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VUPPALAPATI BALIAH

(1917 – 2000)

Elected Fellow 1972

India lost a pioneer physical organic chemist, an outstanding teacher and a researcher in the demise of PROFESSOR V BALIAH on 26th September 2000 at his son's residence in Baroda. He spent most part of his life in the development of higher education by serving in Annamalai University, Annamalainagar, Tamil Nadu. Baliah was largely responsible for motivating a number of young students to undertake research from 1950 and particularly in the area of physical organic chemistry. It is no exaggeration and certainly redounds to his credit that he may be considered to be the leader in this area of chemistry.

FAMILY BACKGROUND, EARLY EDUCATION & PERSONAL LIFE

Vuppalapati Baliah was born on 15th August 1917 at Penugudurupadu, Andhra Pradesh. He took his B. Sc (Hons)., and M.Sc., degrees from the Andhra University. He was a student of Professor TR Seshadri in the Andhra University. He served for some time as Head of the Department of Chemistry in Sir CR Reddy College, Eluru, Andhra Pradesh and later moved to Pachiappa's College, Madras now Chennai.. Then he proceeded to USA under Government of India financial assistance to carry out research in Stanford University (USA) with Professor CR Noller and earned his Ph. D. in 1948. He was blessed with two daughters and two sons who are well settled in life. His wife passed away in 1987.

PROFESSIONAL CAREER

Professor Baliah returned to India and joined Annamalai University as the Head of the Department of Chemistry and served there till his retirement. At the time of joining he also helped to strengthen the Chemical Engineering Department there. He served as a Member of Syndicate and Dean, Faculty of Science, Annamalai University for more than two terms. He had the distinction of working as Acting Vice-Chancellor of Annamalai University. He was invited to become the first Vice-Chancellor of Nagarjuna University, Andhra Pradesh and he accepted the invitation and served there for a period of three years.

SCIENTIFIC CONTRIBUTIONS

Since his Ph. D. research project involved the preparation of piperidones by simple condensation reaction, it is not surprising that he developed deep interest in heterocyclic chemistry. The urge in him to investigate heterocyclics, led him to explore organic



sulphur compounds. In the early years of his research activities in Annamalai, a number of α,β -unsaturated sulphones were prepared by simple methods. The availability of a number of sulphones in his hands kindled his interest to understand the nature of S-O bonds in sulphones. The influence of solvent on the UV absorption spectra of sulphones and ketones (the structural analogues of the sulphones) and the measurements of diamagnetic susceptibilities of a number of sulphones, sulphoxides and sulphides pointed out that the S-O bond in sulphones and sulphoxides is semipolar in nature.

A number of heterocyclics like thiazines, tetrahydrothiapyran-4-ones, tetrahydrothiapyran-4-ols, azabicyclononanes, 1,4-dithia-7-azacyclononane, benzothiamorpholine-1,1-dioxides, 2,6-diaryl 1,4-dithian 4,4-dioxides, thiaazabicyclooctanes, tetrahydropyran-4-ones, tetrahydropyran 4-ols, 5-aryl-4,6-bis[alkoxycarbonyl]-1,3-dithiane 1,1,3,3-tetroxides were prepared by new techniques.

At the time of his active research period only two sophisticated instruments, UV-Vis Spectrophotometer and Dipole meter were available in his laboratory. He was, therefore, instrumental in inspiring his team to study the dipole moments of some of these compounds and also the UV spectra and IR spectra (recorded in a company in USA) of various compounds. These studies were not routine, but undertaken with the objective of understanding some hidden beauties in the molecules like the intra- and intermolecular hydrogen bonding, internal rotation etc.

Indeed his important and excellent contribution *Steric Enhancement of Resonance*, his pet baby was born in 1960 as a result of a careful analysis of the dipole moments of substituted 4-nitroanisoles and similar compounds. Compared to various concepts proposed from UK, this is considered to be the most novel concept in physical organic chemistry originating from India. After nearly three decades of the discovery of 'steric enhancement of resonance', Prof. Gadre, University of Pune, confirmed the existence of this phenomenon by theoretical calculations. Another important area in which he contributed richly was the study of conformational analysis of several heterocyclics by kinetic, spectral and dipole moment measurements.

