was extracted with CH_2Cl_2. After workup, the crude product was dissolved in benzene (3 mL) containing pyridine (155 μL) and refluxed for 2 h. The residue obtained by evaporation was purified by TLC with CH_2Cl_2 as eluent to afford **46a** (36 mg, 60%): IR (CCl_4) 1705, 1730, 1640, 1624 cm^{-1}; ^1H NMR 2.36 (s, 3 H), 3.80 (s, 3 H), 6.62 (d, 1 H, J = 16), 7.03 (d, 1 H, J = 16).

Methyl 4-Oxo-2-hexenoate (46b). A solution of mCPBA (85% assay, 108 mg, 0.5 mmol) in CH_2Cl_2 (3 mL) was added to a stirred solution of **26′** (126 mg, 0.5 mmol) in the same solvent (3 mL) at −78 °C, and stirring was continued for 3 h at the same temperature. Water was added, and the product was extracted with ether. The extract was washed with aqueous $NaHCO_3$, water, and then brine. The residue obtained by evaporation was heated in a mixture of benzene (4 mL) and pyridine (161 μL, 2 mmol) for 2 h, and then the benzene was removed by evaporation. The unsaturated ester **46b** (48 mg, 68%) was obtained from the residue by TLC with CH_2Cl_2 as eluent: IR (CCl_4) 1730, 1705, 1690, 1640, 1628 cm^{-1}; ^1H NMR 1.14 (t, 3 H, J = 6), 2.68 (d, 2 H, J = 6), 3.80 (s, 3 H), 6.68 (d, 1 H, J = 16), 7.07 (d, 1 H, J = 16).

Methyl 2-(1-Methyl-2-oxocyclohexyl)-4-oxopentanoate (48a) and Methyl 2-(1-Methyl-2-oxocyclohexyl)-4-oxohexanoate (48b). $TiCl_4$ (110 μL, 1.0 mmol) was added to a stirred solution of **46a** (128 mg, 1 mmol) at −78 °C under Ar, and the mixture was stirred for 30 min. 2-Methyl-1-((trimethylsilyl)oxy)cyclohexene (**47**) (330 μL, 1.5 mmol)[14] was then added dropwise to the above solution at the same temperature, and the mixture was allowed gradually to raise to room temperature over 3 h. After addition of water, the product was extracted with ether, and the extract was washed with water and brine. The residue obtained by evaporation of the solvent was purified by TLC with CH_2Cl_2 as eluent to yield **48a** (197 mg, 82% yield): bp 120 °C (1.5 mmHg); IR 1725, 1710 cm^{-1}; ^1H NMR[18] 1.02 and 1.04 (two s in ca. 1:1 ratio, 3 H in total), 1.2–2.1 (m, 7 H), 2.08 and 2.16 (two s in ca. 1:1 ratio, 3 H in total), 2.2–3.5 (m, 4 H), 3.52 and 3.62 (two s in ca. 1:1 ratio, 3 H in total). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.70; H, 8.77.

By the same manner, **48b** (64 mg, 71% yield) was obtained from **46b** (51 mg): bp 120 °C (3 mmHg); IR 1740–1705 cm^{-1}; ^1H NMR[18] 0.9–1.2 (overlapped singlet and triplet, 6 H in total), 1.2–2.2 (m, 7 H), 2.42 (q, 2 H, J = 7), 2.2–3.2 (m, 4 H), 3.56 and 3.65 (two s in 1:1 ratio, 3 H in total). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.33; H, 8.98.

4,4a,5,6,7,8-Hexahydro-4a-methyl-4-carboxy-2(3*H*)-naphthalenone (49a) and 4,4a,5,6,7,8-Hexahydro-1,4a-dimethyl-4-carboxy-2(3*H*)-naphthalenone (49b). A mixture of **48a** (96 mg, 0.4 mmol), KOH (86% assay, 261 mg, 4.0 mmol), water, (0.4 mL), and ethanol (4 mL) was heated at 70 °C for 4 h. After dilution with water, the product was extracted with ether, and the aqueous layer was acidified with dilute HCl. Acidic product **49a** (74 mg, 89% yield) was obtained by extraction with ether: ^1H NMR 1.29 and 1.42 (two s in ca. 1:1 ratio, 3 H in total), 1.0–3.1 (m, roughly 11 H), 5.80 and 5.82 (two s in ca. 1:1 ratio, 1 H in total), 8.64 (br s, 1 H).

By the same procedure, **49b** (106 mg, 86% yield) was obtained from **48b** (141 mg): ^1H NMR 1.24 and 1.40 (two s in ca. 1:1 ratio, 3 H in total), 1.0–3.0 (m, approximately 11 H), 1.78 (s, 3 H), 8.80 (br s, 1 H).

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Registry No. **6**, 142-62-1; **7**, 97-61-0; **8**, 103-82-2; **9**, 103-04-8; **10**, 17431-94-6; **11**, 4749-28-4; **12**, 2783-12-2; **13**, 2562-37-0; **14**, 4812-23-1; **15**, 26817-75-4; **15′**, 77903-61-8; **16**, 84796-99-6; **16′**, 84796-95-2; **17** (isomer 1), 84797-00-2; **17** (isomer 2), 84797-01-3; **17′** (isomer 1), 84805-09-4; **17′** (isomer 2), 55311-10-9; **18** (isomer 1), 90670-05-6; **18** (isomer 2), 90670-06-7; **18′** (isomer 1), 88869-02-7; **18′** (isomer 2), 88869-03-8; **19**, 84797-02-4; **19′**, 84796-96-3; **20**, 84797-03-5; **20′**, 84796-97-4; **21**, 72349-79-2; **21′**, 75436-61-2; **22**, 4439-87-6; **22′**, 74457-44-6; **23**, 13122-69-5; **23′**, 84796-94-1; **24** (isomer 1), 84805-10-7; **24** (isomer 2), 84796-98-5; **24′** (isomer 1), 84805-07-2; **24′** (isomer 2), 84805-08-3; **25**, 84796-81-6; **25′**, 84796-82-7; **25′**-ol, 90670-14-7; **26**, 84796-89-4; **26′**, 84796-83-8; **27** (isomer 1), 84796-90-7; **27** (isomer 2), 84796-91-8; **27′** (isomer 1), 84796-84-9; **27′** (isomer 2), 84796-85-0; **28** (isomer 1), 84805-03-8; **28** (isomer 2), 84805-04-9; **28′** (isomer 1), 84796-86-1; **28′** (isomer 2), 84805-00-5; **28′**-ol, 90670-09-0; **29**, 84796-92-9; **29′**, 84796-87-2; **30**, 84796-93-0; **30′**, 84796-88-3; **31** (isomer 1), 84805-05-0; **31** (isomer 2), 84805-06-1; **31′** (isomer 1), 84805-01-6; **31′** (isomer 2), 84805-02-7; **32**, 106-70-7; **33**, 110-42-9; **34**, 4630-82-4; **35**, 101-41-7; **36**, 17277-58-6; **37**, 75436-60-1; **38**, 88869-08-3; **39**, 88869-09-4; **40**, 53138-46-8; **41**, 591-11-7; **42**, 53183-56-5; **43** (isomer 1), 53390-35-5; **43** (isomer 2), 90670-15-8; **44**, 3727-53-5; **45**, 15174-78-4; **46a**, 2833-24-1; **46b**, 90670-10-3; 47, 19980-35-9; **48a** (isomer 1), 90670-11-4; **48a** (isomer 2), 90670-07-8; **48b** (isomer 1), 90670-12-5; **48b** (isomer 2), 90670-08-9; **49a** (isomer 1), 67800-09-3; **49a** (isomer 2), 90670-16-9; **49b** (isomer 1), 90670-13-6; **49b** (isomer 2), 90670-17-0; propanoic acid, 79-09-4; cyclohexanecarboxylic acid, 98-89-5.

