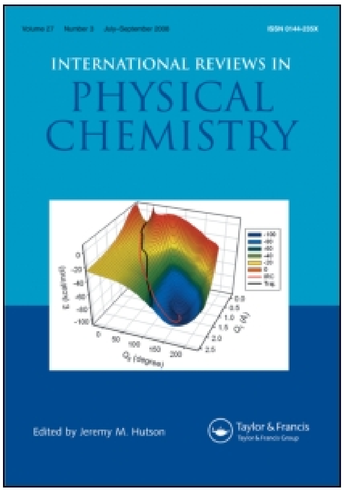

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Changes in the phase of the barrier to internal rotation upon electronic excitation

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Changes in the phase of the barrier to internal rotation upon electronic excitation

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Molecules with CX_3NO, CX_3CHO, and related structures have eclipsed conformations in their ground electronic states, but adopt a staggered equilibrium conformation in their $n\pi^*$ excited states. This dramatic difference in the torsional barrier in different electronic states of the same molecule is an important clue towards a fuller understanding of the relation between electronic structure and preferred conformation. Results to date are reviewed, and suggestions are made for further experimental and theoretical studies.

1. Introduction

The problem of hindered internal rotation, or torsion, about single bonds in the ground states of molecules had been the subject of many studies (see, for example, Lister *et al.* (1978) and *Journal of Molecular Structure* (1985)). Barrier heights and phases (preferred conformations) in series of related molecules have been compared in an attempt to understand the delicate balance of forces responsible for torsional barriers. Another approach, with considerable promise for probing the relation between electronic structure and torsional barriers, is to compare the barriers in different electronic states of the same molecule. Cases are known in which the barrier height changes upon excitation: for example, there is a substantial increase in the C–OX torsional frequency upon excitation of phenol (Bist *et al.* 1967), but a more modest increase in anisole (Balfour 1985). However, it was only with a study of the 690 nm $n\pi^*$ absorption of CF_3NO (Gordon *et al.* 1976) that a change in both the magnitude and *phase* of the barrier was first shown to accompany electronic excitation. The same conformational change has since been shown to accompany $n\pi^*$ electronic excitation in a variety of molecules with CX_3NO, CX_3CHO, or related structures. In each case the double bond is eclipsed by a CX bond in the ground state, but the staggered equilibrium conformation is preferred in the $n\pi^*$ excited state. The purpose of this paper is to review existing studies of this effect with the hope of stimulating further experimental and theoretical work.

2. Experimental methods

A change in conformation upon excitation manifests itself in the electronic spectrum as a progression of bands in the torsional mode, in accordance with the Franck–Condon principle as shown in figure 1 (*a*). For example, in the absorption spectrum of CF_3NO (figure 2), a progression in the low-frequency torsional mode is observed (Gordon *et al.* 1976), and the separation between bands ($\sim 60\,cm^{-1}$) leads to an estimate of the torsional barrier in each electronic state. This spectrum, recorded at $-68°C$, is complicated by many torsional hot bands. DeKoven *et al.* (1981) obtained a much sharper and simpler spectrum, devoid of hot bands, by cooling CF_3NO in a supersonic jet. Fluorescence excitation, and dispersed single-vibronic-level

