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CORRELATION OF INFRA-RED FREQUENCIES AND INTENSITIES WITH REACTIVITY DATA

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CORRELATIONS of various physico-chemical quantities with reactivity parameters often lack a physical meaning (1). An exception are spectral transitions in the IR-region which are considered to be controlled by similar factors as the reactivity, provided that the reduced mass is practically independent of substitution (1). In such a case the reactivity of a given functional group could be predicted on the basis of its measured characteristic frequency (2) and the reactivity parameters (constant σ) could be calculated, especially for some sensitive substituents (3). The correlation with IR-intensities has a similar meaning (3) (4); in both cases in addition to the use in the spectroscopy itself.

The correlations described both with frequencies and with intensities are of a relatively low accuracy (3) (4) (5). This can be caused either by experimental unaccuracies which can be relatively considerable when compared with differences between individual compounds or by specific substituent effects affecting one of the quantities correlated. To decide between these possibilities we consider necessary to study a great number of systematically chosen substituents and to compare only data in a single solvent and from one laboratory. We chose the valence vibration of the $C\equiv N$ bond as one of the most simple possibilities and measured the frequencies and integrated intensities of about 80 meta and para substituted benzonitriles in chloroform solution. The substituents were Me, CH_2X, CF_3, COX, CN, Ph, NH_2, NMe_2, NHAc, NO_2, OX, SO_2X, Hal. Our results were mostly in good accordance with previous measurements in the same solvent (5). We believe to have achieved a relative accuracy of about 0.3 cm^{-1} with the frequencies and 10% with the intensities.

On plotting $\nu_{C\equiv N}$ vs. substituent constants σ (6) we found that the substituents can be divided into three classes (Fig.1) : 1. para-Substituents with no free electron pair in the α position (NFE-substituents, denoted as in Fig.1), considered by us as being negligibly conjugated with benzene nucleus (6), raise the frequency proportionally to their σ_p constant. The slope is cca 6.8 cm^{-1} and the scatter exceeds about twice the experimental error. 2. para-Substituents with a free electron pair in the α-position (FE-substituents, denoted as ◑) strongly conjugated as donors with benzene nucleus as well as with cyano group cause a larger lowering of the frequency than corresponds to their σ_p constant; the deviation is greater with stronger donors. This behaviour cannot be accounted for quantitatively by using σ_p^+ constants which express an enhanced conjugation (7); such a correction is still too small with the strong donors and at the same time too large with the weaker ones. 3. The most remarkable results were obtained with meta-substituents (denoted as ○) where the found frequency is in all cases higher than corresponds to the electronic effect of the substituent as expressed by the constant σ_m. We have to deal with a specific effect, probably of kinematic nature, acting on IR frequencies only. In no instance there is a simple relation between the frequency enhancement and the mass of the substituent or its electronic effect. Likewise the simple distortion of molecular symmetry in meta derivatives cannot be regarded as an explanation since with symmetrical 3,5-bisderivatives a twice as great deviation is encountered. For the kinematic nature of this effect an evidence is given by the different behaviour of pyridine derivatives (aza "substituent"); here the 3-derivative shows a higher frequency.

As to the correlations of IR intensities there is a controversy which function of A should be proportional to the σ constant (8) (9). In view of the physical meaning of the quantity A we consider it most correct to plot

