

the shape predicted by the matrix elements calculated by Delabaye *et al.* on the basis of extreme single particle model as shown in Fig. 2.

CONCLUSIONS

(1) The present experimental results regarding the shape of the 693 keV beta transition show a small deviation from the exact allowed shape reported by Lehmann, which is within the ξ -approximation. This might be due to the incorrect choice of the end point energy on the part of Lehmann.

(2) The present shape is consistent with the shape predicted by the matrix elements calculated from extreme single particle model.

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SYNTHESIS OF SOME BENZOTHAZOLYL HYDRAZONES

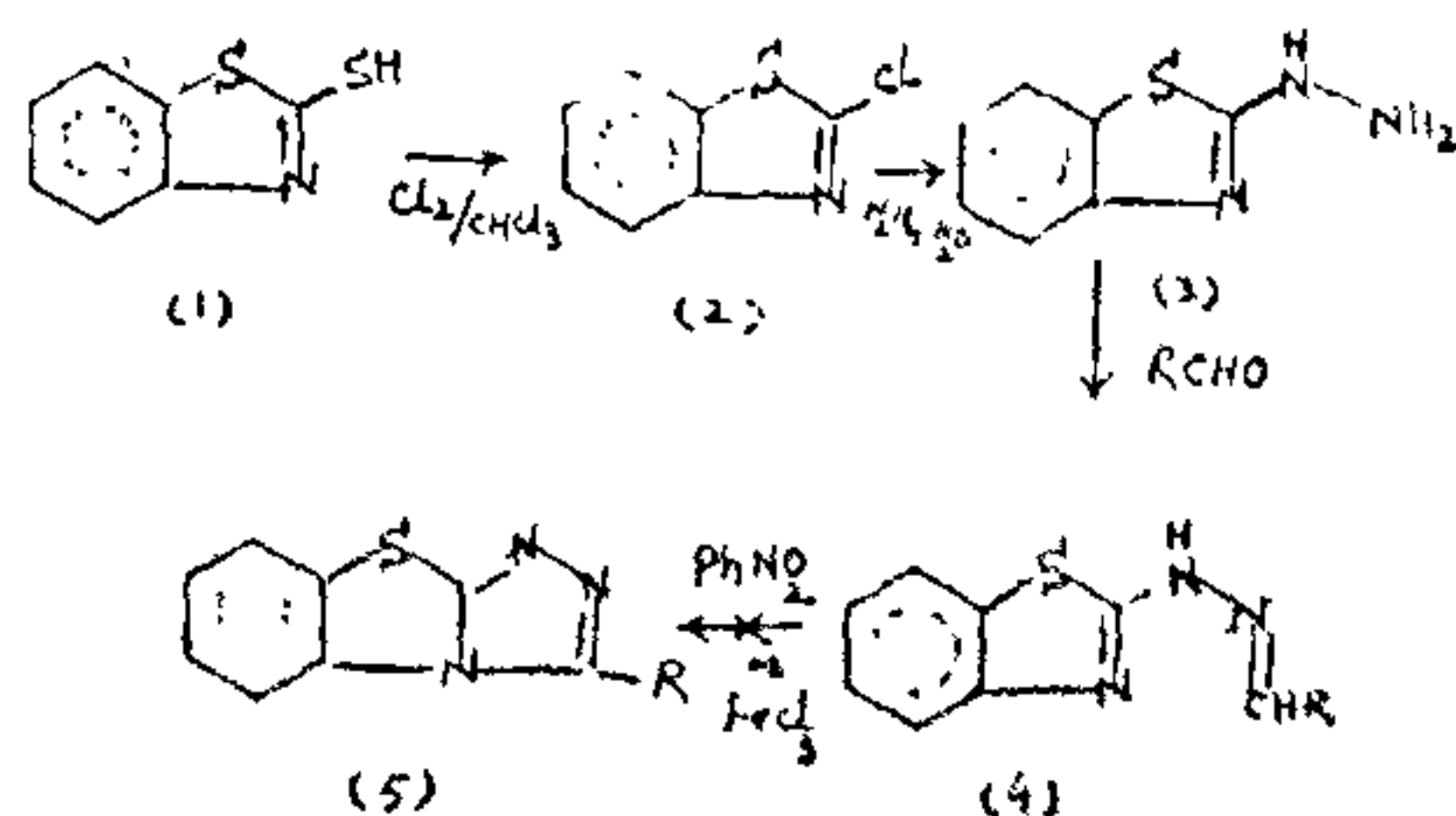
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ALTHOUGH a large amount of work has been carried out on 1, 2, 4 triazoles, very little information is available on *s*-triazolo (3, 4-*b*) benzothiazoles possessing various functional groups. This gap may perhaps be due to non-availability of efficient methods for the synthesis of starting material. The method for the synthesis of this system involving the use of hydrazine has been discussed earlier by various workers^{1,2}. Hydrazino benzothiazole is generally prepared from 2 mercapto³ or 2-chloro benzothiazole by the action of hydrazine hydrate. The reaction was carried out with varying concentrations of hydrazine hydrate for different durations. There is no significant improvement in the yield. The reported chloro compound obtained from mercapto benzothiazole and sulfur monochloride was formed only in low yields. Heterocyclic thiols on oxidative chlorination are generally known to yield sulfonyl chlorides and this method finds a general use for the synthesis of the corresponding sulfonamides^{4,5}.

