Tetrahedron. Vol 33, pp 2993 to 2995 Pergamon Press 1977 Printed in Great Britain

INFRARED SPECTRA AND STRUCTURES OF CARBANIONS—XI

ESTIMATION OF σ^+ CONSTANTS OF ANIONIC SUBSTITUENTS[1]

I. N. JUCHNOVSKI* and I. G. BINEV
Institute of Organic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

(*Received in UK* 17 *March* 1977; *Accepted for publication* 16 *May* 1977)

Abstract—σ^+ constants of $H_2\overset{\ominus}{C}$– (−11.2), $HN\overset{\ominus}{-}$ (−7.6), $C_2H_5OOC\text{-}H\overset{\ominus}{C}$– (−5.0), $NC\text{-}H\overset{\ominus}{C}$– (−5.4) and some other anionic substituents were estimated on the basis of ν_{CN} of the corresponding benzonitrile anions and by using the correlations ν_{CN}/σ^+ for benzonitriles, in polar aprotic solvents.

The idea of determining substituent constants on the basis of IR spectral data was put forward with the first satisfactory correlations of IR frequencies and intensities with substituent constants;[2] this is the manner in which σ, σ^0, $\sigma_R{}^0$, etc. values have been determined for a large number of substituents.[3] On the other hand, this method has been criticized quite recently by Exner[4] on the basis of solvent and "meta"[5] effects, and by Deady *et al.*,[6] where series showing no excellent fit are found. In spite of these limitations, the correlations with IR data present a convenient means of estimating sigma-values particularly for substituents with which the standard chemical methods are unapplicable.

RESULTS AND DISCUSSION

We used the series of nitrile group frequencies (ν_{CN}) of substituted benzonitriles as a standard one for obtaining the electrophillic constants of anionic substituents. Correlations of ν_{CN} of benzonitriles with variety of sigma-constant types have been studied repeatedly;[2,5-7] because of the resonance electron-withdrawing character of the nitrile group ν_{CN} of benzonitriles correlate with σ^+ better than with σ.[6,8] Carbon tetrachloride and chloroform have been used as solvents[2,5-7] to avoid strong solvent-solute interactions.[8] Unfortunately, these solvents are not suitable for ionic species; ethereal solvents are also unsuitable because of ion pairs formation.[9] IR spectra of organic anions containing nitrile group are conveniently studied in polar aprotic solvents.[10-12] For this reason we examined the correlations for this series in dimethyl sulphoxide (DMSO) and hexamethyl phosphoramide (HMPA); the results are shown in Tables 1 and 2.

It is seen from Table 2 that in a variety of solvents, ν_{CN} of substituted benzonitriles correlate with σ^+ much better, than with σ; the use of DMSO and HMPA as solvents does not adversely affect the correlation factors and ρ increases considerably when using polar solvents instead of CCl_4.

In order to evaluate σ^+ constants of a series anionic substituents, we measured ν_{CN} of the anions  C≡N (Table 3 and Experimental). The σ^+ values in Table 3 were obtained from the correlation equations of Series **7** (HMPA) and **8** (DMSO) (Table 2). The inaccuracies in σ^+ (Table 3) were calculated by simultaneously taking into account the quantities S_ρ, S_b and the instrumental error (see Experimental).

The satisfactory agreement between the electrophillic constant of the group p–$\overset{\ominus}{O}$–, found quite recently by Hoefnagel and Wepster ($\sigma^+ = -2.3$)[13] and the one estimated on the basis of IR correlations ($\sigma^+ = -2.5 \pm 0.3$, Table 3) can be considered as some confirmation of the correctness of the σ^+ values reported in Table 3.

It can be pointed out that most of σ^+ in Table 3 are considerably more negative than σ^+ of the strongest neutral conjugative electron-donor ($\sigma_p{}^+$–$(CH_3)_2N$ = −1.7),[14] i.e. the data indicate that the electron-releasing effects of these anionic substituents are many times stronger than that of the dimethylamino group.