Charge–Carbon-13 Empirical Relationships in Organic Ions: An Improvement Extending the Access to Experimental Charge Maps

Silvia Bradamante and Giorgio A. Pagani*

Centro C.N.R. and Istituto di Chimica Industriale dell'Università, via Golgi 19, 20133 Milano, Italy

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An improved empirical relationship between ^{13}C shifts and local π electron densities is proposed for organic ions. Accordingly, the ^{13}C shifts can be predicted by summing two terms: the first takes into account the shielding contributions of neighboring groups and represents the shift of a hypothetically uncharged trigonal carbon with the same chemical environment as that of the ion, while the second term accounts for the effect of π charge upon this shift. The validity and generality of the relationship are tested in a number of carbanions and carbenium ions constituted of a hydrocarbon skeleton only and in which the charge is fully delocalized. A good accord is generally found between empirical and theoretically computed local π electron densities: exceptions, in particular those relative to triphenylmethyl ions, are discussed in detail. The proposed relationship represents an easy and expeditious method for obtaining experimental, empirical charge maps in organic ions starting from their ^{13}C shifts.

Carbanions and carbenium ions are key intermediates in many reactions of organic chemistry. When the charge is delocalized over an extended π system, structure–reactivity relationships require in the first step a detailed knowledge of charge density maps. Although theoretical calculations provide one access to charge distribution, in view of the fact that they usually ignore the effects that different solvents have on the structure of the intermediate, experimental organic chemists prefer to rely on experimental sources of charge density maps. The establishment over 20 years ago of an empirical relationship (eq 1) between charge and an observable quantity (^1H and ^{13}C

$$\delta_c = \delta_n - k(q - 1) \tag{1}$$

$$\delta_c = 290 - kq \tag{2}$$

$$\delta_c = 123 - 167(q - 1) \tag{2a}$$

shifts) represented a long sought goal.[1,2] Equation 1 relates the shift of the charged carbons δ_c of a number of cyclic, symmetric aromatic hydrocarbon ions to the shift of the neutral precursor δ_n through a term which takes care of the effect of charge with a sensitivity for carbon of 160 ppm/electron.

Although the Lautebur–Schaefer–Schneider relationship "has become a part of our grammar",[3] it presents serious practical and theoretical limitations. In fact the value of δ_n becomes practically ill defined in noncyclic, nonsymmetric systems. To circumvent this difficulty, the relationship in eq 2 (k = 167 ppm/electron), obtained by plotting charge densities of a theoretical source (HMO, CNDO) vs. ^{13}C shifts in a number of carbanions and carbenium ions, was proposed;[2c,4] a similar expression (k = 156 ppm/electron) was obtained by plotting *average* chemical shifts and average charge densities in a number of carbanions.[5] Actually, eq 2 is a particular, limited case of the more general eq 1; in fact, for k = 167, eq 2 can be written in the form of eq 2a, identical with eq 1, in which the reference shift δ_n is assumed to be the shift of unsubstituted ethylene (123 ppm). Because of this constraint the prediction of *local* (nonaveraged) charge densities in noncyclic systems becomes imprecise; furthermore carbons, which undergo configurational rehybridization ($sp^3 \rightarrow sp^2$) on going from neutral to the ion, cannot be treated and no account for the influence of α-substitution at the charged atom, in particular when heteroatoms are present,[2c] can be provided.

Serious limitations of linear charge–shift relationships are encountered when a theoretical justification is looked for. Accordingly, Grutzner[6] has recently questioned acritical applications of linear charge–shifts relationships; his view is supported by the failure of such relationships in a number of carbanions, carbenium ions, and neutral molecules. The most striking examples are the norbornadienyl cation,[7,8] phenyl lithium,[7,9] acetylene, and allene.[10] There are three key factors influencing ^{13}C shifts: (a) the orbital symmetry for paracyclic mixing,[6] appropriate to induce electron orbital angular momentum in the presence of a magnetic field; (b) the p orbital size as influenced by charge effects; (c) the energy gap for electron promotion. According to Grutzner's analysis,[6] any variation of one of these factors either within the set of the charged species submitted to correlation or within the couple formed by the charged species and its neutral model will introduce effects which cannot be ascribed to charge effects alone and which will ultimately lead to a failure in the correlation.

We have devised an empirical method for estimating the value of δ_n in open chain organic ions, in such a way that it approaches the incorporation of all the shielding contributions except charge; we believe that in this way the theoretical limitations associated with linear charge–shift relationships are circumvented.

The carbanions and carbenium ions we have considered have been restricted to systems possessing a hydrocarbon skeleton only in order to check the internal consistency of the method; results confirm the validity of the approach and show that the improved form of eq 1 we propose, eq 4, has a much more general and wider predictive scope than older relationships, so far limited to simple, cyclic, symmetric charged species. The application of eq 4 to α-substituted benzyl carbanions containing heteroatoms will be reported shortly.[12]

Results

Since within a set of charged organic species, change in substituent bond character at the charged carbon can generate shift changes which overwhelm the charge effect, it is essential to maintain constant bonding around such a center in order to permit the interpretation of the shift in terms of charge effects alone. Therefore the shift δ_c of the charged species can take as a reference neither the shift of the neutral hydrocarbon they are related to (since the bonding situation is different because of the different hybridization of at least one carbon) nor the aspecific shift of ethylene in which the shielding contributions are ignored. To keep constant bonding character around the charged atom however would prevent *every* charge–shift correlation, since no substituent variation would be pos-

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(7) The 7-norbornadienyl ion[8] shows *upfield* shifts at all positions except the bridgehead carbon, and carbon-1 in phenyllithium and phenyl Grignard shows[9] major *downfield* shifts relative to benzene, in direct contradiction to eq 1. In neutral molecules,[10] the chemical shifts of acetylenic carbons and the central carbon of allenes differ by over 100 ppm despite the fact that they are both sp hybridized and formally neutral. Without questioning Grutzner warning, it appears there are reasons to believe that the 7-norbornadienyl cation has special properties which make it different from common classical carbenium ions. Also, eq 1 was originally proposed for delocalized systems and phenyl carbanion is certainly not one of them; if however other vinyl localized carbanions are considered,[11] a systematic downfield shift is observed relative to the neutral precursor. Even without considering the different situation regarding ionization and dissociation equilibria in a solution of localized and delocalized carbanions, no one would reasonably pretend these species ought present analogous quantitative properties and reactivities.

