Tetrahedron, 1958, Vol. 3, pp. 113–131. Pergamon Press Ltd., London

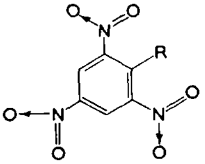
4:6-DINITROBENZOFUROXAN, NITROBENZODIFUROXAN AND BENZOTRIFUROXAN: A NEW SERIES OF COMPLEX-FORMING REAGENTS FOR AROMATIC HYDROCARBONS*

A. S. Bailey and J. R. Case
Dyson Perrins Laboratory, Oxford University

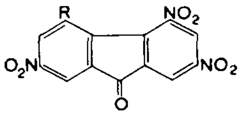
(*Received* 23 *January* 1958)

Abstract—4:6-Dinitrobenzofuroxan, 5:6-dinitrobenzofuroxan, nitrobenzodifuroxan and benzotrifuroxan have been prepared, and the values of the equilibrium constants for complex formation between naphthalene and this series of compounds have been determined in chloroform solution. Benzotrifuroxan has yielded solid complexes with a wide range of aromatic hydrocarbons.

The formation of solid complexes between aromatic compounds containing electron-attracting groups (acceptors, *a*) and aromatic hydrocarbons (donors, *b*) is well known, and over seventy compounds that form solid complexes with naphthalene are listed.[2] The two most important acceptors in general use are 1:3:5-trinitrobenzene (I, R = H) and picric acid (I, R = OH). In 1946–47, 2:4:7-trinitrofluorenone (II, R = H) was introduced as a reagent forming complexes with a wide range of aromatic hydrocarbons, and it appears to be especially useful with polynuclear hydrocarbons.[3] More recently,[4] 2:4:5:7-tetranitrofluorenone (II, R = NO_2) has been used for this purpose. Compounds such as (II) have high melting points and are rather insoluble in cold solvents; this is a disadvantage when dealing with aromatic hydrocarbons whose complex-forming power is small. For example, although 2-*n*-butylnaphthalene forms a solid complex with 1:3:5-trinitrobenzene,[5] it does not give a complex with 2:4:7-trinitrofluorenone.[6]



(I)



(II)

Of the mononuclear acceptors 1:3:5-trinitrobenzene appeared to be the most efficient complex-forming substance; for example, it forms solid complexes with 1- and 2-*n*-pentylnaphthalene, but picric acid does not yield solid complexes with these hydrocarbons.[5] Sinomiya[7] has concluded that maximum stability in complexes is obtained with acceptors in which the nitro groups are allowed to be coplanar with

---

* For preliminary communication, see Bailey and Case.[1]

[1] A. S. Bailey and J. R. Case, *Proc. Chem. Soc.* 176 (1957); erratum, *Ibid.* 211 (1957).

[2] *Encyclopaedia of Organic Chemistry* (Vol. 12B) p. 38. Elsevier, Amsterdam (1948).

[3] M. Orchin and E. O. Woolfolk, *J. Amer. Chem. Soc.* **68**, 1727 (1946); M. Orchin, L. Reggel and E. O. Woolfolk, *J. Amer. Chem. Soc.* **69**, 1225 (1947).

[4] M. S. Newman and W. B. Lutz, *J. Amer. Chem. Soc.* **78**, 2469 (1956).

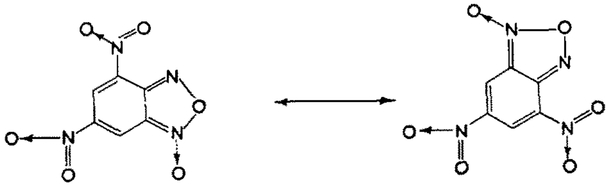
[5] A. S. Bailey, G. B. Pickering and J. C. Smith, *J. Inst. Petrol.* **35**, 103 (1949).

[6] C. M. Staveley, D. Phil. Thesis, Oxford University (1955).

[7] T. Sinomiya, *Bull. Chem. Soc. Japan* **15**, 92, 137, 259, 281 (1940).

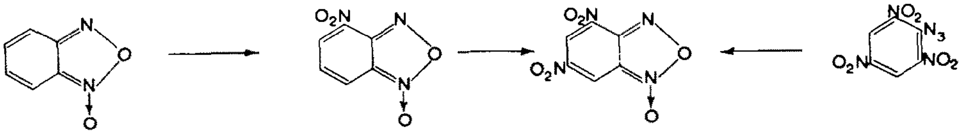
the benzene ring to which they are attached; association constants for the reaction between anthracene and a series of substituted 1:3:5-trinitrobenzenes in chloroform solution have been measured,[8] K decreasing in the order (I, R = H, OH, OMe, Cl, I). These results show that replacement of the hydrogen atoms in (I, R = H) by other groups leads to a decrease in complex-forming ability.

In 1899 Drost[9] reported that 4:6-dinitrobenzofuroxan (III) formed a solid complex with naphthalene. Examination of the structure of a benzofuroxan carrying a nitro group in the benzene ring in the "*ortho*" position to the furoxan ring shows that two identical structures might be written, and that resonance between the two canonical forms would give a planar hybrid structure. Hence this compound is similar to trinitrobenzene, but more highly substituted yet still planar. So one might expect (III) to be a more effective complex-forming reagent than (I, R = H). Drost's report of the formation of a naphthalene complex was confirmed and (III) also gave a complex with 1-*n*-pentylnaphthalene.[6] It was, therefore, decided to prepare a series of benzofuroxans containing nitro groups, to determine their association constants with a given hydrocarbon (naphthalene), and to try to obtain solid complexes, especially with hydrocarbons which do not yield complexes with (I) and (II).

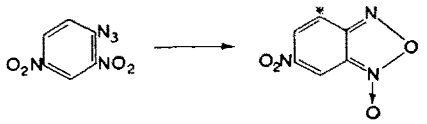


(III)

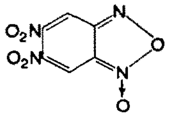
Benzofuroxans are obtained (i) by decomposition of *o*-nitroazides and (ii) by oxidation of *o*-nitroanilines with either alkaline hypochlorite[10,11] or phenyl iodosoacetate.[12] Nitration of benzofuroxan (IV) yields 4-nitrobenzofuroxan (V),[9] and



(IV) (V) (III) (VI)



(VII) (VIII)



(IX)

---

[8] S. D. Ross, M. Bassin and I. Kuntz, *J. Amer. Chem. Soc.* **76**, 4176 (1954).

[9] P. Drost, *Liebigs Ann.* **307**, 49 (1899).

[10] A. G. Green and F. M. Rowe, *J. Chem. Soc.* 2452 (1912).

[11] A. G. Green and F. M. Rowe, *J. Chem. Soc.* 2023 (1913).

[12] K. H. Pausacker and J. G. Scroggie, *J. Chem. Soc.* 4499 (1954).

4:6-dinitrobenzofuroxan (III);[9,11] this compound may also be obtained by decomposition of picryl azide (V).[13] Decomposition of 2:4-dinitrophenyl azide (VII) yields 5-nitrobenzofuroxan (VIII);[9] the azide may be obtained from 2:4-dinitroaniline[14] or by the reaction of 2:4-dinitrochlorobenzene with sodium azide.[15] Benzofuroxans have generally been obtained by heating the solid azide or by heating under reflux a benzene or toluene solution of the compound.[9,13,14] These methods often yield tarry material and the products require extensive purification. Of several solvents tried, glacial acetic acid appears to be the most suitable. Drost stated[9] that nitration of 5-nitrobenzofuroxan (VIII) with fuming acid gave 5:6-dinitrobenzofuroxan (IX) in unspecified yield. The substance was shown to be (IX) by reduction to 1:2:4:5-tetraaminobenzene (identified by colour reactions). (IX) gave a yellow naphthalene complex (m.p. and analysis not stated); unlike 4:6-dinitrobenzofuroxan (III), it did not give a colour with sodium hydroxide solution, and with aniline it gave a red compound, formed by the following reaction:

