

Reduction of 1, 3, 5, 7, 9-Penta-*t*-Butyl-Corannulene: Isomeric Sandwiches With Multiple Lithium Cations Inside and Out

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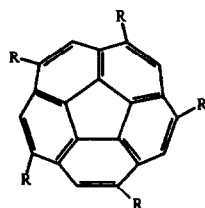
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Abstract

Four reduction stages were observed for 1, 3, 5, 7, 9-penta-*t*-Bu-corannulene(2), two of which exhibited diamagnetic character: a paratropic dianion 2^{2-} and a diatropic tetraanion 2^{4-} . In the last stage of reduction three distinct tetraionic species are detected. Two of them are sandwich-type compounds with eight Li cations each and a tetraionic monomer.

Key Words: Nuclear magnetic resonance spectroscopy, Fullerenes and derivatives.

Introduction



1) R = H
2) R = *t*-Bu

The dimerization of a conjugated π system with lithium cations serving as a "glue" was observed for corannulene (1)¹, which is the smallest subunit of C_{60} that has a curved bowl-type structure. More recently we have managed to detect all oxidation states, from zero to -4 of the corannulene molecule

(1)². This has given a further insight to the corannulenes' electronic properties and helped us to propose a mechanism for the reduction reaction of corannulene (1). The reduction of corannulene (1) to a tetraanion, forming an eight lithium containing dimer, urged further investigation of multiple reductions and dimerization processes in this class of molecules. Thus, we have subjected 1, 3, 5, 7, 9-penta-*tert*-butyl-corannulene (2) to reduction with lithium metal. We followed the reduction process by NMR. Herein we present the results of the multiple reduction of 2.

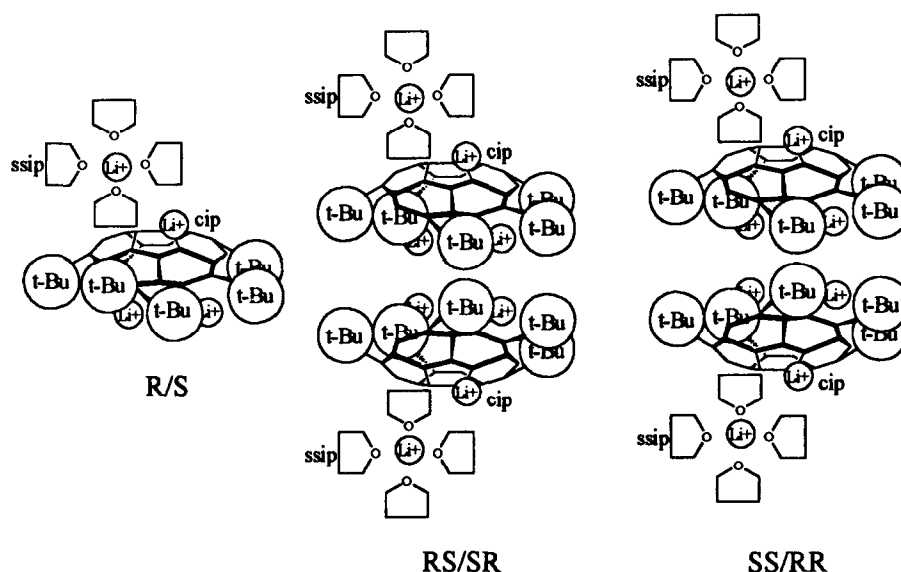
Results and Discussion

1, 3, 5, 7, 9-penta-*tert*-butyl-corannulene (2), was subjected to reduction with lithium metal as the reducing agent. We followed the reduction of (2) by NMR. In the first stage of the reduction the solution exhibited a green color, like the first stage in the reduction of corannulene (1) and no NMR was detected. A second stage was soon observed with a color change of the solution to purple. This time we could obtain a 1H -NMR spectrum. The 1H -NMR exhibits a paratropic character of 2^{2-} and only one broad line is observed at -1.5ppm, assigned to, the

protons of the *tert*-butyl groups. We believe that in the case of 2 the line broadening effect is enhanced, compared with corannulene², and that is the reason for not detecting the line of the ring protons.

A very helpful tool in the research on the lithium salts of polycyclic anions is the Li-NMR. In the 7Li -NMR spectrum of the dianion we observe at 298K one broad signal, only at very low temperatures (173K) we detect two lines. For the corannulene dianion we have observed only one line even at very low temperatures (173K)². We propose two explanations to this, either the location of lithium cations on opposite sides of a slow inverting bowl or, formation of a weak dimer at the dianionic stage.

