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On the Influence of Spiroconjugation and Electron-withdrawing Effects on the Frontier Orbital Energies of 5-Substituted Cyclopentadienes

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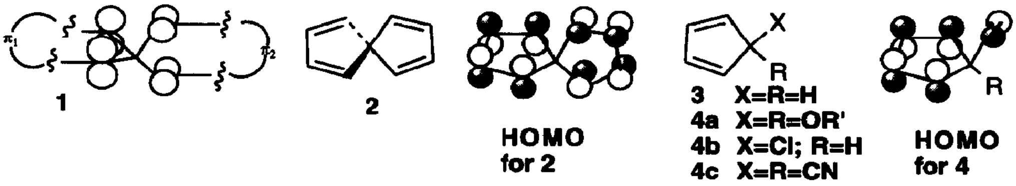
Abstract: Ab initio calculations reveal that the influence of spiroconjugation on the HOMO of 5-substituted cyclopentadienes is weak relative to electron withdrawing effects and that both the HOMO and LUMO energy levels can be lower than in cyclopentadiene contrary to the predictions of qualitative perturbation theory. In accord with these theoretical results, the reaction of 5,5-dicyanocyclopentadiene with cyclopentadiene yields only heterodimers.

The term spiroconjugation was first introduced to describe a form of homoconjugation which arises when the termini of two orthogonal π-systems are held in close proximity by virtue of the fact that they are linked by a common (spiro) tetrahedral carbon atom as illustrated in **Figure 1**.[1,2] The application of qualitative perturbation theory to these so-called spirarenes has led to predictions concerning the influence of such spiroconjugative interactions on the frontier orbitals of the parent isolated π-systems. In the case of spiro[4.4]nonatetraene, **2**[3], perturbation theory arguments predict that the HOMO for such a system will be raised in energy relative to cyclopentadiene as a consequence of the antibonding interaction of the terminal p-orbitals of the two π-systems as shown in **Figure 1** below. On the other hand, since the LUMO of cyclopentadiene is symmetric while the p-orbitals of the orthogonal π-system are antisymmetric with respect to the plane of symmetry in **2**, the energy of the LUMO of **2** is expected to be unaffected by through space orbital overlap.[4]

Figure 1:

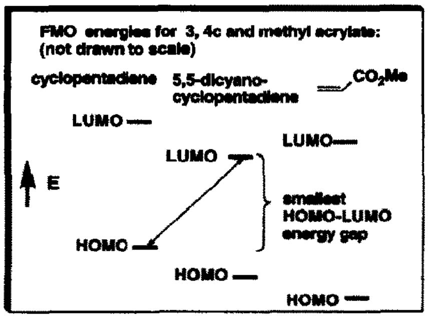


It has been pointed out that a qualitatively similar through space interaction is expected for any 5-substituted cyclopentadiene **4** in which the C-5 substituent bears an appropriately oriented p-orbital.[4,5] It has also been noted that a consequence of the spiroconjugation interaction, which results in an increase in HOMO energy with no effect on the LUMO energy, is that the energy separation between the frontier orbitals decreases. This predicted diminution in the HOMO-LUMO energy gap has been suggested to be the origin of the unusual UV spectroscopic properties of certain 5-substituted cyclopentadienes such as cyclopentadienone ketals, **4a**, and of the tendency of these and other 5-substituted cyclopentadienes, such as the 5-halocyclopentadienes, **4b**, to undergo dimerization in preference to Diels-Alder cycloaddition with other dienophiles.[1a,2,6,7] This qualitative picture of spiroconjugation effects has become entrenched in the literature concerning 5-substituted cyclopentadienes and has been assumed to be correct in more recent studies aimed at the design of new molecules with unusual electronic properties arising from similar through space interactions.[8,9,10]