$$C_6H_2(NO_2)_2(NO)_2 + 2C_6H_5NH_2 = C_6(NO_2)_2(NO)_2(NHC_6H_5)_2 + 2H_2$$

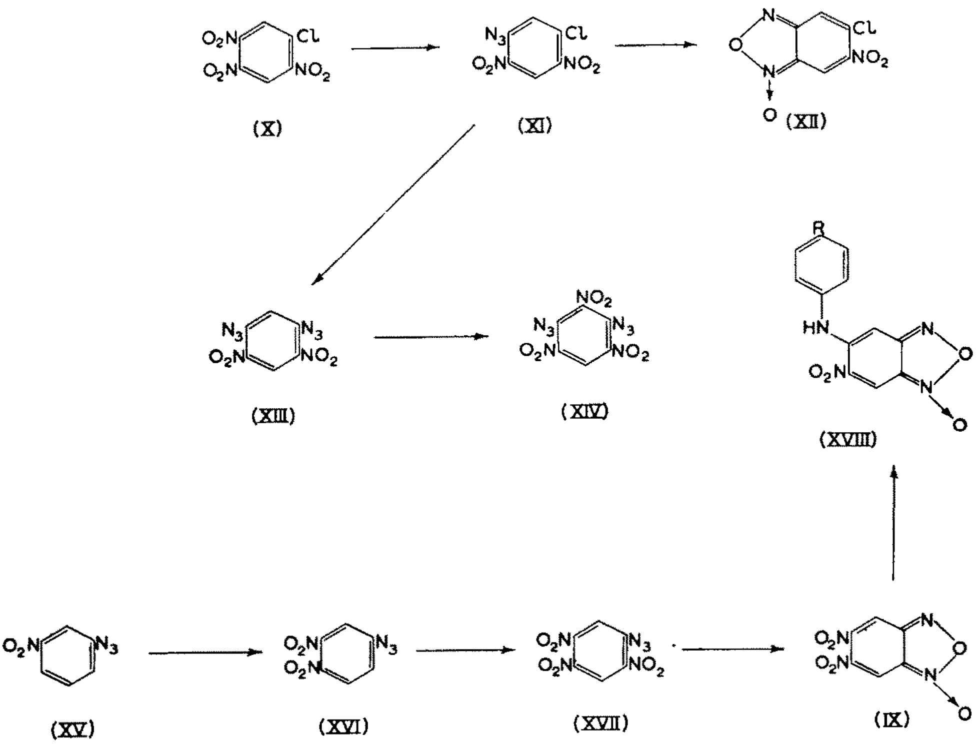
Three features of 5:6-dinitrobenzofuroxan were of interest: (*i*) the m.p. (172°) is identical with the m.p. of (III), (*ii*) the compound should be less efficient as a complex-forming reagent than (III), and (*iii*) the attack on 5-nitrobenzofuroxan to give 5:6-dinitrobenzofuroxan (IX) is unexpected. Benzofuroxan itself is nitrated easily to give over 80 per cent of 4-nitrobenzofuroxan (V), a position "*ortho*" to the furoxan ring being attacked. One would therefore expect that further substitution in (VIII) would occur at the position marked (*), which is *meta* to the nitro group and *ortho* to the furoxan ring, to give 4:6-dinitrobenzofuroxan (III) and not 5:6-dinitrobenzofuroxan (IX). 5-Nitrobenzofuroxan was nitrated with fuming nitric acid as described by Drost. The crude product (50 per cent yield) had m.p. 130–150°, analysed for a dinitrobenzofuroxan and pure (III) was isolated in 30 per cent yield. 5:Nitrobenzofuroxan (VIII) was also nitrated under the conditions used in the nitration of (IV) to give (III) (an excess of concentrated sulphuric acid being used). A small quantity of crystals was obtained, m.p. 169–170°, which on analysis had values for a dinitrobenzofuroxan, but the infra-red and ultra-violet spectra of the compound were different from the spectra of (III).

The synthesis of 5:6-dinitrobenzofuroxan (IX) was next attempted from 2:4:5-trinitrochlorobenzene (X), the latter being obtained by nitration of *m*-chloronitrobenzene.[16] Holleman reports[17] the method as unsatisfactory. A single recrystallisation of the reaction product from trichloroethylene gives a 50 per cent yield of pure material. Treatment of 2:4:5-trinitrochlorobenzene (X) with one equivalent of sodium azide gave 1-azido-5-chloro-2:4-dinitrobenzene (XI), which, on being heated in acetic acid solution, yielded 5-chloro-6-nitrobenzofuroxan (XII). With two equivalents of sodium azide (X) gave 1:5-diazido-2:4-dinitrobenzene (XIII), m.p. 94–95° (dec.), which was further nitrated to form styphnyl azide (XIV); the formation of (XIV) proves the structure of (XIII). The nucleophilic displacement of the nitro group of

---

[13] E. Schrader, *Ber. Dtsch. Chem. Ges.* **50**, 777 (1917).
[14] R. J. Gaughran, J. P. Picard and J. V. R. Kaufman, *J. Amer. Chem. Soc.* **76**, 2233 (1954).
[15] F. Moulin, *Helv. Chim. Acta* **35**, 175 (1952).
[16] A. Laubenheimer, *Ber. Dtsch. Chem. Ges.* **9**, 760 (1876); R. Nietzki and W. Zänker, *Ber. Dtsch. Chem. Ges.* **36**, 3953 (1903).
[17] A. F. Holleman, *Versl. Gerwone Vergad. Akad. Amst.* **31**, 295 (1922); see also ref. 18.

(X) rather than the halogen atom is in agreement with the observation of Van de Vliet on the reactions of (X) with methoxide ion.[18] After we had successfully prepared nitrobenzodifuroxan and benzotrifuroxan by methods involving the nitration of an aromatic azide, we returned to the problem of synthesising (IX) by the nitration of *m*-nitrophenyl azide (XV). Nitration in cold fuming acid gave a solid analysing for a dinitrophenyl azide. The product was probably a mixture consisting largely of the 3:4-dinitro compound (XVI), since very little nitrogen was evolved on heating the compound at 100° in glacial acetic acid. Nitration with mixed acids gave a trinitrophenyl azide (m.p. 73–74°) consisting largely of the required 2:4:5-trinitrophenyl azide (XVII), the 6-position of (XVI) being attacked in preference to the 2-position. The crude trinitrophenyl azide was decomposed to give 5:6-dinitrobenzofuroxan (IX), pale-yellow prisms, m.p. 177°. The compound did not give any colour with sodium hydroxide solution, in agreement with Drost's observations. The ultra-violet spectrum of the compound was identical with that of the product (m.p. 169–170°) obtained in minute amount by nitration of (VIII) with mixed acid. The infra-red spectra of the two specimens were identical, the bands of the "synthetic" specimen being much sharper than those of the compound of m.p. 170°. Structure (IX) is also confirmed by the ultra-violet spectrum of the compound (see later).



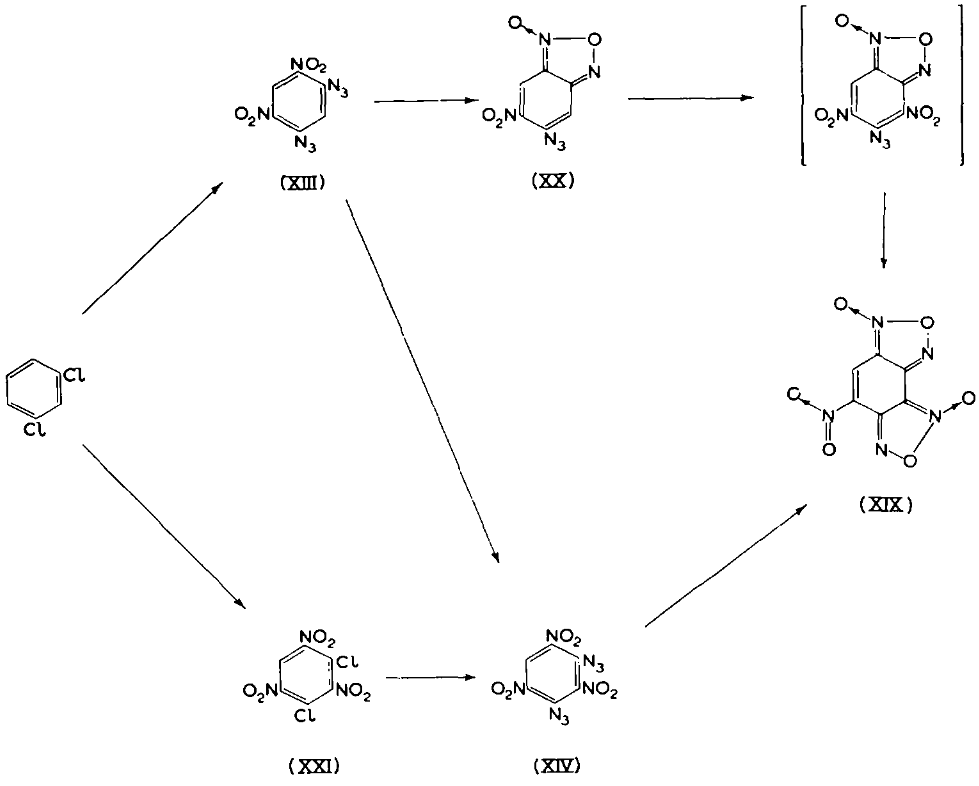
Treatment of the synthetic material with aniline in ethanol gave dark-red needles; the analytical figures agree with those quoted by Drost, who suggested a formula $C_{18}H_{12}O_6N_6$, and are also in agreement with a formula $C_{12}H_8O_4N_4$, suggesting that aniline reacts with (IX) by displacement of a nitro group with the formation of

---

[18] P. G. Van de Vliet, *Rec. Trav. Chim. Pays-Bas* 43, 606 (1924).

5-anilino-6-nitrobenzofuroxan (XVIII, R = H) by analogy with the formation of 5-anilino-2:4-dinitrotoluene from aniline and 2:4:5-trinitrotoluene.[19] The corresponding *p*-bromoanilino compound has been obtained, the two alternative formulae for the product being $C_{18}H_{10}O_6N_6Br_2$ or $C_{12}H_7O_4N_4Br$. The analytical figures are in excellent agreement with the latter formula (XVIII, R = Br). Displacement of one of the nitro groups of 5:6-dinitrobenzofuroxan (IX) by aniline is further evidence that the two nitro groups in (IX) are *ortho* to each other. These results suggest that Drost did obtain an impure specimen (m.p. 5° low) of 5:6-dinitrobenzofuroxan (IX) by nitration of (VIII), since our observations agree closely with his descriptions of the reactions of (IX).

