Tetrahedron Vol. 45, No. 23, pp. 7405 to 7410, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00
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ITERATIVE FORCE-FIELD CALCULATIONS OF CYCLODECANONE

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(*Received in UK* 1 *September* 1989)

Abstract: Iterative force-field calculations have been carried out on conformations and conformational processes of cyclodecanone(**1**). Twentyseven possible conformations of **1** were considered and the lowest energy conformation is calculated to be the [3232]-2-one.

Owing to their unusual reactivities[1] and excessive strain[2] medium-ring ketones have been the subject of extensive experimental and theoretical investigations.[2,3,4] However little structural information is available on these ketones.[4,5] For cyclodecanone(**1**) , low-temperature x-ray data show that it exists as a "crystal-lattice" rectangular conformation with the carbonyl group situated at a non-corner position on a long side of the [2323] conformation of cyclodecane[6]. This same conformation has been employed for the interpretation of the low-temperature ^{1}H and ^{13}C NMR spectra of **1**.[4,7] Two distinct averaging processes have been observed in the dynamic ^{1}H NMR spectra of **1**, and these processes are associated with free energy barriers of 6.5 and 7.3 kcal/mol[7]; only the lower energy process has been observed in the dynamic ^{13}C NMR spectra of **1**.[7] Limited force-field calculations have been carried out on **1**.[8]

RESULTS AND DISCUSSION

Force-field Calculations: Boyd's iterative computer program[9] with modified parameters[10] was employed for the force-field calculations. Approximate coordinates for trial geometries were calculated by means of the program CODRD[11] with torsional angles estimated from Dreiding-Fieser molecular models. Pseudorotation paths were explored by the migration of a specific carbon atom from a corner to an adjacent noncorner position (or sequences of such migrations).[3,12] As a result of the migration three torsional angles change by about 120° : One torsional angle passes through 0° and the other two pass through 120° in a sequential order.[3,13] The appropriate torsional angles were changed by increments of 10-15°. The strain energies reported in this study correspond to molecules in a hypothetical motionless state at 0°K. However zero-point energy and vibrational enthalpy effects are expected to be similar for the different conformations of **1**. The present calculations will converge to either an energy minimum or maximum with respect to distortions corresponding to a normal mode of vibration.[9] Hence the vibrational frequencies of all the conformations of **1** were calculated and in each case 3N-6 real vibrational frequencies were obtained, which indicates that each of these conformations corresponds to a true (local) energy minimum with respect to any small geometric distortion. For the conformational transition states of cyclodecanone 3N-7 real frequencies were obtained.

Conformational Nomenclature: The nomenclature used in this work to describe the conformations of **1** is an extension of the notation proposed for the conformations of cycloalkynes.[14] The number of bonds on consecutive sides of a conformation are indicated within a square bracket starting with the side containing the carbonyl function. The direction of numbering around the ring is then dictated by the carbonyl group and starts at the corner position nearest to this group. In cases where the carbonyl function is symmetrically located on a side, the direction around

the ring is chosen so as to have the second number the smallest possible. The position of the carbonyl group (from the nearest corner position) is indicated outside (after) the square brackets. This conformational labelling system should not be confused with the chemical labelling of cyclodecanone, where 1 refers to the carbonyl carbon, 2 (or α) to the CH_2 next to the carbonyl, and so on. Dale's "wedge" system[3,13] has been employed to represent the three dimensional molecular conformations. The magnitude and sign of each torsional angle are indicated alongside the respective carbon-carbon bond.

