Journal of Organometallic Chemistry, 293 (1985) 131–137
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ION-PAIRING EFFECTS ON ^{1}H NMR CHEMICAL SHIFTS OF CYCLIC CONJUGATED CARBANIONS

HELMUT VOGLER

Max-Planck-Institut für Medizinische Forschung, Abteilung Organische Chemie, Jahnstr. 29, D-6900 Heidelberg (Federal Republic of Germany)

(Received March 21st, 1985)

Summary

The ^{1}H NMR chemical shifts of the cyclic conjugated hydrocarbon carbanions: cyclopentadienyl, cyclooctatetraene, cyclononatetraenyl, benzyl and methylenecyclooctatrienyl anions, have been studied by a semiempirical approach in which the alkali counter ions are explicitly taken into account. The importance of electrostatic and covalent interactions between the ions and the ion-pairing effects on the proton shifts are elucidated.

Introduction

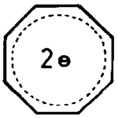
Conjugated hydrocarbon carbanions and their counter ions exist as equilibrium mixtures of solvent-separated ion pairs (SIP's) and contact ion pairs (CIP's), the ratio of which can be influenced by the solvent, temperature, and counter ion [1,2]. The mutual orientation of the ions in the solid state can be deduced from X-ray analysis, but for solutions of organometallic ion pairs no such direct method is available. However, it can be expected that the proton shifts of cyclic conjugated carbanions will provide a sensitive probe for ion-pairing effects, since their ^{1}H NMR spectra exhibit important effects [2] which can be rationalized qualitatively by means of the ring current model [3,4].

In this paper we present the results of calculations of ^{1}H NMR chemical shifts for the species: cyclopentadienyl anion (**1**), cyclooctatetraene dianion (**2**), and cyclononatetraenyl anion (**3**), as well as of benzyl anion (**4**) and methylenecylcooctatrienyl anion (**5**) which can be regarded as representing annulenes with one exocyclic bond, see Fig. 1. Counter ions have not previously been taken explicitely into account in the calculation of proton shifts of negatively charged conjugated systems.

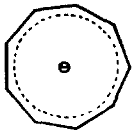
The ^{1}H NMR chemical shifts δ are calculated by means of a π-electronic procedure [5] where δ is obtained as a sum $\delta = \delta^{RC} + \delta^{LA} + \delta^{q} + \delta^{0}$; δ^0 defines the zero of the δ-scale, δ^{RC} represents the ring current contribution of the π-system, δ^{LA}

0022-328X/85/$03.30

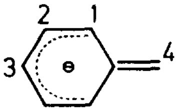
1



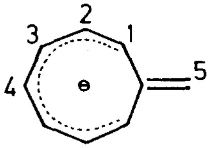
2



3



4



5

Fig. 1. The carbanions studied.

is the local anisotropic contribution of π- and σ-electrons (which has been shown to be important in the case of annulenoid compounds [6]), and $\delta^q(= a \cdot q$ [7]) is the shift due to a net charge q at the carbon atoms bonded to the proton in question.

In a SIP the counter ion interacts with the conjugated system mainly electrostatically whereas covalent binding should also be taken into account in the case of a CIP. Consequently a simple description of a SIP is obtained if the counter ion is represented by a pseudoproton P [8] whose electric field is transmitted by a Coulomb integral γ_{sP} between π-basis functions χ_s at atoms s in the π-network and P. γ_{sP} is calculated by means of the Mataga–Nishimoto formula [9] with a one-centre integral γ_{PP} 20.408 eV. For a CIP we use a supermolecule approach for π-system and counter ion; only alkali ions are considered here although the results can be readily generalyzed. The resonance integrals between the *ns* and *np* valence orbitals of the alkali atom and the π-basis functions are calculated as in ref. 10, by use of the Wolfsberg–Helmholtz equation [11] with $K = 1.75$ and neglecting overlap integrals between non-neighbours in the π-network. The core energies U and the one-centre repulsion integrals for the alkali atoms have been obtained from ionization potentials I [12] and g values [13] according to $U = I + U_C - I_C$ and $\gamma = g\gamma_{CC}/g_C$, where U_C and γ_{CC} are the parameters given in ref. 5 for carbon.

