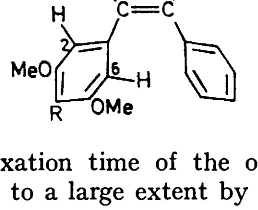
Conformation of *cis*-Stilbene and Some Derivatives studied by Nuclear Magnetic Relaxation Measurements

By **Frank Heatley,* Michael K. Cox,** and **Anne Jones,** Chemistry Department, University of Manchester, Manchester M13 9PL
Brian Jacques, Pharmacy Department, Portsmouth Polytechnic, Portsmouth

The spin–lattice relaxation times and nuclear Overhauser enhancements (NOE) have been measured for the olefinic protons of *cis*-stilbene and a few derivatives in dilute solution in $CDCl_3$. The results confirm the propeller conformation suggested previously on the basis of the electronic spectrum. The angle of twist is in the range 20—40°.

THE conformation of *cis*-stilbene is the result of a compromise between π-orbital resonance, which favours a conformation with the two aromatic rings and the olefinic bond all coplanar, and steric interaction of *ortho*-protons which favours the conformation with both aromatic rings perpendicular to the plane of the olefinic bond. Previous theoretical calculations[1] and experimental studies of u.v. spectra[2,3] have suggested that this conflict is resolved in the form of a propeller conformation of C_2 symmetry in which the aromatic rings are rotated by *ca.* 30° from the plane of the olefinic bond. Direct evidence for this structure is lacking however, and it is the purpose of this paper to fill this gap.

Noggle and Schirmer[4] have shown how measurements of spin–lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE) can provide quantitative details of molecular structure, and many applications have been reported.[5,6] We have made such measurements on *cis*-stilbene and two derivatives (I) and (II) in order to determine the conformation of the aromatic rings.



(I) R = OMe
(II) R = H

The relaxation time of the olefinic proton (H_α) is determined to a large extent by intramolecular dipolar

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[1] H. Stegenmeyer and W. Rapp, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 1165.

[2] D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1965, **87**, 5340.

[3] H. Suzuki, *Bull. Chem. Soc. Japan*, 1960, **33**, 379, 389.

[4] J. H. Noggle and R. E. Schirmer, ' The Nuclear Overhauser Effect,' Academic Press, New York, 1971.

[5] R. Rowan, J. A. McCammon, and B. D. Sykes, *J. Amer. Chem. Soc.*, 1974, **96**, 4773.

[6] R. T. Brown, F. Heatley, D. Moorcroft, and J. A. Ladd, *J.C.S. Chem. Comm.*, 1973, 459.

interactions with the *ortho*-protons. This contribution, designated $T^{\mathrm{d}}_{1\alpha}$, is given by equation (1) where γ_{H} is the

$$1/T^{\mathrm{d}}_{1\alpha} = \gamma_{\mathrm{H}}^{4}\,\hbar^{2}\,\tau_{\mathrm{c}}\,(1/r^{6}_{\alpha 2} + 1/r^{6}_{\alpha 2}) \qquad (1)$$

^{1}H magnetogyric ratio, $\hbar$ is Planck's constant divided by 2π, $r_{\alpha 2}$ and $r_{\alpha 6}$ are the internuclear distances, and τ_{c} is the correlation time for molecular rotation, assumed isotopic. Thus if $T^{\mathrm{d}}_{1\alpha}$ and τ_{c} can be measured, the distances $r_{\alpha 2}$ and $r_{\alpha 6}$ can be determined and hence the conformation of the aromatic ring.

In practice there are other contributions to proton relaxation, such as other intramolecular dipolar interactions, solute–solute and solute–solvent intermolecular interactions, and interactions with paramagnetic impurities. Lumping these other sources into an 'external' relaxation time $T^{\mathrm{x}}_{1\alpha}$, the measured relaxation time $T_{1\alpha}$ is given by: $1/T_{1\alpha} = 1/T^{\mathrm{x}}_{1\alpha} + 1/T^{\mathrm{d}}_{1\alpha}$. $T^{\mathrm{d}}_{1\alpha}$ and $T^{\mathrm{x}}_{1\alpha}$ can be separately determined by measuring the NOE[4] of H_α when the *ortho*-protons are completely saturated. Defining the NOE factor η_α in the usual way by $\eta_\alpha = (I_{\mathrm{d}} - I_{\mathrm{o}})/I_{\mathrm{o}}$ where I_{d} and I_{o} are the H_α signal intensities with the *ortho*-protons saturated and not saturated respectively, then for ^{1}H–^{1}H interactions equation (2) applies. τ_{c} can be obtained from the ^{13}C spin–lattice

