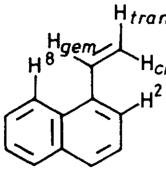
Conformations and Internal Rotation of Simple 1-Alkenylnaphthalenes, studied by Dynamic Nuclear Magnetic Resonance Spectroscopy, Nuclear Overhauser Effects, and Molecular Mechanics Calculations

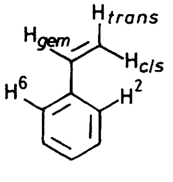
J. E. Anderson,* D. J. D. Barkel, and J. E. Parkin
Chemistry Department, University College London, Gower Street, London WC1E 6BT

A wide range of proton–proton nuclear Overhauser effects have been measured for 1-naphthylethylene and its *gem*, *cis*, and *trans* monomethyl derivatives, and the mean interplane angle in each case is determined. The rotational barrier in the α,β,β-trimethyl derivative is 14.3 kcal mol^{-1}, determined with the help of a chiral shift reagent. The MMP2 program is used to calculate a four-minima potential energy diagram for all these molecules. The measured rotational barrier is reproduced well, while mean interplane angles derived from the n.O.e. measurements agree well with the mean interplanar angle derived from calculations of stable conformations.

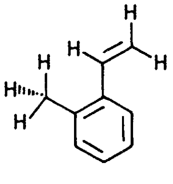
α-Naphthylethylene (**1**) is a simple analogue of styrene (**2**), in which the *peri*-interaction replaces one of the *ortho*-interactions. For styrene, the consensus of opinion is that the aromatic ring and the alkene double bond are coplanar in the ground state.[1] Conjugation diminishes, but not very steeply, as the two systems rotate away from coplanarity and there is a barrier of 2—3 kcal mol^{-1} to rotation through an orthogonal conformation.



(**1**)



(**2**)



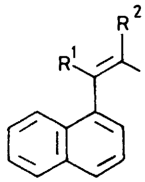
(**3**)

In a planar structure (**2**), the H_{gem} to 6-H distance appears from models to be about 2.4 Å, the sum of two hydrogen van der Waals radii. The H_{cis} to 2-H distance is about 1.8 Å, so there is some repulsive interaction. This, with the barrier,[1] suggests that the stabilising conjugation interaction of the two planar systems is somewhat greater than 3 kcal mol^{-1}.

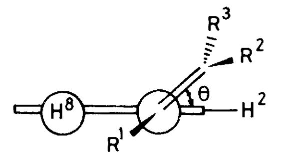
ortho-Substituents on the benzene ring or α- and *cis*-β-substituents on the alkene in styrene introduce destabilising interactions in the planar conformation but ultraviolet,[2] photoelectron,[3,4] and Raman[5] spectroscopic studies suggest that rotation away from the planar conformation to reduce these interactions is quite small. In *ortho*-methylstyrene (**3**), α-methylstyrene, and *cis*-β-methylstyrene the interplane angle appears[4,5] to be 30—40° which undoubtedly represents some residual conjugation. Even 2,6-dimethylstyrene (θ 59—68°) and *cis*-β-(t-butyl)styrene (θ 72°) are not orthogonal.[4,5]

A coplanar representation of 1-naphthylethylene (**1**) is more congested than styrene and appears to be much like *o*-methylstyrene (**3**). Both the u.v.[6] and photoelectron[7] spectrum of (**1**) suggest however that there is some remaining conjugation between the two π-systems.† More highly substituted naphthyl alkenes (**4**), for example 1-(1-naphthyl)cyclopentene, are unstable in any near-to-coplanar structure, and do not show conjugation between the two parts.[6]

The key feature of the structure of such alkenes is the angle θ, [see (**5**)], between the alkene and naphthalene planes. We report in this paper the conformations and rotational barriers for 1-naphthylethylene (**1**), its three derivatives with one methyl group on the ethylene (**6**)—(**8**), and the trimethyl derivative (**9**). The two planar conformations (**4**) and (**10**) (θ = 0 and 180° respectively) should have maximum steric interactions, but as a counterbalance, maximum conjugative stabilisation. Except for very large substituent R^1, (**10**) will be the less stable of these two, so rotation through (**10**) will be much less likely than through (**4**).

