Tetrahedron Letters No. 39, pp 3479 - 3482, 1976. Pergamon Press. Printed in Great Britain.

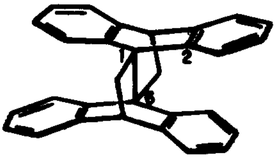
LONG BONDS AND THROUGH-BOND COUPLING

Dennis A. Dougherty, W. Douglas Hounshell, H. Bernhard Schlegel,
Robert A. Bell, and Kurt Mislow*

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

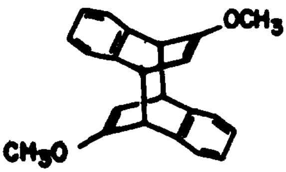
(Received in USA 22 July 1976; received in UK for publication 10 August 1976)

The synthesis[1] and X-ray structure determination[2] of the novel hydrocarbon lepidopterene (1) have recently been reported. The most striking structural feature of 1 is the elongated (1.64 Å) central (1-6) bond, and we were therefore interested in calculating a structure for 1 by use of an empirical force field (EFF) method which had been developed for the determination of ground state structures of aromatic hydrocarbons.[3] Surprisingly, a structure with a 1-6 bond length of 1.570 Å was calculated to be ca. 6 kcal/mol less strained than the X-ray structure with all hydrogens relaxed. It seems unlikely that an error of this magnitude could be attributed to inadequate force field parametrization, considering the success of the force field in application to other aromatic hydrocarbons.[3,4] Since EFF calculations give an adequate description of steric effects on ground state structures, the bond lengthening in 1 had to be the result of an electronic effect not considered by the force field. The formalism of through-bond coupling[5] provides an appealing rationalization of this effect. The same effect accounts for the finding that the 1-2 bond length[2] in 1 (1.526 Å) is significantly shorter than the EFF calculated value of 1.548 Å.

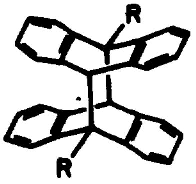


1

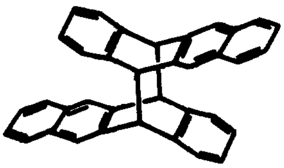
Several other structures (2-5)[6-10] have been reported in which four π orbitals are geometrically constrained so as to be nearly parallel to a central σ bond. All of these show bond lengths significantly greater than those attributable to steric effects, and are thus additional examples of the through-bond coupling.[11]



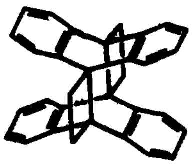
2
(1.610 Å)[6]



3a, R = H
(1.61 Å)[7]
(EFF: 1.557 Å)
3b, R = CHO
(1.61 Å)[8]



4
(1.616 Å)[9]



5
(1.77 Å)[10]
(EFF: 1.574 Å)

The nature of the effect can be illustrated by a qualitative molecular orbital treatment of 1. For the sake of simplicity, each of the four aryl rings is considered as a free benzene, and through-space interactions are assumed to be negligible, giving rise to six sets of four degenerate orbitals (Figure 1). Each set of four orbitals consists of the four symmetry combinations shown on the left. These four combinations, as well as the σ and σ^* orbitals of the 1-6 bond, are given symmetry designations with respect to σ_h and the C_2 axis of 1 (virtual C_{2h} symmetry). The interaction diagram in Figure 1 is obtained by allowing orbitals of the same symmetry to interact, and by considering only interactions of filled with unfilled orbitals. The mixing of the SS orbitals results in a transfer of σ electron density into π^* orbitals, while the SA interaction results in π to σ^* donation. Both effects will bring about a weakening of the 1-6 bond. Similar explanations serve to account for the abnormal bond lengths in 2-5.

In further support of the interpretation advanced above, CNDO/2 calculations[12] performed on 1 and 3a show (Table I) that the presence of the aromatic rings causes a diminution of the σ bond overlap population relative to that of the same bond in the saturated skeleton at the same bond length. The decrease in overlap population indicates a weaker and therefore longer bond. We note that the effect of through-bond coupling on bond length in 1-5 should be enhanced by appropriate ring substitution, and experiments to test this hypothesis are underway.

The present work illustrates anew the power of EFF calculations in the detection of unusual electronic effects.[13]

