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Adducts of Benzotrifuroxan (BTF)

Walter Selig

ABSTRACT

The preparation and some properties of adducts of benzotrifuroxan (BTF) are reported. The adducts contain one or two molecules of the adduct-forming compound (AFC) per molecule of BTF. All AFC's contain an oxygen atom.

INTRODUCTION

Benzotrifuroxan, $C_6H_6N_6$, is an explosive which is of particular interest because it does not contain any hydrogen. Therefore, it might be suspected that this material has different thermodynamic, physical and

hydrodynamic properties than hydrogen-containing explosives. This compound is also called hexanitrosobenzene. However, elucidation of its crystal structure by Cady et. al.¹ has unequivocally proven the trifuroxan structure of this molecule as shown here.

Bailey and Case^{2,3} have studied the preparation of BTF. They have also prepared a number of complexes of this compounds with aromatic compounds which act as electron donors.

This report describes the preparation and properties of a series of adducts mostly with non-aromatic organic compounds.

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EXPERIMENTAL

Adducts were prepared by dissolving 100 - 200 mg of BTF in 0.3 - 0.5 ml of the adduct-forming compound (AFC). The resulting products were dried in vacuo to constant weight or, the products were isolated after precipitation and air-dried to constant weight. If the AFC was a solid at ambient temperature, it was melted prior to solution of BTF.

Preparation of Adducts

BTF^{a*}(I):hexamethylphosphortriamide^b(1:2).

Prepared by drying in vacuo at room temperature to constant weight. Yield, quantitative. Analysis for $C_{18}H_{36}N_{12}O_8P_2$ (610.51):

	C	H	N
Calcd:	35.41	5.94	27.53
Found:	35.07	5.86	27.21

MP 143-144 (dec.)

(I):octamethylpyrophosphoramid^c(1:1).

Prepared by drying in vacuo at room temperature to constant weight, after removing the product from solution. Yield, 64%.

Analysis for $C_{14}H_{24}N_{10}O_9P$ (538.36):

	C	H	N
Calcd:	31.23	4.49	25.02
Found:	31.16	4.42	25.66

MP 163-4 (dec.).

* Superscript letters refer to list of sources of chemicals on p. 6.

(I):2-pyrrolidinone^a (1:1).

Prepared by drying in vacuo at room temperature to constant weight. Yield, quantitative. Analysis for $C_{10}H_7N_7O_7$ (337.21):

	C	H	N
Calcd:	35.62	2.09	29.08
Found:	35.76	2.27	28.57

MP 108.5 - 109.4

(I):2-piperidone^a (1:2).

Prepared by drying in vacuo at room temperature to constant weight. Yield, quantitative. Analysis for $C_{16}H_{18}N_8O_8$ (450.37):

	C	H	N
Calcd:	42.67	4.03	24.88
Found:	41.80	4.19	24.88

The above compound, on further drying in vacuo to constant weight at 45°C yields (I):2-piperidone (1:1).

(I):2-piperidone (1:1).

Analysis for $C_{11}H_9N_7O_9$ (351.24):

	C	H	N
Calcd:	37.62	2.58	27.91
Found:	37.78	2.68	27.29

MP 105.5 - 107.5 (dec)

(I):tetramethyloxamide^d (1:1).

Prepared by drying in vacuo at 55°C to constant weight. Yield, quantitative. Analysis for $C_{12}H_{12}N_8O_8$ (396.28):

	C	H	N
Calcd:	36.37	3.05	28.28
Found:	36.13	3.25	27.82

MP 136-7

(I):N-methyl-2-quinolone^b (1:1).

Prepared by drying in vacuo at 55-60°C to constant weight. Yield, quantitative. Analysis for $C_{16}H_9N_7O_7$ (411.29):

	C	H	N
Calcd:	46.72	2.21	23.84
Found:	47.03	2.33	24.19

MP 165.2-165.4

(I):N-formylhexamethyleneimine^a (1:1).

Prepared by air-drying precipitate to constant weight. Yield, 55%. Analysis for $C_{13}H_{13}N_7O_7$ (379.29):

	C	H	N
Calcd:	41.17	3.45	25.85
Found:	41.13	3.59	25.17

(I):2-methyl-1-isoquinolone^d (1:2).

Prepared by drying in vacuo at room temperature to constant weight. Yield, quantitative. Analysis for $C_{26}H_{18}N_2O_8$ (570.48):

	C	H	N
Calcd:	54.74	3.18	19.64
Found:	54.15	2.98	19.20

MP 66-8

(I):hexaethylphosphortriamide^e (1:2).

