

Figure 4. Contents of core buffer. **a.** After initialization with first row elements. **b, c.** After computation of (2, 1) and (2, 2).

At the end of each row, the contents of the core buffer are saved on the disc to form a record of elements for subsequent computations. Similar steps are adopted for all the rows (NR) and the corresponding records are created on the disc file.

This technique is utilized for solving a flow problem of dimensions 30×21 , involving 630 nodes and three intermediate arrays. The problem could be solved using 360 bytes of memory on EC-1030 computer by the presently developed technique as against 7560 bytes in the conventional methods, thereby reducing about 97% of memory requirement. However, the time requirement in both the methods is same and to be less than two minutes, since the number of accesses to the core has not changed in the core buffer method.

CONCLUSIONS

The conventional decomposition techniques also require extensive memory for several intermediate arrays in solving large matrices. The storing of non-required elements is replaced by the new concept of core buffer method which rendered possible the solution of large matrices on microcomputers with minimum configuration.

1. Remson, I., Hornberger, G. M. and Molz, F. J., *Numerical methods in subsurface hydrology*, (New York: Wiley-interscience), 1971.

ORGANOTIN COMPLEX COMPOUNDS OF N-SUBSTITUTED BENZOHYDROXAMIC ACIDS (2)

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ABSTRACT

Some triphenyl tin derivatives of N-substituted benzohydroxamic acids have been prepared and the stability of these chelates tested. Also, structures of some tin derivatives of N-phenyl benzohydroxamic acid have been discussed.

INTRODUCTION

The authors¹ have reported three classes of new organotin compounds, R_2SnLX , R_2SnL_2X and $R_2SnLX(OM_c)$ along with the preparation and properties of some R_2SnL_2 , where LH is the hydroxamic acid ligand. In this communication, some triphenyl tin

compounds of N-substituted hydroxamic acids have been reported. The tentative structures of $Bu_2Sn(PBHA)_2$, $PhSn(SCN)(PBHA)_2$, $Ph_2Sn(SCN)(PBHA)_2$, $Bu_2Sn(SCN)(PBHA)_2$ and P.M.R. spectra of $PhSnCl(OCH_3)(PBHA)_2$, where PBHA being N-phenyl benzohydroxamic acid also are being reported.

TABLE 1

Ph₃SnL compounds: LH-N-substituted benzohydroxamic acid

LH	Solvent for crystallisation/precipitation	Nature of the compound	M.P. (°C)	Analysis found		
				(Calc.)	(%)	
				C	H	Sn
N-Phenylbenzohydroxamic acid	Benzene/methanol	Colourless crystals	133	65.98 (66.20)	4.73 (4.50)	20.73 (21.10)
N-phenyl-para-chloro-benzohydroxamic acid	Methanol	Colourless crystals	139–40	62.66 (62.37)	4.24 (4.02)	19.90 (19.95)
N-phenyl-para-nitro-benzohydroxamic acid	Methanol/benzene	Bright yellow crystals	188	61.21 (61.28)	4.00 (3.95)	19.45 (19.60)
N-para-chloro-phenyl-benzohydroxamic acid	Methanol	Needle-shaped crystals	129	62.11 (62.37)	3.99 (4.02)	19.85 (19.95)
N-ortho-tolyl-benzohydroxamic acid	Ethanol	White precipitate	55	67.03 (66.67)	4.90 (4.70)	20.10 (20.58)

MATERIALS AND METHODS

N-substituted benzohydroxamic acids were prepared by standard procedures² with necessary modifications. All solvents were purified and dried. Triphenyl tin chloride was prepared by literature method³.

Preparation and properties of organotin hydroxamates

The triphenyl tin derivatives were prepared by following one of the two methods described below for triphenyl tin N-phenyl benzohydroxamate.

