

Photochemical Nitration by Tetranitromethane.

III.[†] On the Anomalous Nitration and Oxidative Substitution of Dibenzofuran and a Novel Test of the Shaik–Pross Model of Radical Cation Reactivity

Lennart Ebersson,^{a,*} Michael P. Hartshorn,^{a,‡} Finn Radner,^a Manuela Merchán,^{b,§} and Björn O. Roos^b

Division of ^aMAX chemistry and ^bTheoretical Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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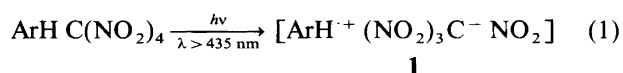
The photochemical reaction of dibenzofuran and tetranitromethane in dichloromethane gives predominantly nitro/trinitromethyl adducts and only a small amount of nitro-substitution products. The adducts originate from the reaction between photochemically produced trinitromethanide ion and (dibenzofuran)⁺, followed by reaction of the trinitromethyl-substituted cyclohexadienyl radical with NO₂. The main sites of attack of trinitromethanide ion are the 1- and the 3-positions. The adducts rapidly eliminate nitroform in the presence of a hindered base. Thus photolysis with such a base present gives directly a mixture containing predominantly 2- and 4-nitrodibenzofuran.

The unexpected attack of trinitromethanide at the 3-position of (dibenzofuran)⁺ is also found in more typical oxidative substitution reactions, such as acetoxylation and cyanation. This isomer distribution is distinctly different from that of electrophilic substitution in dibenzofuran (attack at the 2-position), a non-alternant conjugated system. The Shaik–Pross treatment of the radical cation/nucleophile elementary step predicts that the spin density of the corresponding triplet should govern the isomer distribution, and CASSCF calculations show that (dibenzofuran)⁺ then should react predominantly in the 3-position. Thus the electrophilic reactivity of the radical cations of non-alternant systems constitutes a novel test of the configuration mixing model.

It is also concluded that the unusual substitution pattern of dibenzofuran with respect to electrophilic nitration is due to incursion of the nitrous acid catalyzed (NAC) reaction.

Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

We have recently shown that the photonitration of naphthalene by tetranitromethane (TNM) in dichloromethane occurs predominantly ($\approx 85\%$) via an addition/elimination process.¹ The naphthalene/TNM charge-transfer (CT) complex is excited to give the triad **1** [eqn. (1); ArH = naphthalene],² from which adducts are formed by initial attack of (NO₂)₃C⁻ upon ArH⁺,



followed by reaction of the hydroarenyl radicals with NO₂. Elimination of nitroform during work-up/analysis gives a nitro-product mixture with a low α/β ratio, ca. 3. A closer study of one of the nitro/trinitromethyl adducts from naphthalene, *cis*-1,4-dihydro-1-nitro-4-trinitromethylnaphthalene, showed it to undergo fast elimination of nitroform at 20°C in the presence of a hindered base ($\tau_{1/2}$ ca. 20 s in dichloromethane with 0.2 M 2,6-di-*t*-butylpyridine, DTBPy) and slow, spontaneous elimination of nitroform in acetonitrile ($\tau_{1/2}$ ca. 25 h).³

The remaining 15% reaction involved direct nitration of naphthalene by NO₂,[†] presumably catalyzed by acid

* To whom correspondence should be addressed.

[†] Part II, see Ref. 3.

[‡] Permanent address: Department of Chemistry, University of Canterbury, Christchurch, New Zealand.

[§] On leave from: Universitat València, Departamento de Química Física, Doctor Moliner 50, Burjassot, E-46100 València, Spain.

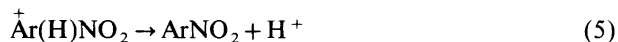
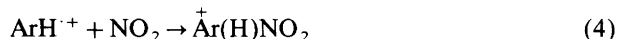
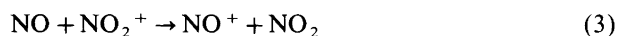
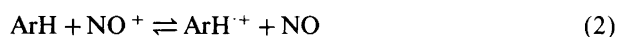
[†] In the following, we represent NO₂/N₂O₄ simply as 'NO₂', in spite of the fact that NO₂ is the minor component of the fast equilibrium between these species.^{4c}

and/or N(III) species⁴ formed during photolysis. This gave an α/β ratio of ca. 20. The origin of NO_2 was leakage from **1**, as shown by EPR spectral analysis.¹ This reaction was suppressed by running the photolysis in the presence of DTBPY, known to prevent nitration by NO_2 .⁴

1-Methoxynaphthalene, which is $>10^2$ times more reactive toward NO_2 than naphthalene, behaved similarly, although the proportion of NO_2 nitration was higher and the photochemistry was complicated by dark nitration reactions of partly unknown origin.¹

In looking for other substrates suitable for further mechanistic exploration of photonitration by TNM, our attention was drawn to the unusual behavior of dibenzofuran (numbering, see Fig. 1). This compound undergoes electrophilic substitution at the 2-position, except for nitration which occurs preferentially at the 3-position with 'normal' NO_2^+ generating reagents, such as 99% nitric acid in sulfuric acid.⁵ Only with NO_2BF_4 in nitroethane or dichloromethane and with alkyl nitrate/ AlCl_3 was a weak preference for the 2-position noticed. Nitration with $h\nu/\text{TNM}$ showed selectivity toward the 3-position in dichloromethane and acetonitrile and an increased proportion of the otherwise insignificant 4-isomer.

