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Structures of lithium salts of substituted 1-phenylpropynes: ^{13}C NMR and MNDO study

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Abstract

^{13}C NMR spectroscopy has been used to study the structure of ambident carbanions in contact (CIP) and solvent-separated (SSIP) ion pairs of lithium salts of substituted 1-phenylpropynes. It was shown that the structures of carbanions in SSIP are close to the propargylic type, whereas, with the decrease in delocalizing ability of substituents at the propargylic centre, their structure shifts to the allenylic type, in fair agreement with theoretical predictions by the MNDO semi-empirical method. In CIP, the structures of carbanions are progressively changed from near-to-propargylic to allenylic with decrease of delocalizing ability of the substituents.

Introduction

The structures and ionic states of carbanions in solutions of alkali metal derivatives of allenes and propynes, important reagents in the syntheses of a broad scope of organic compounds [1], have been little studied [1e,2]. This makes it difficult to understand what factors determine the direction of the reactions of such organometallic compounds with electrophilic reagents, which are known to yield mixtures of substituted allenes and acetylenes as a rule.

A study of the solutions of alkali salts of substituted 1-phenylpropynes by absorption spectroscopy in the visible region have shown [3] that equilibria between CIP, SSIP, and free ions are established in these solutions. This helps to understand the influence of ionic states of the salts on the regioselectivity of their alkylation [4]. UV-VIS spectroscopy is, however, of no use when evidence on the electron density distribution and hybridization states of carbon atoms in ambident propargylic and allenylic carbanions is of interest. These parameters and substituent effects on them can be studied by means of ^{13}C NMR, which has been

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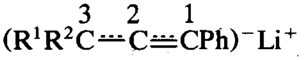
extensively used to probe the structure of allyl carbanions [5], resembling ambident propargylic (allenylic) carbanions in chemical behavior. Nevertheless, ^{13}C NMR has been only occasionally used to study propargylic and allenylic carbanions. Only ^{13}C NMR data on allenyllithium (AL) in THF [6] and on the sodium (potassium) salt of 1,3-diphenylpropyne in liquid ammonia [7] have been published.

In the present work, ^{13}C NMR spectroscopy is applied to lithium salts (**1a–h**) of 1-phenylpropynes (**2a–h**) in THF. Except for the salt **1g** the exhaustively substituted salts have been investigated in order to exclude all possible isomerization pathways [1a,8].



$$(\mathrm{R^1R^2\overset{3}{C}{=}\overset{2}{C}{\equiv}\overset{1}{C}Ph})^-\mathrm{Li}^+$$

(**1a**: $R^1 + R^2$ = 2,2′-biphenylene; **1b**: $R^1 = R^2$ = Ph; **1c**: R^1 = Ph, R^2 = 4-MeOC$_6$H$_4$; **1d**: R^1 = Ph, R^2 = 2-MeOC$_6$H$_4$; **1e**: $R^1 = R^2$ = 2-MeOC$_6$H$_4$; **1f**: R^1 = Ph, R^2 = Me; **1g**: R^1 = Ph, R^2 = H; **1h**: $R^1 = R^2$ = Me)

The NMR data on the structure of salts **1** was corroborated with theoretical computations of the free carbanions and CIP (**1a, b, f, g, h**) by a semi-empirical MNDO procedure [9]. This method has proven its usefulness in studies of the structure of various organolithium compounds [10], where other semi-empirical procedures such as CNDO/2 failed [11].

Experimental

Diethyl ether (DEE), THF and THF-d_8 were thoroughly purified using published procedures and kept degassed over sodium benzophenone ketyl in evacuated bulbs equipped with vacuum stopcocks. After routine purification, pentane was kept similarly over a sodium mirror. THF-d_8 was stored in evacuated ampoules with break-seals. The solvents were vacuum transferred to the reaction vessels over a vacuum line (10^{-3}–10^{-4} Torr).

1,3,3-Triphenylpropyne (**2b**), 1,3-diphenyl-3-(4-methoxyphenyl)propyne (**2c**), 1,3-diphenyl-3-(2-methoxyphenyl)propyne (**2d**), 1-phenyl-3,3-di(2-methoxyphenyl)-propyne (**2e**), were obtained by the method given in [12] for **2b**. 9-Phenylethynylfluorene (**2a**), 1,3-diphenylbutyne-1 (**2f**) and 1-phenyl-3-methylbutyne-1 (**2h**) were prepared by the reduction of the corresponding propargylic alcohols by Et$_3$SiH in the presence of BF$_3$ [13]. 1,3-Diphenylpropyne (**2g**) was obtained by the reduction of 1,3-diphenylprop-1-yn-3-ol by borane–THF complex [14].

Lithium salts **1a–g** were obtained by lithiation with a small excess of ^{n}BuLi of the corresponding acetylenic hydrocarbons dissolved in a mixture of pentane and DEE in all-glass evacuated apparatus. In the same apparatus, the solid crystalline products were thoroughly washed by the same solvent mixtures, dried *in vacuo* and dissolved in DEE or THF-d_8. The solutions of salt **1h** were obtained by lithiation of **2h** by an excess of ^{n}BuLi directly in DEE or THF. The latter was afterwards replaced with THF-d_8.

A proper amount of TMS was vacuum transferred to the 0.1–0.25 *M* solutions of the salts **1**, and the solutions were poured into tubes (o.d. 8.7 mm), which were frozen in liquid nitrogen, sealed off, and inserted into standard 10 mm NMR tubes. The spectra were obtained on a Varian XL-400 spectrometer (400 MHz for

^1H, 100.6 MHz for ^{13}C). Chemical shifts and temperatures were measured with accuracy to 0.03 ppm and 1°C, respectively.

An assignment of ^{13}C NMR signals was made for C(1) and C(3) by an analysis of the signal multiplicities in the spectra: (i) without proton decoupling; (ii) selective heteronuclear NOE with excitation of the protons of methyl groups in **1f**, **h**; (iii) selective decoupling from *ortho*-protons in phenyl groups and from protons at 1- and 8-sites of the fluorenyl moiety in **1a** (assignment of C(1), C(3)). The assignment of C(1), C(2), and C(3) in **1h** was also confirmed by a comparison of the experimental values of chemical shifts with the estimates made in accordance with published correlations [15]. For comparison, the spectra of the starting propynes **2a–h** in THF-d_8, and of the isomeric allenes **3a–h** in $CDCl_3$ have been studied. Allenes **3a–f**, **h** were obtained by vacuum-transfer quenching of solutions of **1a–h** in THF with an excess of aqueous HCl.

Theoretical computations were realized using the MNDO RHF method as implemented in the molecular orbital package MOPAC [16]. The geometric parameters of the free carbanions of the salts **1a, b, f, g, h** were optimized except CH bond lengths (1.089 Å) and CCH bond angles (120°) in phenyl rings. Computations of the lithium salts were run using the geometry of phenyls at C(1) obtained in computations of the corresponding carbanion.

Results and discussion

Contact and solvent separated ion pairs of lithium salts of substituted 1-phenylpropynes

NMR [5,17] and UV-VIS spectrophotometry [18] have been extensively used for distinguishing between types of ion pairs in solutions of alkali derivatives of fluorenes and arylmethanes. The temperature dependences of δH [17e,f] and δC [17a–e] in carbanion spectra were used to determine a position of equilibrium between CIP and SSIP.

Some examples of temperature dependences of δH and δC for the salts **1** are given in Table 1 and Figs. 1, 2. These data confirm that only monomeric CIP exist in 0.1–0.25 *M* solutions of **1** in DEE. The salt **1h** is an exception: an ethereal solution of this salt contains ion pair aggregates probably even at −78°C. This supposition finds confirmation in the splitting at −78°C of each of the signals of C(1), C(2), C(3), observed as singlets at 27°C (Fig. 3). This is explained by different exchange rates between various aggregates of CIP (**1h**) at 27°C and −78°C. Similar behaviour was observed for other organolithium compounds [10e,19].

SSIP predominate in 0.1–0.25 *M* solutions of **1a–c** between 27°C and −78°C (*cf.*, *e.g.*, Fig. 2). At 27°C, **1d** and **1e** exist in THF mainly as monomeric CIP, while the solution of **1f** contains nearly 40% of SSIP, and CIP **1d, e, f, g** are transformed at −78°C mainly to SSIP. For **1e**, this is confirmed by closeness of the values of δC at −78°C in THF solution and at 27°C in DMSO solution (Table 1) and for **1f**, by the data of Figs. 1 and 2. The fact that **1g** exists in THF at low temperatures (from −60°C to −100°C) in the form of SSIP is evidenced not only by the trends in temperature dependences of chemical shifts for various carbon atoms (Table 1), but also by the closeness of the δC values for **1g** at −60°C and −100°C in THF to the chemical shifts for this salt at −33.4°C in liquid ammonia [7]. It should be expected that in liquid ammonia, which possesses a high dielectric constant and

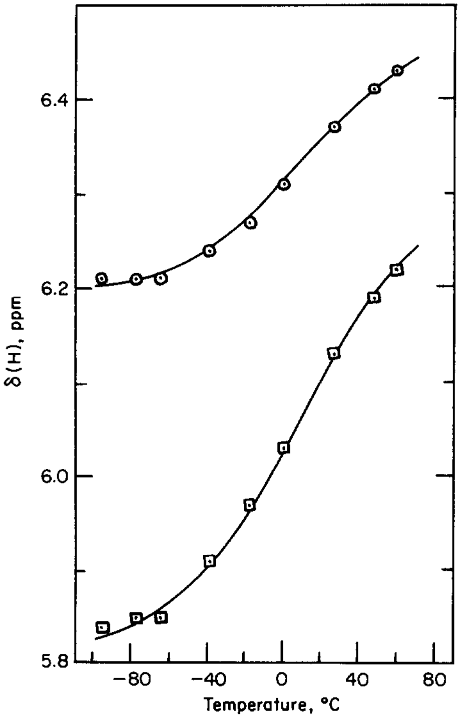


Fig. 1. Temperature dependences of chemical shifts for *para*-protons $H_p(1)$ (⊙) and $H_p(3)$ (⊡) in phenyl groups bonded to the first and third carbons in the triad C(1)–C(2)–C(3) of salt **1f** in THF-d_8.

