THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VII. THE NITRONAPHTHOLS AS FLUORIMETRIC REAGENTS FOR STANNOUS TIN

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INTRODUCTION

In earlier papers of this series, the use of naphthalene compounds has been reported for the fluorimetric detection of various cations[1-6]. In particular, nitronaphthalene derivatives have been utilized for the fluorimetric detection[1,3-6] and determination[7] of stannous tin. For this paper, the nitro derivatives of 1-naphthol and 2-naphthol have been examined and found to be of importance in the detection of tin by fluorimetric methods. Spots of aqueous solutions of 49 metal salts were placed on No. 1 Whatman Chromatographic paper, air dried and then sprayed separately with 0.1% solution of the reagents dissolved in a mixture of equal volumes of 96% ethyl alcohol and 10N hydrochloric acid. The paper was air dried, sprayed with 15N NH_4OH, again air dried and viewed under ultra-violet light. Under these conditions only stannous tin exhibited any marked fluorescence. The addition of 10N HCl to the alcoholic solutions of the nitronaphthols was found to increase the sensitivity of the test. The intensity of fluorescence was found to vary with the position of the nitro group in the naphthol nucleus.

EXPERIMENTAL

Synthesis of reagents

A summary of the methods of synthesis of the nitro-naphthols will be published in the near future by BRYSON[8]. All nitro-naphthols can be synthesized from the corresponding nitro-naphthylamines[4] by a diazotisation procedure and subsequent replacement of the diazo group by hydroxyl. The synthesis of 5-nitro-1-naphthol from 5-nitro-1-naphthylamine is an example of the procedure used for the preparation of the nitronaphthols.

5-Nitro-1-naphthol

5-Nitro-1-naphthylamine** (0.8 g) was warmed in a mixture of sulphuric acid (5 ml, sp.gr. – 1.84) and water (50 ml), then cooled to 0–5° so that the nitronaphthylamine was present in a finely divided state as the sulphate paste, the most suitable form for efficient diazotisation. A solution of sodium nitrite (0.5 g) in water (2.5 ml) was added from a dropping funnel over a period of 10 min at 0–5° and the presence of excess, nitrous acid confirmed by the starch–potassium iodide test. The mixture was stirred for 1 h at 0–5°, then urea (0.1 g) added to destroy excess nitrous acid. The diazo solution was now added slowly over a period of 10 min to 2N H_2SO_4 maintained just below the boiling point. After the addition was completed, the mixture was boiled for a further 10 min, filtered hot and the filtrate chilled. The flocculent yellow crystals of 5-nitro-1-naphthol were separated and recrystallised from boiling water using a trace of activated charcoal to remove the small amount of red dye which unavoidably forms during the sulphuric acid decomposition step.

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* On study leave at Birkbeck College, University of London.

** For the synthesis of this compound see GARNETT AND LOCK[4].

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Yield 0.5 g; m.p. 171–2°; Literature 171°[8]

The same procedure was used for the synthesis of the remaining nitronaphthols, except 8-nitro-1-naphthol and 6-nitro-2-naphthol.

8-Nitro-1-naphthol

When the diazo compound from 8-nitro-1-naphthylamine was decomposed in $2N$ H_2SO_4, following the same procedure as previously reported, excessive coupling appeared to occur, resulting in bad tarring and a very poor yield (approx. 10%) of 8-nitro-1-naphthol. The yield was improved to 30% by using stronger sulphuric acid ($4N$) in the decomposition step. BRYSON[8] suggests that even better yields can be obtained if the diazonium solution is slowly added to the sulphuric acid at 50° (instead of 95°) and the solution slowly brought to the boil. This minimises the loss of 8-nitro-1-naphthol through the competing coupling reaction.

6-Nitro-2-naphthol

This compound can also be readily synthesized from the corresponding nitronaphthylamine by the diazotisation procedure[8], however the authors have used an alternative method of preparation which involves a pressure desulphonation of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid in $10N$ HCl.

A solution of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid* (1.0 g) in $10N$ HCl (10 ml) was carefully heated to 160° for 2 h in a sealed glass tube, then cooled. The solution was diluted with water (90 ml) and the precipitate filtered, dried and recrystallised from benzene in pale yellow needles.