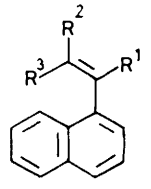


(**4**)

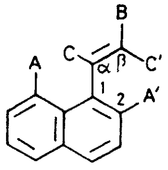


(**5**)

(**6**) R^1,R^3 = H , R^2 = Me
(**7**) R^1,R^2 = H , R^3 = Me
(**8**) R^1 = Me, R^2,R^3 = H
(**9**) R^1 = R^2 = R^3 = Me



(**10**)



(**11**)

In the orthogonal conformation (θ 90° ≡ θ 270°), both steric interactions and conjugative stabilisation should be minimised, so a composite potential energy diagram for rotation as in Figure 1 should obtain, the energy values and angles θ for maxima and minima depending on the nature of groups R.

There are four stable conformations (X, X′, Y, and Y′) during a complete rotation. Owing to the symmetry about the θ 180° and θ 0° points these are enantiomeric pairs, so it is sufficient to discuss the system in terms of the 0—180° diagram. There are thus two different kinds of minimum energy orientations (X and Y), and there will be a Boltzmann distribution of molecules between these two minima. We will make the simplifying

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† We have not investigated this matter[6] experimentally, but our calculations suggest that conjugation is reduced to zero only for a dihedral angle of 90°.

Table 1 Proton chemical shifts (δ) for the compounds (**1**) and (**6**)—(**9**). See (**1**) for labelling scheme

Compound	H_{gem}	H_{trans}	H_{cis}	2-H	8-H	Other ArH	Me
(**1**)	7.48	5.51	5.82	7.62	8.12	7.87, 7.81, H_4, H_5 ~7.5 others	
(**6**)	7.17		6.21	7.50	8.14	7.81, 7.71, H_4, H_5 ~7.45 others	1.93 (*trans*)
(**7**)	6.91	6.04		7.35	8.00	7.85, 7.86, H_4, H_5 ~7.48 others	1.76 (*cis*)
(**8**)		5.43	5.09	7.34	8.11	7.79, 7.87, H_4, H_5 ~7.5 others	2.22 (*gem*)
(**9**)				7.20	7.75	7.4, 7.9 others	1.39 *cis* 1.93 *gem* 2.02 *trans*

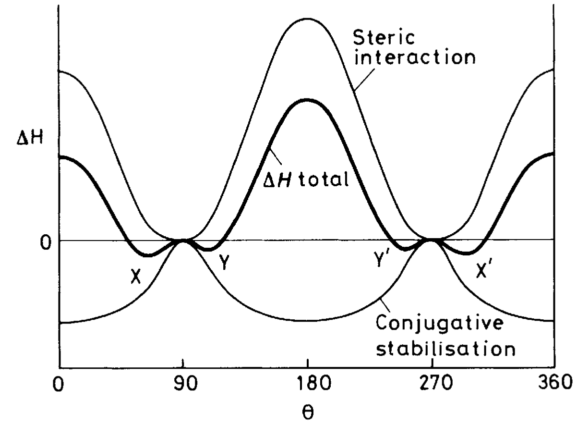


Figure 1. Diagrammatic representation of the variation of conjugative stabilisation and steric destabilisation with interplanar angle for styrene (**2**)

assumption that these minima are symmetrical so that the population at $\theta_{min.} + \delta\theta$ is balanced by an equal population at $\theta_{min.} - \delta\theta$. The real populations near to these minima are thus considered as averaging to the local minimum.

We have shown elsewhere[8,9] that the n.m.r. spectra of more highly substituted compounds (with R^1 = ethyl, *etc.*) are temperature-dependent, indicating that rotation is becoming slow on the n.m.r. timescale. During the course of these studies we found that nuclear Overhauser effects on the proton spectrum are particularly useful for indicating the relative interplane angle of the two parts of the molecule. For compounds (**1**), (**6**), (**7**), and (**8**), however, rotation of the alkene group is rapid with respect to the n.m.r. timescale at all accessible temperatures so any n.m.r. property measured will reflect the weighted average of the different kinds of conformation X and Y.

