$ eV.[5]

Discussion

Possible mechanisms involved. The photochemical reactions of tetranitromethane with aromatics show considerable mechanistic complexity,[2] making clearcut assignments of products to particular mechanisms difficult. The products resulting from the mechanism of interest here, coupling of trinitromethanide ion with 3˙⁺, are relatively easy to identify by their C–C(NO₂)₃ connectivity. The products originating from initial reaction between NO₂ and 3 and/or 3˙⁺ are less easily disentangled. In the case of 3, we have clearly identified one undesired mechanism, namely addition of NO₂ to the 2,3-bond with formation of adducts 4–7, dinitro dimers 19 and 20 and possibly 3-nitrobenzofuran (8) (see below). A further complication is nitration by NO₂, lately shown[15] to proceed by an ET mechanism mediated by NO⁺ [eqns. (3)–(5)], which may be difficult to distinguish from nitration via photochemically produced ArH˙⁺ and NO₂. For dibenzofuran (1), a related substrate, the ET mediated 1–NO₂ reaction has been shown to proceed with ease.[9b]

$$2\,NO_2 \rightarrow N_2O_4 \rightarrow NO^+NO_3^- \tag{3}$$

$$NO^+ + ArH \rightarrow NO + ArH^{˙+} \tag{4}$$

$$ArH^{˙+} + NO_2 \rightarrow Ar^+(H)NO_2 \rightarrow ArNO_2 + H^+ \tag{5}$$
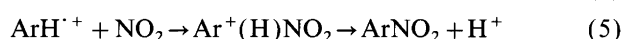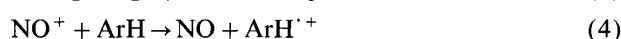
The thermal reaction of 3 with nitrogen dioxide in dichloromethane or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) in the dark at 20 °C. Nitro substitution product and adduct distributions are summarized for both thermal and photochemical reactions in Table 12, whereas the regiochemistry of trinitromethanide ion attack on 3˙⁺ is

Table 11. Transfer orbital (TO) coefficients and spin densities of the radical cation and triplet state of benzofuran (3).

State	Index	Atom no. 1	2	3	4	5	6	7
1 ²A″	Spin density	0.004	0.280	−0.041	0.014	0.046	0.333	−0.061
	TO coefficient	0.31	−0.71	0.33	−0.52	−0.04	0.63	−0.42
1 ³A′	Spin density	0.025	0.494	0.078	0.332	0.051	0.482	0.181

Table 12. Nitro product distributions from reactions of benzofuran at 20 °C (data from Tables 1, 4, 7 and 9).

Reaction conditions	Isomer distribution (%) 3-NO₂ (8)	6-NO₂ (9)	4-NO₂ (22)	Remark on adducts
Tetranitromethane-*hv* in DCM	—	1	5	Dinitro dimers 19 and 20 (3%); (NO₂)₃C based adducts (80%)
Tetranitromethane-*hv* in AN	2	6	2	Dinitro adducts 4–7 (8%); dinitro dimers 19 and 20 (10%); (NO₂)₃C based adducts (57%)
Tetranitromethane-*hv* in HFP	2	14	6	Dinitro dimers 19 and 20 (64%)
Thermal, NO₂ in DCM	12	2	—	Dinitro adducts 4–7 (70%)
Thermal, NO₂ in HFP	1	38	13	Dinitro dimers 19 and 20 (27%)

Table 13. Overview of the regiochemistry of trinitromethanide ion attack on the benzofuran radical cation (3˙⁺) after photolysis for 6 h (data from Tables 4 and 7).

Solvent	$T/°C$	Attack at C2 (%)[a]	Attack at C3 (%)[b]	Attack at C4 (%)[c]	NO_2 based products (%)[d,e]	Nitrobenzo-furans (%)[f]
DCM	20	44	23	15	3	6
DCM	−20	38	22	15	10	7
AN	20	36	13	12	18	10
AN	−20	32	16	7	17	17
HFP	20	0	0	0	64	21

[a]Compounds **10+11+15+16**. [b]Compounds **12+13+14**. [c]Compounds **17+18+21**. [d]Compounds **4+5+6+7+19+20**. [e]Level of unknown adducts ⩽5%, except in HFP (≈10%). [f]Level of unknown aromatics ⩽6%.

summarized in Table 13. These Tables will be the basis for the discussion to follow.

The predominant products **4–7** (total 70%) formed in the thermal reaction between **3** and NO_2 in dichloromethane are formed by radical addition of nitrogen dioxide to the unsaturated system of the enol ether function in the heterocyclic ring. This addition is seen as occurring by initial attack of nitrogen dioxide at C2 to give the benzylic radical **25** (Scheme 1). Subsequent radical coupling of nitrogen dioxide at C3 in **25** could occur *syn* or *anti* to the first nitro group and with both C–NO_2, to give **4** and **5**, or C–ONO bond formation, followed by hydrolysis to give adducts **6** and **7**. 3-Nitrobenzofuran (**8**), formed in 12% yield, is presumably formed by elimination of HNO_2 from **4**, **5** and or H_2O from **6**, **7**. This is similar to the chlorination of **3** by chlorine where addition to the 2,3-bond, followed by elimination of HCl, is the pathway to 3-chlorobenzofuran.[16] It should also be noted that very little 6-nitrobenzofuran **9** is formed, and none at all of the dinitro dimers **19** and **20** (see comment below).
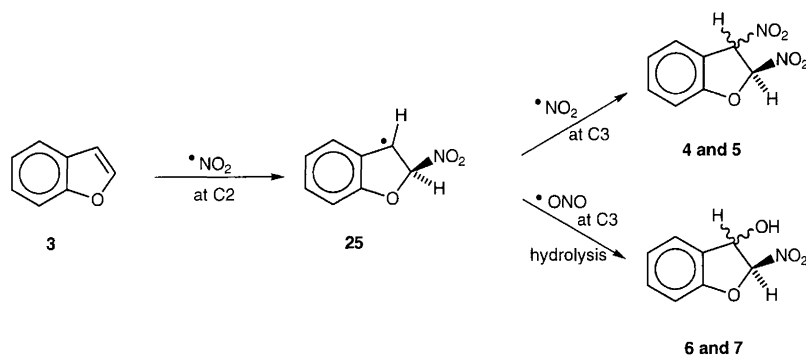
The reaction of **3** in HFP saturated with nitrogen dioxide in the dark gave the dinitro dimers **19** and **20** (total 27%), accompanied by the nitroarenes **8** (1%), **9** (38%) and **22** (13%). We have earlier[17] found that HFP is a favourable solvent for the nitration of ArH by NO_2, no doubt due to its high polarity and capability to solvate negatively charged ions by hydrogen bonding[18] [forcing the equilibrium of eqn. (3) to the right]. The product-forming step of the ET mechanism, eqn. (5),