More than 50 Ph. D. students were benefited by the guidance of Professor Baliah. He was a great teacher and he used to take classes for fresher in the University as he felt that the junior most students can be shaped well by the Senior Faculty, a fact which is neglected by reputed and senior academics in India. He even wrote a book for pre-university students and emphasized the importance of significant figures in presenting the experimental data.



The major highlights of Baliah's research are summarized below:

(i) **Synthesis of Piperidones:** Baliah and his co-workers developed an elegant method of synthesis of 2,6-diarylpiperidin-4-ones by the condensation of ketones with aromatic aldehydes in the presence of ammonium acetate or methylamine. The importance of this method lies not only in the simplicity of the procedure but also in the use of acetone and other aliphatic ketones in the method. The yields are also very high, with practically no side reactions of any consequence.

(ii) **Synthesis and Stereochemistry of Bicyclic Compounds:** A number of bicyclic compounds such as azabicyclononanes, azabicyclodecanones and other related compounds have been synthesised by simple methods. They have also been reduced to alcohols and each ketone yielded a pair of epimeric alcohols. In bridged bicyclic systems containing hetero atoms the probability of a six-membered ring acquiring the boat form has been shown to be even higher due to decrease in some of the interactions present in cyclohexanol and also due to intermolecular hydrogen bonding and other possible interactions between the hetero atoms and substituent groups. Hence the conformations of these compounds have been extensively studied by Baliah and his students.

(iii) **Thiomorpholine Derivatives:** As a result of their interest in cyclic sulphones, Baliah and his co-workers extended simple condensation methods as employed for the preparation of piperidones to synthesise heterocyclics containing nitrogen and sulphur atoms. They obtained thiomorpholine derivatives in excellent yields by the simple condensation reaction of sulphonyldiacetic acid or its esters or diphenacyl sulphones with aromatic aldehydes and ammonium acetate. The condensation of several phenacyl sulphones with ammonia in glacial acetic acid resulted in the formation of 3,5-diaryl-1,4-thiazine 1,1-dioxides. Some 2-arylidene-3,4-dihydro-3-oxobenzo-1,4-thiazines have also been obtained by condensation reactions.

(iv) **Synthesis of other Heterocyclics:** By employing a method similar to the synthesis of piperidones, substituted decahydroquinoline-4-ones have been prepared in a remarkably simple manner. D¹-Acetylcyclohexene and D¹-propionylcyclohexene condense with aromatic aldehydes and ammonium acetate in ethanol to yield 2-aryldecahydroquinolin-4-ones and 3-methyl-2-aryldecahydroquinolin-4-ones, respectively. In view of his interest in the study of sulphur containing heterocyclics, his group developed methods for the synthesis of 1,4-oxathiin derivatives. 2,6-Diaryl-1,4-oxathiin 4,4-dioxides were synthesised by the cyclisation of the corresponding phenacyl sulphones in the presence of POCl₃ / Ac₂O. Dimethyl or diethyl methylene-bis-sulfonylacetate was condensed with aromatic aldehydes in the presence of ammonium acetate to yield the 1,3-dithiane 1,1,3,3-tetroxides.



(v) *Fries Rearrangement of Aryl Arene Sulphonates*: Baliah and his co-workers for the first time made an extensive study of the hitherto uninvestigated rearrangement of arylsulphonates to hydroxydiaryl sulphones. A number substituted diaryl sulphones containing hydroxy group have been prepared by this method and they also examined the presence of intramolecular and intermolecular hydrogen bondings in these compounds by UV-Vis spectral studies.

(vi) *Nature of S-O and P-O Bonds in Sulphones and Phosphine Oxides*: Studies on the solvent effect on the UV spectra of sulphones and phosphine oxides threw light on the nature of the S-O and P-O bonds. With change of solvent from cyclohexane to ethanol for sulphones and phosphine oxides there is practically no change in λ_{max} , while for ketones, there is a considerable bathochromic shift. These observations led Baliah and co-workers to propose that the sulphur-oxygen bond in sulphones and phosphorus-oxygen bond in phosphine oxides are semipolar and not doubly covalent as the carbon-oxygen bond in ketones. An analysis of the diamagnetic susceptibilities of a number of sulphoxides, sulphones, phosphine oxides, arsine oxides and stibine oxides indicated that the oxygen is linked by a co-ordinate covalent bond in these compounds.