Conformations: The initial geometries required for the force-field calculations have been obtained by the formal replacement of methylene groups with carbonyl functions[4] in the five low energy conformations of cyclodecane: [2323], [1414], [2233], [1333], and [1324].[3,13] Such replacements result in a total of twentyseven possible conformations for **1**; three conformations are derived from [2323] and three from [1414] whereas six, five, and ten conformations are derived from [2233], [1333] and [1324] respectively. The calculated torsional angles of the lowest energy member of each group of derived conformations are shown in figure 1.[15] The force-field calculations indicate the existence of eighteen conformations of **1** with relative strain energies lower than about 3 kcal/mol . Contributions to the total strain energy of each of these conformations are listed in Table I. The remaining nine possible conformations of **1** have relative strain energies of 4 kcal/mol or more and in each of these nine conformations the carbonyl function is situated at a corner position.[16]

The lowest energy conformation of **1** is calculated to be the [3232]-2-one (Table I) in agreement with x-ray and NMR data on **1**. The calculated torsional angles of the [3232]-2-one (figure 1) are in excellent agreement with the torsional angles of crystalline **1** as determined by x-ray diffraction methods.[6] The minor differences between the calculated and experimental torsional angles can be mainly attributed to crystal lattice forces in solid **1** which may distort the crystal conformation from that of an isolated molecule. The [2323]-2-one is only 0.4 kcal/mol (Table I) less stable than the preferred [3232]-2-one, and both of these conformations are formally derived from the [2323] conformation of cyclodecane.[13] The next two conformations in order of increasing energy are the [2233]-2-one and [3331]-2-one both of which have virtually the same strain energy and are formally derived from the [2233] and [1333] conformations of cyclodecane respectively.[13] The lowest energy conformations of **1** that can be derived from [1324] and [1414] of cyclodecane are the [3241]-2-one and [4141]-3-one which are 1.19 and 1.92 kcal/mol respectively higher in energy than the preferred [3232]-2-one (figure1). Force-field calculations show that the [3232]-2-one is the only conformation expected to be populated at low-temperatures in agreement with the ^1H and ^{13}C NMR data. However other conformations with relatively low calculated strain energies (0.4-1.9 kcal/mol) may become slightly populated near or above room temperature (Table I). All the conformations of **1** with the carbonyl function at a corner position have relatively high strain energies and are not expected to be important in **1**. Two members of this group namely the [1333]-1-one and [2323]-1-one have relative strain energies of 2.42 and 3.23 kcal/mol respectively while the rest of the group are at least 4.0 kcal/mol higher in energy than the [3232]-2-one conformation of **1**.[16] The replacement of a non-corner methylene group in cyclodecane with the smaller carbonyl function[17] decreases the repulsive proton-proton interactions, whereas such repulsive interactions are generally not affected when the methylene group being replaced is at a corner position.

Conformational Interconversions: The pseudorotation of the lowest energy [3232]-2-one conformation of **1** occurs via two distinct pseuorotation paths. The first path (C_S-pseudorotation) involves the conversion of the [3232]-2-one into its mirror image conformation via the [2323]-2-one as intermediate and pseudorotation partner. The second path (C_2-pseudorotation) involves the conversion of the [3232]-2-one into either the [3223]-1-one or