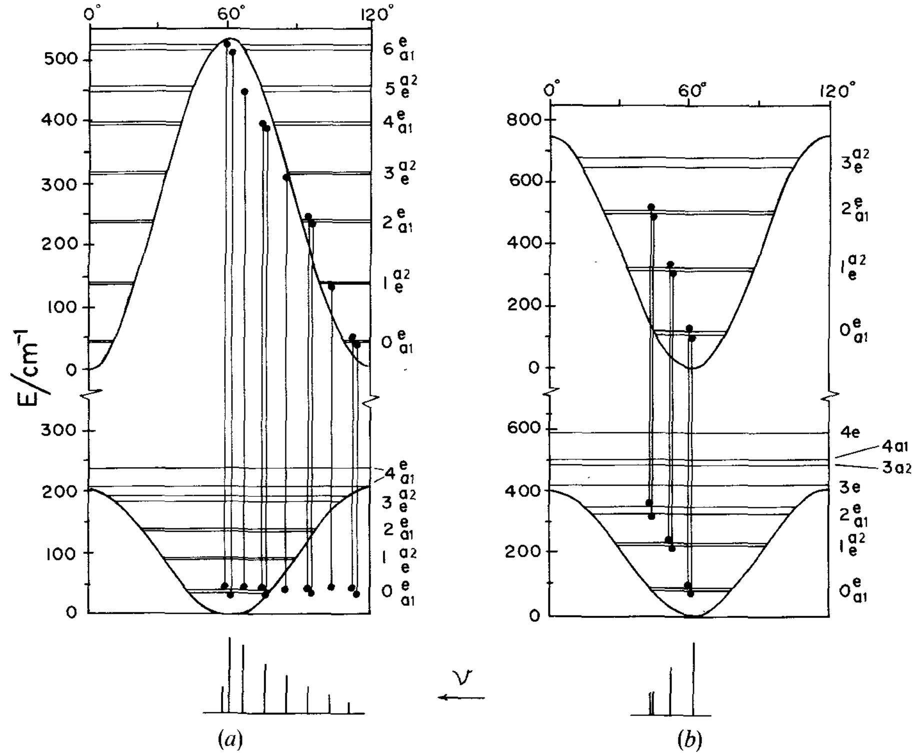

Figure 1. Portions of the ground and excited-state potential curves for internal rotation of a threefold rotor. Staggered conformations occur at 0, 120, and 240°, eclipsed at 60, 180, and 300°. Selection rules a_1–a_1, a_2–a_2, and e–e apply to the transitions shown. (*a*) Potential curves 60° out of phase as in the $n\pi^*$ transition of CF_3NO. The $0 \rightarrow v'$ progression shown is similar to that observed in the jet spectrum. (*b*) Potential curves in phase. The $\Delta v = 0$ sequence bands are similar to those observed in the ($n \rightarrow 3s$) Rydberg transition of CH_3CHO. Note in the lower state of (*b*) how triply near-degenerate torsional vibrational levels below the barrier merge into doubly near-degenerate internal rotational levels above the barrier.

fluorescence spectra, respectively, provided information about the excited and ground-state torsional potential. Goodman and Brus (1978) observed a similar spectrum for CF_3NO in a neon matrix, but found the torsional levels to be significantly displaced from their gas-phase energies.

If, on the other hand, the conformation is the same in both electronic states (figure 1 (*b*)), $\Delta v = 0$ sequence bands, rather than a progression, are expected in the torsional mode. Such a pattern is observed, for example, in a *Rydberg* transition of acetaldehyde (Heath *et al.* 1980, Gordon 1980).

For a threefold rotor connected to an asymmetric frame, the torsional potential is usually assumed to be $V = (V_3/2)(1 - \cos 3\alpha)$ where V_3 is the barrier to internal rotation and α the torsional angle. Torsional (or internal rotational) states (figure 1) are classified a_1, a_2 or e according to the molecular symmetry group of Longuet-Higgins (1963), and their energies calculated as described by Lewis *et al.* (1972). Calculated and observed energies are then compared to obtain values for V_3, and for F, the reduced rotational constant for internal rotation which depends on the molecular structure. This simple approach assumes that torsion is separable from other motions of the molecule.

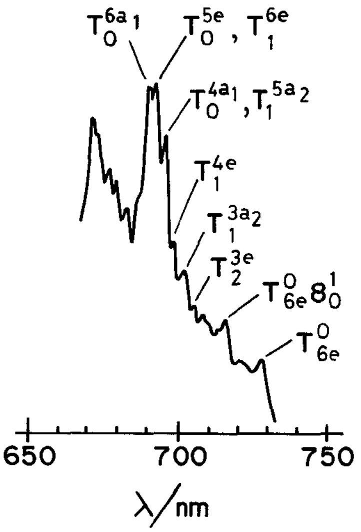

Figure 2. Low-energy portion of the $n\pi^*$ absorption spectrum of CF_3NO gas, showing the progression in the torsional mode T.

