

INTRAMOLECULAR INTERACTIONS IN DIBENZYL

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Dibenzyl, considered in this paper, is the simplest representative of the substituted 1,2 - diphenylethanes, on which our attention is focused, and as it presents an important structural unit in the latter, we attempted a more detailed analysis of its conformations in order to gain some insight into its intramolecular interactions.

In the crystal state by X - ray analysis of dibenzyl, the antiperiplanar conformation with parallel benzene rings angled at 72° with respect to the plane of the three central bonds has been established¹, and this behaviour of the molecule in the crystal environment was successfully reproduced by V. F. Bereznitskaya, A. I. Kitaigorodskii et al.² on the basis of empirical potentials. There is some evidence for the conformational equilibria of the liquid state too. A crude estimation on the basis of the intensity of the lines for the deformation vibration related to the angle $C^{al}-C^{ar}-C^{ar}$ in the solid and liquid states, respectively, is approximately 35 percent for the synclinal conformation (unpublished results of B. Yordanov and A. Oranovats). Unfortunately, there is not experimental data on which to make reasonable conclusions about the gas phase conformational preference and to compare them with our results which are relevant to an isolated molecule. Nevertheless, having in mind the existence of the synclinal conformation in the liquid state, it seems likely that this conformation would be preferable in the gas phase. LCAO - MO treatment of the interaction of benzene nuclei in syn- and anti - periplanar position performed by N. Tyutyulkov and D. Petkov³ led to the conclusion dealing with the probable favoring of conformations with a synclinal position of the two molecular fragments.

For changes only in the dihedral angles for rotation around single bonds the

Table 1

Conformation	ω_1 (deg)	ω_2 (deg)	ω_3 (deg)	ΔE (kcal mol ⁻¹)	$(\det \mathbf{F})^{-1/2^+}$	Normalized statistical weight at 300°K
(sc)-	83.5	57.8	83.5	0.00	5.5	0.385
	-83.5	-57.8	-83.5	0.00	5.5	0.385
(ap)-	90.0	180.0	90.0	0.95	16.0	0.230

$(E_0)_g = -4.29 \text{ kcal mol}^{-1}$ $\Delta E = E_i - (E_0)_g$
 $(E_0)_g$ - The energy at the global minimum.
 (+) - Units are $(\text{deg}^2 \text{ kcal})^{3/2} \times 10^3$.

Table 2

Conformation	ω_1 (deg)	ω_2 (deg)	ω_3 (deg)	φ_i (deg)			ΔE (kcal mol ⁻¹)
				i=1,7	i=2-5,8-11	i=6,12	
(sc)-	84.7	57.7	84.7	110.4	110.3	105.3	0.00
	R(C ^{al} -C ^{al})=1.533 Å, R(C ^{al} -C ^{ar})=1.511 Å, R(C ^{al} -H ^{al})=1.098 Å						
(ap)-	90.0	180.0	90.0	110.9	110.2	105.1	0.57
	R(C ^{al} -C ^{al})=1.531 Å, R(C ^{al} -C ^{ar})=1.511 Å, R(C ^{al} -H ^{al})=1.098 Å						

$(E_0)_g = 1.99 \text{ kcal mol}^{-1}$

Table 3

ω_2^+	Momany & Scheraga	Allinger	CNDO/2
0°	3.61	3.49	1.95
60°	0.00	0.00	0.00
180°	0.77	0.39	1.44

(+) - $\omega_1 = \omega_2 = 90^\circ$. Units are kcal mol⁻¹ and the starting geometry was used.

computational scheme of H. A. Scheraga et al.⁴ was followed and the empirical functions adopted by N. L. Allinger et al.^{5,6}, when bond stretching and angle bending were also taken into account, were used. The conformation is described in terms of the three dihedral angles of internal rotation ω_1 , ω_2 and ω_3 (Figure 1) with $\omega = 0^\circ$ in the eclipsed conformation. From^{2,7} starting geometry was chosen: C^{al}-C^{al} (1.51 Å), C^{al}-C^{ar} (1.52 Å), C^{ar}-C^{ar} (1.40 Å), C^{al}-H^{al} (1.09 Å), C^{ar}-H^{ar} (1.08 Å), C^{ar}-C^{al}-C^{al} (

112.07°), $H^{al}-C^{al}-H^{al}$ (109.47°). The simplifying assumption that all angles $C^{ar}-C^{al}-H^{al}$ and $C^{al}-C^{al}-H^{al}$ are equal to each other was made. The phenyl substituents were treated as rigid parts of the molecule (regular hexagon).

