

DETERMINATION OF THE BARRIER TO ROTATION THROUGH AN ORTHOGONAL
CONFORMATION (THE π -BARRIER) IN SUBSTITUTED STYRENES
BY DYNAMIC NMR SPECTROSCOPY.

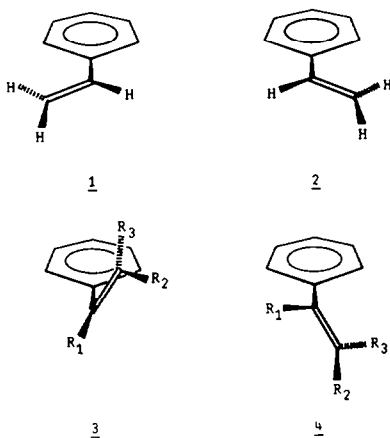
J. E. ANDERSON

Chemistry Department, University College,
Gower Street, London, WC1E 6BT, U.K.

(Received in UK 29 April 1987)

Abstract - The barrier to phenyl group rotation in *p*-dimethylaminocinnamaldehyde and *p*-methoxycinnamaldehyde is 7.3 and 6.2 kcal/mol respectively. These results are discussed in terms of the conformations of styrene and its various substituted derivatives.

Styrene appears to be planar with a barrier to rotation $1 \leftrightarrow 2$ through an orthogonal conformation (π -barrier) estimated to be 3.0 kcal/mol¹. Substitution round the central bond with as little as one methyl group changes the conformation to a non-planar one,² and this introduces the possibility of a second rotational barrier, the steric-barrier to rotation ($3 \leftrightarrow 4$) through a planar conformation.



This latter steric barrier has been much studied, for suitably large ortho-substituents, α -(geminal)-substituents, and cis- β -substituents, alone or in combination, as in for example 5 - 8, see Table 1, produce barriers large enough to be measured by dynamic nmr spectroscopy,³⁻⁶ and even by racemisation of chiral atropisomers e.g. 9, as in the classic work of Adams.⁷ Table 1 shows typical barrier values.

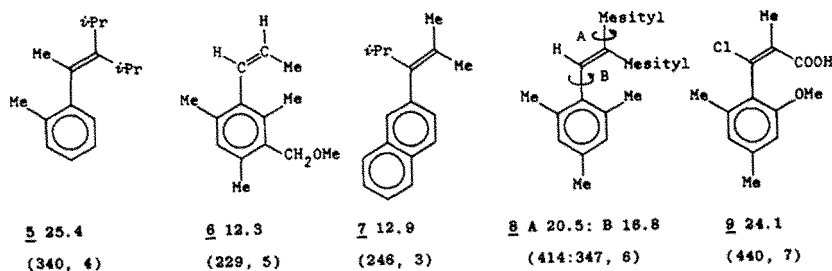
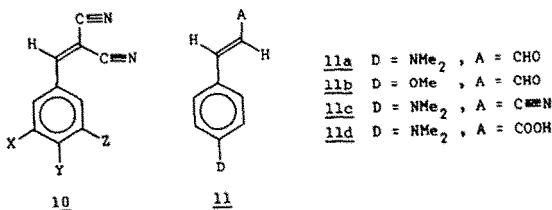


Table 1 Steric Rotational Barriers for Compounds 5 - 9 (kcal/mol). The parentheses contain the temperature of the barrier measurement and the literature reference.

The parent styrene molecule is the only case where rotation of a planar compound through an orthogonal transition state has been considered, although an interesting intermediate series of molecules of the benzylidenemalononitrile type 10 has been reported.⁸⁻¹³ These seem to be non-planar, but have substantial π -barriers to passage through an orthogonal transition state. The discussion contains some comments on the results for these molecules.