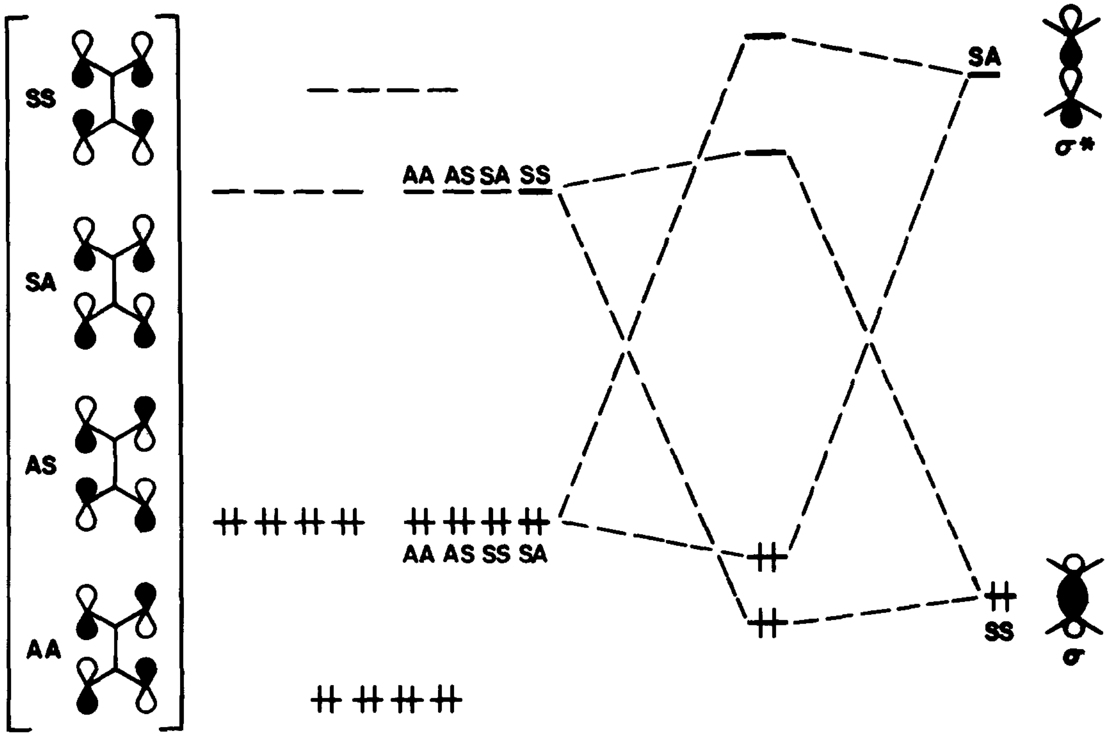


Figure 1

Table I

Cpd	Bond Length (Å)		CNDO Overlap Population[a,b]	
	X-ray	EFF	Parent	Sat'd Skeleton[c]
1	1.638[d]		1.153	1.191
		1.570	1.271	1.297
3a	1.612[e]		1.262	1.288
		1.557	1.348	1.373

[a] R. S. Mulliken, J. Chem. Phys., 23, 1833 (1955). [b] Calculated for an EFF minimized structure with the central bond(s) fixed at the given value. [c] Tetracyclo[$4.4.2^{1,4}.2^{6,9}.0$]tetradecane for 1 and tricyclo[$4.2.2.2^{2,5}$]dodecane for 3a. [d] Molecule A of the unit cell.[2] [e] Calculated from X-ray coordinates.[7]

Acknowledgment. We thank the National Science Foundation (MPS74-18161) for support of this work, and Professors H. Bouas-Laurent, P.v.R. Schleyer, and R. Hoffmann for informative discussions. One of us (H.B.S.) wishes to thank the National Research Council of Canada for a NATO Postdoctorate Fellowship.

References and Notes

1. G. Felix, R. Lapouyade, A. Castellan, and H. Bouas-Laurent, Tetrahedron Lett., 409 (1975).
2. J. Gaultier, C. Hauw, and H. Bouas-Laurent, Acta Cryst., B32, 1220 (1976)
3. J. D. Andose and K. Mislow, J. Am. Chem. Soc., 96, 2168 (1974).
4. K. Mislow, Acc. Chem. Res., 9, 26 (1976) and references cited therein; M. G. Hutchings, J. D. Andose, and K. Mislow, J. Am. Chem. Soc., 97, 4553 (1975); P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, ibid., in press.
5. R. Hoffmann, A. Imamura, and W. J. Hehre, J. Am. Chem. Soc., 90, 1499 (1968); R. Hoffmann, Acc. Chem. Res., 4, 1 (1971); R. Gleiter, Angew. Chem. internat. Ed., 13, 696 (1974).
6. B. K. Selinger and M. Sterns, Chem. Commun., 978 (1969).
7. M. Ehrenberg, Acta Cryst., 20, 177 (1966).
8. M. Ehrenberg, Acta Cryst., B24, 1123 (1968).
9. J. Gaultier, C. Hauw, J. P. Desvergne, and R. Lapouyade, Cryst. Struct. Comm., 4, 497 (1975).
10. M. Ehrenberg, Acta Cryst., 20, 183 (1966).
11. Whether the presence of four π orbitals surrounding a single σ bond is a precondition for the magnitude of the observed bond-lengthening effect is a question under current exploration.
12. P. A. Dobosh, program 141, Quantum Chemistry Program Exchange, Bloomington, Indiana (modified to accomodate 55 atomic centers and 145 basis functions).
13. Cf., for example, N. L. Allinger and J. T. Sprague, J. Am. Chem. Soc., 94, 5734 (1972); G. A. Olah, G. Liang, P.v.R. Schleyer, E. M. Engler, M.J.S. Dewar, and R. C. Bingham, ibid., 95, 6829 (1973).