Tetrahedron Vol 44, No 24, pp 7455 to 7460, 1988
Printed in Great Britain

0040-4020/88 $3.00+.00
© 1988 Pergamon Press plc

THE USE OF SEMIEMPIRICAL ENERGY PARTITIONING TERMS IN THE STUDY OF THROUGH SPACE (HOMOAROMATIC) INTERACTIONS

Richard V. Williams,* Henry A. Kurtz,* and Ben Farley

Department of Chemistry
Memphis State University
Memphis, TN 38152

(*Received in USA* 30 *March* 1988)

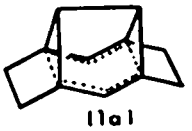
Abstract

MNDO and AM1 calculations, including configuration interactions, were performed on cycloheptatriene (2), 1,6-methano[10]annulene (3), and the tautomeric elassovalenes (4), (5), and (6). The goal of this study is to examine these systems and assess indicators of the importance of through space (homoaromatic) interactions. It is established that the two-center energy partitioning terms are capable of detecting favorable (negative two-center term) through space interactions. In cases of cyclic conjugation (homoconjugation), it is also shown that the inclusion of CI is necessary.

Introduction

We have recently proposed that the bisannelated semibullvalene (1) adopts a symmetrical geometry (1a) due to favorable through space interactions. Furthermore it is postulated that these interactions constitute a homoaromatic stabilization and that (1a) is best regarded as a bishomobenzene.[1] These conclusions were reached by consideration of the results of MNDO and AM1 calculations, in particular the fact that energy lowering interactions must be occurring which force the molecule to become symmetrical. These interactions were correlated with the calculated bond orders and two-center energy partitioning terms.

(1)



(1a)

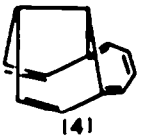
Obviously, it can be argued in light of the limited basis sets and the very nature of these semiempirical calculations that extreme caution must be exercised in reaching any conclusion regarding "homoaromatic" (through space stabilizing) interactions. However, we are confident that our results do indeed indicate the importance of energy lowering through space interactions in (1a). Our conclusions are supported by the fact that restricted basis sets are well known to over emphasize the importance of three membered rings[2] (which clearly disfavors (1a) in comparison with (1)) and that these semiempirical calculations tend to underestimate the importance of extended conjugation.[3,4] In spite of these factors (1a) is calculated to be at least 10 kcal/mole more stable than (1). In an effort to calibrate our calculations and to further substantiate these proposals, the MNDO and AM1 study of known systems capable of similar through space interactions was undertaken. We also wished to establish the reliability of bond order and energy partitioning as indicators of homoaromatic interactions. The molecules chosen were cycloheptatriene (2), 1,6-methano[10]annulene (3), and elassovalene (4), as in each case the importance (or lack there of) of through space interactions has been previously addressed.

Numerous calculations and experimental investigations have been undertaken on cycloheptatriene (2)[5,6,7] and 1,6-methano[10]annulene (3)[2,4,7]. The concensus of these studies is that 1,6-homoaromatic interactions in (2) are of little or no importance, whereas in (3) the interactions are strong and such experimental results as the photoelecton, NMR, and UV spectra can only be satisfactorily explained by consideration of this interaction.[2,7]

Elassovalene (4) has been less well studied.[7] However, experimental evidence (principally NMR spectroscopy) suggests that through space interactions are relatively unimportant.[8]

(2)

(3)



(4)

In each case, valence tautomerism to norcaradiene type structures are possible, although calculations and experiment have established that the groundstates are indeed (2), (3), and (4).[2,7,8]

Method

The methods chosen for this study are the semiempirical MNDO[9] and AM1[10] procedures as implemented in the MOPAC electronic structure program[11]. As has been noted previously,[1,2,4,12] simple SCF calculations alone may not be sufficient to describe the types of conjugated systems investigated here. To address this problem we have also performed configuration interaction (CI) calculations on each of the systems under study. Two types of CI calculation were used: a 2x2 CI and a 4x4 CI, both based on closed shell SCF orbitals. The numbers (nxn) refer to the number of active orbitals in the CI. Within the MOPAC program, a full CI calculation is done by forming all possible microstates by permuting the electron among the orbital subspace.[13] The 2x2 CI calculation contains 4 microstates (leading to 3 singlets and a triplet) and the 4x4 CI has 36 microstates (giving 20 singlets, 15 triplets, and 1 quintet). All reported results in this work are for fully optimized geometries.