(a) To 2.15 g of *bis*-triphenyl tin oxide taken in 50 ml benzene was added 1.25 g of N-phenylbenzohydroxamic acid and the mixture refluxed for 4 hr using water-separator, the light yellow solution was filtered and evaporated to a pasty mass on a water bath, which was crystallised from methanol. Yield 2.5 g; m.p. 133° C. This compound has also been crystallised from benzene and was found to have the same m.p. (lit.⁴ m.p. 115.5–116.5° C; crystallised from benzene).

(b) N-phenylbenzohydroxamic acid (2.13 g) was dissolved in 30 ml of benzene and to this hot solution was added 3.85 g of triphenyl tin chloride with shaking. The mixture was cooled and the clear solution was treated with 2 ml of 25% aqueous ammonia. The mixture was filtered and the organic layer was separated, concentrated to a pasty mass, crystallised from benzene/methanol. Yield 5.0 g; m.p. 133° C.

Properties and analytical data of some triphenyl tin N-substituted hydroxamates are given in table 1.

Phenyl thiocyanato tin *bis* (N-phenyl benzohydroxamate) was prepared by dissolving 1 g phenyl chloro tin *bis* (N-phenyl benzohydroxamate) in 30 ml of benzene and adding 0.3 g of potassium thiocyanate to this solution. The mixture was then stirred for 3 hr. The heavy white precipitate filtered and crystallised from benzene, needle shaped colourless crystals (m.p. 93–95° C; yield 1.1 g).

Analysis

Found: C, 59.5; H, 3.9; Sn, 17.3;

Calculated for C₃₃H₂₅N₃O₄SSn; C, 58.7; H, 3.7; Sn, 17.5 per cent.

Preparation and properties of Bu₂Sn(PBHA)₂, Ph₂Sn(SCN)(PBHA), Bu₂Sn(SCN)(PBHA) and PhSnCl(OCH₃)(PBHA) were reported earlier¹.

Infrared, ultraviolet and PMR spectra

The infrared spectra were recorded on Beckman IR-20 infrared spectrophotometer equipped with KBr optics, using Nujol mulls. The UV spectra were recorded on a Beckman DU-2 spectrophotometer using 1 cm cells. The PMR spectra (60 MHz) was taken in CDCl₃. The spectral data are given in table 2.

RESULTS AND DISCUSSIONS

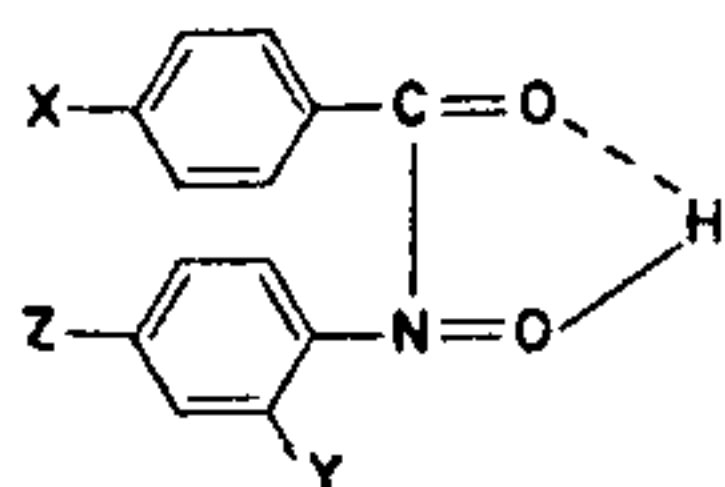
All the organotin derivatives of these N-substituted