This work was interpreted⁶ in terms of an NO_2^+ mechanism involving a late transition state, leading to 2-substitution and an early transition state leading to 3-substitution. However, one important aspect of nitration by NO_2^+ was omitted, namely the necessity of controlling the competing and sometimes dominating nitrous acid catalyzed (NAC) nitration, as emphasized by Ridd *et al.*⁷ and by us.⁴ We have therefore run experiments designed to delineate the contribution from the NAC reaction, assumed to proceed via an electron-transfer mechanism [eqns. (2)–(5)].⁷ In combination with the results from photonitrations and some oxidative



substitution reactions,^{8,9} these data suggest a different explanation for the curious behavior of dibenzofuran in nitration.

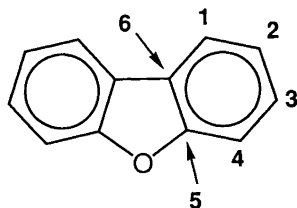


Fig. 1. Numbering scheme of dibenzofuran.

Results and discussion

Electrochemistry of dibenzofuran. Upon cyclic voltammetry at 100 mV s^{-1} , dibenzofuran displayed an irreversible wave at $E_p \approx 1.9$ vs. Ag/AgCl in dichloromethane/tetrabutylammonium hexafluorophosphate (0.16 M), its redox reactivity thus being similar to that of naphthalene. As expected, dibenzofuran gives a CT complex with TNM, as shown in Fig. 2.

Formation of nitro/trinitromethyl adducts. Irradiation of a dichloromethane solution of dibenzofuran (1.0 M) and TNM (2.0 M) with filtered light ($\lambda > 435 \text{ nm}$) at $\approx 20^\circ\text{C}$ for 51 h produced a slightly acidic solution which was worked up by evaporation at or below 0°C . NMR spectral examination of the crude product mixture showed that the predominant components were three major adducts ($\approx 50\%$) and that nitrobenzofurans were present in a total amount of only 4.5% (1-/2-/3-/4- equal to 1/15/72/12). Unchanged dibenzofuran constituted 8% of the mixture. According to NMR spectral analysis two of the adducts in all probability consisted of the two stereoisomers of 4-nitro-1-trinitromethyl-1,4-dihydrodibenzofuran, the third adduct being *trans*-4-nitro-3-trinitromethyl-1,4-dihydrodibenzofuran.

The crude product mixture above upon GLC analysis gave elimination products (nitrobenzofurans and dibenzofuran) exactly as described for an analogous adduct of naphthalene, *cis*-1-nitro-4-trinitromethyl-1,4-dihydronaphthalene.³ It was also ascertained that the dibenzofuran adducts underwent fast elimination in dichloromethane upon treatment with a hindered base (2,6-di-*t*-butylpyridine; $k_2 \approx 2.5 \text{ M}^{-1} \text{ s}^{-1}$). NMR spectral examination of the base-induced elimination process showed that the three adducts disappeared completely and were replaced by 4-nitrobenzofuran (ca. 45% of the mixture). This confirms the attachment of the nitro group to the 4-position in all three adducts. The chemical behavior of these adducts, as well as adducts from several other systems, will be described in a future publication.

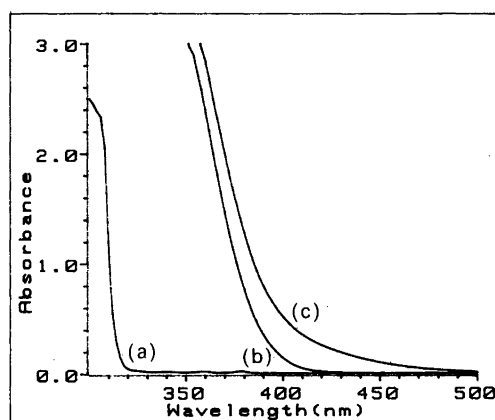


Fig. 2. UV/VIS spectra of (a) dibenzofuran (12 mM), (b) tetranitromethane (0.27 M) and (c) dibenzofuran (12 mM) + tetranitromethane (0.27 M) in dichloromethane.

Thus it should be stressed that the photonitration results reported below were obtained by GLC analysis of reaction mixtures that originally contained predominantly adducts. Only runs with hindered base present gave nitro products directly, owing to fast elimination of nitroform from adducts. We assume, nevertheless, that we have obtained unambiguous information about the location of the nitro group in the adducts.

