Tetrahedron Letters,Vol.24,No.39,pp 4169-4172,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

STRAIN ENERGIES OF SOME BRIDGEHEAD DIENES VIA MM2 CALCULATIONS

Philip Warner*
Iowa State University, Department of Chemistry, Ames, IA 50011

Stephen Peacock*
Molecular Design Ltd., Hayward, CA 94541

Abstract: Strain energy calculations (MM2) are reported for 36 bridged dienes; the relationship between strain energy and stability is discussed.

We recently reported[1] MM2[2] calculations on a series of bridgehead alkenes; these complemented similar calculations[3] using the MM1 force field.[4] Our interest in bridged dienes[5] has led us to perform MM2 calculations for a representative series of these compounds, which we now report.

Table I summarizes the data we have obtained. In addition to the calculated ΔH_f°'s and strain energies (SE), we list DS, defined as the difference in SE between a diene and its saturated counterpart (this is an extension of the OS concept[3]), and DS-OS, which is the difference in SE between a diene and the corresponding monoene (where there may be 2 such values if the diene has non-equivalent double bonds). This latter value is a measure of the incremental strain necessary to introduce a second bridgehead double bond into a bridgehead alkene. The last column of Table I lists the ring size in which each double bond is transoid.[6] Table II shows the structure and conformation for each diene calculated.

The most generally reliable structural statement about bridgehead alkenes is that the olefinic strain energy (and, hence, instability) increases as the size of the ring in which the double bond is transoid decreases.[6] Fig. I pictorially represents the relationship between dienic strain (DS) and transoid double bond ring sizes. In general, the strain does increase with smaller ring size, but there are quite a few cases where this is not true. In fact, one of the trans-9,9 dienes (**36**) has more dienic strain than half the trans-8,8 dienes, and a larger strain increment (DS-OS) than all but 2 of the dienes calculated. This somewhat exceptional case (**36**) is a bicyclo[6.1.1]decadiene; all the bicyclo[n.1.1]alkadienes (**2**, **19**, **20**, **35**, **36**) have rather high DS values. Models clearly show that it is rather difficult to bridge a 1,3-dimethylenecyclobutane without very large distortions of the π-bonds.

In earlier work on monoenes,[1,3] an OS value of ca. 17 kcal/mole was deemed to be the maximum allowable value for an isolatable species. What should the corresponding value be for dienes? The 2 known dienes which we have calculated (**15**, **23**) are shown in heavy type in Table I. Compound **23**,[5b] which is stable at room temperature and considerably above, has a DS value well below 17 kcal/mole. Contrariwise, **15**,[7] which undergoes Cope rearrangement slowly at 25°C, has a DS value (and also DS-OS value) considerably above 17 kcal/mole. The dashed horizontal lines in Figure I correspond to the strain level of **23**. Dienes below the dashed line should be stable, while those above may not be. This issue needs to be addressed by future experiment.

Dienes exhibit greater complexity than monoenes partly because, in appropriate cases, they may be parallel or perpendicular to each other. A simple case, trans, trans-1,5-cyclooctadiene,