Nitrobenzodifuroxan (nitrotetranitrosobenzene, XIX) has been prepared by the nitration of tetranitrosobenzene [20] and, more recently,[14] from 1:5-diazido-2:4-dinitrobenzene (XIII) via 5-azido-6-nitrobenzofuroxan (XX) and 5-azido-4:6-dinitrobenzofuroxan (not isolated). These two methods give poor yields and the compound has



now been obtained from styphnyl chloride (XXI),[21,22] which, on treatment with sodium azide, gave an excellent yield of styphnyl azide (XIV), thermal decomposition of (XIV) yielding nitrobenzodifuroxan (XIX). 1:5-Diazido-2:4-dinitrobenzene (XIII) is easily obtained from 1:5-dichloro-2:4-dinitrobenzene and sodium azide;[14] (XIII) was smoothly nitrated to form styphnyl azide. The over-all yield of (XIX) from

---

[19] P. Hepp, *Liebigs Ann.* **215**, 366 (1882).

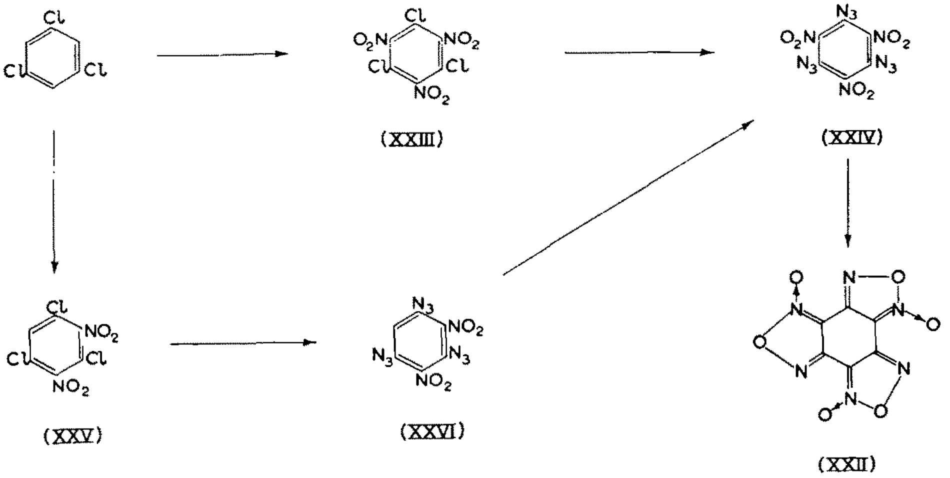
[20] R. Nietzki and W. Geese, *Ber. Dtsch. Chem. Ges.* **32**, 506 (1899).

[21] J. J. Sudborough and N. Picton, *J. Chem. Soc.* 591 (1906).

[22] A. T. Dann, *J. Chem. Soc.* 2461 (1929).

1:3-dichlorobenzene via styphnyl chloride (XXI) is 54 per cent; via (XIII) the yield is 55 per cent.

Benzotrifuroxan (hexanitrosobenzene, XXII) was described by Turek,[23] who obtained it from 1:3:5-trichlorobenzene via 1:3:5-trichloro-2:4:6-trinitrobenzene (XXIII) and 1:3:5-triazido-2:4:6-trinitrobenzene (XXIV). Although two nitro groups may easily be introduced into trichlorobenzene to form (XXV), the preparation of (XXIII) requires extremely vigorous conditions. When the method described by Turek was attempted, the mixture exploded, in agreement with the observations of Backer and Van der Baan,[24] and (XXIII) was obtained by a preparation involving the use of 60 per cent oleum.[25] We were unable to prepare triazidotrinitrobenzene (XXIV) by Turek's method; the transformation of (XXIII) into (XXIV) by shaking an acetone solution of the halide with moist sodium azide has been briefly reported.[26]



To avoid the preparation of (XXIII) the following route was devised. Reaction of the dinitro compound (XXV) with sodium azide affords 1:3:5-triazido-2:4-dinitrobenzene (XXVI).[27] The yield of (XXVI) is moderate, since it slowly decomposes at the temperature of its formation. Turek found that purification of (XXVI) was difficult, the m.p. of the substance being very sensitive to traces of impurity. We therefore nitrated the crude material, and triazidotrinitrobenzene (XXIV) crystallised from the nitrating mixture. The optimum reaction time for the step (XXV) → (XXVI) was determined by nitrating the crude reaction product and weighing the yield of pure (XXIV) produced. Turek decomposed the triazide in xylene; we first attempted its decomposition in acetic acid, but the compound only decomposed slowly in this solvent. Benzotrifuroxan was obtained by heating a solution of (XXIV) in propionic acid to 130–135°. The yields in all the stages of the preparation are good apart from the step (XXV) → (XXVI).

For the preparation of complexes we required a specimen of 2-phenylnaphthalene. This has been prepared[28] by a five-stage synthesis from benzyl cyanide and by heating

---

[23] O. Turek, *Chim. et Ind.* **26**, 785 (1931).
[24] H. J. Backer and S. Van der Baan, *Rec. Trav. Chim. Pays-Bas* **56**, 1178 (1937).
[25] P. Engelbertz, *Ger. Pat.* 767,510; *Chem. Abstr.* **49**, 14803d (1955).
[26] F. P. Bowden and H. T. Williams, *Proc. Roy. Soc.* A **208**, 176 (1951); A. Yoffé, *Ibid.* **208**, 188 (1951).
[27] O. Turek, *Chim. et Ind.* Special number 885 (June, 1933).
[28] N. Campbell and D. Kidd, *J. Chem. Soc.* 2154 (1954).

phenylethylene glycol with hydrobromic acid.[29] The glycol is converted into phenylacetaldehyde, which then undergoes self-condensation as soon as formed, and little polymeric material is produced. The hydrocarbon may also be obtained by heating phenylacetaldehyde at 170° with dilute hydrochloric acid.[30] By adding a solution of phenylacetaldehyde in acetic acid to boiling hydrobromic acid 2-phenylnaphthalene has been obtained in 52 per cent yield; this is a very simple method of obtaining small quantities of the hydrocarbon.

Spectral properties of the nitrobenzofuroxans and related compounds

The following ultra-violet spectra were measured in chloroform solution by means of a Cary recording spectrophotometer model 14M–50 (wavelengths in mμ.):

Benzofuroxan	λ_{max}	236	240	355	367		
	ε_{max}	1400	1700	7300	6500		
4-Nitrobenzofuroxan	λ_{max}	234	267	407	412		
	ε_{max}	9700	3100	8300	8200		
5-Nitrobenzofuroxan	λ_{max}	240*		262	335	390	
	ε_{max}	8000		13,100	1800	5200	
4:6-Dinitrobenzofuroxan	λ_{max}	234	260	277	330	412*	420
	ε_{max}	7950	12,500	13,400	1700	4900	7700
5:6-Dinitrobenzofuroxan	λ_{max}	262	387				
	ε_{max}	17,150	5,050				
Nitrobenzodifuroxan	λ_{max}	238*		241	244	247*	
	ε_{max}	10,600		11,150	11,000	10,200	
	λ_{max}	287*	291*	294	338	345*	356
	ε_{max}	7900	8200	8300	9800	9600	10,300
Benzotrifuroxan	λ_{max}	252*		258	280*		293*
	ε_{max}	23,600		27,900	10,000		7600

* Inflexion.

These spectra show several interesting features. 5-Nitrobenzofuroxan (VIII), 4:6-dinitrobenzofuroxan (III) and 5:6-dinitrobenzofuroxan (IX) all show strong absorption at 260–262 mμ, (IX) having the largest ε_{max}. This is probably associated with a nitro group not adjacent to the furoxan ring (nitrobenzene has λ_{max} 252 mμ, ε_{max} 10,000).[31] 4-Nitrobenzofuroxan (V) has a weak maximum at 267 mμ (see Fig. 1.) Introduction of a nitro group into the benzofuroxan nucleus alters the position of the longest wavelength band, (VIII) and (IX) both having maxima at 387–390 mμ. When a nitro group is *ortho* to the furoxan ring, the bathochromic effect is greater, (III) and (V) having λ_{max} 412–420 mμ. Thus the spectral properties of (IX) show that the two nitro groups are not *ortho* to the furoxan nucleus. Benzotrifuroxan has a strong band λ_{max} 255 mμ, ε_{max} 35,000 (in ethanol, slightly different from the values in chloroform). *cyclo*Hexenefuroxan has λ_{max} 262–263 mμ, ε_{max} 6700 (in ethanol).[32]

Infra-red spectra were determined in paraffin paste. Main bands above 1290 cm^{-1}

---

[29] H. E. Carter and E. J. Van Loon, *J. Amer. Chem. Soc.* **60**, 1077 (1938).

[30] K. Auwers and G. Keil, *Ber. Dtsch. Chem. Ges.* **36**, 3902 (1903).

[31] E. A. Braude, *Ann. Rep. Chem. Soc.* **42**, 126 (1945).

