

共轭效应和芳香性本质的争论和它们的历史发展

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**摘要** “共轭效应是稳定的”是有机化学的最基本原理之一。但是,自30年代起,键长平均化,  $4N+2$  芳香性理论, 苯环D~6~h构架的起因, 分子的构象和共轭效应的因果关系,  $\pi$ -电子离域的结构效应等已经受到了广泛的质疑。其中, 最引人注目的是Vollhardt等合成了中心苯环具有环己三烯几何特征的亚苯类化合物, Stanger等合成了键长平均化, 但长度在0.143~0.148nm的苯并类衍生物。最近(1999年), Stanger又获得了在苯环中具有单键键长的苯并类化合物。在理论计算领域, 争论主要表现在计算方法上, 集中在如何将作用能分解成 $\pi$ 和 $\sigma$ 两部分。随着论战的发展, 作用能分解法在有机化学中的应用不断地发展和完善, Huckel理论在有机化学中的绝对权威也受到了挑战。为此, 简要地介绍了能量分解法的发展史, 对kollma法的合理性提出了质疑。此外特别介绍了我们新的能量分解法, 及在共轭效应和芳香性的研究中的新观点和新的思维模式。

**关键词** [共轭效应](#) [芳香性](#) [电子离域](#)

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## The controversy over the nature of aromaticity and conjugation

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**Abstract** It is the most important general concept in organic chemistry that the  $\pi$  electron delocalization is stabilizing. However, this concept, together with the ability of the  $\pi$  electron delocalization to level out of differences in bond lengths between formal double and single bonds, the Huckel  $4N+2$  theory, and the high stability of the  $\pi$  system in benzene, was argued during the period of 1930's through 1990's. The compounds, such as star-phenylene, linear and angular N-phenylene, tris(tri-carbonylironcyclobuta-dieno)benzene, 2,7-di-tert-butyl-4,5,9,10-tetraphenylbenzo-1,2,4,5-dicyclobutadiene were synthesized, and their crystallographic data were brought up as the experimental examples. these experimental results appear to support Shaik's viewpoint. On the other hand, the role of Mills-Nixon distortion in triannulated benzene was doubted by Siegel, and the stabilizing effect of the  $\pi$  electron delocalization in benzene was reconfirmed by the Streitwieser. Meanwhile, various methods for energy partition, such as those of Morokuma, Shaik, Kollma, Jug, Streitwieser, Wolfe and Ichikawa, were reviewed and commented. Kollma's and related methods, in which the effects of the  $\pi$  electron delocalization on the  $\pi$  framework and on the Fock matrix have been neglected completely, were questioned. At last, our novel energy partition was introduced. More than 50 references were cited.

**Key words** [CONJUGATIVE EFFECT](#)

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