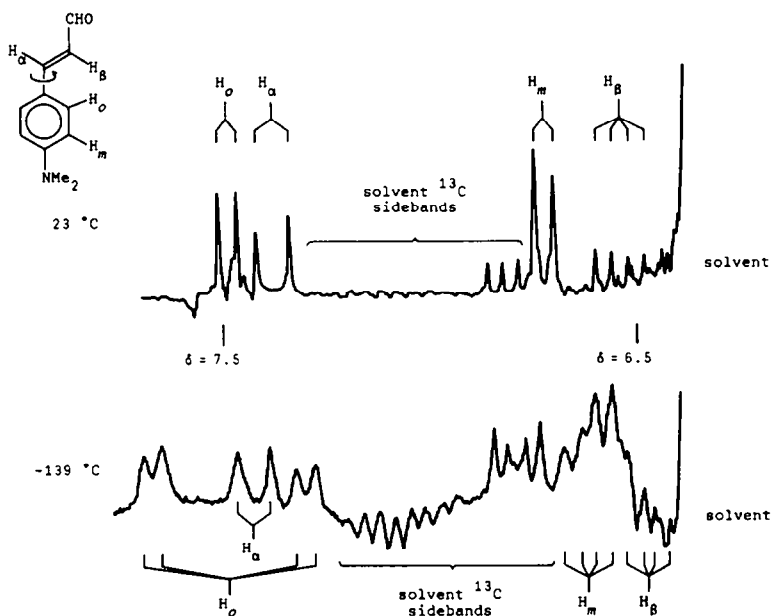
The styrene π -barrier is too low for measurement by dynamic nmr spectroscopy for which technique the practical limit is between 4 and 5 kcal/mol. I now want to report dynamic nmr measurements of π -barriers for suitably substituted planar styrenes.



The origin of the π -barrier is the loss of conjugation between the benzene and ethylene parts of the molecule when these become orthogonal, so any substitution which enhances the conjugation should lead to a higher barrier. Substituents which diminish the conjugation should be avoided. I therefore chose to examine molecules with no ortho-, α -, or cis- β -, substituents which disfavour coplanarity, but with electron releasing substituents in the benzene ring and electron attracting substituents in the trans- β -position.

Results and Discussion

The four substituted styrenes studied were the cinnamic compounds 11a-11d. The proton nmr spectrum of p-dimethylaminocinnamaldehyde 11a in very dilute solution in vinyl chloride, see Figure, shows an AA'BB' spectrum for the aromatic protons, which superficially resembles two doublets, see Figure 1. As the temperature is lowered below about -100° , these doublets broaden and below about -113° they split and appear as an ABMN spectrum, superficially four equal doublets, see also Table 2. The two ortho-protons are now different from each other on the nmr timescale (as are the two meta ones), yet no other signal shows significant changes. Similar changes at rather lower temperatures are observed for p-methoxy cinnamaldehyde, (11b, except that the spectrum appears as an ABNM' at low temperatures). See Table 2. p-Dimethylaminocinnamalonitrile 11c shows no significant spectral changes at -140° (aside from those that could be attributed to diminishing solubility at these temperatures). p-Dimethylaminocinnamic acid 11d was not sufficiently soluble in vinyl chloride (or other solvents) at low temperatures to allow

Figure 1: Downfield Region of ^1H nmr spectrum of 11a.

an investigation of what is expected to be a very low barrier.

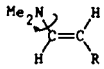
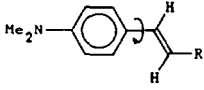
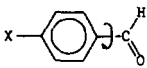
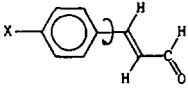
Table 2 NMR Data for *para*-Substituted Cinnamic Compounds, *p*-R-phenyl- $\text{CH}=\text{CH}_2$ -X

Compound	R	X	Chemical shifts (δ), multiplicity, and coupling (Hz)						
			H-C=O	H_β	H_α	H_m to R	H_o to R	Methyl	
<u>11a</u>	-NMe ₂	-CHO	9.63 d 8.0	6.53 dd 8.0 16.1	7.37 d 16.1 7.32 (-140° 7.69)	7.49 ~d 8.2 6.69 6.77	6.73 ~d 8.2	3.02	
<u>11b</u>	-OMe	-CHO	9.67 d 7.8	6.63 dd 7.8 15.3	7.46 d 15.3 7.64 (-145° 7.33)	7.58 ~d 8.3 6.98	6.98 ~d 8.3	3.85	
<u>11c</u>	-NMe ₂	-C≡N		5.46 d 16.8	7.23 d 16.8	7.28 ~d 8.8	6.62 ~d 8.8	3.00	

The changes in the nmr spectrum of 11a and 11b indicate that rotation of a planar styrene molecule through an orthogonal transition state like $\underline{1} \rightleftharpoons \underline{2}$, has become slow on the nmr timescale. A barrier to rotation of 7.3 kcal/mol at -118° can be calculated for 11a, and one of 6.2 kcal/mol at -141° can be calculated for 11b. The barrier in 11c is less than 6.5 kcal/mol, and probably at least 1 kcal/mol less, since no kinetic broadening was observed.

