

NOTIZEN

Comment on the Relationship between ^1H Chemical Shifts and Net Charges

Helmut Vogler

Max-Planck-Institut für medizinische Forschung,
Abteilung Organische Chemie,
Jahnstraße 29, D-6900 Heidelberg, GermanyZ. Naturforsch. **40b**, 1415–1416 (1985);
received April 9, 1985Proton Shifts, Charged Conjugated Hydrocarbons,
Charge-Shift Correlations

The relationship between net charges and ^1H chemical shifts in cyclic conjugated charged hydrocarbons is investigated by taking into account explicitly ring current and local anisotropic contributions and the effect of ion-pairing.

The ^1H chemical shifts δ of cyclic conjugated compounds can be partitioned [1] according to

$$\delta = \delta^{\text{RC}} + \delta^{\text{LA}} + \delta^{\text{q}} + \delta^{\circ} \quad (1)$$

with the ring current (RC) and local anisotropic (LA) contributions δ^{RC} and δ^{LA} . δ° contains all isotropic contributions to δ . δ^{q} is related to the electronic charge distribution [2]. Experimental and theoretical studies [3, 4] provided evidence that

$$\delta^{\text{q}} \cong \alpha q \quad (2)$$

where q is the π net charge ($q < 0$ for excess electron density) on the adjacent carbon atom. A value of $\alpha \cong 10.7$ ppm/electron has been obtained [4] by a regression analysis between observed shifts and net charges in the diatropic [5] annulenes C_5H_5^- , C_6H_6 , C_7H_7^+ , and $\text{C}_8\text{H}_8^{2-}$. Herewith it was assumed that RC and LA terms do not differ considerably in these compounds and that the counterion does not affect the shifts. However, later work [6–8] demonstrated that proton shifts of charged annulenes depend significantly on the kind of counterion and so it was concluded [7] that the observed shifts cannot be rationalized by the simple relationship (2).

In this paper we report on our calculations of ^1H chemical shifts of annulenes C_5H_5^- , C_6H_6 , C_7H_7^+ , $\text{C}_8\text{H}_8^{2-}$, and C_9H_9^- according to eq. (1) utilizing the procedure of ref. [1] which was successfully applied to a considerable number of conjugated hydrocar-

bons [1, 9]. In solution counterion and annulene can form a free ion pair (FIP), a solvent-separated ion pair (SIP), or a contact ion pair (CIP) [6–8]. In a SIP the counterion interacts with the annulene mainly electrostatically. Thus the counterion can be represented by a pseudoproton [10]. In a CIP also covalent interaction between the valence orbitals of the counterion and the π system of the annulene has to be taken into account. Details of the parametrization are given elsewhere [11].

A uniform net charge distribution is encountered in the studied annulenes. Consequently the resulting electrostatic potential directs the counterion over the centre of the perimeter. Such an ion-pairing was found by X-ray analysis [12] for a derivative of $\text{C}_8\text{H}_8^{2-}/2\text{K}^+$ and by *ab initio* calculations [13] for $\text{C}_5\text{H}_5^-/\text{Li}^+$. Furthermore it rationalizes the fact that only one signal is observed in the proton NMR spectra for the charged annulenes [6, 7]. The distance between the counterion and the plane of the annulenes was fixed at 237.5 pm (K^+) [12] and 175 pm (Li^+) [13] for a CIP and 300 pm for a SIP.

The experimental and calculated proton shifts and net charges q are given in Table I. The K^+ counterion forms exclusively CIP's [6–8]. For $\text{C}_5\text{H}_5^-/\text{Li}^+$ it was shown [14] that it exists in solution as a CIP whereas $\text{C}_9\text{H}_9^-/\text{Li}^+$ forms a SIP and C_7H_7^+ a FIP or a SIP [7]. RC and LA terms and the net charges for a FIP do not differ from those of a SIP. Therefore the observed shifts δ_{exp} are uniquely related to calculated ones. It is possible to determine the constants α and δ° by a regression analysis between $(\delta_{\text{exp}} - \delta^{\text{RC}} - \delta^{\text{LA}})$ and q . We obtain the regression line

$$(\delta_{\text{exp}} - \delta^{\text{RC}} - \delta^{\text{LA}}) \pm 0.12 = (11.1 \pm 0.5)q + (5.2 \pm 0.05) \quad (3)$$

with a correlation index of 0.995. The value $\alpha = 11.1$ ppm/electron is similar to the one proposed earlier [4]. $\delta^{\circ} = 5.2$ ppm agrees approximately with those values given for benzenoid and olefinic protons [1]. Using these α and δ° parameters we calculate proton shifts δ which agree well with the observed ones. The maximum deviation is less than 0.2 ppm.

The proton shifts for the CIP's of C_5H_5^- , $\text{C}_8\text{H}_8^{2-}$, and C_9H_9^- are larger by 0.3 ppm (C_9H_9^-) and 1.2 ppm (C_5H_5^- , $\text{C}_8\text{H}_8^{2-}$) than those of the FIP's or SIP's. The difference is mainly due to the electron transfer from the annulene to the counterion leading to a numerical reduction of the net charges q and hence of δ^{q} . Table I reveals that the sum $(\delta^{\text{RC}} + \delta^{\text{LA}})$ varies between 1.2 ppm (C_5H_5^-) and 2.9 ppm



Table I. Calculated (δ^{RC} , δ^{LA} , δ^{q} , δ) and experimental (δ_{exp}) ^1H chemical shifts (in ppm) and net charges q for neutral and charged [n]annulenes.