A major goal of this paper is to correlate two-center interaction energy values from the MOPAC program with stabilizing and destabilizing through space interactions. These energies are obtained from an energy partitioning into one-center (atomic) and two-center (bond) contributions based on a procedure of Dewar and Lo.[14]

Results

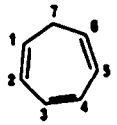
The results for cycloheptatriene (3) are summarized in Table 1. This molecule is an example of a system which is claimed to exhibit a weak to nonexistent "homoaromatic" interaction across the nonbonded (1,6) atoms. Both SCF and 2x2 CI calculations were performed using MNDO and AM1 for (2), the CI having little effect. The calculated SCF and CI heats of formation were 33.89 and 32.24 kcal/mole, respectively, from MNDO and 38.30 and 36.93 kcal/mole, respectively, from AM1. The 1,6 atom distance from all procedures was predicted to be about 2.5 Å. To determine the nature of the interactions, the bond orders and two-center energy terms are 0.02 and +0.31 eV. These indicate a weak destabilizing interaction, entirely consistent with experimental results.[6,7]

For comparison, calculations were also performed on norcaradiene (7). The MNDO heats of formation are 41.84 and 38.96 kcal/mole by SCF and 2x2 CI, respectively. As expected, this molecule is predicted to be less stable than cycloheptatriene (2) (6.7 kcal/mole at the 2x2 CI level). The 1,6 distance is 1.56 Å with a bond order of 0.94 and a two-center interaction energy of -11.9 eV, indicative of the single bond between 1 and 6. The AM1 values for the heat of formation are 51.03 and 48.56 kcal/mole by SCF and 2x2 CI, respectively.

The results for 1,6-methano[10]annulene (3) are summarized in Table 2. For this system a 4x4 CI calculation was necessary because of a near degeneracy between the two highest occupied orbitals and also between the two lowest unoccupied orbitals. The computed SCF and CI heats of formation were 79.97 and 71.20 kcal/mole, respectively, from MNDO and 81.06 and 70.27 kcal/mole, respectively, from AM1.

The 1-6 nonbonded interaction is again of main interest. The distance is predicted to be about 2.3 Å from the SCF and CI calculations based on both the MNDO and AM1 procedures. Even though the CI does not seem to make a very big difference in the interatomic distances, it has a large effect on the other quantities of interest: heats of formation, bond orders, and two-center interaction energies. The MNDO SCF result has a very small bond order and a positive (destabilizing) interaction energy. In contrast, when the CI is included, the bond order increases appreciably and the interaction energy becomes negative (stabilizing). The AM1 results are qualitatively the same except that the interaction energies are always stabilizing.

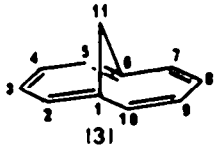
TABLE 1. CYCLOHEPTATRIENE RESULTS



[21]

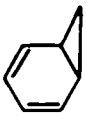
Atom Pairs	2-3	1-2	3-4	1-7	1-6
			Distance (Å)		
MNDO	1.46	1.35	1.36	1.50	2.55
MNDO-CI	1.46	1.35	1.36	1.51	2.55
AM1	1.44	1.34	1.35	1.48	2.46
AM1-CI	1.44	1.34	1.35	1.48	2.46
Exp (ref 15)	1.45	1.36	1.36	1.50	2.51
			Bond Orders		
MNDO	1.04	1.87	1.83	0.98	0.02
MNDO-CI	1.04	1.87	1.82	0.98	0.02
AM1	1.06	1.86	1.81	0.99	0.03
AM1-CI	1.06	1.86	1.80	0.99	0.03
			Two-Center Energy (eV)		
MNDO	-16.82	-23.62	-23.29	-15.44	+0.31
MNDO-CI	-16.90	-23.59	-23.16	-15.41	+0.30
AM1	-16.20	-22.92	-22.58	-14.73	+0.20
AM1-CI	-16.28	-22.88	-22.47	-14.71	+0.20