Yield 0.48 g; m.p. 158–9°

This compound showed no depression of melting point when mixed with an authentic sample of 6-nitro-2-hydroxynaphthalene prepared from 6-nitro-2-naphthylamine by a diazotisation procedure.

The observed and reported melting points of the nitro-naphthols are listed in Table I and compared with those of the parent *α*- and *β*-naphthols.

TABLE I

MELTING POINTS OF THE NITRONAPHTHOLS

Substituent		*Observed m.p.*	*Literature m.p.*
NO_2	*OH*	°C	°C
	1	95.5	96
	2	122	122
2	1	127.5	128
3	1	168–9	167–8
4	1	166	164
5	1	171–2	171
6	1	181–2	181–2
7	1	212[a]	—
8	1	242[d]	212[d]
1	2	103	103
4	2	120	120
5	2	148	147
6	2	159	156–8
7	2	163	159
8	2	145	145

[a] 7-Nitro-1-naphthol is a new compound, the synthesis of which will be described elsewhere[8].

[d] decomposed without melting.

It will be noticed that the observed and reported melting points for 8-nitro-1-naphthol do not agree. BRYSON[8] discusses this anomaly and presents strong evidence to support the observed melting point.

From Table I, it can be seen that 13 of the theoretically possible 14 nitro-naphthols

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* See ANDERSON, GARNETT AND LOCK[6] for the synthesis of this compound.

are listed, 3-nitro-2-naphthol being the exception. This compound can be synthesized from 3-nitro-2-naphthylamine. However, this is the most difficult of all nitronaphthylamine preparations and was unavailable in sufficient quantity for the preparation of the corresponding nitronaphthol.

Technique of spot testing

The standard procedure reported in previous communications[1,3] was used. The reagents employed are listed in Table II. The results obtained are shown in Table III.

TABLE II

REAGENTS USED FOR SPRAYING METAL IONS

Reagent No.	*Reagent 0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl*	*Reagent No.*	*Reagent 0.1% Solution in a mixture of equal volumes of 96% ethyl alcohol and 10N HCl*
1	2-Nitro-1-naphthol	8	1-Nitro-2-naphthol
2	3-Nitro-1-naphthol	9	4-Nitro-2-naphthol
3	4-Nitro-1-naphthol	10	5-Nitro-2-naphthol
4	5-Nitro-1-naphthol	11	6-Nitro-2-naphthol
5	6-Nitro-1-naphthol		
6	7-Nitro-1-naphthol	12	7-Nitro-2-naphthol
7	8-Nitro-1-naphthol	13	8-Nitro-2-naphthol

TABLE III

FLUORESCENCE OBTAINED ON SPRAYING SPOTS OF IONS WITH VARIOUS REAGENTS, BEFORE (B) AND AFTER (A) QUENCHING WITH 15N NH_4OH

	Reagent																									
	1		*2*		*3*		*4*		*5*		*6*		*7*		*8*		*9*		*10*		*11*		*12*		*13*	
Ion	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A
Sn^{+2}	F(s)	F(s)	F	F	F	F	F	F	F(s)	F	F(s)	F	F(s)	F(h)	F(s)	F	F	F	F(s)	F	F(s)	F	F(s)	F(s)	F(s)	F
Sn^{+4}																			F(t)							
As^{+5}										F(t)																
Al^{+3}																			F(t)					F(t)		
Li^{+}																					F(t)					
Be^{+2}								F(t)		F(t)				F(t)				F(t)	F(t)	F(t)	F(t)	F(t)		F(t)		
Th^{+4}																			F(t)							
ZrO^{+2}										F(t)								F(t)	F(t)					F(t)	F(t)	
Ti^{+4}																								F(t)		
In^{+3}																				F(t)				F(t)		

Other ions tested included: Fe^{+2}, Fe^{+3}, Hg^{+}, Hg^{+2}, As^{+3}, Sb^{+3}, Bi^{+3}, Cr^{+3}, Mn^{+2}, Zn^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Mg^{+2}, Cu^{+2}, Co^{+2}, Ni^{+2}, Pb^{+2}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Ce^{+3}, Ce^{+4}, Mo^{+6}, Pt^{+2}, Pt^{+4}, Au^{+3}, Pd^{+2}, Tl^{+}, Tl^{+3}, W^{+6}, UO_2^{+2}, VO^{+2}, V^{+5}, Ru^{+3}, Ti^{+3}, Cd^{+2}, Ag^{+}.