Hence the use of gaseous chlorine was investigated under mild condition. The conditions of reactions were so adjusted that the variation of both the time of reaction and the chloroform: water ratio in the suspending medium was possible. When gaseous chlorine was bubbled through mercapto benzothiazole suspended in chloroform and water it was noticed that the product after 50 to 60 min was indeed a 2-chloro benzothiazole. The chloro compound thus obtained

was converted into the hydrazino compound in 72-75% yield. In this particular case reaction of chloro derivative with hydrazine, proceeded well to give good yields in contrast to some reports where the conversion of halo heterocycle to the corresponding hydrazine, proceeded with poor yields⁶; excessive heating with hydrazine⁷ resulted in the decomposition of the mixed heterocycles, possessing sulfur and nitrogen. With excess of hydrazine for a period of 40 minutes, the yield is better than that reported by Veltman⁸.



In the hope of obtaining biologically active compounds, hydrazino benzothiazole was condensed with various aldehydes. Cyclization of these hydrazines through nitrobenzene did not proceed and the oxidation with ferric chloride did not give satisfactory results. These were cyclized by bromine in acetic

acid. Details of this will be published at a later date. Since heterocyclic compounds have featured prominently in biological activity, the compounds were screened for antifungal and plant growth activity. Benzothiazolyl hydrazones with heteryl substituents like pyridyl, furyl and thienyl were specifically selected in view of biological importance.

In the case of *T. vulgare*, the data presented in Table II indicate that the activity of benzothiazol-

2-yl hydrazone of pyridine 3-aldehyde is equal to that of gibberellic acid and superior to 2, 4 dichlorophenoxy acetic acid and other heteryl derivatives. In the case of *P. deveus* benzothiazolyl-pyridine 3-aldehyde hydrazone is superior to all, as far as the percentage of germination is concerned, though there is a slight decrease in the length of the radicle compared to No. 5. It thus appears that among these three, the pyridyl derivative is more active.

TABLE I
Benzothiazolyl-hydrazones

No.	R	Melting point °C	Yield %	Molecular formula	C	Analysis (found) H N
1.	2-Hydroxy phenyl-	240	85	C ₁₄ H ₁₁ N ₃ OS	64.9 ;	4.09 ; 15.53 %
2.	2, 4-Dihydroxy phenyl-	250	78	C ₁₄ H ₁₁ N ₃ O ₂ S	59.74 ;	3.71 ; 13.2 %
3.	3-Hydroxy 4-methoxy phenyl-	182	78	C ₁₅ H ₁₃ N ₃ O ₂ S	59.92 ;	4.21 ; 14.11 %
4.	m-Nitro phenyl-	236	86	C ₁₄ H ₁₀ N ₄ O ₂ S	56.89 ;	3.29 ; 18.34 %
5.	2-Pyridyl-	220	61	C ₁₃ H ₁₀ N ₄ S	61.60 ;	3.96 ; 22.22 %
6.	3-Pyridyl-	234	58	C ₁₃ H ₁₀ N ₄ S	61.8 ;	3.81 ; 22.89 %
7.	4-Pyridyl-	224	80	C ₁₃ H ₁₀ N ₄ S	61.49 ;	3.56 ; 20.99 %
8.	2-Thienyl-	210	77	C ₁₂ H ₉ N ₃ S ₂	55.28 ;	3.58 ; 15.99 %
9.	2-Furyl	180	74	C ₁₂ H ₉ N ₃ OS	58.88 ;	3.52 ; 17.51 %

Solvent for crystallisation = Ethanol.