σ^+ of substituents **1**, **2** and **3** (Table 3) increase with the increase in the electronegativity of the corresponding elements in the order C < N < O. Because of the absence

Table 1. ν_{CN} of "basic set"[6,8] benzonitriles  C≡N in polar aprotic solvents

R	in DMSO	in HMPA
m-$(CH_3)_2N$	2224.9	2224.6
p-$(CH_3)_2N$	2211.4	2212.8
m-CH_3O	2228.3	2228.6
p-CH_3O	2223.3	2223.1
m-CH_3	2227.1	2227.1
p-CH_3	2226.4	2226.3
H	2227.2	2226.8
m-F	2233.1	2232.6
p-F	2230.3	2229.4
m-Cl	2231.8	2231.2
p-Cl	2229.8	2229.2
m-CF_3	2234.7	2233.8
p-CF_3	2232.8	2231.6
m-CN	2234.6	2234.2
p-CN	2230.8	2229.9
m-NO_2	2235.1	2235.1
p-NO_2	2232.8	2232.2

Table 2. "Basic set"[6,8] correlations of ν_{CN} (benzonitriles) with σ and σ^+

SERIES	SOLVENT	SIGMA	ρ^a	b^b	r^c	s^d	Notes
1.	CCl_4	σ	9.925	2231.7	0.9193	1.74	e
2.	$CHCl_3$	σ	12.436	2230.4	0.9212	2.16	f
3.	HMPA	σ	11.562	2226.5	0.9199	2.03	-
4.	DMSO	σ	12.527	2226.7	0.9200	2.19	-
5.	CCl_4	σ^+	7.000	2232.9	0.9573	1.28	e
6.	$CHCl_3$	σ^+	8.832	2231.9	0.9658	1.44	f
7.	HMPA	σ^+	8.104	2227.9	0.9519	1.58	g
8.	DMSO	σ^+	8.814	2228.3	0.9563	1.64	h

[a]slope; [b]intercept; [c]correlation coefficient; [d]standard deviation; [e,f]calculated by using data from refs. 6 and 5, resp.; [g]in this series: $S_\rho = 0.632$, $S_b = 0.4$ (inaccuracies in ρ and b, resp.); [h]in this series: $S_\rho = 0.654$, $S_b = 0.4$.

Table 3. σ^+ constants of anionic substituents $Z^\ominus$ and ν_{CN} of the anions Z–C≡N

No.	SUBSTITUENTS $Z^\ominus$	ν_{CN} (cm^{-1}) OF THE ANIONS	$\sigma^+_{Z^\ominus}$
1.	p-$H_2C^\ominus$–	2137[a]	−11.2 ± 1.1
2.	p-$HN^\ominus$–	2166[a]	−7.6 ± 0.8
3.	p-$^\ominus O$–	2206[b]	−2.5 ± 0.3
4.	m-$^\ominus O$–	2215[b]	−1.5 ± 0.3
5.	p-NC-$HC^\ominus$–	2181[b]	−5.4 ± 0.5
6.	m-NC-$HC^\ominus$–	2219[b]	−1.1 ± 0.2
7.	p-EtO_2C-$HC^\ominus$–	2184[b]	−5.0 ± 0.5
8.	p-$^\ominus O_2C$-H_2C–	2223.0[a]	−0.6 ± 0.1
9.	p-$^\ominus O_2C$-$HC^\ominus$–	2157[a]	−8.7 ± 0.9
10.	p-$^\ominus O_2C$–	2223.5[a]	−0.5 ± 0.1
		2224.7[b]	−0.4 ± 0.1

[a]in HMPA; [b]in DMSO.

of direct resonance with the nitrile group, the meta-substituents show considerably lower σ^+ values (absolute values).

The negative values obtained for the $\sigma^+_{CO_2^\ominus}$ constant show that the carboxylate anion appears as a conjugative electron-donor in the series studied. The comparison:

$\sigma^-_{CO_2^\ominus} = +0.145$ to $+0.351$ (Refs. 13, 15);

$\sigma_{CO_2^\ominus} = 0.0$ (Ref. 16);

$\sigma^+_{CO_2^\ominus} = -0.4, -0.5$ (This work);

can be considered as an evidence for the ±resonance character of the carboxylate anion, in agreement with the data of Lindberg.[17] Indeed by contrast, the same group acts as electron-acceptor in the dianion **9** (Table 3, cf. σ^+'s for substituents **1** and **9**).

There are no data in the literature on σ^+ constants of the substituents studied. Despite the considerable inaccuracy in their values (*ca.* ±10%), the constants reported here may be used as an approximate measure of the electron-releasing effects of the studied anionic substituents.

EXPERIMENTAL

The anions $^{\ominus}Z\text{-}C_6H_4\text{-}CN$ were obtained by metalating the corresponding neutral benzonitriles $HZ\text{-}C_6H_4\text{-}CN$ with naphthalene-disodium (in HMPA), and with dimsyl-sodium or sodium methoxide (in DMSO). We identified the ν_{CN} bands of the anions by the approach used in previous work[10,12] and having in mind the results of protonation of the anions, viz. regeneration of the parent benzonitriles.[12]

The spectra were recorded on a UR-20 Zeiss spectrophotometer using calcium fluoride cells. ν_{CN} were reproducible to about 0.3 cm^{-1} for the neutral nitriles in Table 1 and for the anions **8** and **10** in Table 3, and to about 0.5 cm^{-1} in the other cases.

