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ELECTRONIC EFFECTS INDUCED BY METHYL SUBSTITUENTS: INTERPRETATIONS OF REACTIONS AND N.M.R. RESULTS

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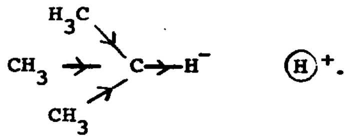
Jackman and Kelly[1] have published an account of extensive studies by N.M.R. (^1H and ^{13}C) of methyl substituted alcohols and ketones. On the basis of their findings they propose a reversal of the presently assumed polarity of the methyl group as a source of an induced electrical effect. That is, the displacement is predicated to be $C \rightarrow CH_3$ instead of the widely recognised $C \leftarrow CH_3$, where the arrow indicates the direction of displacement of electrons.

The facts generalised by this electron-push of methyl (replacing H) cover a wide range of phenomena: dipole moments, e.g. that of p-nitrotoluene; strengths of acids and bases; and a veritable host of comparative rates of reactions. In this class, the consistent electron-push[2] of a substituting methyl in OR, shown in the nitration of a series of p-methoxyphenyl ethers[3], was unequivocally demonstrated. Such results cannot be explained away by any of the considerations mentioned by Jackman and Kelly (l.c.), including 'hyperconjugation', itself a very dubious conception.

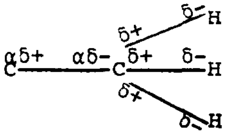
Recent studies by Hogeveen and Bickel[4] give strong support to the electron push of substituting CH_3. For example, isobutane reacts reversibly with $HSbF_6$ with formation of H_2 (and presumably t-butyl hexafluoroantimonate).



This is the converse of the formation of hypo-iodite from CI_4 and $O\bar{H}$.

Nevertheless, the whole of the above evidence refers to comparisons of R——H with R——CH_3, and not to an intrinsic polar property of the CH_3 group. The C——H bond is very probably $\overset{\delta+}{C}\overset{\quad\delta-}{\text{——}}H^{(5)}$ and one of us has recently suggested[6] that the electron-push of CH_3 replacing H, is not due to a reversal of the dipole, but to a reduction of its value.

$$C\overset{\delta+\quad\delta-}{\text{————}}H$$



Here, the dipole αδ+ — αδ- is induced by 3 δ+ — δ- in the β-position. The value of this induced effect is less than δ+ — δ- due to $\bar{H}$ in the α-position. Thus, the symbol $C \leftarrow CH_3$ should not imply, as has usually been assumed, a dipole $C\overset{\delta-\quad\delta+}{\text{———}}CH_3$ but, rather a reduction of the $C\overset{\delta+\quad\delta-}{\text{———}}H$ separation of the charges. This hypothesis of a differential effect is applicable to all comparisons of organic chemical mechanisms and rates of reaction made between RH and R·CH_3 as reactants under the same conditions. The CH_3 group remains — $\overset{+}{C}\overset{-}{H}_3$, and it may be found that this polar character is relevant to constitutive effects on values, although in a manner not yet fully understood. In regard to the questions posed by chemical shifts we submit the following considerations.

There are many instances in which quantitative correlation of shielding with strength of negative electrical field breaks down, and therefore the interpretation of chemical shifts in terms of an inductive effect is unconvincing. Other factors, some not yet fully understood, can play a part in determining the shielding of ^{13}C in simple alkyl substituted compounds.

Jackman and Kelly[1] state that the contribution of an α-alkyl substituent to the deshielding of carbinol carbon atoms is -6.8 p.p.m., while α-alkyl substitution reduces the chemical shift of the ^{13}C nucleus in hydrocarbons[8] by -9.09 p.p.m. They attribute this difference to the fact that the electron density of the hydroxy-substituted carbon atom has already been seriously depleted by the much stronger electron withdrawing effect of the attached oxygen atom, and correlated this deshielding effect of the α-alkyl substituent with electron withdrawal by the alkyl group.

Comparison of the difference of the ^{13}C-shift of the 1-carbon in ethyl halides with that of the ^{13}C-nucleus in methyl halides gives the following results: fluorides -3.9 p.p.m., chlorides -14.5 p.p.m., bromides -19.0 p.p.m., and iodides -24.3 p.p.m.[7] Even assuming that these figures can change somewhat when averages are derived from measurements of a larger number of compounds, they show that alkyl substitution in halides (with the exception of the fluorides) produces a _greater_ shift than in the hydrocarbon series. This appears to be in direct contradiction of Jackman and Kelly's suggestion that the chemical shift of the ^{13}C-nucleus attached to an electron withdrawing substituent should be _less_ affected by alkyl substitution than the ^{13}C chemical shifts in similarly substituted hydrocarbons.

Even more relevant is a comparison of the progressive downfield shifts for the ^{13}C and ^{17}O nuclei in the series methanol, ethanol, isopropyl alcohol and _t_-butyl alcohol. Jackman and Kelly[1] use these figures, together with the increasing gas phase acidities along the series, to support their electron withdrawal theory.

Although, however, the α and β ^{13}C shifts in propanol, as in isopropanol, are lower than those in ethanol[9], and the gas phase acidity is higher[10], the ^{17}O shift is this time to _higher_ field.[11] There is, therefore, no systematic behaviour applicable to both ^{13}C and ^{17}O chemical shifts which can be correlated with an electron withdrawal effect of the methyl substituent.

These inconsistencies illustrate some of the difficulties encountered in attempts to equate chemical shifts purely with inductive effects in the bonds of the carbon chains. Other factors have to be taken into consideration.

Perhaps the first question that arises is the possibility of direct field effect from the Cδ+——δ-H dipoles of the C—H bonds in the methyl group(s) on the ^{13}C nucleus. However, the contrast between response of ^{13}C and ^{17}O to effects of substituents strongly suggests that they could hardly be explained in this relatively simple manner. The conclusion appears to be inescapable that the solution of the problem must be sought in the N.M.R. processes themselves. We submit that in view of the present, limited state of knowledge of the origin of shielding effects, proposals to set aside the well-supported concept of the electron donation by methyl substituents, are unacceptable.

REFERENCES

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(2) The terms electron-push and -pull (or withdrawal) are used instead of electronegative etc., in order to avoid a possible ambiguity.

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This is a Foreword to a memoir by H.D. Scharf, F. Fleischhauer and F. Korte, including references to other papers of Korte *et al* concerning nitration of quinol ethers.

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ADDENDUM:

We are grateful to Professor A.R. Katritzky, for drawing our attention to a Communication by P.R. Schleyer and C.W. Woodworth [J. Amer. Chem. Soc., 90, 6528 (1968)] in which the polar property of methyl replacing hydrogen in saturated compounds is discussed. We concur in the conclusions of these authors and especially in the emphasis they lay on the importance of steric effects. These often operate in a reverse sense to that of the induced polar effect. It was mainly for this reason that the work on the nitration of mixed ethers of catechol and quinol was undertaken. Here a steric effect should be minimal.