Prepared by drying in vacuo at room temperature to constant weight. Yield, quantitative. Analysis for $C_{30}H_{60}N_{12}O_8P_2$ (778.84):

	C	H	N
Calcd:	46.27	7.77	21.58
Found:	45.85	7.91	21.72

MP 100-102 (dec)

(I):N-methyl-2-piperidone^a:H₂O (1:1:1).

Prepared by air-drying precipitate to constant weight. Yield, 51%. Analysis for $C_{12}H_{13}N_2O_8$ (383.28):

	C	H	N
Calcd:	37.61	3.42	25.58
Found:	37.21	3.19	25.40

MP 99-100

* Source of Chemicals

- a Aldrich Chemical Co., Milwaukee, Wisconsin
- b Eastman Organic Chemicals, Rochester, New York
- c City Chemical Corp., New York, New York
- d Reef Laboratory, Lafayette, Indiana
- e Orgmet, Hampstead, New Hampshire

Analysis of Adducts

X-ray diffraction patterns made with $\text{CuK}\alpha$ (Ni-filtered) radiation were determined as relative intensities for d spacings in Angstroms.

Melting points were determined on a Mettler FPI melting point apparatus. Infrared spectra were run on a Beckman IR8 spectrophotometer in potassium bromide pellets.

RESULTS

The stable adducts of BTF synthesized are listed in Table 1.

Table 1. Stable Adducts of BTF

AFC	AFC/BTF
hexamethylphosphoramide	2
hexaethylphosphoramide	2
octamethylpyrophosphoramide	1
2-pyrrolidinone	1
2-piperidone	2,1
tetramethyloxamide	1
N-methyl-2-quinolone	1
2-methyl-1-isoquinolone	2
N-methyl-2-piperidone	1
N-formylhexamethyleneimine	1

Compounds forming labile adducts with BTF, as determined from X-ray diffraction patterns, are listed in Table 2; compounds not yielding adducts under the experimental conditions used are listed in Table 3. The probable ratio of AFC/BTF of some of the labile adducts was judged by comparison of the X-ray

Table 2. Compounds forming labile adducts with BTF

AFC	probably AFC/BTF
* N,N-dimethylformamide	2,1
N,N-dimethylacetamide	1
N,N-dimethylpropionamide	2
N,N-dimethylbutyramide	2
N,N-dimethylpivalamide	
* dimethylsulfoxide	1
* N-methyl-2-pyrrolidinone	1
N-isopropyl-2-pyridone	1
γ-butyrolactone	2
4-valerolactone	
* N-formylpyrrolidine	
N-formylpiperidine	

Table 3. Compounds not forming adducts with BTF

N-n-propyl-2-pyridone
N-n-butyl-2-pyridone
N,N-dimethylbenzamide
ε-caprolactam

diffraction patterns with those of known stable adducts. The diffraction patterns of twelve of the adducts are listed in Table 4.

The IR spectra of the adducts are additive, showing the peaks of the components. However, the peaks of BTF seem to be of higher intensity than those of the AFC's. The IR spectrum for BTF is presented in Figure 1, while those for the adducts with 2-piperidone and octamethylpyrophosphoramidate are shown in Figures 2 and 3.

The compounds in Table 2 marked with an (*) fall into a group of quasi-isomorphous powder patterns.

Those working with benzotrifuroxan should be aware of its great tendency to form both stable and labile complexes and adducts with a wide variety of organic compounds.

Figure 1

Figure 2

Figure 3

REFERENCES

1. H. H. Cady, A. C. Larson, and D. T. Cromer, Acta Cryst. 20, 336 (1966).
2. A. S. Bailey and J. R. Case, Tetrahedron 3, 113 (1958).
3. A. S. Bailey, J. Chem. Soc. 1960, 4710.

