

Photochemical Nitration by Tetranitromethane Part XXX. † Product Isolation and Identification in the Photochemical Reaction of Dibenzofuran

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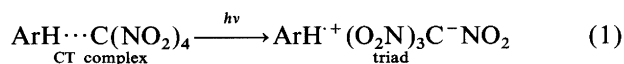
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The photolysis of the charge-transfer complex of dibenzofuran (1) and tetranitromethane in either dichloromethane or acetonitrile gives *t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydrodibenzofuran (4), the epimeric 4-nitro-1-trinitromethyl-1,4-dihydrodibenzofurans 5 and 7, the epimeric 4-hydroxy-1-trinitromethyl-1,4-dihydrodibenzofurans 6 and 8, 3-trinitromethyl dibenzofuran (13), and the four isomeric nitrodibenzofurans 9–12. The five adducts 4–8 are formed via attack by trinitromethanide ion at C1 of the dibenzofuran radical cation, while 3-trinitromethyl dibenzofuran is formed by decomposition of an adduct, itself formed via initial attack of trinitromethanide ion at C3 of the dibenzofuran radical cation. The regiochemistry of attack of trinitromethanide ion on the radical cation of the non-alternant dibenzofuran system is in keeping with earlier theoretical predictions.

In 1,1,1,3,3,3-hexafluoropropan-2-ol solution the analogous photolysis of the charge-transfer complex of dibenzofuran (1) and tetranitromethane gives only the four nitrodibenzofurans 9–12, the attack of trinitromethanide ion on the radical cation of dibenzofuran being suppressed by the solvent.

X-Ray crystal structures are reported for compounds 4, 6 and 13, compound 6 representing the first hydroxytrinitromethyl adduct to be unambiguously assigned this structure.

The photochemical addition of tetranitromethane (TNM) to aromatic compounds (ArH) by excitation of the ArH–TNM charge-transfer (CT) complex by light matching the wavelength of the CT band has been shown² to occur by recombination of a triad consisting of ArH^+ , trinitromethanide ion, and nitrogen dioxide.



The first chemical step which occurs, leading to the formation of adducts, is reaction between ArH^+ and trinitromethanide ion [eqn. (2)] to give a carbon radical which then reacts with nitrogen dioxide to give adducts [eqn. (3)].²

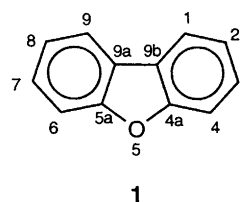


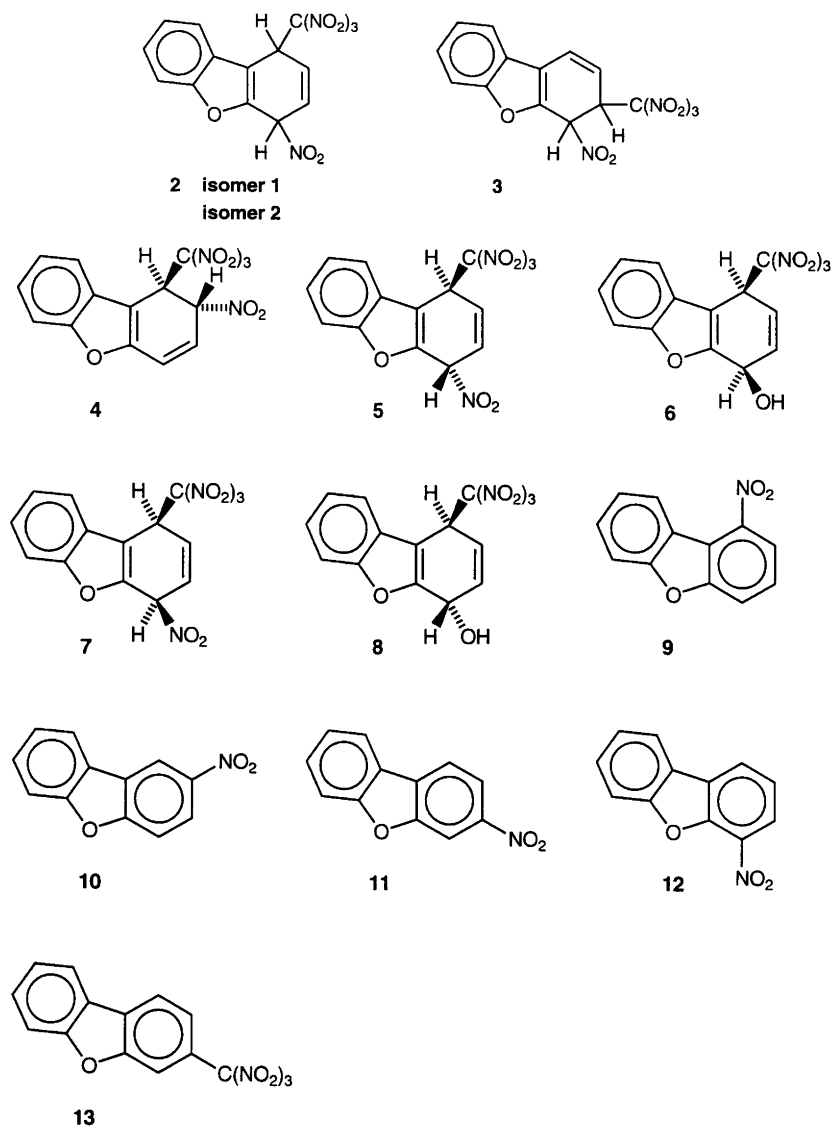
† Part XXIX, see Ref. 1.

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Recently we reported the formation of adducts in the photolysis of the charge-transfer complex of tetranitromethane with dibenzofuran 1.³ At that time the adducts were not isolated, but were identified tentatively as adducts 2 (isomers 1 and 2) and adduct 3 on the basis of the NMR spectra of the crude product of the photochemical reaction. We now report a full study of this photolysis reaction, including the isolation and structure determination of the adducts 4–8, the nitrodibenzofurans 9–12 and the 3-trinitromethyl dibenzofuran 13.





