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FOREWORD

For some years it has been the policy of the Chemistry Department of Indiana University to hold occasional conferences on timely subjects in specialized fields of chemistry. It is hoped that these meetings of specialists from diverse parts of the United States and abroad render a service to the advancement of science. The first such conference, in 1951, was on "Organic Sulfur Chemistry". Its success prompted the organization of a second conference held in 1954 on "Coordination Compounds". It is perhaps symptomatic of the trends in modern science that the subject of the most recent conference, "Hyperconjugation", represents probably an even narrower field of specialization than those of the first two.

The possibility of C–H electron delocalization as a means of explaining the effects of certain alkyl substituents on reaction rates was first suggested by J. W. Baker and W. S. Nathan in 1935. In 1941 R. S. Mulliken, C. A. Rieke and W. G. Brown published a quantum theoretical consideration of C–H electron delocalization with particular reference to ground state and spectroscopically excited states and introduced the term "hyperconjugation" to refer to this effect. The term met with quick general acceptance and has since been used, perhaps rather loosely with at least in some cases an implied meaning which was not envisaged by these authors. Many results from spectroscopic, thermochemical, molecular dimensional and reaction kinetic observations have been presented in the literature and interpreted with reference to hyperconjugation. A certain degree of self-consistency has been achieved in the interpretation of data in each of the different fields. However, the development of a unified picture of hyperconjugation has been plagued by apparent mutual inconsistencies in the ideas derived from the several different areas. As an example of this, the so-called "Baker-Nathan Order" of electron-releasing effects of alkyl groups ($\mathrm{Me} > \mathrm{Et} > \mathrm{Pr}^i > \mathrm{Bu}^t$) in reaction kinetic and equilibrium data has been considered to be indicative of important hyperconjugative interaction between the group and an electron-deficient center. But such orders are generally not characteristic of spectroscopic, thermochemical or molecular dimensional data where hyperconjugation has nevertheless been thought to be important. This introduces the problem of C–C electron delocalization or C–C hyperconjugation which has been suggested by several authors but never examined from a quantum theoretical view. These and other problems combined with the diverse nature of the evidences pertaining to hyperconjugation seemed to make the topic an ideal one for the type of conference which we at Indiana University like to sponsor.

The Conference on Hyperconjugation was held at Indiana University 2–4 June, 1958. The total registration was 117, including 61 participants from 23 states other than Indiana and 3 from the United Kingdom.

The conference heard the sixteen scheduled major papers as well as the results of several important investigations presented by participants from the floor during discussion sessions. The discussions were lively and, as befits a growing vital science, at times controversial. Considerable discussion evolved around Professor Dewar's idea that conjugation as well as hyperconjugation is unimportant in "classical" molecules such as butadiene or propene. Other high points in the discussions centered on the appropriateness of linear free energy equations in treating hyperconjugation, the usefulness of various theoretical models in hyperconjugation calculations, the roles of carbon–carbon vs. carbon-hydrogen hyperconjugation, conformation influences on hyperconjugation and the rather small but persistent Baker-Nathan orders observed in reactivity studies. A number of participants seriously questioned the existence of important hyperconjugation effects and offered alternative explanations of some of the relevant data. It seemed agreed that the Baker-Nathan order usually involves very small effects and may well have an origin different from that which accounts for the much larger discrepancy between the electron-releasing abilities of hydrogen and the alkyl groups.

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