Compound	Ion-pairing	Counterion	δ^{RC}	δ^{LA}	q	δ^{q}	δ	δ_{exp}	Ref.
C_5H_5^-	FIP/SIP		0.40	0.81	-0.200	-2.22	4.19		
	CIP	Li^+	0.10	0.68	-0.011	-0.12	5.86	5.71	[6]
	CIP	K^+	0.14	0.70	-0.057	-0.63	5.41	5.51	[6]
C_6H_6			0.72	1.37	0	0	7.29	7.27	[17]
C_7H_7^+	FIP/SIP	^a	1.04	1.44	0.143	1.59	9.27	$9.28 \pm 0.12^{\text{b}}$	[7]
$\text{C}_8\text{H}_8^{2-}$	FIP/SIP		1.32	0.68	-0.250	-2.78	4.42		
	CIP	K^+	1.80	0.47	-0.160	-1.78	5.69	$5.80 \pm 0.05^{\text{c}}$	[7]
C_9H_9^-	FIP/SIP	Li^+	1.83	1.05	-0.111	-1.23	6.85	6.77	[7]
	CIP	K^+	1.83	0.94	-0.073	-0.81	7.16	7.03	[7]

^a Several cations; ^b several solvents excluding those which contain oxygen; ^c several solvents.

(C_9H_9^-) but is less affected by ion-pairing than δ^{q} . This was to be expected for diatropic annulenes according to qualitative theoretical considerations [15].

The results of this investigation demonstrate that in a semi-empirical π -electronic approach for the calculation of proton shifts in charged alternant hydrocarbons according to eq. (1) the effect of net charges can be described well enough by the simple relationship (2) if the ion-pairing is explicitly taken into account. Non-vanishing net charges and hence

δ^{q} terms are also encountered in neutral non-alternant or heteroconjugated compounds. However, there is some indication [16] that in such systems different α parameters will have to be used if the σ -core polarization is neglected.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out in the Universitätsrechenzentrum Heidelberg on the IBM 3081 D.

- [1] H. Vogler, *J. Am. Chem. Soc.* **100**, 7464 (1978).
 [2] M. Karplus and J. A. Pople, *J. Chem. Phys.* **38**, 2803 (1963).
 [3] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.* **82**, 5846 (1960); H. Spiesscke and W. G. Schneider, *Tetrahedron Lett.* **1961**, 468; C. MacLean and E. L. Mackor, *Mol. Phys.* **4**, 241 (1961); J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron, Suppl. 2*, **19**, 65 (1963); P. J. Black, R. D. Brown, and M. L. Heffernan, *Aust. J. Chem.* **20**, 1305 (1967).
 [4] T. Schaefer and W. G. Schneider, *Can. J. Chem.* **41**, 966 (1963).
 [5] F. Sondheimer, *Acc. Chem. Res.* **5**, 81 (1972).
 [6] J. B. Grutzner, J. M. Lawlor, and L. M. Jackman, *J. Am. Chem. Soc.* **94**, 2306 (1972).
 [7] R. H. Cox, L. W. Harrison, and W. K. Austin (Jr.), *J. Phys. Chem.* **77**, 200 (1973).
 [8] K. Müllen, *Chem. Rev.* **84**, 603 (1984) and references therein.
 [9] H. Vogler, *Tetrahedron Lett.* **1979**, 229; *Tetrahedron* **35**, 657 (1979); *Org. Magn. Reson.* **12**, 306 (1979); *J. Mol. Struct.* **51**, 289 (1979); *Croat. Chem. Acta* **57**, 1177 (1984); *J. Mol. Struct. (Theochem)* **122**, 333 (1985); *Org. Magn. Reson.*, in press.
 [10] J. Spanget-Larsen, *Mol. Phys.* **32**, 735 (1976).
 [11] H. Vogler, *Mol. Phys.*, in press; T. Meul, K. Müllen, and H. Vogler, in preparation.
 [12] S. Z. Goldberg, K. N. Raymond, C. A. Harmon, and D. H. Templeton, *J. Am. Chem. Soc.* **96**, 1348 (1974).
 [13] E. D. Jemmis and P. v. R. Schleyer, *J. Am. Chem. Soc.* **104**, 4781 (1982).
 [14] R. H. Cox and H. W. Terry (Jr.), *J. Magn. Reson.* **14**, 317 (1974).
 [15] H. Vogler, *Chemica Scripta* **24**, 188 (1984).
 [16] G. Ege and H. Vogler, *Mol. Phys.* **30**, 1511 (1975); S. Fliszár, G. Cardinal, and M.-T. Bérardin, *J. Am. Chem. Soc.* **104**, 5287 (1982).
 [17] C. W. Haigh and R. B. Mallion, *Mol. Phys.* **18**, 737 (1970).