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Table I. Shielding Contributions to Trigonal Carbon

group	position[a]	shielding, ppm
Ph	α	13.0
CH_3	α	13.0
$CH{=}CH_2$	α	14.4
C	β	4.5
C	γ	−1.5
C	α'	−7.9

[a] As defined in ref 15.

sible. Therefore, the effect of variation of substituent bond character must be poured into the δ_n term of eq 1. If positively and negatively charged carbons in delocalized carbanions and carbenium ions are trigonally hybridized, it is possible to define what the δ_n term should represent. It is the shift, in an appropriate (hypothetical) model, of a neutral trigonal carbon atom which, presenting the same substitution pattern as that of the charged carbon of the ion, would mimic as close as possible its bonding situation with substituents.

In recent years, much has been learned about the effects of several groups on the ^{13}C shifts of substituted ethylenes; a number of correlations of predictive power have been proposed.[10,13–15] In particular, it is possible to estimate, empirically but with considerable precision, ^{13}C shifts of substituted ethylenes, correcting the shift of ethylene itself by additive increments, typical for each substituent and dependent from the site of substitution along the chain. Thus, in view of the fact that for $q = 0$ the intercept of eq 2 is indeed the shift of parent ethylene and in the light of the foregoing discussion defining the meaning of δ_n, we propose that δ_n should assume the expression in eq 3, and, consequently, eq 1 should be transformed into eq 4.

$$\delta_n = 122.8 + \sum A_i \qquad (3)$$

$$\delta_c = 122.8 + \sum A_i - k(q - 1) \qquad (4)$$

The A terms of eq 4 represent the contributions to the shielding of the trigonal carbon due to polar inductive effects of the adjacent substituents, devoid of any mesomeric influence. The check for the validity and generality of the extended eq 4 requires that the charged substrates under consideration are made up exclusively of a hydrocarbon skeleton; in fact, only in this case it is possible to sum all the π charge densities on each carbon atom to obtain the total π charge. Therefore, we shall restrict the range of substituents under consideration to phenyl, vinyl, and alkyl groups. The shielding effects of these groups are collected in Table I; therein are also reported effects of further neighboring groups, as tabulated by Wehrli and Wirthlin.[15] In contrast with the treatment of olefinic carbons,[15] eq 3 does not include correction terms for α,α-disubstitution and, by extension, for α,α,α-trisubstitution. This choice appears experimentally justified at least in two cases. The shielding effect of phenyl groups on α carbons is almost additive on going from ethylene to styrene to α,α-diphenylethylene as reported in Chart I. Furthermore, it appears that the predictive power of eq 4 is already sufficiently precise, particularly when substitution with more than one methyl group is considered as in examples of Table II, for not requiring correction terms. As an exception, the α,α-correction term has been considered for the special structure of Grutzner's benzyl anion[16] (see Experimental Section).

Chart I

$CH_2{=}CH_2$	$PhCH{=}CH_2$	$Ph_2C{=}CH_2$
$\delta C_\alpha = 122.8$	$\delta C_\alpha = 135.8$	$\delta C_\alpha = 150$
	$(\Delta = 13)$	$(\Delta = 14.2)$

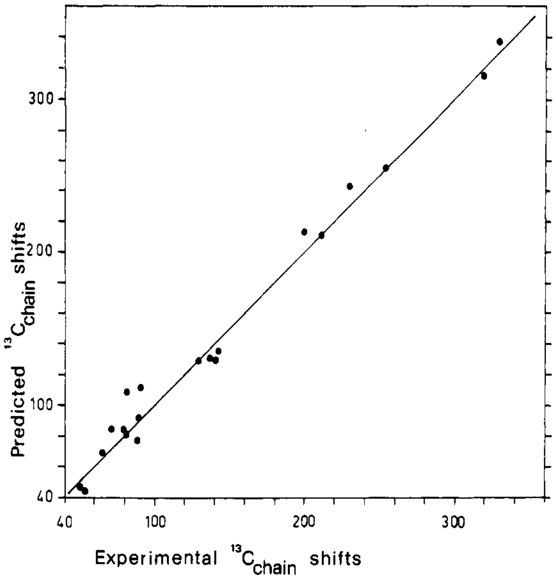

Figure 1. Experimental vs. predicted ^{13}C shifts for chain carbons in ions 1–14. Hückel π charges have been used as input for q of eq 4.

Details of the calculation of the δ_n value in a number of cases are reported in the Experimental Section. For the aromatic carbons the δ_n values are the shifts of the corresponding carbons of the related neutral hydrocarbon; thus for benzyl anion and for both the diphenylmethyl carbanion and carbenium ion, toluene and diphenylmethane are taken as a reference.

A delicate decision concerned the choice of the numerical value of the constant k of eq 4; in view of the widely accepted value of 160 ppm/electron,[1] very close to the value of 156 ppm/electron found by O'Brien,[5] we elected this value for carbanions, while the value of 167 ppm/electron, first proposed by Olah,[4] appeared preferable for carbenium ions.

