Conformational Analyses of Some *trans*-2-Decalones

By WOLFGANG SCHUBERT and LOTHAR SCHÄFER*
(*Department of Chemistry, University of Arkansas, Fayetteville, Arkansas* 72701)
and G. H. PAULI
(*Department of Chemistry, Lafayette College, Easton, Pennsylvania* 18042)

Summary For a series of substituted *trans*-2-decalones the ground state energies of their minimum energy conformations and the structural effects of steric strain on fused rings are described as evaluated on the basis of molecular mechanics calculations.

WE report the results of a conformational analysis of *trans*-2-decalone (I), 10-methyl-*trans*-2-decalone (II), 1,1-dimethyl-*trans*-2-decalone (III), and 1,1,10-trimethyl-*trans*-2-decalone (IV). This project was initiated to study the effects of increasing sterical strain exerted on a fused-ring system by an increasing number of methyl substituents. At the same time these investigations are intended to help guide future interpretation of the electron diffraction data of these molecules[1] and to continue a series of combined vibrational, conformational, and electron diffraction studies of cyclic systems.[2] These compounds can only alleviate sterical strain by flattening their rings, or by converting them into a flexible form; and the situation is very similar to that found in some keto-steroids.[3] So, our conformational energy calculations were intended to discover to what extent must the chairs of compounds (I)—(IV) be expected to be flattened, and which of these compounds, if any, can be expected to exist in a flexible form.

The calculations were executed using our conformational energy program.[2,4] This program uses internal co-ordinates as a trial input set to construct the geometry of a molecule; and the parameters are optimized by a second-order Taylor expansion of the energy function. The force field applied in this study is that by Lifson and Warshel.[5] It includes bond stretching, angle bending, torsional strain, and non-bonded interactions. Since this field does not contain terms involving a carbonyl group, the C·C(=O)·C group was kept as a planar unit; and the oxygen was treated like a carbon atom in evaluating its non-bonded interactions. This represents a slight deviation from the design of this force field.[5] It should not introduce any serious errors, however, since all investigated systems do not contain more than one C=O group; and the application of this thoughtfully justified field should be preferable over the use of any other which may include C = O interactions but is less consistent otherwise. All parameters were allowed to change simultaneously during the optimization process.

TABLE 1. Conformational energies (kcal/mol) for the minimum energy chair–chair (ch–ch); chair–boat (ch–bt); boat–chair (bt–ch); and boat–boat forms (bt–bt) for molecules (I)—(IV) calculated using the force field by Lifson and Warshel.[5] Numbers without parentheses refer to the chair–chair form of each conformation as zero point. Numbers in parentheses refer to the chair–chair form of (I) as energy zero point.

	ch–ch	ch–bt	bt–ch	bt–bt
(I)	0·0	8·5	8·3	17·0
(II)	0·0	8·2	7·9	16·7
	(5·2)	(13·4)	(13·1)	(21·9)
(III)	0·0	8·8	7·3	15·2
	(9·4)	(18·2)	(16·7)	(24·6)
(IV)	0·0	8·1	4·9	13·6
	(17·7)	(25·8)	(22·6)	(31·3)

TABLE 2. Torsional angles (degrees) for the minimum energy chair–chair forms of compounds (I)—(IV) calculated using the Lifson and Warshel[5] force field.

	(I)	(II)	(III)	(IV)
(C)1–(C)9–(C)10–(C)4 ..	59·0	59·3	56·9	52·9
9–10–4–3	−58·7	−57·2	−58·0	−56·4
10–4–3–2	55·3	53·6	56·9	58·3
1–9–10–5	180·3	176·7	177·1	169·1
9–10–5–6	58·0	56·6	58·0	59·0
10–5–6–7	−57·1	−55·5	−57·1	−56·1
5–6–7–8	56·2	54·2	56·7	53·7
Average deviation from normal torsion	2·3	3·8	2·8	4·9

For each molecule the ground-state energies of four local conformational energy minima were investigated. One in which both rings are in the chair conformation (chair-chair form, henceforth); one in which the cyclohexanone ring (A-ring) is in the chair, and the cyclohexane ring (B-ring) is in the flexible form (chair-boat form, henceforth); one with the A-ring in the flexible and the B-ring in the chair conformation (boat-chair form); and one with both rings in the flexible form (boat-boat form). The final energies obtained by our calculations are listed in Table 1. To give an impression of the geometrical differences of systems (I)—(IV), we also list the independent torsional parameters of all chair–chair forms (Table 2) which best reflect the changing sterical strain. Numbering of atoms follows standard procedures, with atoms 9 and 10 as the bridge-carbon atoms.

The increasing sterical pressure caused by increasing substitution is well reflected by the conformational ground state energies of compounds (I)—(IV). If one compares a specific type of conformation, there is an energy difference of about 14—17 kcal/mol between (I) and (IV).

Ring A is the centre of stereochemical changes. Consequently it takes 8·3 kcal/mol in (I) to convert ring A into the flexible form; it takes considerably less (4·9 kcal/mol) to convert A in the trimethyl compound (IV). Similarly, the boat–boat forms are 17·0 (in I) and only 13·6 kcal/mol (in IV) less stable than the corresponding chair–chair forms. In contrast, the energy to convert ring B into the flexible form is nearly constant (about 8 kcal/mol) in all the compounds investigated.

An interesting trend is also observed by comparing the chair–chair forms of (I)—(IV). For these conformations it takes 5·2 kcal/mol to introduce the axial 10-methyl group [(II) compared to (I)]; less than twice that much [9·4 kcal/mol, (III) compared to (I)] is needed for two methyl groups in the 1-position; but more than three times that much (17·7 kcal/mole) is required to introduce the three methyl groups in the 1-, 1-, and 10-positions. These numbers reflect very well the more modest requirements of the equatorial methyl in (III) and the additional strain from diaxial repulsions in (IV). Such repulsions may also explain the fact that (IV) shows the largest deviation of its independent torsions from a normal torsion (60° or 180°). As is seen from Table 2, this deviation is 4·9° in (IV), compared to 3·8° in (II), 2·8° in (III), and 2·3° in (I). Parallel to this the connection of rings A and B [torsion angle C(1)–C(9)–C(10)–C(5)] changes from 180° in (I) to about 169° in (IV). It is also seen from Table 2 that distortions caused by substituents in ring A also have some impact on the geometry of B.

As far as flexible forms are concerned it seems that all four compounds can be expected to exist purely in the chair–chair conformation. However, for large systems, the applied field may somewhat overestimate energy differences.[2] So, if one allows for relatively large error limits, and if one takes into account the entropy term supporting the flexible forms, then it is not impossible to expect 1,1,10-trimethyl-*trans*-2-decalone to exist to a minor extent in the flexible form at about 110 °C, the temperature of the electron diffraction study.[1]

The authors thank the Dreyfus Foundation for support and the University of Arkansas Computing Centre for executing the calculations.

(*Received*, 13*th August* 1973; *Com.* 1161.)

---

[1] Electron diffraction data for molecules (I)—(IV) taken by G. H. Pauli at Indiana University.
[2] W. Schubert, J. F. Southern, and L. Schäfer, *J. Mol. Structure*, 1973, **16**, 403.
[3] N. L. Allinger, J. Allinger, and M. A. DaRooge, *J. Amer. Chem. Soc.*, 1964, **86**, 4061.
[4] W. Schubert, Thesis, University of Arkansas, 1973.
[5] S. Lifson and A. Warshel, *J. Chem. Phys.*, 1968, **49**, 5116.