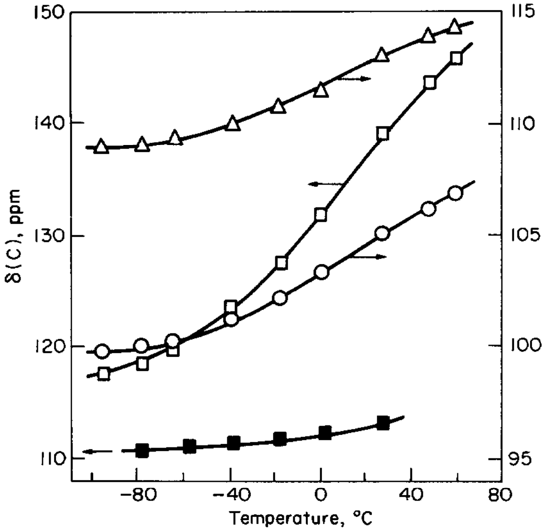


Fig. 2. Temperature dependences of chemical shifts for carbon atoms C(1) (○), C(2) (□) and $C_p(3)$ (△) in salt **1f** and for C(2) (■) in salt **1b** in THF-d_8.

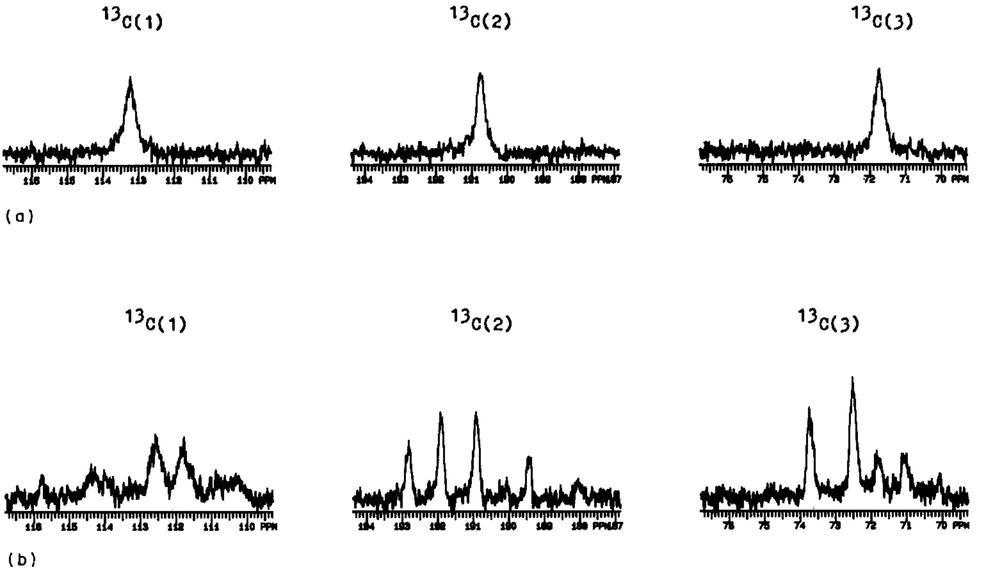


Fig. 3. ^{13}C NMR spectra of salt **1h** in DEE at 27°C (a) and −78°C (b).

strongly solvates the alkali metal cations, **1g** is expected to exist in the form of SSIP and free ions. Lithium salt **1h** in the whole temperature range under investigation (from 27°C to −78°C) exists in THF as monomeric CIP. The above conclusions are in a fair agreement with: (i) spectrophotometric data on the equilibria between CIP and SSIP in dilute (10^{-3}–10^{-5} M) solutions of **1a–f**, **h** [3,4]; (ii) ^1H, ^7Li, ^{13}C NMR data for concentrated solutions of fluorenyllithium (FL) in DEE and THF [5,17a,c,d], diphenylmethyllithium (DPML) [5,17a,c], α-methylbenzyllithium (α-MBL) [17f], all of which can be regarded as direct precursors of salts **1a**, **b**, **f**; and of triphenylmethyllithium (TPML) [5,17c,20]. The latter from the viewpoint of structure is close to the salts **1b**, **c**, **d**.

The structure of carbanions in solvent separated ion pairs

Chemical shifts of different carbon atoms in CIP and SSIP of salts **1** differ essentially (Tables 1, 2). The largest differences between δC in CIP and SSIP are observed for C(2). These differences obviously should not be neglected as occurred in [21]. Therefore, later in this paper ^{13}C NMR data on CIP and SSIP will be treated separately.

Attention will first be paid to SSIP. Since, in such types of ion pairs, alkali cations exert a negligible effect on carbanions, spectral properties [18] and reactivities [22] of SSIP weakly depend on the nature of the cation, being close to those of free carbanions. This is also true for alkali salts of 1,3,3-trisubstituted propynes [3,4a,23]. The cations in SSIP have a small influence on δC [5,17c]. Thus, the influence of lithium cation in SSIP of the salts **1** on the values of δC can be neglected. Also important is the fact that in the case of SSIP of lithium derivatives **1**, an equilibrium between their propargylic and allenylic forms need not be considered. Such equilibria have been established by many authors [1,8]. This part of the present paper deals with ^{13}C NMR data obtained at −78°C for **1a–e**, at

Table 1

Chemical shifts values for C(1), C(2) and C(3) in lithium salts **1**, acetylenic hydrocarbons (AH) **2**, allenes **3**, and the values of $\Delta C = \delta C(\text{salt}) - \delta C(\text{AH})$ [a] (ppm relative to TMS) in THF-d_8 and diethyl ether (DEE)

Compound	Solvent	Temperature (°C)	Type of ion pairs	$\delta C(1)$	$\Delta\delta C(1)$	$\delta C(2)$	$\Delta\delta C(2)$	$\delta C(3)$	$\Delta\delta C(3)$
1a	THF	27, −78	SSIP	95.3	12.9	99.2	11.5	78.0	37.6
1a	DEE	27	CIP	96.2	13.8	94.1 [b]	6.4	70.4	30.0
2a	THF	27		82.4		87.7		40.4	
3a	$CDCl_3$	27		101.9		204.5		109.3	
1b	THF	27	SSIP	94.3	9.0	113.1	22.3	72.5	28.4
1b	THF	−78	SSIP	93.6	8.3	110.9	20.1	72.2	28.1
1b	DEE	27	CIP	99.3	14.0	126.3 [b]	35.5	70.1	26.0
1b	DEE	−78	CIP	97.3	12.0	121.7 [b]	30.9	70.5	26.4
2b	THF	27		85.3		90.8		44.1	
3b	$CDCl_3$	27		97.3		207.9		114.2	
1c	THF	27	SSIP	95.8	10.8	117.8	26.7	71.4	28.1
1c	THF	−78	SSIP	94.3	9.3	112.7	21.7	70.6	27.3
1c	DEE	27	CIP	101.7	16.7	133.2 [b]	42.1	71.3	28.0
2c	THF	27		85.0		91.1		43.3	
3c	$CDCl_3$	27		97.3		207.5		113.2	
1d	THF	27	CIP	95.2	11.1	116.2	24.8	62.9	25.6
1d	THF	−78	SSIP	92.7	8.6	114.3	22.9	64.2	26.9
1d	DEE	27	CIP	96.0	11.9	116.7 [b]	25.3	60.3	23.0
2d	THF	27		84.1		91.4		37.3	
3d	$CDCl_3$	27		96.7		207.2		111.2	
1e	THF	27	CIP	92.1	9.1	118.6	26.9	58.7	27.0
1e	THF	−78	SSIP	90.7	7.7	117.0	25.3	63.9	32.2
1e [c]	DMSO	27	SSIP	90.7	7.7	117.8	26.1	63.0	31.3
2e	THF	27		83.0		91.7		31.7	
3e	$CDCl_3$	27		93.7		208.8		111.4	
1f [d]	THF	27	[e]	105.1	22.2	139.0	46.2	62.1	29.3
1f [d]	THF	−78	SSIP	100.1	17.2	118.7	25.9	57.9	25.1
1f [d]	THF	−96	SSIP	99.7	16.8	117.6	24.8	57.5	24.8
1f	DEE	40	CIP	108.9	26.0	149.1 [b]	56.3	66.0	33.2
1f	DEE	27	CIP	108.8	25.9	148.8 [b]	56.0	65.3	32.5
1f	DEE	20	CIP	108.7	25.8	148.2 [b]	55.4	64.4	31.6
1f	DEE	−78	CIP	108.1	25.2	145.4 [b]	52.6	62.9	30.1
2f	THF	27		82.9		92.8		32.8	
3f	$CDCl_3$	27		96.4		206.3		104.3	
1g	THF	25	SSIP [f]	102.1	13.8	127.7	44.5	55.3	29.4
1g	THF	−20	SSIP [f]	100.7	12.4	123.3	40.1	55.0	29.1
1g	THF	−60	SSIP [f]	99.8	11.5	117.6	34.4	55.3	29.4
1g	THF	−100	SSIP [f]	99.5	11.2	114.9	31.7	55.3	29.4
2g	THF	25		88.3		83.2		25.9	
1g [g]	NH_3 liq.	−33	[g]	99.5	11.8	[h]	[h]	54.2	28.5
2g [g]	$CDCl_3$			87.7		82.8		25.7	
1h	THF	27	CIP	116.2	35.8	184.7	89.1	62.1	40.8
1h	THF	−18	CIP	116.3	35.9	183.7	88.1	61.5	39.8
1h [i]	THF	−78	CIP	116.0	35.6	183.3	87.7	61.3	39.6
1h	DEE	27 [j]	Aggregates of CIP	113.4	33.0	191.0	95.4	72.0	50.3
2h	THF	27		80.4		95.6		21.7	
3h	$CDCl_3$	27		92.4		202.7		98.8	