Results

General. The photochemical experiments were performed with filtered light (cut-off 435 nm, 5 cm water IR-filter, 300 W incandescent lamp) as described before,⁴ 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 $\leq 0^\circ\text{C}$. The crude product mixtures were stored at -20 or -78°C and were analysed (^1H NMR spectroscopy, see Experimental section; Tables 1 and 2) as soon as possible.

Photochemistry in dichloromethane at 20°C and identification of adducts 4–8, nitrodibenzofurans 9–12, and 3-trinitromethyldibenzofuran (13). A solution of dibenzofuran 1 (0.37 mol dm^{-3}) and tetranitromethane (0.74 mol dm^{-3}) in dichloromethane was irradiated at 20°C . The composition of the mixture was monitored by withdrawing samples for NMR spectral analysis (Table 1).

The final solution (after 8 h) contained a mixture of adducts 4 (2%), 5 (9%), 6 (6%), 7 (8%) and 8 (6%), nitrodibenzofurans 9 (4%), 10 (1%), 11 (5%) and 12 (7%), and 3-trinitromethyldibenzofuran 13 (30%). The components of the mixture were separated partially by HPLC on a cyanopropyl column using hexane–dichloromethane mixtures as the eluting solvents.

The first material eluted was a mixture of the nitrodibenzofurans 9–11, and 3-trinitromethyldibenzofuran 13, which was separated into its components by chromatography on a silica gel Chromatotron plate. The three nitrodibenzofurans 9–11 were identified by comparison with authentic materials, and the structure of 3-trinitromethyldibenzofuran 13, $\text{C}_{13}\text{H}_7\text{N}_3\text{O}_7$, was determined by single-crystal X-ray analysis. A perspective drawing is presented in Fig. 1, and corresponding atomic coordinates are given in Table 3. In the solid state the trinitromethyl group is orientated such that the C(13)–N(1) bond is close to eclipsed with the C(3)–C(2)

Table 1. Overview of yields of products from the photolysis of dibenzofuran (0.37 mol dm⁻³) and tetranitromethane (0.74 mol dm⁻³) in dichloromethane.

t/h	Conversion (%)	Yield (%)										Total aromatics (%) ^b	
		4	5	6	7	8	Total adducts (%) ^a	9	10	11	12		13
At 20 °C													
2	43	6.0	10.6	8.9	9.6	8.1	56.5	1.0	1.0	3.1	5.1	26.1	43.5
4	65	3.2	11.7	7.6	10.8	6.1	61.5	0.7	0.5	2.4	3.6	25.8	38.5
8	82	2.3	9.3	6.1	7.9	5.5	47.1	3.6	1.2	4.8	7.0	29.5	52.9
At -20 °C													
2	32	7.7	9.7	7.3	7.5	8.7	56.3	0.9	1.5	3.8	6.5	19.5	43.7
4	42	5.6	7.9	4.7	6.4	8.3	52.7	0.6	1.0	5.7	6.7	25.0	47.3
8	69	6.0	7.4	7.2	7.4	4.7	47.7	2.3	2.0	5.5	5.7	28.5	52.0

^a Including unidentified adducts. ^b Including unidentified aromatics.

Table 2. Overview of yields of products from the photolysis of dibenzofuran (0.37 mol dm⁻³) and tetranitromethane (0.74 mol dm⁻³) in acetonitrile.

t/h	Conversion (%)	Yield (%)										Total aromatics (%) ^b	
		4	5	6	7	8	Total adducts (%) ^a	9	10	11	12		13
At 20 °C													
2	20	4.1	6.6	5.2	3.9	8.9	37.2	3.9	2.3	13.2	9.7	28.3	62.8
4	34	5.6	4.9	8.1	4.7	9.1	40.1	4.2	4.2	16.4	5.8	24.6	59.9
8	55	2.5	3.7	4.2	2.6	4.8	31.6	4.6	3.3	20.8	6.8	27.0	68.4
At -20 °C													
2	19	5.5	5.9	5.1	3.5	5.2	36.9	4.2	2.5	11.0	8.5	32.7	63.1
4	26	5.6	6.6	6.8	4.8	7.6	41.8	4.6	2.0	17.6	9.1	20.3	58.2
8	40	5.4	6.8	5.1	4.9	6.5	40.4	5.1	2.7	15.6	9.2	23.5	59.6

^a Including unidentified adducts. ^b Including unidentified aromatics.

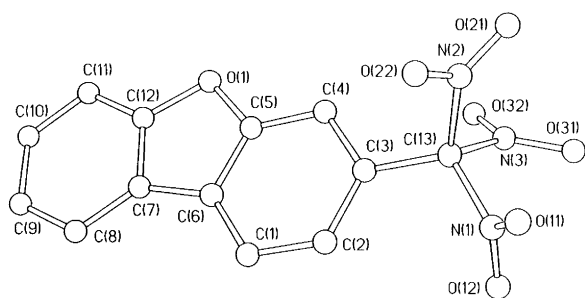


Fig. 1. Perspective drawing of compound 13.

bond [torsional angle: C(2)–C(3)–C(13)–N(1) 3.5(3)°], the remaining two nitro groups being approximately symmetrically disposed either side of the mean plane of the aromatic ring system. The limited spectroscopic data obtainable on a small sample were consistent with the established structure.

The remaining 4-nitrodibenzofuran (12) was the second material eluted from the HPLC column and was identical with an authentic sample.

