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# Ab initio evaluation of the equilibria between isomeric cyclooctadienes

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## Abstract

Thermodynamic properties of the equilibria between 1,3-, 1,4- and 1,5-*cis-cis*-cyclooctadienes in the gas phase were determined by ab initio Hartree–Fock calculations. The populations of cyclooctadienes at different temperatures are in good agreement with the experimental data reported in literature. The results may be used to optimize the preparation process of 1,4-cyclooctadiene via catalytic isomerisation of 1,5-cyclooctadiene.

**Keywords:** Cyclooctadienes; Isomerisation; Ab initio calculations

## 1. Introduction

Catalytic isomerisation of the *cis-cis*-1,5-cyclooctadiene (1,5-COD) to *cis-cis*-1,4-cyclooctadiene (1,4-COD) has been recently considered [1,2] because of the interest on using 1,4-COD in copolymerisation reaction together with 1,5-COD, employing homogeneous or heterogeneous catalysts, for obtaining a polybutadiene-like rubber [1] with good oil drying properties. In fact, due to difficulties in achieving 1,4-COD by organic synthesis [1], the only route available to 1,4-COD seems to be the catalytic one.

Supported metal catalysts are generally preferred to homogeneous ones for the easier separation and purification of the products and for the stability in the reaction medium. Attempts to isomerize 1,5-COD were performed employing heterogeneous Pd/pumice catalysts [3] but a pressure of hydrogen was needed [4]. Therefore, the competitive hydrogenation of cyclooctadienes to cyclooctene must be reduced to a minimum level for reaching a high yield in 1,4-COD. Optimisation of the results requires the knowledge of all the details of the kinetic conditions such as temperature, hydrogen pressure, and 1,3/1,5-COD ratio.

A good approach for studying the kinetic properties of this reaction system is the method described by Silvestri et al. [5], which develops an approach by Wei and Prater [6], requiring the knowledge of the composition of the isomer mixture at the equilibrium at different temperatures. In fact, this method allows to find the

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solutions of a system of differential equations where the kinetic constants of isomerisation processes are the unknowns, if the equilibrium constants of the same processes are determined.

Thermodynamic data concerning the equilibrium involving *cis-cis*-cyclooctadienes were obtained theoretically by using the force-field method [7] and, experimentally, by chemical equilibration in DMSO solution [8]; however, the theoretical method above is not always sufficiently accurate and the experimental data are not directly transferable to the gas phase case. Therefore, we decided to perform an ab initio calculation on *cis-cis*-1,3-COD, 1,4-COD, and 1,5-COD in order to obtain an accurate evaluation of  $\Delta G^\circ$  for the isomerisation equilibria in the gas phase.

## 2. Method of calculation

All calculations were performed at Hartree-Fock (HF) level using the Gaussian 90 program package [9], with the polarised split valence 6-31G\*\* basis set. A full geometry optimisation was carried out for each isomer (1,3-, 1,4- and 1,5-*cis-cis*-COD), without any symmetry constraint. In all cases only the absolute minimum was found, despite a number of different starting geometries; this seems to indicate that other secondary minima, reported in the litera-

ture [7,10] and observed either theoretically or experimentally, are not located in so a deep region of the potential energy surface to be detected through the optimisation procedure. The existence of the minima was confirmed by inspection of the hessian matrix eigenvalues. After obtaining the minimum energy structure, a calculation of the zero point energy and entropy values was performed. Moreover, an evaluation of the correlation energy was carried out at MP2 level, without further geometry optimisation.

## 3. Results and discussion

The optimised structures of the three isomers are depicted in Fig. 1; 1,3-COD and 1,4-COD show  $C_1$  symmetry, whereas a  $C_s$  symmetry was found for 1,5-COD.