Table II reports all the charged species which have been submitted to the treatment of eq 4; this collection, far from being exhaustive is intended to offer some of the most representative examples. Table II also reports ^{13}C shifts for carbanions 11, 12, and 14 obtained in the present investigation. Although they were already known in a variety of solvents, we wanted to have both the neutral precursors and the anions recorded in the same solvent, in order to avoid possible errors due to solvent effects, which might be incorporated finally in the charge term of eq 4. Among the charged species taken from the literature and collected in Table II, only the ion 7 has been studied in the same solvent used for the neutral.[16] Results indicate however that solvent effects are relatively small. Carbanions 11, 12, and 14 were prepared in Me_2SO by using sodium dimsyl as a base. ^{13}C shifts of the corresponding neutrals were available from our previous investigation.[17]

For estimating how good eq 4 works, it is possible to compare the experimental shifts with those predicted from eq 4 using charge densities obtained from theoretical calculations. Figures 1 and 2 report such plots while their

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Table II. Comparison between Experimental and Predicted ^{13}C Shifts (ppm) and Empirical and Computed π Electron Densities in Carbanions and Carbenium Ions[a]

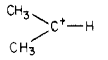
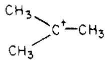
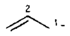
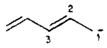
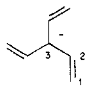
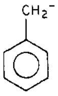
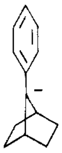
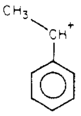
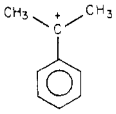
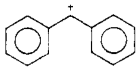
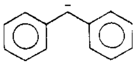
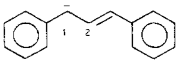
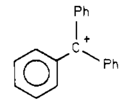
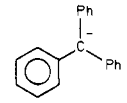
			^{13}C predicted[b]					π electron density				
system	no.	position	H[c]	CNDO	other	^{13}C exptl.	ref	empirical[d]	H[c]	CNDO	other	ref
 $\delta_n = 148.8$	**1**		315.8			319.61	*e*	0.023	0.0			
 $\delta_n = 161.8$	**2**		328.7			330.02	*e*	0.007	0.0			
 $(\delta_1)_n = 126.3$ $\Sigma q = 3.87$	**3**	1	46.3			52.8	*f*	1.46	1.50			*g*
		2	135.7			144.0		0.95	1.00			
 $(\delta_1)_n = 122.4$ $(\delta_2)_n = 131.7$ $(\delta_3)_n = 136.7$ $\Sigma q = 6.03$	**4**	1	69.6			65.0	*h*	1.359	1.33			*g*
		2	131.7			138.7		0.956	1.00			
		3	83.9			73.2		1.397	1.33			
 $(\delta_1)_n = 121.16$ $(\delta_2)_n = 130.0$ $(\delta_3)_n = 149.60$ $\Sigma q = 7.90$	**5**	1	81.1			83.6	*h*	1.23	1.25			*g*
		2	130.0			141.8		0.93	1.00			
		3	109.6			82.1		1.42	1.25			
 $(\delta_\alpha)_n = 135.8$ $\Sigma q = 7.84$	**6**	ipso	137.8	158.6	151.2	153.0	*f,i*	0.91	1.00	0.87	0.92	*g,j,l*
		ortho	106.9	106.9	99.4	110.9		1.12	1.14	1.14	1.19	
		meta	128.5	117.3	130.3	130.7		0.99	1.00	1.07	0.99	
		para	103.2	88.8	85.6	95.7		1.19	1.14	1.23	1.25	
		α	44.6	55.8	58.7	52.8		1.52	1.57	1.50	1.48	
 $(\delta_\alpha)_n = 169.0$ $\Sigma q = 8.0$	**7**	ipso	141.9	162.7	155.3	127.7	*k*	1.03	1.00	0.87	0.92	*g,l,m*
		ortho	105.9	105.9	98.4	107.6		1.13	1.14	1.14	1.19	
		meta	128.6	117.4	130.4	129.3		0.99	1.00	1.07	0.99	
		para	103.7	89.3	85.1	90.9		1.22	1.14	1.23	1.25	
		α	77.8	89.0	91.9	88.1		1.51	1.57	1.50	1.48	
 $(\delta_\alpha)_n = 148.8$ $\Sigma q = 6.01$	**8**	ipso	144.1	129.9		141.5	*n,i*	1.01	1.00	1.08		*g,n*
		ortho	151.5	151.0		155.1		0.84	0.86	0.86		
		ortho′	151.5	149.0		143.6		0.91	0.86	0.87_5		
		meta	128.5	125.8		133.8		0.97	1.00	1.01_5		
		para	149.3	156.1		161.6		0.79	0.86	0.82		
		α	244.0	240.8		230.0		0.51	0.43	0.45		
 $(\delta_\alpha)_n = 161.8$ $\Sigma q = 6.09$	**9**	ipso	148.7	133.0		140.0	*n,i*	1.05	1.00	1.09		*g,n*
		ortho	150.0	145.0		142.4		0.91	0.86	0.89		
		meta	128.6	126.9		133.3		0.97	1.00	1.01		
		para	149.5	151.6		155.9		0.82	0.86	0.85		
		α	257.0	251.8		254.0		0.45	0.43	0.46		
 $(\delta_\alpha)_n = 148.8$ $\Sigma q = 11.81$	**10**	ipso	141.1	130.1		138.3	*n,o*	1.02	1.00	1.07		*g,n*
		ortho	143.9	148.1		149.1		0.87	0.90	0.87		
		ortho′	143.9	142.6		143.4		0.90	0.90	0.91		
		meta	127.2	113.9		133.7		0.96	1.00	1.08		
		para	143.9	151.3		150.9		0.85	0.90	0.85		
		α	215.6	220.3		200.6		0.69	0.60	0.57		
 $(\delta_\alpha)_n = 148.8$ $\Sigma q = 13.89$	**11**	ipso	141.1	163.5		145.3	*o,p*	0.97	1.00	0.86		*g,j*
		ortho	111.2	116.0		116.1		1.07	1.10	1.07		
		meta	127.2	117.6		127.5		1.00	1.00	1.06		
		para	109.8	89.0		105.7		1.12	1.10	1.23		
		α	84.8	97.6		80.3		1.43	1.40	1.32		
 $(\delta_1)_n = 140.2$ $(\delta_2)_n = 129.2$ $\Sigma q = 16.02$	**12**	ipso	139.9			143.5	*o,p*	0.98	1.00			*g*
		ortho	117.1_5			117.5		1.07	1.07			
		meta	128.3_5			127.9		1.00	1.00			
		para	117.1			111.2		1.09	1.07			
		1	93.8			90.1		1.30	1.29			
		2	129.1			129.0		1.00	1.00			