should be regiochemically controlled by the spin density distribution of 3˙⁺ (see below) since it is a simple coupling
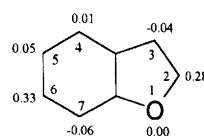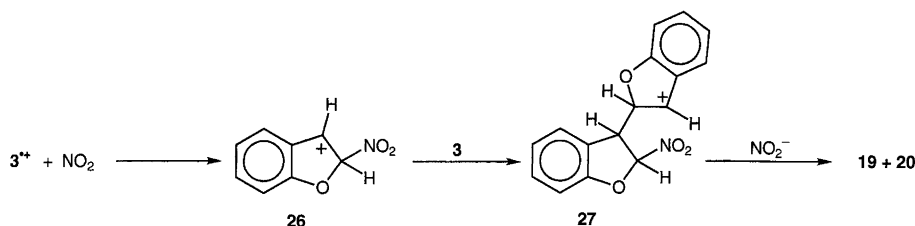

between two radicals. Thus we predict that the 6-position should be the most reactive one, followed by the 2-position; experimentally we observe that 6-nitrobenzofuran **9** is the major isomer (39%), followed by the 4-isomer **22** (13%). This would seem to be at odds with the prediction that the 2-nitro isomer should be nearly as prevalent as the 6-nitro isomer, but one can resolve this apparent anomaly by assuming that the dinitro dimers **19** and **20** (together formed in 27% yield) are the final products from coupling between NO_2 and the 2-position of 3˙⁺. The intermediate carbocation formed, **26** in Scheme 2, should be very reactive toward the 2-position of a second molecule of **3**, analogously to the extreme reactivity of furans in acid-catalyzed oligomerizations,[19] thus affording the dimeric carbocation **27** which can react with nitrite ion or nitrous acid present.
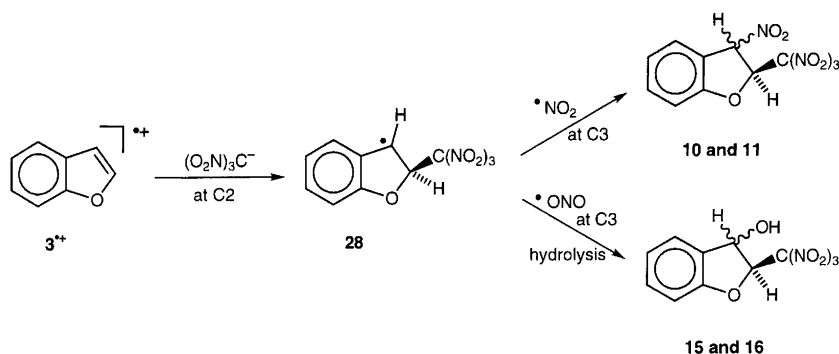
The formation of **19** and **20** can also be formally thought of as a radical process in which radical **25** attacks a second molecule of **3** at C-2 with formation of a dimeric radical which gives **19** or **20** by reaction with a second NO_2. However, we deem this mechanism less likely in view of the outcome of the dichloromethane
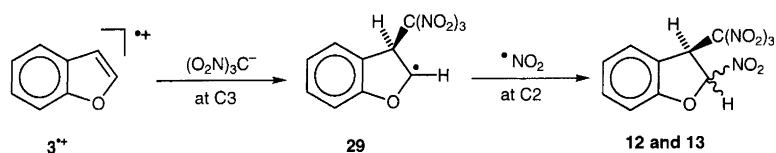

Scheme 1.

$$3^{\cdot+} + NO_2 \longrightarrow \mathbf{26} \xrightarrow{3} \mathbf{27} \xrightarrow{NO_2^-} 19 + 20$$

Scheme 2.

$$3^{\cdot+} \xrightarrow[\text{at C2}]{(O_2N)_3C^-} \mathbf{28}$$

at C3 → **10 and 11**

·NO₂ at C3 / ·ONO at C3 / hydrolysis → **15 and 16**

Scheme 3.

$$3^{\cdot+} \xrightarrow[\text{at C3}]{(O_2N)_3C^-} \mathbf{29} \xrightarrow[\text{at C2}]{·NO_2} \mathbf{12 \text{ and } 13}$$

Scheme 4.

reaction; no dinitro dimer is formed in spite of the fact that the intermediacy of radical **25** is strongly implicated by the formation in 70% yield of monomeric adducts **4–7**. On the contrary, the low yield of 6-nitrobenzofuran **9** is consistent with the absence of **19** and **22**, indicating that NO_2 nitration of **3** via the mechanism of eqns. (3)–(5) is a slow process in dichloromethane.

The regiochemistry of trinitromethanide ion attack on the radical cation of 3 in the photochemistry of the 3–tetranitromethane CT complex in dichloromethane. Adducts **10**, **11**, **15** and **16** arise by initial attack of trinitromethanide ion at C2 of the benzofuran radical cation **3**$^{·+}$ to give the benzylic radical **28** (Scheme 3). Radical coupling of nitrogen dioxide at C3 in **28** occurs predominantly, but not exclusively, *anti* to the trinitromethyl group and with both $C–NO_2$ and $C–ONO$ bond formation; hydrolysis of the intermediate nitrite esters occurs either in the reaction medium or during the work-up procedure.

Adducts **12**, **13** and **14** arise by initial attack of trinitromethanide ion at C3 in **3**$^{·+}$ to give the radical **29** (Scheme 4). Radical coupling of **29** with nitrogen dioxide with $C–NO_2$ bond formation at C2 would yield adducts **12** and **13**. The nitronic ester **14** arises from the carbon radical **29** by a process in which the radical centre

interacts with the proximate trinitromethyl group leading to cyclization and extrusion of a molecule of nitrogen dioxide from the former trinitromethyl group (Scheme 5). This reaction is analogous to earlier reports of denitrocyclizations of trinitromethyl derivatives to give nitronic esters.[20]

Adducts **17** and **18** and 4-trinitromethylbenzofuran (**21**) clearly arise from attack of trinitromethanide ion at C4 in **3**$^{·+}$ to give the delocalized carbon radical **30** (Scheme 6). Radical coupling at C7 of **30** with nitrogen dioxide would yield the epimeric adducts **17** and **18**. The mode of formation of 4-trinitromethylbenzofuran (**21**) from radical **30** remains uncertain.

A low yield (3%) of dinitro dimers **19** and **20** is consistent with the low level of nitro products via the $3^{·+}–NO_2$ coupling pathway.

$$\mathbf{29} \longrightarrow \mathbf{14}$$
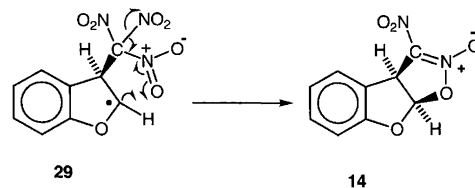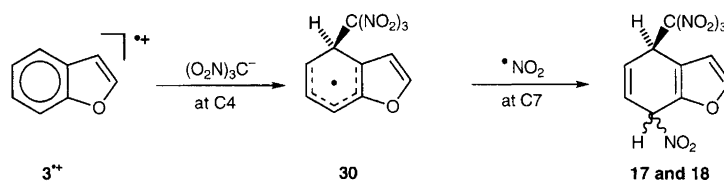
Scheme 5.

