

THE SOLUTION CONFORMATION OF 1,2-DIPHENYLPROPANE

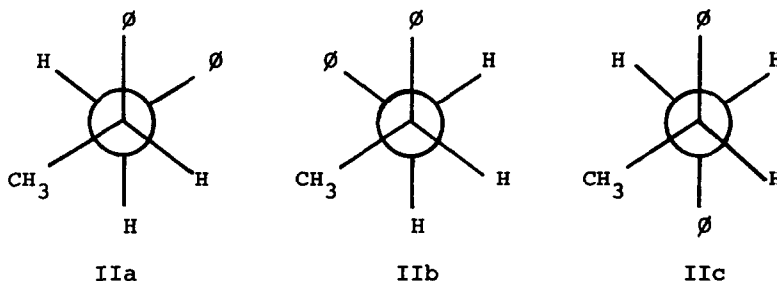
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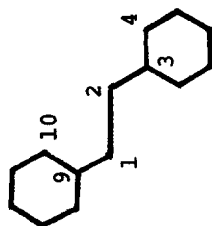
Recently, on the basis of molecular mechanics calculations, Ivanov *et al.*¹ concluded that the gauche conformer of 1,2-diphenylethane (I) is 0.57 kcal/mole more stable than the anti conformer. The stabilization of gauche I relative to that of anti I was concluded to arise from non-bonded interactions (attractive) between the atoms of the benzene nuclei.

We have performed similar calculations² on I and 1,2-diphenylpropane (II). The results of these steric energy minimization calculations are presented in Table I. Our calculations also indicate that the gauche conformer of I is more stable than the anti conformer of I (by 1.15 kcal/mole), and, surprisingly, that both gauche conformers of II are more stable than the anti conformer of II (by 1.22 and 0.42 kcal/mole, respectively, for IIa and IIb relative to IIc). Intuitively, it might be expect-



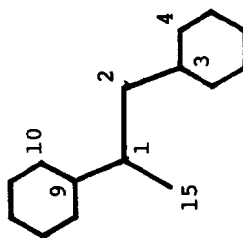
ed that the steric interactions in gauche I might be more severe than those experienced in anti I and that IIc should predominate over IIa or IIb. The calculations indicate that this is not the case.

Table I



Dibenzyl

Calculation	Dihedral Angles (deg)		Δ Strain Energy (kcal/mole)
	10,9,1,2	9,1,2,3	
Present Work (gauche)	78.7	57.1	0.0 ^a
Ivanov <u>et al.</u> (gauche)	84.7	57.1	0.0
Present Work (anti)	90.8	180.0	1.15 ^b
Ivanov <u>et al.</u> (anti)	90.0	180.0	0.57



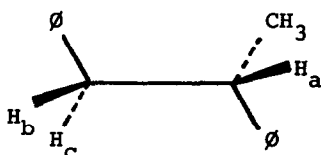
1,2-Diphenylpropane

Conformation	Dihedral Angles (deg)		Δ Strain Energy (kcal/mole)
	2,1,9,10	9,1,2,3	
Gauche (IIa)	69.5	53.4	0.0 ^c
Gauche (IIb)	75.9	62.0	0.80 ^d
Anti (IIC)	104.6	-173.4	1.22 ^e

^a $E_0 = 3.94$ kcal/mole; ^b $E_0 = 5.09$ kcal/mole; ^c $E_0 = 4.64$ kcal/mole; ^d $E_0 = 5.44$ kcal/mole;

^e $E_0 = 5.86$ kcal/mole

Experimentally, we have examined specifically deuterated analogues of II. The coupling constants of II, in CCl_4 solution, are presented below.



$$J_{ab} = 6.50 \pm 0.04 \text{ Hz}$$

$$J_{ac} = 8.20 \pm 0.04 \text{ Hz}$$

$$J_{bc} = -13.25 \pm 0.04 \text{ Hz}$$

Granted any reasonable theoretical coupling constants (J_g and J_t) in

$$J_{ab} = n_a J_t + n_b J_g + n_c J_{g'}$$

and
$$J_{ac} = n_a J_{g''} + n_b J_{g'''} + n_c J_t$$

where n_i is the mole fraction of the i^{th} conformer (see above), it can only be concluded that the predominant conformer (EXPERIMENTALLY) is actually IIc (with $J_t = J_{t'} = 13.0$ Hz and $J_g = J_{g'} = J_{g''} = J_{g'''} = 3.0$ Hz, $n_a = 0.35$, $n_b = 0.13$, and $n_c = 0.52$). Thus, the calculated conformational strain energies bear no resemblance to the experimentally determined conformations. By analogy, we believe that the calculations on 1,2-diphenylethane are also suspect. X-ray crystallographic³ and spectroscopic studies⁴ both indicate that 1,2-diphenylethane exists predominantly, if not exclusively, in the anti conformation in both the solid and solution states.

As has been noted previously,⁵ "...From a knowledge of the dependence of strain energy on geometry, it is in principle possible to arrive at a description of the molecular conformation under consideration. Unfortunately the accent is on the provisional "in principle," for although the mathematical apparatus for performing the required computations is more than adequate, the same cannot often be said of the functions describing the dependence of energy on geometry." This caveat should most probably be considered when energy differences between computed conformations are small, as in the present case. A complete discussion of the computational and experimental work described herein will be presented in a full paper.

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