Table 2

The comparison of ^{13}C NMR data for CIP (DEE, 27°C) and SSIP (THF, −78°C) of lithium salts **1**

Salt	dC [a]					$\Delta\delta C(CIP)/\Delta\delta C(SSIP)$	
	C(1)	C(2)	C(3)	$C_p(1)$	$C_p(3)$	$C_p(1)$	$C_p(3)$
1a	0.9	−5.1	−7.6	2.4	3.3	1.6	1.7
1b	5.7	15.4	−2.1	3.5	5.1	1.5	1.7
1c	7.4	20.5	0.7	4.3	6.3	1.6	1.8
1d	3.3	2.4	−3.9	3.6	4.4	1.5	1.4
1e [b]	1.4	1.6	−5.2	1.9		1.2	
1f [c]	9.1	31.2	7.7	6.1	8.8	1.9	2.0
1h		34.1 [d]					

[a] $dC = \delta C(CIP) - \delta C(SSIP)$. [b] The data for CIP (THF, 27°C) and SSIP (THF, −78°C) compared. [c] The data for CIP (DEE, 27°C) and SSIP (THF, −96°C) compared. [d] Calculated based on $\delta C(2) = 150.6$ ppm, estimated for SSIP **1h** (see text) and of $\delta C(2) = 184.7$ ppm for CIP **1h** in THF at 27°C.

−96°C for **1f**, and at −100°C for **1g** in THF solution, since these salts exist under stated conditions predominantly as SSIP (Table 1).

Lack of data on the acidity of acetylenic hydrocarbons (AH) **2a–h** makes it difficult to order their salts by decrease in net delocalizing ability of R^1 and R^2. However, our analysis of earlier NMR data helped to reveal a convenient parameter correlating with the acidity of hydrocarbons and thus reflecting the properties of substituents at the carbanionic centre. Chemical shifts δC_α in fluorene, 9-methylfluorene, 9-benzylfluorene, and 9-phenylfluorene show almost perfect linear correlation with the pK_a of these hydrocarbons (Table 3). A similar relation between δC_α and pK_a (Table 3) is observed for phenylmethanes. Hence, at least for these series of hydrocarbons the values of δC_α can be used for estimates of relative values of pK_a for these compounds. The larger is the downfield shift of $^{13}C_\alpha$ resonance, the lower is pK_a. Thus, δC_α values can be used as a measure of the relative thermodynamic stability of carbanions derived from hydrocarbon acids, and the delocalizing ability of the substituents at the carbanionic centre C_α.

Analysis of the earlier data has led to another important conclusion. A good linear correlation (Fig. 4) exists between δC_α in the SSIP of FL, 9-methylfluorenyllithium (MFL), 9-phenylfluorenyllithium (PFL) and δC_α in corresponding hydrocarbons in THF [21]. Arylmethane salts satisfy a similar relation. Since in THF solution, the differences between δC_α in SSIP and CIP of alkali salts of arylmethanes might vary from several ppm to 10 ppm [17c], the correlation is better for ion pairs of the same sort. Figure 4 shows the correlation between δC_α for

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Notes to Table 1:

[a] Positive values of $\Delta\delta C$ indicate lowfield shift relative to the resonances of parent AH in THF-d_8. [b] The signal of C(2) is broad. [c] Chemical shifts are measured relative to DMSO signal with $\delta = 39.5$ ppm. [d] Chemical shifts are measured relative to THF resonance with $\delta C = 67.2$ ppm. [e] 60% of CIP and 40% of SSIP, calculated by O'Brien's method [17c] with the values of $\delta C(SSIP)$ in THF at −96°C and $\delta C(CIP)$ in DEE at 40°C. [f] A small portion of CIP exists in solution. [g] Bushby's data [7] for sodium (potassium) salt of 1,3-diphenylpropyne in liquid ammonia, where these salts have to exist mainly as SSIP and free ions. [h] The values have not been obtained [7]. [i] The half-widths for $^{13}C(1)$, $^{13}C(2)$ and $^{13}C(3)$ resonances in $\{^{13}C\text{-}^{1}H\}$ spectra are 24.6, 5.4 and 1.7 Hz. [j] The ^{13}C NMR spectrum in DEE at −78°C is shown in Fig. 3.

Table 3

Chemical shifts for C_α and acidities of fluorenes and phenylmethanes in THF

Hydrocarbon	δC_α	pK_a
Fluorene	37.2 [a]	22.41 [b]
9-Methylfluorene	43.1 [a]	21.85 [b]
9-Benzylfluorene	48.6 [c]	20.92 [b]
9-Phenylfluorene	55.1 [a]	18.49 [b]
Toluene	21.3 [d], 21.5 [e,f]	41.2 [g], 40.9 [h]
Phenylethane	29.1 [i]	42.0 [h]
Diphenylmethane	42.4 [d], 42.6 [f]	33.09 [j], 33.01 [b]
Triphenylmethane	57.5 [d], 58.2 [f]	30.2 [j], 31.02 [b]

[a] [21]. [b] Caesium ion-pair acidity [24]. [c] In $CDCl_3$. The data of this work. [d] [6]. [e] [25]. [f] [26]. [g] Caesium ion-pair acidity [27]. [h] Potassium ion-pair acidity [28]. [i] In dioxane [29]. [j] Lithium ion-pair acidity [28].

hydrocarbons and δC_α for SSIP of TPML and triphenylmethylsodium (TPMS) in THF [17c], DPML [6], SSIP of DPML and diphenylmethylsodium (DPMS) [17c], as well as for CIP of triphenylmethylpotassium (TPMP) and diphenylmethylpotassium (DPMP) [17c], α-methylbenzylpotassium (α-MBP) [17f], benzylpotassium (BP), *ortho-* and *para-*methoxybenzylpotassium (*o*-MBP, *p*-MBP) [25]. The larger cation in the CIP of potassium salts of arylmethanes makes their spectral parameters close to those of SSIP [5,17c,18], and the hybridization of C_α in α-MBP [17f], BP [5,25], *o*-MBP and *p*-MBP [25] is closer to sp^2 than in the corresponding lithium

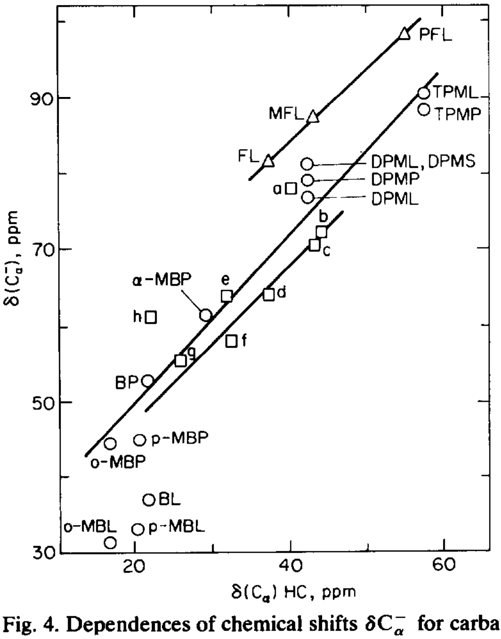
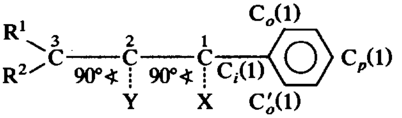


Fig. 4. Dependences of chemical shifts δC_α^- for carbanion centres in alkali derivatives of fluorenes (△) and arylmethanes (○), and in lithium salts **1** (□) *versus* the chemical shifts δC_α HC in the parent hydrocarbons. For **1**, δC_α^- is δC(3), and for AH, δC_α HC is δC(3) AH. The abbreviations are given in the text.