The geometrical data of the optimised structures are reported in Table 1, along with the available electron diffraction data [11] in the gas phase for 1,3-COD. In this case the agreement between theoretical and experimental data of bond lengths and angles is good, except in the case of C5–C6–C7 and C6–C7–C8 bond angles, where the experimental values are about  $10^\circ$  lower; the experimental C5–C6–C7–C8 and C6–C7–C8–C1 torsional angles show also noticeable differences with respect to the theoretical findings. In the case of the other two iso-

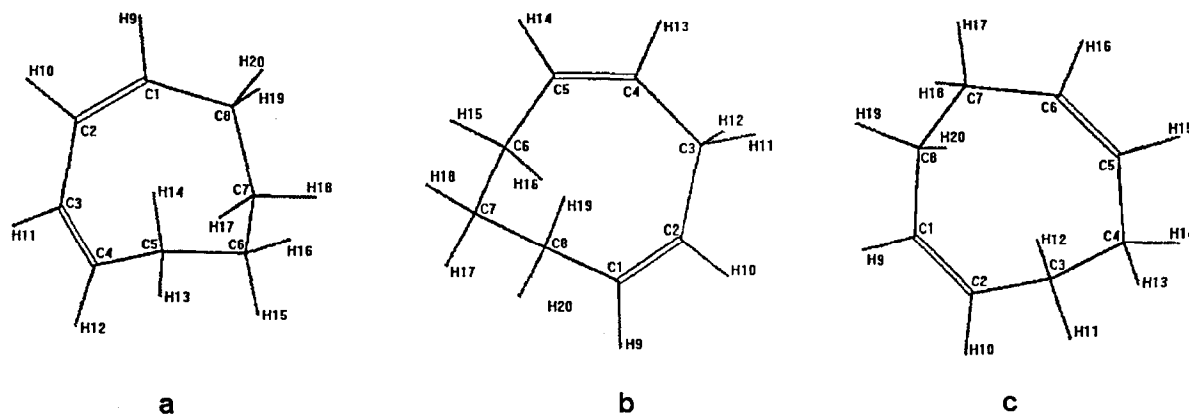


Fig. 1. The optimized structure of 1,3-COD (a), 1,4-COD (b) and 1,5-COD (c).

mers, no experimental data are available, so that a comparison with our theoretical results was not feasible.

Molecular mechanics data [7] are in good agreement with the ab initio results as what concerns the bond lengths, whereas bond angles and dihedral angles generally show considerable differences.

Table 2 summarises the results of our calculations for the total and relative energies of the considered systems with an estimate of the relative Gibbs free energies and the relative populations of the isomers at different temperatures. The most stable form appears to be 1,3-COD, which is favoured by about  $18 \text{ kJ} \cdot \text{mol}^{-1}$  with respect to 1,4-COD and by about  $34 \text{ kJ} \cdot \text{mol}^{-1}$

Table 1  
Bond lengths (Å), bond angles (°) and torsional angles (°) for 1,3-COD, 1,4-COD, and 1,5-COD. Values in parenthesis are from Ref. [8]. The C–H bond distances and C–C–H bond angles are average values

	1,3-COD	1,4-COD	1,5-COD
C1–C2	1.324 (1.347)	1.322	1.319
C2–C3	1.478 (1.475)	1.516	1.506
C3–C4	1.327 (1.347)	1.515	1.531
C4–C5	1.513 (1.509)	1.323	1.514
C5–C6	1.534 (1.542)	1.511	1.326
C6–C7	1.532 (1.542)	1.538	1.514
C7–C8	1.536 (1.542)	1.538	1.531
C8–C1	1.504 (1.509)	1.508	1.506
C–H (C with double bond)	1.080 (1.102)	1.079	1.080
C–H (C with single bond)	1.087 (1.109)	1.087	1.088
C1–C2–C3	126.8 (129.0)	129.1	124.0
C2–C3–C4	130.8 (129.0)	121.9	113.4
C3–C4–C5	133.0 (129.0)	131.8	121.2
C4–C5–C6	119.9 (117.2)	128.4	137.6
C5–C6–C7	115.4 (105.9)	113.4	137.6
C6–C7–C8	114.2 (105.9)	113.2	121.2
C7–C8–C1	112.4 (117.2)	112.4	113.4
C8–C1–C2	124.9 (129.0)	126.5	124.0
C–C–H	110.7 (113.3)	110.8	110.4
C1–C2–C3–C4	–42.4 (–37.8)	–37.2	–87.1
C2–C3–C4–C5	–4.2 (0.0)	–16.5	65.1
C3–C4–C5–C6	–6.7 (–18.2)	2.2	–11.2
C4–C5–C6–C7	80.6 (75.2)	79.9	0.0
C5–C6–C7–C8	–54.2 (–77.5)	–53.5	11.2
C6–C7–C8–C1	–53.7 (–32.3)	–51.2	–65.1
C7–C8–C1–C2	86.4 (79.7)	85.8	87.1
C8–C1–C2–C3	3.3 (0.0)	–39.1	–38.0

