

NMR Studies of the Electronic Structure of Benzocycloheptatriene Ions. Absence of Ion Pair Effects in Carbenium Salts

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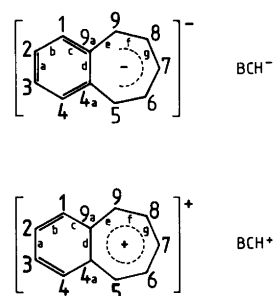
An NMR chemical shift study of benzocycloheptatrienyl ions has shown that ion pair effects are insignificant for the estimated charge distribution. The carbon shifts induced by varying the solvent or by the presence of various counterions are small compared with the shifts induced for the corresponding paratropic anion and the isoelectronic indenide system.

It is well established that ion pair changes of delocalized alkali metal carbanion salts significantly perturb the charge distribution of the carbanion system. Such field and polarization effects are reflected in induced NMR shifts, especially in induced ^{13}C NMR shifts.¹ In the case of delocalized carbocations one would expect such changes to be suppressed, when the counterions are bulky and therefore have a limited tendency to form specific solvates. However, the possibility of ion pairing effects for carbenium salts can not safely be excluded. It has been suggested that such effects can rationalize the variation observed in hydride transfer reactions of alkyl carbocations in superacidic solutions.² So far, no spectroscopic evidence for the presence or absence of such ion pairing effects has been presented. In a ^1H NMR study of the tropylium ion a negligible ion pairing effect was suggested.³ This delocalized cation, however, is not suitable for such studies, since π -polarization changes are not expected due to molecular symmetry.

In this study the benzocycloheptatriene (BCH) cation was used as a model system. This cation can be compared to the isoelectronic indenide compound.⁴ NMR and molecular orbital data (HMO) are also presented for a reference molecule, the BCH anion, in order to build a complete electronic picture of the BCH system.

The anion and cation of BCH (Fig. 1) have $4n\pi$ and $(4n+2)\pi$ electron systems, respectively. The expected paratropicity and diatropicity of the two systems have earlier been confirmed.⁵ MNDO calculations of the BCH^- system resulted in two structures of C_s and C_{2v} symmetry, both of approximately the same heat of formation.⁶ The C9–C9a and C5–C4a bonds are essentially single bonds, especially so in the C_{2v} structure. The two 6π -electron systems are therefore, to a large extent, repulsive.⁶

In this report, ^{13}C NMR chemical shifts have been used to estimate ion pair effects on charge distribution. Carbon shifts are less sensitive than proton shifts, with regard to



changes in ring susceptibilities. The ^{13}C shift data reported in Table 1 were determined in various solvents, and by varying temperature and counterions.

The data for BCH^+ indicate that the variation in the ^{13}C chemical shifts is only to within 1 ppm. This is a considerably smaller range than for the observed shift variance for the isoelectronic indenide system. Significantly, ^{13}C chemical shift changes, $\Delta\delta_c$ ca. 6 ppm, have been observed for the delocalized indenide system by varying the solvent.⁴ In the case of BCH^+ , no systematic pattern in the data is observed that may indicate any changes in the degree of polarization of the benzocycloheptatrienium ion. The change from an acidic to an organic medium, dichloromethane, did not induce significant shift changes. Additional support for the absence of ion pairing effects comes from a comparison with the solid-state NMR data of $\text{BCH}^+\text{ClO}_4^-$. The shift values are almost identical with the solution values (Table 1).

The situation is quite different for BCH^- . The shielding of the carbon atom of highest charge in the seven-membered ring is increased, when solvent effects favour intimate ion pairs. Significant counterion-induced charge polarization is thus clearly manifested.

In order to estimate the charge distribution of the BCH ions, one has to rely on either MO calculations or experimental estimates, in our case charge values based on the induced carbon shifts. Provided that one can account for

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Table 1. NMR chemical shifts of benzocycloheptatrienium and benzocycloheptatrienide ions on variation solvent, temperature and counterion.^a