Table 4

Geometries, bond orders and charges (ρ) on the carbon atoms in carbanions of salts **1**, calculated by the MNDO method (X and Y are dummy atoms shown for reference)



	1a	**1b**	**1f**	**1g**	**1h**	**1i** [a] $R^1 = R^2 = H$	$(C_3H_3)^-$
Bond length C(1)–C(2) (Å)	1.213	1.216	1.220	1.222 1.24 [b]	1.234	1.23	1.267 [c] 1.271 [d] 1.276 [e] 1.288 [f]
Bond order C(1)–C(2)	2.620	2.556	2.519	2.487	2.337		
Bond length C(2)–C(3) (Å)	1.388	1.386	1.383	1.370 1.38 [b]	1.354	1.36	1.337 [c] 1.340 [d] 1.346 [e] 1.356 [f]
Bond order C(2)–C(3)	1.157	1.217	1.252	1.289	1.463		
C(1)–C(2)–C(3) (°)	179.9	180.0	178.2	177.5	179.4		
C(2)–C(1)–C_i(1) (°)	180.0	180.0	179.8	180.0	179.5	175.2	118.5 [g] 120.9 [h] 122.7 [i] 122.9 [j]
C_i(1)–C(1)–X–C(2) (°)	180.0	180.0	180.0	180.0	180.0		
C_o(1)–C_i(1)–C(1)–X (°)	0.0	0.0	0.0	0.0	0.0		
C_o(1)–C'_o(1)–C_i(1)–C(1) (°)	180.0	180.0	180.1	180.0	180.0		
C(1)–C(2)–Y–C(3) (°)	180.0	180.0	179.5	180.0	180.0		
C(2)–C(3)–R^1 (°)	125.8	117.8 [k]	121.9 [k]	125.4 [k] 125 [b]	120.4	111.2 [l]	115.7 [m] 116.6 [n] 122.2 [o]
C(2)–C(3)–R^2 (°)	125.8	117.7	115.5	117.8	120.3		
Y–C(2)–C(3)–R^1 (°)	−0.2 [p]	0.1 [p]	−0.8 [p]	−1.9 [p]	0.0 [q]		
Y–C(2)–C(3)–R^2 (°)	179.8 [r]	180.1 [r]	180.9 [s]	182.0 [t]	180.0 [u]		179.1 [v]
ρ_t, C(1) (a.u.)	−0.336	−0.366	−0.387	−0.389 −0.24 [b]	−0.428	−0.28	−0.772 [f]
ρ_π [w], C(1) (a.u.)	−0.211	−0.252	−0.267	−0.276	−0.336		
ρ_t, C(2) (a.u.)	+0.104	+0.095	+0.104	+0.089	+0.090	+0.06	+0.111 [f]
ρ_t, C(3) (a.u.)	−0.244	−0.325	−0.371	−0.317 −0.25 [b]	−0.445	−0.34	−0.580 [f]
ρ_π [w], C(3) (a.u.)	−0.353	−0.444	−0.442	−0.402	−0.475		
ρ_t, C_p(1) (a.u.)	−0.120	−0.136	−0.145	−0.150	−0.194	−0.08	
ρ_π [w], C_p(1) (a.u.)	−0.077	−0.097	−0.108	−0.115 −0.06 [b]	−0.170		
ρ_t, C_p(3) (a.u.)	−0.147	−0.146	−0.186	−0.196			
ρ_π [w], C_p(3) (a.u.)	−0.116	−0.052	−0.148	−0.171			

[a] Bond lengths for the propargylic form of carbanion calculated by MINDO/2, charges calculated by CNDO/2 [33]. [b] CNDO/2 data [7]. [c] 4–31 G [34a]. [d] 4–31 G [34c]. [e] 6–31 G [34d]. [f] SCEP for the equilibrium form $(C_3H_3)^-$ [34b]. [g] C(2)–C(1)—H [34d]. [h] C(2)–C(1)–H [34b]. [i] C(2)–C(1)–H [34a]. [j] C(2)–C(1)–H [34c]. [k] R^1 = Ph(3) groups are twisted relative to the planes of carbanions **1b** ($R^1 = R^2$ = Ph(3)) by 34.2°, **1f** by 12.4°, and **1h** by 6.9°. [l] Average value for C(2)–C(3)–H. [m] H–C(3)–H [34c]. [n] H–C(3)–H, hydrogen atoms are out of plane C(1)–C(2)–C(3) by 2.7° [34b]. [o] C(2)–C(3)–H [34a]. [p] Y–C(2)–C(3)–C_i(3), in which C_i(3) is the 9a carbon atom of fluorenyl fragment in **1a** or the *ipso*-carbon atom of Ph(3) in **1b**, **1f**, and **1g**. [q] Y–C(2)–C(3)–C(Me^1). [r] Y–C(2)–C(3)–C_i(3), in which C_i(3) is the 8a carbon atom of the fluorenyl fragment in **1a** or the *ipso*-carbon atom of the second group Ph(3) in **1b**. For the related data for C_i(3) of the first group Ph(3) in **1b** see footnote *p*. [s] Y–C(2)–C(3)–C(Me). [t] Y–C(2)–C(3)–H. [u] Y–C(2)–C(3)–C(Me^2). [v] C(2)–C(3)–0, where 0 is a bisector of H–C(3)–H [34c]. [w] Calculated from the values of p_z-AO electron populations.

derivatives [5,17f,25]. It is an essential deviation from sp^2-hybridization of C_α that accounts for a heavy scatter of points of benzyllithium (BL) [2,5,25,30], *ortho*- and *para*-methoxybenzyllithium (*o*-MBL and *p*-MBL) [25] from the straight line in Fig. 4.

The data given and the relationship between δC_α and pK_a discussed above prompt a conclusion that for the salts of fluorenes and arylmethanes with sp^2-hybridized carbanion centres, the relative variations in δC_α values for the ion pairs are accounted for mainly be delocalizing abilities of substituents at C_α. The stronger is this ability, that is the larger is the value of δC_α for CH-acid, the larger is the downfield shift of $^{13}C_\alpha$ in carbanions in the given series of these acids.

The α-carbons in FL [5,21], DPML [5,26,30], α-MBP [17f] are sp^2-hybridized. Atom C(3) in the alkaline salt of 1,3-diphenylpropyne is also sp^2-hybridized [7]. This fact shows that the introduction of phenylethynyl substituent at α-site of benzyl carbanion stimulates sp^2-hybridization of C_α [7]. Therefore, it is possible to conclude that in **1a–g**, C(3) atoms are also trigonal. Indeed, MNDO calculations of the free carbanions **1a**, **b**, **f**, **g**, **h** show that C(3) and the neighbouring atoms lie practically in the same plane with bond angles close to 120° (Table 4). Figure 4 shows that δC(3) for SSIP of **1b–d** (−78°C), **1f** (−96°C), **1g** (−100°C) in THF are linearly correlated with δC(3) of AH, with ^{13}C(3) resonance in SSIP being shifted upfield with the decrease of δC(3) of AH. The deviation from the line in Fig. 4 observed for the point of **1h** is accounted for by this salt being CIP in THF at −78°C.

The resonances of $^{13}C_p(1)$ and $^{13}C_p(3)$, *i.e.* of *para*-carbons in phenyl rings Ph(1) and Ph(3) bound to C(1) and C(3) of the triad C(1)–C(2)–C(3) of SSIP of salts **1**, also shift systematically to a higher field in accordance with the decrease of δC(3) for AH (Fig. 5). The latter may thus serve as a probe for the net delocalizing ability of substituents R^1 and R^2. It is noteworthy that for a lot of α-substituted

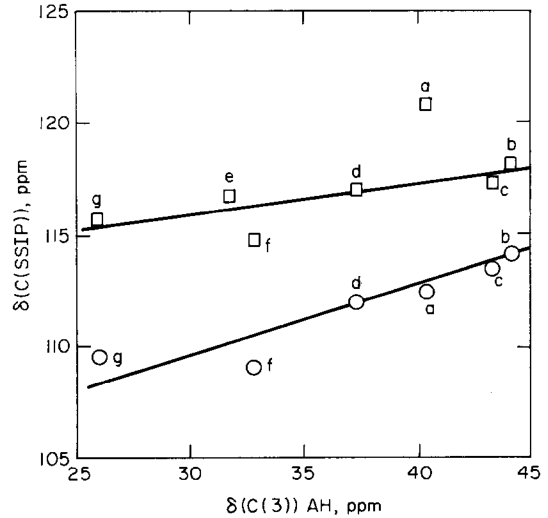


Fig. 5. Chemical shift dependences for $C_p(1)$ (□) and C_p^3 (○) atoms in SSIP of salts **1** (THF-d_8) *versus* the total delocalizing abilities of R^1 and R^2 (δC(3) in AH).