When the solution reaches the brown color we can again observe an NMR spectrum. Being the second diamagnetic stage detected in the course of the reduction, we conclude that finally a tetraanion is formed. A sharp proton NMR was detected even at room temperature. Much to our surprise it exhibited three lines in the low field region ($\delta = 7.86, 7.18$ and $6.98ppm$) and three more signals in the high field region assigned to the *tert*-butyl group. The carbon NMR spectrum of 2^{4-} also exhibits extra lines, each of the high field signals assigned to the *t*-Bu groups is tripled. To exclude a chemical reaction, due to the reduction with the lithium, we carried out a quench reaction with oxygen that yielded only the pure starting material and this confirms that no chemical reaction (e. g. protonation) took place. Our assumption at this stage was, that what we are observing are spectra of three different species in the solution with no exchange at room temperature in the NMR time scale. We carried out at this stage a NOESY experiment to show NOE interactions. We see that the three species do not show NOE interactions between them. However, each *tert*-butyl group and the adjacent proton shows an NOE interaction. This result confirms that the three species are distinct and it also excludes



Scheme 1: The Three Tetraionic Species.

the possibility of an exchange process between them, at a time scale shorter than the mixing time. Much to our surprise the Li-NMR of 2^4 consists of nine sharp lines at room temperature. We can see three groups of signals in Li-NMR of 2^4 centered around 1.6ppm, -7.7ppm and -11.65ppm. In the ^7Li -NMR spectrum of the corannulene tetraanion (1^4) two lines were observed at low temperature (210K)¹. One line, at -11.78 was assigned to the inner lithium cations of the contact ion pair (c.i.p.) and a much broader line ($\delta = -4.5\text{ppm}$) to the outer Li cations of the corannulene sandwich. On this basis we propose our interpretation of the Li-NMR. We assign the signals of the very high field group (-11.65ppm) to the inner c.i.p. Li cations. Taking the average of the Li shifts of the two groups, (in -1.6 and -7.7ppm) we reach the value of -4.9ppm which is close to the shift value assigned to the outer Li cations of corannulene tetraanion (1^4). Thus, we assigned the group of signals at -7.7ppm to the outer c.i.p. cations and the signals at -1.6ppm to the outer solvent separated ion pair (s.s.i.p.) cations. Monosubstituted corannulene forms diastereoisomeric dimers with corannulene. Since 2 is also chiral it can be expected that it will form four stereoisomers in the solution i. e. the meso, RS, SR and the two enantiomers RR and SS. Thus one can expect to have two diastereoisomers to which two of the high field signals at the ^1H -NMR ($\delta = 7.18$ and 6.98 ppm) can be assigned. We have assigned the third signal ($\delta = 7.86\text{ppm}$) to the two enantiomers of a monomeric tetraanion specie. Each of the dimers has one line in the Li-NMR for the inner c.i.p. cations at -11.57 and -11.77ppm. For each of them there are also two lines, at each group of signals, -7.7ppm and -1.7ppm, for the exterior c.i.p. and s.s.i.p. cations, respectively. There is one more line at each group that can be related to the c.i.p. and s.s.i.p. lithiums of the monomer. The fourth signal seen in the high field group (-7.7ppm) also belongs to the monomer and is assigned to the c.i.p. lithium cation trapped between the t-Bu groups. We wish to present our model for the reduction reaction of

1, 3, 5, 7, 9-penta-tert-butyl-corannulene (2) to a tetraanion with Li. The reduction to the tetraanionic stage proceeds on the same route as in the case of corannulene (1). There is however, an exception to this and that is the unknown structure of the dianion 2^{2-} , we believe that it exists as a monomer. In the tetraionic stage we have three species one monomer and two diastereoisomers of the dimer (scheme1). The differences in the chemical shifts between the dimers require further comment.

In the tetraanion dimers one can assume that each interior Li cation "wants" to sit directly between the faces of two benzene rings. This will require the corannulene rings to be "eclipsed" in the geometry that is most favorable for the lithium atoms. That will enhance the differences between the two diastereoisomers seen in the ^1H -NMR and ^{13}C -NMR. Only one benzene ring, on each deck, is left unoccupied by the inner Li cations and that is where the exterior c.i.p. lithiums sit. The last lithium on each side of the dimer can exist only as a s.s.i.p.. That is the place where a fifth lithium cation can come in and let one of the original interior lithiums go out, thus leading to inside-outside exchange. The five t-Bu groups slow down this exchange which we call, "the merry-go-round model".

References

1. A. Ayalon, A. Sygula, P.-Ch. Cheng, M. Rabinovitz, P. W. Rabideau and L. T. Scott, *Science*, **265**, 1065-1067, (1994).
2. M. Baumgarten, L. Ghergel, M. Wagner, A. Weitz, M. Rabinovitz, P.-Ch. Cheng and L. T. Scott, *J. Am. Chem. Soc.*, **117**, 6254-6257, (1995).