TABLE 2. 1,6-METHANO[10]ANNULENE RESULTS



[31]

Atom Pairs	3-4	4-5	5-6	6-7	7-8	8-9	1-6
				Distance (Å)			
MNDO	1.37	1.46	1.37	1.47	1.36	1.47	2.32
MNDO-CI	1.41	1.42	1.41	1.44	1.39	1.44	2.31
AM1	1.36	1.44	1.36	1.44	1.35	1.44	2.30
AM1-CI	1.40	1.39	1.40	1.40	1.39	1.43	2.30
Exp (Ref 16)	1.42	1.38	1.41	1.40	1.38	1.42	2.24
				Bond Orders			
MNDO	1.77	1.08	1.77	1.02	1.83	1.05	0.05
MNDO-CI	1.50	1.29	1.51	1.13	1.68	1.15	0.13
AM1	1.71	1.13	1.70	1.05	1.79	1.08	0.06
AM1-CI	1.33	1.47	1.32	1.29	1.50	1.31	0.14
				Two-center Energy (eV)			
MNDO	-22.76	-17.11	-22.73	-16.76	-23.27	-16.88	+0.16
MNDO-CI	-20.67	-19.18	-20.63	-17.76	-22.04	-17.98	-0.29
AM1	-21.74	-16.94	-21.72	-16.16	-22.43	-16.47	-0.12
AM1-CI	-18.81	-19.90	-18.72	-18.52	-20.08	-18.61	-0.54



(7)

(8)

For the norcaradiene-like structure (8), the results are more interesting. By MNDO the SCF and CI heats of formation are 77.32 and 70.89 kcal/mole, respectively. For AM1, they are 88.11 and 82.25 kcal/mole, respectively. It was noted earlier by Dewar and McKee[4] that MNDO fails to give the proper relative energies (even with CI) and predicts that the norcaradiene geometry is the most stable. However, our AM1 calculations give the correct ordering with the 1,6-methano[10]annulene structure (3) as the ground state.

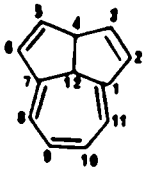
For elassovalene, three different valence tautomers were found ((4), (5), and (6)) and their results are shown in Tables 3-5. The lowest energy form is the only one to have been isolated and studied experimentally.[7,8] The heat of formation is 74.57 and 86.21 kcal/mole by MNDO and AM1, respectively. By both methods the nonbonded atoms of interest (1,7 and 3,5) are over 2.5 Å apart, have very small bond orders, and have positive interaction energies (destabilizing). This implies that there is no "homoaromatic interaction" between these atoms, once more in accord with experimental evidence.[8]

The structure (5) of next higher energy has an MNDO heat of formation of 99.68 kcal/mole and an AM1 value of 117.11 kcal/mole. This corresponds to a geometry with a single bond across the 3,5 terminus. For these two atoms, the distance is 1.58 Å, the bond order is 0.91, and the two-center energy is -11.7 eV. The other atom pair of interest (the 1,7 pair) are 2.38 Å apart, with a bond order of 0.02 and a two-center energy of +0.29 eV.

The highest energy structure (6) has a calculated heat of formation of 103.43 and 119.46 kcal/mole from MNDO and AM1, respectively. This structure has a single bond across the 1,7 atom pair. Now the 1,7 distance is 1.62 Å, with a bond order of 0.88 and a two-center interaction energy of -10.8 eV, compared with the 3,5 distance of 2.43 Å, bond order of 0.01 and two-center energy of +0.32 eV.