The first adduct eluted from the HPLC column was identified as *t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydro-

dibenzofuran 4, C₁₃H₈N₄O₈, by single-crystal X-ray analysis. A perspective drawing is presented in Fig. 2, and corresponding atomic coordinates are given in Table 4. The structure consisted of two crystallographically independent molecules, the differences in conformation between them being minor and of no chemical significance. The conformation of the alicyclic ring is such that the orientations of the C(1)–C(13) and C(2)–N(1) bonds are given by the torsional angle (molecule 1): N(1)–C(2)–C(1)–C(13) –145.0(4)°, presumably the result, at least in part, of the minimization of steric interaction between the trinitromethyl group and the aromatic ring [torsional angle (molecule 1): C(7)–C(6)–C(1)–C(13) 79.4(7)°]. The diene system in the alicyclic ring is consequentially somewhat twisted from coplanarity [torsional angle (molecule 1): C(3)–C(4)–C(5)–C(6) –8.4(8)°], leading to torsional angles (molecule 1): H(2)–C(2)–C(3)–H(3) –36.1(2)° and H(1)–C(1)–C(2)–H(2) 88.4(1)°, torsional angles consistent with the observed coupling constants, $J_{H1,H2}$ ca. 0 Hz, $J_{H2,H3}$ 5.4 Hz. The remainder of the spectroscopic data for the nitro-trinitromethyl adduct 4 were also consistent with the established structure. The ¹H

Table 3. Fractional coordinates for atoms in 3-trinitromethyl-dibenzofuran (13).^a

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(1)	337(1)	218(2)	3624(1)	31(1)
O(11)	-5337(2)	1334(4)	3489(1)	60(1)
O(12)	-5015(2)	-1584(4)	3138(2)	68(1)
O(21)	-3117(3)	1835(4)	5301(2)	115(1)
O(22)	-3359(3)	3453(4)	4147(2)	93(1)
O(31)	-4072(2)	-1934(4)	4930(2)	95(1)
O(32)	-2347(2)	-2323(3)	4938(1)	45(1)
N(1)	-4727(2)	-43(4)	3505(1)	40(1)
N(2)	-3283(2)	1974(4)	4556(2)	44(1)
N(3)	-3273(2)	-1569(3)	4690(1)	41(1)
C(1)	-2483(2)	73(3)	2046(2)	29(1)
C(2)	-3168(2)	33(3)	2561(2)	28(1)
C(3)	-2701(2)	57(3)	3465(2)	28(1)
C(4)	-1512(2)	168(3)	3872(2)	30(1)
C(5)	-847(2)	169(3)	3338(2)	27(1)
C(6)	-1296(2)	146(3)	2442(1)	25(1)
C(7)	-313(2)	172(3)	2140(2)	26(1)
C(8)	-163(2)	169(3)	1334(2)	34(1)
C(9)	948(2)	188(3)	1298(2)	37(1)
C(10)	1883(2)	222(3)	2049(2)	33(1)
C(11)	1758(2)	242(3)	2856(2)	32(1)
C(12)	645(2)	215(3)	2878(2)	27(1)
C(13)	-3457(2)	83(3)	4016(2)	30(1)

^a The equivalent isotropic temperature factor in Tables 3–5 is defined as one-third of the orthogonalized U_{ij} tensor (Å²).

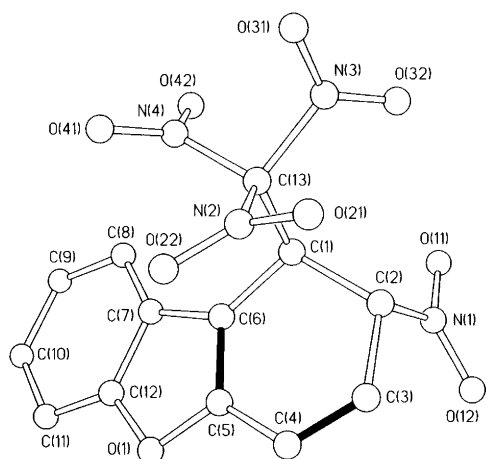


Fig. 2. Perspective drawing of compound 4. Double bonds are shown in black.

and ¹³C NMR spectra were substantially assigned from a consideration of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra (HMQC). Notable among the data was the chemical shift for H1 (δ 6.37); this unusual extent of deshielding may arise from the close proximity of the proton to the plane of the aromatic ring and also to the deshielding effect of the proximate O(11), O(32) and O(42) atoms of three nitro groups.

The epimeric *t*-4-nitro-*r*-1-trinitromethyl adduct 5 and *c*-4-nitro-*r*-1-trinitromethyl adduct 7 could be isolated only in low yield and in an impure state. Nonetheless, the connectivity in each adduct was established by a

Table 4. Fractional coordinates for atoms in *t*-2-nitro-*r*-1-trinitromethyl-1,2-dihydrodibenzofuran (4).