Temp./°C	Solvent	Counterion	Position					
			5, 9	7	4a, 9a	6, 8	2, 3	1, 4
Carbocation								
+20	HF	F ^{-b}	160.9	158.5	144.9	141.2	139.1	137.8
+20	DCI	Cl ^{-b}	160.9	158.3	144.7	141.1	139.1	137.9
+20	HBr	Br ⁻	160.7	158.5	144.6	141.3	139.1	137.9
+20	HSO ₃ Cl	SO ₃ Cl ⁻	161.1	158.3	145.2	141.2	139.6	138.2
-30	CH ₂ Cl ₂	ClO ₄ ⁻	161.5	158.8	145.0	141.7	139.6	138.4
			(9.45)	(8.95)	(8.65)	(8.30)	(-)	(8.55)
-30	CH ₂ Cl ₂	BF ₄ ⁻	161.3	158.7	145.0	141.6	139.5	138.3
			(9.50)	(9.05)	(8.70)	(8.40)	(-)	(8.60)
-30	FCISO ₂	SO ₃ Cl ⁻	161.3	158.7	145.4	141.4	139.8	138.4
			(9.45)	(9.00)	(8.65)	(8.45)	(-)	(8.65)
-30	HSO ₃ Cl	SO ₃ Cl ⁻	161.2	158.4	145.1	141.3	139.6	138.3
-60	FCISO ₂	SO ₃ Cl ⁻	161.5	158.8	145.4	141.6	139.9	138.5
+20	Solid	ClO ₄ ^{-c}	161	158	145	140	140	140
Carbanion								
-25	THF- <i>d</i> ₆	Li ⁺	109.5	86.2	161.7	151.0	127.2	123.1
			(0.1)	(-0.5)	(-)	(1.9)	(3.9)	(2.3)
+20	THF- <i>d</i> ₆	Li ⁺	108.8	84.2	159.3	150.2	127.0	123.9
			(0.7)	(0.0)	(-)	(2.5)	(4.3)	(2.9)
-30	THF- <i>d</i> ₆	K ⁺	108.9	90.3	160.7	151.2	128.3	123.9

^aThe NMR spectra of BCH⁺ were obtained on a Bruker AC-P250 spectrometer using an external lock as the reference. The NMR spectra of the anions were obtained on an AM500 spectrometer using cyclohexane as an internal reference (27.7 ppm). The values in parentheses are the proton chemical shifts when recorded. ^bThese salts were not stable in acidic solution and decomposed within a few hours to the covalently halo-substituted benzocycloheptenes. ^cThe resonances of the CP/MAS spectrum were broadened, probably due to dipolar coupling to the oxygens of the perchlorate anion. The three high-field resonances are merged into one broad peak around 140 ppm.

paramagnetic contributions arising from differences in HOMO–LUMO gaps in the ion and its reference molecule, ‘experimentally’ derived charges are often preferred to MO-calculated charges.⁷ The MO-calculated values either neglect counterion or solvent effects or describe them only poorly.

The sum of the induced carbon shifts on going from the cation to the anion of BCH, leads to a sensitivity-to-charge ratio (K_C) of 89 ppm per electron. This value is much smaller than the commonly quoted value of 160 ppm per electron for cyclic aromatic ions. We have previously demonstrated that low K_C values are observed when the reduction affords a paratropic carbanion.^{7a} The low shift/charge factor is thus a confirmation of the paratropicity of the BCH anion, i.e. a decreased HOMO–LUMO gap relative to the gap of BCH⁺.⁷ The paramagnetic contributions related to the differences in tropicity can be accounted for as previously described.⁷ The carbon shifts, corrected for such anisotropy changes, are then used to calculate the experimental charges (Table 2). The overall agreement between calculated and experimental charges is particularly satisfying for the diatropic BCH⁺, where ion pairing is suggested to be insignificant. For BCH⁻, however, the estimated ‘experimental’ charge is higher than the calculated one at the carbon atom of highest charge in the seven-

Table 2. Experimental π -charges, derived from ¹³C chemical shifts together with HMO π -charges.

	BCH	Position				
		5, 9	7	6, 8	2, 3	1, 4
$\delta^{13}\text{C}^a$	+	161.1	158.3	141.2	139.6	138.2
$\delta^{13}\text{C}$ (corr.) ^b	+	161.7	159.0	141.9	140.3	138.9
$\delta^{13}\text{C}^c$	-	109.5	86.2	151.0	127.2	123.1
$\delta^{13}\text{C}$ (corr.) ^b	-	99.0	75.5	140.5	116.7	112.6
exp. q_π ^d (corr.)	+	+0.19	+0.17	+0.08	+0.07	+0.06
HMO q_π	+	+0.19	+0.18	+0.08	+0.05	+0.03
exp. q_π ^d (corr.)	-	-0.21	-0.39	+0.09	-0.08	-0.11
HMO q_π	-	-0.26	-0.29	+0.07	-0.05	-0.12

