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On Secondary Isotope Effects in Molecular Structure⁺

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Primary isotope effects in structure and kinetics are well-known. The increase in length of a bond when one of the atoms is replaced by a lighter isotope is attributed to the greater amplitude of vibration of the lighter isotope in a Morse-like anharmonic potential field. The greater ease of rupturing a bond containing a lighter isotope is accounted for by its greater zero-point energy.

In spectroscopic structure analyses of polyatomic molecules, however, isotope effects on bond lengths are frequently ignored. Moreover, it seems to be universally assumed that if isotopic shifts in atomic positions occur at all, they occur only in those bonds which contain the varied isotopes. On the other hand, in kinetic studies it was shown several years ago by Lewis¹ and Shiner² that rates of bond breakage may be influenced appreciably by isotopic substitution, not only when the substitution occurs in the bond itself (primary isotope effect) but also when it occurs at more distant sites (secondary isotope effect). It is of interest, then, to inquire whether secondary effects also occur in molecular structure.

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Recent studies^{3,4} indicate that secondary deuterium isotope effects in kinetics can be ascribed, at least in part, to effects of repulsions between nonbonded atoms. Hydrogen atoms, with their greater amplitudes of vibration, behave as if they are larger than deuterium atoms, and hence exert stronger repulsions on neighboring atoms. Accordingly, it was predicted⁴ that a decrease of the order of 0.003 Å in the C-C bond in ethane might be expected to accompany the replacement of hydrogens by deuteriums. It was also estimated⁵ that perhaps 20% of the deuterium isotope effect on CD₄ bond lengths arises from nonbonded interactions and hence could plausibly be interpreted as secondary in origin rather than primary (due to Morse asymmetry). Further considerations, to be reported later, have suggested an additional small interaction which probably enhances the secondary effect in ethane but which may counteract it in certain other molecules listed below.

In order to test predictions we have initiated an electron diffraction study of ethane and deuterioethane. Preliminary results are now available. In C₂H₆ the mean C-C and C-H bond lengths found agree very closely with values determined in this laboratory for other paraffin hydrocarbons,^{6,7} and the C-H bond shows a normal primary isotope effect (~0.005 Å) very nearly the same as that found in methane when H is replaced by D.⁶ Most interesting, however, is the output of our least squares analysis indicating that the mean C-C bond length in C₂D₆ is indeed shorter than in C₂H₆, and by about 0.004 Å. The decrease seems to be real, for the apparent uncertainty is not much greater than 0.001 Å.

Electron diffraction offers the advantage over spectroscopy, in principle, that it affords a much more direct measure of bond lengths for individual isotopic species. Nevertheless, in view of the difficulty in attaining accuracies greater than 0.001 Å by electron diffraction, it would be desirable to bring an intrinsically more precise method, microwave spectroscopy, to bear on the problem. The spectroscopic parameter r_0 would probably not be adequate in reliability for the comparisons required, according to evidence cited by Costain⁸ and others. The parameter r_s , determined independently for, say, the C-X bond in CH_3X and in CD_3X molecules would appear to be more reliable, but not entirely free of objection. Costain considers that r_s closely approximates the equilibrium parameter, and the secondary isotope effects postulated here for mean (time-average) structures should vanish for equilibrium structures.

While it is not possible to study ethane by microwave spectroscopy there are many analogous molecules which would be amenable ^{to investigation}. Information on the interactions giving rise to secondary effects on structure is so scanty that it is premature to claim sufficient understanding has been achieved yet to permit predictions for other molecules. Still, after stressing such reservations, it may be useful to venture a few guesses of types of molecules likely to exhibit secondary deuterium shrinkages like ethane, and types where opposing factors may be stronger. In the former class might be found hydrazine, CD_3 derivatives of silane, phosphine, and chlorine, and perhaps CH_3ND_2 . In none of these compounds, however, does the number of nonbonded deuterium interactions across a bond rival that in ethane. In the latter class might be found SiD_3 derivatives of methane and ammonia, the compounds CD_3F , CD_3OH ,

and perhaps CD_3NH_2 . In addition, shifts in angle may be encountered as well as shifts in length. For example, the XCX angle in HCX_3 may be the order of 10^{-1} degrees smaller than in DCX_3 , at least for $\text{X} = \text{carbon}$.

In any event, a careful study of secondary isotope effects on time-average structures might be helpful in elucidating the origin of secondary isotope effects in kinetics, which remains speculative. It would also provide useful information on intramolecular force fields.

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