Professor Zhi-Tang Huang
A Tribute

Dedicated to Professor Zhi-Tang Huang on the Occasion of His 75th Birthday

It is a privilege to be invited to write a tribute for this commemorative issue of Arkivoc which is dedicated to Professor Zhi-Tang Huang, a highly respected scientific mentor, a nice person and fine friend to all of his former students.

Zhi-Tang Huang was born on May 20, 1928 in Shanghai, East China, but was raised by his grandparents and grew up in his hometown Huangyan, Zhejiang Province, China. Huangyan is a pleasant, small city on the southeast coastline of East China with thriving fine chemicals and pharmaceutical industries, while Zhejiang has earned a reputation for having nurtured outstanding academicians as well as great scholars since the early days of the history of China.

Zhi-Tang Huang went to Shanghai in 1946 and was educated in the Department of Chemistry, Shanghai Tongji University, which at that time was one of the few renowned old universities in China. Immediately after having graduated from Tongji University in 1951, he was appointed to the position of Research Assistant at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences; subsequently, he was promoted to Assistant Research Professor of Organic Chemistry. It seems likely that he developed his lifetime interest in organic chemistry and polymer chemistry research during that period.

When the Institute of Chemistry of the Chinese Academy of Sciences in Beijing was established in 1956, Zhi-Tang Huang moved to the North to join this newly established Institute as Assistant Research Professor. There, he initiated research in polymer chemistry and later in organic chemistry, with specialization in heterocyclic chemistry and supramolecular chemistry. He remained at the Institute of Chemistry during the next 46 years, during which time he worked his way through the academic ranks and finally was appointed Full Professor in 1982. As he approaches his 75th birthday, Zhi-Tang Huang remains an enthusiastic researcher and dedicated mentor of Ph. D. students at the Institute of Chemistry.

As one of the principal scientists who has been associated with the Institute of Chemistry since its inception, Zhi-Tang Huang has contributed significantly to its development. He has been a primary driving force behind the Institute's program in organic chemical research, which

at one time was denigrated by the early policy-makers as a "minor branch" and "unimportant subject". Under his aegis, organic chemistry has survived as a discipline and currently continues to prosper at the Institute of Chemistry, where polymer physics and chemistry and physical chemistry rather than organic chemistry historically have been considered to be the strategically important research areas. However, having suffered very poor working conditions, tight budgets, and meager administrative support during the early years, Zhi-Tang Huang remained active in the research areas of heterocyclic chemistry and supramolecular chemistry and made notable achievements in those areas. In retrospect, he now must be highly gratified to have been privileged to witness the rapid growth in organic chemical research at the Institute, and he must certainly be pleased to note that increased numbers of scientists are joining this branch.

In addition to being a loyal staff member at the Institute, Zhi-Tang Huang has traveled extensively around the world, appearing regularly at important international organic chemistry conferences and. He has served as Visiting Researcher at several institutions abroad, including the Department of Chemistry, McGill University, Canada (July 1985 to September 1985) and the Institut für Organische Chemie und Biochemie der Universität Bonn, Germany (May 1981 to September 1982, July 1987 to September 1987, July 1993 to September 1993)

During his more than 50 year academic career, Zhi-Tang Huang has made remarkable and considerable contributions to research in organic chemistry and in polymer science in China. Renowned as a distinguished scientist in organic chemistry as well as in polymer chemistry, Zhi-Tang Huang has a broad range of research interests and has been a positive influence upon the research areas in which he has been involved, especially in the research areas of heat-resistant polymers, heterocyclic chemistry and supramolecular chemistry. Indeed, he pioneered research on heat-resistant polymers, organosilicon chemistry and polymers in China in the mid-1950s; he was one of the first to initiate research on supramolecular chemistry, and he also established himself as a leading heterocyclic chemist in China. To date, he is author or co-author of more then 210 published research papers and reviews.

His academic achievements led to his having been awarded several prestigious prizes and awards, which include, among others, the National Science Congress Award (1978), the Third National Invention Award (1987, 1996), the First Natural Science Award of the Chinese Academy of Sciences (1994) and the Third National Natural Science Award (1995). He was elected a Member of the Chinese Academy of Sciences in 1991 for his scientific achievements in organic chemistry and polymer science.

Apart from his research work, Zhi-Tang Huang has also played an important role in many scientific affairs in China. He had served as Chairman of the Academic Committee of the Institute of Chemistry for more than a decade (1989-2001). He was also Chairman of the Academic Degrees Committee of the Institute of Chemistry from 1995 to 2001. He also serves as a member of the editorial boards of several academic journals in China. He is currently the Editor-in-Chief of *Polymer Bulletin* and the Executive Editor of *Chinese Chemical Letters*.