^a¹³C chemical shifts of BCH⁺ in HSO₃Cl at +20 °C. ^bWhen using benzene as a shift reference, the calculated ring current anisotropy X_H is -4.4 and 0.4 ppm for the anion and cation, respectively. The corresponding X_C values, 10.5 and -0.7 ppm, are subtracted from the experimental shift values. See Ref. 7 for details. ^c¹³C chemical shifts of lithium BCH⁻ in THF-*d*₆ at -25 °C. ^dCharges calculated using corrected shift values and 180 and 134 ppm per electron for the cation and anion, respectively.⁷ Benzene is used as a reference for zero charge.

membered ring. This is as expected, if charge polarization to the seven-membered ring is significant, i.e. in a contact ion pair. One may also note that charge alternation is more pronounced in the paratropic BCH^- system.

The present results lead to the conclusion that ion pair effects are insignificant for a delocalized carbenium ion such as the benzocycloheptatrienium ion. The carbon shifts induced by the presence of various counterions or by varying the solvent are very small compared with the shifts induced for the corresponding anion and the isoelectronic indenide system.

Experimental

The ^{13}C NMR spectra were assigned by using C,H-correlated 2D NMR spectroscopy. Identification of the proton resonances of the carbanion was performed by DQF-COSY 2D due to the low concentration and interference from larger signals. Benzocycloheptatrienium ions were prepared by treatment of benzocycloheptatrien-5-ol with acid.⁸

Benzocycloheptatrienyl anions were prepared by treatment of a mixture of 5*H*- and 7*H*-benzocycloheptatriene with trimethylsilylmethyl-lithium (or -potassium) at $-78^\circ C$ in THF- d_8 following the procedure for the preparation of benzyl anions.⁹

Benzocycloheptatrien-5-ol was prepared by treating benzocycloheptatrien-5-one with $LiAlH_4$ in diethyl ether ($-17^\circ C$).¹⁰ The benzocycloheptatriene mixture was prepared by treatment of benzocycloheptatrien-5-one with diisobutylaluminium hydride in hexane and refluxing overnight, following the procedure for the preparation of phe-

nalene from phenalene.¹¹ The product was purified by column chromatography using Florisil (mesh 200–300) with hexane as the eluent. Benzocycloheptatrien-5-one was prepared from the commercially available 6,7,8,9-tetrahydrobenzocycloheptatrien-5-one (benzosuberone).¹²

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References

1. Young, R. N. *Prog. NMR Spectrosc.* 12 (1979) 261.
2. Arnett, E. M. and Hofelich, T. C. *J. Am. Chem. Soc.* 104 (1982) 3522.
3. Cox, R. H., Harrison, L. W. and Austin, W. K. *J. Phys. Chem.* 77 (1973) 200.
4. Eliasson, B., Johnels, D., Wold, S. and Edlund, U. *Acta Chem. Scand., Ser. B* 36 (1982) 155.
5. Staley, S. W. and Orvedal, A. W. *J. Am. Chem. Soc.* 95 (1973) 3382.
6. Glidewell, C. and Lloyd, D. *Tetrahedron* 40 (1984) 4455.
7. (a) Eliasson, B., Edlund, U. and Müllen, K. *J. Chem. Soc., Perkin Trans. 2* (1986) 937; (b) Eliasson, B., Johnels, D., Sethson, I., Edlund, U. and Müllen, K. *J. Chem. Soc., Perkin Trans. 2. In press.*
8. Rennhard, H. H., Heilbronner, E. and Eschenmoser, A. *Chem. Ind. (London)* (1955) 415.
9. Hart, A. J., O'Brien, D. H. and Russell, C. R. *J. Organomet. Chem.* 72 (1974) C19.
10. Rennard, H. H., Di Modica, G., Simon, W., Heilbronner, E. and Eschenmoser, A. *Helv. Chem. Acta* 40 (1957) 957.
11. Boudjok, P. and Johnson, P. D. *J. Org. Chem.* 43 (1978) 3979.
12. Collington, E. W. and Jones, G. *J. Chem. Soc. C* (1969) 2656.

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Den kgl. Veterinärhögskolan, Uppsala