How n.O.e.s are applied to such problems is simply explained.[10] If a proton C relaxes between its nuclear spin energy levels by nuclear dipole–dipole interaction with two protons A and B among others, then the intensity of the signal C will be enhanced if it is observed while irradiating at the frequency of A or B. The relative magnitude of the enhancements $E\{A\}$ and $E\{B\}$ varies as the inverse sixth power of the distance of C from A and from B. Structure (**11**) shows two such examples, and if the B,C distance can be estimated from model compounds, the n.O.e. measurements should allow a determination of the sixth root mean of the A,C distance. This can be related to the mean angle θ between the planes by assuming reasonable structural parameters, as discussed in detail in the Experimental section. We have measured n.O.e. values between groups within the alkene, and at the 2- and 8-position in the naphthalene ring, A, B, C, and A′, B′, C′ in (**11**).

Allinger[11] has recently published a revised force field program MMP2 for computing the energies of structures with interactions between π-systems. We have used this to calculate the potential energy diagram for rotation of the ethylene group in (**1**), (**6**)—(**8**), and (**9**) and to compute the two stable kinds of conformations X and Y suggested in Figure 1. These results are compared with our experimental conclusions. For (**9**) we have measured a barrier to rotation and MMP2 was used to predict and determine in some detail the structure and energy of the rotational transition state. The calculations also provided a good estimate of the variation of interproton distances with the rotational angle θ for the various compounds. This was needed to relate the relative magnitudes of significant nuclear Overhauser effects to the average rotational angle between the alkene and naphthalene planes.

Results

N.M.R. Measurements.—Table 1 shows proton chemical shift data for the compounds (**1**), (**6**), (**7**), (**8**), and (**9**). Table 2 shows all n.O.e. values measured; of these the most significant are as follows.

1-*Naphthylethylene* (**1**). There are n.O.e. enhancements to H_{cis} of 17.3 and 4.5% from H_{trans} and 2-H respectively. This suggests that the 2-H to H_{cis} distance is 2.35 Å and θ = 38°. There are n.O.e. enhancements to H_{gem} from H_{trans} and 8-H respectively, the latter being considerably the larger. Since the H_{gem} signal overlaps several aromatic proton signals, the relative n.O.e.s could not be measured accurately.

trans-1-*Naphthylprop*-1-*ene* (**6**). There are n.O.e. enhancements to H_{gem} of 12.7 and 13.7% from Me_{trans} and 8-H respectively. If the methyl group adopts a conformation with one hydrogen eclipsing the double bond, this suggests that the H_{gem} to 8-H distance is 2.10 Å and that θ = 43°.

cis-1-*Naphthylprop*-1-*ene* (**7**). There are n.O.e. enhancements to H_{gem} of 12.8 and 11.8% from H_{trans} and 8-H respectively. This suggests that the 8-H to H_{gem} distance is 2.43 ± 0.06 Å, and depending on the assumed geometry, that θ = 65 ± 5°.

gem-1-*Naphthylprop*-1-*ene* (**8**). There are n.O.e. enhancements to H_{cis} of 32.5 and 3.4% respectively from H_{trans} and 8-H respectively. This suggests that the 8-H to H_{cis} distance is 2.74 Å and that θ = 114°.

Other n.O.e. values measured for these compounds and shown in Table 2 give qualitative support to these determinations. In particular, relative n.O.e. values at 2- and 8-H, when H_{cis} or H_{gem} is irradiated, vary among the compounds in a way which agrees well with the values of θ determined above.

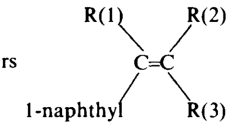
Some relatively large negative n.O.e. effects are reported but can invariably be interpreted as the indirect type,[10] that is the decrease in population difference (negative n.O.e.) observed at D is the consequence of a marked enhancement of population

Table 2. Proton–proton nuclear Overhauser enhancements (%) observed in the compounds (**1**), (**6**), (**7**), and (**8**). Structure (**1**) shows the labelling scheme