$$\eta_\alpha = T_{1\alpha}/2T^{\mathrm{d}}_{1\alpha} \qquad (2)$$

relaxation times of ^{13}CH groups by measuring the contribution from dipolar interaction with protons. This is given by equation (3) where the sum is over the various C–H distances in the molecule. In the majority of

$$1/T^{\mathrm{d}}_{1\mathrm{C}} = \gamma_{\mathrm{C}}^{2}\,\gamma_{\mathrm{H}}^{2}\,\hbar^{2}\,\tau_{\mathrm{c}}\,\Sigma 1/r^{6}_{\mathrm{CH}} \qquad (3)$$

molecules, this contribution is the only significant one and moreover for ^{13}CH groups it is dominated by the interaction with the directly bonded proton. It can easily be separated if necessary from other relaxation sources by measuring the ^{13}C NOE factor (η_{c}) when the protons are saturated. η_{c} is related to $T^{\mathrm{d}}_{1\mathrm{C}}$ and the overall ^{13}C relaxation time $T_{1\mathrm{C}}$ by $\eta_{\mathrm{c}} = 1.988T_{1\mathrm{C}}/T^{\mathrm{d}}_{1\mathrm{C}}$.

EXPERIMENTAL

^{1}H and ^{13}C spin–lattice relaxation times were determined at 100 and 25.14 Mhz respectively on a Varian Associates XL-100 fourier transform n.m.r. spectrometer using the standard π–τ–$\pi/2$ pulse sequence. ^{13}C NOE factors were obtained in the Fourier transform mode from the ratio of the intensity with the protons completely noise-decoupled to the intensity with the decoupling irradiation set 30 kHz off-resonance and in the continuous wave mode. ^{1}H NOE factors were obtained with the spectrometer in the continuous wave mode by comparing the integrals of spectra recorded first with the decoupling field set on the protons to be irradiated and then with the decoupling field set an equal offset on the order side of the peak being recorded.

ca. 10% (w/w) Solutions in CDCl$_3$ were used for ^{13}C measurements, and 1% (*cis*-stilbene) and 5% [derivatives (I) and (II)] for ^{1}H measurements. All solutions were degassed and sealed *in vacuo*.

RESULTS AND DISCUSSION

The ^{13}C spectra of all compounds showed the appropriate number of peaks, assuming that rotation of the aromatic rings was rapid enough to make the two *ortho*- and two *meta*-positions in each ring equivalent on average. The chemical shifts were in no way remarkable, and a complete assignment was not made especially in view of the fact that for each compound the ^{13}C spin–lattice relaxation times for all ^{13}C–H groups were identical within experimental error. This observation establishes that the molecular rotation is isotropic and therefore all dipolar relaxation mechanisms have the same correlation time. Furthermore the ^{13}C relaxation times were independent of concentration in the range 4—10% w/w. The correlation time is therefore independent of concentration and can be transferred without correction from ^{13}C data for the more concentrated solutions to ^{1}H data for the more dilute solutions.

For all solutions η_{c} was found to lie in the range 2.0 ± 0.1. The ^{13}C relaxation times are therefore determined entirely by intramolecular dipolar interaction with protons. The major interaction is with the directly bonded proton but a small contribution arises from more distant protons, amounting to 4% in *cis*-stilbene and 1.5% in the derivatives (I) and (II).

This has been taken into account when evaluating the rotational correlation times which are listed in Table 1 together with the ^{13}C relaxation times. The geometry used to calculate internuclear distances is given in Figure 1, and is taken from published data on *trans*-stilbene.[7]

TABLE 1

Relaxation times, NOE factors, and correlation times in CDCl$_3$ solution at 30°

Compound	$T_{1\alpha}$/s	η_α	$T_{1\mathrm{C}}$/s	$10^{12}\tau_{\mathrm{c}}$/s
cis-Stilbene	10.5 ± 0.5	0.095 ± 0.01	6.0 ± 0.4	8.6 ± 0.6
(I)	6.0 ± 0.3	0.36 ± 0.05	1.1 ± 0.1	48 ± 4
(II)	5.6 ± 0.3	0.34 ± 0.05	1.4 ± 0.1	36 ± 3

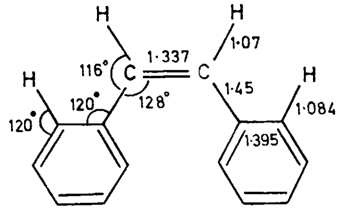

FIGURE 1 Geometry used for *cis*-stilbene: bond lengths in Å

The ^{1}H n.m.r. spectra of *cis*-stilbene and some derivatives have been discussed at length elsewhere.[8] In *cis*-stilbene itself, the olefinic protons lie 0.7 p.p.m. upfield of the aromatic protons which themselves lie very close together, and it is straightforward to measure the relaxation times and Overhauser enhancements. The spectra

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[7] 'Tables of Interatomic Distances,' ed. L. E. Sutton, Special Publication No. 11, The Chemical Society, London, 1958, Supplement 1962.

