

ROTATIONAL BARRIERS OF BENZALDEHYDES IN THE FRAMEWORK OF THE INTERSECTING-STATE MODEL

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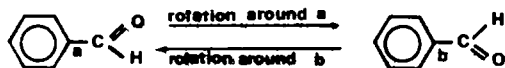
Abstract - A general intersecting-state model has been applied to the rotational barriers of benzaldehydes. It is found that in the gas phase the transition state bond order, n^\ddagger , is greater than 1.0, implying a siphoning of electronic density from the oxygen lone pairs into the transition state. In solution such siphoning is hindered due to the interactions of the oxygen lone pairs with the solvent molecules and $n^\ddagger=1.0$. For protonated benzaldehydes rotation around a carbon-carbon double bond seems to occur and $n^\ddagger=1.0$, which is in agreement with a bond breaking at the transition state. Substituent effects are studied and estimations of rotational energy barriers for several benzaldehydes in the vapour phase are presented.

There is a considerable interest in rotational barriers around single bonds, particularly in what concerns the formyl group.¹⁻⁷ Theoretical calculations have been performed on such systems by Jost⁸ and by Drakenberg *et al.*⁷ without a great success and at the expense of a considerable amount of work. Although force field calculations⁹⁻¹¹ are becoming increasingly popular in this field, the applicability of simpler models to the study of internal rotation and conformational reorganization energy barriers continues to be investigated. Recently, Chen and Murdoch¹² have shown that the theory of Marcus¹³ can describe the energy barriers of internal rotations in several molecules.

Recently a theory was developed by Formosinho and Varandas^{14,15} that employs a general intersecting-state model (ISM) and that has been found more general than the Marcus and BEBO theories. As this theory has been successfully applied to proton transfer reactions¹⁶ and nucleophilic substitutions¹⁷ among others, we found it of interest to see whether this model could throw some light on the rotational barriers of benzaldehydes.

Theory

The theory has been described in detail^{14,15}, but we shall show here its important features. Consider the benzaldehyde and its two equivalent forms A and B, where bonds *a* and *b* are necessarily equal



One can view this internal rotation as controlled by the bond stretches of *a* and *b* followed by a free rotation around the extended bonds. The potential energy curves for distension and compression of bonds *a* and *b* can be represented by Morse curves and approximated by parabolas

depicting harmonic oscillators. In accordance with ISM the transition state for the rotation corresponds to the crossing point of the two curves,

$$(1/2) f_a x^2 = (1/2) f_b (d-x)^2 + \Delta G^0 \quad (1)$$

where f_a and f_b are the harmonic force constants of the bonds a and b , x is the extension of the harmonic oscillator corresponding to a , d is the sum of the bond extensions from a and b to the transition state and ΔG^0 is the free energy difference between conformers A and B, which in the present case is zero. The activation free energy for the rotation is given by

$$\Delta G^\ddagger = (1/2) f_a x^2 \quad (2)$$

where x is estimated from equation (1) once d is known. It has already been shown that the sum of bond extensions is proportional to the equilibrium bond lengths of a and b ^{14,15}, $d = \eta(l_a + l_b)$ where η is the reduced bond extension. This proportionality constant is related to the chemical bond order at the transition state^{14,15}, n^\ddagger , and to the configuration entropy¹⁶, λ ,

$$\eta = (a' \ln 2 / n^\ddagger) + (a' / 2) (\Delta G^0 / \lambda)^2 \quad (3)$$

where $a' = 0.156$. For conformers such as A and B, with two equivalent sites, $l_a = l_b$ and $\Delta G^0 = 0$, which gives $d = 2x$ and

$$x = (a' \ln 2 / n^\ddagger) l_a \quad (4)$$

Rotational barriers

The free energy barriers ΔG^\ddagger for the rotation of the formyl group in benzaldehydes has been determined by Drakenberg *et al.*³ and the relevant f and l data were given in references 19 and 20. In the rotation around a single bond there is no bond breaking process. So the transition state bond order is similar to the reactant, and ISM can be applied as in the spin conversion of transition metal complexes.²¹ However, studies of several kinds of reactions^{15-17,21,22} have revealed that an increase in the transition state bond order can occur due to a siphoning of electronic density from nonbonding and antibonding electrons of atoms close to the reactive bonds, which acquire a bonding character at the transition state.