[32] J. H. Boyer, U. Toggweiler and G. A. Stoner, *J. Amer. Chem. Soc.* **79**, 1748 (1957).

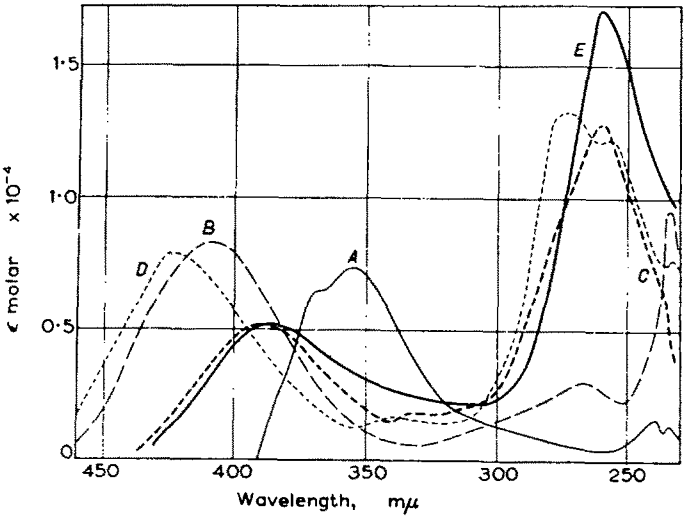


FIG. 1. Absorption spectra of:
A, benzofuroxan (———)
B, 4-nitrobenzofuroxan (— — —)
C, 5-nitrobenzofuroxan (- - - -)
D, 4:6-dinitrobenzofuroxan (. . . . . .)
E, 5:6-dinitrobenzofuroxan (———)

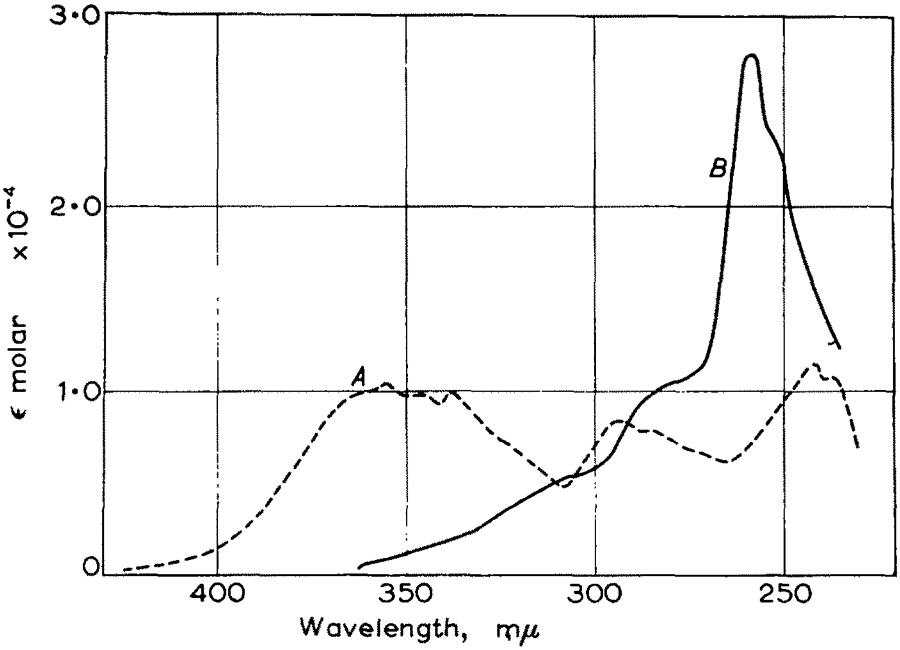


FIG. 2. Absorption spectra of:
A, nitrobenzodifuroxan (- - - -)
B, benzotrifuroxan (———)

are given, except for benzotrifuroxan for which the complete spectrum is quoted:

4-Nitrobenzofuroxan	3077;	1629;	1592;	1529;	1490;
	1439;	1359;	1326 cm^{-1}		
5-Nitrobenzofuroxan	3077;	1795;	1608;	1533;	1520;
	1484;	1403;	1351;	cm^{-1}	
4:6-Dinitrobenzofuroxan	3077;	1605;	1595;	1570;	1543;
	1456;	1344;	1328 cm^{-1}		
5:6-Dinitrobenzofuroxan	3077;	1766;	1626;	1608;	1563;
	1548;	1531;	1348;	1312 cm^{-1}	
Nitrobenzodifuroxan	3077;	1828;	1656;	1623;	1597;
	1563;	1529;	1522;	1429;	1342;
	1325;	1309;	1295 cm^{-1}		
Benzotrifuroxan	1656;	1608;	1572;	1540;	1508;
	1416;	1304;	1287;	1105;	1075;
	962;	935;	807;	735 cm^{-1}	

The N=O stretching vibration for monomeric nitrosobenzene is reported[33] as 1520 cm^{-1}; the absence of this band in the spectrum of (XXII) suggests it is not a simple nitroso compound. Boyer *et al.*[34] assigns the band at 1625–1600 cm^{-1} in the spectrum of simple benzofuroxans to the stretching vibration of $C{=}\overset{+}{\underset{|}{N}}{-}$. The intense band at 1656 cm^{-1} in the spectrum of (XXII) probably corresponds to this vibration.

Determination of spectrophotometric association constants

The equilibrium constants for complex formation between this series of compounds and naphthalene in chloroform solution have been determined

$$a + \text{naphthalene} \rightleftharpoons a\,.\,\text{naphthalene}$$

spectrophotometrically by the method of Foster *et al.*[35] Two master solutions were prepared, one containing the acceptor (a), the other containing pure naphthalene (b), and from them solutions containing a fixed amount of the acceptor and varying amounts of naphthalene were made up in calibrated flasks, the naphthalene being in large excess. One solution was prepared containing only (a) at the fixed concentration. This solution was placed in one of a pair of matching 1 cm cells fitted with lids and used as a blank instead of pure solvent. The optical densities of the solutions were measured in a Unicam SP 500 spectrophotometer. By using the solution containing only (a) in the "solvent" cell, the increase in optical density, ΔD, of the solution of $a + b$ was obtained directly from the spectrophotometer reading.[36]

For a 1:1 complex the equation relating ΔD, b and K is: $\Delta D/b =$ constant $-K\Delta D$. Hence a plot of $\Delta D/b$ against ΔD should be a straight line of slope $-K$. The equation of the line of closest fit was obtained using the method of "least squares,"

---

[33] P. Tarte, *Bull. Soc. Chim. Belg.* **63**, 525 (1954).

[34] N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, *J. Amer. Chem. Soc.* **77**, 4238 (1955).

[35] R. Foster, D. Ll. Hammick and A. A. Wardley, *J. Chem. Soc.* 3817 (1953); see also R. Foster, D. Ll. Hammick and P. J. Placito, *J. Chem. Soc.* 3881 (1956); K. H. Takemura, M. D. Cameron and M. S. Newman, *J. Amer. Chem. Soc.* **75**, 3280 (1953); S. D. Ross and M. M. Labes *J. Amer. Chem. Soc.* **77**, 4916 (1955); *Ibid.* **79**, 76 (1957).

[36] W. Slough and A. R. Ubbelohde, *J. Chem. Soc.* 914 (1957); J. W. Watts, Part II Thesis, Oxford University (1956).

thus giving K. The equilibrium constant was determined at two wavelengths for each compound.

Purification of materials

Chloroform was washed with water six times, dried over calcium chloride, distilled and stored in the dark. A good specimen of *naphthalene* was crystallised from ethanol four times and the same batch was used for all our experiments; it had m.p. 80°. 1:3:5-*Trinitrobenzene* was crystallised from ethanol, m.p. 122°. 2:4:7-*Trinitrofluorenone* (obtained from Messrs. Hopkin & Williams Ltd.) was crystallised from acetic acid and it had m.p. 176·5°. The preparation and purification of other acceptors has been described elsewhere in this paper.

Ross and Labes reported a value of 1·30 at 24·8° for the equilibrium constant of the reaction between naphthalene and 1:3:5-trinitrobenzene in chloroform solution.[35]

TABLE 1. DETERMINATION OF THE EQUILIBRIUM CONSTANT FOR REACTION BETWEEN 2:4:7-TRINITROFLUORENONE AND NAPHTHALENE (b) IN CHLOROFORM SOLUTION

Concentration of trinitrofluorenone (a) = $4{\cdot}85 \times 10^{-4}$M

Wavelengths used 450 and 460 mμ. Temperature = 18°

	450 mμ		460 mμ	
(b) M	ΔD	$\frac{\Delta D}{b}$	ΔD	$\frac{\Delta D}{b}$
0·312	0·144	0·461	0·117	0·375
0·390	0·170	0·449	0·140	0·359
0·468	0·197	0·421	0·166	0·355
0·546	0·222	0·407	0·186	0·340
0·702	0·265	0·377	0·220	0·313
0·858	0·302	0·352	0·249	0·290

The lines of closest fit are:

$\Delta D/b = -0{\cdot}72\,\Delta D + 0{\cdot}590$ at 450mμ

$\Delta D/b = -0{\cdot}67\,\Delta D + 0{\cdot}444$ at 460 mμ

Mean value of K = 0·69 (l./mole)

TABLE 2. RESULTS FOR ASSOCIATION CONSTANTS IN CHLOROFORM SOLUTION

Acceptor	Temp (°C)	K [wavelength used (mμ)]	K [wavelength used (mμ)]	Mean value of K (l./mole)
2:4:7-Trinitrofluorenone	18	0·72 (450)	0·67 (460)	0·69
5:6-Dinitrobenzofuroxan	18	1·21 (440)	1·24 (450)	1·2
1:3:5-Trinitrobenzene	16	1·31 (410)	1·27 (420)	1·3
4:6-Dinitrobenzofuroxan	16	2·64 (478)	2·61 (482)	2·6
Nitrobenzodifuroxan	16	3·65 (470)	3·71 (480)	3·7
Benzotrifuroxan	19	4·13 (365)	4·09 (370)	4·1

These figures show clearly that complex-forming power increases steadily from 1:3:5-trinitrobenzene to benzotrifuroxan and that the position of the nitro group in the benzofuroxan nucleus is important, the value of *K* for 4:6-dinitrobenzofuroxan being twice the value of *K* for 5:6-dinitrobenzofuroxan.

