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# Extending Ball and Stick Models by Using Three-Center, Two-Electron Bonding Components

Though some molecular model sets make an attempt to represent the delocalized $\pi$-electron systems found on benzene and other conjugated species, most are restricted to representing the localized bonding components corresponding to the kernels, bonds, and lone electron pairs of classical structural theory (1). This restriction to localized bonding components is for the most part a natural consequence of the mechanical limitations inherent in the models themselves. It is important to realize, however, that a delocalized MO or bonding component and a multicentered MO or bonding component are not necessarily the same thing. Thus both empirical experience and MO studies of the localized bonding (2) in certain classes of molecules suggest the existence of multicentered, but localized, bonding components other than the two-center, two-electron (2c-2e) bonds and one-center, two-electron (1c-2e) lone pairs of conventional Lewis structures and ball and stick models. Once this distinction is made it becomes apparent that standard ball and stick models can be extended easily and profitably by incorporating such localized multicentered components without, at the same time, unduly increasing their mechanical complexity.

## Use of Localized Multicentered Bonding Components

Perhaps the most common and best known of these components is the closed three-center, two-electron (3c-2e) bond found in localized borane and carborane structures and generally symbolized as

$$\begin{matrix} & A & \\ & \diagup \diagdown & \\ B & & C \end{matrix} \qquad (1)$$

This component finds use not only in localized borane and carborane structures but in a number of other inorganic species, such as $Al_2(CH_3)_6$, $[Be(CH_3)_2]_{1D}$, $K[PtCl_3(C_2H_4)]$, and $B_4Cl_4$. It is also employed in describing the bonding in a number of donor-acceptor or charge-transfer complexes, such as that between the $Ag^+$ ion and benzene

$$\text{\includegraphics{benzene}} \diagdown_{\text{- -}}Ag^+ \qquad (2)$$

where broken lines are used in the 3c-2e symbol to represent its incipient nature relative to the other bonds in the benzene ring. Even more importantly, the use of 3c-2e bonds is becoming increasingly prevalent in organic chemistry, particularly in the area of electrophilic substitution and addition reactions.

More than 30 years ago Dewar (3) proposed that electrophilic attack at a double bond proceeded initially through the formation of a weak $\pi$ complex between the attacking electrophile and the multiple bond, a process involving 3c-2e bond formation. Thus in the case of addition of $Cl_2$ over the double bond in ethene we would have

$$\begin{matrix} & Cl^{\delta-} & \\ & | & \\ & Cl^{\delta+} & \\ & \diagup \diagdown & \\ H & & H \\ \diagdown & & \diagup \\ & C = C & \\ \diagup & & \diagdown \\ H & & H \end{matrix} \qquad (3)$$

Olah (4) has extended this concept to electrophilic attack at

single or $\sigma$ bonds as well and again postulates the use of a 3c-2e bonding component in the initial complex to explain the apparent existence of pentavalent carbon without the necessity of invoking high-lying $d$ orbitals. Thus in the nitration of $CH_4$ in liquid HF using the $NO_2^+$ cation as the attacking electrophile, one obtains

$$CH_4 + NO_2^+ \rightleftharpoons \left[ H_3C\text{-}\text{-}\diagup\diagdown^{NO_2}_{H} \right]^+ \rightleftharpoons H_3CNO_2 + H^+ \qquad (4)$$
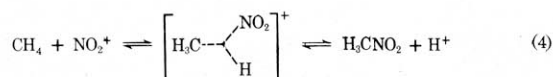
Olah has also suggested that conventional trivalent carbonium ions (e.g., $CH_3^+$) be called carbenium ions, as they correspond to protonated carbenes (e.g., $CH_2$), and that the term carbonium ion, in keeping with the terms ammonium ion ($NH_4^+$) and oxonium ion ($H_3O^+$), be reserved for the corresponding protonated neutral hydrocarbons instead. The simplest member of this class would be the methonium cation

$$\left[ \begin{matrix} & H & \\ & | & H \\ H\text{-}C\diagup\diagdown \\ & | & H \\ & H & \end{matrix} \right]^+ \qquad (5)$$

Carbonium ions and carbenium ions together would constitute the general class of carbocations in analogy with the term carbanion used to describe negatively-charged hydrocarbon ions. As with the methonium cation, carbonium ions in general would all have 3c-2e bonding components in their structures.

## Construction of Models

In light of both the widespread use of the 3c-2e bonding component in inorganic and organic chemistry and the long established use of a symbol to represent it, it is surprising that no commercially available molecular model kit appears to offer it as a model component (5). We have constructed such a kit by modifying a standard student molecular model kit consisting of $3/4$ in. wooden balls and spring connectors sold by Laboratory Supplies Co., Inc. of Hicksville, New York. Y-shaped 3c-2e bonding components were made by melting together sections of $1/8$ in. solid polyethylene tubing with a microtorch and then trimming off any excess with a razor knife. It is necessary that these components be made of a flexible material as considerable bending, both in the plane and out of the plane of the Y, occurs in the construction of
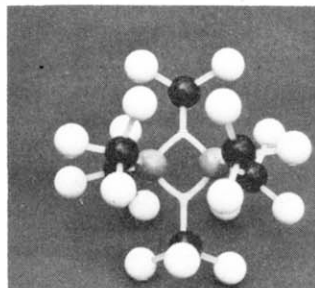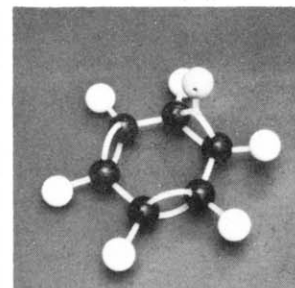