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
Molecule 1				
O(1)	9215(3)	2726(4)	3255(1)	24(1)
O(11)	11762(4)	2046(5)	4857(2)	65(2)
O(12)	10694(4)	114(5)	4742(2)	49(1)
O(21)	8066(3)	5053(4)	4971(2)	36(1)
O(22)	8018(3)	5578(5)	4207(2)	35(1)
O(31)	9628(3)	7339(5)	5233(1)	40(1)
O(32)	10638(3)	5243(5)	5333(1)	31(1)
O(41)	9466(3)	7836(5)	4091(2)	38(1)
O(42)	11113(3)	7125(4)	4300(1)	30(1)
N(1)	10874(4)	1497(6)	4766(2)	34(1)
N(2)	8489(3)	5430(5)	4584(2)	23(1)
N(3)	10030(4)	6103(6)	5107(2)	27(1)
N(4)	10112(4)	7008(5)	4293(2)	22(1)
C(1)	10286(5)	4079(6)	4415(2)	20(1)
C(2)	9882(4)	2616(6)	4712(2)	22(1)
C(3)	8911(4)	1764(6)	4515(2)	28(1)
C(4)	8658(5)	1845(6)	4054(2)	29(2)
C(5)	9312(4)	2808(6)	3746(2)	20(1)
C(6)	10103(4)	3813(6)	3889(2)	18(1)
C(7)	10592(4)	4456(6)	3452(2)	17(1)
C(8)	11451(4)	5448(6)	3333(2)	23(1)
C(9)	11705(5)	5698(6)	2845(2)	26(2)
C(10)	11084(5)	4977(6)	2490(2)	31(2)
C(11)	10233(5)	3970(6)	2599(2)	28(2)
C(12)	10006(4)	3724(6)	3083(2)	24(1)
C(13)	9711(4)	5592(6)	4592(2)	18(1)
Molecule 2				
O(1')	3247(3)	2461(4)	2601(1)	29(1)
O(11')	465(3)	3268(4)	1382(1)	39(1)
O(12')	1499(4)	4992(5)	1048(2)	52(1)
O(21')	4164(3)	205(5)	850(2)	51(1)
O(22')	4340(3)	-253(5)	1625(2)	45(1)
O(31')	2601(4)	-2165(4)	648(1)	44(1)
O(32')	1520(3)	-137(5)	589(1)	36(1)
O(41')	3036(3)	-2631(5)	1778(2)	47(1)
O(42')	1331(3)	-2065(4)	1629(1)	35(1)
N(1')	1322(4)	3700(6)	1213(2)	26(1)
N(2')	3822(4)	-163(6)	1244(2)	31(1)
N(3')	2201(4)	-949(6)	790(2)	27(1)
N(4')	2316(4)	-1848(5)	1596(2)	28(1)
C(1')	2000(4)	1068(6)	1476(2)	20(1)
C(2')	2307(4)	2545(6)	1180(2)	23(1)
C(3')	3316(4)	3392(6)	1330(2)	27(1)
C(4')	3698(5)	3312(6)	1789(2)	26(2)
C(5')	3077(4)	2349(6)	2113(2)	27(2)
C(6')	2281(4)	1336(6)	2003(2)	23(1)
C(7')	1852(4)	749(6)	2447(2)	22(1)
C(8')	977(5)	-240(7)	2591(2)	28(2)
C(9')	788(5)	-436(7)	3076(2)	33(2)
C(10')	1428(5)	317(7)	3414(2)	33(2)
C(11')	2296(5)	1298(7)	3295(2)	31(2)
C(12')	2453(5)	1478(6)	2802(2)	25(1)
C(13')	2604(4)	-384(6)	1289(2)	20(1)

combination of nuclear Overhauser experiments coupled with reverse detected heteronuclear correlation spectra (HMQC). In particular, for each adduct the H(1)–C(1)–C(NO₂)₃ structural feature was placed on the basis of a nuclear Overhauser enhancement of the H9 proton at δ 7.54 on irradiation at the H1 resonance.

The assignment of the stereochemistry of the two adducts **5** and **7** is based on the known elution order of epimeric 1-nitro-4-trinitromethyl-1,4-dihydro aromatic systems from a cyanopropyl HPLC column using hexane-dichloromethane mixtures as the eluting solvent system.⁵ On the basis of comparisons of ¹H NMR data it is clear that the *t*-4-nitro-*r*-1-trinitromethyl adduct **5** is the compound described previously as compound **2** (isomer 2),³ and that the *c*-4-nitro-*r*-1-trinitromethyl adduct **7** is the compound described previously as compound **2** (isomer 1).³

The hydroxy-trinitromethyl adduct **6** was eluted in admixture with the nitro-trinitromethyl adduct **7**, but could be separated from **7** by crystallization from ether-pentane mixtures. The structure of *c*-4-hydroxy-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran **6**, C₁₃H₉N₃O₈, was determined by single-crystal X-ray analysis of a crystal of barely adequate quality. A perspective drawing is presented in Fig. 3, and corresponding atomic coordinates are given in Table 5. In the solid state the alicyclic ring exists in a flattened boat conformation [torsional angles: C(2)–C(1)–C(6)–C(5) 13(2)°; C(3)–C(4)–C(5)–C(6) –8(2)°] with the C(1)–C(13) bond close to perpendicular to the plane of the aromatic system [torsional angle: C(7)–C(6)–C(1)–C(13) 83(1)°]. The orientation of the C(4)–O(4) bond is indicated by the torsional angle: O(4)–C(4)–C(5)–O(5) –73(1)°. The spectroscopic data for hydroxy-trinitromethyl adduct **6** were consistent with the established structure. This 1,4-dihydrodibenzofuran (**6**) is clearly identical with the material described earlier as compound **3**.³

The epimeric hydroxy-trinitromethyl adduct **8** could be isolated only in small amounts and unfortunately afforded only microcrystalline material on crystallization. Comparison of the spectroscopic data for **8** and those for the hydroxy-trinitromethyl adduct **6**, for which the structure is established above, allows the assignment of adducts **6** and **8** simply as epimers. It should be noted that the observed elution order from the cyanopropyl HPLC column is consistent with the expectation that a *c*-4-hydroxy-*r*-1-trinitromethyl-1,4-dihydro system **6** will

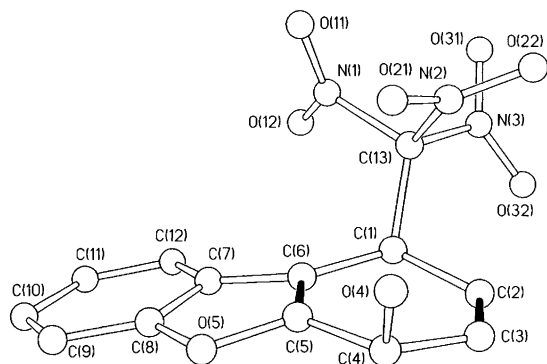


Fig. 3. Perspective drawing of compound **6**. Double bonds are shown in black.

Table 5. Fractional coordinates for atoms in *c*-4-hydroxy-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**6**).

