

## Letters

## More on the Nature of Resonance

I would like to supplement the recent insightful article by Kerber (1) on the interpretation of resonance theory with three additional observations—one historical in nature and the other two conceptual.

1. It is important to realize that both the concept of mesomerism, as developed by Ingold, and the concept of *Zwischenstufe*, as developed by Arndt and Eistert, had a purely chemical origin which predates Pauling's attempt to link them with quantum mechanics. In particular, both evolved out of the attempts of Fry, Jones, Noyes, Stieglitz, and others to develop an ionic theory of organic reactivity in the first three decades of the 20th century (2, 3). In order to explain homoatomic bonding using the ionic model, Fry introduced the concept of "electronic tautomerism", a literal time-dependent equilibrium analogous in all respects to classical molecular tautomerism in which the net positive and negative charges of the two bonded atoms continuously exchanged places. The two dynamically interconverting forms were called "electromers" to differentiate them from classical molecular isomers. Interaction of the homoatomic bond with various charged reagents or substituents could radically shift this equilibrium in one direction or another thereby permanently locking the previously fluctuating charge into either the positive or negative mode and giving rise to the possibility of isolating one or the other of the two electromers. This concept permeated much of the thinking on the electronic theory of organic reactivity in the first third of the century, including that of G. N. Lewis, and no doubt contributed to Pauling's confusion over resonance as revealed by his notorious calculation of the frequency of bond oscillation in benzene found in all three editions of the *Nature of the Chemical Bond* (4).

2. It should be noted that use of resonance structures in connection with qualitative Lewis diagrams has long been known to be an artifact of an impoverished chemical symbolism and the conventions used to link that symbolism to the components of a simple wave function. The single line used to connect two atoms denotes an equally shared 2c–2e bond in which both atomic centers contribute equally to the wave function. Any deviation from this ideal requires the use of resonance, whether due to bond polarity (ionic-covalent resonance), multicentered bonding (bond–no bond resonance), nonintegral bond orders (single bond–multiple bond resonance), or so-called hypervalence (bond–lone pair resonance). The moment one agrees on a new valence symbol, such as the Y used to denote the localized 3c–2e bonds in the boron hydrides or the circle inside the benzene ring, and agrees on its relationship to the corresponding wave function, the qualitative need for 2c–2e bond resonance evaporates. Likewise, as Harcourt showed many years ago, if we did not have the line to represent a 2c–2e bond, but only a dot to represent a single shared electron, we would have to use resonance of these dot formulas to represent conventional 2c–2e bonds as well (5). Though many proposals, such as those of Linnett, have been made for extending our current valence symbolism beyond that of the conventional line for 2c–2e bonds, none of these, with the exception of the symbols for the 3c–2e bond

and the benzene  $\pi$ -system, have seen general acceptance, thus necessitating the continued widespread use of resonance structures in undergraduate chemistry (6).

3. The above point also calls into question Kerber's proposal that we replace the terms "resonance" and "resonance energy" with the terms "delocalization" and "delocalization energy". Deviations from the idealized 2c–2e bond requiring the use of resonance do not always literally imply increased delocalization (e.g., ionic-covalent resonance, localized multicentered bonding, etc.) of the kind imagined for conjugated hydrocarbons. There is no simple one-to-one relationship between the appearance of delocalized orbitals in an MO picture and the presence or absence of resonance in the corresponding VB picture. After all, the spectroscopic MOs for methane are delocalized (7, 8). As pointed out in several previous articles in this journal, most delocalized MOs can be converted into an equivalent set of localized MOs which closely approximate a single VB structure by using a suitable unitary transformation which maintains the same overall total energy and electron density for the species (8–11). Consequently, I would suggest that the terms "delocalization" and "delocalization energy" have the potential to be as physically misleading as the terms "resonance" and "resonance energy" which they are intended to replace.

## Literature Cited

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### *The author replies:*

I thank Prof. Jensen for his interesting and informative expansion on some of the history underlying the resonance concept. I particularly like his characterization of the use of contributing structures as “an artifact of an impoverished chemical symbolism”. Nevertheless, I continue to find the use of delocalization preferable to resonance. The former is misleading only if taken in an absolute sense, as implying that electrons in methane (for example) are totally locked in place and those in benzene are totally free. Understanding

delocalization as a relative term reduces the potential for misunderstanding, in my opinion. And, empirically, generations of students have been confused by the resonance terminology. If Pauling was confused, how can we expect our students not to be confused? Perhaps we need a clean new term, or perhaps mesomerism should rise again?

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