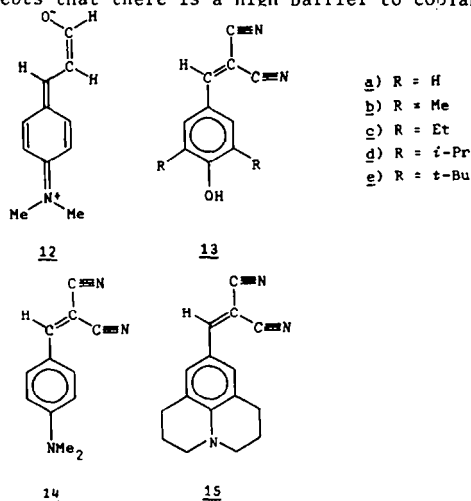
These results indicate that the dimethylamino-substituent is a better donor than a methoxy one, and that an aldehyde group is a better acceptor than a nitrile, quite in keeping with previous investigations,^{14,15} see Table 3.

Table 3 Effect of Substituents on Rotational Barriers (kcal/mol).

	Barrier		Reference
	R = -CHO	R = C≡N	
	14.7	12.9	14
	7.3	< 6.5	This work
	10.6	8.7	15
	7.3	6.2	This work

The push-pull picture of enhanced conjugation implies that the aldehyde-ethylene bond should have as much double bond character as the phenyl-ethylene bond, see 12. Hindered rotation about the former bond might therefore be detectible. We looked for broadening or doubling of the aldehyde proton signal down to low temperatures (about -150°), but in no case did we see evidence of rotation slow on the nmr timescale. The barrier to rotation must therefore be less than about 6 kcal/mol or alternatively, one conformation about the bond in question must be much more stable than any other.

There have been several recent publications on conformations and rotational barriers in compounds of type 10 which merit comment in the light of the present results. The nmr spectrum of 13b¹¹ and 13c¹⁰ show changes with temperature in the signal of hydrogens *ortho* to the olefin substituent, quite analogous to those in 11a and 11b. Similarly Safarzadeh-Amiri¹² has observed like behaviour in malononitriles 14 and 15. The interpretation of these results has been confused by earlier CNDO/2 calculations⁸ which suggest that the ground state of 13b has an angle of $\sim 40^{\circ}$ between the two planar parts, that there is a barrier of about 18 kcal/mol to passage through a coplanar conformation, and a much smaller barrier to rotation through an orthogonal one. *ab initio* (STO3G) Calculations are reported⁹ to suggest a ground-state conformation with an interplanar angle of $\sim 60^{\circ}$ and a barrier to rotation through the plane of 38 kcal/mol. All experimental evidence suggests that the results of these calculations are far-removed from reality, and that insofar as they have influenced the interpretation of the nmr results for 13, 14 and 15, these interpretations are less than satisfactory. Safarzadeh-Amiri's interpretation of his results is reasonable except that he accepts that there is a high barrier to coplanarity.

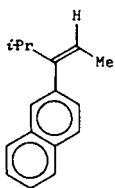


The ground-state conformation of 13 - 15 has the two planes either coplanar or near-to-coplanar with a small barrier to passage through the plane, small in terms of the timescale of nmr used to observe these compounds.

The evidence for this is as follows. A X-ray diffraction study of 13e shows a coplanar structure.¹³ This does not necessarily carry over to solution, but it suggests that there could be such a structure in solution and certainly does not agree with the barrier to a coplanarity of 18 - 38 kcal/mol, suggested by calculations.^{8,9} In spite of statements to the contrary there is nothing in the nmr spectrum of 13a - 13e as reported, which opposes a coplanar or near to coplanar conformation as ground state. These nmr data show only that there is a substantial barrier to rotation through an orthogonal conformation. If on the other hand there were a high barrier to rotation through a planar conformation clear evidence of this should come from the spectra of 13c and 13d, which are known.⁹ When rotation is slow on the nmr timescale (and a barrier of 18 kcal/mol implies this should be so at room temperature), the methylene protons of the ethyl groups in 13c and the isopropyl methyl groups in 13d are diastereotopic and should give separate signals in the nmr. The nmr spectra of these compounds have not been reported explicitly, but the point is so cardinal that one can infer that diastereotopicity is not observed.

On the contrary, Safarzadeh-Amiri shows¹² that the two protons of any CH₂-group in 15 are equivalent in the nmr at room temperature and implicitly at -94°. This suggests a maximum value of 8 kcal/mol for the through-the-plane rotational barrier, and there is nothing to suggest that the barrier is not very much less than that value.