TABLE 2
Spectral Data

Compound	IR(cm^{-1}) data (Nujol mulls)			Solvent	U.V. DATA	
	$\nu(\text{O—H})$ (s = strong)	$\nu(\text{C=O})$	$\nu(\text{N—O})$		λ_{max} (nm)	$\log \epsilon_{\text{max}}$
PhCO.NOHPh	3100s	1635s	920s	Cyclohexane	275	3.81
				Dichloromethane	271	3.87
				Methanol	265	3.94
Ph ₃ Sn(PhCO.NOHPh)	—	1543s	935s	Cyclohexane	296	3.75
p-ClC ₆ H ₄ CO.NOHPh	3165s	1618s	900s	Cyclohexane	281	—
				Methanol	274	—
Ph ₃ Sn(p-ClC ₆ H ₄ CO.NO.Ph)	—	1538s	928s	Cyclohexane	298	3.90
p-NO ₂ C ₆ H ₄ CO.NOHPh	3165s	1605s	910s	Cyclohexane	252	—
				Methanol	249	4.12
Ph ₃ Sn(p-NO ₂ C ₆ H ₄ CO.NO.Ph)	—	1545s	932s	Cyclohexane	254	—
				Methanol	252	4.15
p-ClC ₆ H ₄ NOHCOPh	3160s	1612s	896s	Cyclohexane	275	—
Ph ₃ Sn(p-ClC ₆ H ₄ NO.CO.Ph)	—	1545s	932s	Cyclohexane	296	3.90
O—CH ₃ C ₆ H ₄ NOH.COPh	3120s	1625s	910s	Cyclohexane	269	3.80
Ph ₃ Sn(O—CH ₃ C ₆ H ₄ NO.COPh)	—	1535s	930s	Cyclohexane	291	3.84

benzohydroxamic acids show a shift to a lower frequency of the C=O band of $60\text{--}90\text{ cm}^{-1}$ compared to that in the free ligand with a concomitant increase of $15\text{--}35\text{ cm}^{-1}$ in the N—O frequency. The O—H frequency due to intramolecular hydrogen bonding in the ligand at $\sim 3150\text{ cm}^{-1}$ is absent in the tin derivatives. In N-phenyl para nitrobenzohydroxamic acid the two strong absorptions at 1512 and 1342 cm^{-1} which are absent in the N-phenyl benzohydroxamic acid have been assigned respectively to $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$ modes which remain practically intact in the triphenyl tin derivative indicating the non-involvement of the NO_2 group in the co-ordination with tin.

All the triphenyl tin N-substituted benzohydroxamates show a bathochromic shift *i.e.* shift to higher wavelengths of the longest wavelength absorption maxima in the UV region in cyclohexane compared to that in the free ligands. Thus in accordance with the work of Sone and his co-workers^{5,6} these organotin benzohydroxamates are all chelated in solution. For $X=Y=Z=H$ (figure 1). The UV spectral shift is



(A)

greater than that when $X=\text{Cl}$, $Y=Z=H$ which is again greater than that when X is a strong perturbing substituent (like NO_2). The IR shift in carbonyl frequency follows the same sequence *i.e.* greater shifting when