Signal irradiated	Signal observed/ Compound	2-H	8-H	H_{cis}	H_{trans}	H_{gem}	Me	Other
H_{cis}	**(1)**	2.7	*a*	*b*	5.9	−0.8	*b*	
	(6)	13.6	*a*	*b*	*b*	3.5	1.8	
	(8)	3.3	4.6	*b*	33.0	*b*	*a*	3-H, −0.5
H_{trans}	**(1)**	−2.1	*a*	17.3	*b*	2.8	*b*	
	(7)	0.6	*a*	*b*	*b*	12.8	2.1	
	(8)	*a*	*a*	32.5	*b*	*b*	1.5	
H_{gem}	**(1)**	*a*		*a*	*a*	*b*	*b*	
	(6)	*a*	19.0	6.3	*b*	*b*	2.8	
	(7)	1.4	9.2	*b*	7.0	*b*	1.1	other ArH, 1.0
2-H	**(1)**	*b*	*a*	4.5	*a*	*a*	*b*	
	(6)	*b*	*a*	*a*	*a*	*a*	*a*	
	(7)	*b*	*a*	*a*	1.0	−1.0	0.5	
	(8)	*b*	*a*	1.0	−0.3	*a*	0.3	
8-H	**(1)**	*a*	*b*	−1.1	*a*	8.5	*b*	7-H, 11.6
	(6)	*a*	*b*	1.1	*a*	13.7	*a*	7-H, 14.0
	(7)	*a*	*b*		−1.9	11.8	*a*	7-H, 5.3
	(8)	*a*	*b*	3.4	1.5		2.4	7-H, 7.0
Me	**(6)**	−3.4	−1.7	21.8	*b*	12.6	*b*	4-H, 0.8
	(7)	6.0	3.4	*b*	8.5	*a*	*b*	5-H, 1.2
	(8)	8.6	9.6	−2.9	7.6	*b*	*b*	3-H, −0.5

[a] No effect was observed. [b] Entries which have no physical or chemical meaning.

Table 3. MMP2 Calculations of naphthylethylenes ground-state geometry and rotational barriers



Naphthalene All R = H except:	Value of θ in ground-state conformation/°	Value of θ in other stable conformations and its relative energy (kcal mol⁻¹)		Magnitude of barrier relative to ground state (kcal/mol⁻¹)			Calculated weighted mean minimum angle/°	Experimental mean angle/°
				0°	180°	90°		
(**1**) Parent none	30	140	1.34	0.42	4.59	3.18	41	38
(**6**) *trans* R(2) = CH_3	32	133	1.45	0.45	4.59	2.95	42	43
(**8**) *gem* R(1) = CH_3	53	130	0.02	7.05	5.83	1.20	91	114 (49, 131. See text)
(**7**) *cis* R(3) = CH_3	49	120	0.55	4.39	5.67	1.34	69	65
(**9**) All R = CH_3	110	70	0.13	14.04—14.79		0.34	92	

difference (strong positive n.O.e.) at B due to irradiation of A. For (**8**) and (**9**) some long-range positive n.O.e.s particularly to aromatic hydrogens other than 2- or 8-H from the alkene, or from 2- or 8-H to H_{trans} were observed. In these cases the planes are near to orthogonal, and the groups in question are relatively near in space.

Dynamic N.M.R.—At −40 °C, the methyl region of the spectrum of (**9**), when recorded in the presence of a chiral shift reagent[12] and a silver salt,[13] shows three methyl signals at δ 1.37, 1.88, and 1.94, the middle one of which is a doublet, δv 4.2 Hz at 200 MHz. On raising the temperature, the doublet broadens and coalesces at *ca.* −10 °C to a singlet. This corresponds to a rotational barrier of 14.3 kcal mol⁻¹ at 263 K.

Molecular Mechanics.—Figure 2 shows the potential energy diagram for rotation of the alkene group for the compounds (**1**), and (**6**)—(**9**) generated by driving the C(2)–C(1)–C(α)–C(β) dihedral angle θ through 180°. Table 3 reports important values on the diagram. For each compound there is a rather flat-bottomed minimum on either side of θ 90°. In the unsubstituted compound it is calculated that the minimum with θ at about 30° is more stable by 1.34 kcal mol⁻¹. Substitution either with a *gem* or a *cis* methyl group makes the $\theta > 90°$ minimum relatively less disfavoured with respect to the $\theta < 90°$ minimum, and in (**9**) with both *cis* and *gem* substituents, the minimum with $\theta > 90°$ is calculated to be more stable.