Complexes with aromatic hydrocarbons

The formation of solid complexes between this series of compounds and other aromatic hydrocarbons was next investigated. In all the examples examined the solvent has been an acetic acid–ethanol mixture (1:4). Dimroth[37] has discussed the effect of the solubility of the various components on the formation of a solid complex, and this solvent mixture may not be the most suitable for all the pairs of compounds tried. To obtain some idea of the complex-forming ability of these compounds the formation of complexes with naphthalene (*A*), 2-phenylnaphthalene (*B*), 1-*n*-hexylnaphthalene (*C*), 1-phenylnaphthalene (*D*) (a hydrocarbon that is non-planar)[38] and tetrahydronaphthalene (*E*) was examined; the results are summarised in Table 3.

TABLE 3. COMPARISON OF COMPLEX-FORMING ABILITY

Acceptor	*A*	*B*	*C*	*D*	*E*
(IX)	+				
(III)	+	+	+		
(XIX)	+	+	(+)	+	+
(XXII)	+	+	+	+	+

(IX). (*A*) was unstable at room temperature, whilst the isomeric (III). (*A*) was quite stable. (XIX). (*C*) was a sticky solid, which was not obtained pure or analysed. (XIX). (*E*) was a complex $C_{10}H_{12}\cdot 3C_6HO_6N_5$, whilst (XXII). (*E*) separated as a 1:1 complex. The scope of complex-formation was then extended more fully for benzotrifuroxan (XXII) for the following reasons. It alone formed sharp-melting complexes with (*D*) and (*E*); the 1:1 complex (XXII). (*A*) was the most stable in solution (as shown by the value of the association constant, *K*); and (XXII) was more soluble in the solvent used than (XIX). Twenty-four complexes have been prepared with benzotrifuroxan, of which the following are of interest, since the hydrocarbons do not form complexes readily with other reagents: 1:2:3-trimethylbenzene, mesitylene, 1:2:3:4-tetramethylbenzene, styrene, diphenyl, diphenylmethane, tetrahydronaphthalene, 6-methyltetrahydronaphthalene, 5-ethyltetrahydronaphthalene 5:7-dimethyltetrahydronaphthalene, 1:7-dimethyl-3:4-dihydronaphthalene, 2-α-naphthylbutane, 1-*n*-hexylnaphthalene, 2-*n*-octylnaphthalene, 1-phenylnaphthalene and indene. The complexes obtained from hydrocarbons such as alkylbenzenes, alkylnaphthalenes and tetrahydronaphthalenes gave clear melts (unless the m.p. was considerably over 200°); the complexes from "unsaturated" hydrocarbons such as styrene, indene and 1:7-dimethyl-3:4-dihydronaphthalene blackened and decomposed at the m.p.

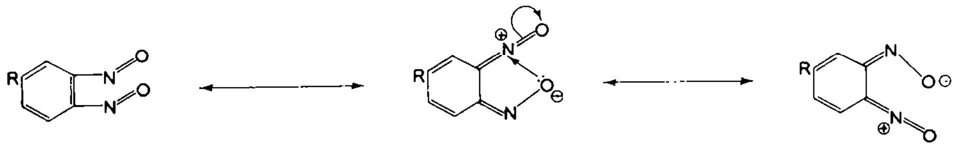
---

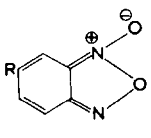
[37] O. Dimroth and C. Bamberger, *Liebigs Ann.* **438**, 67 (1924); G. W. Wheland, *Advanced Organic Chemistry* p. 63. Wiley, New York (1949).

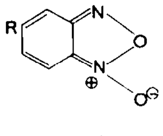
[38] R. A. Friedel, M. Orchin and L. Reggel, *J. Amer. Chem. Soc.* **70**, 199 (1948); M. Orchin and R. A. Friedel, *Ibid.* **71**, 3002 (1949).

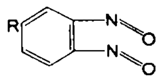
The three xylenes, 2:3-di-*n*-hexylnaphthalene and 1:2:3:4:5:6:7:8-octahydroanthracene gave solids that on being analysed did not give values for a simple hydrocarbon to acceptor ratio; *p*-cymene, phenylacetylene, 1-phenyldialin, 6-ethyl tetrahydronaphthalene, 6-*n*-butyltetrahydronaphthalene and *cyclo*octatetraene all failed to give solid complexes. Although indole yielded a complex, no solid was obtained from quinoline or *iso*quinoline. We were interested to find that dimethylfulvene gave a stable solid derivative with (XXII). Trinitrobenzene also gave a yellow solid with dimethylfulvene. After standing at room temperature for 3–4 hr, the yellow product became colourless and had the same m.p. as trinitrobenzene. We were, however, able to obtain analytical results that showed that a complex had been formed.

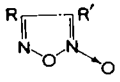
The structure (XXVII a, b, c) and the name ψ-*o*-dinitrosobenzene have been suggested recently for the benzofuroxans.[39] Structures of type (XXVII) are important, especially in explaining why a monosubstituted benzofuroxan exists in only one form whilst isomers of type (XXXI) and (XXXII) are known in simple furoxans.[40] Resonance stabilisation of the benzene ring will result in (XXVII a) contributing more to the final state of a benzofuroxan than (XXXIII) will contribute to the final state of a simple furoxan. As transition states which permit interconversion of the isomers, (XXVII a) and (XXX) are more favourable energetically than (XXXIII).

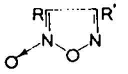

(XXVII a) (XXVII b) (XXVII c)

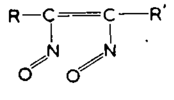

(XXVIII)


(XXIX)


(XXX)


(XXXI)


(XXXII)


(XXXIII)

---

[39] J. H. Boyer, R. F. Reinisch, M. J. Danzig, G. A. Stoner and F. Sahhar, *J. Amer. Chem. Soc.* **77**, 5688 (1955).

[40] J. Meisenheimer, H. Lange and W. Lamparter, *Liebigs Ann.* **444**, 94 (1925).

It is, however, difficult to explain the well known stability of the benzofuroxans towards oxidation in terms of formula (XXVII). We have observed that benzofuroxan is not oxidised by performic and peracetic acids, reagents that oxidise *o*-nitronitrosobenzene to *o*-dinitrobenzene.[41] The placing of a double-headed arrow between (XXVII b) and (XXVII c) implies resonance between two canonical forms. This is unlikely, since *both* the oxygen atoms are in different positions in (XXVII b) and (XXVII c), and it is generally accepted[42] that "resonating structures must correspond to very nearly the same positions of all the atomic nuclei." In structure (XXVII b) there will be strong attraction between the positively charged nitrogen atom and the negatively charged oxygen atom leading directly to (XXVIII), the benzofuroxan structure. The compounds are hybrid structures, the canonical forms being (XXVII a, XXVII b, XXVIII) for one structure and (XXVII c, XXIX, XXX) for the other. We have, therefore, retained the well established name benzofuroxan for this class of compound to which it is impossible to assign a single formula.

EXPERIMENTAL

Benzofuroxan was prepared by hypochlorite oxidation of *o*-nitroaniline.[10,11] 4-Nitrobenzofuroxan (IV) formed orange needles from methanol, m.p. 142°; Drost[9] reports m.p. 143°. Dinitration[11] of benzofuroxan afforded 4:6-dinitrobenzofuroxan (III) as long, yellow needles from acetic acid, m.p. 172° (lit.[9] 172°)

2:4-*Dinitrophenyl azide* (VII). A solution of sodium azide (9·0 g) in a mixture of methanol (20 ml), water (20 ml) and acetone (10 ml) was added slowly to a solution of 2:4-dinitrochlorobenzene (28 g) in acetone (20 ml) and methanol (20 ml) with vigorous shaking. After an hour the solution was poured into cold water, and the solid was collected, washed and dried. Yield 28·0 g (96 per cent), m.p. 66–67° (Moulin[15] gives m.p. 67–68°). A solution of 2:4-dinitrophenyl azide (25·0 g) in glacial acetic acid (50 ml) was heated on a steam-bath until evolution of nitrogen ceased (approximately 30 min). Next day 5-nitrobenzofuroxan (VIII) was collected, washed and dried (18·0 g), m.p. 71°. The mother-liquors were poured into water to give a further 5 g, m.p. 70° (Gaughran *et al.*[14] report m.p. 72°).