Scheme 6.

The regiochemistry of trinitromethanide ion attack on the radical cation of 3 in the photochemistry of the 3–tetranitromethane CT complex in acetonitrile. As seen from Tables 12 and 13, the yield of products formed by trinitromethanide ion attack upon $3^{\cdot +}$ decreases from 70 to 57% at the expense of NO_2 initiated ones on going from dichloromethane to acetonitrile. Dinitro adducts 4–7 appear in acetonitrile, as well as dinitro dimers 19 and 20 and an increased level of nitro substitution products. This points to increased competitiveness of the $3-NO_2$ and $3^{\cdot +}-NO_2$ reactions, presumably caused by the attenuation of trinitromethanide ion reactivity in acetonitrile relative to dichloromethane. Similar changes in product distribution have been observed for other substrates, for example 1,3-dimethylnaphthalene.[21]

The photochemistry of the 3–tetranitromethane CT complex in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP). Although some traces of 4-trinitromethylbenzofuran (21) were obtained from the title reaction, the majority of the products identified did not contain a trinitromethyl function. This outcome was expected in the light of the known suppression of nucleophilicity by HFP.[18] The dinitro dimers 19 and 20 were the major products (total 64%), accompanied by the nitroarenes 8 (2%), 9 (14%) and 22 (6%). It seems likely that the nitroarenes are formed by radical coupling of nitrogen dioxide with the benzofuran radical cation $3^{\cdot +}$. This is neatly accommodated within eqns. (3)–(5) and Scheme 2, where HFP would favour pathways involving $3^{\cdot +}-NO_2$ coupling.

Regioselectivity of trinitromethanide ion attack upon $3^{\cdot +}$. An overview of the regiochemistry of trinitromethanide ion attack on the benzofuran radical cation in dichloromethane and acetonitrile, as judged by the criteria discussed above, is given in Table 13. HFP is included to reiterate that the trinitromethanide ion reactivity is very low in that solvent. To compare experimental results with the theoretical calculations, the combination of TO coefficients at the various sites of the radical cation and spin densities of the triplet are shown below. From the principles mentioned above, the sites of highest reactivity are predicted to be C-2, C-4 and C-6. This is not entirely in agreement with the experimental results, which indicate the expected high reactivity at C-2 and C-4 but an unexpectedly high reactivity at C-3 and none at C-6. The reason(s) for the discrepancy is(are) not obvious, but one possibility is that the $ArH^{\cdot +}-(NO_2)_3C^-$ reaction is reversible and thus the regiochemistry is determined by

the stability of the neutral radicals formed (28, 29 or 30; Schemes 3, 4 and 6). A possibly similar situation was encountered for $1^{\cdot +}$-nucleophile reactions.[9]
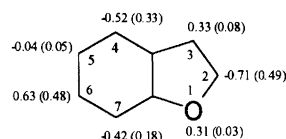
Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer with $SiMe_4$ as an internal standard. HPLC separations were carried out on a Varian 5000 liquid chromatograph equipped with an Alltech cyanopropyl column, and using a Varian UV-50 ultraviolet spectrometric detector and hexane–dichloromethane as solvent mixtures. Benzofuran and tetranitromethane were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH. 1,1,1,3,3,3-Hexafluoropropan-2-ol was purchased from Acros Organics.

WARNING. While we did not experience any incidents in working with tetranitromethane, it should be noted that its mixtures with hydrocarbons are detonative within certain concentration limits and that due care should be taken in handling mixtures of tetranitromethane and organic molecules.[22]

Reaction of benzofuran (3) with nitrogen dioxide in dichloromethane at 20 °C in the dark and the identification of 2,3-dinitro-2,3-dihydrobenzofurans (4 and 5), 3-hydroxy-2-nitro-2,3-dihydrobenzofurans (6 and 7) and 3-nitrobenzofuran (8). A solution of 3 (0.53 mol dm^{-3}) in dichloromethane saturated with nitrogen dioxide was stored in the dark at 20 °C. Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at $\leqslant 0$ °C, and the product composition determined by ^1H NMR spectral analysis (Table 1). After 6 h the product was a mixture of 3-nitrobenzofuran (8) (12%), 6-nitrobenzofuran (9) (2%), the epimeric 2,3-dinitro adducts (4) (11%) and (5) (24%), the epimeric 3-hydroxy-2-nitro adducts (6) (24%) and (7) (12%), and unidentified products (total 16%). The mixture was par-

tially separated into its components by HPLC and gave the following in elution order:

3-Nitrobenzofuran (8), m.p. 101–103 °C (X-ray crystal structure determined, see below). IR: v_{max} (liquid film) 1601, 1560, 1508 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.46–7.52 (m, 2 H), 7.57–7.61 (m, 1 H), 8.17–8.20 (m, 1 H), 8.59 (s, H2).

r-2-c-3-Dinitro-2,3-dihydrobenzofuran (4), isolated as an oil containing impurities (10%). ^{1}H NMR (CDCl$_3$): δ 6.23 (s, H2), 6.58 (s, H3), 7.16–7.26 (m, 2 H), 7.49–7.55 (m, 2 H). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.23 gave an enhancement at δ 6.58 (0.5%); irradiation at δ 6.58 gave enhancements at δ 6.23 (1.3%) and at δ 7.51 (0.32%). ^{13}C NMR (CDCl$_3$): δ 83.9 (C3), 106.4 (C2), 111.3 (C7), 123.8 (C5), 126.5 (C4), 133.2 (C6); these assignments were made from reverse-detected heteronuclear correlation spectra (HMQC).

r-2-t-3-Dinitro-2,3-dihydrobenzofuran (5), m.p. 88–90 °C (X-ray crystal structure determined, see below). ^{1}H NMR (CDCl$_3$): δ 6.23 (s, H3), 6.82 (s, H2), 7.17–7.24 (m, H5, H7), 7.54 (ddd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H4}$ 1.0 Hz, H6), 7.66 (dd, $J_{H4,H5}$ 7.8 Hz, $J_{H4,H6}$ 1.0 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.23 gave an enhancement at δ 7.66 (0.2%); irradiation at δ 6.82 gave an enhancement at δ 6.23 (0.6%); irradiation at δ 7.21 gave enhancements at δ 7.54 (4.3%) and at δ 7.66 (3.6%); irradiation at δ 7.54 gave an enhancement at δ 7.21 (5.1%); irradiation at δ 7.66 gave enhancements at δ 6.23 (0.9%) and at δ 7.21 (1.6%). ^{13}C NMR (CDCl$_3$): δ 88.1 (C3), 105.0 (C2), 111.3 (C7), 123.9 (C5), 126.2 (C4), 133.3 (C6); these assignments were made from reverse-detected heteronuclear correlation spectra (HMQC).