TABLE II

Effect of benzothiazol-2-yl (heteryl-aldehyde) hydrazone on germination of *T. vulgare* and *P. deveus* seeds

No.	Name of the compound	<i>T. vulgare</i>		<i>P. deveus</i>	
		Percentage germination	Length (cm)	Percentage germination	Length (cm)
Benzothiazolyl-					
1.	-Pyridine 3-aldehyde hydrazone	100	5	100	3
2.	-Furyl 2-aldehyde hydrazone	100	1.5-3	90	1.5-3.5
3.	-Thiophene 2-aldehyde hydrazone	80	1.5-2.5	70	2-3
4.	Gibberellic acid (standard)	100	2-5	70	1-2.5
5.	2, 4 dichlorophenoxy acetic acid (standard)	100	0.5-3	90	0.5-4.5
6.	Control	90	2-3	70	1-2

Surprisingly one of the compounds was found to be very active as plant growth promoter. None of these was found to be antifungal.

EXPERIMENTAL

2-Chloro benzothiazole (2)

2-Mercapto benzothiazole (1) (0.03 mole) was suspended in chloroform and water 2:1 mixture. The mixture was cooled to 5°C. Chlorine gas was passed for 1.5 hr. Chloroform layer was tapped off and the remaining liquid was distilled under reduced pressure (yield 2.8 g). B.P. 158–162°C/50 mm.

2-Hydrazino benzothiazole (3)

This is prepared by condensation of 2-chloro benzothiazole with hydrazine hydrate.

Benzothiazolyl hydrazones (4)

Equimolar proportions of 2-hydrazino benzothiazole and the required aldehyde in ethanol were condensed by heating on a water bath for 20–45 min. The reaction mass was poured into water. Crude hydrazone was filtered off and recrystallised from ethanol. The yields, melting points and analytical data, etc. are included in Table I.

The hydrazones were taken in nitrobenzene and refluxed for 2 hours. Then nitrobenzene is removed by steam distillation. The products were not the cyclised *s*-triazolo (3, 4-*b*) benzothiazole derivatives (5) but were found to be starting materials (4). Similarly ferric chloride oxidation also failed to give *s*-triazole (3, 4-*b*) benzothiazole derivatives.

Biological screening

After surface disinfection with a solution of sodium hypochlorine (2% available chlorine) for 10 min., the

seeds of *T. vulgare* and *P. deveus* were soaked for five hours in the solution. Then seeds were sown on blotter in a petri dish. The blotters were sterilized at 15 psi for 20 min. before use. The blotters were moistened with 5 ppm solution of the compounds. Along with these compounds gibberellic acid and 2, 4-dichlorophenoxy acetic acid were also used as standards and sterile water was kept as control. The results are presented in Table II.

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DETERMINATION OF STABILITY CONSTANTS OF 2-HYDROXY-1-NAPHTHALIDENE-*p*-N-DIMETHYLANILINE COMPLEXES WITH SOME BIVALENT METAL IONS

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ABSTRACT

Potentiometric studies have been carried on metal complexes of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Cd²⁺ and Mg²⁺ with 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline. The dissociation constants (*pK₁* and *pK₂*) of the reagent and the formation constants of its metal complexes have been determined by Bjerrum's method at 30 ± 0.1°C and at ionic strength 0.1 M in 75:25% (v/v): dioxan-water medium. The order of stability is found to be Cu > Co > Ni > Zn > Cd > Mg.

LITERATURE survey indicates that no systematic study of the stabilities of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline and its metal chelates with bivalent metal ions appears to have been carried out.

In the present communication the successive stability constants of the complexes of 2-hydroxy-1-naphthalidene-*p*-N-dimethylaniline with various bivalent metal ions have been determined potentiometrically following the Calvin-Bjerrum pH titration technique as adopted by Irving and Rossotti¹,

EXPERIMENTAL

The Corning Model 12, a precision research pH meter with a wide range glass electrode and a calomel reference electrode, was used for pH determination. The meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale reads 0.005 pH unit.

2-Hydroxy-1-naphthalidene-*p*-N-dimethylaniline was prepared by dissolving 10 g of 2-hydroxy-1-naphthal