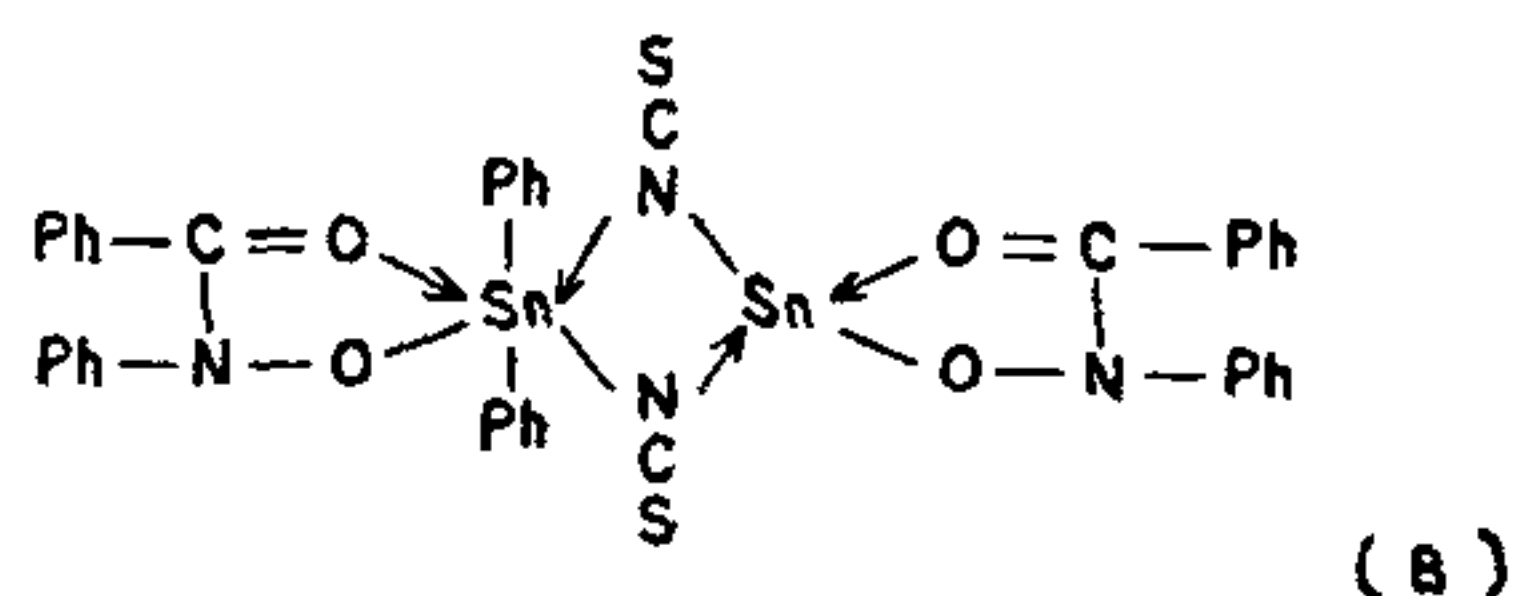
- (1) $X=Y=Z=H$,
- (2) $X=\text{Cl}$, $Y=Z=H$,
- (3) $X=\text{NO}_2$, $Y=Z=H$,
- (4) $X=H$, $Y=H$, $Z=\text{Cl}$,
- (5) $X=H$, $Y=\text{CH}_3$, $Z=H$,

X is NO_2 . This is expected since the electron withdrawing capacity is $\text{NO}_2 > \text{Cl} > H$ which is reflected in the UV spectral shift for these complexes. Thus, the stability of the chelates increases in the reverse direction *i.e.* greater the UV spectral shift in non-polar solvents, the greater is the stability of chelates¹. Substitution for $Y=H$ or $Z=H$ of Cl or CH_3 has practically little effect on chelation.

The organotin derivatives of N-substituted benzohydroxamic acids show new bands at $550 \pm 5\text{ cm}^{-1}$, which is absent in the ligands. This band can be assigned as due to $\nu_{\text{s}}(\text{OSnO})$ mode in these compounds, the corresponding asymmetric stretching vibration $\nu_{\text{as}}(\text{OSnO})$ being at $\sim 690\text{ cm}^{-1}$. For the dibutyl tin bis (N-phenylbenzohydroxamate) the IR spectrum shows an intense broad band at 490 cm^{-1} which is absent in the ligands. This band can be

assigned as due to ν_{as} (Sn-C) mode, the corresponding asymmetric stretching vibration ν_{as} (Sn-C) being the weak absorption at 565 cm^{-1} since no such band is present in the diphenyltin bis (N-phenylbenzohydroxamate). The absence of a symmetric Sn-C stretching vibration in the IR spectra of $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2\text{Py}$, $(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}$ and $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ around 500 cm^{-1} has been shown to have trans alignment of the CH_3 group around tin atom^{7,8}. So $\text{Bu}_2\text{Sn}(\text{Ph} \cdot \text{CONOPh})_2$ can be suggested to have a configuration in which the two butyl groups are probably *cis*—as in the related dimethyl tin bis-oxinate, which has a *cis*-dimethyl tin group⁹.