(vii) *d-Orbital Resonance Involving Sulphur and Halogens Other than Fluorine*: Elements below the first row of the Periodic Table can in certain circumstances expand their valence shells by the utilization of their vacant d-orbitals. The observed acidities and the basicities of p-halogenophenols and N,N-dimethylanilines have been explained by invoking d-orbital resonance in chloro, bromo and iodo compounds. Careful examination of the dipole moments, UV spectra and diamagnetic susceptibilities of a number of organic compounds containing sulphur and also chlorine, bromine and iodine has established the existence of d-orbital resonance (expansion of the valence shells of S, Cl, Br and I).

(viii) *Steric Enhancement of Resonance*: The most important contribution of Baliah is the discovery of the concept of Steric Enhancement of Resonance and this is considered to be the first major concept in physical organic chemistry to be proposed from India. Though this phenomenon was first discovered in 1960 while analysing the dipole moments of some substituted anisoles, in the past forty years a number of papers based on different studies by his co-workers furnished additional evidence for the phenomenon. He himself pointed out that the kinetic data of Baddeley *et al.* on the solvolysis of benzyl chlorides (*J. Chem. Soc.*, 2455, 1956) and the rate data of Jones and Robinson on the alkaline hydrolysis of substituted ethyl benzoates (*J. Chem. Soc.*, 3845, 1955) also support the existence of this phenomenon. Later he cited the already published bond distances in some anisoles as evidence for this new idea. ^{13}C NMR spectral evidence for steric enhancement of resonance is provided on the basis of comparison of calculated and observed chemical shifts of the various carbons in 4-methoxyacetophenone, 4-methoxy-3-methylacetophenone and 4-methoxy-3,5-dimethylacetophenone.



(ix) **Conformational Analysis of Heterocyclics and Cyclohexane Derivatives:** Baliah was attracted by conformational analysis as his group obtained two alcohols by the reduction of a piperidone even before the concept of conformational analysis was proposed. He extensively studied the conformations of a number of heterocyclic compounds and cyclohexane derivatives by dipole moment and kinetic measurements. Because of the limited conformational studies on sulphur heterocyclics, Baliah extensively studied the conformations of several types of heterocyclic compounds. Dipole moments were used to calculate the relative populations of rotamers. The conformations of several bicyclic compounds containing hetero atoms were also investigated. By studying the kinetics of quaternization of some substituted N,N dimethylcyclohexylamines, very valuable and interesting information about the conformations of these cyclohexane derivatives were obtained. From the kinetic data conformational free energies of the NMe₂ and Ph groups were determined.

(x) **Studies on Linear Free-Energy Relationship:** He was very much interested in testing the applicability of linear free-energy relationships like the Hammett Equation in interpreting the rate and equilibria data of a number of systems and particularly his studies with naphthalene derivatives were some of the earliest attempts in this type of work. The rate data obtained in the kinetics of reaction of semicarbazide with *o*-, *m*-, and *p*-substituted acetophenones have been analysed with Hammett type of relations. In the study of the kinetics of oxidation of some methyl phenyl sulphoxides by Cr(VI), the correlation of rate constants of *para*-substituted phenyl methyl sulphoxides with σ^+ values has been observed to be good.

HONOURS AND AWARDS

Baliah was an elected Fellow of the Indian Academy of Sciences, Bangalore and elected Fellow of the Indian National Science Academy, New Delhi. He was a UGC National Lecturer in 1971. He visited Rumania under the Indo-Rumanian Cultural Exchange Programme in 1975. Nagarjuna University awarded him D. Sc. (Honorary). He was member of several committees of the Government of India, UGC, CSIR etc. He also served in the Editorial Board of the *Journal of Indian Chemical Society*.

LAST DAYS

Eventhough he was not serving in any educational institution after his superannuation, he was writing research papers and review articles and published them. Nearly seventy papers have been published after his retirement. He used to stay in his children's places depending on the weather conditions.

Baliah will be remembered for grooming a large number of young people who in course of time rose to do good work in different areas of Chemistry and make significant



cant contributions in different fields. His honesty, devotion to science and warm affection, left a mark on all those who have been associated with him.

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