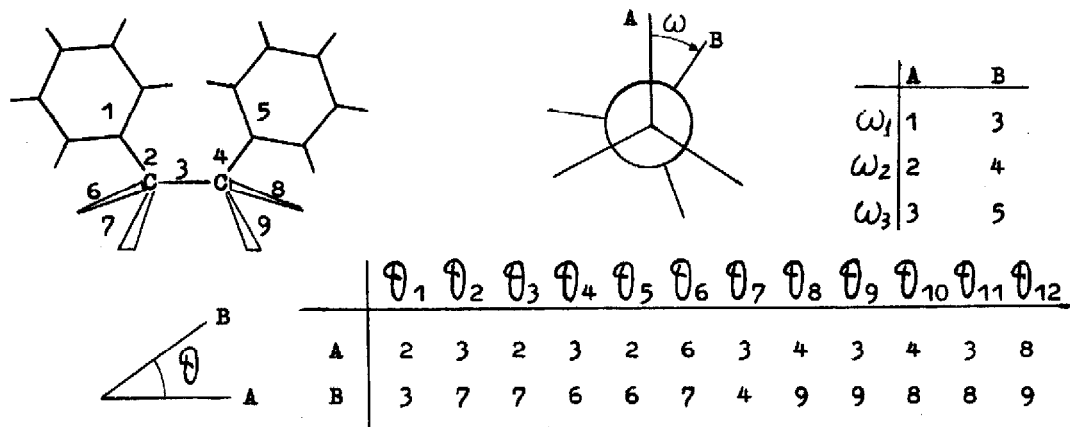


Figure 1. Description of the molecular geometry.

Except for the three dihedral angles, when the potential functions of Momany and Scheraga were used, the valence angles around C^{al} atoms and the valence bonds of the ethane framework also underwent variations.

An estimation of the conformational potential energy on a two dimensional lattice with "constants" $\Delta\omega_2 = 10^\circ$ and $\Delta\omega_1 = \Delta\omega_3 = 10^\circ$, using the potential functions of Momany and Scheraga, was made. Two low energy regions for the synclinal and antiperiplanar conformations were obtained. Starting points for minimization of the conformational energy with respect to the dihedral angles were chosen on this basis. After one cycle of minimization some of them converged to the local minimum (90° , 180° , 90°) and the remaining points approached closely the conformations (\ddagger sc) - of Table 1. After the next cycle of minimization the first derivatives of the conformational energy with respect to the dihedral angles for these two conformations became also $\leq 10^{-4}$ kcal mol $^{-1}$ deg $^{-1}$. At this point the matrix of second derivatives and the statistical weights (see ⁴) for the three low energy conformations (two of them are of the same energy because of symmetry) were computed. The obtained population of the conformations corresponds to a difference of 0.7 kcal mol $^{-1}$ in the free energy between the (ap) - conformation and the (+ sc) - and (- sc) - ones, taken together. These

local minima ((ap) - and (+ sc) -) were starting points for the minimization of the potential energy with respect to the dihedral angles and the valence bonds and angles of the ethane framework. After two to three cycles of minimization, with minimum increments of 0.02° for the valence and dihedral angles, and 0.0005 \AA for the valence bonds, the geometries in Table 2 were obtained. The results from the CNDO/2 - calculations (Table 3) also show preference of the synclinal conformation to the antiperiplanar one and quite well agree with those obtained with the empirical energy functions.

For the synclinal and antiperiplanar conformations, with geometries given in Table 2, an evaluation of the contributions from the different energy terms to the total strain energy was made. There is no difference in the stretch, bend, torsion and stretch - bend interactions, but there is a difference in the nonbonded interactions. Subsequent detailed analysis of the atom - atom interactions showed that the preference of the synclinal conformation to the antiperiplanar one is due to the attraction between the atoms of the benzene nuclei.

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