Atom	10 ⁴ X/a	10 ⁴ Y/b	10 ⁴ Z/c	10 ³ U/Å ²
O(4)	–902(7)	7918(6)	2637(2)	34(2)
O(5)	525(7)	6171(5)	1874(2)	22(2)
O(11)	–2619(7)	8796(6)	672(2)	41(2)
O(12)	–551(6)	8971(6)	316(2)	31(2)
O(21)	–2309(7)	9017(6)	1694(2)	32(2)
O(22)	–2232(8)	10998(6)	1623(2)	44(2)
O(31)	–1469(7)	11468(6)	603(2)	35(2)
O(32)	591(8)	11609(5)	978(2)	38(2)
N(1)	–1378(8)	9112(7)	653(3)	22(2)
N(2)	–1885(8)	9952(8)	1509(3)	26(2)
N(3)	–552(9)	11090(7)	875(3)	31(2)
C(1)	626(10)	9253(8)	1325(3)	21(3)
C(2)	915(10)	9901(9)	1822(3)	30(3)
C(3)	796(10)	366(9)	2272(4)	34(3)
C(4)	441(11)	8058(9)	2365(3)	27(3)
C(5)	444(10)	7430(9)	1855(3)	25(3)
C(6)	549(11)	7894(7)	1405(3)	14(2)
C(7)	766(11)	6867(9)	1063(3)	23(3)
C(8)	713(10)	5843(8)	1366(3)	19(3)
C(9)	849(10)	4657(8)	1202(4)	24(3)
C(10)	1150(9)	4508(8)	687(3)	25(3)
C(11)	1252(10)	5524(8)	371(3)	28(3)
C(12)	1054(9)	6696(8)	554(3)	18(3)
C(13)	–756(9)	9808(8)	1105(3)	13(2)

be eluted before the corresponding *t*-4-hydroxy-*r*-1-trinitromethyl-1,4-dihydro epimer **8**.⁵ This inversion of the order of elution relative to that for analogous nitro-trinitromethyl adducts, e.g. **5** and **7**, can be rationalized on the basis that the hydroxyl group in hydroxy-trinitromethyl adducts is the dominant feature in determining the elution order, the more hindered hydroxyl group in the *c*-4-hydroxy-*r*-1-trinitromethyl-1,4-dihydro system **6** allowing more ready elution.

Photochemistry in dichloromethane at –20 °C. The photolysis of the dibenzofuran-tetranitromethane charge-transfer complex at –20 °C gave similar product mixtures as the reaction at 20 °C above. The only feature of note was the systematic increase in the yield of the 3-trinitromethyl aromatic compound **13** with reaction time, presumably the consequence of the decomposition of an unidentified labile adduct.

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 2. Generally, the yields of adducts **4–8** are somewhat lower than for reactions in dichloromethane, with correspondingly higher yields of the nitrodibenzofurans **9–12**.

Photochemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20 °C. The photolysis of the dibenzofuran-tetranitromethane charge-transfer complex at 20 °C in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) gave product mixtures containing only the nitrodibenzofurans **9–12**,

Table 6. Overview of yields of products from the photolysis of dibenzofuran (0.37 mol dm^{-3}) and trinitromethane (0.74 mol dm^{-3}) in 1,1,1,3,3,3-hexafluoropropan-2-ol at 20°C .

t/h	Conversion (%)	Yield (%)			
		9	10	11	12
2	15	6.3	9.0	71.2	13.5
4	25	6.0	9.0	75.9	9.0
8	47	4.7	9.4	75.6	10.3

the 3-nitrodibenzofuran **11** being the major component (Table 6). With the exception of the somewhat higher yield of the 4-nitrodibenzofuran **12**, the yields of the four nitrodibenzofurans **9–12** parallel the yields found for the reaction of dibenzofuran with $\text{NO}_2/\text{N}_2\text{O}_4$ in dichloromethane.³ The absence of adducts **4–8** and 3-trinitromethylidibenzofuran **13** from the product mixtures is a clear indication that attack of trinitromethanide ion on the radical cation of dibenzofuran is largely, if not totally, suppressed by HFP.⁶

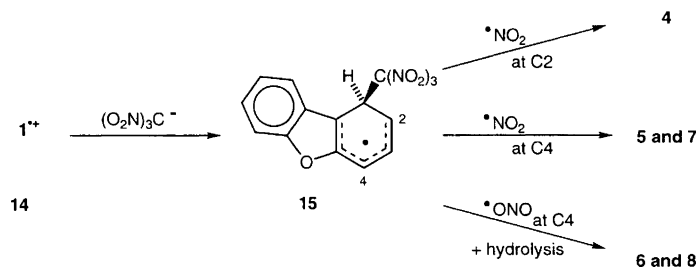
Discussion

The mode of formation of adducts **4–8** and the 3-trinitromethylidibenzofuran **13**. All of the adducts **4–8** arise by initial attack of trinitromethanide ion at C1 of the dibenzofuran radical cation **14** to give the delocalized carbon radical **15** (Scheme 1). Radical coupling of nitrogen dioxide at C2 in the delocalized carbon radical **15**

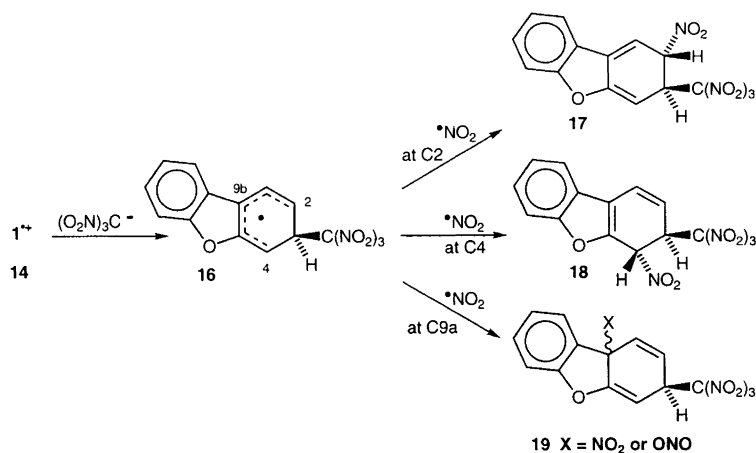
occurs only *anti* to the bulky trinitromethyl group to give the nitro-trinitromethyl adduct **4**. In contrast, radical coupling with nitrogen dioxide, with either C- NO_2 or C- ONO bond formation, can occur at the C4-ring position more remote from the bulky trinitromethyl group in either the *syn* or *anti* sense. These reaction pathways lead either directly to the nitro-trinitromethyl adducts **5** and **7**, or to the hydroxy-trinitromethyl adducts **6** and **8** after hydrolysis of the intermediate nitrite esters which probably occurs under the prevailing acidic reaction conditions.