The 0 and 180° values are no doubt near representations of the rotational transition states, although driving the C(2)–C(1)–C(α)–C(β) dihedral angle is an unrealistically clumsy way of approaching the transition state in the case of (**7**), (**8**), and (**9**). For these three, this state is likely to occur when a methyl group (rather than the β-carbon) passes through the plane. This point was investigated in more detail for the trimethyl compound (**9**), with its measured barrier of 14.3 kcal mol⁻¹. There ought to be two potential maxima of different magnitude when the *gem*-methyl and the *cis*-methyl in turn pass through the plane.

The 11.30 kcal mol⁻¹ barrier calculated for (**9**) by driving the C(2)–C(1)–C(α)–C(β) dihedral angle to coplanarity is unrealistic since both interfering methyl groups are still far displaced on either side of the naphthalene plane. The state where Me_{gem} and C(β) are both held in the plane suggests a barrier of 16.72 kcal mol⁻¹, but both need not pass through the plane simultaneously. Relaxing the β-carbon from this point while holding the geminal methyl in the plane leads to a barrier of 14.73 kcal mol⁻¹, and a

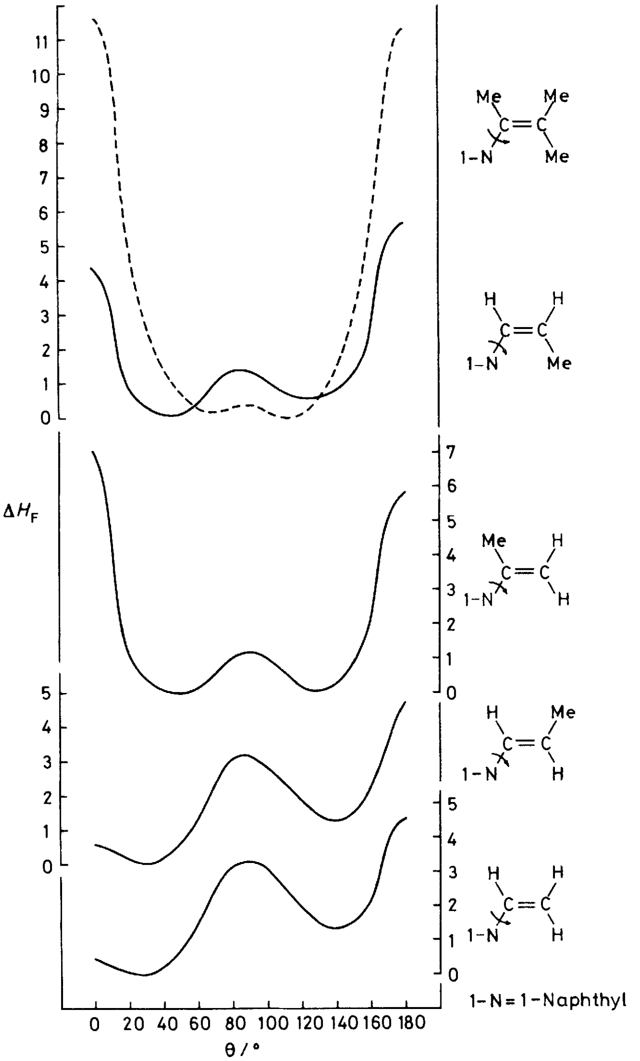


Figure 2. Rotational potential (kcal mol^{-1}) calculated by molecular mechanics for various alkenylnaphthalenes (4)

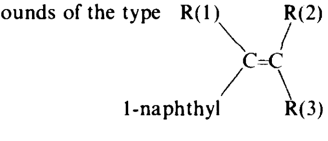
structure with the *cis*-methyl *ca.* 20° out of the plane. The state where the *cis*-methyl is in the plane as well as the β-carbon suggests a barrier of 14.04 kcal mol^{-1}, with the *gem*-methyl about 23° out of the plane. Driving the β-carbon out of the plane from here so as to drag the *gem*-methyl towards the plane, suggests a barrier of 15.39 kcal mol^{-1}, an unrelaxed equivalent of the 14.73 kcal mol^{-1} value found earlier.

