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AN EXPERIMENTAL PROBE INTO THE LUMO OF TRIPTYCENE

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From the regioselectivity of deprotonation of 1,3-dimethyltriptycene the LUMO of triptycene was concluded on some presently acceptable assumptions to be such e′ orbitals as expected from the significant contribution of the through-bond interaction.

The electronic structure of triptycene has been attracting much attention because of its unique structure with high symmetry (D_{3h}). The HOMO of triptycene is now established by the photoelectron spectroscopy together with the molecular orbital calculations to be an $a_2{}'$ orbital.1) That is an out-of-phase combination of the three e_{1g} π orbitals of benzene rings symmetric with respect to the reflection in the plane perpendicular to the C_3 axis. This is what is predicted from the dominant through-space interaction. The HOMO has greater extension at the β than α carbons. According to the frontier orbital theory, electrophiles should attack on the β carbons preferentially. In fact, the prediction of the regioselectivity has been substantiated by various electrophilic aromatic substitution reactions.2) We here report our experimental approach to the LUMO of triptycene.

The LUMO of triptycene (Fig. 1) is supposed to be composed of the LUMOs of benzene (e_{2u}). A set of orbitals ($a_1{}''$, e'') are antisymmetrical with respect to the reflection in the plane perpendicular to the C_3 axis, the other ($a_2{}'$, e') symmetrical. When the through-space interaction is allowed, the doubly degenerate orbitals (e' and e'') are of lower energy in each set. The overlap integral between the antisymmetrical LUMOs of benzene is greater due to the greater extension on the fused carbons or on the interacting sites. When the difference in the magnitude of the overlapping is furthermore taken into account, the e" orbitals are lower than the e' orbitals in energy. The LUMO of triptycene should then be the e'' orbitals. This is the result on the assumption that the through-space interaction is completely dominant.

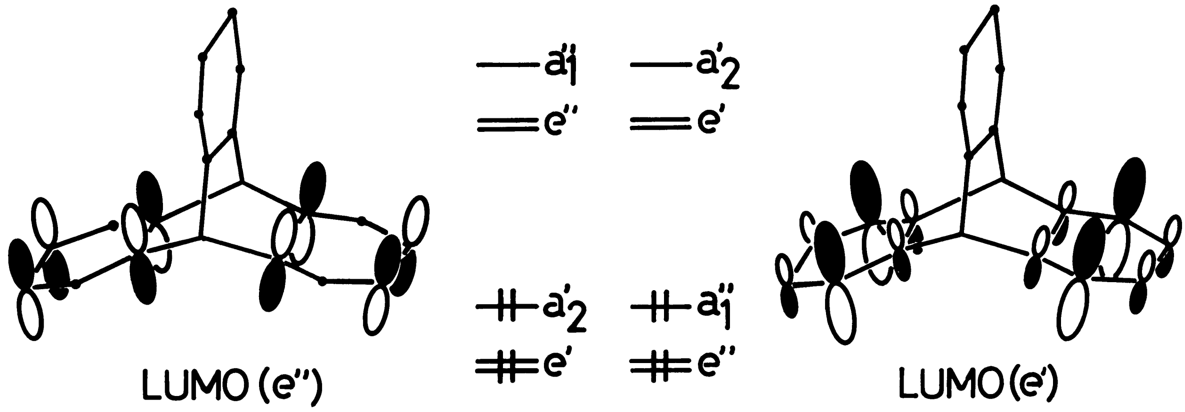
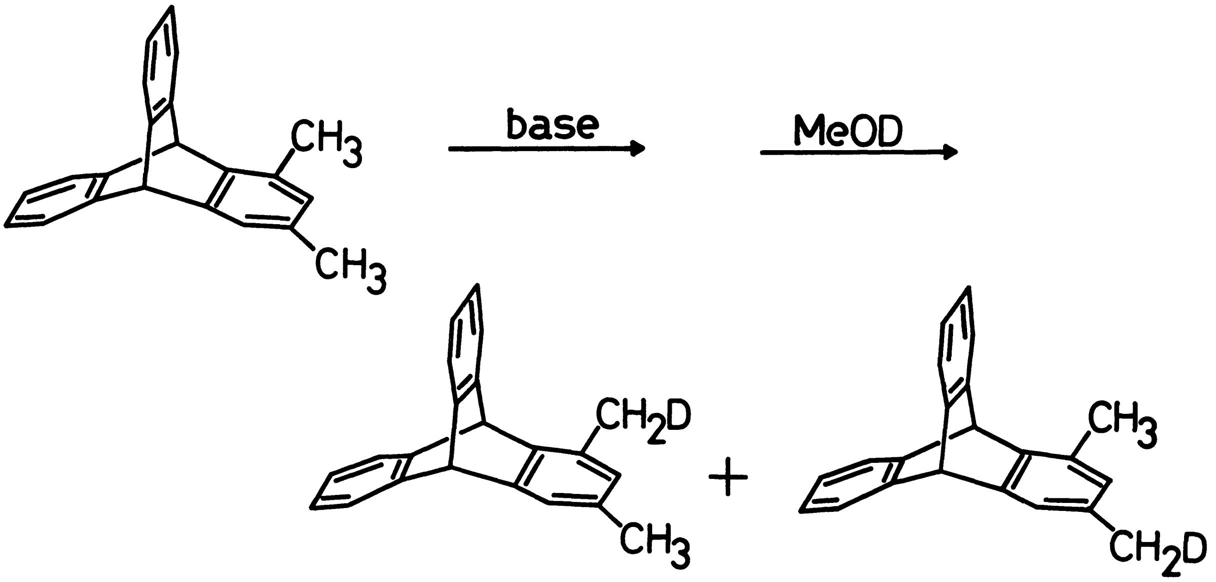


Fig. 1. The low-lying vacant orbitals of triptycene.