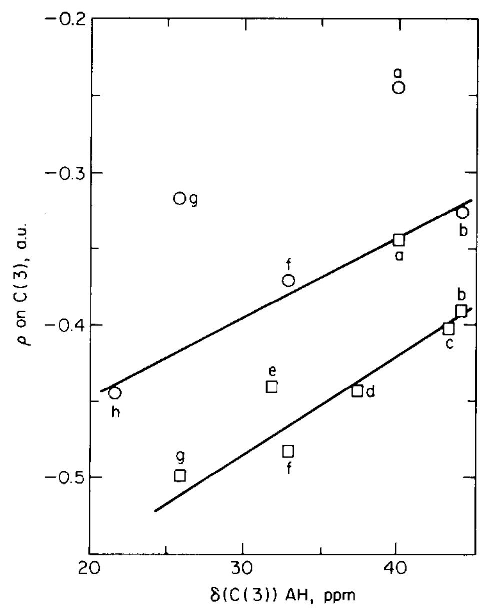


Fig. 6. Variations of charges at C(3) atoms in SSIP of salts **1** *versus* the change of delocalizing abilities of substituents (δC(3) AH). π-Charges (□) are calculated from the ^{13}C NMR data by method B (see text). Total charges (○) are calculated by the MNDO semi-empirical method.

benzylsodiums in DMSO, good linear correlations between δC_p and pK_a of the corresponding hydrocarbons have been observed previously [31]. Lack of fit between δC_α in carbanions and the pK_a of the parent hydrocarbons in this case [31] is most probably due to the presence of heteroatoms in the vicinity of carbanion centres.

The formation of carbanions from diphenylmethane and triphenylmethane results in rehybridization of C_α from sp^3 to sp^2 and in the downfield shift of ^{13}C 95 ppm on average, the effect of the π-charge on the upfield shift of the $^{13}C_\alpha$ line being taken to be 160 ppm per electron [26]. If in the transformation of AH **2** to salts **1** the rehybridization of C(3) may be assumed to be followed by a downfield shift of ^{13}C(3) resonance by a constant value, the decrease of ΔδC(3) for the series of SSIP of salts **1a** (37.6) > **1b** (28.1) > **1c**(27.3) > **1d**(26.9) > **1f**(24.8) should be associated with an increase of ρ_π at C(3) atoms along the same series.

Excess (compared to the starting AH) π-charges at C(3) atoms in SSIP **1a** (−0.36), **1b** (−0.42), **1f** (−0.44), **1g**(−0.41), calculated from NMR data by Takahashi's method [26] (Method A), which takes into account rehybridization (95 ppm) and upfield shift (160 ppm per electron) of ^{13}C(3) resonance due to the build-up of π-density, are quite large and close to MNDO charges ρ_π at sp^2-hybridized C(3) atoms in the free carbanions (Table 4). Although, no meaningful trend could be revealed in the variation of π-charges, estimated using Method A for SSIP **1a–d**, **f**, **g**, or using MNDO results for free carbanions **1a**, **b**, **f**, **g**, **h** *versus* delocalizing ability of R^1 and R^2 in salts **1**, that is *versus* the values of δC(3) for AH. The trend is especially sharply pronounced (Fig. 6) for MNDO total charges ρ_t at C(3) atoms (Table 4). This confirms the conclusion made earlier [21] that δC for carbanion centres of lithium derivatives of CH-acids are defined not by π, but rather by the total $(\pi+\sigma)$ charge density at the centres. The π-charges at C(3) atoms calculated from ^{13}C NMR data for SSIP of salts **1** by O'Brien's equation [32] (Method B) vary with the decrease of delocalizing ability of the substituents at C(3) in an almost identical way (Fig. 6) as ρ_t. This fact may be understood if we suppose that Method B actually leads to ρ_t and not ρ_π at the C(3) atoms. However, in order to obtain a reasonable agreement between ρ_t values at C(3) atoms of SSIP of salts **1** computed with Method B and MNDO, the parameters of O'Brien's equation should have different values. This is especially important for the constant term, which should be less than 289.6 ppm in order that the charges are not overestimated.

The deviation of points for SSIP **1a** from the lines (Fig. 6) is probably accounted for by the fact that **1a** belongs to fluorenyllithium compounds in which the p_z-AO of the carbanionic centre is incorporated into the aromatic anionic π-system. The substantial deviation of the point for **1g** from line 2 in Fig. 6 is apparently due to sharp changes in the neighbourhood of the C(3) centre in carbanion **1g** compared with that in the carbanions **1a**, **b**, **f**, **h** (C(3) in **1g** bears a hydrogen and a carbon atom, while in other species it bears only carbons). MNDO is possibly insensitive to these changes. For now it is not possible to give a reasonable explanation for the deviation of the value of δC(3) for **1e** from the relationship in Fig. 4, and the value of ρ at C(3) from the correlation of Fig. 6, although the discrepancies obviously are due to some effect of two methoxy groups adjacent to the carbanion centre C(3).

By redistribution of the negative charge over the mesomeric propargylic (allenylic) carbanion, the atom C(2), as follows from simple reasoning based on resonance structures, should not bear a negative charge, and MNDO calculations (Table 4) give even slightly positive charges at C(2). No correlation is observed between MNDO charges at C(2) and δC(2) for SSIP **1**. However, downfield shifts of ^{13}C(2) resonances in the SSIP relative to the resonances of the same nuclei in the parent AH, denoted as $\Delta\delta$C(2), increase linearly with the increase of bond order between C(2) and C(3), and the decrease of bond order between C(1) and C(2) (Fig. 7). Hence, a conclusion might be drawn that the variation in shielding constant of ^{13}C(2) nuclei in the salts of propynes and allenes is determined not so much by charges at C(2) atoms, but by C(2)–C(3) and C(2)–C(1) bond orders. If so, the values of δC(2) might have been regarded as a probe for testing which structure–propargylic, allenylic or borderline–should be assigned to some allene or propyne salt in solution.

The values of $\Delta\delta$C(2) for SSIP **1a**–**g** are not higher than 11–32 ppm (Table 1). Therefore, the structures of carbanions of these SSIP are closer to acetylenes, and not to allenes, so that these carbanions should be rather propargylic, and not allenylic. The carbanion of the SSIP of salt **1a** has the most developed acetylenic structure, that is probably because the p_z-AO of the C(3) atom in this carbanion is incorporated into the aromatic π-system of the fluorenyl moiety, which is more reluctant to drive electron density towards, the phenylethynyl part than substituents in the carbanions of other salts **1**. The $\Delta\delta$C(2) value and consequently the δC(2) value for SSIP **1h** can be estimated from the dependence shown in Fig. 7. These values are about 55 ppm and 151 ppm. The latter value is almost the average between δC(2) values for **2h** and **3h** (Table 1). In other words, the carbanion in SSIP **1h** has the structure intermediate between propargylic and

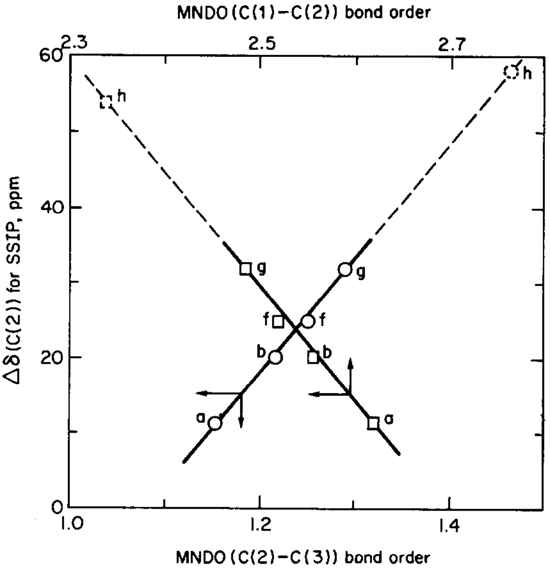


Fig. 7. ^{13}C(2) resonance shift in salts **1** relative to ^{13}C(2) resonance in AH *versus* C(1)–C(2) (□) and C(2)–C(3) (○) bond orders in free carbanions of salts **1**.

allenylic. If we consider, as a measure of allenylic character, the structure of AL with δC(2) = 196.4 ppm [6], one can propose that the carbanion in SSIP **1h** has a structure even closer to allenylic than to propargylic. Thus, the decrease of delocalizing abilities of substituents R^1 and R^2 results in a regular increase of allenylic character in the structures of the anions studied.

MNDO data on substituent effects on the structure of anions in salts **1** agree fairly well with earlier calculations of anions of some other propynes [7,33], and of the allenyl anion ($C_3H_3^-$) [7,34] (Table 4). However, the phenyl group Ph(1) at the C(1) atom of the studied salts ensures an almost planar structure of the anions (Table 4), with parallel p_z-AOs of sp^2-hybridized C(1) atoms and of $C_i(1)$ *ipso*-carbon atoms of Ph(1) groups. The structure thus meets the requirements of the highest possible delocalization of negative charge over both R^1 and R^2 substituents, and Ph(1) groups.