Results and discussion

The annulenes **1**–**3** are characterized by a uniform distribution of the negative charge over the perimeter. The electrostatic potential produced by such a charge distribution will direct the counter ion over the centre of the perimeter resulting in ion pair arrangements **A** (cf. Fig. 2) for **1** and **3** and **B** for **2**. Such an ion-pairing is consistent with the fact that only one signal is observed in the ^{1}H NMR spectra of **1**–**3** [14,15]. Furthermore, structure **B** was found by X-ray analysis [16] for a derivative of **2**/2K$^+$. The experimental proton shifts of **1**–**3** are given in Table 1, together with the calculated values for structures **A** and **B**. The distance between the

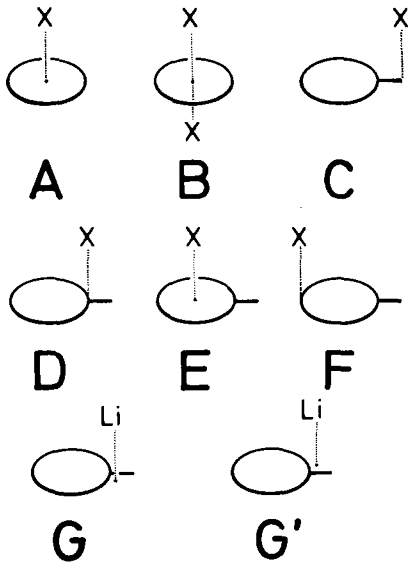


Fig. 2. Schematical representation of ion pair arrangements.

counter ion and the plane of the π-network was fixed at 175 pm (Li^+) [17] and 237.5 pm (K^+) [16] for a CIP and 300 pm for an SIP.

The ^1H NMR chemical shifts derived by assuming an SIP for **1**–**3** do not differ from those of the free ion pair (FIP). The K^+ counter ion forms exclusively CIP's [2,14,15] and it has been shown [18] that **1**/Li^+ exists as a CIP except in solvents with good cation-solvating abilities in which **3**/Li^+ also forms an SIP. Thus the observed proton shifts δ_{exp} are uniquely related to the calculated values δ, and it is possible to determine the constants a and δ^0 by a regression analysis between $(\delta_{exp} - \delta^{RC} - \delta^{LA})$ and the net charges q. We obtain a value for a of 10.2 ppm/electron, which is similar to that proposed earlier [7], and a value of δ^0 of 5.09 ppm; this value agreeing approximately with those for benzenoid and olefinic protons [5]. Using these parameters a and δ^0 we calculate proton shifts δ which agree with the experimental values. The maximum error in the calculated δ values is less than 0.2 ppm.

TABLE 1

CALCULATED (δ) AND EXPERIMENTAL (δ_{exp}) ^1H NMR CHEMICAL SHIFTS (ppm) AND NET CHARGES q FOR 1–3

Compound	Model	Counterion	q	δ	δ_{exp}	Solvent [a]	Ref.
1	FIP/SIP		−0.200	4.26			
	CIP	Li^+	−0.011	5.76	5.71	DME	15
	CIP	K^+	−0.057	5.35	5.51	DME	15
2	FIP/SIP		−0.250	4.54			
	CIP	$2K^+$	−0.160	5.73	5.75	THF	14
3	FIP/SIP	Li^+	−0.111	6.84	6.77	DME	14
	CIP	K^+	−0.073	7.12	7.03	THF	14

[a] DME dimethoxyethane, THF tetrahydrofuran.

The proton shifts for the CIP's of **1**–**3** are larger than those of the FIP's or SIP's by 0.3 ppm for **3** and by more than 1 ppm for **1** and **2**. The differences are mainly due to a numerical reduction of the up-field shifts δ^q. The covalent interaction between the ions, or more specifically, between the occupied orbitals of the annulene and virtual orbitals of the counter ion, induces an electron transfer from the annulene to the counter ion, so that the net charges q, and hence δ^q, are reduced in magnitude. The ring current and local anisotropic contributions δ^{RC} and δ^{LA} to the shift are not greatly affected by the ion-pairing in **1**–**3**. This is to be expected for diatropic annulenes [19] according to qualitative theoretical considerations [20].

