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FORMAL SEQUENCING OF ALKYL GROUPS: APPLICATION TO THE AUGMENTATION, LEVELLING, AND INVERSION OF THEIR STERIC EFFECTS.

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In a prior communication[1] we developed an homogeneous scale of steric effects based on the Taft-Ingold hypothesis[2] and an exact specification of the defining reaction (acid-catalysed esterification of carboxylic acids in MeOH, at 40°). This revised Taft scale, E'_S, permits, for the first time, a sound analysis of the behaviour of the steric effect with increasing substitution. Insofar as this behaviour is not trivial[3,4] its understanding presents an interesting and, we feel, fruitful problem in chemistry.

Previous work by Dubois et al. has shown how it is possible to establish purely formal relationships between the structures of alkyl groups and properties.[5] The nature and utility of these relationships depends on the ordering which is imposed on these structures. The classical notion of homology is logically contained in this study of formal populations. Moreover, though usually associated with linear structures, the term may be generalized to include branching. Since alkyl groups may be derived from one another by the formal replacement of a hydrogen by a methyl group, they can be interrelated by a formal link symbolising the replacement. The structures may then be included in a formal transformation graph termed "hyperstructure"[6] which brings out the formal relationships which exist among them (Fig. 1). Such a general graph permits the evaluation of topological distances between structures and the search for similarity indices useful in data treatments.[7]

We may use this formal filiation of alkyl groups to analyse the influence of introducing a methyl into an alkyl group on its steric parameter E'_S. The hyperstructure in Fig. 1 is equivalent to a labelled and ordered conversion graph of the known alkyl groups, homomorphous to the group t-Bu_3C-. From it, it is evident that groups with the same number of carbon atoms have steric effects of the same order of magnitude. For families of isomers the sequence of increasing steric hindrance is: primary < secondary < tertiary. This is true for all isomer families from i-Pr (3 carbons) to t-$BuMe_2C$- (7 carbons). By indicating on each link of the hyperstructure the difference between the steric parameters of the groups which are derived from one another by monosubstitution one may visualize the variation of E'_S due to the *successive introduction of methyl groups*. The figure shows three regions distinguished, in fact, by the effect of the successive introduction of methyl groups: R I (groups with up to 7 carbons) in which the contribution of successive methyl groups increases monotonically; R II (groups with 8 and 9 carbon atoms), an intermediate region in which this contribution diminishes and becomes nil (except for the group i-Pr_2MeC-); R III (groups with 10 carbon atoms), an extreme region where this contribution changes sign.