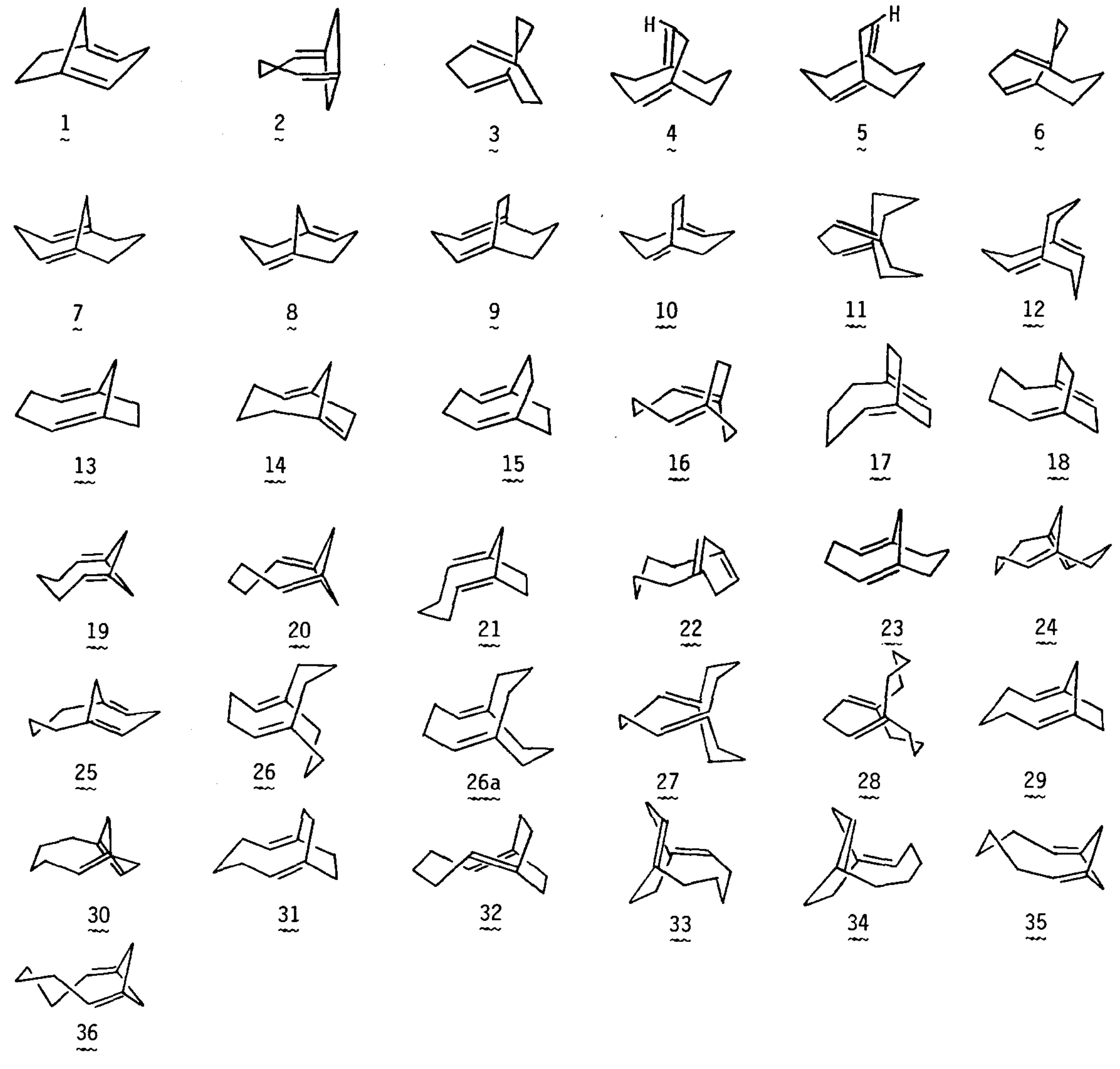
Table I. Calculated energies (kcal/mol) for dienes

