Notes from the Oesper Collections

The Case of the Wandering Model

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The other day, while cleaning out the storage area for the Oesper Museum, I made a unexpected discovery. Among the items slated for disposal was a set of filing cabinets belonging to the late Hans Jaffé (figure 1). These had been sitting in storage for the past 26 years and were assumed to contain nothing more than his extensive set of reprints, now rendered worthless by the rise of online journals which allow one to print down reprints of older papers at the touch of a keyboard. Though I had gone through these shortly after his death in 1989 and removed any items of interest to my own research, I nevertheless quickly checked their contents once again to make certain that nothing of importance had been overlooked. Much to my surprise, this led to the discovery in one of the bottom drawers of a plaster model (figure 2) that I had either previously overlooked or whose existence I had completely forgotten about.

This time, however, I instantly recognized what I was looking at, since, in the intervening years, I had seen a photograph (figure 3) of this very model in the pages of the *Journal of Chemical Physics* in an article published in 1954 by the American physicist, John R. Platt (figure 4), of the University of Chicago (1). Jaffé served as the department's specialist in quantum mechanics for 35 years (2) and, among his early interests, as revealed from the contents of his reprint collection, was a very approximate quantum-mechanical model of chemical bonding known as the "free-electron" or "box model" which became something of a vogue among theoreticians in the period 1948-1964 before improvements in the computer made more sophisticated calculations routine (3).

Figure 1. Hans Jaffé (1919-1989).

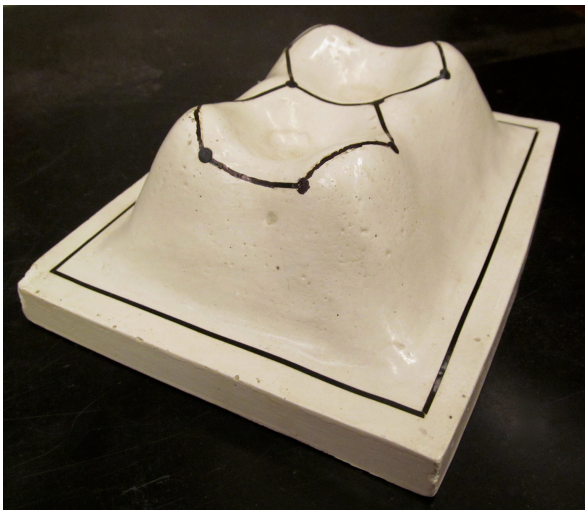

Figure 2. The (2.5" x 6" x 8") plaster π-electron-density model for naphthalene found in the bottom drawer of Hans Jaffé's filing cabinet.

Among the leaders in this field was John Platt and a group of associates at the University of Chicago, who would publish more than 21 papers on this subject between 1949 and 1961 (1). In his 1954 paper Platt summarized the results of an earlier crude version of the free-electron model known as the box model that had been introduced by the German chemist, Otto Schmidt, in 1938 and which Platt used to approximate the π-electron densities of various conjugated hydrocarbons. In this approach each conjugated hydrocarbon molecule was confined to a two-dimensional box of appropriate dimensions and its π-energy levels and π-electron densities obtained by solving the corresponding well-known "particle in a box" problem.

Platt also provided photographs of plaster models

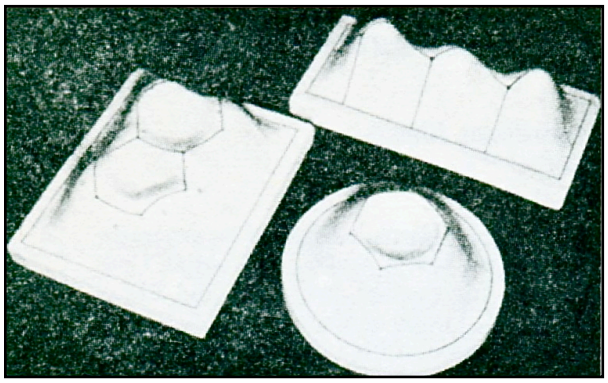

Figure 3. A badly stippled photo of some of Platt's plaster π-electron-density models as they appeared in his 1954 paper. The model for naphthalene is on the left. Note the circular box for benzene.

for the resulting distribution of the π-electron densities for each of the 10 hydrocarbons studied in the paper, one of which is for the compound naphthalene and corresponds to the model found in Hans Jaffé's filing cabinet.

In these models the magnitude of the π-electron density at each point within the box is represented by variations in height and its relation to the molecule in question by the superposition of a framework structure for the molecule on top of this density surface. The size of the box used in the calculation was further indicated by outlining its shape around the outer edge of the model.

Figure 4. John Rader Platt (1918-1992).

Conventional 3D physical models of molecular structure are quite common and many examples have survived, since most molecular model kits were produced commercially. In sharp contrast, surviving 3D physical models of electron-density distributions based on quantum mechanical calculations are quite rare. To the best of my knowledge, they were never available as commercial kits (if such a thing is even possible) and were all one-of-kind productions unique to a particular theoretician or research group. Both kinds of models, as actual 3D physical objects, are now rapidly disappearing thanks to the rise of computer graphics, which are far easier to construct and manipulate. Hence the survival of Jaffé's plaster model has definite value as a museum artifact, though how it made its way from Platt's laboratory at Chicago to the bottom drawer of Jaffé's filing cabinet at Cincinnati is an historical mystery that, in all likelihood, will never be solved (4).

References and Notes

1. J. R. Platt, "The Box Model and Electron Densities in Conjugated Systems," *J. Chem. Phys.*, **1954**, *22*, 1448-1455. Reprinted in J. R. Platt, Ed., *Free-Electron Theory of Conjugated Molecules*, Laboratory of Molecular Structure and Spectra: University of Chicago: Chicago, IL, 1964.

2. W. B. Jensen, "An Interview with Hans Jaffé" in *Cincinnati Chemists*, Oesper Collections: Cincinnati, OH, 2012, pp. 113-126.

3. W. B. Jensen, "The Free-Electron Model From Otto Schmidt to John Platt," in E. T. Strom, A. K. Wilson, Eds., *Pioneers of Quantum Chemistry*, ACS Books: Washington, DC. 2013, pp. 117-137. This paper was based largely on the contents of Hans Jaffé's reprint file on this subject.

4. Of course it is possible that Jaffé's model is a copy of Platt's, though Platt's paper does not indicate that copies of his models were available to interested parties upon request.