Figure 1. (left) $Al_2(CH_3)_6$



Figure 2. (right) $Ag^+$-benzene complex

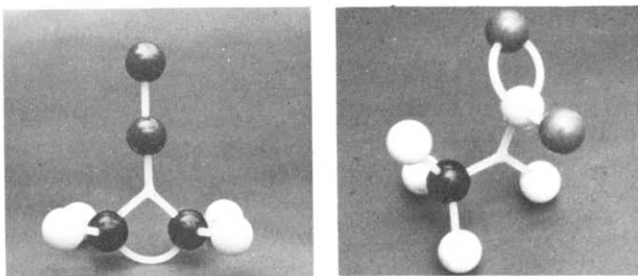Figure 3. (left) Dewar π complex for $Cl_2$-$C_2H_4$

Figure 4. (right) Olah complex for $CH_4$-$NO_2^+$
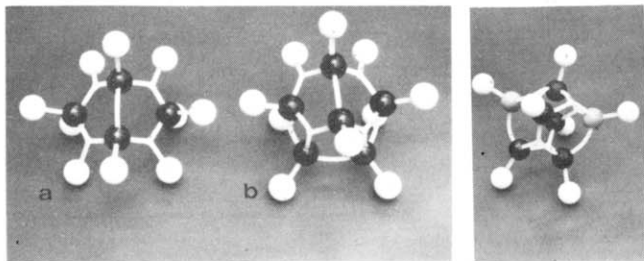


Figure 5. (left) (a) $B_4H_{10}$ (b) $B_6H_{10}$

Figure 6. (right) 2,4-$C_2B_5H_7$

models, especially in the case of cage and polyhedral structures. The conventional spring bonds belonging to the kit were also replaced by straight sections of polyethylene tubing to give a uniform representation of all bonding components. The 3c-2e components were cut so that each arch of the Y roughly spanned a distance equivalent to the longest straight line bonding component (about $1\frac{1}{2}$ in.). The tubing was slightly larger than the holes in the balls and trimming of the ends with a razor insured a secure fit for the bonding components.

Some example models are shown in Figures 1 through 6. Figure 1 shows a model of $Al_2(CH_3)_6$, Figure 2 the $Ag^+$-benzene complex in eqn. 2, Figure 3 the Dewar π complex in eqn. 3, and Figure 4 the $CH_4$-$NO_2^+$ intermediate in eqn. 4. Figure 5 shows models of $B_4H_{10}$ and $B_6H_{10}$ corresponding to the *styx* structures



(6)
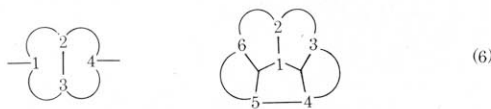
The correct shapes, corresponding to the polyhedra and polyhedral fragments predicted by Wade's rules (6), naturally result from "inflating" these *styx* structures, each boron having an approximately tetrahedral arrangement of bonds and the flexibility of the bonding components allowing for considerable distortion from the ideal angles if necessary. Use of any one of the many possible resonance *styx* structures for the higher boranes also gives the proper geometry for each species, the choice of the *styx* structure used being dictated by the absence of open 3c-2e bonds and (for aesthetic reasons) the symmetry of the components (7). Finally, Figure 6 shows a model for the carborane 2,4-$C_2B_5H_7$ based on the structure



(7)

recently proposed by Lipscomb (2) on the basis of localized MO calculations.

It is apparent from the above examples that commercial production of 3c-2e bonding components (and possibly other localized multicentered components such as the 4c-2e bonds in $Pt_4(CH_3)_{16}$ and $Li_4(CH_3)_4$) would substantially enhance the value of molecular model kits for the inorganic and organic chemist alike.

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### Literature Cited

(1) An extended survey of currently available commercial model kits has recently been given by Walton, A., "Molecular and Crystal Structure Models," Halsted Press, Chichester, England, **1978**.
(2) Readers interested in the theoretical justification of localized bonding components (and consequently of ball and stick models in general) and in the distinction between delocalized, localized, and multicentered should consult the review by England, W., Salmon, L. S., and Ruedenberg, K., *Fortschr. Chem. Forsch.*, **23**, 31 (1971). A review of localized MO results for multicentered bonds in boranes and carboranes can be found by consulting Lipscomb, W. N., *Acc. Chem. Res.*, **6**, 257 (1973). As a result of this work Lipscomb has suggested certain modifications of the conventional *styx* pictures; see Epstein, I. R. and Lipscomb, W. N., *Inorg. Chem.*, **10**, 1921 (1971).
(3) Dewar, M. J. S., "The Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, **1949**.
(4) Olah, G., "Carbocations and Electrophilic Reactions," Wiley, New York, **1974**.
(5) The only molecular models I am aware of which attempt to represent 3c-2e bonds are based on the tangent-sphere model popularized by Bent (see Bent, H., *Fortschr. Chem. Forsch.*, **14**, 1 (1970)) and commonly used to represent Gillespie's VSEPR rules for predicting molecular geometry. Model kits based on the use of plastic spheres and rubber bands have been extensively used by King (see King, L. C., *Chemistry*, **37** (2), 12 (1964)) to represent such tangent-sphere domains, and Sunderwirth (see Sunderwirth, S. G., J. CHEM. EDUC., **47**, 728 (1970)) has given some tangent-sphere models of 3c-2e bonded intermediates in organic chemistry.
(6) Wade, K., *Chem. Brit.*, **11**, 177 (1975).
(7) Lipscomb, W. N., "Boron Hydrides," Benjamin, New York, **1963**.