The Electronic Structure of the *s*-Indacenyl Dianion. Structural Assessment by Nuclear Magnetic Resonance Spectroscopy and Molecular Orbital Calculations

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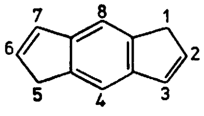
The ^1H and ^{13}C n.m.r. chemical shifts of *s*-indacenyldilithium are reported and the results are compared with the charge pattern given by CNDO and *ab initio* MO calculations. Comparisons are also made with the corresponding data for the indenyl-lithium anion. Our observations are consistent with a delocalized, 14-π electron structure where most of the excess charge is located at the C-1, -3, and -4 positions.

ALTHOUGH the understanding of aromaticity effects has been widely extended during the last ten years, it is still very hard to predict on an *a priori* basis the ground-state electron distribution in molecules capable of sustaining an induced ring current. This problem is especially obvious in charged polycyclic systems and the situation is further complicated in the presence of multiple charges, since, in these cases, the possibility of charge repulsive interactions must be considered.[1,2] As shown earlier for carbocations and carbanions,[3] ^{13}C n.m.r. spectroscopy has proved to be a powerful qualitative tool in probing charge distribution, since the paramagnetic term is usually dominant and should vary substantially with charge for sp^2 carbons. However, a simultaneous variation of the diamagnetic term and the ring currents in adjacent rings could complicate the situation somewhat. Since a separation of the individual contributions to the ^{13}C screening is virtually impossible, it is important to do a complementary MO study and to compare the results with theoretical and spectroscopic data obtained in similar systems.



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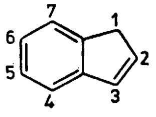

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In this paper we report the preparation and n.m.r. observation of *s*-indacenyldilithium. We also present a discussion of the electronic structure of the dianion based on ^1H and ^{13}C chemical shifts and on *ab initio* and semi-empirical MO calculations. The obtained characteristics will then be compared with the corresponding data for indenyl-lithium.

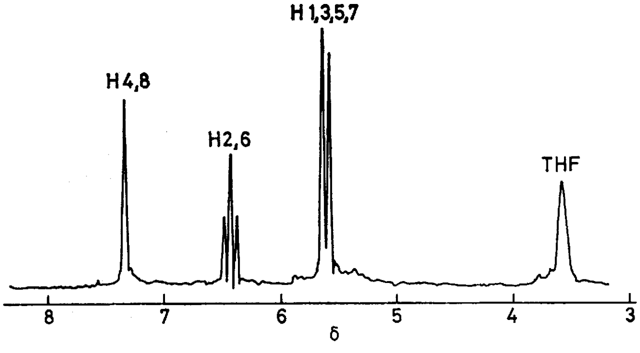
EXPERIMENTAL

The ^1H and ^{13}C n.m.r. chemical shifts were measured on either a JEOL FX-90 Q or a Bruker WM-250 spectrometer. The deuteriated solvents were used without further purification. Hexamethylphosphoroamide (HMPA) was dried overnight over CaH_2, distilled, and finally stored over molecular sieves. Field-frequency lock on the FX-90 Q was maintained by locking on $[^2H_8]$tetrahydrofuran ($[^2H_8]$-THF) or on internal (capillary) D_2O. The ^1H chemical shifts are reported relative to Me_4Si, while ^{13}C chemical shifts are referenced relative to cyclohexane,[4] but reported relative to Me_4Si, using the conversion scale $\delta_{Me_4Si} = \delta_{cyclohexane} - 27.7$. The sample concentrations were 0.3—0.5M in all cases. Each free-induction decay was digitized using 16 K data points. The coupled spectra were obtained with the nuclear Overhauser effect using gated decoupling. The proton frequencies used in the selective decoupling experiments were determined from the proton spectra obtained by using the decoupler coils of the tunable broad-banded probe.