The situation is more complicated in molecules such as acetaldehyde (Noble *et al.* 1983, Noble and Lee 1984) in which the aldehyde group becomes non-planar in the $n\pi^*$ excited states. Here the 'staggered' conformation may not be a full 60° out of phase with the eclipsed (and aldehyde planar) ground state, and there is evidence for substantial interaction between methyl-torsion and aldehyde-inversion motions. The two rotors of acetone (Baba and Hanazaki 1983) and the asymmetric rotor of $CClF_2NO$ (Ernsting 1984) also present complications which have yet to be unravelled in detail.

3. Results and discussion

Microwave spectroscopy shows that all the molecules of the type considered here have eclipsed equilibrium conformations in their ground electronic states. Electronic spectra show that they are staggered in their $n\pi^*$ excited states, but eclipsed, with an increased barrier, in their ($n\rightarrow 3s$) Rydberg states. Molecular orbital calculations of varying degrees of sophistication lead to the same qualitative results, but have had little success in reproducing the magnitude of internal rotation barriers in excited states. Details are given in the table. Error limits in the table are those given by the authors. Some, but not all, include an allowance for systematic error in the simple model used.

This consistent dependence of preferred conformation upon electronic state shows that torsional barriers are very sensitive to electronic structure as well as to other effects such as steric repulsions. Since Rydberg excitation of a non-bonding electron increases the relative stability of the eclipsed conformation, the staggered conformation found in $n\pi^*$ excited states must be due to the promoted π^* electron.

The eclipsed ground-state conformation can be rationalized in terms of π-orbital interactions (Radom *et al.* 1985, Hehre *et al.* 1976), and Devaquet *et al.* (1976) suggest how electronic excitation can lead to a different conformation. Moule and Ng (1985) present a similar argument as follows: The 'π' and 'π^*' orbitals of a $CH_3-A=B$ molecule have the nodal properties shown in figure 3. The methyl group orbital of a″ (or π) symmetry mixes with the π-type orbital localized on the $A=B$ group. In the ground state the highest occupied orbital (π) has an antibonding 1–4 interaction as shown, and

Table 1. Ground and excited state comformations and torsional barriers (cm^{-1}).

	Electronic state and equilibrium conformation				
Molecule	Ground eclipsed	$n\pi^*$ Triplet staggered†	$n\pi^*$ Singlet staggered†	Rydberg eclipsed	Calc. of exc. state barrier
CF_3NO	269 ± 17 MW[1]				
	250 ± 50 A[2]		550 ± 110 A[2]§		
	202 ± 10 JF[3]		533 ± 30 JE[3]		
CH_3NO‡	400 MW[4]		475 ± 50 A[5,6]		5, 6
$CClF_2NO$	~225 JF[7]		>500 JE[7]		
CH_3CHO‡	400 ± 2 MW[8], IR[9]	625 ± 20 *A[10]	660 ± 20 *JE[11]	750 ± 10 MPI[12,13]	12, 13, 14
Acetone‡	274 MW[15]		740 ± 90 *JE[16]		14
Methylglyoxal‡	$269{\cdot}1\pm0{\cdot}3$ MW[17]		190 ± 5 JE[18,19]		19
Biacetyl	269 assumed[19]		~235 JE[18,19]		
CH_3CHS	540 ± 7 MW[20]	A[21]¶	A[21]¶		
Thioacetone‡	454 ± 17 MW[20]	A[22]¶		>450 A[22]	

† In states marked * the carbonyl group is nonplanar so that the 'staggered' conformation may not be a full 60° out of phase with the eclipsed ground state.

‡ Deuterated species have also been studied.

§ Some low-energy bands were incorrectly assigned to a second conformer. These are now known (figure 2) to be hot bands, involving torsional levels above the ground-state barrier.

¶ Conformation established, but barrier not measured.