These ions gave either no fluorescence or coloured spots with only a faint trace of fluorescence.

B = Before quenching with 15N NH_4OH
A = After quenching with 15N NH_4OH
F = Fluorescence
F(s) = Slight fluorescence
F(t) = Trace of fluorescence
F(h) = Coloured spot with faint fluorescent ring

Effect of acid upon the test

Two series of sensitivity tests were performed using (a) the nitronaphthols dissolved in 96% ethyl alcohol and (b) the nitronaphthols dissolved in equal volumes of 96% ethyl alcohol and 10N HCl. The results are summarised in Table IV.

TABLE IV

EFFECT OF ACID UPON THE INTENSITY OF FLUORESCENCE

Reagent	*Reaction with Sn^{+2}*		*Reagent*	*Reaction with Sn^{+2}*	
Series I *0.1% in 96% ethyl alcohol*	*B*	*A*	*Series II* *0.1% in equal volumes of 96% ethyl alcohol and 10N HCl*	*B*	*A*
2-Nitro-1-naphthol	WF	WF	2-Nitro-1-naphthol	WF	WF
3-Nitro-1-naphthol	F	F	3-Nitro-1-naphthol	F	SF
4-Nitro-1-naphthol	WF	F	4-Nitro-1-naphthol	F	F
5-Nitro-1-naphthol	WF	WF	5-Nitro-1-naphthol	F	F
6-Nitro-1-naphthol	WF	WF	6-Nitro-1-naphthol	WF	F
7-Nitro-1-naphthol	WF	F	7-Nitro-1-naphthol	WF	F
8-Nitro-1-naphthol	WF	F(h)	8-Nitro-1-naphthol	WF	F(h)
1-Nitro-2-naphthol	WF	WF	1-Nitro-2-naphthol	WF	F
4-Nitro-2-naphthol	F	F	4-Nitro-2-naphthol	F	SF
5-Nitro-2-naphthol	F	F	5-Nitro-2-naphthol	WF	SF
6-Nitro-2-naphthol	WF	WF	6-Nitro-2-naphthol	WF	F
7-Nitro-2-naphthol	WF	WF	7-Nitro-2-naphthol	WF	WF
8-Nitro-2-naphthol	WF	F	8-Nitro-2-naphthol	WF	SF

SF = Strong fluorescence
F = Fluorescence
WF = Weak fluorescence
F(h) = Coloured spot surrounded by a faint fluorescent ring
B = Before quenching with 15N NH_4OH
A = After quenching with 15N NH_4OH

The above results are in agreement with the data reported for the nitronaphthylamines[4] where the presence of strong hydrochloric acid in the reagent solution improved the fluorescent properties of the particular reagent in the detection of stannous tin.

Sensitivity tests

Sensitivity tests were carried out on freshly prepared dilute solutions of stannous chloride containing 2 ml of 30% hypophosphorous acid per 100 ml of solution[3]. All the nitronaphthols exhibited a blue fluorescence under the conditions of test except reagent No. 7 which yielded a purple spot with a fluorescent ring. Reagent Nos. 1, 8 and 12 gave only slight fluorescence. Reagent Nos. 2, 9, 10 and 13 gave the most intense fluorescence of the series and were capable of detecting 10^{-5} g stannous tin whilst the remaining reagents were sensitive to 10^{-4} g stannous tin. The nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Blank experiments were performed on the dilute hypophosphorous acid solutions described previously and were found to yield no fluorescence.

DISCUSSION

In earlier papers of this series, it has been shown that both the nitronaphthylamines[4] and nitro-aminonaphthalene monosulphonic acids[1,3,5] can be used as fluorimetric reagents for stannous tin, the species responsible for the fluorescence being the excited state of the naphthylammonium ion. More recent evidence indicates that the test will also be given by other nitronaphthalene derivatives, in particular 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid[5] and the reagents reported in this paper, the nitro-naphthols.

In general, the trend of the results with the nitronaphthols confirms the earlier work reported for the nitronaphthylamines, bearing in mind that the nature of the tests enables only a semi-quantitative study to be made of the type and intensity of the fluorescence exhibited by each compound.

From evidence available at present, the following conclusions can be made when attempting to correlate the effect of structure of reagent with intensity of fluorescence.