Total and π-charges (Table 4) at allenylic centres C(1), calculated by MNDO, are increasing with the decrease of delocalizing ability of R^1 and R^2 and with the growth of charges at propargylic centres C(3) (Fig. 8). This explains why the charges at $C_p(1)$ grow (Table 4) and $^{13}C_p(1)$ resonances in SSIP of salts **1** shift upfield (Fig. 5) together with the decrease of delocalizing ability of R^1 and R^2, *i.e.* with the decrease of the values of δC(3) of AH. As was observed for sp^2-hybridized carbon atoms [5,35], the increase of negative charge density at *sp*-hybridized C(1) atoms might be expected to result in an upfield shift of ^{13}C(1) resonance. Actually, in carbanions of salts **1** a decrease in delocalizing ability of R^1 and R^2 and growing charge density at C(1) atoms (Table 4) is followed by a downfield shift of ^{13}C(1) resonance (Table 1). To explain this the shielding constants of ^{13}C(1) in free carbanions and carbanions of SSIP of salts **1** may be argued to be dominated by factors other than charge, *e.g.* by C(1)–C(2) bond

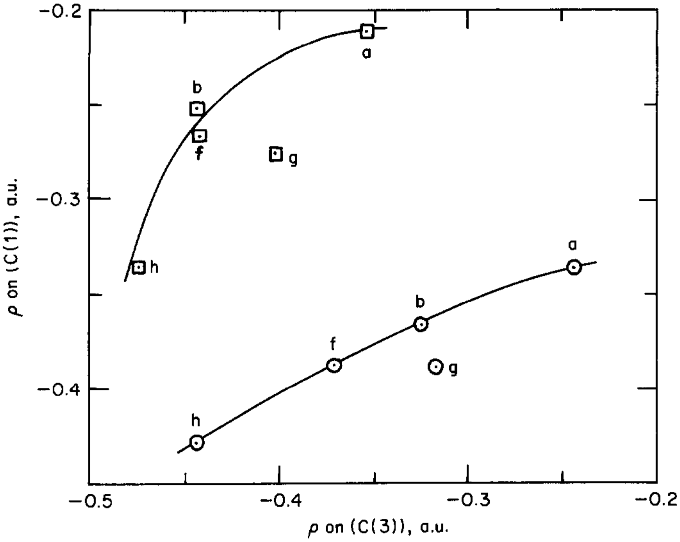


Fig. 8. The relation between total (⊙) and π (⊡) charges at C(1) and C(3) atoms calculated for free carbanions of salts 1 by the MNDO method.

order, which decreases with weakening of delocalizing ability of R^1 and R^2 (Table 4). The substantial deviation of δC(1) for **1d, e** from the general trend in the variation of δC(1) with the decrease of delocalizing ability of R^1 and R^2 is most likely due to the proximity of methoxy groups to propargylic centres C(3) in these salts. However, the effect of MeO groups on the negative charge distribution in carbanions **1d, e** is not quite clear.

The structure of contact ion pairs

Chemical shifts of C(1), C(2), C(3) in CIP of salts **1a–d, f** in DEE solutions are given in Table 1. Poor solubility of **1e** and aggregation of **1h** in DEE interfered with the measurement of the ^{13}C NMR spectra for the CIP of these salts. Therefore, for CIP **1e** and **1h** the data obtained in THF (Table 1) will be considered. That is a reasonable assumption, since spectral parameters of CIP are known to depend weakly on the nature of the solvent [18b]. Small temperature effects on δC in the CIP of **1b, f** in DEE, and of **1h** in THF (Table 1) enable the data obtained for all of the salts **1** at 27°C to be used in further discussion.

Chemical shifts for different carbon atoms in CIP and SSIP of salts **1** as has been mentioned above, differ significantly. Quantitative measures of these differences, the values of $dC = \delta C(CIP) - \delta C(SSIP)$ and $\Delta\delta C(SSIP)/\Delta\delta C(CIP)$ for some carbon atoms are given in Table 2. It is a matter of convention that the $\Delta\delta$C values for carbon atoms of aromatic rings in carbanions are proportional to excess (relative to the corresponding hydrocarbons) π-electron densities at these atoms ($\rho_\pi = \Delta\delta C/160$ [5,35]). Application of this relation to the data from Table 2 yields the values of ρ_π at $C_p(1)$ and $C_p(3)$ in the CIP 1.2–2 times lower than in the SSIP. The decrease of π-charges at $C_p(1)$ and $C_p(3)$ in the CIP relative to the SSIP is a result of polarization by the lithium cation [5], withdrawing electron density from aromatic rings to those carbon atoms with which the lithium cation is bound most

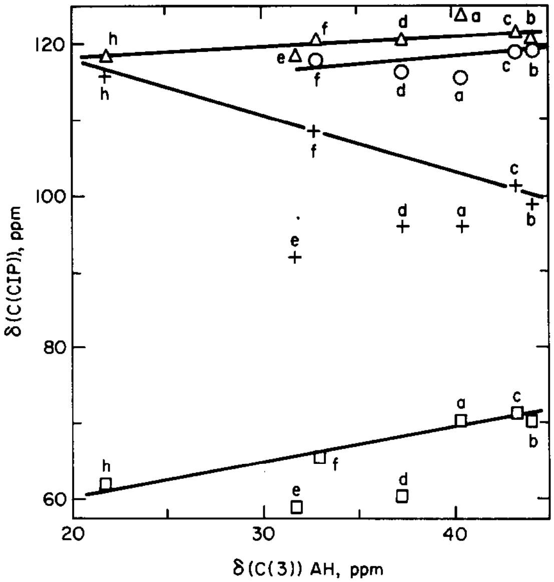


Fig. 9. The dependences of chemical shifts for $C_p(1)$ (△), $C_p(3)$ (○), C(1) (+) and C(3) (□) atoms in CIP of salts 1 on the total delocalizing abilities of R^1 and R^2 (δC(3) AH). For CIP **1e** and **1h**, data obtained in THF-d_8 at 27°C have been used.

tightly. The polarization induced by the lithium cation, however, cannot exclude the growth of π-charges at $C_p(1)$ and $C_p(3)$ in Ph(1) and Ph(3) which results in an upfield shift of $^{13}C_p(1)$ and $^{13}C_p(3)$ resonances occurring together with the decrease of total delocalizing ability of R^1 and R^2 in carbanions of salts **1** (Fig. 9). Similar behaviour is observed for $C_o(1)$ and $C_o(3)$ in Ph(1) and Ph(3).

The ^{13}C(2) nuclei in the CIP of salts **1** except for salt **1a** are more deshielded than those in the corresponding SSIP (Table 2). Moreover, the difference between δC(2) in CIP and SSIP increases with the decrease in delocalizing ability of R^1 and R^2 in the series **1b**, **c**, **f**, **h**.

A possible explanation for these observations, based upon fast equilibria between the covalent forms A and B,

$R^1R^2C(Li)\text{--}C{\equiv}CPh$ (A) $R^1R^2C{=}C{=}C(Li)Ph$ (B)

should be rejected since both the theoretical computations [10c, 34d, 36] and X-ray analysis of some derivatives of AL [10c,34d,37], and allenylsodium (AS) [34d,38] are against the existence of the extremes A and B even in the solid state. This is not unexpected since the C–Li bond in organolithiums is mostly ionic and multicentred, especially in those compounds where the charge is highly delocalized [10i,37–39].

For carbanions of salts **1** in which there are two centres with the highest charge density, the position of a cation might be assumed to be determined principally by the relative charges on these centres. The data of Table 4 show that along the series of carbanions **1a**, **b**, **f**, **g**, **h** the ratio of π-charges at C(1) and C(3) varies slightly, whereas the ratio of total charges at these centres decreases from 1.38 to

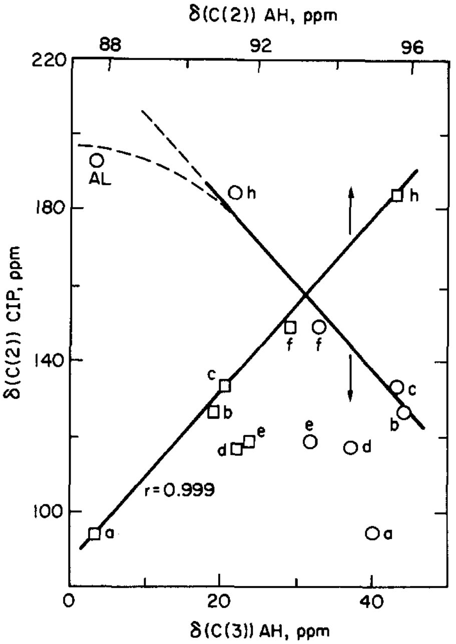


Fig. 10. The dependences of chemical shifts for C(2) atoms in CIP of salts 1 and in allenyl lithium [6] on the total delocalizing abilities of substituents R^1 and R^2 (δC(3) AH) (○) and on δC(2) AH (□). For δC(3) in propyne the value of 3.4 ppm, which is the same as δC(1) for 2-tridecyne [45], has been used.

