INFRARED SPECTRA AND STRUCTURE OF CARBANIONS.III[*]. HAMMETT STUDY OF THE

FREQUENCIES OF THE NITRILE GROUP IN INTERMEDIATES FORMED BY NUCLEOPHILLIC

ADDITION TO TRANS-α-CYANOSTILBENES

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The presence of electronoaccepting substituents in ethylenes favours the nucleophillic addition reactions [1]:

(A , N^- and E^+ are acceptor , nucleophile and electrophile , respectivelly)

When the nucleophillic attack is carried out in aprotic solvents (E^+ is usually H^+) the intermediate (I) has been isolated in several cases . The participation of such intermediates has been considered in almost all mechanisms proposed for this kind of reactions.[1]

When CH_3ONa (or another nucleophile) is added to substituted trans-α-cyanostilbenes (II) adducts are formed , the structure (III) of which is consistent with their UV [2] and NMR [3] spectra. A discussion of the structure of the adducts , based on their IR spectra is also to be reported. [4]

The conjugation of the nitrile group with the carbanionic center negative charge , marked in (III) reduces strongly the C≡N bond order , which ought to be accompanied by a lowering of the nitrile group frequency (ν_{CN}).[5]

Indeed , upon adding CH_3ONa (solid or dimethyl sulfixide solution) to dry DMSO solutions of (II) , under pure argon , the bands at 2218-2202 cm^{-1} (ν_{CN} of the neutral compounds (II)) disappeared , and very intense bands in the 2147 -

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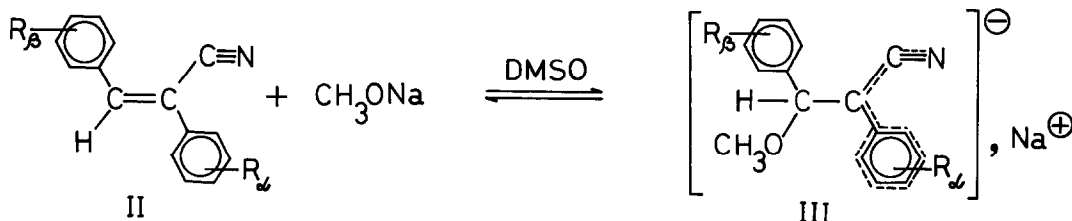[*]For parts I and II see ref.5 .

- 2064 cm^{-1} region (ν_{CN} of the carbanions (III)) appeared.

The characteristic group infrared frequencies can be in good many cases described satisfactorily by Hammett-type equations.[6,7] Because of the electronoaccepting character of the $C{\equiv}N$ group, ν_{CN} of substituted benzonitriles correlate with σ^+ better, than with σ,[8,9] but there exists only a general relationship between ν_{CN} of benzonitriles and substituent constants (a correlation coefficient (r) of only 0,965 has been found for a basic set of substituents)[9], and the m-substituted compounds have shown in chloroform systematic deviations from the correlation line (meta-effect).[10] On the other hand, ν_{CN} of (II) and some other substituted cyanoethylenes (in CCl$_4$ and CHCl$_3$) correlate well with σ^+ and considerably more poorly - with σ .[11]

Correlating the IR characteristics of carbanions with substituent constants can afford some insight data about the electronic structure of these important reaction intermediates , and also data on the mechanism of transmission of substituent polar effects through an carbanionic center.

The frequencies ν_{CN} of the carbanions studied (III , R_β = H) correlate well with the σ^- constants (r = 0,979 , Fig.1) and much more poorly - with σ and σ^+ (r = 0,88 and 0,82 , respectivelly). The steep correlation slope (ρ= 41,0) can be explained by the competitive conjugation of the carbanionic center on the one hand with the nitrile group , and on the other - with the substituent R_α . Since in the present case the characteristic group $[C{\doteq}C{\equiv}N]^\ominus$ is electron-rich , by analogy with the data from Hammett studies of organic reactivity of compounds with a nucleophillic reaction center ,[12] the best fit with the nucleophillic substituent constants is not surprising.

