Vibrationally-induced Barriers to Hindered Rotation

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The factors which determine the most stable conformation of a β-substituted ethyl radical are shown to be dominated by the zero-point energy.

In conformational analysis it is generally assumed that a molecule can be approximately described as two rigid groups contra-rotating about a connecting bond.[1] This model clearly ignores structural, and concomitant vibrational changes[2,3] which can contribute to the internal rotation barrier. In this communication we describe calculations on isotopically substituted ethyl radicals which show that the barrier height is dominated by these contributions. In particular the radical, $CH_2D\dot{C}H_2$, is the first example of a molecule where the most stable conformation is determined by the zero-point energy.

The eclipsed conformation in the β-substituted ethyl radical, $XCH_2\dot{C}H_2$, is when the C–X bond lies in the plane which bisects the $\dot{C}H_2$ group, that is, it eclipses the orbital containing the unpaired electron. The staggered conformation is when the C–X bond lies in the plane of the $\dot{C}H_2$ group. Experimentally the staggered conformation is observed (that is, the barrier conformation is the eclipsed conformation) for X = Me[4] and X = D (deuterium)[5] but for X = Mu (the positive muon)[5] the eclipsed conformation is observed. The geometries of both conformations were optimised using the standard 3–21G basis set in the UHF method[6] and showed that there is a large structural change associated with the $-\dot{C}H_2$ group, which makes an angle of 10° with the C–C bond in the eclipsed conformation but is co-planar in the staggered conformation, the former being more stable by 0.385 kJ mol^{-1}. The barrier for each radical was evaluated by adding the UHF barrier height (0.385 kJ mol^{-1}) to the difference in the zero-point energies of the staggered and eclipsed conformations respectively. In calculating the zero-point energies the vibration coincident with the internal rotation is excluded. The results are compared with experimental data in Table 1.

Table 1. Calculated (assuming 0.0 K) and experimental barriers (J mol^{-1}) to internal rotation for isotopically substituted ethyl radicals in the liquid phase.

	Experimental[a]			
Radical	Table 2	Table 3	Table 5	This work
$Me\dot{C}H_2$				121.9
$CD_3\dot{C}D_2$				153.7
$CDH_2\dot{C}H_2$	−340	−352		−238.4[b]
$CHD_2\dot{C}H_2$	376	379		348.9
$CH_2Mu\dot{C}H_2$	2845	2710		1881.6
$CH_2Mu\dot{C}HD$	2483	2649	2963	1793.3; 2027.8[c]
$CHDMu\dot{C}H_2$	2704	2665	3030	1965.9
$CD_2Mu\dot{C}HD$	2898	2894	3222	1955.7; 2202.5[c]
$CHDMu\dot{C}D_2$	2927	2906	3280	2054.0
$CD_2Mu\dot{C}D_2$	3452	2710		2138.2
$CH_2Mu\dot{C}D_2$			3076	1971.1
$CD_2Mu\dot{C}H_2$			3186	2051.9

[a] The results are taken from Tables 2, 3, and 5 of ref. 5. Tables 2 and 3 derive barriers from the experimental data in different ways. Table 5 is obtained from the analysis of the results in Table 2. [b] A negative barrier means that the staggered conformation is more stable. [c] The symmetry of the isotopic substitution gives rise to two barriers.

All the qualitative trends are well reproduced, and within the limitations of the method, the basis set used, and the neglect of anharmonicity in the vibrational modes, which is most serious for the muon, the quantitative comparison is satisfactory. We conclude that the barrier height to internal rotation in the ethyl radical is dominated by the difference in the zero-point energies of each conformation, and that it will be temperature dependent.

It is advisable in the light of these calculations to re-examine the interpretation of the experimental results for all radicals and molecules with a barrier less than about 3 kJ mol^{-1}. It should be emphasised, however, that these results depend only on two UHF calculations, one for each geometrically optimised conformation. Therefore, in the harmonic oscillator approximation to the molecular vibrations used here, there is no alteration in the bond lengths by isotopic substitution. In particular, the controversial steric isotope effect[7] and hyperconjugative electron release[8] models used to rationalise the barriers and preferred conformations of these radicals must now be considered to have, if any, only a minor effect. In addition, if there is a substantial vibrational contribution to the barrier it is doubtful whether the normal interpretation of the term 'hindered internal rotation' is correct. It is clear from the differences in the optimised geometries used in these calculations that the unobservably small barrier for $Me\dot{C}H_2$ cannot be associated with freely contra-rotating groups.

We thank the Institute of Physics and Rank Xerox for a 'Women Returners Fellowship' grant to A. M. G. and Professor M. C. R. Symons and Dr. S. Cox for discussions.

Received, 9th March 1987; Com. 288

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