t-3-Hydroxy-r-2-nitro-2,3-dihydrobenzofuran (6), isolated as an oil (Insufficient for elemental analysis. Found: M^+ 181.03770. C$_8$H$_7$NO$_4$ requires 181.03751). IR: v_{max} (liquid film) 3339, 1572 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.44 (br s, H3), 6.06 (br s, H2), 7.10–7.14 (m, H5, H7), 7.39–7.44 (m, H4, H6). ^{13}C NMR (CDCl$_3$): δ 77.2 (C3), 110.8 (C2), 110.9 (C7), 123.3 (C5), 125.2 (C4), 131.5 (C6); these assignments were made from reverse-detected heteronuclear correlation spectra (HMQC).

c-3-Hydroxy-r-2-nitro-2,3-dihydrobenzofuran (7), m.p. 114–116 °C (preliminary X-ray crystal structure determined). ^{1}H NMR (CDCl$_3$): δ 5.85 (d, $J_{H3,H2}$ 6.9 Hz, H3), 6.29 (br d, $J_{H2,H3}$ 6.9 Hz, H2), 7.06 (d, $J_{H7,H6}$ 8.3 Hz, H7), 7.12 (ddd, $J_{H5,H6}$ 8.3 Hz, $J_{H5,H4}$ 7.3 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.37 br dd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H7}$ 8.3 Hz, H6), 7.41 (br d, $J_{H4,H5}$ 7.3 Hz, H4). ^{13}C NMR (CDCl$_3$): δ 72.9 (C3), 107.4 (C2), 110.4 (C7), 123.1 (C5), 124.9 (C4), 131.1 (C6); these assignments were made from reverse-detected heteronuclear correlation spectra (HMQC).

General procedure for the photonitration of benzofuran (3) with tetranitromethane. A solution of **3** (500 mg, 0.53 mol dm^{-3}) and tetranitromethane (1.06 mol dm^{-3}) in dichloromethane (at 20 or −20 °C), in acetonitrile (at 20 or −20 °C), or in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C was irradiated with filtered light ($\lambda_{cut-off}$ 435 nm) exciting only the CT band. Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤ 0 °C, and the product compositions determined by NMR spectral analysis (Tables 4, 7 and 8).

Photochemical reaction of benzofuran 3 in dichloromethane at 20 °C, and the identification of adducts (10–19), 4-trinitromethylbenzofuran (21) and 4-nitrobenzofuran (22). Reaction of **3**–tetranitromethane in dichloromethane at 20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 4) of adducts (**10–20**) (total 83%), aromatic compounds (**9, 21** and **22**) (total 9%), unidentified adducts (total 6%) and unidentified aromatic products (total 2%). The mixture was partially separated into its components by HPLC and gave the following in elution order:

4-Trinitromethylbenzofuran (21) (X-ray crystal structure determined, see below, on the only crystal obtained) (Found: parent ion not visible, MH^+–NO$_2$ 222.02758. C$_9$H$_6$N$_2$O$_5$ requires 222.02767). IR: v_{max} (liquid film) 1616, 1593 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.54 (br d, $J_{H3,H2}$ 2.5 Hz, H3), 7.45–7.53 (m, H5, H6), 7.84 (d, $J_{H2,H3}$ 2.5 Hz, H2), 7.90 (br d, $J_{H7,H6}$ 7.8 Hz, H7).

Dinitro dimer (19) was isolated only as an impure oil (10% impurity). ^{1}H NMR (CDCl$_3$): δ 4.45 (d, $J_{H3,H2}$ 5.9 Hz, H3), 5.21 (d, $J_{H2A,H3A}$ 4.8 Hz, H2A), 5.55 (d, $J_{H3A,H2A}$ 4.8 Hz, H3A), 6.43 (d, $J_{H2,H3}$ 5.9 Hz, H2), 6.89 (d, J 7.8 Hz), 6.91 (dd, J 7.8 Hz, J' 7.8 Hz), 6.98 (d, J 7.9 Hz), 6.99 (dd, J 7.9 Hz, J'' 7.3 Hz), 7.25 (dd, J 7.3 Hz, J' 7.3 Hz), 7.32 (dd, J 7.8 Hz, J' 7.8 Hz), 7.36 (d, $J_{H4,H5}$ 7.3 Hz, H4), 7.42 (d, $J_{H4A,H5A}$ 7.8 Hz, H4A). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.45 gave enhancements at δ 5.21 (1.3%), at δ 6.43 (3.2%), and at δ 7.36 (0.6%); irradiation at δ 5.21 gave enhancements at δ 4.45 (1.9%), at δ 5.55 (5.2%), and at δ 7.36 (1.3%); irradiation at δ 5.55 gave enhancements at δ 5.21 (3.8%) and at δ 7.42 (0.7%); irradiation at δ 6.43 gave an enhancement at δ 4.45 (2.7%). ^{13}C NMR (CDCl$_3$): δ 53.5 (C3), 83.6 (C3A), 91.8 (C2A), 111.1 (C2), 124.6 (C4), 125.75 (C4A); these assignments were made from reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

t-3-Nitro-r-2-trinitromethyl-2,3-dihydrobenzofuran (10) was isolated only as an impure oil (15% impurities). ^{1}H NMR (CDCl$_3$): δ 6.39 (d, $J_{H3,H2}$ 4.9 Hz, H3), 6.81 (br d, $J_{H2,H3}$ 4.9 Hz, H2), 7.03 (d, $J_{H7,H6}$ 8.3 Hz, H7), 7.16 (dd, $J_{H5,H4}$ 7.9 Hz, $J_{H5,H6}$ 7.8 Hz, H5), 7.48 (dd, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H5}$ 7.8 Hz, H6), 7.61 (d, $J_{H4,H5}$ 7.9 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.81 gave an enhancement at δ

6.39 (1.4%); irradiation at δ 7.03 gave an enhancement at 7.48 (1.6%); irradiation at δ 7.16 gave enhancements at δ 7.48 (2.0%) and at δ 7.61 (4.6%); irradiation at δ 7.48 gave enhancements at δ 7.03 (6.1%) and at δ 7.16 (2.6%); irradiation at δ 7.61 gave enhancements at δ 6.39 (1.4%) and at δ 7.16 (1.9%). ^{13}C NMR (CDCl$_3$): δ 81.1 (C2), 87.8 (C3), 111.8 (C7), 125.2 (C5), 126.4 (C4), 133,2 (C6); confirmed by reverse-detected heteronuclear correlation spectra (HMQC). Attempted crystallization of t-3-nitro-r-2-trinitromethyl-2,3-dihydrobenzofuran (10) from dichloromethane-hexane at ⩽20 °C gave crystals of 3-nitrobenzofuran (8), identical with the material isolated above.