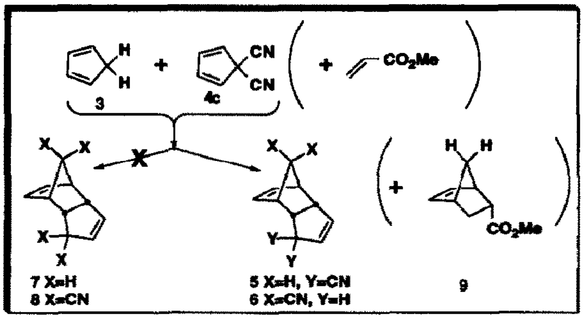
Some time ago we described the synthesis of 5,5-dicyanocyclopentadiene, **4c** and Diels-Alder trapping by the use of a large (≈ 40 fold) excess of appropriate activated dienophiles.[11] We have now carried out experimental and ab initio molecular orbital studies in order to determine if the Diels-Alder reactivity of **4c** is explicable on the basis of spiroconjugation arguments. Disclosed herein are the results of these studies which demonstrate that *the influence of spiroconjugation on the frontier orbitals of 5-substituted cyclopentadienes can be weak relative to the consequences of electron withdrawing effects of the C-5 substituents and that both the HOMO and LUMO energy levels of such systems can be lower than the corresponding orbitals in cyclopentadiene itself.*

Gaussian 90 calculations were performed for **4c** and cyclopentadiene **3** with full geometry optimization using the 3-21G basis set [14] As indicated in **Figure 2** below, 5,5-dicyano-substitution lowers the energies of the HOMO and the LUMO of **4c** relative to the HOMO and LUMO of the parent system **3** by comparable amounts.

Figure 2:



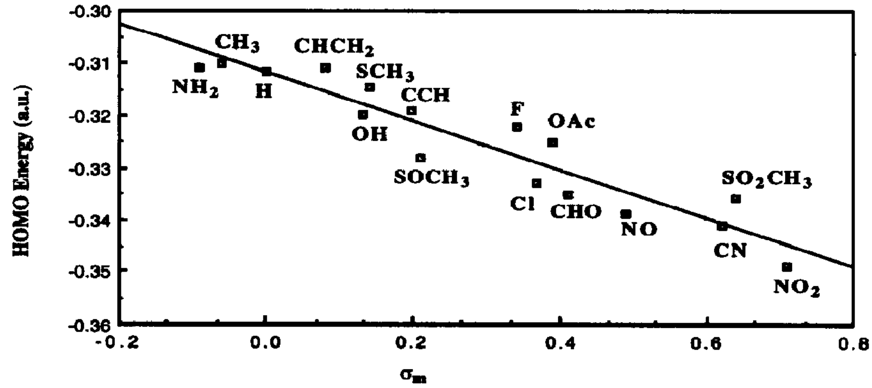
Scheme 1:



The sluggishness of **4c** in reactions with typical dienophiles such as acrolein or methyl acrylate is explicable in this model in terms of a larger HOMO$_{\text{diene}}$-LUMO$_{\text{dienophile}}$ energy gap which results in a diminution in the stabilizing frontier orbital interaction in the early stages of the cycloaddition process. Closer inspection of the frontier orbital energy relationships illustrated in **Figure 2** revealed that the smallest orbital energy gap is that between the HOMO of cyclopentadiene and the LUMO of **4c** and led us to carry out experiments to explore the possibility that the computed frontier orbital energies might be useful for understanding the reactivity of **4c**. It was predicted that in a Diels-Alder reaction of a mixture of **3** and **4c** the heterodimers **5** and **6** should predominate over the known homodimers **7** and **8**. In practice it was found that reaction of equimolar amounts of **3** and **4c** at room temperature proceeded smoothly to yield a mixture of the adducts **5** and **6** in a 1 to 1.3 ratio, as estimated by NMR analysis, and little or none of the known homodimers.[15] The heterodimers also predominated when the same reaction was carried out in the presence of an equimolar amount of methyl acrylate. In this case a small amount of the adduct **9** (5 %) was isolated in addition to the mixture of adducts **5** and **6** (89 %) as expected from the FMO energy levels shown qualitatively in **Figure 2**.[14]