In the case of elassovalene and its tautomers, 2x2 CI calculations failed to give results that differed significantly from the SCF results.

TABLE 3. ELASSOVALENE TAUTOMER (4).



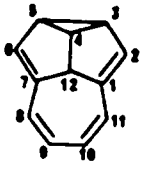
(4)

Atom Pair	1-2	2-3	1-11	10-11	9-10	1-7	3-5
				Distance (Å)			
MNDO	1.48	1.36	1.36	1.46	1.36	2.54	2.60
AM1	1.46	1.35	1.34	1.44	1.35	2.48	2.54
Exp[a]	1.46	1.34	1.39	1.43	1.39	2.40	2.54
Exp[b]	1.44	1.32	1.33	1.45	1.43	2.44	2.54
				Bond Order			
MNDO	1.02	1.88	1.80	1.05	1.81	0.02	0.01
AM1	1.03	1.87	1.78	1.07	1.79	0.03	0.01
				Two-center (eV)			
MNDO	-16.31	-23.44	-23.28	-16.89	-23.15	+0.28	+0.33
AM1	-15.69	-22.81	-22.54	-16.40	-22.40	+0.11	+0.29

a) X-ray structure of $Cr(CO)_3$ complex (Ref. 17).
b) X-ray structure of benzannelated compound (Ref. 18).

TABLE 4. ELASSOVALENE TAUTOMER (5)

151

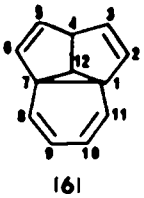


151

Atom Pair	1-2	2-3	1-11	10-11	9-10	1-7	3-5
				Distance (Å)			
MNDO	1.37	1.49	1.46	1.36	1.46	2.38	1.58
AM1	1.36	1.48	1.44	1.35	1.44	2.35	1.55
				Bond Order			
MNDO	1.84	1.01	1.02	1.84	1.04	0.02	0.91
AM1	1.81	1.02	1.04	1.82	1.06	0.02	0.90
				Two-center Energy (eV)			
MNDO	-23.12	-15.88	-16.75	-23.35	-16.86	+0.29	-11.72
AM1	-23.38	-15.34	-16.22	-22.65	-16.31	+0.10	-11.31

TABLE 5. ELASSOVALENE TAUTOMER (6)

161



161

Atom Pair	1-2	2-3	1-11	10-11	9-10	1-7	3-5
				Distance (Å)			
MNDO	1.50	1.36	1.48	1.36	1.46	1.62	2.43
AM1	1.49	1.35	1.46	1.35	1.44	1.58	2.39
				Bond Order			
MNDO	0.99	1.91	1.01	1.83	1.06	0.87	0.01
AM1	1.00	1.90	1.03	1.81	1.08	0.85	0.02
				Two-center Energy (eV)			
MNDO	-15.64	-23.60	-16.36	-23.24	-16.95	-10.85	+0.32
AM1	-15.06	-23.00	-15.86	-22.56	-16.37	-10.57	+0.23

Conclusions

There are three main conclusion to be drawn from the above results: 1) the two-center interaction energies are good indicators of nonbonded (homoaromatic) interactions, 2) as pointed out by Dewar and McKee[4], CI is necessary in many instances and, more importantly, also appears to be a good discriminator for the presence of cyclic conjugation (homoconjugation), and 3) the AM1 method seems to be better parameterized for the types of systems studied here, than MNDO. A fourth point to be noted is that the bond orders seem to be of no use as a discriminator of favorable interactions.

1) Two-Center Terms. In the case of the bridged [10]annulene (3), where the existence of a strong homoaromatic interaction is well accepted, the two-center terms from both the MNDO and AM1 (CI) results are negative -- indicating energy lowering interactions. For cycloheptatriene (2) and elassovalene (4), where

homoaromatic interactions are generally regarded to be of much less importance, the two-center terms are positive -- indicative of destabilization. Finally in the case of the bisannelated semibullvalene (1), where energy lowering (homoaromatic) interactions are assumed to force a symmetrical ground state, the two-center terms are negative once more indicative of stabilization. In the systems thus far studied for which the importance of homoaromatic interactions has been assigned by other means, the two-center energy partitioning terms reinforce these conclusions. We therefore suggest that these two-center terms be added to the armory of discriminators for homoaromatic interactions.