4-Nitrobenzofuran (22), isolated as an oil (Insufficient for elemental analysis. Found: M^+ 163.026 88. C$_8$H$_5$NO$_3$ requires 163.026 94). ^{1}H NMR (CDCl$_3$): δ 6.94 (d, $J_{H3,H2}$ 2.5 Hz, H3), 7.39 (dd, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H5}$ 7.9 Hz, H6), 7.85 (d, $J_{H2,H3}$ 2.5 Hz, H2), 7.94 (dd, $J_{H5,H6}$ 7.9 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 8.17 (dd, $J_{H7,H6}$ 8.3 Hz, $J_{H7,H5}$ 1.0 Hz, H7). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.94 gave an enhancement at δ 7.85 (1.5%); irradiation at δ 7.85 gave an enhancement at δ 6.94 (1.2%); irradiation at δ 7.94 gave an enhancement at δ 7.39 (1.4%); irradiation at δ 8.17 gave an enhancement at δ 7.39 (1.1%).

r-2-Nitro-t-3-trinitromethyl-2,3-dihydrobenzofuran (12) was isolated only as a minor component in a complex mixture of substituted arenes. ^{1}H NMR (CDCl$_3$): δ 5.61 (br s, H3), 6.36 (d, $J_{H2,H3}$ 1.9 Hz, H2), 7.29 (d, H4), the remainder of the spectrum was obscured. Nuclear Overhauser experiments gave the following results: irradiation at δ 5.61 gave enhancements at δ 6.36 (0.7%) and at δ 7.29 (0.4%); irradiation at δ 6.36 gave an enhancement at δ 5.61 (1.3%). ^{13}C NMR (CDCl$_3$): δ 52.1 (C3), 105.0 (C2), 125.2 (C4), located by reverse-detected heteronuclear correlation spectra (HMQC).

t-7-Nitro-r-4-trinitromethyl-4,7-dihydrobenzofuran (17) was isolated as an impure oil (10% impurity). ^{1}H NMR (CDCl$_3$): δ 5.28 (m, H4), 6.03 (ddd, $J_{H7,H6}$ 4.9 Hz, $J_{H7,H4}$ 4.4 Hz, $J_{H7,H5}$ 1.0 Hz, H7), 6.41 (d, $J_{H3,H2}$ 2.4 Hz, H3), 6.45 (ddd, $J_{H5,H6}$ 9.8 Hz, $J_{H5,H4}$ 3.9 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 6.67 (ddd, $J_{H6,H5}$ 9.8 Hz, $J_{H6,H7}$ 4.9 Hz, $J_{H6,H4}$ 1.5 Hz, H6), 7.63 (d, $J_{H2,H3}$ 2.4 Hz, H2); the H,H-coupling constants, above, were confirmed by double irradiation experiments. Nuclear Overhauser experiments gave the following results: irradiation at δ 5.28 gave enhancements at δ 6.41 (0.6%) and at δ 6.45 (1.9%); irradiation at δ 6.03 gave an enhancement at δ 6.67 (1.78%); irradiation at δ 6.41 gave enhancements at δ 5.28 (1.7%) and at δ 7.63 (1.6%); irradiation at δ 6.45 gave enhancements at δ 5.28 (3.3%) and at δ 6.67 (6.7%); irradiation at δ 6.67 gave enhancements at 6.03 (2.8%) and at δ 6.45 (6.9%); irradiation at δ 7.63 gave an enhancement at δ 6.41 (1.5%). ^{13}C NMR (CDCl$_3$): δ 41.4 (C4), 75.3 (C7), 108.8 (C3), 125.1 (C5), 127.3 (C6), 145.6 (C2); the above

assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

The next material eluted was a mixture (ca. 2:1) of c-3-nitro-r-2-trinitromethyl-2,3-dihydrobenzofuran (11) and c-7-nitro-r-4-trinitromethyl-4,7-dihydrobenzofuran (18). These compounds were inseparable by chromatography and their structures were determined from spectra of the mixture.

c-3-Nitro-r-2-trinitromethyl-2,3-dihydrobenzofuran (11). ^{1}H NMR (CDCl$_3$): δ 6.11 (d, $J_{H2,H3}$ 7.4 Hz, H2), 6.48 (d, $J_{H3,H2}$ 7.4 Hz, H3), 7.08 (br d, $J_{H7,H6}$ 7.8 Hz, H7), 7.23 (ddd, $J_{H5,H4}$ 7.8 Hz, $J_{H5,H6}$ 7.3 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.53 (ddd, $J_{H6,H7}$ 7.8 Hz, $J_{H6,H5}$ 7.3 Hz, $J_{H6,H4}$ 1.4 Hz, H6), 7.63 (dd, $J_{H4,H5}$ 7.8 Hz, $J_{H4,H6}$ 1.4 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.11 gave an enhancement at δ 6.48 (4.1%); irradiation at δ 6.48 gave an enhancement at δ 6.11 (5.0%); irradiation at δ 7.08 gave an enhancement at δ 7.53 (2.3%); irradiation at δ 7.63 gave an enhancement at δ 7.23 (2.7%). ^{13}C NMR (CDCl$_3$): δ 78.9 (C2), 85.3 (C3), 111.2 (C7), 123.4 (C5), 126.9 (C4), 133.2 (C6); these assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

c-7-Nitro-r-4-trinitromethyl-4,7-dihydrobenzofuran (18). ^{1}H NMR (CDCl$_3$): δ 5.40 (m, H4), 5.97 (ddd, $J_{H7,H4}$ 5.6 Hz, $J_{H7,H6}$ 3.9 Hz, $J_{H7,H5}$ 1.0 Hz, H7), 6.58 (ddd, $J_{H5,H6}$ 9.8 Hz, $J_{H5,H4}$ 3.5 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 6.65 (ddd, $J_{H6,H5}$ 9.8 Hz, $J_{H6,H7}$ 3.9 Hz, $J_{H6,H4}$ 1.5 Hz, H6), 6.73 (d, $J_{H3,H2}$ 2.0 Hz, H3), 7.44 (d, $J_{H2,H3}$ 2.0 Hz, H2). ^{13}C NMR (CDCl$_3$): δ 40.5 (C4), 77.5 (C7), 110.0 (C3), 123.0 (C5), 126.2 (C2), 128.6 (C6), located by reverse-detected heteronuclear correlation spectra (HMQC).

