Dynamic Properties of Bicyclic Compounds related to Sesquinorbornene. A Computational Study

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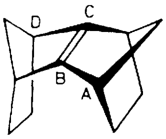
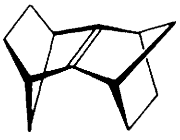
Empirical force field calculations for several bicyclic compounds related to sesquinorbornene reveal that the ground state structures are bent at the double bond, and that the diastereoisomerization or topomerization barriers may be as high as 6.2 kcal mol^{-1} (25.9 kJ mol^{-1}).

Extensive bending (16—18°) about carbon–carbon double bonds has been observed in *syn*-sesquinorbornene derivatives,[1] a class of polycyclic compounds in which the rings containing the double bond are not rigidly constrained.[‡] Hinge-like bending motions about the double bond are therefore a possibility for this class of compounds, and may lead to observable dynamic processes.[§] This paper describes a computational study of this process for *syn*-sesquinorbornene (1), *anti*-sesquinorbornene (2), and for two related but as yet unknown compounds, tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-2-ene (3), and tetracyclo[5.1.1.1^{3,5}.0^{2,6}]deca-2-ene (4), using the empirical force field (EFF) approach.

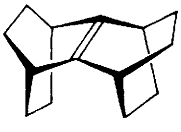
EFF calculations were carried out using the force field from Allinger's MM2 program[4] with steepest descent and full matrix Newton–Raphson geometry optimization as implemented by the program BIGSTRN-3.[5] The atomic co-ordinates of the *syn*-sesquinorbornene frame of 2-*exo*-(phenylsulphonyl)-*syn*-sesquinorbornene[1a] were used for the input geometry of (1). Full geometry optimization gave a ground state structure (**1a**) with exact C_{2v} symmetry, and with an 18° bend about the double bond. This and other structural parameters are in agreement with the corresponding *X*-ray values.[1a] Two other stationary points, both also with exact C_{2v} symmetry, were located using (**1a**) as the input geometry and changing the dihedral angle ($\phi = C_A\text{–}C_B\text{–}C_C\text{–}C_D$; see Table 1). One of these is a minimum (**1b**) 2.9 kcal mol^{-1} (1 cal = 4.184 J) above the ground state, and corresponds to a structure which is bent 35° in the opposite direction from planarity. The third stationary point corresponds to a transition state (**1c**) which separates the two minima and lies 4.2 kcal mol^{-1} above the ground state.[6] The transition state structure is bent 14° from planarity. These results suggest that a diastereoisomerization process is unlikely to be observed for *syn*-sesquinorbornene because <1% of the minor diastereoisomer is expected to be present at room temperature.



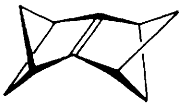
(1)



(2)



(3)



(4)

However, if the nonsymmetric double-well potential in (1) were converted into a symmetric potential, dynamic bending about the double bond would correspond to a potentially observable topomerization process. Such is the case for (2), (3), and (4). The atomic co-ordinates of the *anti*-sesquinorbornene frame of *anti-endo*-sesquinorbornene anhydride[1a] were used for the input geometry of (2). Full geometry optimization gave a ground state structure (**2a**) with exact C_s symmetry, and bent 27° about the double bond. A transition state structure (**2b**), C_{2h} symmetry, lies 1.7 kcal mol^{-1} above the ground state (see Table 1). The large angle of bend about the double bond calculated for (2) is in contrast to the 3° bend found by *X*-ray diffraction for the anhydride of (2). A partial explanation may be that (2) has a weak bending force constant (as suggested by the low topomerization barrier) and that packing forces are responsible for the small angle of bend observed in the crystal.

Addition of one methylene group to each of the two $-CH_2-$ bridges results in the hypothetical compound (3). EFF calculations on (3) were performed by inputting structures having either exact C_{2v} or exact D_{2h} symmetry. The ground state structure (**3a**) was found to have exact C_{2v} symmetry and to be bent 7° about the double bond. A planar transition state structure (**3b**) of exact D_{2h} symmetry was found to lie 0.1 kcal mol^{-1} above the ground state (see Table 1). Thus a topomerization process is unlikely to be observed for (2) or (3). In addition, it is predicted that the structure of (3) is likely to be nearly or exactly planar.

However, if one methylene group is removed from each of the two $-CH_2CH_2-$ bridges, the hypothetical compound (4) results. EFF calculations for (4) were performed as for (3). The ground state structure (**4a**) was found to have exact C_{2v} symmetry and to be bent 35° about the double bond, as in (**1b**). A planar transition state (**4b**) of exact D_{2h} symmetry was found to lie 6.2 kcal mol^{-1} above the ground state (see Table 1). Therefore, inversion of the pyramidalized olefinic carbon

Table 1

Conformer	ϕ/°	Relative steric energy/kcal mol^{-1}
(**1a**)	162.2	0.0
(**1b**)	−144.8	2.9
(**1c**)	−166.3	4.2
(**2a**)	152.7	0.0
(**2b**)	180.0	1.7
(**3a**)	172.5	0.0
(**3b**)	180.0	0.1
(**4a**)	145.4	0.0
(**4b**)	180.0	6.2

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[‡] As they are, for example, in 9,9′,10,10′-tetradehydrodianthracene ref. 2a, 9,10-benzotricyclo[3.3.2.0^{3,7}]deca-3(7),9(10)-diene, ref. 2b, or in *syn*-13,14′,15,16-dibenzotricyclo[6.4.2.2^{2,7}]hexadeca-1,3,5,7,9,11,13,15-octaene (ref. 2c).

[§] A similar prediction was made for the hypothetical molecule bicyclobutene. For this molecule, the planar conformation was calculated to be higher in energy than the bent ground state structure (ref. 3).

atoms, which corresponds to hinge-like bending about the double bond, might be observable for (**4**) on the n.m.r. time-scale.

It is of interest that the transition states for diastereoisomerization, as for (**1**), or topomerization, as for (**2**), (**3**), and (**4**), do not result from twisting about the double bond,¶ but instead result only from bending. These EFF calculations do not point to the source of the energy difference between the two conformations for (**4**); however the short (1.987 Å) non-bonded H–H distance (between methylenes in different cyclobutane rings) for (**4a**) suggests an attractive interaction that stabilizes the bent structure relative to the planar structure.[7] Clearly, the phenomenon of dynamic bending which appears to be general for this class of fused bicyclic compounds warrants additional investigation.

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5 R. B. Nachbar, Jr., and K. Mislow, unpublished work. This program is being prepared for submission to QCPE. A listing is available upon request. In the full matrix Newton–Raphson optimization, all the elements of the $3N \times 3N$ second derivatives matrix are used. Also, all the atoms are moved simultaneously, and symmetry is thus conserved. The signs of the eigen-values of the second derivatives matrix are used to determine whether the structure corresponds to a minimum or maximum on the potential energy surface.

6 This is in contrast to Extended Huckel calculations for (**1**). See: R. Gleiter and J. Spanget-Larsen, *Tetrahedron Lett.*, 1982, **23**, 927.

7 For a related molecule with short H–H distances, see O. Ermer and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1983, **53**.

¶ Examination of the eigenvalues of the second derivatives matrix indicates that twisting is a much lower energy process.