Table II (Continued)

system	no.	position	^{13}C predicted[b] H[c]	^{13}C predicted[b] CNDO	^{13}C predicted[b] other	^{13}C exptl.	ref	π electron density empirical[d]	π electron density H[c]	π electron density CNDO	π electron density other	ref
	**13**	ipso	143.6	141.9	143.0	141.7	*n,o*	1.01	1.00	1.01	1.00	*g,n,q*
		ortho	141.5	139.9	136.5	145.1		0.90	0.92	0.93	0.95	
		meta	128.9	131.4	133.9	132.1		0.98	1.00	0.98	0.97	
		para	139.4	139.4	134.3	144.9		0.89	0.92	0.92	0.95	
$(\delta_\alpha)_n =$ 161.8 $\Sigma q =$ 17.66		α	213.6	203.5	215.2	212.7		0.69	0.69	0.75	0.68	
	**14**	ipso	143.6	167.6		148.1	*o,p*	0.97	1.00	0.85		*g,j*
		ortho	115.4	120.2		122.8		1.03	1.08	1.05		
		meta	128.9	119.3		127.6		1.01	1.00	1.06		
		para	113.3	95.7		112.7		1.08	1.08	1.19		
$(\delta_\alpha)_n =$ 161.8 $\Sigma q =$ 19.88		α	112.2	121.8		89.9		1.45	1.31	1.25		

[a] Σ represents the sum all over the charged molecule of the local π electron densities. [b] The predicted shift δ_c as obtained from eq 4 by using the theoretical π electron densities computed with the different methods of columns 10–12. [c] H = Hückel. [d] *q* values of eq 4. [e] Reference 4b. [f] Reference 5. [g] Reference 28. [h] Reference 29. [i] Shifts of the neutral are from ref 30. [j] SCF calculations reported in ref 2c. [k] Reference 16. [l] Reference 18d. [m] Charge distribution assumed as in 6. [n] Reference 4b. [o] Shifts of the neutrals from ref 17. [p] This work. [q] Electron densities computed on assuming a twist angle of 60° for the phenyl rings; see ref 27.

Table III. Fittings of Correlations of Experimental vs. Predicted ^{13}C Shifts

entry	carbons	source of π charges[a]	slope	intercept	*r*	*n*
1	α, chain	H	1.01 ± 0.03	1.11 ± 2.58	0.996	14
2	chain	H	0.995 ± 0.03	3.07 ± 2.48	0.992	20
3	chain	*b*	0.967 ± 0.03	9.43 ± 2.63	0.991	20
4	para	H	0.71 ± 0.03	36.31 ± 0.7	0.995	9
5	para	*c*	1.03 ± 0.06	−10.30 ± 1.82	0.992	9
6	ortho	H	1.08 ± 0.09	−11.93 ± 1.53	0.968	11
7	ortho	*c*	1.12 ± 0.09	−18.79 ± 1.51	0.971	11
8	para + ortho	H	0.83 ± 0.06	21.14 ± 1.22	0.960	20
9	para + ortho	*c*	1.09 ± 0.06	−16.61 ± 1.42	0.969	20

[a] Hückel. [b] Hückel, CNDO, STO-3G as available from Table II, the more sophisticated being preferred. [c] All other non-Hückel calculations, the more sophisticated being preferred.

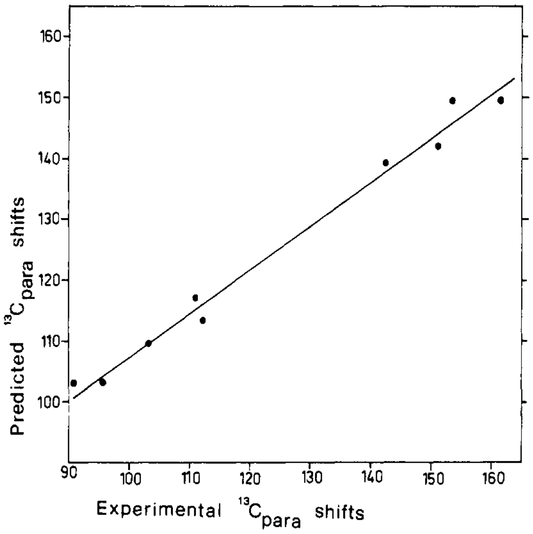
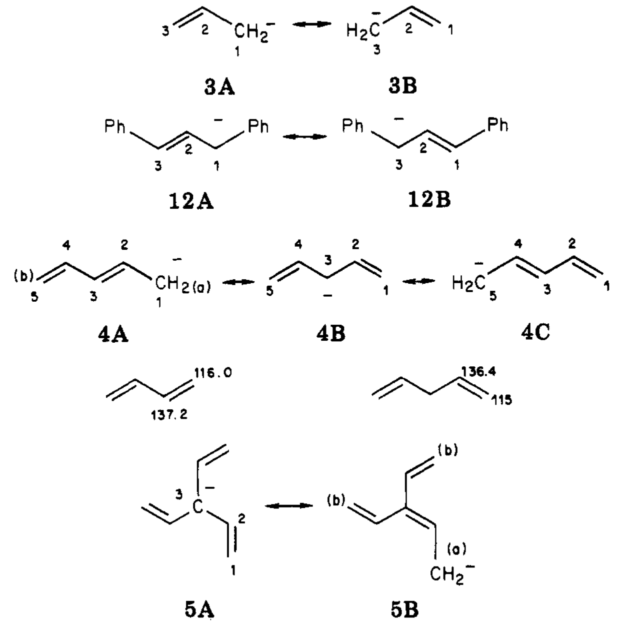


Figure 2. Experimental vs. predicted ^{13}C shifts of ions **6–14**. Hückel π charges have been used as input for *q* of eq 4.

analysis in statistical terms is in Table III. It is evident that the goodness of the fit will also depend upon the degree of sophistication of the calculation. It should be expected therefore that on increasing the complexity of the system under consideration, the reliability of the available, relatively unsophisticated, calculations will decrease. Unfortunately, it appears that ab initio calculations are available only for extremely simple systems.[18] Despite these limitations, the validity of eq 4 can be nonetheless estimated on comparing the total number of π electrons of the species with the summation, extended all over the charged molecule, of the local π densities.

Chart II



Experimental Section

Data from ref 17 are for Me_2SO solutions. Whenever these shifts are used for neutrals, it should be noted that they are relative to (trimethylsilyl)propanesulfonic acid sodium salt (TPS). To convert them relative to Me_4Si the following relationship is used $\delta_{Me_4Si} = \delta_{TPS} - 1.63$.

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[18] (a) Hopkinson, A. C.; Lien, M. H. *Int. J. Quantum Chem.* **1980**, *18*, 1371. (b) Pross, A.; De Frees, D. J.; Levi, B. A.; Pollack, S. K.; Radom, L.; Hehre, W. J. *J. Org. Chem.* **1981**, *46*, 1693 and references therein. (c) Reynolds, W. F.; Dais, P.; MacIntyre, D. W.; Topsom, R. D.; Marriot, S., Nagy-Felsobuki, E. Taft, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 378. (d) Keminster, G.; Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 1056.