With our confidence in the theoretical model bolstered by these experimental observations we turned our attention to exploring the validity of the predictions of qualitative perturbation theory in regard to other 5-substituted cyclopentadienes for which spiroconjugative interactions are possible a priori. Gaussian 90 calculations were performed with full geometry optimization using the 3-21G and (where appropriate) the 3-21G* basis sets for fifteen C-5 monosubstituted cyclopentadienes. For twelve of the fifteen examples studied the HOMO energy was found to be lower than that of the parent system contrary to the qualitative predictions of the perturbation treatment of spiroconjugation. Exceptions to this generalization were found only for 5-methyl, 5-vinyl and 5-amino cyclopentadiene in which cases the HOMO energies were found to be slightly elevated relative to that of cyclopentadiene. That the energy lowering effect is related to an inductive electron withdrawing influence of the C-5 substituent is indicated by the approximate correlation of HOMO energies with Hammett σ_m values shown in **Figure 3**.[16,17]

Figure 3: Plot of HOMO Energy (3-21G*//3-21G*) for 5-Monosubstituted Cyclopentadienes, 4, versus Hammett σ_m for the C-5 Substituent:



Examination of the atomic orbital coefficients in the HOMO's of the C-5 heteroatom substituted cyclopentadienes reveals that the antibonding interaction between the p_y orbital of the substituent heteroatom and the p_z orbitals at the termini of the cyclopentadiene HOMO , predicted on the basis of perturbation theory arguments, is indeed present. However the magnitude of this interaction is small and the effect is clearly outweighed by the energy lowering influence of the electronegative substituents. As a result, it is clear that the validity of explanations for the unusual reactivity and ultraviolet spectroscopic properties of C-5 heteroatom substituted cyclopentadienes which were based on the qualitative application of perturbation theory to the spiroconjugation phenomenon must be reconsidered. It is also clear that in the design of new materials with anticipated optical or electronic properties which are a consequence of through-space orbital interactions attention must be paid to the influence of the electron withdrawing capacity of substituent groups.

Acknowledgments: Preliminary semi-empirical calculations were carried out at the University of Oxford while two of us (LAB and GID) were visiting on sabbatical leave. We would like to thank Professor Jack E. Baldwin for making the facilities of the Dyson Perrins Laboratory available to GID and Professor Norman Marsh for making the facilities of the Department of Theoretical Chemistry available to LAB. One of us (GID) would also like to thank the Royal Society for a fellowship and the Natural Sciences and Engineering Research Council of Canada (NSERC) for an operating grant. All of the ab initio calculations were carried out at the University of Waterloo using a molecular modeling facility purchased with a University-Industry Collaborative Research and Development grant (to GID) jointly from Uniroyal Chemical Ltd. Research Laboratories, Guelph, Ontario and NSERC.

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14. The HOMO and LUMO energies for **4c** are -0.3665 and 0.0820 a.u. respectively as compared with -0.3118 and 0.1427 a.u. respectively found for **3**. The HOMO and LUMO energies for *s*-cis methyl acrylate are -0.3959 and 0.1117 and for *s*-trans methyl acrylate are -0.3960 and 0.1117 a.u. respectively.
15. The cycloaddition of **3** and **4c** was effected by adding one equivalent of **3** to a solution of **4c**, prepared as previously described[13], at -78°C in CH_2Cl_2 and allowing the solution to stir at room temperature for 30 minutes. The crude product was concentrated to dryness in vacuo and analyzed by ^{1}H NMR at 200 MHz. Comparison with ^{1}H NMR spectra of authentic **7** and **8**, revealed that the product contained less than 5% of either of the homodimers. Detailed analysis of the product by ^{1}H and ^{13}C NMR including ^{1}H-^{1}H decoupling, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C HETCOR experiments allowed unambiguous determination of the structures of **5** and **6**. The ratio of **5**:**6** was determined to be 1.3:1 by integration of the ^{1}H NMR and inverse-gated ^{13}C NMR spectra.
16. Ab initio calculations were performed with geometry optimization using the 3-21G* basis set in Gaussian 90.*Gaussian 90*, Frisch, M.J.; Head-Gordon, M.; Trucks, G.W.; Forseman, J.B.; Schlegel, H.B.; Raghavachari, K.; Robb, M.A.; Binkley, J.S.; Gonzalez, C.; Defrees, D.J.; Fox,D.J.; Whiteside, R.A.; Seeger, R.; Melius, C.F.; Baker, J.; Martin, R.L.; Kahn, L.R.; Stewart, J.J.P.; Topiol, S.; Pople, J.A., Gaussian, Inc., Pittsburg PA, **1990**.
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