Although the HOMO candidates (a_2', a_1'') are forbidden by symmetry to interact with the σ-bond orbitals (e', e'') on the bridgehead carbons, the through-bond interaction is allowed in the LUMO candidates (e', e''). The interaction raises the e'' π-orbital energy to a greater extent due to greater orbital overlapping with the σ-bond orbitals. The LUMO could be the e' π-orbitals if the through-bond interaction is significant.

We designed an experiment (Scheme 1) to probe the LUMO of triptycene. That is the deprotonation reaction of 1,3-dimethyltriptycene. If the LUMO is the e'' π-orbitals, the deprotonation should occur from the 3-methyl group due to the greater extension on C_β. On the other hand, if the LUMO is the e' π-orbitals, the deprotonation from the 1-methyl group should be preferential due to the greater extension on C_α.

The 1,3-, 1,4-,and 2,3-dimethyltriptycenes were prepared by the addition reactions of benzyne with the corresponding dimethylanthracenes.[3)] As the deprotonating reagents were employed three complex bases, n-butyl lithium (n-BuLi)/tetramethylethylenediamine (TMEDA),[4)] n-BuLi/potassium t-butoxide (t-BuOK),[5)] and lithium diisopropylamide (LDA)/t-BuOK or n-BuLi/diisopropylamine/t-BuOK.[6)] The deprotonation by 5-fold excess of bases followed by MeOD quenching was run in hexane solution at room temperature under an atmosphere of argon. After the purification by preparative TLC on silica gel with hexane the product was subjected to the ^{1}H NMR spectroscopy. 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). The ^{13}C NMR spectroscopy showed no signs of the deuteration on the aromatic rings and the bridgeheads. The figures listed in Table 1 are the ratios of the integrated intensity of methyl protons to the bridgehead protons (2.0).



Scheme 1.

Table 1. The NMR Integrated Intensity of Methyl Protons

Bases	1-CH_3	3-CH_3
n-BuLi/TMEDA	2.8	2.9
n-BuLi/t-BuOK	2.2	2.6
LDA/t-BuOK	2.3	2.9

The deprotonation of 1,3-dimethyltriptycene was shown to preferentially occur at the 1-methyl group. On the assumptions that the quenched intermediates are the carbanions, of which the stability is controlled by the interaction of the nonbonding orbital of the anionic center with the LUMO of triptycene, the present results lead to the following conclusions. The LUMO of triptycene has greater extension on C_α. In other words, the LUMO is the e′ π-orbitals. In addition, the through-bond interaction plays a critical role in the LUMO, in contrast to the HOMO where the through-bond interaction is forbidden by symmetry.

The electron tranmission spectroscopy (0.04 - 0.05eV resolution) of triptycene7) showed no appreciable splitting between the E′ and E" anion states. This order of energy difference can be observed in the chemical equilibrium. The major component may exist a few times in excess. We think we have, fortunately, observed the small difference in the regioselectivity.

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References

1) E. Haselbach, L. Neuhaus, R. P. Johnson, K. N. Houk, and M. N. Paddon-Row, Helv. Chim. Acta, 65, 1743 (1982); T. Kobayashi, T. Kubota, and K. Ezumi, J. Am. Chem. Soc., 105, 2172 (1983); H.-D. Martin, B. Mayer, R. Gleiter, W. Schäfer, and F. Vögtle, Chem. Ber., 116, 2546 (1983).

2) C. J. Paget and A. Burger, J. Org. Chem., 30, 1329 (1965); R. Taylor, G. Wright, and A. J. Homes, J. Chem. Soc., B, 1967, 780; B. H. Klanderman and W. C. Perkins, J. Org. Chem., 34, 630 (1969); J. H. Rees, J. Chem. Soc., Perkin Trans.2, 1975, 945; V. K. Shalaev, and V. R. Skvarchenko, Vestn. Mosk. Univ. Khim., 15, 726 (1974); Chem. Abstr. 82, 497 (1975); Z. R. H. Schaasberg-Nienhuis, H. Cerfontain, and T. A. Kortekaas, J. Chem. Soc., Perkin Trans. 2, 1979, 844.

3) L. F. Fieser, "Organic Experiments," Maruzen, Tokyo (1964), Chap. 62.

4) G. G. Eberhardt and W. A. Butte, J. Org. Chem., 29, 2928 (1964).

5) L. Lochmann, J. Pospisil, and D. Lim, Tetrahedron Lett., 1967, 257; M. Schlosser, J. Organomet. Chem., 8, 9 (1967).

6) B. Renger, H. Hügel, W. Wykypiel, and D. Seebach, Chem. Ber., 111, 2630 (1978); S. Raucher, and G. A. Koolpe, J. Org. Chem., 43, 3794 (1978).

7) V. Balaji and K. D. Jordan, submitted for publication.

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