Nitro substitution in dibenzofuran. Table 1 shows the isomer distributions from nitration of dibenzofuran by different reagents. Key results by Keumi *et al.*⁶ have been included for comparison. As shown by entry 5, it is also possible to obtain preferential 2-substitution by HNO₃, provided azide ion is present in high concentration (≈ 0.07 M) to trap any N(III) species formed.⁷ This result compares well with those of entries 1–4 which represent nitronium-ion-mediated nitrations. However, as we go to established nitrous acid catalyzed processes (entries 10–12) nitration is directed towards the 3-position. This indicates that reactions employing 99% HNO₃ in various solvents as the nitrating reagent (entries 6–9; further examples, see Ref. 5) are influenced by the nitrous acid catalyzed process.

For the photochemical nitration of dibenzofuran by TNM two features are outstanding. First, as long as the NO₂ nitration process (from triad leakage) and other dark nitration mechanisms¹ are not inhibited by addition of DTBPy, substitution at the 3-position is still favored (entries 13–17), but the previously insignificant 4-isomer starts to appear, especially in dichloromethane.

Obviously, this isomer is formed by elimination of nitroform from the adduct described above. Second, prevention of NO₂ nitration and promotion of elimination from adducts by addition of 10 mol% DTBPy changes the substitution pattern to predominantly 2-/4-substitution and gives as little as 18% 3-substitution.

Reaction of (dibenzofuran)⁺ with nucleophiles. Since the nitration results, especially those for photochemical reactions, are not easily understandable without some knowledge of the reactivity of (dibenzofuran)⁺, we have investigated oxidative cyanation⁸ and acetoxylation⁹ of dibenzofuran, both archetypal radical cation/nucleophile reactions. Isomer distributions of these reactions are listed in Table 2, and it is immediately noticeable that they differ significantly from those of the electrophilic substitution reactions of dibenzofuran, some of which are given for comparison in the lower part of Table 2. The radical cation/nucleophile reaction gives mainly 3-substitution, whereas electrophilic attack upon neutral dibenzofuran gives mostly 2-substitution product.

This behavior contrasts with the known behavior of aromatic radical cations where isomer distributions from ArH⁺/nucleophile reactions are similar to those of ArH/electrophile reactions. We suggest an explanation of this difference based on the following reasoning.

The Shaik–Pross treatment of the reactions of radical cations of non-alternant systems with nucleophiles. The transition state of the elementary reaction between a radical cation, RH⁺, and a nucleophile, Nu⁻, is described by the Shaik–Pross configurational mixing (CM) model¹⁰ as

Table 1. Nitration of dibenzofuran with different reagents.

Entry	Reagent	Solvent	Temp/°C	Isomer distribution					Ref.
				1-	2-	3-	4-	2-/3- Ratio	
1	EtONO ₂ /AlCl ₃	EtNO ₂	20	11	52	35	2	1.5	6
2a	CMN ^a /AlCl ₃	MeNO ₂	20	10	51	37	2	1.4	6
2b				13	51	33	3	1.5	This work
3	NO ₂ BF ₄	EtNO ₂	0	22	43	33	2	1.3	6
4	NO ₂ BF ₄	CH ₂ Cl ₂	-50	21	41	36	2	1.1	6
5	NaNO ₃ , N ₃ ⁻	HOAc/H ₂ SO ₄ ^b	20	13	52	34	1	1.5	This work
6	99% HNO ₃	Ac ₂ O	20	11	39	48	2	0.81	6
7	99% HNO ₃	Ac ₂ O	20	9	14	77	<0.1	0.18	This work
8	99% HNO ₃	TFA	0	3	4	93	1	0.04	6
9	100% HNO ₃	TFA	0	3	10	87	<0.1	0.11	This work
10	NaNO ₂ ^c	CH ₂ Cl ₂ /TFA ^d		10	12	78	<0.1	0.15	This work
11	NO ₂ /N ₂ O ₄	CH ₂ Cl ₂	20	10	13	77	<0.1	0.17	This work
12	NO ₂ /N ₂ O ₄ /NO ⁺ ^e	CH ₂ Cl ₂	20	10	12	78	<0.1	0.15	This work
13	TNM/hν (UV)	TFA	0	6	11	83	1	0.13	6
14	TNM/hν (λ > 430 nm)	TFA	20	7	10	83	<0.1	0.12	This work
15	TNM/hν (UV)	CH ₃ CN	0	10	22	63	5	0.35	6
16	TNM/hν (λ > 430 nm)	CH ₃ CN	20	11	17	69	3	0.25	This work
17	TNM/hν (λ > 430 nm)	CH ₂ Cl ₂	20	8	11	57	24	0.19	This work
18	TNM/hν (λ > 430 nm)/10 mol% DTBPy	CH ₃ CN	20	8	40	18	33	2.2	This work
19	TNM/hν (λ > 430 nm)/10 mol% DTBPy	CH ₂ Cl ₂	20	6	31	18	45	1.7	This work

^a 1-Cyano-1-methylethyl nitrate. ^b HOAc/H₂SO₄ = 4/1 (v/v). ^c See Ref. 4(d): 'nitration under standard conditions.'

