This is a short review dealing mainly with my work on the quantitative conformational analysis of substituted 1,3-dioxanes and 1,3-dithianes. The methodology used involves acid-catalyzed equilibration combined with proton nuclear magnetic resonance spectroscopy; the most important conclusion is that unshared electron pairs are "smaller" than hydrogen atoms. This conclusion is that unshared electron pairs are "smaller" than hydrogen atoms. The significance of this result has been generally recognized by chemists and physicists.

Our next surprise came when we equilibrated 2R, 3,5-di-butyl-1,3-dioxanes and 2-methyl, 2,5-di-butyl-1,3-dioxane. The corresponding preference at C(4) is 2.3 kcal/mol. These values are much larger than the 1.7 kcal/mol value in methylecyclohexane, presumably because the smallness of the C-C bond compared to C-O bond leads to enhanced syn-axial CH interaction in the oxygen systems.

Two circumstances saved the day. One was a conversation with S.J. Angyal (Sydney), I decided to test this assumption. The other was the arrival of a six-membered ring with axial t-buty1; evidently the latter's interaction with the syn-axial lone pairs on oxygen is much less than corresponding interactions with syn-axial hydrogen atoms. Shortly after publishing this result, we learned that Riddell and Robinson at Oxford had arrived at the same conclusion.

Subsequent work dealt with 1,3-dithianes. Conformational energies in this system are smaller than in 1,3-dioxanes because of the much longer C-C bonds (as compared to C-O-C) distances. For the same reason, the 1,3-dithiane system readily assumes the twist or boat conformation. The account has been widely quoted presumably because it was one of the first to lay out the conformational factors particular to saturated heterocycles and to summarize the magnitude of such factors, including dipolar ones.

In 1980 an entire book dealing with conformational analysis in saturated heterocycles appeared.