Nitronic ester (14), m.p. 112–114 °C (X-ray crystal structure determined, see below). I.R.: ν_{max} (liquid film) 1655, 1516 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.64 (d, $J_{H3,H2}$ 7.8 Hz, H3), 6.79 (d, $J_{H2,H3}$ 7.8 Hz, H2), 7.03 (br d, $J_{H7,H6}$ 8.3 Hz, H7), 7.08 (ddd, $J_{H5,H6}$ 8.3 Hz, $J_{H5,H4}$ 7.8 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.36 (ddd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H4}$ 1.0 Hz, H6), 7.59 (d, $J_{H4,H5}$ 7.8 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.64 gave enhancements at δ 6.79 (1.7%) and at δ 7.59 (0.5%); irradiation at δ 6.79 gave an enhancement at δ 5.64 (2.5%); irradiation at δ 7.03 gave an enhancement at δ 7.36 (3.9%); irradiation at δ 7.08 gave enhancements at δ 7.36 (3.1%) and at δ 7.59 (4.1%); irradiation at δ 7.36 gave enhancements at δ 7.03 (3.9%) and at δ 7.08 (1.4%); irradiation at δ 7.59 gave enhancements at δ 5.64 (0.8%) and at δ 7.08 (1.6%). ^{13}C NMR (CDCl$_3$): δ 48.7 (C3), 101.2 (C2), 110.4 (C7), 122.8 (C5), 125.8 (C4), 130.8 (C6); these assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

t-3-Hydroxy-r-2-trinitromethyl-2,3-dihydrobenzofuran (15), isolated only as an impure oil (10% impurity). ^{1}H NMR (CDCl$_3$): δ 5.67 (d, $J_{H2,H3}$ 3.9 Hz, H2), 5.77 (br d, H3), 6.94 (br d, $J_{H7,H6}$ 8.3 Hz, H7), 7.11 (ddd, $J_{H5,H6}$

8.3 Hz, $J_{H5,H4}$ 7.3 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.37 (ddd, $J_{H6,H5}$ 8.3 Hz, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H4}$ 1.0 Hz, H6), 7.43 (d, $J_{H4,H5}$ 7.3 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.67 showed no enhancements; irradiation at δ 5.77 gave an enhancement at δ 7.43 (0.9%); irradiation at δ 6.94 gave an enhancement at δ 7.37 (2.3%); irradiation at δ 7.43 gave enhancements at δ 5.77 (1.2%) and at δ 7.11 (4.0%). ^{13}C NMR (CDCl$_3$): δ 75.4 (C3), 87.5 (C2), 110.6 (C7), 122.8 (C5), 124.9 (C4), 131.2 (C6); these assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

c-*3*-Hydroxy-r-*2*-trinitromethyl-*2,3*-dihydrobenzofuran (*16*), isolated only in admixture with impurities (15% impurities). ^{1}H NMR (CDCl$_3$): δ 5.78 (d, $J_{H2,H3}$ 7.3 Hz, H2), 5.96 (br d, H3), 6.97 (br d, $J_{H7,H6}$ 8.8 Hz, H7), 7.11 (ddd, $J_{H5,H4}$ 8.3 Hz, $J_{H5,H6}$ 7.4 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.38 (ddd, $J_{H6,H7}$ 8.8 Hz, $J_{H6,H5}$ 7.4 Hz, $J_{H6,H4}$ 1.5 Hz, H6), 7.45 (br d, $J_{H4,H5}$ 8.3 Hz, H4). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.78 gave an enhancement at δ 5.96 (5.5%); irradiation at δ 5.96 gave enhancements at δ 5.78 (6.6%) and at δ 7.45 (0.5%); irradiation at δ 6.97 gave an enhancement at 7.38 (2.2%); irradiation at 7.45 gave enhancements at δ 5.96 (0.6%) and at δ 7.11 (2.9%). ^{13}C NMR (CDCl$_3$): δ 72.7 (C3), 82.1 (C2), 110.7 (C7), 122.8 (C5), 125.1 (C4), 131.4 (C6); these assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

r-*2*-Nitro-c-*3*-trinitromethyl-*2,3*-dihydrobenzofuran (*15*), isolated only as an impure oil (20% impurities). ^{1}H NMR (CDCl$_3$): δ 4.86 (br s, H3), 6.11 (d, $J_{H2,H3}$ 1.4 Hz, H2), 6.94 (d, $J_{H7,H6}$ 8.3 Hz, H7), 7.02 (ddd, $J_{H5,H4}$ 7.9 Hz, $J_{H5,H6}$ 7.3 Hz, $J_{H5,H7}$ 1.0 Hz, H5), 7.24 (d, $J_{H4,H5}$ 7.9 Hz, H4), 7.38 (dd, $J_{H6,H7}$ 8.3 Hz, $J_{H6,H5}$ 7.3 Hz, H6). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.86 gave enhancements at δ 6.11 (0.9%) and at δ 7.24 (0.6%); irradiation at δ 6.11 gave an enhancement at δ 4.86 (1.5%); irradiation at δ 6.94 gave an enhancement at δ 7.38 (2.1%); irradiation at δ 7.02 gave enhancements at δ 7.24 (3.7%) and at δ 7.38 (2.1%); irradiation at δ 7.24 gave enhancements at δ 4.86 (1.1%) and at δ 7.02 (1.6%). ^{13}C NMR (CDCl$_3$): δ 54.4 (C3), 100.1 (C2), 111.0 (C7), 122.3 (C5), 125.2 (C4), 131.8 (C6); these assignments were confirmed by reverse-detected heteronuclear correlation spectra (HMQC).

Photochemical reaction of benzofuran (3) in dichloromethane at −20 °C. Reaction of 3–tetranitromethane in dichloromethane at −20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 4) of adducts (*10–19*) (total 82%), aromatic compounds (*9, 21* and *22*) (total 8%), unidentified adducts (total 7%) and unidentified aromatic products (total 2%).

Photochemical reaction of benzofuran (3) in acetonitrile at 20 °C. Reaction of 3–tetranitromethane in acetonitrile at 20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 7) of adducts (*4–7, 10–20*) (total 75%), aromatic compounds (*8, 9, 21* and *22*) (total 14%), unidentified adducts (total 7%) and unidentified aromatic products (total 4%).

Photochemical reaction of benzofuran (3) in acetonitrile at −20 °C. Reaction of 3–tetranitromethane in acetonitrile at −20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra to be a mixture (Table 7) of adducts (*4–6, 10–20*) (total 68%), aromatic compounds (*9, 21* and *22*) (total 19%), unidentified adducts (total 7%) and unidentified aromatic products (total 6%).

Photochemical reaction of benzofuran (3) in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C, and the identification of compounds 9 and 20. Reaction of benzofuran–tetranitromethane in HFP at 20 °C, as above, for 6 h gave a product which was shown by ^{1}H NMR spectra (Table 8) to be a mixture of 6-nitrobenzofuran (*9*) (13%), the isomeric dinitro dimers (*19*) (29%) and (*20*) (35%), and small amounts of the nitroarenes *8* (2%) and *22* (6%). Chromatography on a silica gel Chromatotron plate gave in elution order:

4-Trinitromethylbenzofuran (21), identical with the material isolated above.

