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BOND LENGTH CALCULATIONS FOR NORBORNANE, BICYCLO[2.2.2]OCTANE, AND RELATED OLEFINS USING A CONSISTENT FORCE FIELD. INFLUENCE OF STRETCH–BEND CROSSTERMS

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Abstract—It is shown that a valence force field CCC stretch-bend crossterm which is consistent in sign and magnitude with vibrational spectroscopic calculations leads to bond stretchings in norbornane, norbornenes, and bicyclo[2.2.2]octenes. The bond length effects are in satisfactory agreement with most of the available experimental results and have not been obtained by earlier force field calculations.

Most experimental structural studies of norbornane[1] (**1**), norbornadiene[1a,1b,2] (**3**), bicyclo[2.2.2]-octane[3] (**4**), bicyclo[2.2.2]octene[4] (**5**), and bicyclo[2.2.2]octadiene[4] (**6**) yield abnormally long CC bond distances if the adjacent CCC bond angles are abnormally small. In some cases however the experimental data were interpreted in terms of normal CC bond lengths, and the results of different workers differ appreciably. For instance in the case of norbornadiene the extreme C(1)–C(7) bond lengths reported are 1·514 Å[2a] and 1·573 Å.[1b] A number of published strain calculations [1a,3-5] did not give bond stretchings in the above systems. The purpose of the present communication is to show that calculations using a consistent force field (CFF) the force constants of which are derived not only from structural and thermochemical but also from vibrational data lead to appreciable bond stretchings. The force field for the present calculations was derived for nonconjugated olefins and saturated hydrocarbons, and has been described previously.[6]

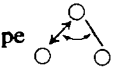
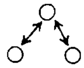
The abnormally long calculated bond lengths in the bicyclic compounds discussed here are a consequence of exceptionally short 1,3-C . . . C distances and corresponding strong 1,3-repulsions.[5a,5c] These short 1,3-distances are connected with unusually small CCC angles which have their ultimate origin in geometric constraints of the small bicyclic compounds **1**–**7**. (It is, for instance, evident that a planar 5-membered ring cannot accommodate a double bond with favourable CCC angles simultaneously at all C atoms since the average of these angles must be 108°. In case of nonplanar 5-membered rings as occurring in the norbornane skeleton even higher angle strain is inevitable when introducing double bonds.) 1,3-interactions are usually formulated either in terms of 1,3-distances (Urey-Bradley force field, UBFF), or as stretch–bend and stretch–stretch crossterms of the type  ($F_{R\omega}$ for CCC and $F_{R\gamma}$ for CCH) and  (F_{RR} for CCC), respectively (valence force field, VFF). Both formulations are essentially equivalent.[7] Our force field is a modified VFF including important bilinear crossterms.[6] The potential constants were determined by a least-squares procedure so as to fit optimally a large set of experimental vibrational, structural, and thermochemical molecular properties. These constants are not always equally influenced by all three different types of experimental quantities. The stretch–bend crossterm $F_{R\omega}$, for instance, which is discussed here, was mainly ($F_{R\gamma}$ almost entirely) determined by the vibrational frequencies incorporated into the least-squares process. The contribution of the frequencies to the respective diagonal element of the least-squares matrix was about 8 times higher than the contribution of the structural and thermochemical data. It is shown subsequently that $F_{R\omega}$ has a severe effect on calculated bond lengths in systems with high angle strain. Being smaller than $F_{R\omega}$ and of the same sign the influence of $F_{R\gamma}$ is less severe and opposite to that of $F_{R\omega}$ since on the average opening of a CCC angle is accompanied by closing of adjacent CCH angles. The present study thus provides a good illustration of the CFF concept which attempts to make use of the interplay of vibrational, structural, and thermochemical effects when determining force field parameters. The stretch–bend crossterms would have been poorly defined constants had the vibrational frequencies been omitted from the least-squares process since no sensitive geometrical data were incorporated. (In particular, no experimental data of the systems discussed here were considered.) The inclusion of the frequencies lead to well defined stretch–bend crossterms which can be used for more reliable geometry calculations of systems such as **1–7** where these terms lead to significant effects.