The thiocyanato complexes, $\text{PhSn}(\text{SCN})(\text{PBHA})_2$, $\text{Ph}_2\text{Sn}(\text{SCN})(\text{PBHA})$ and $\text{Bu}_2\text{Sn}(\text{SCN})(\text{PBHA})$ show very intense absorption bands at 2035, 2030 and 2060 cm^{-1} respectively in nujol mull. These have been assigned as due to $\text{C} \equiv \text{N}$ stretching frequency. The ambidentate ligand, $-\text{SCN}$, can co-ordinate to tin either through S or N or it can act as a bridge. The ligand PBHA has so many absorptions in the region of the $\text{C}-\text{S}$ stretching vibrations that they may obscure the $\text{C}-\text{S}$ stretching band and hence on the basis of the $\text{C} \equiv \text{N}$ stretching frequency, the thiocyanate group may be considered to be linked to tin atom through the nitrogen atom of the group¹⁰. For the $\text{PhSn}(\text{SCN})(\text{PBHA})_2$, the $\nu(\text{C} \equiv \text{N})$ frequency at 2035 cm^{-1} in KBr is shifted to 2045 cm^{-1} in chloroform solution. But for the latter two thiocyanato complexes, it is interesting to note that a medium intensity band at 1982 cm^{-1} for $\text{Ph}_2\text{Sn}(\text{SCN})(\text{PBHA})$ along with the strong absorption band for $\text{C} \equiv \text{N}$ mode have been appeared. The appearance of the secondary weak band is indicative of a bridging SCN group in which nitrogen bridges between the two tin atoms in the solid (figure 2).



This is supported by the similar assignment $\text{N} \equiv \text{C}$ stretching vibrations near 2040 and 1960 cm^{-1} for $(\text{SCN})\text{R}_2\text{SnOSnR}_2(\text{NSC})$ ¹¹. But in solution in chloroform, the secondary lower frequency band has completely disappeared for these two compounds and the strong absorption band shifted to 2040 cm^{-1} for both the compounds suggesting the absence of —

NCS —bridging in solution. Thus in the solid state these compounds are hexa-coordinated but in chloroform solution, the diphenyl and dibutyl thiocyanato tin derivatives are penta-coordinated. Similar assignment has been suggested for $\text{Bu}_2\text{Sn}(\text{SCN})(\text{OX})$ ¹².

The PMR spectrum (60 MHz) of $\text{PhSnCl}(\text{OCH}_3)$ (PBHA) has been taken in CDCl_3 and the structure assigned previously¹ has further been supported. The PMR spectrum showed peaks at $\delta 7.37$, 7.30 and 7.25 ppm for the phenyl protons and a signal (singlet) at $\delta 3.45\text{ ppm}$ due to the $-\text{OCH}_3$ protons. From the integration of the curve the ratio of the phenyl protons and methoxy protons is approximately 5:1, which is consistent with the structure assigned.

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1. Pradhan, B. and Ghosh, A. K., *J. Organometal Chem.*, 1977, 131, 23.
2. Majumdar, A. K., *N-Benzoylphenylhydroxylamine and its analogous*, (London: Pergamon Press), 1972.
3. Gilman, H. and Rosenberg, S. D., *J. Am. Chem. Soc.*, 1952, 74, 5580.
4. Harrison, P. G., *J. Organometal Chem.*, 1972, 38, C5.
5. Yamasaki, K. and Sone, K., *Nature (London)*, 1950, 166.
6. Sone, K., *J. Am. Chem. Soc.*, 1953, 75, 5207.
7. McGrady, M. M. and Tobias, R. S., *J. Am. Chem. Soc.*, 1965, 87, 1909.
8. Tanaka, T., Kumura, M., Kawasaki, Y. and Okawara, R., *J. Organometal Chem.*, 1964, 1, 484.
9. Schlemper, E. O., *Inorg. Chem.*, 1967, 6, 2012.
10. Sabatini, A. and Bertini, I., *Inorg. Chem.*, 1965, 4, 959.
11. Wada, M., Nishino, M. and Okawara, R., *J. Organometal Chem.*, 1965, 3, 70.
12. Poller, R. C. and Ruddick, J. N. R., *J. Chem. Soc., (A)* 1969, 2273.