

INFRARED SPECTRA AND STRUCTURE OF CARBANIONS.

VI. TRANSMISSION OF THE SUBSTITUENT EFFECTS THROUGH A CARBANIONIC CENTER.

I.N.Juchnovski, I.G.Binev and Ts.M.Kolev

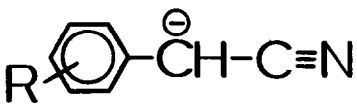
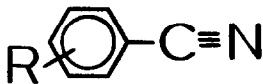
Institute of Organic Chemistry, Bulgarian Academy of Sciences,
1113 Sofia, Bulgaria.

(Received in UK 5 March 1976; accepted for publication 22 March 1976)

The infrared frequencies of characteristic groups can be satisfactorily described in a great number of cases by Hammett-type equations.^{1,2} In the case of carbanions, correlations of I.R. spectral characteristics with substituent constants can provide information on the electronic structure of these important reaction intermediates, insight into the structure of the carbanionic center itself, the mechanism and effectiveness of the transmission of the electronic effects across this center³, etc.

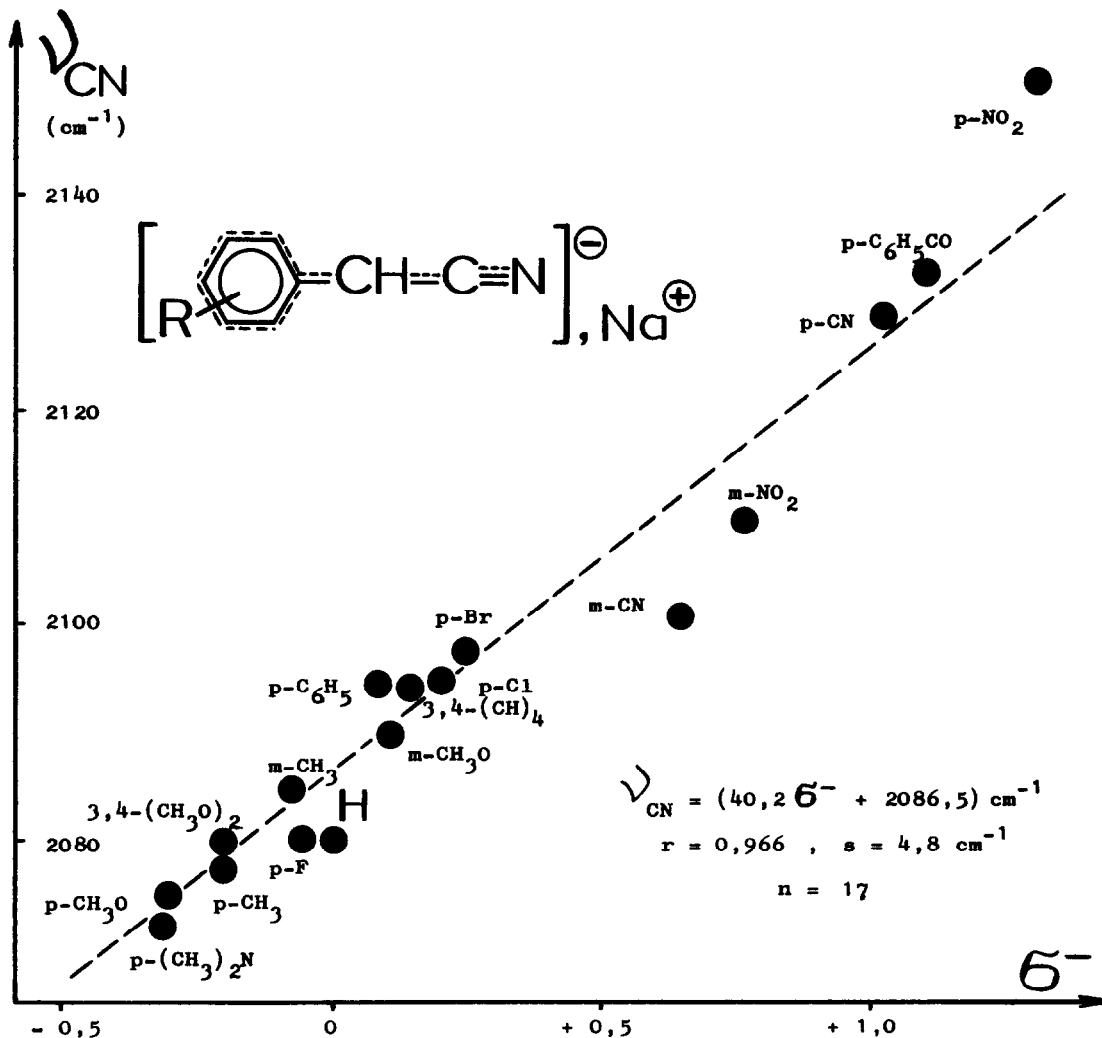
As in the case of the previously studied trans- α -cyanostilbene carbanionic adducts, the ν_{CN} bands of the carbanions of substituted phenyl-acetonitriles appear in a very broad frequency region, viz. 2072 - 2151 cm^{-1} (Fig., Footnote 4).