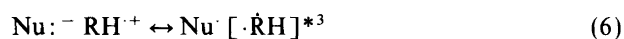
^d CH₂Cl₂/TFA = 3/1 (v/v). ^e Mol% NO⁺ = 5.

Table 2. Oxidative substitution reactions involving nucleophilic attack upon [dibenzofuran]⁺ and electrophilic attack upon dibenzofuran.

Reaction	Isomer distribution (%)				Ref.
	1-	2-	3-	4-	
Oxidative substitutions					
Anodic cyanation in MeOH	8	17	71	4	8
Photocyanation in MeOH	9	27	64	<0.5	8
Anodic acetoxylation in HOAc	32	3	62	3	9
Acetoxylation by 12-tungstocobaltate(III) in HOAc	42	1	55	2	9
Acetoxylation by hexa(nitrato)cerate(IV) in HOAc	32	2	64	2	9
Acetoxylation by Ag(II)/peroxydisulfate in HOAc	29 ^b	1	70		9
Photochemical trinitromethylation in dichloromethane/DTBPy ^a	7	15	71	6	This work
Electrophilic substitutions					
Protiodetrinitration in TFA	3	86	7	4	6
Protiodesilylation by HClO ₄ in MeOH	3	83	10	4	6
Acylation (PhCOCl/AlCl ₃) in nitrobenzene	0.7	92	7	0.4	6
Alkylation (PhCH ₂ Cl/AlCl ₃) in CHCl ₃	12	50	32	6	6
Nitration by HNO ₃ /N ₃ ⁻	13	52	34	1	This work

^a Determined after conversion into nitriles (under GLC conditions). ^b 1- and 4-isomer together.

a hybrid between the initial-state configuration and one in which an electron has been shifted from Nu: ⁻ to RH⁺,



and in order to achieve bonding between the reactants one must assume that RH has undergone excitation to its triplet state. This has led to the prediction that radical cations should react slowly with nucleophiles, relative to reactions between carbocations and nucleophiles. This proposal is currently under discussion.¹¹

In contemplating the initially puzzling chemical behavior of the dibenzofuran radical cation, we realized that this species is not analogous to most radical cations so far studied. Dibenzofuran corresponds to the non-alternant fluorenyl system and thus the spin densities of its radical cation and anion should be distinctly different, in contrast with the situation for alternant hydrocarbons where calculations according to simple MO theory give identical absolute values of the spin densities of the radical cation and anion, respectively (the pairing theorem¹²). Since the Shaik-Pross CM model requires that the spin densities of the radical cation and the triplet state of the neutral molecule are the relevant ones for its reactivity, the reactivity of radical cations of non-alternant systems toward nucleophiles should provide a new way of testing the CM model. The calculations reported below show that this approach holds some promise.

Theoretical calculations. In order to determine the spin densities in the radical cation and triplet state of dibenzofuran, we performed a set of *ab initio* quantum chemical calculations, to our knowledge the first ones performed

on this system. The complete active space (CAS) SCF method¹³ was used. This is a multi-configurational SCF method where the wavefunction comprises all configurations that can be generated by distributing a set of *active* electrons among a set of *active* MOs in all possible ways consistent with overall spin and space symmetry of the wavefunction. In the present case the active orbitals were chosen as the 13 valence π -orbitals, while all σ -orbitals were kept *inactive*, that is, doubly occupied. A CASSCF wavefunction is a true spin eigenfunction, in contrast with the unrestricted Hartree-Fock (UHF) wavefunctions most commonly used to compute spin densities in organic radicals. On the other hand, the CASSCF wavefunction will have unpolarized σ -electrons. We do not believe, however, that this will greatly influence the spin densities in the π -electron system which is the main concern of the present study.

The basis set used was of the atomic natural orbital (ANO) type.¹⁴ For carbon and oxygen 3 s- and 2 p-type ANOs were used and for hydrogen 2 s-type ANOs. The total basis set then consists of 133 ANOs. All calculations were performed at the experimental equilibrium geometry¹⁵ of the dibenzofuran molecule. All calculations were performed on the IBM 9021/500-2NF computer at the University of Valencia using the programs included in the MOLCAS-2 quantum chemistry software.¹⁶ The CASSCF program of MOLCAS-2 has recently been modified to include calculations of spin density matrices.¹⁷ The total and relative energies of the species studied are presented in Table 3, where the number of configurations for the different wavefunctions are also given in order to illustrate the size of these calculations. Actually they are the largest so far performed with the MOLCAS-2 system. It might be of interest to compare the present data with similar data obtained with the STO-3G

Table 3. SCF and CASSCF energies, relative energies and dipole moments for the different electronic states of dibenzofuran (DBF) and its radical cation (DBF⁺).