0.96 in the series **1a**, **b**, **f**, **h** and for **1g** is equal to 1.23. In CIP formed from the carbanions under study, the equilibrium position of lithium is likely to be determined mainly by relative magnitudes of total charges at C(1) and C(3). In this case, relative weakening of the bond between the lithium cation and the allenylic centre C(1) in the series of CIP **1a**, **b**, **f**, **h** should have resulted in a decrease of allenylic character in the structure of CIP. However, ^{13}C NMR data show that, in reality, δC(2) values increase in the series of CIP **1b**, **c**, **f**, **h** with the decrease of delocalizing ability of R^1 and R^2, *i.e.* with the decrease in δC(3) values for AH (Fig. 10). Consequently, in these series, the allenylic character of the carbanions increases. The discrepancy between the above reasoning and experiment is certainly due to the neglect of the interactions of the lithium cation with all other atoms but the negatively charged C(1) and C(3).

The observed changes in the structures of CIP of salts **1**, as well as the ratios of products formed in alkylation of SSIP [4b,c] may be successfully treated using the electrostatic potential maps [40] showing the Coulomb interaction of a charged particle q^+ with not only C(1) and C(3), but all other carbon atoms in the carbanions studied. The electrostatic potential maps, drawn with MNDO atomic charges at a distance of 2 Å from the molecular plane [41*], show that potential wells for carbanions **1a**, **b** are located near C(3), for carbanion **1h** near C(1), and for carbanion **1f** between C(1) and C(3). The energy gap $E_{el} = E_1 - E_3$ of the

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* Reference with asterisk indicates a note in the list of references.

electrostatic interaction of q^+ with C(1) and C(3) centres amounts, for anions **1a**, **b**, **f**, **h**, to 0.35, 1.01, −0.22, −1.02 eV, respectively.

Thus, the decrease in total delocalizing ability of R^1 and R^2 in the studied carbanions should result in stronger interaction of the cation with the allenylic centre C(1) and weaker interaction with the alternative centre C(3). We have not been able to confirm this conclusion by theoretical computations, since MNDO overestimates covalent bonding of lithium to carbons [10a,c,d,f,g,i,42]. For salts **1** the interaction of lithium with *ortho*-carbons of aromatic rings is highly overestimated.

The bridging character of the lithium cation between C(1) and C(3) in the CIP of the salts **1** is in fair agreement with a similar structure pattern found in AL, AS, and some other compounds of a similar kind [10c,34d,36–38], where the cation is stated to lie closer to C(1) than to C(3). In dilithiated propyne the bridging cation between C(1) and C(3) is located, from computational evidence [39b], closer to C(3). This effect nicely conforms with the expectations based on our data, since the negative charge on the *sp*-orbital of C(1) is bound to cause shift of charge at the orthogonal orbital towards C(3). Lithium cation balancing against the mesomeric part of the dianion is shifted in the same direction. The cation is also shifted towards the C(3) atom due to the interaction with lithium bonded to the acetylenic centre C(1). In allyllithium compounds related to metallated propynes and allenes the cation is able to take its place unsymmetrically between C(1) and C(3) [19g,43].

In the alkali metal derivatives of propynes and allenes mentioned above, the angle between the atoms C(1), C(2), and C(3) is considerably smaller than 180° [10c,34d,36–38,39b], so the cation may come closer to C(2), than to C(1) and/or to C(3). However, the data [36,39b] show that lithium only weakly interacts with C(2). The interaction of lithium with the C(1)–C(2) bond π-system, as well as in allyllithium compounds [43c,44], is supposed to be relatively weak. Therefore, one can propose that the cation possibly should not strongly influence the δC(2) values in CIP of salts **1**. Therefore, the values of δC(2) in CIP, as in the case of SSIP, are determined probably by C(1)–C(2) and C(2)–C(3) bond orders. This is why these values can be used for making decisions on the propargylic and/or allenylic character of carbanions in the systems with organolithium compounds under investigation.

As the delocalizing ability of R^1 and R^2 decreases, the cation shifts stepwise towards C(1) and the bond between lithium and this centre strengthens, resulting in enhanced polarization of the π-electron system of the carbanion by the cation towards the C(1) atom. As a consequence, on going from CIP **1a** to CIP **1h**, C(2)–C(3) bond order would increase, C(1)–C(2) bond order would decrease, which should cause downfield shift of the ^{13}C(2) resonance not only relative to the resonance of ^{13}C(2) in the corresponding SSIP (Table 2), but also in the cited range of CIP. Indeed, the values of δC(2) in the CIP **1b**, **c**, **f**, **h** are increasing in a regular manner (Fig. 10) together with the decrease of δC(3) in AH, δC(2) for CIP **1h** coming close to δC(2) in AL [6]. It is noteworthy that the shifts δC(2) for the CIP **1a**, **b**, **c**, **f**, **h** and δC(2) for AH show a good linear correlation (Fig. 10), which might be of use in estimating the magnitude of δC(2) in CIP of some similar salts left out of the scope of the present study, by the known shifts of δC(2) in the corresponding AH. A possible source of the deviation of points for **1a**, **d**, **e** from the lines in Fig. 10 will be discussed further. Thus, the decrease of delocalizing

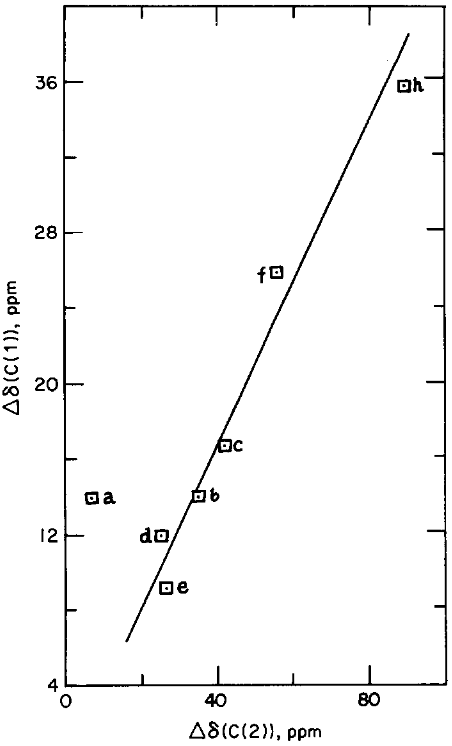

Fig. 11. Relations between differences in chemical shifts for C(1) and C(2) atoms in CIP of salts 1.

ability of R^1 and R^2 results in growing allenylic character of the structures of carbanions in the CIP of allenes and propynes [46*]. This might be a reason to consider organolithiums with structures similar to CIP of **1a-e** or SSIP of **1a-g** as propargyllithiums, and those resembling CIP of **1f**, **h** or SSIP **1h** as allenyllithiums.

The values of δC(3) in the CIP **1a–c**, **f**, **h** decrease almost proportionally with the decrease of total delocalizing ability of R^1 and R^2 (Fig. 9). As in the case of SSIP **1**, this is likely to be associated with the increase of total charge at C(3) in this series of CIP. The decrease of delocalizing ability of R^1 and R^2 results in a downfield shift of ^{13}C(1) resonances in both CIP (Fig. 9) and SSIP. The shift of ^{13}C(1) resonances in the carbanions relative to the resonances of these nuclei in the parent AH parallels the trend towards a more allenylic character of the structure in carbanions in CIP (Fig. 11). Up to now, these findings have been hard to rationalize, since in the series of CIP of salts **1** not only the charge at C(1), but a lot of other factors, such as the distance from lithium to C(1), C(1)–C(2) bond order, and hybridization state of C(1), are likely to vary. The change in hybridization state is clearly seen from MNDO computations. While in SSIP of **1** the dihedral angles C_i(1)–C(1)–X–C(2) and bond angles C(1)–C(2)–C(3) are close to 180° (Table 4), some preliminary results show that in CIP **1a**, **b**, **f** these angles are about 174–178°. In CIP **1h** the angles shrink to 136° and 166°, respectively, and the bond angle C(2)–C(1)–Li is equal to 76°. Although these results are in good agreement with both computational and X-ray structure evidence for alkali metal derivatives of some propynes and allenes [10c,34d,36–38], the data for **1h** might be challenged since MNDO so greatly overestimates the interaction of lithium with $C_o(1)$-*ortho*-carbons of phenyl ring attached to C(1)–that the dihedral angle $C_o(1)$–$C'_o(1)$–$C_i(1)$–C(1) significantly deviates from 180° (Table 4). In the case of CIP **1b, f** the overestimation by MNDO of the interaction of lithium with *ortho*-carbons of phenyl rings attached to C(3) leads to skewing of these rings around the C(3)–$C_i(1)$ bond, as compared to SSIP.

Figures 9–11 show that the points for the CIP of salt **1a** deviate from almost all the lines. The salt represents a class of substituted fluorene carbanions, while a majority of the salts (**1b–g**) under study are of arylmethane kind. This factor is likely to account for the observed discrepancies of the ^{13}C NMR parameters not only for CIP but for SSIP **1a**. As has been shown above, another peculiar property of CIP **1a** is that the resonances of not only ^{13}C(3), but ^{13}C(2) are upfield compared to the signals of the same nuclei in SSIP: the values of dC in Table 2 for both the nuclei are negative. Such behaviour cannot be ascribed solely to specific feature of fluorenyl carbanion being an integral π-electron system. The most probable explanation is that in CIP **1a**, the cation prefers a location over the atom C(3) and one of the *ortho*-carbons of the fluorenyl moiety. The suggestion is confirmed by preliminary data of MNDO calculations for CIP **1a**, as well as by structures of externally solvated CIP of FL in the solid state [47]. In such a location, the cation cannot effectively interact with C(1), but induces a significant polarization of the carbanion towards C(3). Polarization results in a decrease of charge density at $C_p(3)$ (carbon atoms at *para*-sites to C(3)–C(3) and C(6) of the fluorenyl moiety), at C(1) and $C_p(1)$. An increase of C(1)–C(2) bond order, a decrease of C(2)–C(3) bond order, and buildup of charge on C(3) are also observed. As a consequence, the signals of C(1), $C_p(1)$, $C_p(3)$ are shifted downfield, the signals C(2) and C(3) are shifted upfield relative to those in SSIP (Table 2), where the cation exerts negligible influence on the charge density distribution in the carbanion.