Compound	ΔH_f°	strain energy (SE)	DS[a]	DS-OS[b]	ring sizes of trans double bonds[c]
bicyclo[3.2.1]octa-1,4-diene (Z,Z) (1)	88.87	74.72	60.7	32.0	7,7
bicyclo[4.1.1]octa-1,5-diene (DL) (2)	108.93	94.78	60.7	28.4	7,7
bicyclo[3.2.2]nona-1,4-diene (DL) (3)	90.66	82.26	64.0	42.2	7,7
bicyclo[3.3.2]deca-1,5(10)-diene (Z,E) (4)	66.42	63.78	37.7	20.2,32.9	7,8
bicyclo[3.3.2]deca-1,5(10)-diene (Z,Z) (5)	66.44	63.80	37.7	20.2,32.9	7,8
bicyclo[3.3.2]deca-1,4-diene (Z,E) (6)	69.77	67.13	41.0	7.0,36.2	7,8
bicyclo[3.3.1]nona-1,4-diene (Z,Z) (7)	56.74	48.34	36.0	19.9	8,8
bicyclo[3.3.1]nona-1,5-diene (Z,Z) (8)	57.25	48.85	36.6	20.5	8,8
bicyclo[3.3.2]deca-1,4-diene (Z,Z) (9)	57.18	54.54	28.4	23.6	8,8
bicyclo[3.3.2]deca-1,5-diene (Z,Z) (10)	49.65	47.01	20.9	16.1	8,8
bicyclo[3.3.3]undeca-1,4-diene (DL) (11)	47.69	50.81	20.8	12.5	8,8
bicyclo[3.3.3]undeca-1,5-diene (Z,E) (12)	48.92	52.03	22.0	13.7	8,8
bicyclo[4.2.1]nona-1,5-diene (Z,Z) (13)	63.67	55.27	36.9	19.6	8,8
bicyclo[4.2.1]nona-1,6-diene (Z,Z) (14)	61.13	52.73	34.3	18.1,23.3	8,8
bicyclo[4.2.2]deca-1,5-diene (meso) (15)	**56.03**	**53.39**	**28.5**	**19.2**	**8,8**
bicyclo[4.2.2]deca-1,5-diene (DL) (16)	61.33	58.69	33.8	24.5	8,8
bicyclo[4.2.2]deca-1,6-diene (Z,Z) (17)	59.91	57.27	32.4	23.1,25.0	8,8
bicyclo[4.2.2]deca-1,6-diene (E,Z) (18)	57.74	55.10	30.2	20.9,22.8	8,8
bicyclo[5.1.1]nona-1,6-diene (meso) (19)	87.54	79.15	38.4	22.5	8,8
bicyclo[5.1.1]nona-1,6-diene (DL) (20)	97.92	89.52	48.7	32.8	8,8
bicyclo[5.2.1]deca-1,6-diene (E,E) (21)	62.23	59.59	34.2	22.7	8,8
bicyclo[5.2.1]deca-1(9),7(10)-diene (Z,Z) (22)	83.05	56.77	31.4	27.6,29.8	8,9
bicyclo[4.3.1]deca-1,5-diene (Z,Z) (23)	**33.81**	**31.17**	**12.8**	**9.4**	**9,9**
bicyclo[4.3.1]deca-1,6-diene (Z,Z) (24)	33.45	30.81	12.4	9.0,9.2	9,9
bicyclo[4.3.1]deca-1(9),6-diene (Z,Z) (25)	36.95	34.31	15.9	12.7	9,9
bicyclo[4.3.3]dodeca-1,5-diene (meso) (26)	23.67	32.54	-8.2	-4.0	9,9
(26a)	25.45	34.33	-6.4	-2.2	9,9
bicyclo[4.3.3]dodeca-1,5-diene (DL) (27)	23.61	32.49	-8.3	-4.1	9,9
bicyclo[4.4.3]triadeca-1(11),6(13)diene(DL) (28)	23.46	38.10	----	-7.1[d]	9,9
bicyclo[5.2.1]deca-1,6-diene (Z,Z) (29)	40.53	37.89	12.5	10.5	9,9
bicyclo[5.2.1]deca-1,7-diene (Z,Z) (30)	44.28	41.65	16.3	14.3,14.7	9,9
bicyclo[5.2.2]undeca-1,6-diene (meso) (31)	32.26	35.38	3.4	5.9	9,9
bicyclo[5.2.2]undeca-1,6-diene (DL) (32)	39.18	42.30	10.3	12.8	9,9
bicyclo[5.2.2]undeca-1,7-diene (E,Z) (33)	39.34	42.46	10.5	13.0,-	9,9
bicyclo[5.2.2]undeca-1,7-diene (Z,Z) (34)	41.28	44.40	12.4	14.9,-	9,9
bicyclo[6.1.1]deca-1,7-diene (meso) (35)	75.65	73.01	26.4	25.6	9,9
bicyclo[6.1.1]deca-1,7-diene (DL) (36)	82.07	79.43	32.8	32.0	9,9
cyclohexa-1,4-diene (37)	26.13	3.27	0.7[e]	0.9[e]	----

[a] DS is "Diene Strain" = SE (Diene)-SE (corresponding alkane); the calculated strain energies of the appropriate saturated hydrocarbons are given in ref. 1; [b] DS-OS (olefinic strain[3]) has 2 values where the diene double bonds are not equivalent; the OS values are from ref. 1; [c] *i.e.*, size of ring in which each of the double bonds is transoid; [d] in this case DS has not been determined because the saturated alkane failed to energy minimize in the usual fashion; however, bicyclo[4.4.3]triadec-1(11)-ene did minimize, thereby affording a DS-OS value; [e] the MM2 strain energies for cyclohexane and cyclohexene were 2.61 kcal/mole and 2.35 kcal/mole, respectively.

is thought to adopt the perpendicular (DL or racemic) conformation.[8] What are interconvertible conformers in monocyclic dienes become stable configurational isomers in bridgehead dienes. As an example, it is seen that the parallel arrangement gains stability over the perpendicular one in the bicyclo[4.2.2] (15 *vs.* 16) and bicyclo[5.2.2] (31 *vs.* 32) systems. However, all attempts to calculate a meso(parallel) isomer of 3 resulted in the MM2 program finding only 3 as the

Table II. Structures and conformations calculated.[a]