State	Number of CSFs ^a	Total energy/au	Excitation energy/eV	Dipole moment/au
DBF				
¹ A ₁	368432	-533.877598	—	-0.7765
³ B ₂	644406	-533.744972	3.61	-0.8588
³ A ₁	643881	-533.724946	4.15	-0.6935
DBF ⁺				
² A ₂	644056	-533.578217	8.15	—
² B ₁	644231	-533.576988	8.18	—

^a Number of spin projected configurations in the CASSCF wave function.

basis set commonly used in calculations on these types of system. The CASSCF energy for dibenzofuran radical cation obtained with such a basis set is -527.2315 au, more than 6 au higher than the energy obtained with the ANO basis set.

The lowest excited state of dibenzofuran is ³B₂, with a calculated energy of 3.61 eV (83 kcal mol⁻¹) above the ground state. The next state is ³A₁ with an energy 4.15 eV above the ground state. There are, to our knowledge, no experimental data with which these results can be compared. Based on earlier experience on similar systems we estimate the accuracy of the computed excitation energies to be about 0.5 eV.

The radical cation has an interesting electronic struc-

ture. The two lowest electronic states are almost degenerate, with ²A₂ only 0.03 eV below ²B₁. There is no experimental evidence to confirm this result, but the calculations are accurate enough to establish that the two states are close in energy. As a result dibenzofuran radical cation is predicted to be a very polarizable system, where the positive charge is easily localized on one of the benzene rings. Attack of a nucleophile will immediately lead to such localization. The solvent interaction will, in fact, in most cases be sufficient for localization of the charge, probably resulting in deformation of the geometry.

The calculated spin densities are given in Table 4. They were obtained by a Mulliken population analysis of the spin density matrices obtained from the CASSCF wavefunction. The spin density of the lower triplet state (³B₂) is largest in positions C1 and C3, the value for C3 being somewhat larger. If a nucleophilic attack on dibenzofuran radical cation follows the Shaik-Pross model [eqn. (6)], spin densities on both radical cation and neutral triplet state indicate that the preferred position of attack should be C3, in agreement with experimental findings (see below).

We also calculated the spin densities for the radical cation and *anion*, using the smaller basis set commonly used in studies of this type, namely STO-3G. The same CASSCF calculations as with the larger ANO basis set were performed, as were also UHF calculations using the GAUSSIAN program system.¹⁸

We first notice (Table 4) that the spin densities for (dibenzofuran)⁺ (²B₁) differ somewhat from the ANO results but show the same qualitative features. The UHF

Table 4. Spin density populations for different states of dibenzofuran (DBF).^a

State	Spin density at						
	O	C1	C2	C3	C4	C5	C6
ANO basis set							
DBF(³ B ₂)	0.011	0.292	-0.007	0.322	0.116	0.122	0.149
DBF(³ A ₁)	0.028	0.322	0.156	0.039	0.325	0.128	0.015
DBF ⁺ (² A ₂)	-0.013	0.083	-0.029	0.263	-0.074	0.148	0.115
DBF ⁺ (² B ₁)	0.336	0.018	0.185	-0.080	0.187	-0.025	0.047
STO-3G basis set, CASSCF results							
DBF ⁺ (² B ₁)	0.529	-0.019	0.155	-0.072	0.168	-0.069	0.075
DBF ⁻ (² B ₁)	0.011	0.212	-0.089	0.229	0.039	0.017	0.085
STO-3G basis set, UHF results							
DBF ⁺ (² B ₁)	0.675	-0.463	0.543	-0.520	0.540	-0.404	0.467
DBF ⁻ (² B ₁)	0.064	0.493	-0.486	0.529	-0.322	0.319	-0.065
DBF ⁺ in an electric field (see the text)							
(Benzene) ¹	0.065	-0.092	0.367	0.104	-0.018	0.288	0.210
(Benzene) ²	—	0.076	-0.032	0.060	-0.016	0.040	-0.051

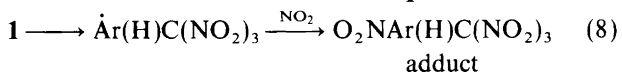
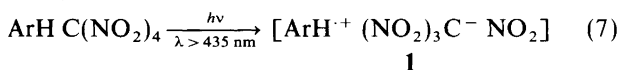
^a Obtained from a Mulliken population analysis of the spin density matrices.

results differ strongly, with large and alternant spin densities on all carbon atoms. The UHF wavefunction has a large spin contamination with an S^2 value of 2.17. It is obvious that the UHF approach is not reliable for extended π -electron systems which commonly have large near-degeneracy effects.

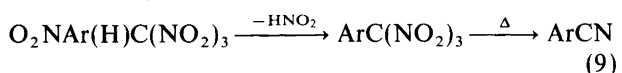
An EPR spectral study¹⁹ of (dibenzofuran)⁻ gave the following proton hyperfine constant assignments: C1 4.90, C2 0.93, C3 4.74 and C4 1.95. This is in excellent agreement with the CASSCF results from which the McConnell equation²⁰ gives the following a^H : C1 4.9, C2 2.0, C3 5.3 and C4 0.9 G, assuming that $Q_{C-H}^H = -23$ G. In fact, there is no strong reason why the assignments of the 2- and 4-couplings might not be interchanged, thus making the agreement perfect. This contrasts with the corresponding values obtained from the UHF calculations: C1 11.3, C2 11.2, C3 12.2 and C4 7.4.