T A B L E¹⁰

<u>No</u>	<u>S E R I E S</u>	<u>C O R R E L A T I O N</u>	<u>ρ</u>	<u>a</u>	<u>r</u>	<u>n</u>
1.		(a) $\nu_{\text{CN}}/\bar{\sigma}^-$ (b) $\nu_{\text{CN}}/\bar{\sigma}$ (c) $\nu_{\text{CN}}/\bar{\sigma}^+$	40,2 43,1 24,4	2086,5 2091,2 2097,0	0,966 0,844 0,746	17 17 17
2.		(a) $\nu_{\text{CN}}/\bar{\sigma}$ (b) $\nu_{\text{CN}}/\bar{\sigma}^+$	13,61 9,50	2225,4 2227,7	0,940 0,944	34 30

The correlation of ν_{CN} with substituent constants (Table) showed best fit with $\bar{\sigma}^-$ values¹¹ (Fig.).

Part V: J.Organometal.Chem., **92**, 1 (1975). Parts III and IV: ref.3.



Since on the contrary, in a variety of solvents ν_{CN} of conjugated nitriles (e.g. substituted benzonitriles; see ref.5 and the Table) correlate best with the σ^+ constants, the results reported in the Table (series 1) are an evidence for a change in the mechanism of transmission of the substituent effects when a carbanionic center is placed between the substituents and the indicator group.

A measure of the effectiveness of transmission of the substituent effects through a bridging function, is the transmission coefficient of the bridging group ($\tilde{\pi}'$), defined as $\tilde{\pi}'_B = \rho_B / \rho^0$, where ρ_B and ρ^0 are the slopes of a given correlation for series with and without the bridge B.

The introduction of an additional bridging function between the

substituent and the reaction center (or indicator group) usually^{1,6} leads to a lowering of ρ , i.e. $\pi' < 1$. Exceptions are characteristic of bridges of the kind - O -, - NH -, - S - etc.; in these cases an increase in the substituent effects has been observed. This phenomenon has been termed⁷ as a "positive bridge effect"; the highest π' values have been obtained in the case of - NH - and - S - groups as bridges ($\pi' = 1,4 - 1,6$)⁶ (see also ref. 8).

It was previously found⁹ that the structure of the alkali-metal derivatives of arylacetonitriles in dimethylsulfoxide and hexamethyl-phosphor-triamide corresponds to the Formula on the Figure - "free" ionic particles, the mesomeric anions and the alkali-metal counter-ions being separately solvated. This fact allows us to define π' in the usual manner^{1,6}, i.e. the carbanions of substituted phenylacetonitriles may be considered as substituted benzonitriles, in which the substituent and the indicator group are additionally separated by the carbanionic center (see the Formulae in the Table).