Nitration of 5-nitrobenzofuroxan. (*a*) 5-Nitrobenzofuroxan (4·0 g) was dissolved in ice-cold fuming nitric acid (sp. gr. 1·51, 6 ml), and the solution was set aside at room temperature for 15 hr and then poured into ice–water. The solid was collected, washed with water and dried; yield 2·5 g (50 per cent), m.p. 130–150° (Found: C, 32·6; H, 0·67; N, 25·2. Calc. for $C_6H_2O_6N_4$: C, 31·9; H, 0·89; N, 24·8 per cent). The infra-red spectrum of this material was almost identical with the infra-red spectrum of pure 4:6-dinitrobenzofuroxan. A naphthalene complex was obtained by mixing equimolecular quantities of the crude nitration product and naphthalene in hot methanol, long bright-red needles, m.p. 145–155° (Found: C, 54·0; H, 3·1; N, 15·9. Calc. for $C_6H_2O_6N_4{\cdot}C_{10}H_8$: C, 54·3; H, 3·3; N, 15·8 per cent). The infra-red spectra of this complex and of the complex from pure 4:6-dinitrobenzofuroxan were identical. A small amount of the complex was decomposed by warming with trichloroethylene. On cooling, long yellow needles of pure 4:6-dinitrobenzofuroxan separated, m.p. 172° (mixed m.p. and infra-red spectra). The crude nitration product (1·0 g) was crystallised from a small amount of concentrated nitric acid to give 4:6-dinitrobenzofuroxan (0·6 g), (mixed m.p. and infra-red spectra). (*b*) 5-Nitrobenzofuroxan (5·0 g)

---

[41] R. Kuhn and W. van Klaveren, *Ber. Dtsch. Chem. Ges.* **71**, 779 (1938).

[42] G. W. Wheland, *op. cit.* p. 415.

was dissolved, by warming, in concentrated sulphuric acid (25 ml) and the solution was cooled to 0°. To the stirred solution was added an ice-cold mixture of fuming nitric acid (7·5 ml) and concentrated sulphuric acid (15 ml) during 30 min, the temperature being kept below 10°. The solution was then kept at room temperature for 30 min, slowly warmed to 40°, kept at that temperature for 15 min, cooled and poured on to ice. The semi-liquid mass was collected and dissolved in the minimum of boiling ethanol, and the solution was left to crystallise. Brown crystals separated; these were collected, washed and dried (2·0 g, 30 per cent), m.p. 128–145°. This material was crystallised three times from ethanol, the m.p. at each stage being 135–155°, 155–164° and 169–170°; the final yield of product was 20 mg (Found: C, 32·4; H, 0·93; N, 24·4. Calc. for $C_6H_2O_6N_4$: C, 31·9; H, 0·89; N, 24·8 per cent).

2:4:5-*Trinitrochlorobenzene* (X). Crystallisation from trichloroethylene gave a product, m.p. 113–115·5° (Found: C, 29·5; H, 0·85; N, 17·0. Calc. for $C_6H_2O_6N_3Cl$: C, 29·1; H, 0·81; N, 17·0 per cent). Accepted value[15] of m.p. 116°.

1-*Azido*-5-*chloro*-2:4-*dinitrobenzene* (XI). 2:4:5-Trinitrochlorobenzene (1·2 g) was dissolved in a mixture of acetone (3 ml) and methanol (3 ml). To this solution was added sodium azide (0·35 g) in water (1 ml) and methanol (1 ml). After 1 hr at room temperature the mixture was poured into water, and the solid was collected, washed and dried (1·1 g, 90 per cent). The *azide* was recrystallised from chloroform, to give yellow prisms, m.p. 80° (dec.) (Found: C, 30·0; H, 0·76; N, 27·2. $C_6H_2O_4N_5Cl$ requires C, 29·6; H, 0·83; N, 28·4 per cent). The azide was decomposed by heating in glacial acetic acid at 100° for 30 min. 5-*Chloro*-6-*nitrobenzofuroxan* (XII) separated from benzene–ethanol as fine, yellow needles, m.p. 88–89° (Found: N, 19·3; Cl, 15·9. $C_6H_2O_4N_3Cl$ requires N, 19·5; Cl, 16·5 per cent). Treatment of 2:4:5-trinitrochlorobenzene exactly as described before, except that sodium azide (0·7 g, 2 equiv.) was used, gave a product (1·10 g, 89 per cent), which crystallised from chloroform as yellow prisms, m.p. 94–95° (dec.) (Found: C, 29·2; H, 0·90; N, 45·6. Calc. for $C_6H_2O_4N_8$: C, 28·8; H, 0·80; N, 44·8 per cent). The substance was shown to be 1:5-diazido-2:4-dinitrobenzene (XIII) by the following method. The compound (0·2 g) was dissolved in cold fuming nitric acid (sp. gr. 1·51, 2 ml), and the solution was left overnight and then poured into water. The solid was collected, washed and dried (0·18 g). Crystallisation from chloroform gave pale-yellow needles, m.p. 91° (dec.). The infra-red spectrum of the compound was identical with that of styphnyl azide.

3:4-*Dinitrophenyl azide* (XVI). *m*-Nitrophenyl azide[43] (0·50 g, m.p. 52–53°) was dissolved in fuming nitric acid (3 ml), and next day the solution was poured into water, and the solid was collected, washed and dried (0·6 g, m.p. 89–91°). Crystallisation from methanol gave 3:4-*dinitrophenyl azide*, m.p. 91–92° (slight dec.) (Found: C, 34·7; H, 1·3; N, 33·2. $C_6H_3O_4N_5$ requires C, 34·5; H, 1·4; N, 33·5 per cent). When a solution of the compound in acetic acid was heated to 100°, very little nitrogen was evolved; the solution was diluted with a small quantity of water and left to crystallise. Pure 3:4-dinitrophenyl azide formed pale-yellow needles, m.p. 100–101°. This heating would convert any 2:3-dinitrophenyl azide into 4-nitrobenzofuroxan (orange needles, m.p. 142°) and any 2:5-dinitrophenyl azide into 5-nitrobenzofuroxan (m.p. 72°).

5:6-*Dinitrobenzofuroxan* (IX). *m*-Nitrophenyl azide (3·0 g) was dissolved in fuming nitric acid (14 ml) and the solution was added slowly to a cold mixture of fuming

---

[43] E. Noelting and O. Michel, *Ber. Dtsch. Ges.* **26**, 87 (1893).

nitric acid (14 ml) and concentrated sulphuric acid (14 ml), the temperature being kept below 20°. The dark brown solution was left overnight, when it became much paler. It was then poured on to ice, and the sticky yellow mass that separated was collected, rubbed with glacial acetic acid (10 ml) so that it solidified, water (30 ml) was added, and the whole mass was vigorously shaken. The solid that separated was collected, washed and dried, m.p. 60–70° (3·2 g, 76 per cent). Crystallisation gave the *trinitrophenyl azide*, yellow prisms (from methanol), m.p. 73–74° (dec.) (Found: C, 28·6; H, 0·57; N, 32·9. $C_6H_2O_6N_6$ requires C, 28·4; H, 0·79; N, 33·1 per cent). A solution of 2:4:5-trinitrophenyl azide (3·2 g) in acetic acid (10 ml) was heated on a water bath until evolution of nitrogen ceased (2 hr). The solution was cooled, water was added, and the solid was collected, washed and dried (2·3 g, m.p. 160–170°). The compound was crystallised from concentrated nitric acid to form hexagonal yellow prisms (1·4 g), m.p. 177° (without dec.), unchanged by further crystallisation (Found: C, 32·0; H, 1·2; N, 24·6. Calc. for $C_6H_2O_6N_4$: C, 31·9; H, 0·89; N, 24·8 per cent). Drost[9] reports m.p. 172° (dec.). Unlike (III), (IX) did not give a deep-red coloration when added to cold 2 N sodium hydroxide solution.

5-Anilino-6-nitrobenzofuroxan (XVII, R = H) was obtained by dissolving 5:6-dinitrobenzofuroxan in hot ethanol and adding 1 mol. of aniline. Clusters of dark-red needles separated, m.p. 168° (lit.[9] 168°) (Found: C, 53·4; H, 2·9; N, 20·3. $C_{12}H_8O_4N_4$ requires C, 52·9; H, 2·9; N, 20·6 per cent).

P-5-Bromoanilino-6-nitrobenzofuroxan (XVII, R = Br) formed dark-red needles, m.p. 151° (Found: C, 41·3; H, 2·1; N, 15·8; Br, 23·1. $C_{12}H_7O_4N_4Br$ requires C, 41·1; H, 2·0; N, 16·0; Br, 22·8 per cent).

1:5-*Dichloro*-2:4-*dinitrobenzene*. *m*-Dichlorobenzene (16·0 g) was dissolved in fuming nitric acid (40 ml), and the solution was heated on a steam bath for 1 hr, cooled and poured on to ice and the solid was collected (24 g). Crystallisation from ethanol gave a product (18 g), m.p. 101°. (lit. [21,22] m.p. 101°). This is more convenient than using a sulphuric–nitric acid mixture,[22] which requires vigorous stirring of the two phases.