Techniques: MW, microwave; IR, infrared; A, room temperature absorption; JE, fluorescence excitation in a supersonic jet; JF, dispersed fluorescence in a jet; MPI, multiphoton ionization.

References: [1] Turner and Cox (1976). [2] Gordon *et al.* (1976). [3] DeKoven *et al.* (1981). [4] Turner and Cox (1978). [5] Ernsting *et al.* (1978). [6] Gordon and Luck (1979). [7] Ernsting (1984). [8] Bauder and Günthard (1976). [9] Hollenstein and Winther (1978). [10] Moule and Ng (1985). [11] Noble *et al.* (1983), Noble and Lee (1984). [12] Heath *et al.* (1980), Eichelberger and Fisanick (1981). [13] Gordon (1980). [14] Peterson *et al.* (1981). [15] Swalen and Costain (1959). [16] Baba and Hanazaki (1983). [17] Dyllick-Brenzinger and Bauder (1978). [18] Gurnick *et al.* (1981), Chaiken and McDonald (1982). [19] Soulard *et al.* (1984). [20] Kroto *et al.* (1974). [21] Judge and Moule, to be published, quoted in Moule and Ng (1985). [22] Paone *et al.* (1984).

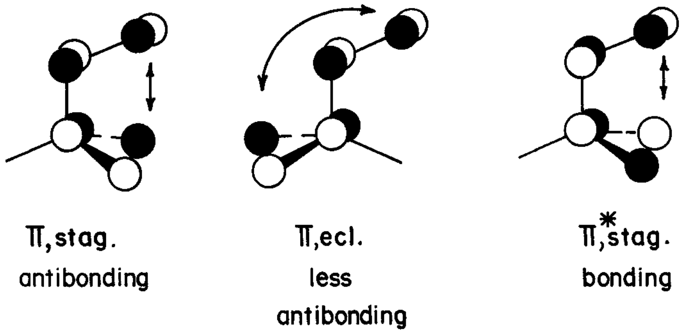

Figure 3. Nodal properties of the π and π^* orbitals in a $CH_3-A=B$ molecule. The 1–4 interaction is shown by arrows.

this is minimized in the preferred eclipsed conformation. When an electron is promoted to the π^* orbital, however, in which the 1–4 interaction is bonding, a staggered conformation is adopted to maximize the overlap.

This simple picture deserves extension and further testing. Can it be supported by *ab initio* excited state calculations? Hehre *et al.* (1976) argue that the ground-state barrier should increase as the $A=B$ bond becomes less polar, and this is consistent with the increase in ground-state barrier from acetaldehyde to thioacetaldehyde. Can a similar argument be applied to excited-state barriers? Why is the ground-state barrier higher in CH_3NO than in CF_3NO while the reverse is true in their $n\pi^*$ excited states? How might the barrier change in magnitude and phase upon $\pi\pi^*$ excitation of propene?

The non-bonding electron in CH_3CHO has its greatest density on the oxygen atom, and its Rydberg excitation increases the stability of the eclipsed conformation. Would the same effect occur upon Rydberg excitation of CH_3NO where the highest-energy non-bonding electron is localized more on nitrogen?

Because of the change of equilibrium conformation upon $n\pi^*$ excitation, the Franck–Condon principle allows us to excite selectively a molecule to a series of excited torsional levels (figure 1 (*a*)), and this facilitates the study of various phenomena as a function of torsional energy. For example, Spears and Hoffland (1981) found that the fluorescence lifetime of $n\pi^*$ CF_3NO decreases rapidly with increasing torsional energy, and that torsion is a promoting mode for radiationless transitions. DeKoven *et al.* (1981) found evidence for a′–a″ symmetry breaking in highly-excited torsional levels of $n\pi^*$ CF_3NO, and for mixing between CF_3 rocking and torsional motions in ground state levels above the internal rotation barrier. Noble and Lee (1984) found significant coupling between torsion and *a*-axis rotation in higher torsional levels of acetaldehyde.

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