6-Nitrobenzofuran (9), isolated as a yellow oil, mass spectrum identical with that of an authentic sample. ^{1}H NMR (CDCl$_3$): δ 6.91 (m, H3), 7.70 (d, $J_{H4,H5}$ 8.8 Hz, H4), 7.89 (d, $J_{H2,H3}$ 2.5 Hz, H2), 8.19 (dd, $J_{H5,H4}$ 8.8 Hz, $J_{H5,H7}$ 1.9 Hz, H5), 8.43 (br s, H7). Nuclear Overhauser experiments gave the following results: irradiation at δ 6.91 gave enhancements at δ 7.70 (0.4%) and at δ 7.89 (1.6%); irradiation at δ 7.70 gave enhancements at δ 6.91 (0.6%) and at δ 8.19 (5.2%); irradiation at δ 7.89 gave an enhancement at δ 6.91 (0.7%); irradiation at δ 8.19 gave an enhancement at δ 7.70 (2.5%); irradiation at δ 8.43 gave no enhancements.

Dinitro dimer (19), identical with the material isolated above.

Dinitro dimer (20), isolated as an oil containing impurities (total 10%). ^{1}H NMR (CDCl$_3$): δ 4.20 (dd, $J_{H3,H2A}$ 8.8 Hz, $J_{H3,H2}$ 6.3 Hz, H3), 5.44 (dd, $J_{H2A,H3}$ 8.8 Hz $J_{H2A,H3A}$ 6.9 Hz, H2A), 6.02 (d, $J_{H3A,H2A}$ 6.9 Hz, H3A), 6.43 (d, $J_{H2,H3}$ 6.3 Hz, H2), 6.49 (d, J 8.3 Hz), 6.81 (ddd, J 7.4 Hz, J' 7.3 Hz, J 1.0), 6.85 (ddd, J 7.3 Hz, J 7.3 Hz, J 1.0 Hz), 7.00 (dd, 2 H, J 7.8 Hz, J'' 7.8 Hz), 7.29 (d, J 7.3 Hz), 7.29 (d, $J_{H4,H5}$ 7.3 Hz, H4), 7.33 (d, $J_{H4A,H5A}$ 7.3 Hz, H4A). Nuclear Overhauser experiments gave the following results: irradiation at δ 4.20 gave enhancements at δ 5.44 (4.5%), at δ 6.43 (3.2%), and at δ 7.29 (0.6%); irradiation at δ 5.44 gave enhancements at δ 4.20 (4.2%) and at δ 6.02 (5.6%); irradiation at δ 6.02 gave enhancements at δ 4.20 (0.3%), at δ 5.44 (2.5%) and at δ 7.33

(0.4%); irradiation at δ 6.43 gave an enhancement at δ 4.20 (1.8%). ^{13}C NMR (CDCl$_3$): δ 51.3 (C3), 84.2 (C2A), 84.8 (C3A), 109.5 (C2), 124.9 (C4A), 126.0 (C4); these assignments were made from reverse-detected heteronuclear correlation spectra (HMBC, HMQC).

Reaction of benzofuran (3) with nitrogen dioxide in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C in the dark. A solution of **3** (0.53 mol dm^{-3}) in HFP saturated with nitrogen dioxide was stored in the dark at 20 °C. Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at ≤0 °C, and the product composition determined by ^{1}H NMR spectral analysis (Table 9). After 6 h the product was a mixture of nitrobenzofurans (**8, 9** and **22**) (total 52%), dinitro dimers (**19** and **20**) (total 27%), and unidentified products (total 21%).

Crystallography

Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, λ(Mo *K*α) 0.710 69 Å from a crystal monochromator] are given below. The space group was, in each case, determined unambiguously as a result of the structure analyses reported below, but initially indicated by conditions limiting possible reflections. ω-Scans were used to collect reflection intensities out to a maximum Bragg angle θ, given below. The cell parameters were determined by least-squares refinements for which the setting angles of accurately centred high-angle reflections were used.

Crystal data. r-2-t-3-Dinitro-2,3-dihydrobenzofuran *(5)*, C$_8$H$_6$N$_2$O$_5$, *M* 280.20, monoclinic, space group *C2/c, a* 16.149(3), *b* 6.593(2), *c* 15.775(3) Å, β 94.01°, *V* 1675.5(7) Å^3, *D*$_c$ 1.666 g cm^{-3}, *Z* 8, μ(Mo *K*α) 1.42 cm^{-1}. The crystal was colourless and of approximate dimensions 0.80–0.44–0.32 mm. Data were collected at 153(2) K out to a maximum Bragg angle θ 25.0°. Number of independent reflections measured 1470, 1225 with *I*>2σ(*I*). Absorption corrections were not applied; *g*$_1$ 0.0311, *g*$_2$ 1.8255; *R*$_{(obs)}$-factor 0.033, *wR*$_{(all\ data)}$ 0.081.

3-Nitrobenzofuran (8), C$_8$H$_5$NO$_3$, *M* 163.13, triclinic, space group *P*Ī, *a* 6.511(2), *b* 6.846(2), *c* 8.819(2) Å, α 71.36(3), β 70.79(2), γ 73.54(3)°, *V* 344.7(2) Å^3, *D*$_c$ 1.572 g cm^{-3}, *Z* 2, μ(Mo *K*α) 1.23 cm^{-1}. The crystal was colourless and of approximate dimensions 0.80 × 0.38 × 0.30 mm. Data were collected at 153(2) K out to a maximum Bragg angle θ 27.49°. Number of independent reflections measured 1579, 1307 with *I*>2σ(*I*). Absorption corrections were not applied; *g*$_1$ 0.0542, *g*$_2$ 0.1042; *R*$_{(obs)}$-factor 0.039, *wR*$_{(all\ data)}$ 0.104.

Nitronic ester (**14**), C$_9$H$_6$N$_2$O$_5$, *M* 222.16, monoclinic, space group *P*2$_1$/*n, a* 9.809(1), *b* 5.355, *c* 17.100(2) Å, β 101,20(1)°, *V* 881.1(1) Å^3, *D*$_c$ 1.675 g cm^{-3}, *Z* 4,

μ(Mo *K*α) 1.40 cm^{-1}. The crystal was yellow in colour and of approximate dimensions 0.80 × 0.44 × 0.42 mm. Data were collected at 153(2) K out to a maximum Bragg angle θ 24.99°. Number of independent reflections measured 1554, 1244 with *I* >2σ(*I*). Absorption corrections were not applied; *g*$_1$ 0.0577, *g*$_2$ 0.0501; *R*$_{(obs)}$-factor 0.031, *wR*$_{(all\ data)}$ 0.091.