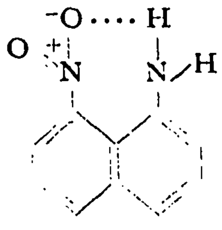
(1) Those substituted naphthalene derivatives (either naphthylamines or naphthols) containing a nitro group in the second ring appear to yield a more intense fluorescence than the corresponding homonuclear substituted nitro compounds.

(2) The nitro derivatives of the β-substituted naphthalenes (naphthylamines or naphthols) produce a more intense fluorescence than the corresponding nitro derivatives of the α-substituted compounds.

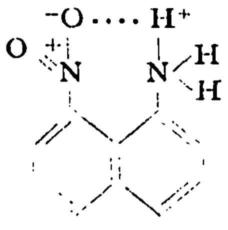
These results are in agreement with the data reported by ALLEN and his co-workers[9] who studied the effect of substituents in the naphthalene ring upon the fluorescent properties of the individual compounds, also the results of TOMASCHEK[10] who reports that the presence of substituents —OH and $-NH_2$ intensify the fluorescence of a particular compound and displace it towards the longer wavelengths.

The exceptions to the above conclusions are the 8-nitro-1-substituted naphthalene derivatives which exhibit poor reactivity in the stannous tin test when compared with the remaining isomers of each particular series. Both 8-nitro-1-naphthylamine[4] and 8-nitro-1-naphthol, in either weakly or strongly hydrochloric acid solution yield poor fluorescence with stannous tin. It is suggested that hydrogen bonding is responsible for this phenomenon *i.e.* the ease of reduction of the nitro group is impaired by a hydrogen bond to, either the amino group in the case of 8-nitro-1-naphthylamine[4], or to the hydroxyl group in the case of 8-nitro-1-naphthol. This hydrogen bonding will be exhibited by both the free base and the acidic forms of the compounds as figures (I, II and III) illustrate.

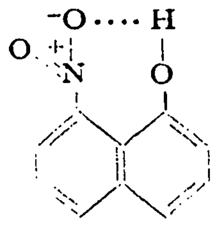
E.g.



(I)



(II)



(III)

Further support for the presence of an intramolecular hydrogen bond in these compounds is shown by the relatively poor reactivity already observed when 8-nitro-1-naphthylamine[4] is diazotised and the diazonium group replaced by hydroxyl. 8-Nitro-1-naphthylamine[4] exhibits the least reactivity of the nitronaphthylamine series in this

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reaction and the slow rate of diazotisation may be attributed to the existence of a hydrogen bond between the nitro and amino groups.

In the *ortho*-substituted compounds (*i.e.* 2-nitro-1- and 1-nitro-2-derivatives) this same lack of reactivity is not as appreciable as with the 8-nitro-1-compounds. Both *ortho* derivatives are readily diazotised and yield a positive stannous tin test, although the fluorescence is not so intense as with the remaining isomers of the series (except for the 8-1 derivative). Obviously the hydrogen bonding in the *ortho* derivatives (IV, V) does not influence the ease of reduction of the compounds as markedly as the hydrogen bonding does in the 8-1 derivative.

This observation is consistent with the effect of *ortho* nitro substituents on the acidity of phenols and anilinium ions[11]. With these systems, it is found that such factors do not appreciably affect the basic strength except in N-substituted anilines. Some indication of this effect can be seen from an analysis of Table V[11].

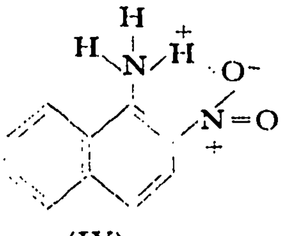
TABLE V

IONIZATION CONSTANTS OF SOME PHENOLS IN WATER SOLUTION

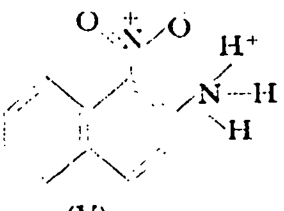
Compound	*K*
Phenol	$1.2 \cdot 10^{-10}$
o-Nitrophenol	$6.8 \cdot 10^{-8}$
m-Nitrophenol	$5.0 \cdot 10^{-9}$
p-Nitrophenol	$7.0 \cdot 10^{-8}$
2-Nitroresorcinol	$1.59 \cdot 10^{-6}$
4-Nitroresorcinol	$1.04 \cdot 10^{-6}$

It will be observed that it makes relatively little difference to the *K* value whether a nitro group is placed *ortho* or *para* to a hydroxyl group. This indicates two significant features.