Acknowledgements—The authors are highly indebted to Drs. I. Pojarlieff and V. Yomtova (Inst. Org. Chem., Bulgarian Acad. Sci.) for their interest and helpful advice on the papers in the present series.

REFERENCES

[1]Part VI: I. N. Juchnovski, I. G. Binev and Ts. M. Kolev, *Tetrahedron Letters* 1519 (1976); Parts VII–X: in press. Part VII: I. G. Binev, R. Todorova-Momcheva and I. Juchnovski, *C.R. Acad. Bulg. Sci.* **29**, 1301 (1976); Part VIII: I. Juchnovski, V. Radomirska, I. Binev and E. Grekova, J. *J. Organometal. Chem.* **128**, 139 (1977); Part IX: I. Binev, I. Juchnovski, Ts. Kolev, *Commun. Dept. Chem. Bulg. Acad. Sci.* **10**, 76 (1977); Part X: G. Andreev, Z. Demireva, I. Juchnovski, R. Kuzmanova and I. Binev, *Commun. Dept. Chem. Bulg. Acad. Sci* (in press).

[2]M. St. C. Flett, *Trans. Faraday Soc.* **44**, 767 (1948); L. J. Bellamy, *J. Chem. Soc.* 4221 (1955); C. N. R. Rao and R. Venkatarghavan, *Can J. Chem.* **39**, 1757 (1961).

[3]H. W. Thompson and G. Steel, *Trans. Faraday Soc.* **52**, 1451 (1956); R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell and R. D. Topsom, *J. Am. Chem. Soc.* **90**, 1757 (1968); B. J. Lindberg and B. Schröder, *Acta Chem. Scand.* **24**, 3089 (1970); A. A. Kane and I. F. Tupitzyn, *Trudy G.I.P.Kh.* **66**, 148 (1970); M. Berthelot, C. Laurence and B. Wojtkowiak, *J. Chim. Phys.* **70**, 1629 (1973).

[4]O. Exner, In *Advances in LFER* (Edited by N. B. Chapman and J. Shorter), Chap. 1. Plenum Press, London (1972).

[5]O. Exner and E. Svatek, *Coll. Czech. Chem. Commun.* **36**, 534 (1971); O. Exner and K. Boček, *Ibid.* **38**, 50 (1973).

[6]L. Deady, A. R. Katritzky, R. A. Shanks and R. D. Topsom, *Spectrochim. Acta* **A29**, 115 (1973).

[7]C. Laurence and B. Wojtkowiak, *Bull. Soc. Chim. Fr.* 3124, 3833, 3870, 3874 (1971); I. N. Juchnovski, *C.R. Acad. Bulg. Sci.* **19**, 743 (1966).

[8]A. R. Katritsky and R. D. Topsom, *Chap.* 3 in Ref. 4.

[9]M. Szwarc (Ed.) *Ions and Ion Pairs in Organic Reactions*, Vol. 1. Wiley-Interscience, New York (1972).

[10]I. N. Juchnovski, *Teoret. Eksp. Khim.* **3**, 410 (1967); I. N. Juchnovski and I. G. Binev, *Tetrahedron Letters* 3645 (1974); I. N. Juchnovski, I. G. Binev and Ts. M. Kolev, *Ibid.* 1519 (1976); I. N. Juchnovski and I. G. Binev, *J. Organometal. Chem.* **99**, 1 (1975); I. G. Binev and I. N. Juchnovski, *Commun. Dept. Chem. Bulg. Acad. Sci.* **9**, 33 (1976); Z. I. Demireva, I. G. Binev and I. N. Juchnovski, *Tetrahedron Letters* 1523 (1976).

[11]I. N. Juchnovski and I. G. Binev, *Chem. Phys. Letters* **12**, 40 (1971).

[12]I. G. Binev, Thesis, Inst. Org. Chem., *Bulg. Acad. Sci. Sofia* (1975).

[13]A. J. Hoefnagel and B. M. Wepster, *J. Am. Chem. Soc.* **95**, 5357 (1973).

[14]H. C. Brown and Y. Okamoto, *Ibid.* **80**, 4979 (1958).

[15]L. A. Cohen and W. M. Jones, *Ibid.* **85**, 3397 (1963); A. V. Willi and J. F. Stoker, *Helv. Chim. Acta* **38**, 1279 (1955); Tseng Kuang Chih, *Acta Chim. Sinica* **32**, 107 (1966).

[16]D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).

[17]B. J. Lindberg, *Acta Chem. Scand.* **22**, 571 (1968).