MOLECULAR ORBITAL STUDIES ON THE CONFORMATION OF N-PHENYL MALEIMIDE

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SUBSTITUTED maleimides have found several biological and technical applications[1-8]. They have been used as heat stabilisers and thermal discoloration inhibitors in polymers, adhesives for metals, vulcanization agents, fungicides and choline transfer inhibitors to mention a few. Such compounds form complexes with oxy and deoxy hemoglobin[5-7] and are reactive to biological species[8]. Due to such a wide variety of interests, it was thought worthwhile to investigate the conformation of a substituted maleimide, namely N-phenyl maleimide. It may be mentioned that NMR investigations on a related molecule N-p-chlorophenyl maleimide have been reported[9]. From the analysis of the NMR spectrum of the molecule oriented in a nematic solvent, it was found that there are only two nonequivalent dipolar couplings [D(i, j) as defined in literature[10]] between phenyl and the maleimide protons, i.e., D(H3, H7) = D(H4, H7) = D(H3, H11) = D(H4, H11) and D(H3, H8) = D(H3, H10) = D(H4, H8) = D(H4, H10). Two possible interpretations can satisfy the NMR observations : (a) a rapid exchange between planar and orthogonal conformations with appropriate weighting factors and (b) a twisted conformation with C_2 symmetry for the molecule with a rapid exchange between the four equivalent conformers.

Since both the rings are planar, the conformational structure of N-phenyl maleimide is determined by a single torsional angle α around the C–N bond. We choose a convention in which the 0° for α corresponds to the conformation in which both the rings lie in the same plane. Two semiempirical molecular orbital methods namely, CNDO and PCILO[11,12], were used for the calculation of total energy (V) of the molecule as a function of angle α. Both these methods have been extensively used for conformational energy calculations and found quite successful for predicting conformational structure[13,16]. Standard bond lengths and bond angles (shown in Fig. 1.) were used to fix the primary geometry of this molecule. The results of the energy calculations are also included in the figure. The energy curves show a four-fold behaviour, because of the molecular symmetry. For this reason only 0–90° section has been shown in the

figure. It is found that both the planar and orthogonal (α = 90°) conformations correspond to maxima in the energy profiles. Energy curves from both the methods are parallel to one another and
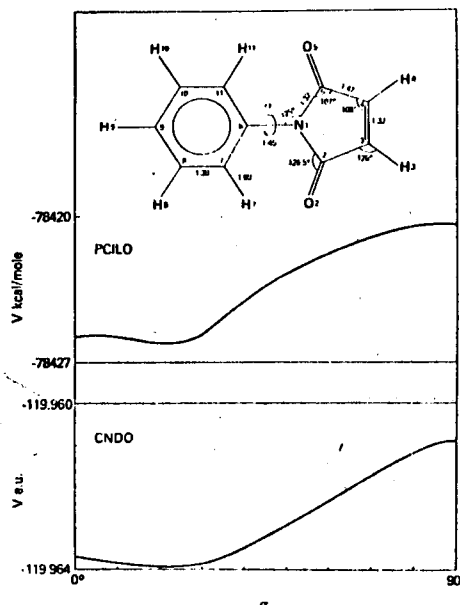

FIG. 1. Potential energy (V) of N-Phenyl maleimide as a function of torsional angle α.

show minima at an angle of about 25°. The potential energy curve is relatively flat in the region of 0–40° but the energy rises sharply as the conformation tends towards an orthogonal arrangement of the two rings. The four equivalent minima are connected by barrier heights which are low on the NMR time-scale. The theoretical results reported here clearly exclude the possibility of an equilibrium between planar and orthogonal conformations, but are consistent with the alternative interpretion of the NMR results and suggest a twisted conformation with a low barrier for rotation around C–N bond.

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