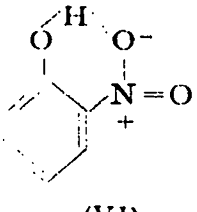
Firstly, it might have been expected that hydrogen bonding in the *ortho* compounds such as (VI) might preferentially stabilize the neutral forms of the *ortho* compounds.



(IV)



(V)



(VI)

Secondly, there is a possibility that the *ortho* nitro group will be forced out of the plane of the benzene ring and thus lose part of its potency as an acid-strengthening substituent. The results indicate that neither effect is large. This conclusion is fortified by the comparison of 2- and 4-nitro-resorcinol. In the former compound both hydroxyl groups are *ortho* to the nitro function and so distortion from planarity should be increased if it were of measurable significance.

By comparison, recent unpublished work[8] in the naphthalene series indicates that

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small "*ortho*" effects do occur with the nitro-naphthylamines and nitronaphthols. In each particular series, infrared studies and pK_a determinations show that intramolecular hydrogen bonding is present to a small degree with the 1-2 and 2-1 compounds, and to a more appreciable extent with 8-1 derivatives. These observations are confirmed by our stannous tin tests where the relative magnitude of the hydrogen bonding appears to be slightly greater with the 8-1 derivative than with either of the 1-2 or 2-1 compounds.

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SUMMARY

Thirteen nitronaphthols have been examined and found to be of use in the fluorimetric detection of stannous tin. The reagents were capable of detecting 10^{-4} to 10^{-5} g stannous tin whilst the nitro derivatives of 2-naphthol produced more intense fluorescence than the corresponding derivatives of 1-naphthol. Of the series examined, 8-nitro-1-naphthol was the least reactive, and this was attributed to the presence of intramolecular hydrogen bonding between the nitro and hydroxyl groups in this compound.

RÉSUMÉ

Les nitronaphtols ont été examinés en vue de leur utilisation comme réactif fluorimétrique de l'étain(II). On peut déceler ainsi jusqu'à 10^{-4} – 10^{-5} g de cet élément. Les dérivés nitrés du β-naphtol donnent une fluorescence plus intense que les dérivés de l'α-naphtol.

ZUSAMMENFASSUNG

Eine Anzahl Nitronaphtole wurden auf ihre Eignung als fluorimetrisches Nachweisreagenz für Zinn(II) geprüft. Es lassen sich hiermit noch 10^{-4} – 10^{-5} g Zinn nachweisen. Die Nitroderivate von β-Naphtol zeigen eine intensivere Fluoreszenz als die entsprechenden Derivate des α-Naphtols.

REFERENCES

[1] J. R. A. Anderson and J. L. Garnett, *Anal. Chim. Acta*, 8 (1953) 393.
[2] J. L. Garnett and L. C. Lock, *Anal. Chim. Acta*, 17 (1957) 351.
[3] J. R. A. Anderson and J. L. Garnett, *Anal. Chim. Acta*, 17 (1957) 452.
[4] J. L. Garnett and L. C. Lock, *Anal. Chim. Acta*, 17 (1957) 574.
[5] J. R. A. Anderson, B. Crawford and J. L. Garnett, *Anal. Chim. Acta*, 19 (1958) 1.
[6] J. R. A. Anderson, J. L. Garnett and L. C. Lock, *Anal. Chim. Acta*, 19 (1958) 256.
[7] J. R. A. Anderson and S. Lenzer-Lowy, *Anal. Chim. Acta*, 15 (1956) 246.
[8] A. Bryson, *Trans. Faraday Soc.*, (to be published).
[9] A. J. Allen, R. Franklin and E. McDonald, *J. Franklin Inst.*, 215 (1933) 705.
[10] R. Tomaschek, *Phosphoreszenz, Fluoreszenz, und chemische Reaktionsleuchten*; *Handbuch der physikalischen Optik*, Vol. 2, Leipzig, 1927.
[11] G. S. Hammond, *Steric Effects in Organic Chemistry*, John Wiley and Sons, Inc., New York, Chapter 9, 1956, p. 436.

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