Zhi-Tang Huang's research interests have touched upon a variety of areas of organic and

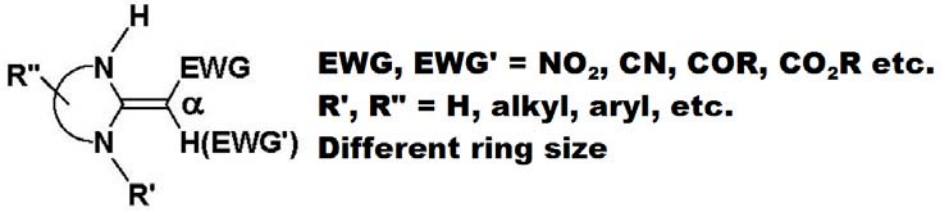
polymer chemistry, but his research work might be categorized roughly into three major parts: heat-resistant polymers and oragnosilicon polymers, heterocyclic chemistry and supramolecular chemistry.

Zhi-Tang Huang is one of the leading scientists in the area of heat-resistant polymers in China. He engaged in research of this field between the mid-1950s and the late 1980s. One of his major areas of research concentration during that period involved the synthesis of heat-resistant polymers and resins, e.g., epoxy resins and phenol-formaldehyde resins. Huang's group invented several novel heat-resistant resins and curing agents, which later were manufactured in bulk and subsequently were utilized as heat-shielding materials in Chinese industries in the 1960s.

Huang and his co-workers continued their efforts to search for even better heat-resistant resins that might be capable of resisting higher temperature. By the mid-1970s, Huang's group developed another type of novel, heat-resistant resin based on triazine-crosslinked polymers. This success was followed by a systematic and detailed investigation of aromatic dinitrile polymerization. A series of important research papers resulted from those projects; however, in those days, their publications could only appear in Chinese journals. Their published results paved the way for future development of research on heat-resistant polymers in China.

Zhi-Tang Huang was also one of the first scientists to perform research on organosilicon chemistry and organosilicon polymers in China. His research results, together with subsequent results published by Professor Bao-Ren Wang in the 1950s, actually pioneered organosilicon chemistry research in China.

Zhi-Tang Huang became interested in the chemistry of heterocyclic ketene aminals in the early 1980s. Subsequently, he engaged in systematic and thorough study of this intriguing class of compounds, with the result that his research group has dominated research in this field. Heterocyclic ketene aminals, also referred to as cyclic ketene *N*,*N*-acetals or cyclic 1,1-enediamines, generally can be depicted by the following formula:



These polyfunctionalized heterocyclic compounds are remarkable in that they are generated readily from inexpensive starting materials. Although they react with many kinds of reagents, they nevertheless have proved to be unusually stable species.

The combined structural and chemical features of heterocyclic ketene aminals render them powerful synthons for heterocyclic synthesis and, thus, attractive targets for further study. Huang's group developed, and improved upon, some convenient methods for large-scale synthesis of heterocyclic ketene aminals, e.g., condensation of diamines with imino esters or ketene dithioacetals, which facilitated subsequent detailed study of these compounds.

Huang and co-workers have made a comprehensive study of the interesting structural and spectroscopic properties of these special kinds of cyclic enamines. In addition, they exploited extensively the reactions of heterocyclic ketene aminals with a wide range of electrophilic reagents and 1,3-dipoles. These reactions can be controlled regioselectively or regiospecifically on the -NH-C=C- segment in most cases, and they usually afford good to excellent product yields. In the case of acyl-substituted heterocyclic ketene aminals (EWG=acyl), nucleophilic reactions with a number of electron-deficient reagents can be performed regioselectively or regiospecifically upon the *NH*, α-*C* and *O* moieties in the NH-C=C-CO- segment.

Zhi-Tang Huang studies various mechanistic aspects of these reactions, and some interesting results were obtained from these studies. Highlighted here are: (i) the mechanism of reaction between heterocyclic ketene aminals with α,β-unsaturated ketones and esters, which was found to be an aza-ene reaction rather than a Michael addition type reaction, as previously had been suggested, and (ii) the mechanism of the reaction with 1,3-dipoles, in which heterocyclic ketene aminals act as nucleophiles rather than as 1,3-dipolephiles. In addition to having published more than 90 published research papers, members of Huang's group thus far have prepared *ca*. 1,500 new heterocycles from these synthons. Their contributions to the development of the chemistry of heterocyclic ketene aminals certainly make a nice addition to enamine chemistry as well as to heterocyclic chemistry.