The complete details of the mode of formation of the 3-trinitromethylidibenzofuran **13** are not known. Clearly it arises by initial attack of trinitromethanide ion at C3 of the dibenzofuran radical cation **14** to give the delocalized carbon radical **16** (Scheme 2). Potentially radical coupling of nitrogen dioxide could occur at C2, C4 or C9b of the delocalized carbon radical **16**, but none of the consequential adducts **17–19** have been identified among the products. It seems unlikely that either of the two potential adducts **17** and **18** would decompose efficiently by loss of HNO_2 to give the 3-trinitromethylidibenzofuran **13**. In contrast, loss of HNO_2 must occur from adduct **19** ($\text{X} = \text{NO}_2$ or ONO) if rearomatization is to be achieved, and it appears likely that such, possibly photochemical decomposition of the sterically compressed adduct **19** is the source of the 3-trinitromethylidibenzofuran **13** (cf. Ref. 7).

The regiochemistry of trinitromethanide ion attack on the dibenzofuran radical cation. Given in Table 7 are the



Scheme 1



Scheme 2

Table 7. Overview of the regiochemistry of trinitromethanide ion attack on the dibenzofuran radical cation as judged by the formation of adducts **4–8** and 3-trinitromethylidibenzofuran **13** after photolysis for 2 h.

$T/^\circ\text{C}$	Attack at C1 (%)	Attack at C3 (%)
In dichloromethane		
20	43	26
–20	41	20
In acetonitrile		
20	29	28
–20	25	33

yields of products formed by trinitromethanide ion attack at C1 and C3 of the dibenzofuran radical cation; in all cases the composition of the 2 h sample is quoted as this reaction time will minimize subsequent decomposition of adducts. Clearly, for both dichloromethane and acetonitrile as reaction solvent, the influence of reaction temperature on the regiochemistry of trinitromethanide ion attack is minimal. Further, although there is a tendency for a shift in favour of C3-attack in acetonitrile relative to the regiochemistry of attack observed in dichloromethane, this shift is not dramatic. Overall, adducts **4–8** and 3-trinitromethylidibenzofuran **13** are formed by attack of trinitromethanide ion at C1 and C3 respectively, in keeping with theoretical predictions for this non-alternant system.³

The chemoselectivity of the dibenzofuran–tetranitromethane– $h\nu$ reaction in HFP. HFP has been found to stabilize radical cations strongly,^{6,8} presumably by making any nucleophilic species present exceedingly unreactive.^{8d} Thus the ESR spectrum of the radical cation of 1,4-dimethoxybenzene appeared with high intensity during irradiation of 1,4-dimethoxybenzene-tetranitromethane in HFP at room temperature, despite the fact that trinitromethanide ion was generated simultaneously.

We therefore anticipated that HFP should inhibit the attack of trinitromethanide ion on the radical cation and thus by default favour the occurrence of the radical cation– NO_2 coupling process. The results of Table 6 show this assumption to be correct: no adducts are formed, and the distribution of nitro products is such as would be expected for the $\text{ArH}^{\cdot+}$ – NO_2 reaction if the spin density of $(\text{dibenzofuran})^{\cdot+}$ determines the regioselectivity.³

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer; ^1H 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 ultra-

violet spectrometric detector and hexane–dichloromethane as solvent mixtures. Tetranitromethane and dibenzofuran were purchased from Aldrich. Dichloromethane (AR) and acetonitrile (HiPerSolv) were from BDH and 1,1,1,3,3,3-hexafluoropropan-2-ol from Sigma.

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 compounds.⁹

General procedure for the photonitration of dibenzofuran (1) with tetranitromethane. A solution of dibenzofuran (**1**) (500 mg, 0.37 mol dm^{-3}) and tetranitromethane (0.74 mol dm^{-3}) in dichloromethane (at 20 or -20°C) or acetonitrile (20 or -20°C) was irradiated with filtered light ($\lambda_{\text{cut-off}}$ 435 nm). Aliquots were withdrawn from the reaction mixture at appropriate time intervals, the volatile material removed under reduced pressure at $\leq 0^\circ\text{C}$, and the product composition determined by NMR spectral analysis (Tables 1 and 2).

Photochemistry in dichloromethane at 20°C and the identification of the products. Reaction of dibenzofuran–tetranitromethane in dichloromethane at 20°C , as above, for 8 h gave a product which was shown by ^1H NMR spectra to be a mixture (Table 1) of adducts (**4–8**) (total 31%), nitrodibenzofurans (**9–12**) (total 17%), trinitromethylidibenzofuran (**13**) (30%), unidentified adducts (total 16%) and unidentified aromatic compounds (total 7%). The mixture was partially separated into its components by HPLC and gave the following in elution order:

The first material eluted was a mixture of the nitrodibenzofurans (**9–11**) and trinitromethylidibenzofuran (**13**), which was separated into its components by chromatography on a silica gel Chromatotron plate (see below).