Materials.—Treatment of 1,5-(1) and 1,7-dihydro-*s*-indacenes in $[^2H_8]$THF or HMPA–$[^2H_8]$THF with BuLi (90% in cyclohexane) resulted in the desired dianion $(1)^{2-}$. The dihydro-*s*-indacenes were obtained starting from 1,2,4,5-tetrakis(bromomethyl)benzene and ethyl acetoacetate by means of extractive alkylation.[5] The solutions of $(1)^{2-}$ could be stored overnight at room temperature without any detectable decomposition. The dianion is not soluble in alkyl ethers or dioxan and slowly decomposes in glymes, probably through deprotonation of the solvent. An alternative synthesis method of $(1)^{2-}$, starting from the very unstable, so far not isolated *s*-indacene, has been mentioned in a review article.[6]

RESULTS AND DISCUSSION

The ^1H n.m.r. spectrum of $(1)^{2-}$ in $[^2H_8]$THF is shown in the Figure and the coupling pattern indicates very



^1H N.m.r. spectrum of *s*-indacenyldilithium $(1)^{2-}$ (0.3M) in $[^2H_8]$THF similar AB_2 characteristics (J 3.5 Hz) as noticed for the indenyl anion.[7] By changing the solvent to HMPA–$[^2H_8]$THF, increased shieldings ($\Delta\delta$ 0.23—0.36) were observed for all protons, most significant though for the five-membered ring protons. The observed shifts move upfield by increasing the HMPA–$[^2H_8]$THF ratio but level off at a HMPA–$[^2H_8]$THF ratio of 4 : 1. These increased shieldings are attributed to decreased C–H bond polarization effects by going from a predominantly, at least on the average, contact ion-pair complex to a solvent-separated ion-pair structure.[8] Very similar polarization effects were recently noted in the indenyl[9] and fluorenyl systems.[10] In a solvent study of cyclopentadienyl-lithium we found a similar trend, an upfield shift of 0.20 p.p.m. when the equilibrium is changed from contact ion pairs to solvent-separated ion pairs. The sign and magnitude of this shielding differential is quite similar to that observed on increasing the cation radii on going from Li^+ to Rb^+.[7]

TABLE 1

^1H and ^{13}C n.m.r. chemical shifts of (1) and (2) and their corresponding anions[a]

Species	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-7a	C-4a, -8a	C-3a, -7a	Reference
(1)	$CDCl_3$	38.6 (3.26)	133.1 (6.30)	132.1 (6.70)	116.4 (7.30)					141.1	142.1	5
$(1)^{2-}$	$[^2H_8]$THF	83.6 (5.57)	116.8 (6.40)	83.6 (5.57)	105.1 (7.30)					127.8		
$(1)^{2-}$	HMPA	84.2 (5.21)	115.7 (6.07)	84.2 (5.21)	103.1 (7.07)					128.5		
(2)	$CDCl_3$	39.0 (3.31)	133.8 (6.47)	132.1 (6.86)	120.9 (7.12)	126.1 (7.03)	124.5 (6.94)	123.6 (7.09)	143.5		144.7	5
$(2)^-$	$[^2H_8]$THF	91.7 (5.81)	115.3 (6.54)	91.7 (5.81)	119.8 (7.35)	114.4 (6.46)			129.1			
$(2)^-$	HMPA	93.4 (5.73)	118.2 (6.37)	93.4 (5.73)	118.2 (7.06)	110.3 (6.08)			131.4			

[a] ^1H N.m.r. chemical shifts in parentheses. Chemical shifts reported relative to Me_4Si.

The ^{13}C n.m.r. chemical shifts of $(1)^{2-}$ were assigned by the aid of selective decoupling and by comparisons of the long-range CH coupling patterns observed in the coupled spectra of $(1)^{2-}$ and $(2)^-$. The most significant upfield shifts for $(1)^{2-}$ compared with $(2)^-$ are observed for the C-1, -3, and -4 positions, and those signals are also those appearing at highest field. The observed solvent-induced changes in $(1)^{2-}$, using the same solvent systems as for the ^1H n.m.r. study, are small especially if compared with the differentials for $(2)^-$. Moreover, no significant changes in the chemical shifts of $(1)^{2-}$ were observed going from $[^2H_8]$THF to a less cation-co-ordinating solvent such as 2-methyltetrahydrofuran.[10] In the indenyl system, a decreased polarization of the π-charge toward the five-membered ring and a more delocalized structure was noticed upon increasing the solvation of the cation.[9-12] The relative minor solvent shifts and the observation that the C-2 position is shifted to low-field in $(1)^{2-}$ relative to $(2)^-$ using $[^2H_8]$THF indicates that the excess charge in the dianion structure $(1)^{2-}$ is well delocalized in both solvents. A decreased cation dependence on charge distribution in a small perimeter dianion system, and an ion-pair structure of $(1)^{2-}$ in $[^2H_8]$THF which is less tight on the average than for $(2)^-$, is in fact very plausible. For multiply charged systems like $(1)^{2-}$, the electrostatic repulsion between the counter-ions must be taken into account. A similar observation has been reported for tetraphenylethylenedilithium,[13] where under contact ion-pair conditions, the equilibrium, due to coulombic repulsion between cations, is described by: tight-Li^+ : dianion : solvated-Li^+ $\rightleftharpoons$ solvated-Li^+ : dianion : tight-Li^+.