The ^1H NMR spectra of **4**/K^+ [21], **4**/Li^+ [22], and **5**/K^+ [23] reveal that these systems possess C_s symmetry, where the mirror plane is perpendicular to the plane of the hydrocarbon and contains the exocyclic bond. Thus the counter ion is confined to this mirror plane within the time scale of the NMR experiment. Four possible ion-pairings **C**–**F** with C_s symmetry are displayed in Fig. 2. We assume the same distances between counter ion and π-network as for **1**–**3**, and arrive at the calculated proton shifts which are shown in Table 2 together with the corresponding experimental values and the maximum and mean errors Δ_{max} and $\bar{\Delta}$ of calculated shifts.

The calculated shifts for an SIP of **4** and **5** do not differ significantly from those of the FIP as long as no unrealistic short ion pair separation is assumed. The observed proton shifts of **4**/K^+ and **5**/K^+ deviate considerably from those for an SIP, in agreement with experimental findings [2,14,15] that K^+ forms CIP's. As with the annulenes **1**–**3** the covalent interaction between the ions causes an electron transfer from the organic ligand to the counterion, thus reducing the up-field shift δ^q. In contrast to the situation for **1**–**3**, the covalent interaction also affects the diamagnetic ring current effect in **4** ($\delta^{RC} > 0$) and the paramagnetic one in **5** ($\delta^{RC} < 0$). The magnitude of the mean ring current term varies according to **C** > **D** ≅ FIP/SIP > **E** > **F**. However, the mean of the total proton shift δ increases according to FIP/SIP < **E**, **F** < **D** < **C** for **4**/K^+ and **C** < FIP < **D** < **E** < **F** for **5**/K^+ since δ^q and δ^{RC} are of opposite sign in **4** but not in **5**.

The calculated ^1H NMR chemical shifts for **4**/K^+ agree best with experimental values if an ion-pairing similar to **E** or **F** is assumed. For an equilibrium between 48% **E** and 52% **F** the mean (maximum) error is only 0.3 (0.5) ppm. For **5**/K^+ the comparison of calculated and observed proton shifts suggests the ion-pairing **F**, since the error in the calculated values increases if the counterion is moved towards structures **E**, **D**, and **C**. There are no experiments to the best of our knowledge which give any indication of the SIP to CIP ratio in the case of **4**/Li^+. The calculated shifts for an SIP and the CIP's indicate that in this system neither the SIP or a CIP structure predominates. Good agreement between observed and calculated ^1H NMR chemical shifts with a mean (maximum) error of less than 0.2 (0.4) ppm is obtained if a rapidly equilibrating mixture of 46% SIP and 54% CIP with ion-pairing **C** is assumed.

For the FIP, SIP, and all studied CIP's the largest net charge q of **4** is located at the exocyclic carbon atom, whereas ring atoms 1 and 3 carry most of the negative charge in **5**. Thus the ion pair structures **C** for the CIP in the **4**/Li^+ system and **F** for **5**/K^+, which have been deduced from the comparison of calculated and experimental ^1H chemical shifts, appear plausible at first sight. However, the charge distribution in **4** would not be consistent with ion-pairing **F** for **4**/K^+. Furthermore, the

TABLE 2

EXPERIMENTAL (δ_{exp}) AND CALCULATED (δ) ^{1}H NMR CHEMICAL SHIFTS (IN ppm) FOR A FIP OR SIP AND ION PAIR ARRANGEMENTS C–G. ALSO GIVEN ARE MAXIMUM DEVIATION Δ_{max} AND MEAN ERROR $\bar{\Delta}$ OF CALCULATED SHIFTS