4-Nitrodibenzofuran (12), identical with authentic material.^{3,10} ^1H NMR (CDCl_3) δ 7.45 (dt, H8), 7.47 (dt, H7), 7.59 (dt, H2), 7.76 (dd, H9), 8.01 (dd, H6), 8.26 (dd, H1), 8.29 (dd, H3).

t-2-Nitro-r-1-trinitromethyl-1,2-dihydrodibenzofuran (4), m.p. 100°C (decomp.) (X-ray crystal structure determined, see below). ^1H NMR (CDCl_3) δ 5.73 (d, $J_{\text{H}_2,\text{H}_3}$ 5.4 Hz, H2), 6.20 (dd, $J_{\text{H}_3,\text{H}_4}$ 9.7 Hz, $J_{\text{H}_3,\text{H}_2}$ 5.4 Hz, H3), 6.37 (br s, H1), 6.96 (d, $J_{\text{H}_4,\text{H}_3}$ 9.7 Hz, H4), 7.30–7.55 (m, H6, H7, H8, H9). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.73 gave enhancements at δ 6.20 (2.5%) and at δ 6.37 (2.2%); irradiation at δ 6.20 gave enhancements at δ 5.73 (4.6%) and at δ 6.96 (5.7%); irradiation at δ 6.37 gave enhancements at δ 5.73 (1.9%) and at δ 7.50 (1.1%); irradiation at δ 6.96 gave an enhancement at δ 6.20 (3.4%). ^{13}C NMR (CDCl_3) δ 40.9 (C1), 77.5 (C2), 120.3 (C3), 112.5, 119.1, 124.7, 124.9, 126.6 (C4, C6, C7, C8, C9), signals

for C4a, C5a, C9a, C9b not observed in a weak spectrum. The above assignments were confirmed by reverse detected heteronuclear correlation spectra (HMQC).

t-4-Nitro-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**5**), isolated only in low yield as an impure solid. ¹H NMR (CDCl₃) δ 5.79 (ddd, *J*_{H1,H4} 4.4 Hz, *J*_{H1,H2} 3.9 Hz, *J*_{H1,H3} 1.2 Hz, H1), 6.25 (ddd, *J*_{H4,H1} 4.4 Hz, *J*_{H4,H3} 2.5 Hz, *J*_{H4,H2} 2.5 Hz, H4), 6.61 (ddd, *J*_{H3,H2} 10.0 Hz, *J*_{H3,H4} 2.5 Hz, *J*_{H3,H1} 1.2 Hz, H3), 6.72 (ddd, *J*_{H2,H3} 10.0 Hz, *J*_{H2,H1} 3.9 Hz, *J*_{H2,H4} 2.5 Hz, H2), 7.35–7.6 (m, H6, H7, H8, H9). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.79 gave enhancements at δ 6.72 (2.9%) and at δ 7.54 (0.8%); irradiation at δ 6.25 gave an enhancement at δ 6.61 (1.0%); irradiation at δ 6.61 gave enhancements at δ 6.25 (6.4%) and at δ 6.72 (7.2%); irradiation at δ 6.72 gave enhancements at δ 5.79 (6.5%) and at δ 6.61 (7.2%). ¹³C NMR (CDCl₃) δ 42.6 (C1), 77.8 (C4), 131.0 (C3), the remainder of the spectrum could not be assigned because of initial impurities and some decomposition of **5** during the spectrum acquisition; the signals assigned were confirmed by reverse detected heteronuclear correlation spectra (HMQC). This adduct **5** is clearly identical with compound **2** (isomer 2) previously detected by ¹H NMR in a reaction mixture.³

c-4-Hydroxy-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**6**), eluted with *c*-4-nitro-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**7**), was separated in low yield from the mixture by crystallization from ether–pentane mixtures to give m.p. 106–108 °C (X-ray crystal structure determined, see below). ¹H NMR (CDCl₃) δ 5.28 (dd, *J*_{H4,H3} 4.4 Hz, *J*_{H4,H1} 3.7 Hz, H4), 5.60 (dd, *J*_{H1,H4} 3.7 Hz, *J*_{H1,H2} 3.5 Hz, H1), 6.43 (dd, *J*_{H2,H3} 9.8 Hz, *J*_{H2,H1} 3.5 Hz, H2), 6.53 (dd, *J*_{H3,H2} 9.8 Hz, *J*_{H3,H4} 4.4 Hz, H3), 7.27–7.65 (m, H6, H7, H8, H9). Nuclear Overhauser experiments gave the following results: irradiation at δ 5.28 gave an enhancement at δ 6.53 (2.9%); irradiation at δ 5.60 gave enhancements at δ 6.43 (2.9%) and at δ 7.50 (0.5%); irradiation at δ 6.43 gave enhancements at δ 5.60 (3.9%) and at δ 6.53 (5.3%); irradiation at δ 6.53 gave enhancements at δ 5.28 (3.0%) and at δ 6.43 (3.7%). ¹³C NMR (CDCl₃) (on a mixture of adducts **6** and **7**) δ 42.9 (C1), 60.3 (C4), 123.3 (C2), 136.5 (C3), the assignment of the remainder of the spectrum was uncertain; the signals assigned were confirmed by reverse detected heteronuclear correlation spectra (HMQC). This adduct **6** is clearly identical with compound **3** previously detected by ¹H NMR in a reaction mixture.³

c-4-Nitro-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**7**) was obtained only in admixture with adduct **6**, above. ¹H NMR (CDCl₃) δ 5.72 (br dd, *J*_{H1,H2} 3.4 Hz, *J*_{H1,H4} 3.4 Hz, H1), 6.14 (dd, *J*_{H4,H3} 4.9 Hz, *J*_{H4,H1} 3.4 Hz, H4), 6.75 (m, H2, H3), the remainder of the spectrum obscured by adduct **6**. Nuclear Overhauser experiments gave the following results: irradiation at δ 5.72 gave

enhancements at δ 6.73 (1.7%) and at δ 7.54 (0.7%); irradiation at δ 6.14 gave an enhancement at δ 6.76 (1.4%); irradiation at δ 6.75 gave enhancements at δ 5.72 (4.3%) and at δ 6.14 (3.7%). ¹³C NMR (CDCl₃) δ 42.9 (C1), 76.3 (C4), 126.9 (C2), 128.2 (C3), the assignment of the remainder of the spectrum was uncertain; the signals assigned were confirmed by reverse detected heteronuclear correlation spectra (HMQC). This adduct **7** is clearly identical with compound **2** (isomer 1) previously detected by ¹H NMR in a reaction mixture.³