A CASSCF calculation, using the same STO-3G basis set, was also performed on (dibenzofuran)⁺ in an electric field in the plane of the molecule and perpendicular to the symmetry axis. This was done in order to obtain a qualitative picture of the spin densities of the molecule in a polarizing medium or when approached by a polarizing reagent, e.g., a nucleophile. A field strength of 0.01 au was assumed. The results are presented at the bottom of Table 4. The spin densities of the two benzene rings are now different, as expected. One of the rings, (benzene)², is almost neutral in the field with a total π -charge of only +0.01, whereas (benzene)¹ carries most of the charge (+0.75) and most of the spin density.

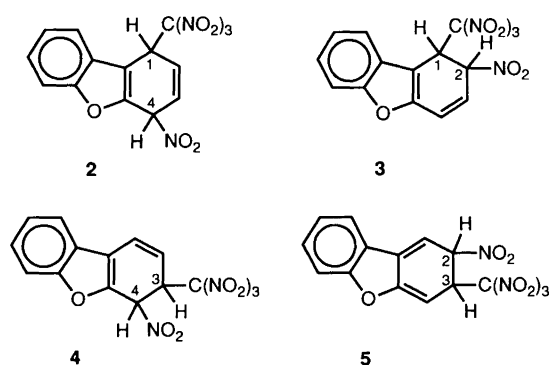
Comparison between theory and experiment. To start with the photonitrations, it is evident that the predominant components of the crude product mixture are nitro/trinitromethyl adducts. As with naphthalene, these are formed via **1** [eqn. (7), ArH = dibenzofuran]. The product-determining step is assumed to be attack of $(NO_2)_3C^-$ upon ArH^+ to give a hydroarenyl radical



[eqn. (8), left-hand side]. In the final step NO_2 coupling with the radical completes the formation of the addition product [eqn. (8), right-hand side]. The formation of nitro products occurs by base-catalyzed or slow, spontaneous (in acetonitrile) elimination of nitroform; this reaction also takes place thermally during work-up (e.g., by GLC or column chromatography). Decomposition of adducts during GLC, especially at high injector-chamber temperatures, also causes some elimination of nitrous acid, leading, in the dibenzofuran case, to a mixture of trinitromethylbenzofurans. In the course of the GLC analysis, these compounds are eventually transformed into nitriles [eqn. (9)].



The isomer distributions of entries 18 and 19 accord with expectations based on the Shaik-Pros model of the reactivity of a non-alternant radical cation (see Table 4 for spin densities of dibenzofuran triplet state and radical cation). The photochemical process produces adducts formed predominantly by the attack of trinitromethanide upon the 1- and 3-positions, leading in principle to adducts **2-5**. Two of these regioisomers, **2** and **4**, were the major components of the crude product mixture. Fast elimination of nitroform by the hindered base then gives 2- and 4-nitrodibenzofuran as the major isomers. The elimination of nitrous acid to give trinitromethyl-dibenzofurans and, upon GLC, eventually dibenzofurancarbonitriles, gave an isomer mixture consisting predominantly of the 3-cyano compound (71%; Table 2).

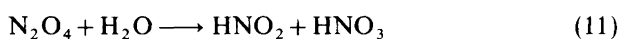


At first sight, another mechanistic problem finds a neat solution in the spin density distributions given in Table 4. NAC nitration, if following the mechanism of eqns. (2)–(5), has ArH^+/NO_2 coupling [eqn. (4)] as the product-determining step. For this reaction the spin density of ArH^+ should determine the selectivity and thus we would expect to find predominant 3-substitution of dibenzofuran from NAC nitration, exactly as observed (Table 1, entries 10–12).

However, this reasoning might be too simple. As noted above, the calculations suggest that (dibenzofuran)⁺ is easily polarizable, as shown in Table 4 by the data describing the influence of an electric field. At least hypothetically, this might have repercussions on the substitution pattern. Thus if one assumes that NO_2 approaches the radical cation via the positive nitrogen atom, the spin density of the almost uncharged ring, (benzene)², would be so low that coupling might not occur at all. If, for some reason, NO_2 instead induces the charged (benzene)¹ ring to be the product-determining ring, one would predict 2-/3-substitution to predominate. In principle, this prediction could be tested by polarizing the radical cation with a suitable substituent, e.g., chlorine, in one ring and thus direct the reactivity towards a nucleophile or radical to the 2-/3-positions of the second ring.²¹

Yet another, not too implausible, suggestion might explain the predominant 3-substitution observed for NAC nitration. From the reasoning imposed by the

Shaik-Pröss model, one would then require a nucleophile as a reactant toward the radical cation. The logical choice under the prevailing acidic conditions would be nitrous acid, a weak nucleophile [eqn. (10)], which would be easily accessible via reaction (11) (water is needed as a catalyst only in the full scheme). Nitrous acid would be expected to react mainly at the 3-position, as outlined above. The introduction of eqn. (10) does not affect the



catalytic nature of the reaction since both HNO_2 and H_2O act as catalysts in a properly modified version of the NAC mechanism.

