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FORMATION OF BIS(1-AMINO-2-NAPHTHALENE) TRISULPHIDE BY FUSION OF 1-NAPHTHYLAMINE AND SULPHUR

by

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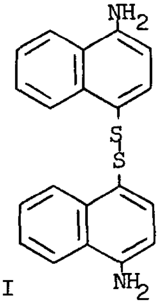
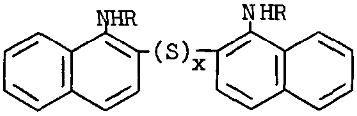
In connection with work on aromatic disulphides, it was our intention to utilise the well known fusion process[1] employing sulphur and an aromatic amine. This method has been used recently by Elix et al.[2] who claimed that the reaction between 1-naphthylamine and sulphur afforded a high yield of bis(1-amino-4-naphthalene) disulphide I. In this note we report our results which show that bis(1-amino-2-naphthalene)trisulphide IIa is formed under these conditions.



I



IIa; R=H, x=3
IIb; R=Ac, x=3
IIc; R=H, x=2
IId; R=Ac, x=2

An intimate mixture of 1-naphthylamine (100g.) and sulphur (25g.) after heating at 185° under nitrogen for 30 minutes, gave bis(1-amino-2-naphthalene) trisulphide (IIa) as a yellow crystalline solid (32g.) m.p. 173-4° (Lit.[2] 172-3°). Found[3]:C=62.89, H=4.27, N=7.11, S=25.09 %. $C_{20}H_{16}N_2S_3$ requires C=63.12, H=4.24, N=7.36, S=25.28%. A number of TLC systems showed only IIa and a little unchanged 1-naphthylamine. The fusion was repeated at 165° and 205° for varying periods of time with only the formation of IIa.

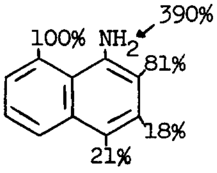
The following chemical transformations have been performed to confirm the trisulphide assignment:

(i) Acetylation of IIa with acetyl chloride in pyridine at 0° gave bis(1-acetylamino-2-naphthalene) trisulphide IIb, m.p. 262-3°. Found:C=61.81, H=4.41, N=6.20, O=6.98, S=20.64 %. $C_{24}H_{20}N_2O_2S_3$ requires C=62.05, H=4.35, N=6.03, O=6.89, S=20.71%.

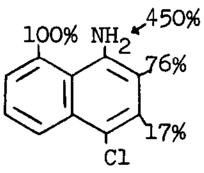
(ii) Treatment of IIa with triethyl phosphite in dry toluene at 95° for three hours gave bis(1-amino-2-naphthalene) disulphide (IIc), m.p. 132-3° (Lit.[4] 131-132°). Found:C=68.53, H=4.87, N=7.90, S=18.22%. $C_{20}H_{16}N_2S_2$ requires C=68.93, H=4.63, N=8.04, S=18.41%. The diacetylamino derivative (IId) was prepared in an analogous way to compound IIb and had m.p. 202°. Found:C=66.68, H=4.64, N=6.53, O=7.63, S=14.54%. $C_{24}H_{20}N_2O_2S_2$ requires C=66.64, H=4.66, N=6.48, O=7.40, S=14.83%.

The position of the sulphur bridge in IIa and IIc was indicated by NMR spectroscopy. Comparison of the coupling constant for the two AB type protons of the amino substituted ring (J=8.0-8.2 Hz) with the relevant J values for 1, 2 and 1, 4 di-substituted naphthalenes[5] was inconclusive. The problem was resolved using the lanthanide shift reagent Eu(dpm)$_3$[6].

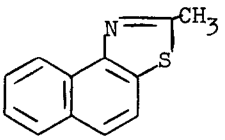
Two model compounds, viz. 1 naphthylamine (IIIa) and 4-chloro-1-naphthylamine (IIIb) were dissolved in $CDCl_3$ and small increments of Eu(dpm)$_3$ were added. All of the protons showed downfield shifts which were internally referenced to the shift of the fastest moving (8) ring proton as 100%. Assignments were made by means of spin decoupling experiments.



IIIa



IIIb



IV

The disulphide, IIc, treated with the Europium reagent (Figures A-C) gave shifts of 19% and 18% for the AB system (calculated in the same manner) in obvious agreement with the shifts of the 3- and 4- protons of IIIa and the 3- proton of IIIb and markedly different from the much larger shifts of the 2-protons in these models. The same result was obtained for solutions of the trisulphide IIa. Thus the disulphide and trisulphide bridges link the naphthalene rings at each 2 position.

It was of interest to note that the shift of the amino protons of the trisulphide, IIa, (467%) was much higher than of the disulphide (293%). A cause of this behaviour may lie in the ability of the trisulphide to fold and allow the naphthalene rings to approach one another, thus permitting the Europium atom to accept the naphthalene molecule as a bidentate donor. This flexibility is not possible for a disulphide bridge[7].

Chemical confirmation of the position of substitution of the sulphur bridge was obtained by reduction of the disulphide IId with Sn/HCl and subsequent ring closure[8] to give the known naphthaleno (1,2-d) thiazole (IV), m.p. 96-7° (Lit.[4,9] 95-7°). Hence, it would appear that the product isolated by Elix et al.[2] was compound IIa since the m.p.'s are almost identical.

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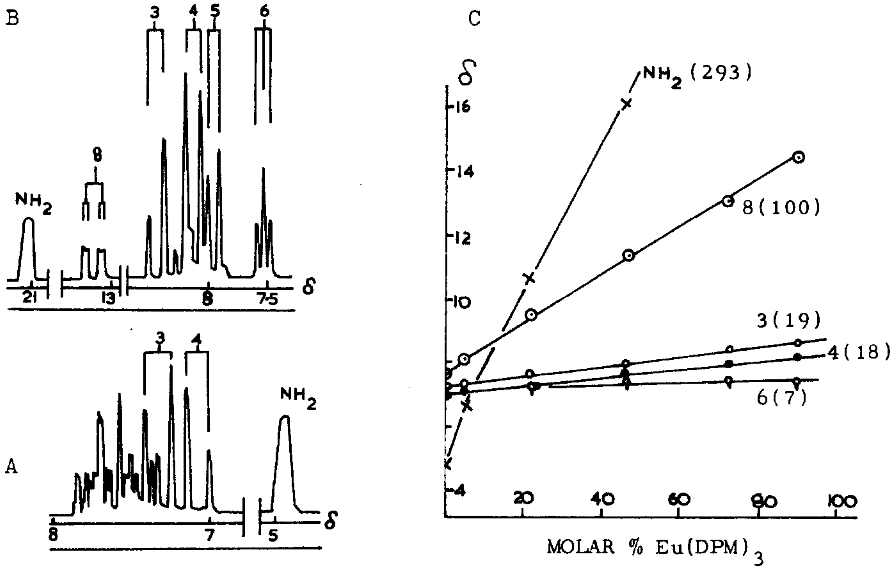

FIGURES A-C

100 MHz NMR spectra of disulphide IIc without (Figure A) and with (Figure B) a 0.91 molar equivalent of Eu(dpm)$_3$. For clarity the assignment of the 7-proton in Figure B has been omitted. Figure C: downfield shifts of IIc with increase in shift reagent concentration. Figures in parentheses indicate magnitude of slopes relative to the 8-proton as 100.

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