Fig. 1

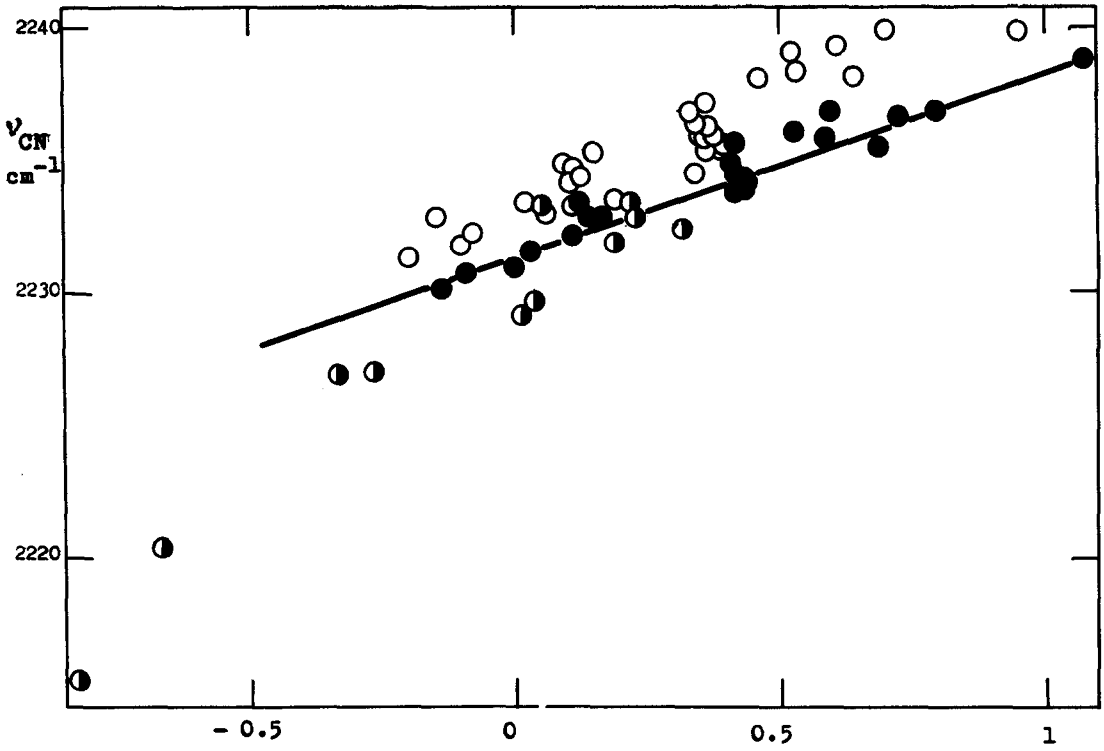
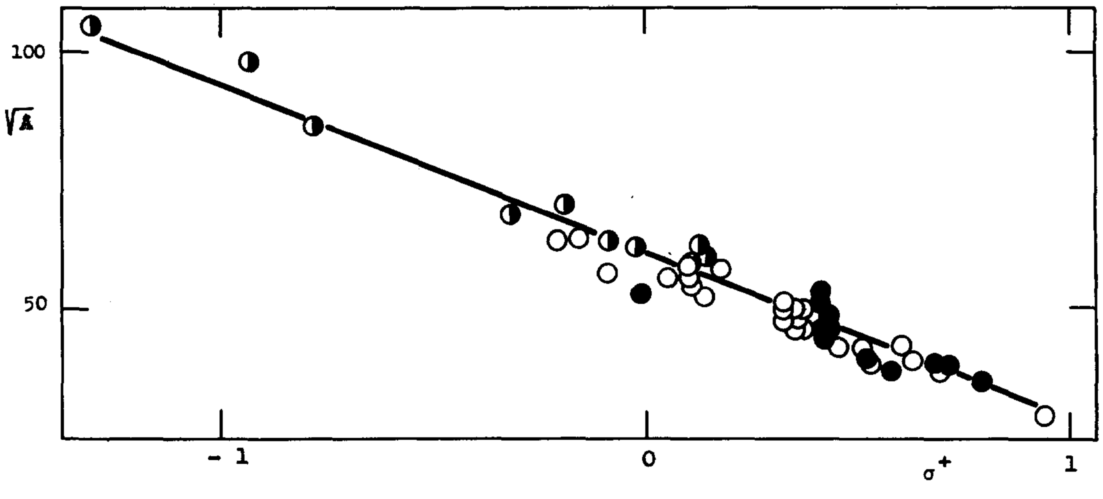


Fig. 2



the value $\sqrt{A}$ (9) but by using log A the same accuracy was achieved (3). From Fig.2 it follows that the correlation with σ^+ constant (7) shows a reasonable linearity in view of the considerable experimental errors. There is no difference between meta and para substituents. The use of σ^+ constants expressing a direct conjugation between the substituent and the CN group is substantiated by the strong electron demanding character of the stretching process (8) (9). With the strongest donor even a normal σ^+ value is not large enough. Similar conclusions were reached at by Brown (9) on a set of 17 compounds.

The main result of the present paper is that the IR frequencies and reactivities cannot be immediately compared as they are controlled by different effects even with most simple model substances. A further task is to find out to which extent the phenomenon on Fig.1 is a common one and to give its theoretical interpretation. The relation of IR intensities to the reactivity is probable a closer one but its greater practical application is still hindered by the unsufficient experimental accuracy.

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