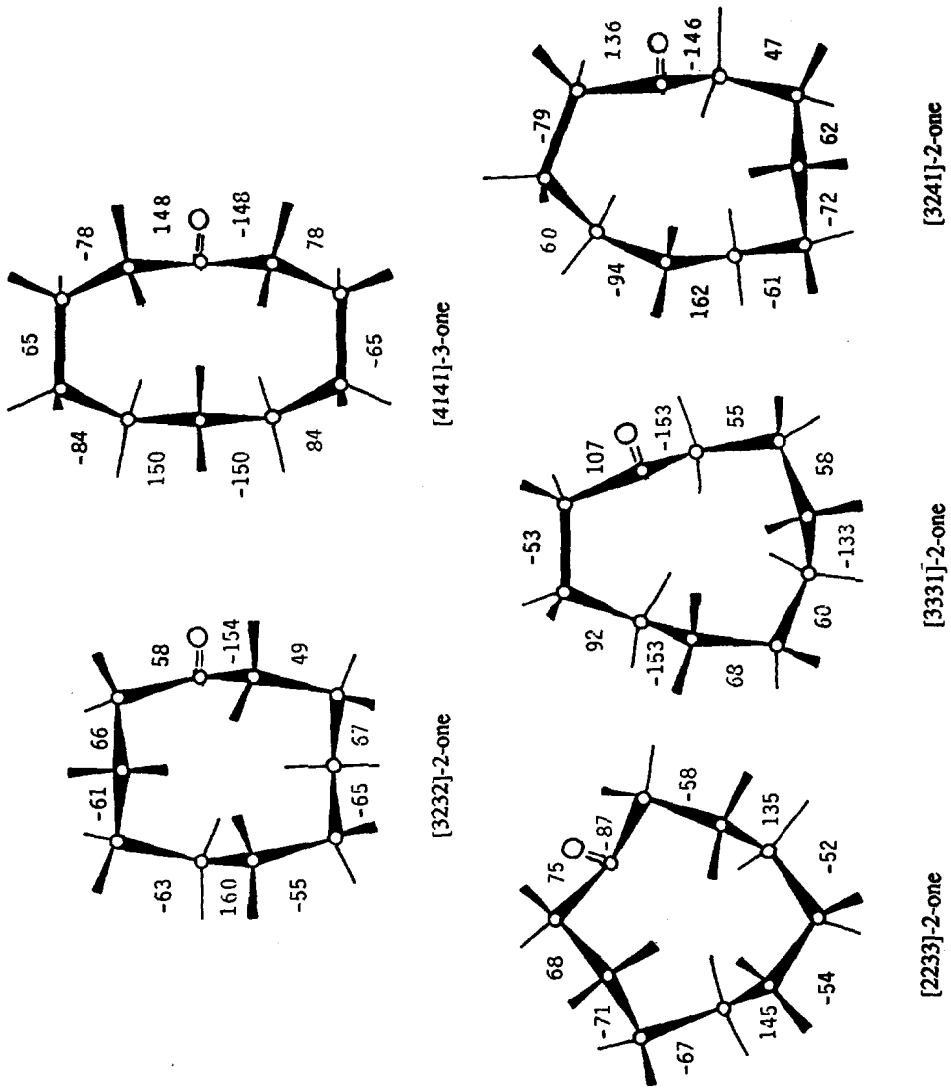
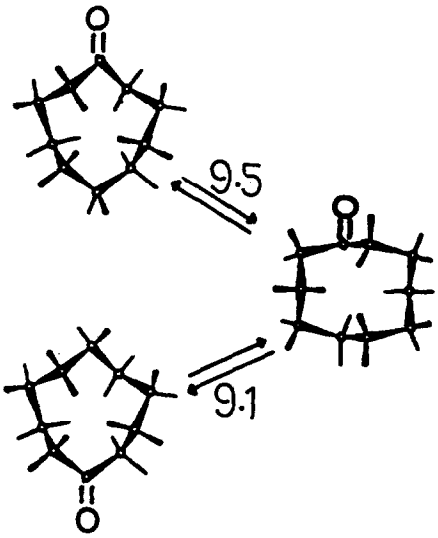
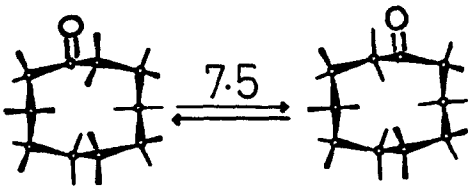


Figure 1 Calculated torsional angles of various conformations of cyclodecanone[15]

otherwise the [2332]-1-one as intermediate and pseudorotation partner. Force-field calculations on two possible C_2-peudorotation cycles : ([3232]-2-one -> [3322]-2-one -> [2323]-1-one -> [3223]-1-one) and ([3232]-2-one ->[3322]-2-one -> [2323]-1-one -> [2332]-1-one) show that the transition states associated with these two paths have barriers of 9.1 and 9.5 kcal/mol respectively, relative to the [3232]-2-one.