4-Trinitromethylbenzofuran (21), C$_9$H$_5$N$_3$O$_7$, *M* 267.16, triclinic, space group *P*Ī, *a* 7.474(1), *b* 7.612(1), *c* 9.658(1) Å, α 92.71(1), β 92.25(1), γ 104.11(1)°; *V* 531.5(1) Å^3, *D*$_c$ 1.669 g cm^{-3}, *Z* 2, μ(Mo *K*α) 1.48 cm^{-1}. The crystal was colourless and of approximate dimensions 0.36 × 0.17 × 0.16 mm. Data were collected at 168(2) K out to a maximum Bragg angle θ 22.5°. Number of independent reflections measured 1382, 938 with *I*>2σ(*I*). Absorption corrections were not applied; *g*$_1$ 0.0234, *g*$_2$ 0.0000; *R*$_{(obs)}$-factor 0.029, *wR*$_{(all\ data)}$ 0.054.

Structure determination. The structures were solved by direct methods and difference-Fourier syntheses. Full-matrix least-squares refinements (SHELXL-93)[23] were employed. This program is based on intensities and uses all data. The observed threshold *I*>2σ(*I*) was used only for calculating *R*$_{(obs)}$, shown here as a comparison for the refinements based on *F*. Reflection weights $1/[\sigma^2(F_o^2)+(g_1 P)^2+g_2 P]$, where $P=(F_o+2F_c^2)/3$, were used. All non-hydrogen atoms were assigned anisotropic thermal parameters. Final Fourier syntheses show no abnormal discrepancies between observed and calculated structure factors.

References

1. Butts, C. P., Eberson, L., Hartshorn, M. P., Radner, F. and Wood, B. R. *Acta Chem. Scand. 51* (1997) 476.
2. Eberson, L., Hartshorn, M. P. and Radner, F. In Coxon, J. M., Ed., *Advances in Carbocation Chemistry*, Vol. 2, JAI Press, London 1995, p. 207; Eberson, L., Hartshorn, M. P. and Radner, F. *Acta Chem. Scand. 48* (1994) 937.
3. Eberson, L., Hartshorn, M. P. and Svensson, J. O. *J. Chem. Soc., Chem. Commun.* (1993) 1614.
4. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *J. Chem. Soc., Perkin Trans. 2* (1994) 1719.
5. Eberson, L., Hartshorn, M. P., Radner, F. and Svensson, J. O. *Acta Chem. Scand. 50* (1996) 885; Butts, C. P., Eberson, L., Hartshorn, M. P. and Persson, O. *Acta Chem. Scand. 51* (1997) 718.
6. For reviews on radical cations: Bard, A. J., Ledwith, A. and Shine, H. J. *Adv. Phys. Org. Chem. 13* (1976) 156; Hammerich, O. and Parker, V. D. *Adv. Phys. Org. Chem. 20* (1984) 55.
7. Eberson, L., González-Luque, R., Merchán, M., Radner, F., Roos, B. O. and Shaik, S. *J. Chem. Soc., Perkin Trans. 2* (1997) 463.

8. The choice of non-alternant systems was partly dictated by the fact that the radical ions of such systems do not obey the pairing theorem (Dewar, M. J. S. and Dougherty, R. C. *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975, p. 75). Thus the regiochemistry of nucleophile (or radical) attack upon radical cations is expected to show synthetically significant differences from those of the corresponding substrate-electrophile reactions. For alternant systems, no such differences are expected.

9. (a) Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T. and Wood, B. R. *Acta Chem. Scand. 50* (1996) 587; (b) Eberson, L., Hartshorn, M. P., Radner, F., Merchán, M. and Roos, B. O. *Acta Chem. Scand. 47* (1993) 176.

10. Butts, C. P., Eberson, L., Hartshorn, M. P., Radner, F., Robinson, W. T. and Wood, B. R. *Acta Chem. Scand. 51* (1997) 835.

11. Katritzky, A. and Taylor, R. *Adv. Heterocycl. Chem. 47* (1990) 181.

12. Eberson, L. and Radner, F. *J. Am. Chem. Soc. 113* (1991) 5825.

13. Wells, P. R. and Alcorn, P. G. E. *Aust. J. Chem. 16* (1963) 1108.

14. Shaik, S. S. *J. Am. Chem. Soc. 103* (1982) 3692; Pross, A. *Adv. Phys Org. Chem. 21* (1985) 99; Shaik, S. S. *Progr. Phys. Org. Chem. 15* (1985) 197; Pross, A. and Shaik, S. S. *Acc. Chem. Res. 110* (1983) 3537; Shaik, S. S. and Pross, A. *J. Am. Chem. Soc. 111* (1989) 4306; Shaik, S. S. and Dinnocenzo, J. P. *J. Org. Chem. 55* (1990) 3434; Shaik, S., Reddy, A. C., Ioffe, A., Dinnocenzo, J. P., Danovich, D. and Cho, J. K. *J. Am. Chem. Soc. 117* (1995) 3205.

15. Bosch, E. and Kochi, J. K. *J. Org. Chem. 59* (1994) 3314.

16. Baciocchi, E., Clementi, S. and Sebastiani, G. V. *J. Heterocyclic Chem. 14* (1977) 359.

17. Butts, C. P., Eberson, L., Fulton, K. L., Hartshorn, M. P., Robinson, W. T. and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 50* (1996) 991; Eberson, L., Hartshorn, M. P.

and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 50* (1996) 1121; Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *J. Chem. Soc., Perkin Trans. 2* (1996) 1877; Eberson, L., Persson, O., Radner, F. and Hartshorn, M. P. *Res. Chem. Intermed. 22* (1996) 799.

18. For a review of the solvent properties of HFP, see: Eberson, L., Hartshorn, M. P., Persson, O. and Radner, F. *J. Chem. Soc., Chem. Commun.* (1996) 2105; and references cited therein.

19. Sargent, M. V. and Dean, F. M. In: *Comprehensive Heterocyclic Chemistry*, Vol. 4 (Katritzky, A. and Ress, C. W., Eds.) Pergamon Press, Oxford 1984, Chap. 11.

20. Butts, C. P., Eberson, L., Hartshorn, M. P., Robinson, W. T., Timmerman-Vaughan, D. J. and Young, D. A. W. *Acta Chem. Scand. 50* (1996) 29; Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *Aust. J. Chem. 48* (1995) 1989; Butts, C. P., Eberson, L., Hartshorn, M. P. and Robinson, W. T. *Acta Chem. Scand. 49* (1995) 389.

21. Eberson, L., M. P. Hartshorn, O. Persson, W. T. Robinson and Timmerman-Vaughan, D. J. *Acta Chem. Scand. 49* (1995) 482.

22. Tschinkel, J. G. *Ind. Eng. Chem. 48* (1965) 732.

23. Sheldrick, G. M. *J. Appl. Crystallogr. In preparation.*

24. Schott-L'vova, E. A. and Syrkin, Y. K. *J. Phys Chem. 12* (1938) 479.

25. Koller, J. and Azman, A. *Z. Naturforsch., Teil A 29* (1974) 624.

26. Zander, M. and Kirsch, G. *Z. Naturforsch., Teil A 44* (1989) 205.

27. Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys. 2* (1969) 471.

28. Selby, R. G. and Grimison, A. *Int. J. Quantum. Chem. 12* (1977) 527.