Styphnyl azide (XIV). Styphnyl chloride was prepared as described by Sudborough and Picton.[21] A solution of sodium azide (13 g) in water (20 ml) and methanol (20 ml) was added slowly with stirring to a solution of styphnyl chloride (24 g) in acetone (20 ml) and methanol (20 ml). After 1 hr at room temperature the solution was poured into water, and the solid was collected, washed and dried (24·2 g), m.p. 85–87°. Crystallisation from methanol gave *styphnyl azide* as pale-yellow plates (21·2 g), m.p. 91–92° (dec.) (Found: C, 24·2; H, 0·68; N, 43·0. $C_6HO_6N_9$ requires C, 24·4; H, 0·34; N, 42·7 per cent).

Nitrobenzodifuroxan (XIX). A solution of styphnyl azide (2·5 g) in acetic acid (10 ml) was heated on a steam-bath until evolution of nitrogen ceased (2 hr). The solution was cooled, water (30 ml) was added, and the solid was collected (2·0 g, m.p. 154–156°). Crystallisation from chloroform–methanol (1:2) gave pale-yellow needles (1·7 g, 85 per cent), m.p. 158° (lit.[14] 156°) (Found: C, 30·4; H, 0·5; N, 29·1. Calc. for $C_6HO_6N_5$: C, 30·1; H, 0·4; N, 29·1 per cent).

1:5-Diazido-2:4-dinitrobenzene (XIII) was prepared from 1:5-dichloro-2:4-dinitrobenzene.[12] The compound crystallised as yellow plates from ethanol, m.p. 96–97° (dec.) (lit.[14] 78°) (Found: C, 29·0; H, 1·2; N, 45·9. Calc for $C_6H_2O_4N_8$: C, 28·8; H, 0·8; N, 44·8 per cent). Heating a solution of this azide in glacial acetic acid for 30 min gave 5-azido-6-nitrobenzofuroxan (XX), as hexagonal plates from chloroform, m.p. 90° (lit.[12] 89°) (Found: C, 32·7; H, 0·85; N, 37·4. Calc. for $C_6H_2O_4N_6$: C, 32·4; H, 0·90; N, 37·8 per cent). The preparation of styphnyl azide by the nitration of (XIII) has been described earlier.

1:3:5-*Triazido*-2:4:6-*trinitrobenzene* (XXIV). Trichloroaniline[44] was deaminated[23] to form 1:3:5-trichlorobenzene, which was nitrated to give trichlorotrinitrobenzene.[25] Treatment of the last-named compound with sodium azide as described by Turek[23] gave an orange solid, m.p. 55–60°, which was not examined further. 1:3:5-Trichlorobenzene was nitrated[45] to give 1:3:5-trichloro-2:4-dinitrobenzene (XXV), m.p. 129–130°. (lit[45] 129–130°). 1:3:5-Trichloro-2:4-dinitrobenzene (10 g) was dissolved in a boiling mixture of acetone (55 ml) and methanol (20 ml) and a hot solution of sodium azide (8·2 g) in water (30 ml) and methanol (30 ml) was added. This mixture was boiled under reflux for 55 min and then filtered, and the residue of sodium chloride was washed with boiling ethanol (5–10 ml) and the filtrate and washings were cooled to 0° overnight. The crude triazidodinitrobenzene (XXVI) was collected and air-dried (6–7 g), m.p. 106–108°. Turek reported[27] that the product had m.p. 107–108° and that protracted crystallisation gave a solid of m.p. 116–117°. The crude material was slowly added to fuming nitric acid (5 ml per g of azide). When all the material was in solution, concentrated sulphuric acid (1 ml per g of azide) was added dropwise and the mixture was set aside at room temperature. After approximately 1 hr pale-yellow plates started to separate and 4 hr later the mixture was cooled to 0°. Next day the solid was collected and washed with water, m.p. 128–130°. The filtrate was diluted with an equal volume of water, and the impure material that separated was crystallised from acetic acid (total yield 4–5 g). The compound formed pale-yellow plates from acetic acid, m.p. 130–131° (lit.[23,26] 130–131°) (Found: C, 21·5; H, 0·19; N, 51·7, 48·3. Calc. for $C_6O_6N_{12}$: C, 21·4; H, 0·0; N, 50·0 per cent). The crystals were observed to darken on the surface. Decomposition of this azide was investigated in xylene, *iso*amyl acetate and propionic acid.

Benzotrifuroxan (XXII). Triazidotrinitrobenzene (3·0 g) was added to propionic acid (15 ml) and the mixture was kept in an oil-bath at 110-115° until all the solid had dissolved. The temperature of the bath was raised rapidly to 135° and maintained at that temperature for 5 min, and the temperature was then raised to 145° for a further 5 min. The pale-brown solution had then almost ceased to evolve nitrogen. It was filtered if necessary, cooled to ca. 60°, warm water (30 ml) was added, and the mixture was cooled to 0°. Next day the cream-coloured solid was collected (2·3 g, 86 per cent), m.p. 192–194°. Crystallisation from aqueous acetic acid or ethanol–acetic acid gave almost colourless prisms, m.p. 194–195° (slight dec.) (Found: C, 28·9; H, 0·08; N, 32·8. Calc. for $C_6O_6N_6$: C, 28·6; H, 0·0; N, 33·3 per cent). Turek[23] reports m.p. 195° (misquoted by Yoffé[26] as 159°). Crystallisation from ethanol gives crystals that turn slightly pink on the surface. The substance sublimes unchanged at 170°/15 mm. Crystallisation from benzene yields a *1:1 complex*, which loses benzene at 100° *in vacuo* (Found: C, 42·5; H, 1·8. $C_6H_6{\cdot}C_6O_6N_6$ requires C, 43·6; H, 1·8 per cent. Loss at 100°, 23·4, 23·8. Required loss, 23·6 per cent. Found on residue, C, 29·2 per cent). The residue from heating this complex is almost pure-white benzotrifuroxan. Instead of adding water to the propionic acid solution of (XXII),

---

[44] F. D. Chattaway and H. Irving, *J. Chem. Soc.* 142 (1933).

[45] E. J. E. Hüffer, *Rec. Trav. Chim. Pays-Bas* **40**, 451 (1921).

benzene (twice the volume of acid) may be added to precipitate benzotrifuroxan as its benzene complex. For reasons of safety we have never decomposed more than 5 g of this azide at once, although the reaction has never shown any sign of getting out of control.

2-*Phenylnaphthalene*. A solution of phenylacetaldehyde (10 g) in acetic acid (40 ml) was added dropwise to boiling hydrobromic acid (48 %, 100 ml) during 40 min, and the mixture was then heated under reflux for a further 25 min and allowed to cool. The oily layer solidified. It was washed with water twice by decantation and crystallised from acetic acid (30 ml), to yield a solid (5·0 g), m.p. 98–101°. This was dissolved in benzene–light petroleum (boiling range 60–80°) mixture (1:2), the solution was passed through a short alumina column, the solvents were evaporated, and the residue was crystallised from methanol–ethanol to give 2-phenylnaphthalene (4·1 g), m.p. 102–103°. Evaporation of the mother-liquors yielded a further 0·3 g, m.p. 101–102° (lit.[28] 101–102°).

Preparation of complexes with aromatic hydrocarbons

The solvent used was a mixture of acetic acid and ethanol (1:4). Usually a slight excess (10 per cent) of the more soluble component (the hydrocarbon) was taken, the majority of the hydrocarbons forming 1:1 complexes. The solids that formed were collected, washed with a little methanol and dried at room temperature.

5:6-*Dinitrobenzofuroxan–naphthalene complex*. This formed orange needles, m.p. 115–150° (Found: C, 54·1; H, 2·6; N, 16·0. $C_{16}H_{10}O_6N_4$ requires C, 54·2; H, 2·9; N, 15·8 per cent). The compound decomposed on being kept at room temperature.

4:6-*Dinitrobenzofuroxan complexes*

Naphthalene, dark-red needles, m.p. 172° (dec.) in agreement with Drost.[9]

1-*n-Pentylnaphthalene*, soft red needles, m.p. 67·5–68·5° (Found: C, 59·4; H, 4·8; N, 12·9. $C_{21}H_{20}O_6N_4$ requires C, 59·4; H, 4·7; N, 13·2 per cent).*

1-*n-Hexylnaphthalene*, scarlet needles, m.p. 146–150° (Found: C, 60·1; H, 5·0; N, 12·6. $C_{22}H_{22}O_6N_4$ requires C, 60·5; H, 4·6; N, 12·8 per cent).

2-*Phenylnaphthalene*, shiny red plates, m.p. 130° (Found: C, 61·2; H, 3·0; N, 16·5. $C_{22}H_{14}O_6N_4$ requires C, 61·4; H, 3·3; N, 16·3 per cent).

Nitrobenzodifuroxan complexes

Naphthalene, orange needles, m.p. 183° (dec.) (Found: C, 52·3; H, 2·6; N, 18·6. $C_{16}H_9O_6N_5$ requires C, 52·3; H, 2·5; N, 19·1 per cent).