Calculation of δ_n. The value of δ_n for ions **1**, **2**, **6**, **8**, **9**, **10**, **11**, **13**, and **14** is straightforwardly calculated from eq 3 upon adding various shielding contributions reported in Table I. In Grutzner's benzyl anion **7**[16] account must be taken for the shielding effects of the phenyl group (+13), the two α carbons (2 × 13), the four β carbons (4 × 4.5),[15] the four γ carbons (4 × −1.5), and the correction for α,α-disubstitution (−4.8). Thus $\delta_n = 122.8 + 13 + 26 + 18 - 6 - 4.8 = 169$.

α positions of the allylic ions **3** and **12** need to be averaged. The actual shift of the carbanionic carbon in **3** is thought as an average between the limit (identical) structures **3A** and **3B**. (Chart II). Thus $(\bar{\delta}_1)_n = {}^1/_2[(\delta_1)_{3A} + (\delta_1)_{3B}] = {}^1/_2[(122.8 + 14.4) + 115.4] = 126.3$, where 115.4 is the shift of the methylene in propene.

An analogous procedure is done for 1,3-diphenylpropenyl anion **17**. Thus, $(\bar{\delta}_1)_n = {}^1/_2[(122.8 + 13 + 14.4) + 129.17] = 139.68$, where 129.17 is the shift of carbon 1 in 1,3-diphenylpropene. For the pentadienyl carbanion **4**, shifts have to be averaged among limit structures **4A**, **4B**, **4C** (Chart II). Since structure **4A** = **4C**, they contribute statistically twice as much as structure **4B** and then $(\bar{\delta}_1)_n = {}^1/_3[2(\bar{\delta}_1)_{4A} + (\delta_1)_{4B}]$, where $(\bar{\delta}_1)_{4A}$ is the averaged shift of carbon 1 between chemical environment a and b. The model shift for carbon 1 in the limit structure **4B** is assumed to be as in 1,4-pentadiene, the ^{13}C shifts of which are reported in Chart II; for carbons 2 and 3 models are 1,4-pentadiene and 1,3-butadiene. Assuming a negligible shielding effect of the vinyl group at carbon 3 of the limit structure **4A**, then $(\bar{\delta}_1)_{4A} = {}^1/_2[(122.8 + + 14.4) + 115] = 126.1$; thus $(\bar{\delta}_1)_n = {}^1/_3 [2 \times 126.1 + 115] = 122.4$. Analogously, $(\bar{\delta}_2)_n = {}^1/_3[2(137.2 - 7.9) + 136.4] = 131.61$, and $(\bar{\delta}_3)_n = {}^1/_3[2(137.2 - 7.9) + (122.8 + 2 \times 14.4)] = 136.7$.

For trivinyl carbanion **5** allowance should be made for resonance between structures **5A** and **5B**, the latter contributing statistically three times as much than the former; thus $(\bar{\delta}_1)_n = {}^1/_4[(\delta_1)_{5A} + 3(\bar{\delta}_1)_{5B}]$. Carbon 1 in the limit structure **5B** should be averaged among chemical environments a and b, the latter contributing twice as much as the former. Thus $(\bar{\delta}_1)_n = {}^1/_4[(\delta_1)_{5A} + 3(\bar{\delta}_1)_{5B}] = {}^1/_4[[(122.9 + 14.4) + 2(122.8 - 7.2)] + 116] = 121.1$. Analogously $(\bar{\delta}_2)_n = {}^1/_4[[(122.8 + 13 - 7.2 \times 2) + 2(122.8 + 13 - 2 \times 1.5)] + (122.8 + 13 - 1.5 \times 2)] = 129.95$, and $(\bar{\delta}_3)_n = {}^1/_4[(122.8 + 3 \times 14.4) + 3(122.8 + 14.4 \times 2 - 7.2)] = 149.6$.

Preparation of the Dimsyl Solution for Magnetic Resonance Experiments. The dimsyl solution was prepared from $NaNH_2$ and twice distilled Me_2SO, according to directions given elsewhere.[19] The $NaNH_2$ as a 50% suspension in toluene was obtained from Merk as a pure reagent. The $NaNH_2$ suspension was placed in a tared 125-mL Schlenk flask, which was fitted with an air tight septum cap and stopcock. The solvent was removed by evaporation under high vacuum and dry N_2 was then added. The Schlenk flask was then weighed to determine the actual amount of dry $NaNH_2$ inside. An appropriate amount of twice distilled Me_2SO was added by syringe. Complete reaction was ensured by using vacuum to remove the NH_3 gas byproduct.

Preparation of the Anions. The anion samples were prepared for ^{13}C analysis directly in the 12-mm NMR tubes by the addition of 2.0 mL of 0.6 M dimsyl solution to 0.6 mmol of organic substrate. The resulting solution was 0.6 M in base and 0.3 M in substrate. This 2-fold excess of base was used to ensure complete deprotonation of the substrate. The ^{13}C NMR spectra were obtained at 25.18 MHz with a Varian XL-100 spectrometer. Chemical shifts (δ) of the anions were obtained in parts per million downfield from the methyl resonance of the sodium salt of (trimethylsilyl)propanesulfonic acid (TPS) and then converted into values relative to Me_4Si. The deuterium lock required by the XL-100 was provided by $(CD_3)_2SO$ in a sealed internal, coaxial 5-mm NMR tube. The 5-mm tube was held in place inside the 12-mm tube by rubber spacers. The spacers were vertically notched in three places so that the needle adding the dimsyl solution could go past the spacers. Into the 12-mm NMR tube were placed 0.6 mmol of substrate, 25 mg of TPS, and the 5-mm $(CD_3)_2SO$ tube with its spacers. The 12-mm tube was capped with a rubber septum cap, and the septum cap tube interface was wrapped in Parafilm. The atmosphere within the 12-mm tube was then replaced with dry N_2 via syringe through the septum cap by alternating between vacuum and N_2, both of which were connected to the syringe through a three-way stopcock. The 2 mL of 0.6 M dimsyl solution was then syringed directly into the 12-mm tube; the tube was cooled to −30 °C and disconnected from the line, and the rubber capped head was covered with a thin layer of melted paraffin.

Discussion

Three points are relevant for discussion: (a) whether ^{13}C shifts would correlate with local π or with local total $(\sigma + \pi)$ electron densities, (b) whether the empirical eq 4 survives the criticism put forward by the theoretical treatment on the origin of ^{13}C shifts, (c) the predictive power of eq 4. Fliszar[3] has shown that even for the systems which served to propose the original Spiesecke–Schneider relationship, ^{13}C shifts are linearly related not only to total local $(\sigma + \pi)$ but also to σ and to π electron densities; however in the last two cases the slope is of opposite sign, that is π electron excess induces high-field shifts while σ electron excess induces low-field shifts.

