Tetrahedron Letters No. 50, pp 4815 - 4818, 1971. Pergamon Press. Printed in Great Britain.

A ^{7}Li NMR Investigation of the Structure and Ring Currents in Some Aromatic Dianion Systems

Richard H. Cox, Harold W. Terry, Jr., and Lester W. Harrison

Department of Chemistry, University of Georgia, Athens, Georgia 30601

(Received in USA 16 August 1971; received in UK for publication 15 November 1971)

Recently, in an investigation of the proton nmr spectra of some aromatic dianions[1] it was reported that the proton chemical shifts did not correlate well with the electron density of the attached carbon atoms as has been observed in other aromatic systems.[2] It was suggested that the high field shifts observed in these dianions could possibly result from these dianions possessing induced paramagnetic ring currents, even though some of the dianions are formally 4n + 2 π-electron systems. Since we have shown previously that information concerning the ring currents in planar aromatic anions and structural features of the ion pairs may be obtained from ^{7}Li nmr[3], it appeared that this technique could provide evidence concerning the induced ring currents in the previously reported aromatic dianions. We wish to report the results of our investigation of the ^{7}Li nmr spectra obtained from several aromatic dianions along with their implications concerning the electron delocalization in these systems.

Previously, both theoretical[4] and experimental work with the annulenes and their dianions[5] have shown that 4n + 2 monocyclic π-electron systems possess an induced diamagnetic ring current whereas an induced paramagnetic ring current is found for unsaturated monocyclic rings with 4n π-electrons. Although these results are not strictly applicable to polycyclic unsaturated systems, Platt[6] has suggested that 4n + 2 polycyclic systems can be treated in terms of their peripheries by considering the cross links as small perturbations. Similarly, 4n polycyclic systems appear to be consistent with this model as the proton nmr spectrum of the dibenzopentalenyl dianion suggests that this dianion behaves as a perturbed [12] annulene with the π-electron delocalized around the periphery of the ring systems.[2d]

The ^{7}Li chemical shifts obtained[3] from thirteen aromatic dianion systems[2c,7] in THF solution are given in Table 1. With the exceptions of the dianions of azulene(IV) and 15,16-dimethyldihydropyrene[8] (V) the ^{7}Li chemical shifts are upfield from the external reference of aqueous 1.0 M lithium chloride and the majority are clustered around +1.0 ppm.[9] Proton nmr data indicates that I forms predominately contact ion pairs in THF solution.[10] Conductance studies and electronic spectra suggest that some of the other dianions reported here form only contact ion pairs in solution.[11] Therefore, if the lithium cations are coordinated with the π-cloud of these dianions as is found for certain other planar aromatic anions, they should experience an upfield or downfield shift, due to their being located in the shielding or deshielding regions of the induced diamagnetic and paramagnetic ring current, respectively.[12]

The ^{7}Li chemical shift observed for (I) is similar to that observed for cyclopentadienyl lithium.[3] The large upfield ^{7}Li shift indicates that the lithium cations are coordinated with the π-cloud of the 10 π-ring and are experiencing a shielding effect from the induced diamagnetic ring current in this dianion. Likewise, the large upfield shift observed for the biphenylene dianion (II), a 14π-periphery, indicates that the lithium cations

Table 1

^{7}Li Chemical Shifts in Some Aromatic Dianion Systems

Dianion	δ, ^{7}Li^{a}
Cyclooctatetrene (I)	+8.55
Biphenylene (II)	+6.10
Acenaphthylene (III)	+4.13
Azulene (IV)	-2.05
15,16-Dimethyldihydropyrene (V)	-3.15
Pyrene (VI)	+1.10
Perylene (VII)	+1.33
Fluoranthene (VIII)	+0.93
3,4-Benanthracene (IX)	+0.48
Anthracene (X)	+1.15
1,2-Benanthracene (XI)	+0.94
Chrysene (XII)	+0.90
Tetracene (XIII)	+0.11

a. In ppm from external aqueous 1 M LiCl. A positive value denotes upfield. The formal concentration of the starting hydrocarbon is 0.3 M in THF.