Table 4-1. X-ray powder pattern of BTF: Hexamethylphosphoramide (1:2)

d(A)	I	d(A)	I
10.6	s-	4.60	s
7.4	m	4.15	s
6.9	s	3.78	w
6.4	s-	3.69	w
5.15	s-	3.56	w
(4.80	m	3.21	w
(4.75	w		
		3.10	w
		2.92	w

Table 4-2. X-ray powder pattern of BTF: Octamethylpyrophosphoramidate

d(A)	I	d(A)	I
9.0	m	4.14	s-
8.3	m	4.05	m
8.0	s	3.94	s-
7.2	s	3.65	w
5.85	m	3.48	m
5.35	s	3.41	w
4.90	w	3.30	m
4.75	w	3.20	s-
4.55	w	3.12	m
4.35	w	2.99	m

Table 4-3. X-ray powder pattern of BTF: 2-pyrrolidinone

d(A)	I	d(A)	I
9.0	s+	4.30	s-
7.3	w	4.10	w
6.5	w	3.93	s
6.1	m	3.80	s
5.3	m	3.70	w
5.1	w	3.38	m
4.90	m	3.24	w
4.70	w	3.03	s+
4.60	m	2.92	w
4.50	m		

Table 4-4. X-ray powder pattern of BTF: N,N,N',N'-tetramethyloxamide

d(A)	I	d(A)	I
8.1	m	4.12	s
7.7	s+	3.99	s
6.1	w	3.70	s-
5.75	w	3.64	m
5.05	s	3.48	w
4.85	w	3.35	w
(4.60	m	3.24	w
(4.55	w		
4.25	w	3.16	w
		3.09	s
		2.92	s-

Table 4-5. X-ray powder pattern of BTF: N-methyl-2-quinolone

d(A)	I	d(A)	I
9.2	m	4.45	w
7.2	s	4.05	w
6.7	w	3.80	w
6.25	w	3.75	w
5.80	w	3.63	m
5.50	m	3.53	w
5.30	w	3.19	s++
4.95	s-	3.10	w
4.85	s-	3.00	w
4.55	w	2.90	w

Table 4-6. X-ray powder pattern of BTF: 2-methyl-1-isoquinolone (1:2)

d(A)	I	d(A)	I
10.5	m	3.96	w
7.6	s	3.84	m
6.3	s	3.75	w
5.9	w	3.65	w
5.5	w	3.51	w
5.3	m	3.42	s
4.75	m	3.33	m
4.60	w	3.15	s-
4.15	m	3.02	w

Table 4-7. X-ray powder pattern of BTF: 2-piperidone, 1:1

d(A)	I	d(A)	I
9.4	s+	3.97	s-
6.5	w	3.88	w
6.1	w	3.80	s-
5.45	m	3.57	w
5.15	w	3.38	w
4.70	m	3.20	w
4.55	w	3.07	s
		3.05	
4.33	m		
4.13	s-	2.99	w

Table 4-8. X-ray powder pattern of BTF: hexaethylphosphortriamide, 1:2

d(A)	I	d(A)	I
9.5	s	4.23	m
8.1	s-	3.99	m
7.6	s+	3.75	m
6.1	m	3.69	w
5.8	w	3.60	w
5.25	w	3.40	w
4.95	w	3.29	w
4.85	w	3.05	m
4.55	s-		

Table 4-9. X-ray powder pattern of BTF: N-methyl-2-piperidone:H₂O, 1:1:1

d(A)	I	d(A)	I
10.8	s+	3.73	w
5.9	w	3.50	m
5.25	s	3.45	m
5.15			
4.25	m	3.38	w
4.15	w	3.33	w
4.03	w	3.08	m
3.94	m	3.00	m
		2.97	s-

Table 4-10. X-ray powder pattern of BTF: N,N-dimethylformamide (labile)

d(A)	I	d(A)	I
11.0	s+	3.94	w
6.0	m	3.80	w
5.8	w	3.72	m
5.5	m	3.50	s-
		3.46	
5.15	s-	3.31	w
5.00	w	3.25	w
4.86	m	3.11	w
4.72	w	3.00	s-
4.59	w	2.96	m
4.40	s-	2.91	m
4.15	w	2.88	m
4.03	s-		

Table 4-11. X-ray powder pattern of BTF: Dimethylsulfoxide (labile)

d(A)	I	d(A)	I
9.6	s	3.92	s
6.1	m	3.76	w
5.7	w	3.67	m
5.1	s-	3.38	w
4.9	w	3.30	w
4.75	w	3.22	w
4.53	s-	3.06	s-
4.35	w	3.01	w
4.25	w	2.92	m
4.08	m		

Table 4-12. X-ray powder pattern of BTF: 1-methyl-2-pyrrolidinone (labile)

d(A)	I	d(A)	I
10.4	s	3.81	w
6.5	w	3.70	w
5.7	w	3.58	w
{ 5.15 5.05	s-	3.48	m
4.60	m	{ 3.43 3.39	w
4.20	s-	3.25	w
4.10	w	3.04	m
3.89	m	2.99	m
		2.95	m

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