Tetrahedron Letters No. 7, pp 653 - 656.
0040-4039/79/0208-0653$02.00/0

THE ACTION OF MOLECULAR DISTORTION ON THE STERIC PARAMETER E_S' - THE X-RAY STRUCTURE OF *tri-iso*-PROPYLACETIC ACID.

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The behaviour of the steric effect of alkyl groups, measured by the E_S' parameter, as a function of increasing degree of substitution has recently been analysed.[1a-c] This work brings out the existence of three regions of distinct behaviour in which the variation of the steric effect with substitution follows different trends: a "normal" behaviour region extending over ca. 6 log units in which the contribution of the introduction of successive methyl groups to the overall steric effect *increases monotonically* (groups with 1 to 7 carbons); a region in which a "levelling" effect is observed, i.e. the contribution diminishes and becomes nil (groups with 8 and 9 carbons); and a region where this contribution changes sign, an " inversion" effect (groups with 10 carbons). This latter effect, exemplified by the group $i\text{-}Pr_3C$-, presents an intriguing problem since it represents a rather substantial and unexpected rate enhancement with increasing substitution. In view of this and some recent interest[2] in the biological properties of *tri-iso*-propylacetic acid (TIPA) we decided to investigate the molecular structure of this compound.

Structural Sequences Illustrating the Anomalous Steric Effect of the Group $i\text{-}Pr_3C$-

$$i\text{-}Pr_2CH\text{-}(E_S' = -5.01) \rightarrow i\text{-}Pr_2MeC\text{-}(-7.38) \searrow$$
$$i\text{-}Pr_2EtC\text{-}(-7.38) \rightarrow i\text{-}Pr_3C\text{-}(-6.78)$$
$$Et_3\text{-}(-5.29) \rightarrow i\text{-}PrEt_2C\text{-}(-6.20) \nearrow$$

Figure 1 illustrates the structure obtained for TIPA by X-ray crystallography. The acid is, of course, a dimer in the solid state. It is immediately evident that the molecule has a highly distorted structure: tha angle $C_1C_2C_3$ (104.0°) is considerably compressed and the bonds C_2C_3, C_2C_4 and C_2C_5 elongated. Mutual repulsions among the three i-Pr groups produces an umbrella-like opening of the molecule. The disposition of these i-Pr groups is not symmetrical with respect to the OCO plane. One group lies above the plane with its methyls directed away from the back-side of the molecule; the two others are directed below the OCO plane each with its pair