The increase in n^\ddagger seems to be associated with a change from linear to nonlinear geometries of the reactive site at the transition state.^{22,23} This is not possible for the C=O group of the conformers A and B and consequently $n^\ddagger = 1$, but it can occur with the C-O group¹⁷ which resembles the configuration of the twisted molecule at $\theta = \pi$.²⁴ For this configuration the interaction of the nonbonding orbitals of oxygen with the p-orbital of the phenyl carbon is predicted to lead to $n^\ddagger = 1.5$.^{15,22,23} So one expects that for the internal rotation of benzaldehyde in the vapour phase n^\ddagger ranges between 1.0 and 1.5.

The rotational barrier for benzaldehyde in the gas phase has been determined from i.r. measurements²⁵, as well as in solution. As i.r. values are traditionally lower than nmr values, ΔG^\ddagger for the gas phase has been corrected taking into account refs. 3, 25 and 26. With the force constant and bond length data of Table 1 we obtain $n^\ddagger = 1.25$. This value can be interpreted in terms of identical contributions of the normal and twisted configurations for the transition state bond order. However, in solution nonconservation of the total bond order can be prevented by interactions of the oxygen lone-pairs with the solvent molecules, and n^\ddagger is expected to be close to 1 (vide Table 1)¹⁷.

Table 1. Transition state bond orders for rotational barriers of benzaldehydes.^a

X	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$1/A^0$ ^b	x	n	n^\ddagger
CF ₃	28.5 ^c	1.5	0.145	0.097	1.12
F	35.1 ^d	1.5	0.161	0.107	1.01
Cl	32.6 ^c	1.5	0.155	0.103	1.05
CH ₃	34.3 ^c	1.48	0.159	0.107	1.01
(CH ₃) ₂ CH	32.6 ^c	1.48	0.155	0.105	1.03
H	31.8 ^e	1.48	0.153	0.103	1.04
H (gas phase)	(19.5 ^e) 21.7 ^f	1.48	0.127	0.086	1.26

^a $f_a = 2.7 \times 10^3 \text{ kJ mol}^{-1} A^0^{-2}$, X substituent in the para position; ^b ref. 20; ^c ref. 3 (CHCl₂F/CCl₂F₂); ^d ref. 26 (CH₂Cl₂/CH₂=CHCl); ^e ref. 25; ^f corrected.

The present model is easily applied to substituted benzaldehydes, on the assumption of a constant f and l , except where stated otherwise. The results are presented in Table 1. The small substituent effects on n^\ddagger can be interpreted in terms of electronic effects of the aromatic ring on the reactive site due to resonance interactions. The Hammett σ_p correlates with n^\ddagger (Figure 1); the difference in the two correlations can be attributed to a small difference in f of the electron-withdrawing and electron-donating groups.