Investigations on ^{13}C shift–charge correlations in other cyclic substrates either containing heteroatoms or of lower symmetry than those chosen by Spiesecke and Schneider afforded equivocal answers.[20] At best, correlations have been found between ^{13}C shifts and the total $(\pi + \sigma)$ charge as for azines,[20] indolizines,[21] and xanthylium ions.[22]

The slopes of these correlations varied widely from substrate to substrate. In phenyl carbenium ions ^{13}C shifts correlate with local π charge with a sensitivity of 167 ppm/electron; however, no correlation whatsoever is found for ipso and α-charged carbons.[4] These contradictory results have led to the belief that all these correlations are unwarrented and fortuitous.[6] In agreement with Grutzner's view[6] we also believe that any approach which assumes a simple, crude relationship between shift and charge is devoted to partial or total failures; at the best, even if a successful correlation exists within a limited set of analogous systems, the sensitivity is expected to be different from one to another class of substrates. It is naive[20] to expect that, for instance, the shift of any carbon of anthracene dianion and of pyrimidine differ only because of a different amount of local charge. An improved approach has been devised recently by Fraenkel; ^{13}C shifts in a variety of cyclohexadienylic cations and anions have been separated into contributions due to the neutral framework, charge effects, and interaction between ion and solvent molecules.[23] Results unequivocally show that a change in π charge of ±1 of the neutral model brings about a change of 165 ppm, thus confirming the linearity of ^{13}C shifts with local π charge.

In evaluating the second point, that is whether the present approach survives a criticism based on the principles about the origin of chemical shifts, it can be recalled that while the contribution of charge to the diamagnetic term σ^d is minor and approximately constant (for carbon ~10 ppm/electron), most of the effect of charge comes from its influence on the paramagnetic terms σ^p, whose components depend on the carbon p orbital size, the π character of bonding, and the excitation energy. Furthermore the effect of charge may be anisotropic on σ^p tensors. The degree of appropriateness with which the neutral model mimics, case by case, these factors as actually present in the ions, will determine the degree of confidence with which one can rely on results given by eq

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[19] Greifenstein, L. G.; Lambert, J. B.; Nienhuis, R. J.; Drucker, G. E.; Pagani, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7753.

[20] Baumann, H.; Olsen, H. *Helv. Chim. Acta* **1980**, *63*, 2202.

[21] Witanowski, M.; Stefaniak, L.; Sicinska, W.; Webb, G. A. *J. Mol. Struct.* **1980**, *64*, 15.

[22] Dradi, E.; Gatti, G. *J. Am. Chem. Soc.* **1975**, *97*, 5472.

4. In this equation the quantity dependent from local π charge is the experimental shift corrected for contributions due to substituents; this correction is strictly analogous to the one which allows the prediction of the shift of carbons in substituted ethylenes starting from the shift of parent ethylene by adding proper substituent parameters, an approach widely accepted and highly successful.[10,13–16] in doing so, we meet the criteria envisaged by Grutzner[6] for lending credibility to charge–shift correlations and we conform to the treatment of Fraenkel[23] for handling corrected shifts which depend solely on local π charge and not from total ($\sigma + \pi$) charge. Additive parameters A in eq 4 take care in fact, in terms of σ and π charge distribution, of the bonding situation between the substituent and the carbon which, being neutral in the model, becomes positively or negatively charged in the investigated ion. This treatment for the neutral model finds firm foundations in recent results of Miyajima and co-workers;[14] they have shown in fact that the shielding of the α-carbon in α-substituted ethylenes depends on the local π electron density, in turn dominated by the adjacent substituent.

While the preceding discussion leaves little doubt that the π bonding character and the orbital size term, as modelled by the interaction of the substituent with an adjacent trigonal carbon part of an ethylene fragment, are good enough to be taken as a reference for the interaction of the same substituent with an adjacent *charged* trigonal carbon, the effect of charge on excitation energies of the model and of the ion may be different. Tokuhiro and Fraenkel in fact have found evidence[24] for a charge dependent change in excitation energies. This point, we believe, may represent the most serious limitation to the predictive power of eq 4. Finally any indiscriminate generalization of eq 4 is without foundation if systems are considered in which bond changes are anticipated either between the neutral model and the ion and among the ions submitted to the charge–shift relationship.

A case of inadequacy of the model pertains to the ipso carbon of the benzenoid frame of some of the ions we have considered. The neutral model to which the δ_c value of the ipso carbon is referred is the shift of the same carbon in the corresponding neutral hydrocarbon. However, while in the model the ipso carbon is flanked by an sp^3 carbon (e.g., in diphenylmethane), in the ion (diphenylmethyl carbanion and diphenylmethyl carbenium ion) it is flanked by an sp^2 carbon. We concede therefore that the prediction of the ^{13}C shifts of ipso carbons on the basis of π charge and relying on such models may be unwarrented.

Being aware of the limitations of every charge–shift relationship and of eq 4 in particular, we are now in a position for evaluating results obtained by the present approach. Inspection of Table II reveals that eq 4 affords predictions for total π charge of quality ranging from excellent to good; in fact the largest discrepancies found between theoretically computed and empirical π charges are in the order of 0.15 of electrons for relatively large systems (diphenyl- and triphenylmethyl systems). The potentiality of eq 4 in predicting individual ^{13}C shifts, starting from theoretically calculated electron densities, varies from excellent to poor, depending upon the site in the molecule and the theoretical calculation taken as a start. The situation is clearly borne out on examining Figures 1 and 2, which report plots of experimental vs. calculated shifts, and Table III where the analysis of the correlations is given in statistical terms.

For charged carbons present at the termini of a chain (α carbon) experimental shifts are excellently correlated with unit slope with those predicted starting from Hückel π charge (entry 1). Also, excellent predictions can be made for all carbons of the chain, both starting from π charges computed by Hückel, and where available, by more sophisticated methods (CNDO, modified CNDO, STO-3G). In both cases the slope is close to unity but the intercept is sizably different from zero. This supports anyhow that the experimental ^{13}C shifts, upon correction with terms present in eq 4, are indeed linearly related to π charge densities and provides evidence for the potentiality of eq 4 in predicting empirical local π charge densities starting from experimental ^{13}C shifts. Aromatic carbons behave differently; for ipso and meta carbons no relationship is found between experimental shifts and values predicted by eq 4 starting from π charges either computed by the Hückel and/or by more sophisticated methods. Instead, para and ortho carbons show successful correlations. Experimental shifts of para carbons are linearly related in an excellent way to predicted values. However, when π charges computed by non-Hückel methods are used the slope is unity, and when Hückel π charges are used the slope is far from being unity; in both cases the intercept is different from zero. This means that eq 4, while still predicting very efficiently shifts which are linearly related to experimental values, does not provide numerical values which are coincident with the experiment. A similar situation holds also for ortho carbons (entries 6 and 7); in this case however the fit between predicted and experimental values is not as good as in the case of para carbons. Entries 8 and 9 of Table III report correlations of experimental vs. predicted shifts of para and ortho carbons. As expected, the fit, although acceptable, is only fair.