Fig 1 summarises the results of our calculations. The top values for the bond lengths and the bond angles were calculated using the full CFF as described earlier,[6] the second values resulted from energy minimisations after removing $F_{R\omega}$ from this CFF, and the third values were obtained after minimising without $F_{R\omega}$ *and* $F_{R\gamma}$. The opposite effects of $F_{R\omega}$ and $F_{R\gamma}$, and the dominating influence of $F_{R\omega}$ are evident. The lower quantities are the result of gas phase electron diffraction studies of Kuchitsu *et al*[1a,3,4] which we believe to be the most reliable structural investigations available for these systems. The calculated CCC angles do not depend very much on the stretch–bend crossterms and change at most by 1·0° when excluding these terms. Therefore in Fig 1 only the CCC angles calculated with the full force field (top) and the experimental angles (bottom) are given. Below the molecular diagrams the minimum energy contributions are given which change most significantly when omitting both $F_{R\omega}$ *and* $F_{R\gamma}$. (In kcal mole^{-1}; ΔV_{tot} is the difference of the total energies after minimisations including and omitting $F_{R\omega}$ *and* $F_{R\gamma}$, respectively. No vibrational contributions are considered since they don't enter the energy minimisation.) A few details of the energy minimisations are discussed in the appendix.

The bond stretching effects of $F_{R\omega}$ are clearly evident from Fig 1. They are most pronounced the smaller the adjacent CCC angles. Fig 2 shows this quantitatively with a plot of the bond length changes in **1–7** on omission of $F_{R\omega}$ from the force field *vs* the sums of the differences of the CCC angles adjacent to the bond considered from their reference values. The points for single and double bonds lie approximately on straight lines through the origin. If one considers $F_{R\omega}$ as mainly responsible

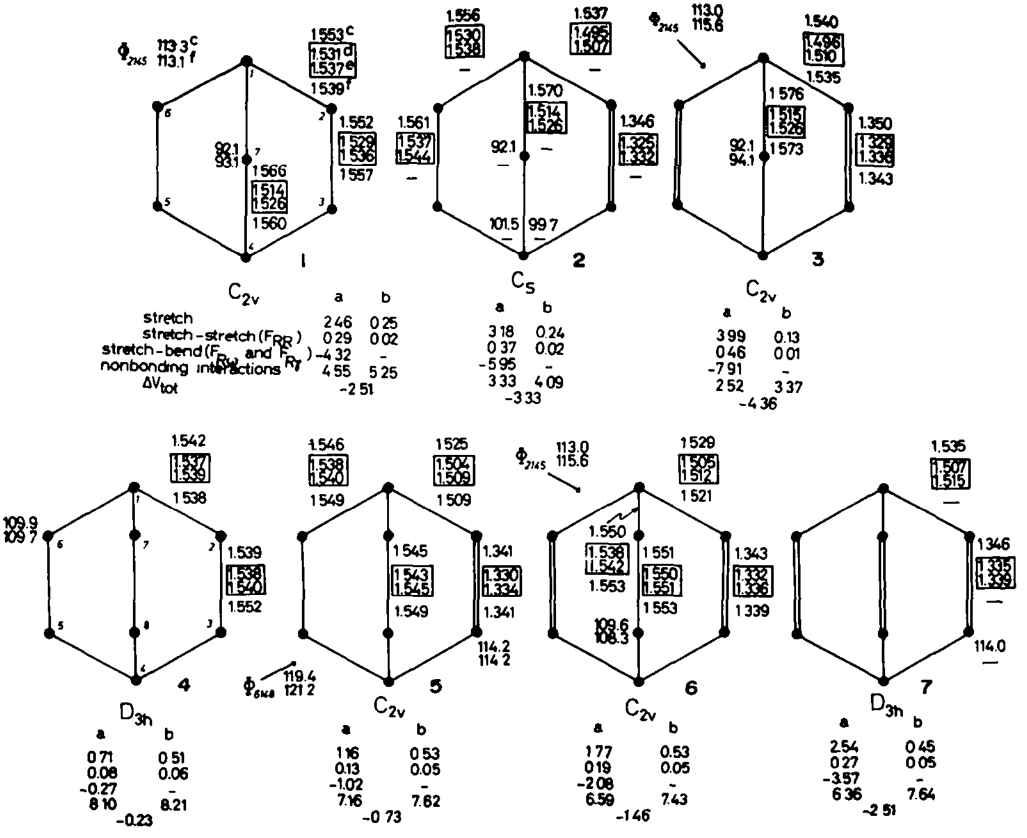


Fig 1. Molecular geometries (Å, degrees) and strain energy contributions (kcal mole^{-1}; a: with, b: without stretch-bend terms). The meaning of the geometry parameters is: ^{c}calculated; ^{d}calculated, excluding $F_{R\omega}$ from the force field; ^{e}calculated, excluding $F_{R\omega}$ *and* $F_{R\gamma}$ from the force field; ^{f}experimental. Superscripts and energy descriptions are given only for molecule **1** and hold accordingly for the other systems. The Φ-values correspond to Kuchitsu's θ-values and are formulated here as "improper" torsion angles. (Φ_{abcd} denotes a dihedral angle between the two planes defined by the positions of atoms *a*, *b*, *c* and *b*, *c*, *d*, respectively). See text for further details.