Table 2

Energy values (a.u.), relative energies ( $\text{kJ} \cdot \text{mol}^{-1}$ ),  $\Delta S^\circ$  ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),  $\Delta G^\circ$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) and percentages at the equilibrium of the cyclooctadienes at different temperatures

	1,3-COD	1,4-COD	1,5-COD
Total energy (HF)	–309.9110	–309.9042	–309.9002
Correl. energy (MP2)	–1.1034	–1.1033	–1.1013
$H(298 \text{ K}) - H_0$	0.0068	0.0071	0.0070
ZPE	0.1931	0.1927	0.1929
$\Delta E$	—	17.9	33.6
$\Delta S^\circ$	—	13.0	5.4
$\Delta G^\circ (T = 298 \text{ K})$	—	14.0	32.0
% Eq. ( $T = 298 \text{ K}$ )	99.7	0.3	$2 \cdot 10^{-4}$
% Eq. ( $T = 343 \text{ K}$ )	99.1	0.9	$1 \cdot 10^{-3}$
% Eq. ( $T = 400 \text{ K}$ )	97.9	2.1	$8 \cdot 10^{-3}$
% Eq. ( $T = 500 \text{ K}$ )	93.9	6.0	0.1

with respect to 1,5-COD at  $T = 0 \text{ K}$ ; when the contribution due to zero point energies is considered, these differences do not change. If we account for the entropic term, it is possible to evaluate the relative free energies at different temperatures; the entropy contributions shift the equilibrium towards 1,4-COD and 1,5-COD. The percentage values at the equilibrium of the three isomers here obtained at 343 K are close to those obtained theoretically by Allinger et al. [7]; in particular, the molecular mechanics data give population values of 98.9, 1.0, and 0.1% versus our values 99.1, 0.9, and  $1 \cdot 10^{-3}\%$  for 1,3-, 1,4-, and 1,5-COD, respectively. However, our results allow for an evaluation of the equilibrium constants between cyclooctadienes at every value of temperature. A comparison can also be made with equilibration experimental data in DMSO at various temperatures [7,8]: even if in this case a larger deviation was expected, due to the fact that experimental conditions are quite different from the isolated molecule scheme, a qualitative agreement was found. In particular, the equilibration study performed at  $70^\circ\text{C}$  [7] gives a mixture of 99.5% of 1,3-COD, with 0.5% of 1,4-COD and an amount of 1,5-COD slightly less than 0.01%; a further equilibration experiment conducted at various temperatures [8] gives, for instance, a mixture of 99.9% of 1,3-COD with 0.1% of 1,5-COD at

343 K and an amount of 99.1%, 0.8%, 0.1% of 1,3-COD, 1,4-COD, and 1,5-COD, respectively, at 403 K.

We think that the data here obtained are accurate enough to allow for determining the experimental kinetic constants of the isomerisation of cyclooctadienes [5] and then for setting the optimal conditions for obtaining a high yield of 1,4-COD in the gas phase.

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