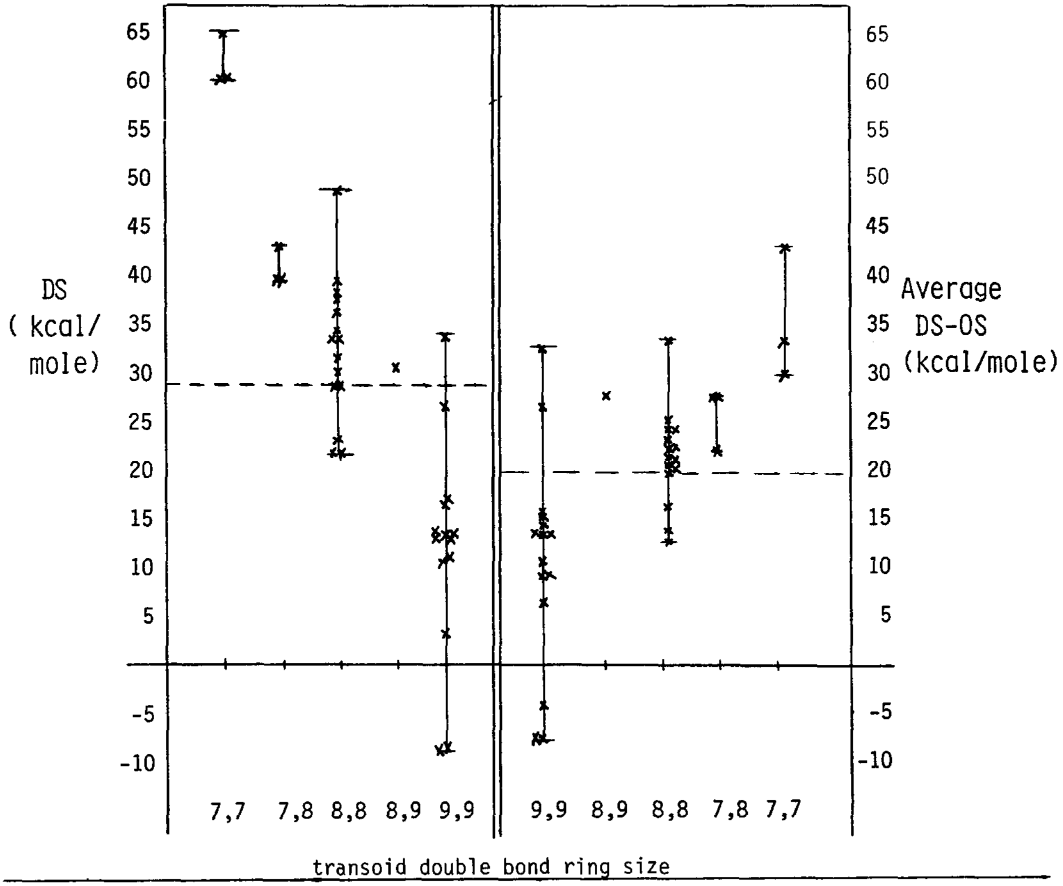


[a] The drawings are schematic rather than exact and are meant to represent the general conformations found to be minima. The exact structures calculated are available on request, addressed to Steve Peacock at Molecular Design, Ltd.

calculated minimum. Similarly, a minimum for the meso isomer of 11 could not be found. After the fact model examination showed that it is extremely difficult to bridge meso-*trans*, *trans*-1,4-cyclooctadiene. Additionally, calculations were made on the (Z,Z) and (E,E) configurational isomers of 12 (Z,E), but these apparently did not find the correct minimum. Nevertheless, the (Z,Z) isomer will clearly be the least stable of the three, with the (E,E) near, or possibly above the (Z,E) isomer [due to methylene-methylene repulsions in (E,E)].

Lastly, it should be noted that 22 is a conjugated diene; such systems are often rejected by the MM2 program. Our version, however, was rather whimsical in this regard--it even provided a SE

Figure I. Diagram of the relationship between transoid double bond ring size and strain energies (DS along left hand ordinate, average (DS-OS) along right-hand ordinate).



for cyclohexa-1,3-diene. We feel that any MM2-generated conjugated diene values should be viewed cautiously; we are reinvestigating such systems with the newer MM2-PI program.

References and Notes

1. P. M. Warner and S. Peacock, J. Comp. Chem., **3**, 417 (1982).
2. N. L. Allinger, J. Am. Chem. Soc., **99**, 8127 (1977).
3. W. F. Maier and P. Schleyer, ibid., **103**, 1891 (1981).
4. N. L. Allinger, Adv. Phys. Org. Chem., **13**, 1 (1976).
5. (a) P. Warner and W. Boulanger, Tetrahedron Lett., 123, (1980); (b) P. Warner, I.-S. Chu and W. Boulanger, accompanying paper.
6. J. R. Wiseman and W. A. Pletcher, J. Am. Chem. Soc., **92**, 956 (1970).
7. J. R. Wiseman and J. J. Vanderbilt, ibid., **100**, 7730 (1978).
8. (a) G. M. Whitesides, G. L. Goe, and A. C. Cope, ibid., **91**, 2608 (1969); (b) N. L. Allinger and J. T. Sprague, ibid., **94**, 5734 (1972).

(Received in USA 21 April 1983)