1-*Phenylnaphthalene*, dark-red needles, m.p. 97·5–98° (Found: C, 59·6; H, 2·9; N, 15·5. $C_{22}H_{13}O_6N_5$ requires C, 59·6; H, 2·9; N, 15·8 per cent).

2-*Phenylnaphthalene*, red plates, m.p. 120–121° (Found: C, 59·3; H, 3·2; N, 15·2 per cent).

Tetrahydronaphthalene, pale-yellow needles, softened at 140°, m.p. 145–148° (Found: C, 39·3; H, 1·9; N, 23·9. $C_{10}H_{12}{\cdot}3C_6HO_6N_5$ requires C, 39·6; H, 1·8; N, 24·3 per cent).

Benzotrifuroxan complexes

A solution of benzotrifuroxan (0·25 g, 0·01 mole) in acetic acid–ethanol (2 ml) was filtered on to the hydrocarbon (solids were dissolved in a small amount of warm

---

* With C. M. Staveley.

solvent); usually a precipitate formed and the mixture was warmed to give a clear solution, which was then allowed to cool.

Benzene, colourless needles, which turned into prisms between 80–100°, m.p. 195° (m.p. of benzotrifuroxan) (Found: C, 32·5; H, 1·0; N, 31·1. $C_6H_6 \cdot 5C_6O_6N_6$ requires C, 32·3; H, 0·5; N, 31·4 per cent).

1:2:3-*Trimethylbenzene*, pale-cream needles, m.p. 170–172° (Found: C, 48·2; H, 3·2; N, 22·5. $C_{15}H_{12}O_6N_6$ requires C, 48·4; H, 3·3; N, 22·6 per cent).

1:3:5-*Trimethylbenzene*, colourless plates, m.p. 162–165° (Found: C, 48·3; H, 3·2; N, 22·7 per cent).

1:2:3:4-*Tetramethylbenzene*, lemon-yellow needles, m.p. 190–193° (Found: C, 49·6; H, 4·0; N, 21·8. $C_{16}H_{14}O_6N_6$ requires C, 49·7; H, 3·7; N, 21·8 per cent).

Hexamethylbenzene, pale-yellow needles, m.p. 207° (dec.) (Found: C, 52·3; H, 4·5; N, 19·9. $C_{18}H_{18}O_6N_6$ requires C, 52·2; H, 4·4; N, 20·3 per cent).

Styrene, pale-cream spears, m.p. 148–150° (dec.) (Found: C, 46·8; H, 2·2; N, 23·6. $C_{14}H_8O_6N_6$ requires C, 47·2; H, 2·3; N, 23·6 per cent).

Diphenyl, pale-yellow needles, m.p. 164–166° (Found: C, 53·7; H, 2·4; N, 20·3. $C_{18}H_{10}O_6N_6$ requires C, 53·2; H, 2·5; N, 20·7 per cent).

Diphenylmethane, white waxy prisms, m.p. 73–83° (Found: C, 64·4; H, 4·0; N, 14·7. $2C_{13}H_{12} \cdot C_6O_6N_6$ requires C, 65·3; H, 4·1; N, 14·7 per cent).

Tetrahydronaphthalene, cream-coloured irregular plates, m.p. 151–152° (Found: C, 49·8; H, 3·2; N, 21·7. $C_{16}H_{12}O_6N_6$ requires C, 50·0; H, 3·2; N, 21·9 per cent).

6-*Methyltetrahydronaphthalene*, colourless needles, m.p. 128–135° (Found: C, 50·9; H, 3·5; N, 21·1. $C_{17}H_{14}O_6N_6$ requires C, 51·3; H, 3·5; N, 21·1 per cent).

5-*Ethyltetrahydronaphthalene*, pale-yellow needles, m.p. 144–147° (Found: C, 52·8; H, 4·0; N, 20·2. $C_{18}H_{16}O_6N_6$ requires C, 52·5; H, 3·9; N, 20·4 per cent).

5:7-*Dimethyltetrahydronaphthalene*, cream-coloured irregular plates, m.p. 132–136°, clearing at 148° (Found: C, 52·3; H, 3·6; N, 20·9 per cent).

1:7-*Dimethyl*-3:4-*dihydronaphthalene*, long lemon-yellow needles, m.p. 128–130° (dec.) (Found: C, 52·6; H, 3·4; N, 20·7. $C_{18}H_{14}O_6N_6$ requires C, 52·7; H, 3·4; N, 20·5 per cent).

Naphthalene, the complex crystallised from acetic acid as pale greenish-yellow needles, m.p. 250–252° (dec.) (Found: C, 51·0; H, 2·4; N, 21·6. $C_{16}H_8O_6N_6$ requires C, 50·6; H, 2·1; N, 22·1 per cent).

1:7-*Dimethylnaphthalene*, long yellow prisms, m.p. 215° (dec.) (Found: C, 53·5; H, 2·8; N, 20·4. $C_{18}H_{12}O_6N_6$ requires C, 52·9; H, 3·0; N, 20·6 per cent).

1-*n*-*Pentylnaphthalene*, pale-yellow needles, m.p. 126° (Found: C, 56·5; H, 3·9; N, 18·5. $C_{21}H_{18}O_6N_6$ requires C, 56·0; H, 4·0; N, 18·7 per cent).

1-n-*Hexylnaphthalene*, pale-yellow needles, m.p. 118° (Found: C, 56·7; H, 4·3; N, 18·0. $C_{22}H_{20}O_6N_6$ requires C, 56·9; H, 4·3; N, 18·1 per cent).

2-n-*Octylnaphthalene*, pale-yellow needles, m.p. 115–118° (Found: C, 58·9; H, 4·9; N, 16·9. $C_{24}H_{24}O_6N_6$ requires C, 58·5; H, 4·9; N, 17·1 per cent).

2-α-*Naphthylbutane*, yellow plates, m.p. 107–117° (Found: C, 55·0; H, 3·6; N, 18·8. $C_{20}H_{16}O_6N_6$ requires C, 55·1; H, 3·7; N, 19·3 per cent).

1-*Phenylnaphthalene*, pale-green crystals, m.p. 162° (Found: C, 51·9; H, 2·0; N, 21·6. $2C_{16}H_{12} \cdot 3C_6O_6N_6$ requires C, 51·6; H, 2·1; N, 21·7 per cent).

2-*Phenylnaphthalene*, bright-yellow needles, m.p. 158° (Found: C, 58·0; H, 2·7; N, 18·3. $C_{22}H_{12}O_6N_6$ requires C, 57·9; H, 2·6; N, 18·4 per cent).

Indene, long pale-yellow laths, m.p. 168–170° (dec.) (Found: C, 49·2; H, 2·2; N, 22·5. $C_{15}H_8O_6N_6$ requires C, 48·9; N, 2·2; N, 22·8 per cent).

Indole (prepared in ethanol), pale-yellow needles, m.p. 180° (Found: C, 45·6; H, 2·1; N, 26·1. $C_{14}H_7O_6N_7$ requires C, 45·5; H, 1·9; N, 26·1 per cent).

Dimethylfulvene (prepared in ethanol), irregular bright-yellow plates, decomposing violently at 140° (Found: C, 46·9; H, 2·6; N, 23·3. $C_{14}H_{10}O_6N_6$ requires C, 46·9; H, 2·8; N, 23·5 per cent).

The following did not give correct results on analysis.

o-*Xylene*, clusters of rectangular plates, m.p. 152–155° (Found: C, 46·0; H, 2·3; N, 24·1. $C_{14}H_{10}O_6N_6$ requires C, 46·9; H, 2·8; N, 23·5 per cent).

m-*Xylene*, cream-coloured rods slowly separated, softened at 140°, m.p. 165–175° (Found: C, 45·2; H, 2·6; N, 24·4 per cent).

p-*Xylene*, irregular plates, m.p. 160–170° (Found: C, 41·5, 48·5; H, 2·8, 2·5; N, 24·9 per cent).

2:3-*Di*-n-*hexylnaphthalene*, pale-yellow needles, m.p. 93–103° (Found: C, 62·8; H, 6·3; N, 14·4. $C_{38}H_{32}O_6N_6$ requires C, 61·3; H, 5·9; N, 15·3 per cent).

1:2:3:4:5:6:7:8-*Octahydroanthracene*, pale-yellow plates, m.p. 110–120° (Found: C, 63·6, 63·7; H, 5·3, 5·7; N, 15·4. $3C_{14}H_{18}{\cdot}2C_6O_6N_6$ requires C, 61·1; H, 5·1; N, 15·8 per cent).

1:3:5-*Trinitrobenzene–dimethylfulvene complex*

The *complex* separated from the ethanol solution of the components as yellow laths, m.p. 72–73° (Found: C, 46·5; H, 3·2; N, 15·2. $(C_6H_3N_3O_6)_9{\cdot}(C_8H_{10})_5$ requires C, 46·1; H, 3·2; N, 15·5 per cent). The compound became white in colour in 3–4 hr at room temperature (m.p. 120°; 1:3:5-trinitrobenzene, mixed m.p. 120°).

Acknowledgements—We thank Drs. B. R. Brown, M. C. Whiting, S. A. Miller and J. C. Smith for gifts of hydrocarbons.