Treatment of aromatics present in carbanions and carbenium ions is thus of scattered predictive value; as a consequence, the sum of the local empirical π charge densities extended to every aromatic site gives a total charge, $\sum q_{\text{ar}}$, numerically different from the value Q_{ar} obtained by substracting from the known total π electrons of the ion the empirical π density residing on the carbons of the chain. For instance, for benzyllithium, $\sum q_{\text{ar}} = 6.32$ electrons (column 8 of Table II) and from $q_{\text{CH}_2} = 1.52$, the expected Q_{ar} on the phenyl ring should be $8 - 1.52 = 6.48$ electrons. Although most of the $\sum q_{\text{ar}}$ are indeed somewhat depressed relative to Q_{ar}, the two quantities are perfectly correlated by the following relationship:

$$Q_{\text{ar}} = 1.016 \sum q_{\text{ar}} + 0.076 \quad (n = 9,\ r = 0.9998)$$

The success of the predictive power of eq 4 depends therefore upon the quantity we choose to compare. Since eq 4 does not account for σ electron densities, the balance of σ electron charge upon summation of the local "empirical" charge densities extended to every position of the charged molecule becomes close to zero by internal cancellation.

Substantial π charge is expected to be present in starred positions, and in particular at the ortho and para positions of the ring of benzyl cations and benzyl anions. In unstarred positions the σ charge is probably dominating over the π term, and deviations between the empirical and computed electron densities are expected. In this respect it should be noted also that, while for starred positions the discrepancy between HMO and CNDO electron densities is not dramatic and is generally limited to a few tenths of me (10^{-3} electrons), for unstarred positions sizable differences exist due to the very serious limitation of the HMO method which assumes unit π electron densities in these positions. Since in these positions the effects of the

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σ and π term probably cancel out, empirical densities obtained from eq 4 are paradoxically closer to values of HMO than to those of CNDO calculations. The foregoing analysis shows that eq 4 has considerable potentiality in mapping electron densities in starred positions but limitations for unstarred positions.

The case of the discrepancy between the empirical charge maps and the CNDO calculated values found for diphenyl- and triphenylmethyl carbanions and carbenium ions **10**–**14** merits a special comment. According to results of CNDO calculations the negative charge in carbanions partitions equally among the deprotonated charged carbon and each of the phenyl rings attached to it following a proportionally additive pattern; thus, each group carries 0.5 excess negative charge in benzyl anion, 0.33 in diphenylmethyl, and 0.25 in triphenylmethyl anions. An increase in charge delocalization in the carbanion is associated with an increase of its stabilization, and hence with an increase of acidity of the precursor carbon acid. On these grounds, if the phenyl groups in the series of benzyl, diphenylmethyl, and triphenylmethyl carbanions would indeed take care of dispersing, respectively $^1/_2$, $^2/_3$, and $^3/_4$ units of π charge from the carbanionic carbon as indicated by CNDO calculations, a steady increase in the acidity of toluene relative to diphenylmethane, in turn relative to triphenylmethane, should also be anticipated. Certainly this is not the case since in Me_2SO diphenylmethane is more acidic than toluene by at least 10 pK_a units,[25] while triphenylmethane is more acidic than diphenylmethane by only 1.5 pK_a units.[26] Empirical charge maps are in much better agreement with acidity data of these methane carbon acids than with CNDO calculated π electron densities. In fact the charge density on the central carbon of triphenylmethyl carbanion turns out to be almost the same, perhaps slightly larger, as that present on the central carbon atom of diphenylmethyl carbanion, a result which parallels closely the experimental acidities which indicate that no extra stabilization is obtained on adding a further third phenyl group in diphenylmethyl anion. While the mesomeric effect of the third phenyl group in **14** does not help in delocalizing the charge better than the two phenyl groups already present in diphenylmethyl carbanion can do, very probably the polar inductive effects are instead additive. As a consequence the small 1.5 pK_a units increase between diphenyl and triphenylmethane would be due to the relatively small polar inductive effect of the third phenyl group.

The inefficiency of the third phenyl group in delocalizing the charge from the central carbon atom of triphenylmethyl carbanion relative to diphenylmethyl carbanion is not restricted to the anionic species but is found also for carbenium ions; in fact also in diphenyl and triphenyl carbenium ions the empirical electron densities of the central carbon atom are quite comparable. This result could be anticipated on considering the close structural analogy of triphenylmethyl carbanion and triphenyl carbenium ion, both species presenting a propeller like shape irrespective of the sign of the charge on the central carbon atom. In accord with this, CNDO calculations, assuming an angle of twist of 60° between the planes of the three phenyl rings relative to the plane defined by the carbenium carbon and the three carbons attached to it, assign[27] to the central carbon a π electron density almost coincident with the value obtained by the present empirical calculations. One final comment concerns the prediction of the shift of the planar methyl carbanion CH_3^-; eq 4 gives for $q = 2$ the value of −37.2 ppm, not too far from that obtained by O'Brien,[5] but considerably different from that proposed by Gompper (+30 ppm).[31] We believe that this latter value is unproperly founded; in fact it has been obtained by extrapolation from symmetrically disubstituted carbanions $[CH(X_2)]^-$ where $X = CO_2R$, Ph, and $CH_2{=}CH$, on the assumption that the shift difference between the carbanide carbons of disubstituted and trisubstituted carbanions is a constant. This treatment furthermore gives no account for the variable charge density present on the carbanide carbon in mono-, di-, and trisubstituted systems. A more detailed, and we believe more successful analysis, of substituent effects in di- and trisubstituted carbanions is forthcoming.[12a]

Conclusion

Equation 4 is certainly of wide predictive scope for charged carbons in linear and branched delocalized systems and accounts in a highly satisfactory way for α-substitution at the charged carbon. Evidence for linearity of experimental with empirically predicted shifts is also obtained for para and ortho carbons of aromatic moieties conjugated with carbons carrying the charge; eq 4 however does not provide directly numerical values coincident with the experiment. Correlations between experimental and predicted shifts fail in the case of ipso and meta carbons. However, since a "charge is a charge and (is) a useful quantity as long as its reliability can be assessed, (even if) simply stolen from critically established empirical correlations",[3] eq 4 undoubtely represents a powerful tool for mapping π electron densities in a large variety of charged organic species.

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