2) Configuration Interaction (CI). From the severe bond alternation observed in the MNDO calculations on several annulenes Dewar and McKee[4] concluded that MNDO did not fully account for the conjugation present. They suggested that CI may redress this imbalance and showed that the bond alternation was reduced and results more aligned with experiment were obtained using UMNDO. Another MNDO study, on semibullvalene[12], showed that results in agreement with experiment were only obtained if CI was included. We wish to extend this requirement of the inclusion of CI for accurate representation of cyclically conjugated systems to a diagnostic level. In all of our calculations the inclusion of CI only had a significant effect (on energy, two-center terms, and bond orders) when cyclic homoconjugation appeared to be important. Hence we suggest that his may be used as a further discriminator in the establishment of homoaromatic interactions.

3) AM1 vs. MNDO. An interesting sidelight of the calculations we have performed is the comparison of the MNDO and AM1 methods. From a comparison of the calculated bond distances with the experimental values in Tables 1-3, both methods do quite well -- with the AM1 results being slightly better. However, when looking at heats of formation data, only the AM1 method predicts the correct energy ordering for the 1,6-methano[10]annulene and its norcaradiene isomer. These calculations are also in excellent agreement with the *ab initio* 6-31G/MP2 results of Haddon and Raghavachari[2], which indicated a bond equalized ground state with the norcaradiene structure about 16 kcal/mole higher in energy. The AM1 energy difference is calculated to be 12 kcal/mole. Part of the differences in results may be explained by the overestimation of repulsion in the MNDO.

References

1. R. V. Williams and H. A. Kurtz, *J. Org. Chem.*, 1988, 53, xxx.
2. R. C. Haddon and K. Raghavachari, *J. Am. Chem. Soc.*, 1985, 107, 289.
3. K. B. Lipkowitz, D. A. Demeter, J. M. Landwer, C. A. Parish, and T. Darden, *J. Computation. Chem.*, 1988, 9, 63.
4. M. J. S. Dewar and M. L. McKee, *Pure and Appl. Chem.*, 1980, 52, 1431.
5. P. Ilic and N. Trinajstic, *Pure and Appl. Chem.*, 1980, 52, 1495.
6. K. Conrow, *J. Am. Chem. Soc.*, 1961, 83, 2958.
7. L. A. Paquette, *Angew. Chem. Int. Ed. Engl.*, 1978, 17, 106.
8. E. Vogel, U. H. Brinker, K. Nachtkamp, J. Wassen, and K. Mullen, *Angew. Chem. Int. Ed. Engl.*, 1973, 12, 758.
9. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, 99, 4907.
10. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, 107, 3902.
11. J. J. P. Stewart, *QCPE Program #455*, 1983, version 3.1 (1986).
12. L. S. Miller, K. Grohmann, and J. J. Dannenberg, *J. Am. Chem. Soc.*, 1983, 105, 6862.
13. D. R. Armstrong, R. Fortune, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc., Faraday 2*, 1972, 68, 1839.
14. M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, 1971, 93, 7201.
15. M. Traetteberg, *J. Am. Chem. Soc.*, 1964, 86, 4265.
16. R. Bianchi, T. Pilati, and M. Simonetta, *Acta Cryst.*, 1980, B36, 3146.
17. L. A. Paquette, C. C. Liao, R. L. Burson, R. E. Wingard Jr, C. N. Shih, J. Fayos, and J. Clardy, *J. Am. Chem. Soc.*, 1977, 99, 6935.
18. L. A. Paquette, T. G. Wallis, T. Kempe, G. G. Christoph, J. P. Springer, and J. Clardy, *J. Am. Chem. Soc.*, 1977, 99, 6946.