Experimental

Materials. Dibenzofuran (Aldrich, 99+%), 2-chloro-nitrobenzene (Fluka, 98%) and 3-bromonitrobenzene (Merck, 98+%) were used without further purification. Dichloromethane (Merck, *zur Rückstandsanalyse*), acetonitrile and trifluoroacetic acid (both Merck UVASOL) were used as supplied. Literature procedures were used for preparing the following compounds: 2- and 3-nitrodiphenyl ether,²² 4-nitrodiphenyl ether²³ and acetone cyanhydrin nitrate.²⁴ Solutions of NO_2 in dichloromethane were made up as previously described.^{4c} All other reagents were of highest purity available and used as supplied.

Instrumentation. The GLC instrument⁸ was equipped with a packed column (2 m \times 0.25 mm 5% NPGS on Chrom W; for ArNO_2) or a fused silica column (25 m, OV-1701; for ArCN). In our hands, 2- and 3-nitrodibenzofuran could not be separated on this capillary column, nor on several other columns including that used previously (Dexil 300),^{5b,6} GLC/MS and NMR spectral analyses were carried out as before.⁸ Column chromatography was performed on silica gel 60 (Merck) using pentane/dichloromethane as the eluent.

Synthesis of authentic nitrodibenzofurans. 1-Nitrodibenzofuran. A mixture of 0.80 g (3.8 mmol) of 3-nitrodiphenyl ether and 1.0 g (4.2 mmol) of palladium(II) acetate in trifluoroacetic acid (20 ml) was heated to 70°C for 1 h.²⁵ After dilution with dichloromethane, filtration, washing with water, drying (MgSO_4), evaporation and column chromatography 0.36 g (1.7 mmol, 44%) of 1-nitrodibenzofuran was isolated, m.p. 129–130°C (EtOH), lit.²⁶ 126–127°C. ¹H NMR (CDCl_3): 8.69 (H8, dd), 8.24 (H2, dd), 7.91 (H4, dd), 7.57 (H3 + H5, m), 7.52 (H7, dt), 7.47 (H6, dt). ¹³C NMR (CDCl_3): 129.75, 126.41, 126.19, 123.66, 120.64, 119.72, 117.76, 111.65. Further elution gave a small amount of 3-nitrodibenzofuran; the 1-/3-isomer ratio in the crude product was ca. 6.

2-Nitrodibenzofuran was prepared analogously from 4-nitrodiphenyl ether, yield 65%, m.p. 167–168°C

(EtOH), lit.²⁷ 151–152°C. ¹H NMR (CDCl_3): 8.86 (H1, dd), 8.40 (H3, dd), 8.02 (H4, dd), 7.65 (H5 + H8, dd + dd), 7.58 (H6, dt), 7.45 (H7, dt). ¹³C NMR (CDCl_3): 128.95, 125.02, 123.94, 123.07, 121.30, 117.12, 112.26, 111.98.

4-Nitrodibenzofuran was prepared analogously from 2-nitrodiphenyl ether, yield 45%, m.p. 136–138°C, lit.²⁸ 138–139°C. ¹H NMR (CDCl_3): 8.29 (H3, dd), 8.26 (H1, dd), 8.01 (H5, dd), 7.76 (H8, dd), 7.59 (H2, dt), 7.47 (H6, dt), 7.45 (H7, dt). ¹³C NMR (CDCl_3): 128.92, 126.95, 124.09, 123.04, 122.70, 120.87, 112.55.

3-Nitrodibenzofuran was prepared by the method of Keumi *et al.*^{5b} and had the same GLC retention time and spectral data as the sample prepared by cyclization of 3-nitrodiphenyl ether (see above), m.p. 192–193°C (EtOH), lit.²⁶ 182–183°C. ¹H NMR (CDCl_3): 8.43 (H4, d), 8.24 (H2, dd), 8.04 (H1, d), 8.03 (H5, dd), 7.66 (H8, dd), 7.61 (H6, dt), 7.43 (H7, dt).

Nitration of dibenzofuran by different reagents. By HNO_3 /azide ion in acetic acid. A cold solution of conc. sulfuric acid (6 ml) in HOAc (14 ml) was slowly added to a mixture of dibenzofuran (890 mg, 5.0 mmol), sodium nitrate (425 mg, 5.0 mmol) and sodium azide (122 mg, 2.0 mmol) in HOAc (10 ml). After 20 h of stirring at ca. 20°C, 60% of the starting material had been consumed. Water (500 ml) and dichloromethane (100 ml) were added. The organic layer was washed with water and dried (MgSO_4). The isomer distribution was determined by GLC (Table 1, entry 5).