More detailed exploration of the transition state did not seem worthwhile except to note that passing the *cis*-methyl by the 8-position involves a much higher barrier.

Discussion

Calculation and experiment agree to suggest that in its ground state unsubstituted 1-naphthylethylene, unlike styrene, is non-planar, with about 35° between the two parts. This is much as *o*-methylstyrene is, and emphasises the similarity between the *peri*-interaction and an *ortho*-interaction with a methyl group. Some conjugative stabilisation is thus being given up to offset the *peri*-interaction. As is to be expected, a broadly similar result is observed for the *trans*-methyl compound (**6**). The methyl substituent has no significant interaction with the naphthalene ring.*

Table 4. Barriers/kcal mol^{-1} to 1-naphthyl-group rotation through the θ = 0° conformation (**4**), for compounds of the type



R(1)	R(2)	R(3)	Barrier	Reference
H	H	H	0.42 (Calc.)[a]	This work
Me	H	H	5.83 (Calc.)	This work
Et	H	H	<7.0 (Exptl.)	8
Pr^i	H	H	11.5 (Exptl.)	8
H	Me	H	0.45 (Calc.)[b]	This work
H	H	Me	4.39 (Calc.)	This work
Me	Me	Me	14.73 (Calc.)	This work
			14.3 (Exptl.)	This work
Et	Me	Me	25.8 (Exptl.)	8
Pr^i	Me	Me	>30 (Exptl.)	8

[a] For this compound there are higher calculated barriers of 3.18 kcal/mol^{-1} to passage through the θ = 90° conformation and of 4.59 kcal/mol^{-1} to passage through the θ = 180° conformation. [b] For this compound there are higher calculated barriers of 2.95 kcal mol^{-1} to passage through the θ = 90° conformation and of 4.59 kcal mol^{-1} to passage through the θ = 180° conformation.

A *cis*-methyl substituent introduces steric interactions towards the 2-position, which along with the *peri*-interaction causes even greater rotation away from planarity to an interplanar angle of 65°. Again, calculation and experiment agree well. With a *gem*-methyl substituent, the *peri*-interaction in a planar state is much increased, and calculations suggest that two conformations with θ 53 and 130° are comparably stable. A conformation with θ 114° is the one which on its own best explains the observed nuclear Overhauser effect, which does not agree very well with the calculated values or their mean. Since calculation suggests two conformations of nearly equal population, we reinterpreted the observed n.O.e. assuming equal populations of two conformations. Noting the symmetry of the calculated potential curve around 90°, we assumed there were minima at $(90 + x)$ and $(90 - x)°$, then found that a value of $x = 41$ best fits the observed n.O.e. value. There is perhaps fortuitously good agreement between the calculated minima of 53 and 130°, and those of 49 and 131° derived from the experimental measurement by this means.

It is gratifying how calculations and n.O.e. measurements, interpreted with reasonable assumptions, suggest similar pictures for the stable conformation. One can credit with some confidence the calculated rotational potential, and the indications of how two different conformations contribute to the average. As for barriers, the parent naphthylethylene and the *trans*-methyl compound have a very low (0°) steric barrier, and rotation through 90° with the loss of conjugation is in fact more difficult. For the compounds with a *gem*-methyl group or a *cis*-methyl group, there is a fairly high steric barrier to rotation, probably just below the practical n.m.r. limit of 5 kcal mol^{-1}. It is notable that the geminal compound probably prefers a 180° transition state, while all others prefer a 0° transition state. For the trimethyl compound (**9**), the measured and calculated barriers agree perhaps fortuitously well, and calculations give indications of small differences between the two likely transition

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* This is perhaps a deceptive simplification. While the best current knowledge is that styrene is planar,[1] *E*-stilbene has an angle of 30—32° between the aromatic and the alkene planes.[14] Insofar as there is no convincing explanation why styrene and *E*-stilbene should contrast thus, we cannot confidently claim that (**1**) and (**6**) should behave identically.

states. These results for (**1**), (**6**), (**7**), (**8**), and (**9**) agree well with what is already known of barriers in slightly more substituted cases,[8,9] as Table 4 shows, and confirm the earlier observation that small changes in substitution can raise barriers dramatically.

