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Inductive Control of Through-Bond Interactions[1)]

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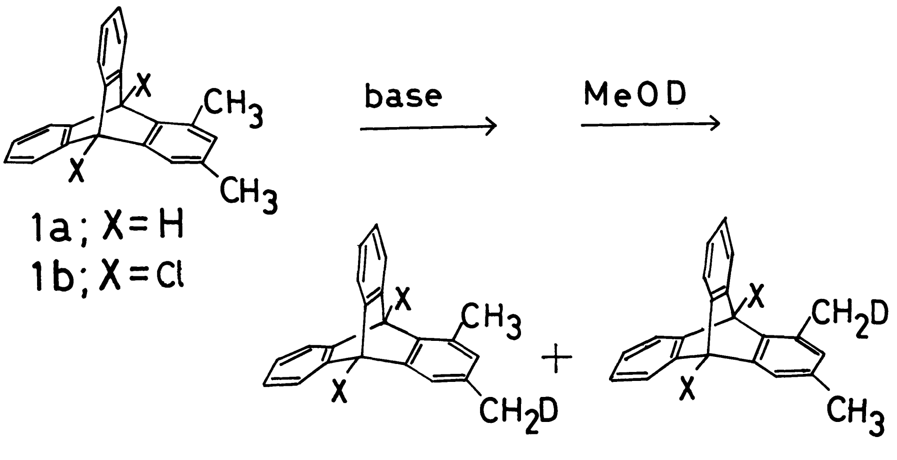
Inductive control of through-bond interactions was substantiated by the reversed site selectivity of the deprotonation reactions of 1,3-dimethyltriptycene and its 9,10-dichloro derivative.

In 1968, Hoffmann, Imamura, and Hehre[2)] proposed the concept of the through-bond interaction, which was first supported by the Heilbronner's analysis[3)] of the vibrational pattern in the photoelectron spectrum of 1,4-diazabicyclo[2.2.2]-octane. The dissection of orbital interaction into through-space and through-bond varieties has proved to be useful in understanding physical and chemical properties of organic molecule.[4)] We now report the attempt to control the through-bond interaction by the inductive effects.[5)] The models examined experimentally were the deprotonation reactions of 1,3-dimethyltriptycenes (Scheme 1; **1a** : X=H, **1b**: X=Cl), where the site selectivities were found to be reversed.



Scheme 1.

The LUMO of triptycene is supposed to be composed of the LUMO's of benzene (e_{2u}). The LUMO candidates are the doubly degenerate e′ and e" orbitals (Fig. 1). From the through-space interaction, the e" orbitals are expected to be lower in energy due to the great overlap between the e_{2u} orbitals. The through-bond interaction may reverse the energy ordering. The interaction with the σ-bonds on bridgehead carbons raises the energies of the e′ and e" orbitals. The through-bond interaction is more appreciable for the e" orbitals due to great orbital overlapping between the σ- and π(e")-orbitals. The LUMO's of triptycene are the e′ orbitals if the through-bond interaction is significant. The LUMO of triptycene can be controled by the through-bond interaction. The energy of the bridge σ-orbital is relatively high in the parent molecule with the electropositive hydrogen atoms on bridgeheads. The through-bond interactions are then appreciable. The LUMO's of triptycene may be the e′ orbitals. The electronegative chlorine atoms, introduced into the bridgeheads, lower the σ-orbital energy to weaken the through-bond interaction, and the LUMO's of 9,10-dichlorotriptycene may be the e" orbitals (Fig. 2).

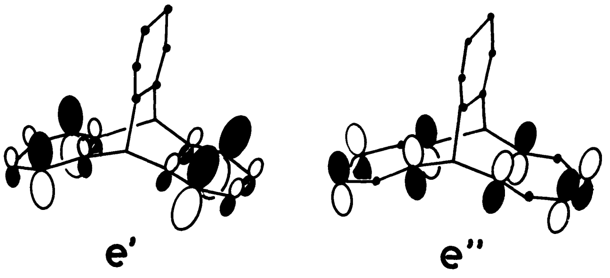


Fig. 1. The LUMO candidates of triptycene.

We designed the deprotonation reactions of the dimethyl derivatives (Scheme 1) to probe the LUMO's of the triptycenes. If the LUMO's are the e′ orbitals, the deprotonation should occur from the 1-methyl group due to the great orbital extension on C_α. This is expected for 1,3-dimethyltriptycene. On the other hand, the deprotonation from the 3-methyl group should be preferential due to the great orbital extension on C_β if the LUMO's are the e" orbitals as is expected for 1,3-dimethyl-9,10-dichlorotriptycene.