In the middle of 1980s, Zhi-Tang Huang initiated research on calixarene-based supramolecular chemistry. At that time, he became first investigator in China to become involved in the chemistry of calixarenes. His Chinese translation for the term "calixarene", i.e., "Bei Fang Ting" (a cup-like aromatic molecule), is widely accepted by Chinese academics. His group has made detailed investigations of a number of important reactions that are essential for chemical modification of calixarenes, e.g., Friedel-Crafts reactions, oxidations, esterification reactions, and halomethylation processes; indeed, Huang's group has synthesized *ca.* 400 calixarene derivatives. A number of functionalized calixarenes, such as calixcrowns, chromogenic and fluorescent calixarenes, chiral calixarenes and oligocalixarenes have been prepared and have been used to study cation and neutral organic molecule recognition, to prepare chemical sensors, and to investigate molecular assembly. More than 40 research papers and reviews have been published in this area by Huang and his
co-workers. Zhi-Tang Huang is undoubtedly one of the pioneers in supramolecular chemistry in China, with the result that his efforts have effectively promoted research in this field in China.

Zhi-Tang Huang's current research interests focus upon combinatorial chemistry of heterocyclic ketene aminals, chiral molecular recognition and self-assembly based on calixarenes.

Mei-Xiang Wang, Chu-Yi Yu, Qi-Yu Zheng, Chuan-Feng Chen and Mei-Xin Zhao
Institute of Chemistry, Center for Molecular Science, Chinese Academy of Sciences, Beijing, 100080, CHINA.

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Selected Publications of Zhi-Tang Huang

Polymer Science:

1. *Review*: The polymerization of aromatic and heterocyclic dinitriles; Z.-T. Huang, *Chin. J. Polym. Sci.* **1988**, *6*, 1-13.

Heterocyclic Ketene Aminals:

1. *Reviews*: (a) Heterocyclic ketene aminals; Huang, Z.-T.; Wang, M.-X. *Heterocycles* **1994**, *37*, 1233. (b) Advances in heterocyclic ketene aminals; Huang, Z.-T.; Wang, M.-X. *Progress in Natural Science* **2002**, *12*, 249.
2. Alkylation of heterocyclic ketene aminals with benzyl chloride and ethyl bromoacetate. Synthesis of heterobicycles containing γ-lactam-fused diazaheterocycles; Huang, Z.-T.; Liu, Z.-R. *Chem. Ber.* **1989**, *122*, 95.
3. The reaction of benzoyl-substituted heterocyclic ketene aminals with aryl azides; Huang, Z.-T.; Wang, M.-X. *J. Org. Chem.* **1992**, *57*, 184.
4. Further investigation on the reaction of heterocyclic ketene aminals with ethyl propiolate: ene-type reaction of enamines and an unusual substituent effect; Huang, Z.-T.; Wang, M.-X. *J. Chem. Soc. Perkin Trans. 1* **1993**, 1085.
5. The regiospecific N-alkylation of heterocyclic ketene aminals with ethyl bromoacetate: A facile route to 3-pyrrolidinone fused diazaheterocycles; Wang, L.-B.; Yu, C.-Y.; Huang, Z.-T. *Synthesis* **1994**, 1441.
6. Regiospecific allylation of benzoyl-substituted heterocyclic ketene aminals and their zinc chloride-promoted 3-aza-Cope rearrangement; Wang, M.-X.; Huang, Z.-T. *J. Org. Chem.* **1995**, *60*, 2807.

Calixarenes:

1. (a) Selective Friedel-Crafts reaction of 26,28-dimethoxycalix[4]arene; Huang, Z.-T.; Wang, G.-Q. *J. Chem. Soc. Perkin Trans. 1* **1993**, 167. (b) Friedel-Crafts reaction of calixarenes; Huang, Z.-T.; Wang, G.-Q. *Chem. Ber.* **1994**, *127*, 519.
2. Synthesis of new chromogenic calix[4]crowns and molecular recognition of alkylamines; Zheng, Q.-Y.; Chen C-F.; Huang, Z.-T. *Tetrahedron* **1997**, *53*, 10345.
3. Synthesis of chiral calix[4]arenes bearing tartaric ester moieties, Yuan, H.-S.; Huang, Z.-T. *Tetrahedron: Asymmetry* **1999**, *10*, 429.
4. Synthesis, Conformation and Metal-binding Properties of Calix[6]arene Derivatives, Zhang, W.-C.; Zhu, Y.; Li, E.-C.; Liu, T.-J.; Huang, Z.-T. *Tetrahedron* **2000**, *56*, 3365.
5. The self-assembly of calix[4]arene derivatives based on an A-T base pairing, Zeng, C.-C.;

Tang, Y.-L; Zheng, Q.-Y.; Huang, L.-J.; Xin, B.; Huang, Z.-T. *Tetrahedron Lett*. **2001**, *42*, 6179.

6. Macrocyclic, linear and starlike assemblies of calix[4]arenes covalently bridged by methylenes at the upper rims: Simple route to novel receptors with defined polycavities; Liu, J.-M.; Zheng, Y.-S.; Zheng, Q.-Y.; Xie, J.; Wang, M.-X.; Huang, Z.-T. *Tetrahedron* **2002**, *58*, 3729.