One of the more striking points about the calculated rotational energy diagram shown in Figure 2 is how relatively flat the profile is away from the coplanar interfering arrangements, particularly for the more substituted compounds. Conjugation becomes a rather small perturbation on steric effects in such cases. Although two minima X and Y persist, a wide range of states around these minima will be populated.

We conclude that in favourable cases, of which this is one, where interacting groups are within van der Waals radius contact, and spectra are relatively simple, proton–proton n.O.e. values are large and give reasonable quantitative estimates of internuclear distances. If a suitable reference distance is available then, as in the present case, the conformation may be defined therefrom. For the present series of compounds, the MMP2 program gives a credible picture of the ground-state conformations and the rotational profile.

The proton chemical shifts (Table 1) of the compounds studied might be expected to reflect the changes in conformation suggested by the n.O.e. results. For (**7**) and (**8**) whose ethylene protons H_{gem} and H_{cis} should be far removed from the aromatic plane and its deshielding influence, upfield shifts are indeed observed.[14] The 2- and 8-H hydrogens also show an upfield shift in these molecules, which agrees with their being in the shielding zone of a more or less orthogonal alkene group. For the trimethyl compound (**9**), shielding* of 2- and 8-H and Me_{cis} is more marked than in any other compound, in agreement with the near orthogonal ground-state conformations.

Experimental

N.m.r. spectra were measured on a Varian XL200 or a Bruker WP400 spectrometer. Solutions were degassed using freeze–pump–thaw techniques. For n.O.e. experiments protons were preirradiated for 30 s, followed by a 90° pulse without irradiation. N.O.e. values used to calculate θ were the result of 60 s preirradiation. The 60 s values were not significantly different from 30 s values. A control experiment was created with irradiation away from any signal, and a difference spectrum was obtained by subtraction. This was usually repeated several hundred times. Line broadening of 2 Hz was used. Spectra were recorded in absolute intensity mode, and n.O.e. values were determined directly from peak heights appropriately corrected for recorder scale.

Certain n.O.e. values were used to calculate the mean distance between H_{gem} or H_{cis} and 2-H or 8-H, and thence the interplane angle θ.[10] It was assumed that there is an inverse sixth power relationship between internuclear distances and the equivalent n.O.e. value. This appears to be valid[16] as long as there is no direct n.O.e. from H_{trans} to the naphthalene protons or *vice-versa*. Only for (**9**) was such a direct effect observed, a small 1% enhancement at 2-H. The calculation of θ in this compound was based, however, on the n.O.e. on irradiation at 8-H. Table 2 shows the complete set of n.O.e. values determined.

The uncertainty in the reported values of θ is *ca.* + 5%; ideally the two n.O.e. values used to determine an internuclear distance should be large and of similar magnitude. This was not true to the same extent in each of the compounds reported here. At different points on the rotation cycle, small changes in the internuclear distances we have exploited can have small or large effects on the value of θ.

Compounds (**1**), (**6**), (**7**), and (**8**) are all well known;[17] (**6**) and (**7**) were separated and all were purified by g.l.c. Compound (**9**) was prepared by dehydrating the tertiary alcohol obtained by refluxing 1-naphthyl-lithium and methyl isopropyl ketone, in toluene with anhydrous copper sulphate.[18] It should be noted that in certain cases, although not the present one, some isomerisation to the equivalent 2-naphthylethylene takes place when this dehydration method is used. There resulted a mixture of (**10**) and the isomeric 2-(1-naphthyl)-3-methylbut-1-ene[8] (Found: C, 91.65; H, 8.35. $C_{15}H_{16}$ requires C, 91.78; H, 8.22%). Preparative g.l.c. separation gave pure (**10**) (Found: M^+, 196.1255. $C_{15}H_{16}$ requires *M*, 196.1252).

References

1 That styrene is planar is not proven, but seems to be the best explanation for the not-completely-consistent evidence available. This is discussed by J. M. Hollas, H. Musa, T. Ridley, P. H. Turner, K. H. Weissenberger, and V. Fawcett, *J. Mol. Spectrosc.*, 1982, **94**, 437.

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* Allowance should be made for the intrinsic substituent effect of the methyl group, but even after this is done,[15] upfield shifts persist.