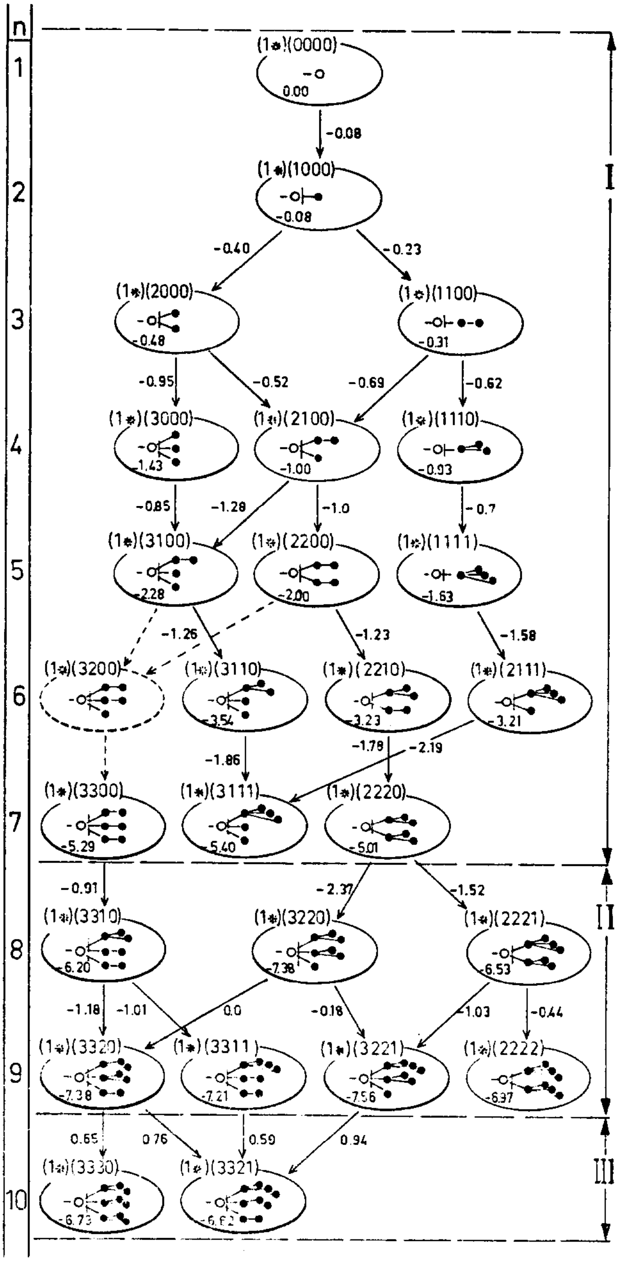

Fig. 1: Hyperstructure (or formal evolution graph) representing the evolution of the steric parameter E'_S of alkyl groups homomorphous to the group t-Bu$_3$C- as a function of substitution. Contained in each oval (i.e. node of the graph) are, from top to bottom, the numerical descriptor (DEL) of the alkyl group,[5] its relevant structure and E'_S value. Over each arrow the E'_S difference between successive groups is given. This hyperstructure brings out the existence of three distinct regions: R I (Augmentation), R II (Levelling), and R III (Inversion).

This behaviour is more strikingly portrayed in Fig. 2 in which the ordinate $\delta E_S'(n \rightarrow n+1)$ represents the average variation of steric effect in alkyl groups and, the abscissa the number of carbon atoms in the corresponding groups. The monotonic (and relatively linear) contribution of successive carbon atoms in Region I is brought out as well as the levelling effect of Region II and the inversion of sign of Region III. It is to be noted that Δ represents *the average contributions to the overall steric effect of atoms possessing different environments* and as such constitutes a qualitative point of view. A more quantitative approach will be forthcoming.

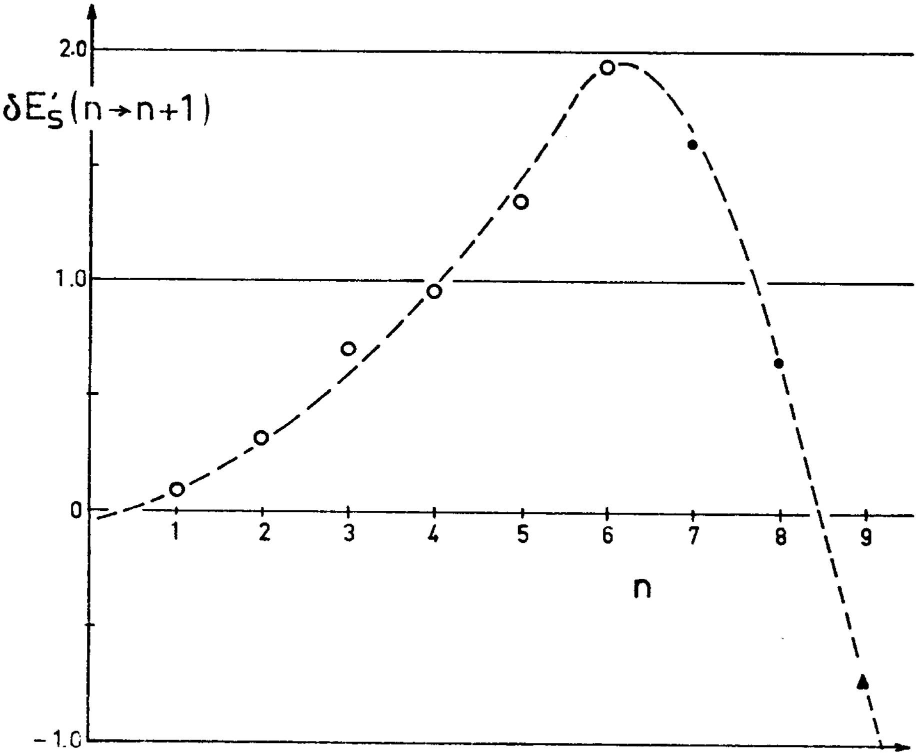

Fig. 2: Variation of E_S' of alkyl groups with changing level of substitution, $\delta E_S'(n \rightarrow n+1)$ versus the number of carbon atoms - n. o - R I, ● - R II, ▲ - R III.

As the effects which are operating are surely distinct, the augmentation (R I), levelling (R II), and inversion (R III) of the steric parameter should be considered separately. Among the elements to be considered in a thorough study of steric effects are the role of conformation and molecular distorsion.

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