There is further indirect evidence to support a planar or near-to-coplanar conformation for 13 - 15. Styrene is known to be coplanar.¹ An electron releasing substituent para and a trans electron withdrawing substituent should enhance the stability of a planar conformation. The only structural feature in 13 - 15 which disfavours a coplanar conformation is the cis---cyano group, which has a steric interaction with an ortho-hydrogen in a coplanar conformation. Bond-angle distortion and rotation of the two planes relative to each other can reduce this interaction but the latter movement will be opposed by the diminution of the very substantial conjugation. Measurements and calculations on 1-vinylnaphthalene, a reasonable comparison for the destabilising steric interactions in 13 - 15, suggest a rotation of about 30° out of the plane and a small 1 or 2 kcal/mol barrier to rotation through the plane.¹⁶



16

Styrenes with rather more substantial interfering substituents on the ethylene than a single cyano-group have been shown to have low barriers to rotation through the plane. The compound 16 with a methylgroup and an isopropyl groups has a barrier³ of only 5.2 kcal/mol. A single cis-cyano group with additional donor-acceptor substituents stabilising the transition state for rotation (i.e. the coplanar form) should lead to a much lower barrier.

All this direct and indirect evidence can be set against the calculations, and suggests that the ground state conformation for 11a - 11d is coplanar, while for 13 - 15 it is near-to-coplanar with a small steric barrier to rotation through the plane. There are much larger π -barriers in the range 6 to 8 kcal/mol to rotation through an orthogonal conformation, which arise from the loss of conjugative stabilisation compared with the ground state.

There is thus a range of styrene structures from coplanar through slightly skewed to strongly skewed, with corresponding high to low degrees of conjugative interaction and steric crowding around the central bond varying in the opposite sense. The transition state conformation for the most sterically crowded cases is near the ground state for the conjugated cases and vice versa.

Experimental

Compounds 11a - 11d were obtained from Aldrich (11a, 11c, 11d) and Lancaster Synthesis (11b),

and examined without purification as very dilute (0.01 M) solution in vinyl chloride solvent in a sealed tube. Deuterated methylene chloride and tetramethylsilane were used as lock and chemical shift references respectively. Rotational barriers refer to observed coalescence temperatures in nmr spectra recorded at 200 MHz operating frequency (Varian XL200 spectrometer), when it is assumed that $k_{\text{rotation}} = \pi \cdot \delta\nu / \sqrt{2}$ where $\delta\nu$ is the relative chemical shift of the two signals for H₂ or H₆ of the styrene.

References

- 1) J.M. Hollas, H. Musa, T. Ridley, P.H. Turner, J.H. Weissenberger, and V. Fawcett, J. Mol. Spec., (1982), 94, 437
- 2) A recent discussion of the evidence for this is given in reference 3.
- 3) J.E. Anderson, D.J.D. Barkel, and C.J. Cooksey, Tetrahedron Lett., (1983), 24, 1077.
- 4) I. Pettersson and U. Berg., J. Chem. Res.(S), (1984), 208.
- 5) C.S.C Yang and R.S.H. Liu, Tetrahedron Lett., (1973), 4811. The ΔG^* value quoted is based on data reported in this reference.
- 6) S.E. Biali and Z. Rappoport, J. Org. Chem., (1986), 51, 2245.
- 7) R. Adams and J.W. Mecorney, J. Amer. Chem. Soc., (1945), 67, 798. The barrier quoted was derived in reference 3.
- 8) K. Yoshikawa, N. Kumazawa, H. Terada, and K. Akagi, Int. Journ. Quant. Chem., (1980), 18, 539.
- 9) K. Yoshikawa, N. Kumazawa, H. Terada and M. Ju-ichi, Bull. Chem. Soc. Japan, (1981), 64, 1108.
- 10) K. Yoshikawa and H. Terada, J. Amer. Chem. Soc., (1982), 104, 7644.
- 11) H. Terada, N. Kumazawa, N. Ju-ichi, and K. Yoshikawa, Biochem. Biophys. Acta, (1984), 767, 192.
- 12) A. Safarzadeh-Amiri, Canad. J. Chem., (1984), 62, 1895.
- 13) M. Itoh, Y. Tanimoto, and Y. Iitaka, J. Chem. Phys., (1978), 69, 816.
- 14) T. Drakenberg, J. Sommer, and R. Jost, J. Chem. Soc. Perkin II, (1980), 363.
- 15) A. Mannschreck, and U. Kolle, Tetrahedron Lett., (1967), 863.
- 16) J.E. Anderson, D.J.D Barkel, and J.E. Parkin, J. Chem. Soc. Perkin II, in press.