Compound	Counterion	Proton	δ(FIP/SIP)	δ(C)	δ(D)	δ(E)	δ(F)	δ(G)	δ [a]	δ [b]	δ_{exp}	Solvent [c]	Ref.
4	K$^+$	1	4.76	6.23	5.63	5.26	5.42			5.34	5.59	THF	21
		2	6.11	6.89	6.99	6.65	6.28			6.46	6.12		
		3	4.29	6.11	5.21	4.46	4.12			4.28	4.79		
		4	0.98	1.62	1.73	1.93	2.49			2.22	2.24		
		Δ_{max}	1.33	1.32	0.87	0.53	0.67			0.51			
		$\bar{\Delta}$	0.84	0.84	0.46	0.38	0.31			0.28			
4	Li$^+$	1	4.76	6.69	5.77	5.53	6.11	6.14 [d]	5.56	5.80	6.09	THF	22
		2	6.11	7.12	7.60	6.99	6.17	7.38 [d]	6.85	6.66	6.30		
		3	4.29	6.64	5.62	5.01	4.30	6.09	5.33	5.56	5.50		
		4	0.98	2.22	2.34	2.27	3.13	2.45 [d]	1.83	1.65	1.62		
		Δ_{max}	1.33	1.14	1.30	0.69	1.51	1.08	0.55	0.36			
		$\bar{\Delta}$	0.84	0.79	0.62	0.60	0.72	0.64	0.37	0.19			
5	K$^+$	1	1.73	−3.64	1.51	2.52	3.98				4.41	LA	23
		2	3.96	−0.22	4.63	4.67	5.40				5.35		
		3	1.32	−2.97	1.99	1.94	3.44				3.76		
		4	3.88	−0.32	4.34	4.55	5.33				5.18		
		5	3.80	1.28	3.76	4.63	4.82				4.99		
		Δ_{max}	2.68	8.05	2.90	1.89	0.43						
		$\bar{\Delta}$	1.80	5.91	1.49	1.08	0.22						

[a] Values for an equilibrium of 42% SIP and 58% **G**/**G**′. [b] Values for an equilibrium of 48% **E** and 52% **F** (**4**/K$^+$) and 46% SIP and 54% **C** (**4**/Li$^+$). [c] THF tetrahydrofuran, LA liquid ammonia. [d] Averaged values.

calculation of the electrostatic interaction [24] $(-Q)\ \Sigma_s\ (q_s/r_s)$ between the counter ion and all carbon atoms s with net charges q_s and distances r_s from the counter ion indicates that **C** and **F** in **4**/Li$^+$, **C** in **4**/K$^+$ and **5**/K$^+$ exhibit the largest electrostatic stabilization. The more sophisticated hard sphere electrostatic model [24] yields another ion pair structure **G** (**G′**) (cf. Fig. 2) for **4**/Li$^+$, which was indeed found in the solid state of **4**/Li$^+$ salts [24,25]. However, **G** emerges only if semiempirically-determined net charges are employed, ab initio values favouring an ion-pairing similar to **E**. The ion pair arrangement **G** destroys the C_s symmetry. Consequently the observed ^{1}H NMR spectrum of **4**/Li$^+$ [22] indicates a rapid equilibrium **G** $\rightleftarrows$ SIP $\rightleftarrows$ **G′**. The best agreement between calculated and observed proton shifts is obtained if a mixture of 42% SIP and 58% **G**/**G′** is assumed (see Table 2), but the mean and maximum errors of calculated shifts still turn out to be significantly larger than those found for a rapidly equilibrating mixture of **C** and an SIP for **4**/Li$^+$.

Conclusion

The results demonstrate that the proton shifts of cyclic conjugated carbanions are significantly affected by ion-pairing with alkali counter ions. The covalent interaction between the ions leads to a charge transfer from the π-system to the counter ion, thus reducing the shielding which is due to the negative net charges. Furthermore the covalent interaction affects significantly the ring current contribution to the shift in the case of **4** and **5**, which are characterized by an exocyclic bond. Obviously a satisfactory quantitative assessment of the ^{1}H NMR spectra in such organometallic compounds can be achieved only if the counterion is explicitely taken into account. The dependence of the ^{1}H NMR chemical shifts of cyclic conjugated organometallics in solution on the ion-pairing can be used to derive information about the ion pair arrangement. The covalent interaction between the ions must also be important for determining their mutual orientation, since it contributes to the binding energy and affects the electrostatic interaction by a significant alteration of the charge distribution in the ion pair. In the case of **1**–**5** the electrostatic interaction between the alkali ion and the negatively charged organic ligand forming an SIP does not significantly affect the proton shifts, and so FIP and SIP cannot be distinguished by their ^{1}H NMR spectra, in contrast to those for paratropic [19] $[4m+2]$ annulene dianions [26].