Force-field calculations on a possible Cs-pseudorotation cycle: ([3232]-2-one -> [2233]-2-one -> [2323]-2-one) show that the transition state associated with this cycle has a barrier of 7.5 kcal/mol relative to the [3232]-2-one. [19]



The calculated barriers for the pseudorotation processes in **1** are in reasonable agreement with the barriers determined experimentally for these two processes. Hence the C_S- and C_2-processes have been determined by dynamic ^1H and ^{13}C NMR to be associated with free energy barriers of 6.5 and 7.3 kcal/mol respectively while the calculated barriers for these processes are 7.5 and 9.1 kcal/mol respectively.

Table I. Calculated Strain Energies[a] (kcal/mol) of various conformations of Cyclodecanone[18]

Conformation	Er	E_θ	E_ϕ	E_δ	Enb	E_T	ΔE
[3232]-2-one	0.714	4.765	1.264	0.050	4.485	11.28	0.00
[2323]-2-one	0.694	4.336	2.519	0.009	4.121	11.68	0.40
[2233]-2-one	0.617	3.176	4.304	0.043	3.752	11.89	0.61
[3331]-2-one	0.549	2.280	5.363	0.029	3.676	11.90	0.62
[3313]-2-one	0.540	2.003	6.117	0.013	3.404	12.08	0.80
[3322]-2-one	0.626	3.825	3.944	0.045	3.826	12.27	0.99
[3241]-2-one	0.635	3.622	3.929	0.050	4.233	12.47	1.19
[4132]-3-one	0.635	3.621	3.930	0.050	4.233	12.47	1.19
[3133]-2-one	0.558	2.187	6.132	0.030	3.737	12.64	1.36
[3142]-2-one	0.600	2.859	5.471	0.026	3.877	12.83	1.55
[4132]-2-one	0.599	2.859	5.471	0.026	3.877	12.83	1.55
[3223]-2-one	0.648	4.411	3.973	0.015	3.940	12.99	1.71
[4231]-2-one	0.630	3.348	5.037	0.012	4.108	13.13	1.85
[4141]-3-one	0.560	2.060	6.578	0.004	3.998	13.20	1.92
[2314]-2-one	0.599	2.469	6.656	0.008	3.725	13.46	2.18
[1333]-1-one	0.601	2.495	6.404	0.001	4.196	13.70	2.42
[4141]-2-one	0.589	2.064	7.167	0.009	4.110	13.94	2.66
[2323]-1-one	0.826	5.835	2.257	0.000	5.593	14.51	3.23

a) The following symbols are used:
E_r, bond length strain; E_θ ,bond angle strain; E_ϕ, torsional strain; E_δ, out-of-plane bending strain; Enb, non-bond strain; E_T, Total strain energy; ΔE, Strain energy relative to [3232]-2-one.

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15. The calculated torsional angles of the conformations of cyclodecanone that are derived from the same cyclodecane conformation e.g. the three conformations from [2323] generally agree within +12° .

16. Examples of conformations of cyclodecanone with the carbonyl group situated at a corner position are : [2332]-1-one(4.01), [3133]-1-one(4.11), [1414]-1-one(4.13), [2233]-1-one(4.15), [3223]-1-one(4.41), where the numbers in brackets following the names of conformations represent calculated strain energies (kcal/mol) relative to the lowest-energy [3232]-2-one.

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19. For the C_2-pseudorotation the first step can alternatively involve the conversion of the [3232]-2-one into the [2233]-1-one. For the C_s-pseudorotation the first step can alternatively involve the conversion of the [3232]-2-one into the [3223]-2-one. However force-field calculations show that these alternative paths are less favorable than the corresponding C_2- and C_s-pseudorotation paths presented above.

ACKNOWLEDGEMENT

This work was supported by grant (CY/KETONES/38) from King Fahd University of Petroleum and Minerals. We thank Dr F.A.L. Anet, University of California, Los Angeles for his constructive discussions.