As the deprotonating reagents were employed three complex bases, n-buthyl lithium (n-BuLi)/tetramethylethylenediamine (TMEDA),6) n-BuLi/potassium t-butoxide (t-BuOK),7) and lithium diisopropylamide (LDA)/t-BuOK.8) The deprotonation by 2-

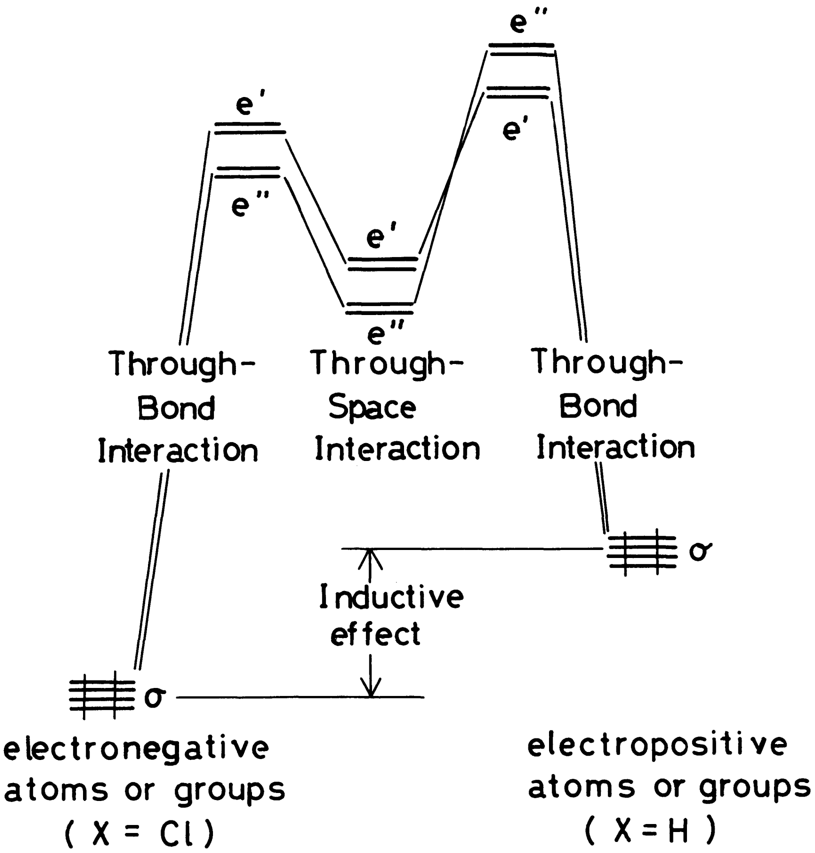


Fig. 2. Inductive effects on the through-bond interactions in the LUMO's of triptycenes.

Table 1. The Percentage (%) of Deuterated Methyl Groups[a)]

Bases	1,3-Dimethyl triptycene		1,3-Dimethyl-9,10-dichlorotriptycene	
	1-CH_3[b)]	3-CH_3[b)]	1-CH_3[c)]	3-CH_3[c)]
LDA/t-BuOK	45	3	7	54
n-BuLi/TMEDA	43	29	6	18
n-BuLi/t-BuOK	34	9	3	25

a) Determined by ^1H NMR spectroscopy. b) The assignment of the methyl protons of 1,3-dimethyltriptycene (δ 2.18, 2.46) was made by the comparison with the 2,3- (δ 2.10) and 1,4-derivatives (δ 2.44).[8)] c) The assignment of the methyl protons of 1,3-dimethyl-9,10-dichlorotriptycene (δ 2.48, 2.76) was made by the comparison with the 2,3- (δ 2.21) and 1,4-derivatives (δ 2.77).

fold excess of bases followed by MeOD quenching was run in hexane solution at room temperature under an atmosphere of nitrogen. After the purification by preparative TLC on silica gel with hexane the product was subjected to the NMR spectroscopy. The results are listed in Table 1.

In summary, the possibility was theoretically predicted that the through-bond interaction could be controlled by the inductive effects. The LUMO's might be the e'-orbitals with the large amplitude on C_α for triptycene where the through-bond interaction is significant, and the e"-orbitals with the large amplitende on C_β for 9,10-dichlorotriptycene where the through-bond interaction is depressed by the inductive lowering of the σ-orbital energy due to the electronegative atoms. This implies that the deprotonation preferentially occurs from the 1-methyl group of **1a** and from the 3-methyl group of **1b**. The prediction was found to be in agreement with the observed reversal of the site selectivities of the deprotonation reactions of 1,3-dimethyltriptycene (**1a** ; X=H) vs. 1,3-dimethyl-9,10-dichlorotriptycene (**1b** ; X=Cl).

References

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