Acknowledgement

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

References

1 M. Szwarc, Ions and Ion Pairs in Organic Reactions, Wiley-Interscience, New York, 1972, Vol. I, II.
2 F. Müllen, Chem. Rev., 84 (1984) 603.
3 C.W. Haigh and R.B. Mallion, Prog. NMR Spectrosc., 13 (1980) 303.
4 H. Vogler, Croat. Chem. Acta, 57 (1984) 1177.

5 H. Vogler, J. Am. Chem. Soc., 100 (1978) 7464.
6 H. Vogler, Tetrahedron, 35 (1979) 657; Org. Magn. Res., 12 (1979) 306; J. Molec. Struct., 51 (1979) 289.
7 G. Fraenkel, R.E. Carter, A. McLachlan, and J.H. Richards, J. Am. Chem. Soc., 82 (1960) 5846; T. Schaefer and W.G. Schneider, Can. J. Chem., 41 (1963) 966; J.P. Colpa, C. MacLean, and E.L. Mackor, Tetrahedron, Suppl. 2, 19 (1963) 65; P.J. Black, R.D. Brown, and M.L. Heffernan, Aust. J. Chem., 20 (1967) 1305.
8 J. Spanget-Larsen, Mol. Phys., 32 (1976) 735.
9 N. Mataga and K. Nishimoto, Z. Physik. Chem. (Frankfurt), 12 (1957) 335, 13 (1957) 140.
10 H. Vogler, Theor. Chim. Acta, 60 (1981) 65.
11 M. Wolfsberg and L. Helmholtz, J. Chem. Phys., 20 (1952) 837.
12 C.E. Moore, Atomic Energy Levels, Natl. Bureau of Standards Circular No. 467, 1949.
13 M.A. Whitehead, in: O. Sinanoğlu, Sigma Molecular Orbital Theory, Yale University Press, 1970, p. 49.
14 R.H. Cox, L.W. Harrison, and W.K. Austin, Jr., J. Phys. Chem., 77 (1973) 200.
15 J.B. Grutzner, J.M. Lawlor, and L.M. Jackman, J. Am. Chem. Soc., 94 (1972) 2306.
16 S.Z. Goldberg, K.N. Raymond, C.A. Harmon, and D.H. Templeton, J. Am. Chem. Soc., 96 (1974) 1348.
17 E.D. Jemmis and P.v.R. Schleyer, J. Am. Chem. Soc., 104 (1982) 4781.
18 R.H. Cox and H.W. Terry, Jr., J. Magn. Res., 14 (1974) 317.
19 F. Sondheimer, Acc. Chem. Res., 5 (1972) 81.
20 H. Vogler, Chemica Sripta, 24 (1984) 188.
21 K. Takahashi, M. Takaki, and R. Asami, Org. Magn. Res., 3 (1971) 539.
22 V.R. Sandel and H.H. Freedman, J. Am. Chem. Soc., 85 (1963) 2328; R. Waack, M.A. Doran, E.B. Baker, and G.A. Olah, J. Am. Chem. Soc., 88 (1966) 1272.
23 S.W. Staley and G.M. Cramer, J. Am. Chem. Soc., 95 (1973) 5051; S.W. Staley and W.G. Kingsley, J. Am. Chem. Soc., 95 (1973) 5804.
24 R.J. Bushby and M.P. Tytko, J. Organomet. Chem., 270 (1984) 265.
25 S.P. Patterman, I.L. Karle and G.D. Stucky, J. Am. Chem. Soc., 92 (1970) 1150.
26 C. Adamek, T. Meul, K. Müllen, and H. Vogler, in preparation.