We believe that similar reasons are responsible for the higher propargylic character of CIP **1d, e** in comparison with CIP **1b, c**, the smaller increase of allenylic character of carbanions on going from SSIP to CIP (dC(2) values in Table 2 are the measure of this increase) and also the larger upfield shift of ^{13}C(3) resonance in CIP in comparison with SSIP for salts **1d, e** relative to SSIP for salts **1b, c** (Table 2). In CIP **1d, e**, coordination of the cation to MeO groups in phenyl rings in *ortho*-positions to the carbanion centre [3b,25,48] draws the cation towards the propargylic centre C(3) closer than in the case CIP **1b, c**, where there are no such specific interactions. The coordination of the lithium cation to the MeO group leads to an increase in dissociation energy of *o*-MBL by approx. 50 kJ/mol [25b], and to more than 18-fold decrease in the dissociation constant in THF [48a]. It is this strong interaction of the lithium cation with the MeO group that causes salts **1d, e** to exist in THF at ambient temperatures exclusively as CIP, while **1b, c** under such conditions almost quantitatively transform to SSIP.

The intramolecular interaction of lithium with MeO group in CIP **1d, e** can be considered as "internal solvation" of the cation [48f], which makes the interaction of the cation with the carbanion much weaker. This is why the carbanions in CIP **1d, e** have features similar to those of SSIP of these salts. Small values of dC(2) and dC for other carbon atoms in salts **1d, e** (Table 2) can thus be explained.

The oxygen atoms of MeO groups of salts **1d**, **e** are at a larger distance from C(3) than the atoms $C_o(3)$ (C(1) and C(8) of the fluorenyl moiety), which can coordinate the lithium cation in **1a**. Therefore, in CIP **1d**, **e**, the cation is supposed to be somewhat more remote from C(3) than in CIP **1a**, but closer than in CIP **1b**, **c**; consequently, it has to polarize carbanions of CIP **1d**, **e** towards the propargylic centre to a lesser extent than in CIP **1a**, but to a larger extent than in CIP **1b**, **c**.

The interaction of carbanion centre C_α with aromatic substituents leads to a significant degree of resonance saturation of these substituents in *ortho*- and *para*-methoxybenzyl carbanions, therefore, MeO groups in the latter are weaker donors than in the corresponding anisols. The polarizing effect of the lithium cation reduces the degree of resonance saturation in carbanions of *o*-MBL and *p*-MBL [25]. Greatly enhanced possibilities of negative charge delocalization in carbanions of CIP **1c**–**e**, than in *o*-MBL and *p*-MBL, should still farther diminish the resonance saturation of the phenyl rings bearing MeO groups. The smallest degree of resonance saturation, at least for one of the substituents R^1 and R^2, has to be exhibited for CIP **1e**. In this case, a higher total electron-donating ability of MeO groups in **1e** compared to that in **1d** should lead to higher electron density at R^1 and R^2 as well as at the atom C(3) in CIP **1e** and, consequently, to a stronger electrostatic attraction of lithium to the $R^1R^2C(3)$ fragment and a shorter distance between lithium and C(3). Then, the carbanion will be polarized to a higher extent towards C(3) in CIP **1e** than in CIP **1d**, and still more in the CIP of **1c**, where there is no coordination of lithium cation with the *para*-MeO group.

Thus, the distance Li–C(1), the degree of polarization of carbanion by lithium cation towards C(3), the relative negative charge at C(3) in CIP compared to SSIP of salt **1** have to vary in the order **1a** > **1e** > **1d** > **1b**, **1c**, which is confirmed by an increase of dC(3) (Table 2) along the series (1).

1a < **1e** < **1d** < **1b** < **1c** < **1f** < **1h** (1)

The ordering (1) shows that for particular salts **1**, the variation of negative charge at C(3) in CIP relative to SSIP is determined in fact not only by the change of the total delocalizing ability of substituents R^1 and R^2, but rather by the ability of the cation to induce polarization of mesomeric carbanions towards the propargylic centre. This ability in its turn depends on the distance Li–C(3), which, as one might judge from the sequence (1), should increase in the same direction, and the distance Li–C(1) should increase in the opposite direction.

In CIP of salt **1a**, the cation may reside not between C(3) and C(1) as in CIP **1b**–**h**, but rather over the plane of the 5-membered central ring of the fluorenyl moiety [10d,17g,39d,49]. In this case, the distance Li–C(3) might even pass beyond the range relevant to the CIP of other salts **1**. Nevertheless, the distance Li–C(1) and the degree of polarization of carbanion from C(1) towards C(3) in CIP **1a** will somehow outweigh these characteristics for the CIP of other salts under study.

The variation of the degree of cation-induced polarization of carbanions towards C(3), occurring within the series (1), results not only in a regular shift of $^{13}C(3)$ resonances in CIP relative to SSIP and consequently, in the increase of dC(3) values (Table 2), but also in a quite regular, corresponding to these latter parameters, trend in shifts of resonances of $^{13}C(2)$, $^{13}C(1)$ (Fig. 12), some other

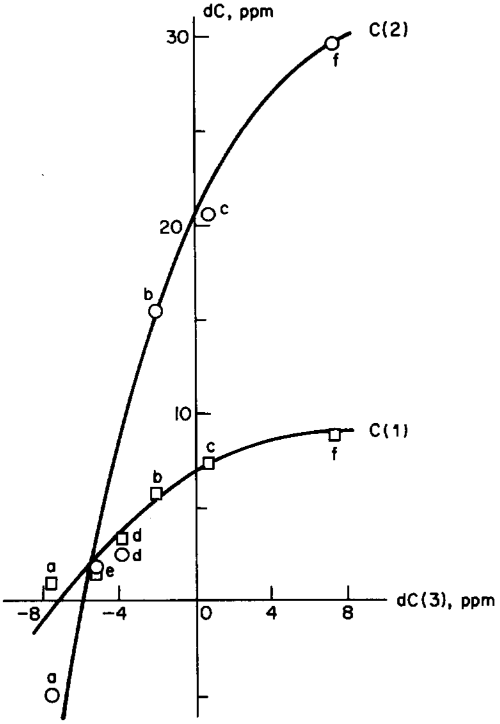

Fig. 12. Dependences of differences in chemical shifts for C(1) (□) and C(2) (○) atoms in CIP and SSIP of salts 1 on similar differences for C(3) atoms.

carbon nuclei (Table 2) in CIP relative to the resonances of the same nuclei in SSIP.

The results reported in the present work show, that in general any unaggregated (to dimers, trimers etc.) alkali salts of propynes or allenes can exist in ethereal solutions in two distinct forms, *i.e.* CIP and SSIP. In these forms, the negative charge distribution of the mesomeric carbanion would resemble a propargylic or near-to-propargylic anion, in another allenylic or near-to-allenylic anion. It seems unfeasible to assert *a priori* which of the two structures will the given carbanion assume in CIP and/or SSIP. However, the evidence gathered until now allows us to exclude the very possibility that lithiated propynes or allenes exist predominantly in allenylic form A [1b] and equilibrate between two of the covalent forms A and B [1,8,50], let alone the existence of the equilibrium between the distinct propargylic and allenylic forms of carbanions [1c,f]. More correct is to discuss the equilibria between CIP and SSIP, in which carbanions might assume any structure, be it propargylic, allenylic or some kind of borderline between these extremes. In media strongly solvating the alkali metal cations, where free carbanions can occur in reasonable concentrations [4a,22b], the structure of such carbanions would also shift depending on the nature of the substituents at the C(1) and C(3) atoms. The structure of carbanions of the type under discussion either in free form, or in CIP or SSIP, might be of prime importance in determining the ratios of acetylenic and allenic products forming in reactions with electrophiles [4,22,51].

The trends in variations of δH and δC for aromatic rings in salts **1** agree well. The ^{1}H NMR spectra are not discussed in the present work since these data bear less information, particularly concerning the structure of the triad C(1)–C(2)–C(3) in the carbanion. On the other hand, ^{13}C NMR provides abundant relevant information, because δC(2) for the studied salts vary over a broad range (approx. 100 ppm) and their values give clear evidence in favour of the form (propargylic, allenylic, or borderline) in which the alkali metal derivatives of propynes and allenes exist in solution.

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[34d,36,37,38,39b]. Our preliminary MNDO computational data show that in CIP of salts **1** the shortest distance between lithium cation and one of carbanion centres C(1) or C(3) is about 2 Å.

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