Chromatography of the non-polar mixture of the nitrodibenzofurans (**9–11**) and trinitromethyldibenzofuran (**13**) on a silica gel Chromatotron plate allowed their separation in elution order:

3-Trinitromethyldibenzofuran (**13**), m.p. 77–78 °C (X-ray crystal structure determined, see below). ¹H NMR (CDCl₃) δ 7.45 (1H), 7.55 (1H), 7.63 (2H), 7.90 (1H), 8.03 (1H), 8.11 (1H).

1-Nitrodibenzofuran (**9**), identical with authentic material.^{3,11} ¹H NMR (CDCl₃) δ 7.47 (dt, H6), 7.52 (dt, H7), 7.57 (m, H3,H5), 7.91 (dd, H4), 8.24 (dd, H2), 8.69 (dd, H8).

2-Nitrodibenzofuran (**10**), identical with authentic material.^{3,12} ¹H NMR (CDCl₃) δ 7.45 (dt, H7), 7.58 (dt, H6), 7.65 (m, H5, H8), 8.02 (dd, H4), 8.40 (dd, H3), 8.86 (dd, H1).

3-Nitrodibenzofuran (**11**), identical with authentic material.^{3,11} ¹H NMR (CDCl₃) δ 7.43 (dt, H7), 7.61 (dt, H6), 7.66 (dd, H8), 8.03 (dd, H5), 8.04 (d, H1), 8.24 (dd, H2), 8.43 (d, H4).

Photochemistry in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) at 20 °C. A solution of dibenzofuran (250 mg, 0.37 mol dm⁻³) and tetranitromethane (0.74 mol dm⁻³) in HFP at 20 °C was irradiated with filtered light ($\lambda_{\text{cut-off}}$ 435 nm) for 8 h. Aliquots were withdrawn from the reaction mixture at appropriate time intervals and, after work-up, the product composition was determined by NMR spectral analysis (Table 6). The exclusive products were the four isomeric nitrodibenzofurans (**9**) (5%), (**10**) (9%), (**11**) (76%), and (**12**) (10%).

Crystallography. Crystal data, established from precession photographs and measured accurately, by means of a Siemens R3m/V four-circle diffractometer [molybdenum X-radiation, $\lambda(\text{Mo K}\alpha)$ 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 25 accurately centred high-angle reflections were used.

Crystal data.

t-2-Nitro-*r*-1-trinitromethyl-1,2-dihydrodibenzofuran (**4**), C₁₃H₈N₄O₈, *M* 348.23, orthorhombic, space group *Pca*2₁, *a* 12.160(3), *b* 8.519(2), *c* 27.78(1) Å; *V* 2877.2 (1) Å³, *D*_c 1.608 g cm⁻³, *Z* 8, μ(Mo Kα) 1.37 cm⁻¹. The crystal was colourless and of approximate dimensions 0.5 × 0.38 × 0.34 mm. Data were collected at 163(2) K out to a maximum Bragg angle θ = 24.0°. Number of independent reflections measured 2306, 1488 with *I* > 2σ(*I*). Absorption corrections were not applied; *g*₁ 0.0207, *g*₂ 0.0000; *R*_(obs)-factor 0.034, *wR*_(all data) 0.057.

c-4-Hydroxy-*r*-1-trinitromethyl-1,4-dihydrodibenzofuran (**6**), C₁₃H₉N₃O₈, *M* 335.23, orthorhombic, space group *Pccn*, *a* 9.386(4), *b* 10.914(4), *c* 26.294(9) Å; *V* 2694(2) Å³, *D*_c 1.653 g cm⁻³, *Z* 8, μ(Mo Kα) 1.41 cm⁻¹. The crystal was colourless and of approximate dimensions 0.54 × 0.25 × 0.1 mm. Data were collected at 166(2) K out to a maximum Bragg angle θ = 22.5°. Number of independent reflections measured 1771, 721 with *I* > 2σ(*I*). Absorption corrections were not applied; *g*₁ 0.0000, *g*₂ 0.0000; *R*_(obs)-factor 0.079, *wR*_(all data) 0.093.

3-Trinitromethylidibenzofuran (**13**), C₁₃H₇N₃O₇, *M* 317.22, monoclinic, space group *P*2₁/*c*, *a* 12.296(4), *b* 6.893(4), *c* 16.337(6) Å, β 108.83(1)°; *V* 1311(1) g cm⁻³, *Z* 4, μ(Mo Kα) 1.34 cm⁻¹. The crystal was pale yellow and of approximate dimensions 0.85 × 0.6 × 0.4 mm. Data were collected at 163(2) K out to a maximum Bragg angle θ = 25.0°. Number of independent reflections measured 2295, 1689 with *I* > 2σ(*I*). Absorption corrections were not applied; *g*₁ 0.0893, *g*₂ 0.0900; *R*_(obs)-factor 0.050, *wR*_(all data) 0.148.

Structure determination. Full-matrix least-squares refinements (SHELXL-93)¹³ 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 refinement based on *F*. Reflection weights 1/[σ²(*F*_o²) + (*g*₁*P*)² + *g*₂*P*], where *P* = [*F*_o² + 2*F*_c²]/3, were used. All non-hydrogen

atoms were assigned anisotropic thermal parameters. Final Fourier syntheses show no significant residual electron density, and there were no abnormal discrepancies between observed and calculated structure factors.

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