are located in the π-cloud of this dianion and that it possesses an induced diamagnetic ring current. The smaller upfield shift observed for II relative to I is consistent with this interpretation since the excess charge can be delocalized over a larger area in II resulting in smaller Coulombic attractions between cations and dianion and hence, a "weaker" contact ion pair. It is difficult to predict the ring current in the acenaphthylene dianion (III) since this dianion represents a 13π periphery if the excess charge is delocalized around the perimeter of the ring. Freedman et. al.[13] have interpreted the delocalization in this dianion in terms of a cyclopentadienyl-heptatrienyl π-system. Assuming one lithium cation to be coordinated with the π-cloud of the cyclopentadienyl part of the dianion and the second lithium cation coordinated with the heptatrienyl part in a fashion similar to that for the allyl anion[14], the ^{3}Li shift for III would be expected to be an average of the two systems if rapid exchange of the lithium cations is occurring. The observed shift for III (Table 1) is in agreement with this prediction lending some support for the cyclopentadienyl-heptatrienyl delocalization in this dianion.[13]

The dianion of azulene (IV) possesses 4n π-electrons and should have an induced paramagnetic ring current. The downfield shift observed for this dianion is consistent with the lithium cations being coordinated with the π-cloud and hence, being in the deshielding region of an induced paramagnetic ring current. An even further downfield shift is observed for the dianion of 15,16-dimethyldihydropyrene (V), a 16 π-dianion. Previous investigations of the proton nmr spectrum of this dianion suggest a strong paramagnetic ring current.[8] The downfield shift observed for this dianion is not as large as expected considering the magnitude of the proton shifts compared to those of the azulene[1c] dianion. However, the methyl groups will inhibit close approach of the lithium cations[8] resulting in a decreasing deshielding effect on the ^{7}Li shifts.

The ^{7}Li chemical shifts for the remainder of the dianions VI-XIII do not appear to follow the above trends. If the periphery model is an accurate model for the electron delocalization in these dianions, their ^{7}Li chemical shifts would be expected to be in the same range since they all possess 4n peripheries, with the exceptions of VIII and IX. The dianions VIII and IX may also be rationalized in terms of a 4n periphery if electron delocalization is mainly restricted to the naphthalene part of these molecules.[15] The proton nmr data for the fluoranthene dianion[1] (VIII) lends some support for this view in that the chemical shifts of the protons on the naphthalene nucleus in this dianion are shifted upfield from 1.5 to 3.6 ppm more than the protons on the remaining ring. Therefore, the ^{7}Li nmr data for VI-XIII are consistent with a periphery model only to the extent that the ^{7}Li shifts are in the same range. The ^{7}Li shifts for VI-XIII are similar to that observed for allyl lithium[14] and 1-phenylallyl lithium.[3] In these anions, the lithium cation is coordinated with the allyl part of the molecule[16] and its chemical shift should not be influenced to any large extent by induced ring currents. If VI-XIII possessed paramagnetic ring currents as the periphery model predicts, their ^{7}Li shifts should be shifted downfield from the reference similar to the dianions of azulene (IV) and 15,16-dimethyldihydropyrene (V). The fact that their ^{7}Li chemical shifts are similar to the allyl anions and not shifted in either direction suggests that they possess essentially no induced ring current.

A consistent explanation for both the proton and ^{7}Li nmr spectra of the dianions (VI-XIII) is that the excess charge is delocalized around the periphery of the ring systems with relatively large perturbations due to the cross links. Perturbations of the delocalization due to the cross links would result in reduced paramagnetic ring currents in the dianions due to an increase in the splitting of the highest occupied and lowest unoccupied molecular orbitals. Evidence in support of reduced ring currents in VI-XIII may be obtained by comparison of the ^{7}Li and proton nmr data of the dianion of 15,16-dimethyldihydropyrene[8] (V) with the dianion of pyrene[1] (VI). The proton chemical shifts of the exterior aromatic protons of V are shifted upfield approximately 12 ppm from their values in the neutral hydrocarbons. In contrast, the proton chemical shifts of VI as well as the other dianions (VII-XIII) reported here are only shifted upfield from 1-6 ppm from their values in the neutral hydrocarbons. Since the excess charge on V and VI is identical, this can only mean that VI possess a smaller ring current than V. Thus, both the proton and ^{7}Li nmr data are consistent and support the idea of smaller ring currents in VI-XII than that expected based on the periphery model above.

Acknowledgments: Partial support of this work by a grant from the Petroleum Research Foundation administered by the American Chemical Society is gratefully acknowledged. We wish to express our appreciation to Professor Boekelheide for his generous donation of the sample of 15,16-dimethyldihydropyrene.

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