In order to gain further information of the electron distribution of $(1)^{2-}$ compared with $(2)^-$, we performed both semi-empirical CNDO[14] and *ab initio* molecular orbital calculations. Standard geometries with regular polygons, using a carbon–carbon bond length of 1.39 Å and a carbon–hydrogen bond length of 1.09 Å, were used. For the non-empirical SCF-LCAO-MO calculations, the atomic basis set consisted of 7*s*-type and 4*p*-type Gaussian type functions (GTFs) for each carbon and 4*s*-type GTFs for each hydrogen, contracted to four *s* functions and two *p* functions for carbons and two *s* functions for hydrogens (double zeta basis set). The exponents and the contraction coefficients have been taken from van Duijneveldt.[15] The calculations have been carried out using the MOLECULE-ALCHEMY program package.[16] The wave functions * have been analysed in terms of Mulliken population analysis.[17] In Table 2, the gross atomic charges on the carbon atoms, π and total, are listed using the CNDO and *ab initio* calculations.

The π-charges computed using both methods in both molecules show similar trends. The most charged positions are C-1 and -3, while position 2 carries little charge. A significant part of the excess charge can also be found in the six-membered ring while the fused carbons have a π-charge of only *ca.* 0.05 electrons. This picture is consistent with the delocalized charge model suggested above.

A somewhat different picture arises if the total charges ($\sigma + \pi$) are considered. The total charges calculated using CNDO display a pattern very similar to that of the π-charges. On the other hand, the *ab initio* calculations place the charge maxima at the bridging positions and predict practically no charge at position 4. A comparison of π and total charges gives the σ-charges. The *ab initio* σ charge distribution in $(1)^{2-}$ alternates between rather large positive and negative values; the variation

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* Additional material available on request.

in *ab initio* calculated σ charges among various carbons in $(2)^-$ is less dramatic but still much more pronounced than in the CNDO calculations. It may in this connection be of interest to mention that opposite behaviour of π and σ charges has been noted by Hinchcliffe [18] in the calculations for naphthalene anion. It is common to relate the ^1H and ^{13}C n.m.r. chemical shifts in aromatic systems to the charges at the carbon atoms. Schaefer and Schneider suggested several years ago,[19] that the ' experimental ' π-electron charge density on a carbon atom, ρ_{exp}, can be expressed as $-a/10.7$, where a is the proton chemical shift, corrected for the ring currents, minus the chemical shift for benzene. The ρ_{exp} values obtained in this fashion, are also listed in Table 2 and agree rather well with the calculated π-charges. The charge-shift relationship in the case of ^1H is based on the assumption that the local diamagnetic term which increases with increasing local charge density,[20] can be isolated. Moreover, this simple relationship does not account for effects, like electric-field CH bond polarizations, which could be present in charged systems.

TABLE 2

Semi-empirical and *ab initio* MO gross atomic charges for the indacenyl and indenyl structures

Species			C-1, -3	C-2	C-4	C-5	C-3a, -7a	C-3a, 8a
$(1)^{2-}$	CNDO	π	-0.344	-0.057	-0.153			-0.051
		$\sigma + \pi$	-0.201	-0.025	-0.109			-0.011
	ab initio	π	-0.334	-0.094	-0.145			-0.046
		$\sigma + \pi$	-0.202	-0.188	$+0.003$			-0.211
		ρ_{exp}[a]	-0.250	-0.148	-0.109			
$(2)^-$	CNDO	π	-0.286	-0.039	-0.047	-0.095	-0.053	
		$\sigma + \pi$	-0.162	-0.013	-0.033	-0.046	-0.005	
	ab initio	π	-0.262	-0.062	-0.040	-0.120	-0.047	
		$\sigma + \pi$	-0.161	-0.179	-0.044	-0.197	-0.228	
		q_{zz}[b]	-0.063	$+0.199$	$+0.233$	$+0.136$	$+0.209$	
		ρ_{exp}[c]	-0.190	-0.111	-0.064	-0.130		