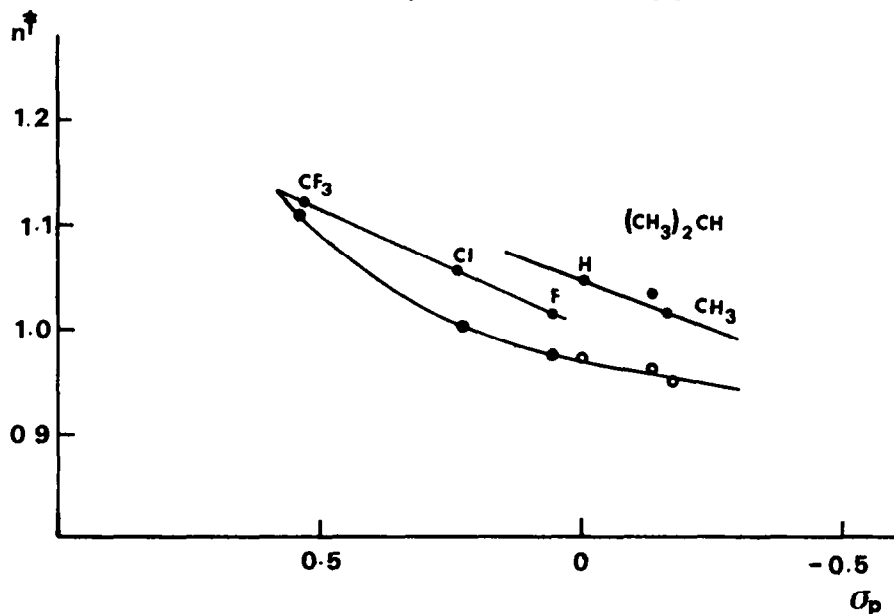
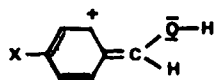


Figure 1 - Correlation between the transition state bond order n^\ddagger and the Hammett coefficient σ_p for the rotational barriers of substituted benzaldehydes (\bullet) and protonated benzaldehydes (\circ).

When benzaldehyde is protonated with "magic acid" its rotational barrier rises considerably and the value of 61.2 kJ mol^{-1} is obtained⁸ for ΔG^\ddagger . For protonated benzaldehyde a structure such as



suggests a double bond character for the reactive bond. However, rotation around a double bond involves a bond-breaking bond-forming process and, consequently, the conservation of the total bond order, $n_a + n_b = m$, leads to $n^\ddagger = m/2$; for a double bond $m=2$ and $n^\ddagger=1$.

The bond length and force constant data for a C=C bond¹⁹ produce n^\ddagger values in good agreement with theoretical predictions (Table 2). The n^\ddagger values of the substituted protonated benzaldehydes correlate with σ_p , although the correlation is nonlinear (Figure 1).

Table 2. Transition state bond orders for rotational barriers of protonated benzaldehydes.^a

X	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ ^b	x	n	n [#]
CF ₃	49.4	0.129	0.097	1.11
F	64.7	0.148	0.111	0.97
Cl	60.7	0.143	0.108	1.00
CH ₃	67.3	0.151	0.114	0.95
(CH ₃) ₂ CH	66.0	0.150	0.112	0.96
H	61.2	0.144	0.108	1.00

^a $f_a = 5.9 \times 10^3 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$, $l_a = 1.33 \text{ \AA}^0$ (ref. 19);
solvent: FSO₃H/SbF₅ in SO₂ClF. ^b ref. 8.

Table 3. Calculated rotational barriers of benzaldehydes in the gas phase.^a

X	n [#]	x	$\Delta G^\ddagger/\text{kJ mol}^{-1}$
CF ₃	1.34	0.121	19.7
F	1.23	0.132	23.4
Cl	1.27	0.128	22.0
CH ₃	1.23	0.130	22.8
(CH ₃) ₂ CH	1.25	0.128	22.0

^a f and l data as in Table 1.

Assuming that these values can be applied to the ferrocenylaldehyde ($\Delta G^\ddagger = 36.8 \text{ kJ mol}^{-1}$)⁵ we can calculate the barrier for its protonated form. The value obtained, $\Delta G^\ddagger = 70 \text{ kJ mol}^{-1}$, is of the order previously admitted,²⁷ but outside experimental confirmation.

On the other hand, the gas phase values for benzaldehyde do allow a calculation of the rotational barriers for the substituted benzaldehydes in the vapour phase (Table 3). The experimental determination of these values would help considerably in confirming the variations of the transition state bond order that arise out of certain inductive and resonance effects, associated with various atoms and groups, particularly the halogens.

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