

Conformational Energy of (+)-Pulegone

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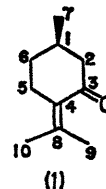
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Summary Temperature-dependent circular dichroism measurements on (+)-pulegone enabled us to estimate its conformational energy.

No attempt has previously been made to estimate the conformational energy of an $\alpha\beta$ -unsaturated carbonyl compound with *s-cis*-geometry. We now describe the estimation of the energy of (+)-pulegone (1) by temperature-dependent c.d. measurements in the region of the $n \rightarrow \pi^*$ transition.

According to the octant projection diagrams¹ for preferred conformers (1a) and (1b) (Figure 1), a positive Cotton effect was predicted for (1a), and a negative one for (1b). The temperature-dependence of the c.d. curves

(Figure 2) showed the presence of a conformational equilibrium between (1a) and (1b). The increase of the positive



(1)

rotational strength with a lowering of the temperature indicated the predominance of conformer (1a).

These c.d. curves were regarded as being coincident with

a Gaussian curve. The observed rotational strength R_K^T at temperature T was estimated from the following equation:²

$$R_K^T = 0.696 \times 10^{-42} \sqrt{\pi} [\theta_K^0] \frac{\Delta_K^0}{\lambda_K^0}$$

where θ_K^0 represents a maximum partial molecular ellipticity, λ_K^0 is the wavelength at θ_K^0 , and Δ_K^0 is the half width.

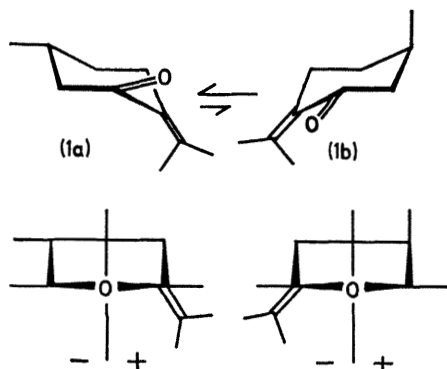


FIGURE 1. Preferred conformations of (+)-pulegone (1) and their octant projections.

Following Moscovitz's procedure,³ the Gibbs free energy change (ΔG^0), the rotational strength of (1a) and (1b) (R_a and R_b), the equilibrium constant (K), and the population of (1a) and (1b) (N_a and N_b) are then as follows: $\Delta G^0 = 1.1$ kcal/mole, $R_a = 2.77 \times 10^{-40}$ c.g.s. units, $R_b = -4.78 \times 10^{-40}$ c.g.s. units, and at 25° , $K = 0.156$, $N_a = 86.5\%$, and $N_b = 13.5\%$. Since ΔG^0 is assumed to be temperature-independent, ΔS^0 is zero and ΔG^0 corresponds to ΔH^0 for the equilibrium (1a) \rightleftharpoons (1b).

The conformational energy of methylcyclohexane has been calculated to be 1.7 kcal/mole. However, one of the 1,3-diaxial interactions between the methyl group and the

hydrogen atom is missing in pulegone as well as in 3-methylcyclohexanone. The conformational energy of 3-methylcyclohexanone is accordingly estimated to be 1.1 kcal/mole by subtracting the energy of the 3-alkyl ketone

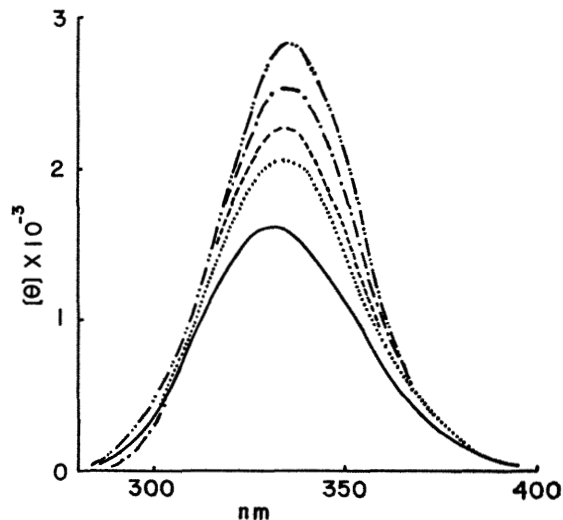


FIGURE 2. C.d. curves of (+)-pulegone (1) in methylcyclohexane-isopentane, 1:3 by volume, at 25° (—), -31° (.....), -67° (-----), -113° (-·-·-), and -148° (- - - -).

effect (0.6 kcal/mole)⁵ from the conformational energy of methylcyclohexane. The conformational energy obtained for (+)-pulegone (1) is coincident with this value. Thus, the introduction of an isopropylidene group at the C-4 position appears not to change the conformational energy of the methyl group, although it would affect the energy barrier of the ring conformation.

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⁵ N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, 1962, **84**, 2201.