[8] H. Guesten and M. Salzwedel, *Tetrahedron*, 1967, **23**, 173.

of the two other derivatives described here are rather different from *cis*-stilbene, though similar to each other. The spectrum of (1) is shown in Figure 2. The H_α proton here is downfield of the aromatic C_6H_5 protons, presumably because of the nitro-group, while the *ortho*-protons are well removed from the C_6H_5 protons to high field. The ^1H relaxation data is also given in Table 1. The two derivatives give high values for η_α, indicating that H_α relaxation is due mainly to the interaction with the *ortho*-protons. η_α for *cis*-stilbene is much lower however because of mutual relaxation of the two H_α protons in close proximity.

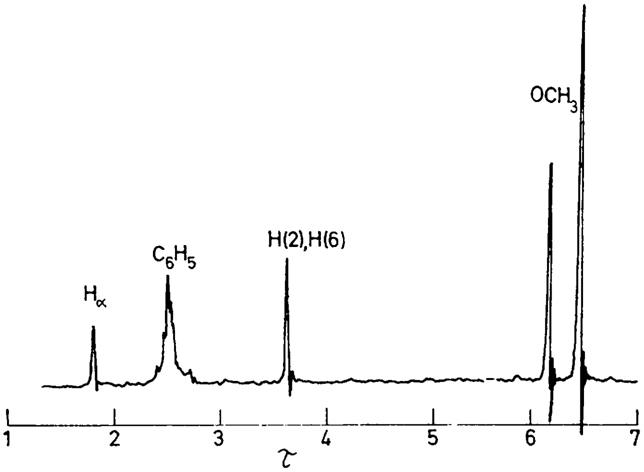

FIGURE 2 ^1H N.m.r. spectrum of compound (I) at 100 MHz in $CDCl_3$ solution

To determine the conformation of the aromatic rings, we have chosen to calculate $T_1{}^d$ expected for various propeller conformations using the correlation times in Table 1 and the geometry in Figure 1, and compare these values with the experimental value calculated using equation (2). The results are shown in Table 2. For *cis*-stilbene, there is reasonable agreement for rotations in the region 30—40°. This agrees well with the 30°/30° propeller conformation suggested by Beveridge and Jaffe [2] and the 28°/28° conformation suggested by Suzuki,[3] both based on u.v. spectra combined with MO calculations. A higher estimate of 50° was given by Stegenmeyer and Rapp [1] based on semi-empirical potential energy calculations. We have also calculated the non-bonded interaction potential energy using potential functions given by Abraham and Parry [9] and Warshel and Lifson.[10] Taking the conformation with both rings perpendicular to the olefinic bond (90°/90°) as zero energy, then according to Abraham and Parry's functions, the non-bonded interaction energy increases to 30 kJ mol^{-1} at the 30°/30° conformation and to 6 kJ mol^{-1} at 40°/40°. Warshel and Lifson's functions give energies of 80 and 16 kJ mol^{-1} for the 30°/30° and 40°/40° conformations respectively. It is obvious that calculations of this type cannot give the angle of rotation with any precision. However steric interactions of this magnitude can easily be accommodated by resonance stabilisation which it is estimated can contribute 50 kJ mol^{-1} or so for rotations of 30—40°.

TABLE 2

Experimental and calculated values of $T_{1\alpha}^d$

Compound	$T_{1\alpha}^d$ (exp)	T_1^d (calc)				
		0°	10°	20°	30°	40°
cis-Stilbene	56 ± 10	35	37	40	45	60
(I)	8.4 ± 1.5	6.8	7.2	7.7	8.7	11.7
(II)	8.5 ± 1.5	8.7	9.2	9.8	11.1	15.0

For the derivatives (I) and (II), the results in Table 2 favour rotation angles for the substituted ring of only 10—20°, a good deal lower than for *cis*-stilbene. A possible explanation for this is that the most favourable electron delocalisation involves donation of electrons into the π-system by the methoxy-groups and withdrawal by the nitro-group. This would lead to a greater partial double bond character of the bond linking the substituted ring and the olefinic group, and therefore a lower rotation ring and the olefinic group, and therefore a lower rotational angle for this ring. The C_6H_5 ring would in consequence be forced by steric repulsion into a greater degree of rotation than *cis*-stilbene, but there is no way of checking this point by the methods employed here.

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[9] R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1970, 539.

[10] A. Warshel and S. Lifson, *J. Chem. Phys.*, 1970, **53**, 582.