Thus, the transmission coefficient of the carbanionic center can be determined by means of the data in the Table (footnotes 10 and 12):

$$\pi'_{\text{CH}^-} = \frac{\rho(\text{ser.1b})}{\rho(\text{ser.2a})} = 3,2$$

In a similar fashion, by using the data in ref.3, we obtained a π' value of 3,5 for the group $\text{C}_6\text{H}_5-\overset{\ominus}{\text{C}}-\text{CHOCH}_3$.

There are no data in the literature concerning the transmission coefficients of carbanionic centers; the values reported here are the highest among all the coefficients known for groups showing a positive bridge effect. The observed strong amplification of the substituent effects on the $\text{C} \equiv \text{N}$ indicator group, when the length of the conjugated system is increased with a carbanionic center is probably due to the high mobility of its electronic charge.

REFERENCES AND FOOTNOTES

1. Yu.A.Zhdanov and V.I.Minkin, Correlation Analysis in the Organic Chemistry, (russ.), izd. Rostovskogo Universiteta (1966).
2. A.R.Katritzky and R.D.Topsom, in Advan. LFER, ed. by N.B.Chapman and J.Shorter, Plenum press, London (1972), Ch. 3.
3. I.N.Juchnovski and I.G.Binev, Tetrahedron Letters, 1974, 3645; I.G.Binev and I.N.Juchnovski, Commun.Dept.Chem.Bulg.Acad.Sci., (in press).
4. We obtained the carbanions studied by adding dimsyl-sodium to the solutions of the corresponding C-H acids, in DMSO; we ran the spectra on a UR-10

"Zeiss" instrument, using calcium fluoride cells.

5. L. Deady, A.R. Katritzky, R.A. Shanks and R.D. Topsom, Spectrochim. Acta, **29A**, 115 (1973);
C. Laurence and B. Wojtkowiak, Bull. Soc. Chim. France, **1971**, 3124;
O. Exner and K. Bocek, Coll. Czech. Chem. Commun., **38**, 50 (1973);
I.N. Juchnovski, Dokl. AN SSSR, **186**, 878 (1969);
I.N. Juchnovski and I.G. Binev, data from spectra of HMPA and tetrahydrofuran solutions, which will be published.
6. V.A. Pal'm, Basic Principles of the Organic Reactions Quantitative Theory, (russ.), Khimiya, Leningrad (1967).
7. L.M. Litvinenko, Izv. AN SSSR (khim.), **1962**, 1737.
8. J.B. Hyne and J.M. Greidanus, Chem. Abstracts, **70**, 28098 (1969).
9. I.N. Juchnovski, Teoret. Eksp. Khim., **3**, 410 (1967);
I.N. Juchnovski and I.G. Binev, Compt. Rend. Acad. Bulg. Sci., **26**, 659 (1973);
I.N. Juchnovski and I.G. Binev, J. Organometal. Chem., **92**, 1 (1975);
I.G. Binev, Thesis, Inst. Org. Chem., Bulg. Acad. Sci., Sofia (1975).
10. Spectra in DMSO solutions only. ρ and a are the slope and the intercept in the correlation equation $\nu = \rho \bar{\sigma} + a$; r and n are the correlation coefficient and the number of the compounds in the corresponding series, resp.
11. Tseng Kuang-Chih, Acta Chim. Sinica, **22**, 107 (1966).
12. The slope of the correlation of ν_{CN} for the substituted benzonitriles depends considerably on the solvent (cf. ref. 5). For this reason it was necessary to obtain data about the correlations in DMSO. On the other hand, because of the dependence of ρ upon the type of the $\bar{\sigma}$ values, series 1b was used for obtaining $\tilde{\rho}$ instead the series, showing the best fit (series 1a).