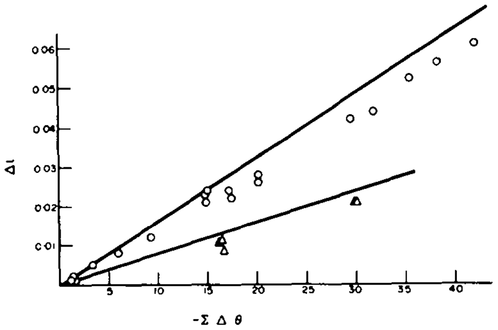


Fig 2. Calculated bond stretching effect of $F_{R\omega}$ for the symmetry independent CC bond lengths of **1–7**. Δl: bond length differences between energy minimisations including and excluding $F_{R\omega}$, respectively; $\Sigma\Delta\theta$: sum of deviations of the CCC bond angles adjacent to the bond considered from their reference values (C—C—C 110·5, C—C=C 122·3°). ○: single bonds, △: double bonds. The significance of the straight lines is explained in the text.

for the bond stretching effects in **1–7** it can be shown that an estimate for the slopes of these straight lines is $-F_{R\omega}/K_R$ (= − 0·00163 Å deg^{-1}) for single bonds and $-F_{R\omega}/K_D$ (= − 0·000803) for double bonds. (K_R and K_D are the bond stretching constants for single and double bonds, respectively.) The straight lines corresponding to these slopes are included in Fig 2.

Our value for $F_{R\omega}$ is + 60·2 kcal mole^{-1} rad^{-2},[6] well compatible with a value of 60·9 derived by Califano *et al*[8] from vibrational spectra for cyclohexene. Evidently only a positive crossterm of this type supports bond stretching energetically when closing adjacent bond angles to values below the respective reference angles. In the calculations of Allinger *et al*[5b,5d] the stretched CC bonds in **1**, **2** and **3** result almost normal. This is probably due to the fact that these workers used a value for $F_{R\omega}$ much smaller than ours (absolute value 13·0 kcal mole^{-1} rad^{-2}) which in addition was given a negative sign in case of the olefins. The recent calculations of Schleyer *et al*[5a] also did not give bond stretchings in norbornane due to the neglect of 1,3-interaction terms. The energetic reason for the calculated bond stretchings is seen from Fig 1. The loss of bend–stretch energy and the increase of nonbonded repulsions when omitting $F_{R\omega}$ and $F_{R\gamma}$ cannot be compensated by the gain of stretch and stretch–stretch energy. Finally it should be noted that the CC single bond lengths in barrelene (**7**) might be even longer in reality than calculated by us since the electronic repulsions of the double bonds in this system[9] are not represented in our CFF.

APPENDIX

The potential energies V of **1–7** were minimised by a steepest descent technique followed by a quadratically convergent Newton-Raphson procedure.[6] The molecular symmetries given in Fig 1 correspond to true minima as verified from the eigenvalues of the matrix of second derivatives **F** ($F_{ij} = \partial^2 V/\partial x_i \partial x_j$; x_i: Cartesian coordinates): The nontranslational and nonrotational eigenvalues at the energy minimum are all positive and nonzero in all cases. The errors in the minimum energies and geometries due to incomplete convergence of the minimisations are negligible. (They are less than 10^{-7} kcal mole^{-1} for energies, and less than 10^{-3} degrees for torsion angles, which are very sensitive indicators of geometry and symmetry changes.)

The potential describing the twisted (around the threefold axis) D_3-structures of bicyclo[2.2.2]octane (**4**) is known to be very shallow along the twisting coordinate.[3,10] With our force field we derive a shallow one-minimum twisting potential corresponding to a molecular D_{3h}-symmetry. (This was verified in this case not only by analysis of the eigenvalues but also by a minimisation starting from a highly twisted D_3-geometry.) The frequency of the twisting mode of **4** (symmetry A_1'') is calculated to be 58 cm^{-1} (harmonic approximation). (All vibrational frequencies of **1–7** were calculated and are available on request.)

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