By acetone cyanhydrin nitrate (CMN)/ AlCl_3 .^{5b} GLC analysis of the crude product (Table 1, entry 2b) showed the presence of 51% of the 2-nitro isomer.

By 100% HNO_3 in trifluoroacetic acid.^{5b} GLC analysis of the crude product showed the presence of 87% of the 3-nitro isomer (Table 1, entry 9).

By NO_2 . A 0.25 M solution of NO_2 in dichloromethane (8 ml) was added to a solution of dibenzofuran (168 mg, 1.0 mmol) in dichloromethane (2 ml). The solution was left at ca. 20°C overnight and then washed with water, dried (MgSO_4) and analyzed by GLC (Table 1, 77% of the 3-nitro isomer).

By HNO_2 . Using the procedure described for the nitrosation of anisole,^{3d} dibenzofuran (5 mmol) in dichloromethane was treated with NaNO_2 (11 mmol) in dichloromethane/trifluoroacetic acid at 0°C. After work-up, the isomer distribution was determined by GLC (Table 1, entry 10).

By TNM/hv. Using the procedure described for naphthalene,¹ dibenzofuran and TNM (molar ratio = 1:2:5) were irradiated in the appropriate solvent (Table 1, entries 14, 16–19).

Formation of adducts in the photolysis of TNM and dibenzofuran. A solution of dibenzofuran (1.0 g, 1.0 M) and TNM (2.33 g, 2.0 M) in dichloromethane was irradiated at 20°C for 51 h with filtered light (cut-off at <435 nm). The solvent and excess TNM were removed under

reduced pressure at 0°C to give a yellow-brown oil (2.31 g), shown by ¹H NMR spectroscopy to be a mixture containing unchanged dibenzofuran (ca. 8%), the nitrodibenzofurans (total ca. 4.5%; ratio 1-/2-/3-/4-, 1/15/72/12), and three major adducts (total ca. 50%; ratio ca. 1/1/1). By means of appropriate double irradiation experiments the ¹H NMR spectral signals of the crude product, upfield of CHCl₃, were tentatively assigned to the following three adducts.

4-Nitro-1-trinitromethyl-1,4-dihydrodibenzofuran (2, isomer 1). ¹H NMR (CDCl₃): 5.70 (H1, dd, $J_{1,4} \approx 3$ Hz, $J_{1,2} \approx 3.2$ Hz), 6.14 (H4, dd, $J_{4,1} \approx 3$ Hz, $J_{4,3} \approx 4$ Hz), 6.73 (H2, app. d,* $J_{2,1} \approx 3.2$ Hz), 6.75 (H3, app. d,* $J_{3,4} \approx 4$ Hz).

4-Nitro-1-trinitromethyl-1,4-dihydrodibenzofuran (2, isomer 2). ¹H NMR (CDCl₃): 5.78 (H1, ddd, $J_{1,4} \approx 3$ Hz, $J_{1,2} \approx 3$ Hz, $J_{1,3} \approx 0.5$ Hz), 6.25 (H4, ddd, $J_{4,1} \approx 3$ Hz, $J_{4,3} \approx 2.4$ Hz, $J_{4,2} = 2.2$ Hz), 6.60 (H3, ddd, $J_{3,2} \approx 9$ Hz, $J_{3,4} \approx 2.4$ Hz, $J_{3,1} \approx 0.5$ Hz), 6.70 (H2, ddd, $J_{2,3} \approx 9$ Hz, $J_{2,1} \approx 3$ Hz, $J_{2,4} \approx 2.2$ Hz).

trans-4-Nitro-3-trinitromethyl-3,4-dihydrodibenzofuran (4). ¹H NMR (CDCl₃): 5.27 (H4, dd, $J_{4,3} \approx 3.5$ Hz, $J_{4,1} \approx 4.7$ Hz), 5.58 (H3, dd, $J_{3,4} \approx 3.5$ Hz, $J_{3,2} \approx 4.5$ Hz), 6.42 (H2, dd, $J_{2,1} \approx 10$ Hz, $J_{2,3} \approx 4.5$ Hz), 6.50 (H1, dd, $J_{1,2} \approx 10$ Hz, $J_{1,4} \approx 4.7$ Hz).

Treatment of the crude product mixture with 2,6-di-*t*-butyl-4-methylpyridine (1 M) in CHCl₃ for 24 h at 20°C resulted in the disappearance of the three adducts and the formation of 4-nitrodibenzofuran (ca. 45%), thus confirming the 4-nitro structure of the adducts. GLC analysis of the crude product mixture resulted in the decomposition of the adducts and the formation of dibenzofuran (24%), 3-(and 2-)nitrodibenzofuran (20%), 4-nitrodibenzofuran (31%), 3-cyanodibenzofuran (12%) and a number of minor products.

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* $\Delta\delta(\text{H3-H2}) \leq$ likely $J_{2,3}$ coupling constant ≈ 10 Hz.

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