Since the β-phenyl ring is insulated from the characteristic group , the effect of R_β on ν_{CN} of the carbanions (III , R_α = H) is ca. one order weaker , and it corresponds in general to the constants σ^o of R_β ($\rho \sim$ 5 cm^{-1}).
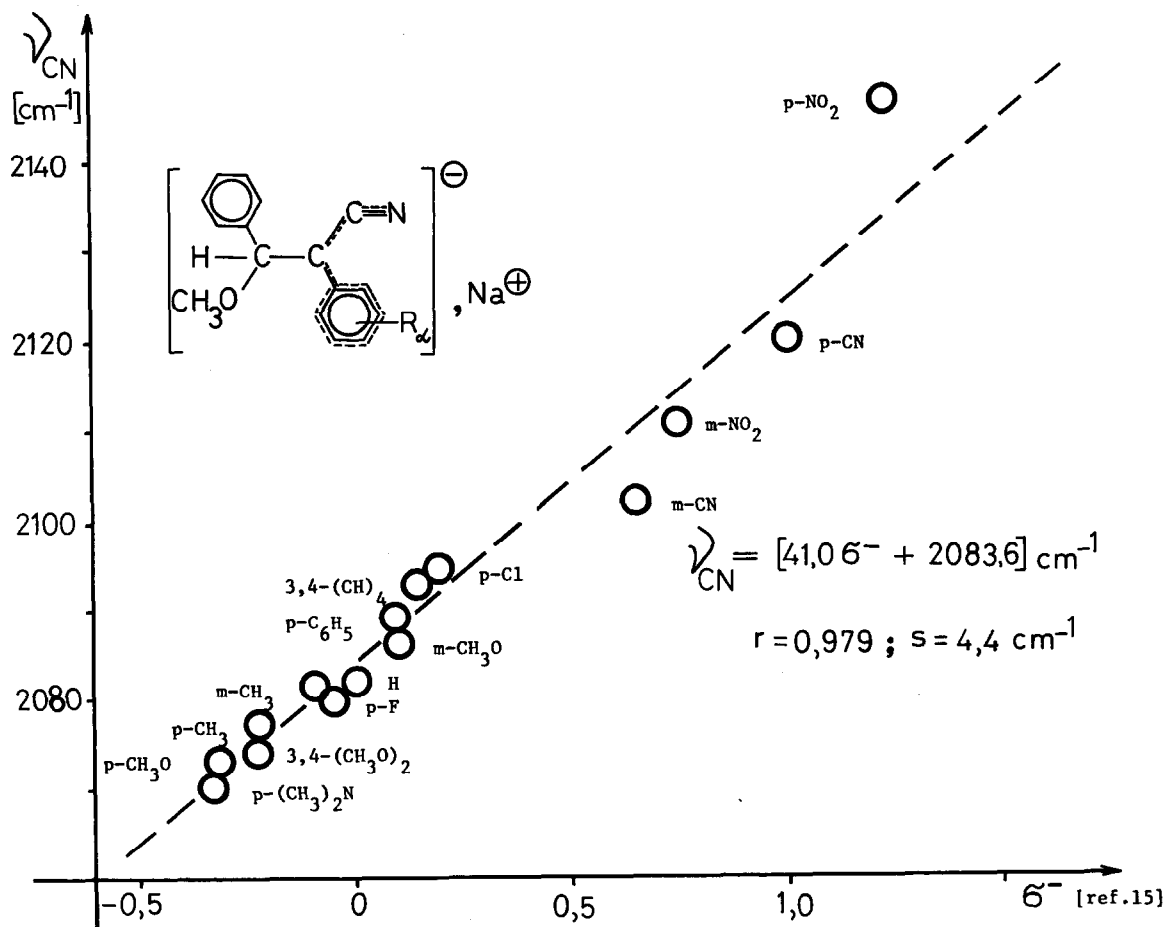
Fig. 1.

On the contrary, in the neutral compounds (II) the effect of R_β is considerably stronger, than the one of R_α, and this is seen from the correlation equations of ν_{CN}/cm^{-1}/ of (II) (in DMSO):

(II, R_α = H, n = 16): ν_{CN} = 2216,4 + 7,5σ (r = 0,92), ν_{CN} = 2217,6 + 4,8σ^+ (r = 0,96)

(II, R_β = H, n = 17): ν_{CN} = 2214,9 + 2,0σ (r = 0,89), ν_{CN} = 2215,2 + 1,2σ^+ (r = 0,82)

Similarly to some other cases of carbanions, containing a nitrile group[5] the unusually high intensity (A $\sim$ /50 - 150/.10^{3}l.mol^{-1}.cm^{-2}) of the ν_{CN}

bands of the adducts studied (while $A = /1,8 - 9,6/.10^3 1.mol^{-1} cm^{-2}$ was found

for (II)[13]) , is obviously due to the strong migration of the carbanionic

negative charge over the conjugated system in the course of the ν_{CN}

vibration. A strong increase in the ν_{CN} intensities is characteristic also

for the anion-radicals of aromatic nitriles.[14]

The results of Hammett investigation of ν_{CN} of the trans-α-cyano-

stilbenes carbanionic adducts thus made , are in good agreement with the

structure ascribed to these intermediates , which structure includes strong

resonance interactions of the characteristic group $[C{=}C{\equiv}N]^{\ominus}$ with the

substituents R_α and weak effects of R_β .

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