[a] ρ_{exp} calculated according to $\rho_{exp} = -a/10.7$. Ring current corrections $\sigma_{1,3} = 0.60$, $\sigma_2 = 0.36$, $\sigma_4 = 0.95$. [b] Expectation values of the zz component of the field gradient tensor. [c] Same conditions as given in a except for ring current corrections: $\sigma_{1,3} = 0.48$, $\sigma_2 = 0.27$, $\sigma_{4,7} = 0.46$, $\sigma_{5,6} = 0.18$.

It has been established empirically that ^{13}C chemical shifts of closely related molecules, such as conjugated hydrocarbons and their ions, can be correlated to carbon π-electron densities by the simple relationship (1) [3a] where

$$\Delta\delta = k\Delta q \qquad (1)$$

$\Delta\delta$ is the change in chemical shift accompanying a change of charge, Δq, and k ranges from 160 to 200 p.p.m. per electron. This observation has been confirmed in the indenyl and fluorenyl anion systems and the constancy of the average chemical shift upon redistribution of charge strengthens this proposal.[10,11] However, the theoretical basis of the simple relationship (1) is rather weak. In the theory of ^{13}C shifts formulated by Karplus and Pople,[21] the dominance of the local paramagnetic term is assumed. This term may be written as (2). Assuming A (a function of various bond orders) and ΔE (the average excitation energy) to be constant, the linearity between charge and ^{13}C n.m.r. chemical shifts stems from the dependence of $\langle r^{-3}\rangle_{2p}$ on the

$$\delta_p = -\frac{A}{\Delta E}\langle r^{-3}\rangle_{2p} \qquad (2)$$

charge; an expansion of the $2p$ orbitals is expected when electrons are added.

Any major change in the ΔE term by going from a monoanion to a dianion system can be ruled out. Based on ^{13}C n.m.r. studies of mostly monion systems, an empirical correlation has been found relating the average carbon shift (δ_{av}) to the average local π-electron density (ρ_{av}) [equation (3)].[22] Thus, ignoring the ΔE term, we

$$\delta_{av} = 289.5 - 156.3\,\rho_{av} \qquad (3)$$

could calculate a δ_{av} of $(1)^{2-}$ as 107.2 p.p.m., a value very close to the experimental one, $\delta_{av}^{exp} = 107.5$ ([$^2H_8$]THF).

A comparison of the ^{13}C chemical shift data for the two ions (Table 1) and the calculated charges (Table 2) conforms to this gross correlation in the case of π charges, as well as the CNDO total charges. No correlation whatsoever can be obtained with the total charges from the *ab initio* calculations. This fact is in excellent agreement with the following observation. For $(2)^-$, we have also used our *ab initio* wavefunction to calculate the expectation values of the zz-component of the field gradient tensor, q_{zz}, at the carbon nuclei (where the z axis is perpendicular to the molecular plane) (see Table 2). This property bears a similarity to the $\langle r^{-3}\rangle_{2p}$ term mentioned above and has been suggested to be related to gross atomic charge.[23] Interestingly, the q_{zz} values obtained for $(2)^-$ correlate nicely with the π-charges, but not with the total charges. Further, we may mention that yet another ' charge index ', the $1s$ orbital energies,[24] do not correlate with the *ab initio* total charges, and not with the ^{13}C chemical shifts either.

In conclusion, if a model is valid, where the partial aromatic contributions of the cyclopentadienyl moieties are significant,[25] it certainly would be revealed in the case of $(1)^{2-}$. Charge repulsions in a small perimeter system such as $(1)^{2-}$, would favour such local aromaticity contributions. However, we find that the n.m.r. experiments as well as the MO calculations give a consistent picture of the s-indacenyl dianion as a peripheral, delocalized, diatropic 14-π-electron system, similar to the 10-π-electron indenyl anion system.

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