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1,3,5-Trineopentylbenzene and Related 1,3,5-Trialkylbenzenes Containing Groups with Both Steric and Conjugative Effects. ^{1}H NMR Band Shape and ^{13}C Spin Lattice Relaxation Time Measurements and Force Field Calculations

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2,4,6-Trialkylsubstituted styrenes, benzaldehydes and *N*-methylbenzaldimines were studied by the ^{1}H NMR band shape and ^{13}C spin lattice relaxation time techniques. The results were in most cases found to be well reproduced by molecular mechanics calculations with the Allinger MMP1 and MMP2 programs. In the case of 2,4,6-trineopentylstyrenes, it was found that a *cis*-β-vinylic methyl group is responsible for the high barrier to internal rotation (74 kJ mol^{-1}) observed. The compound with a *trans*-β-vinylic methyl group has a barrier (<20 kJ mol^{-1}), of similar magnitude to that of 2,4,6-trineopentylstyrene itself. For the benzaldehydes and *N*-methylbenzaldimines, an upper limit to the barrier of <20 kJ mol^{-1} in all cases was estimated by ^{13}C spin lattice relaxation time measurements. A model involving free diffusion in a restricted range was used to calculate internal correlation times from T_1 data. The influence of librational motions on rotational barriers from spin lattice relaxation time measurements is discussed.

Internal rotation in the 1,3,5-trineopentylbenzene (TNB) system has been extensively studied in our laboratories,[1a–n] both experimentally by ^{1}H and ^{13}C MR band shape and spin lattice relaxation methods, and with the aid of molecular mechanics (MM) calculations.[1h,k,m] These studies have included $C_{sp^3}-C_{sp^2}$ (aryl) (neopentyl group)[1a–m] and $C_{sp^3}-C_{sp^3}$(*t*-butyl group)[1e,m] rotations, and have provided insight into the nature of steric effects in the TNB system. For example, the operation of *attractive* steric effects among the t-butyl groups[1g,h,k] was proposed to explain observed (NMR) rotamer ratios in several TNB's, and support for such an interpretation was gained from MM calculations,[1h,k,m] and from a crystallographic investigation on 2,4,6-tribromo-TNB.[1n]

The molecules hitherto studied have almost all contained substituents with predominant *steric* effects, except for a few nitro- and acyl-substituted compounds.[1c–f,i] TNB's with substituents *in conjugation* with the aromatic ring system are of course expected to reflect the operation of both steric and resonance effects, usually working in opposite directions. The preferred conformation of unhindered styrenes, aromatic ketones, aldehydes and aldimines is one in which the vinyl, carbonyl or carbimino group and the aromatic ring are coplanar.[1i,2a] Greater and greater deviations from coplanarity are expected to occur as the effective size of the ortho substituents increases.[1i,2b,c,e,3a] Dahlberg *et al.*[1i] observed large effects on estimated free energies of activation ($\Delta G^{\neq}$) for neopentyl group rotation when acyl groups ranging in size from acetyl to pivaloyl were introduced into the TNB ring: For 2-acetylTNB the estimated $\Delta G^{\neq}$ was 46 kJ mol^{-1}, whereas for 2-pivaloylTNB it was >96 kJ mol^{-1}. In this work, we have extended the series of TNB:s containing groups in conjugation with the aromatic ring, to include vinyl and substituted vinyl groups. In addition, to gain more insight

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Table 1. ^{13}C chemical shifts (in ppm) relative to TMS for some vinyl, formyl, and *N*-methylformylalkylbenzenes (see text) at 28 °C. Solvent $CDCl_3$.

Compound	C-α	C-1	C-2(6)	C-3(5)	C-4	Other
1[a]	136.8	137.5	126.0	128.4	127.6	C-β=113.3
2	137.9	137.2	137.2	131.2	137.2	C-β=121.0, *o*-CH_3=*p*-CH_3=23.7
3	123.0	127.6	142.8	125.2	135.2	C-β=134.2, *trans*-C-γ=19.6, *cis*-C-γ=25.3 *o*-CH_2CH_3=27.2, *p*-CH_2CH_3=27.2, *o*-CH_2CH_3=15.2, *p*-CH_2CH_3=15.4
4	138.6	138.2	136.6	131.4	136.3	C-β=119.2, *o*-CH_2tBu=46.0, *p*-CH_2tBu=50.1, *o*-$CH_2C(CH_3)_3$=33.5, *p*-CH_2-$C(CH_3)_3$=32.2, *o*-$CH_2C(CH_3)_3$=*p*-$CH_2C(CH_3)_3$=30.0
5	135.8	136.7	137.0	131.1	136.3	C-β=129.3, *trans*-C-γ=18.4, *o*-CH_2tBu=46.0 *p*-CH_2tBu=50,1 *o*-$CH_2C(CH_3)_3$=33.5, *p*-$CH_2C(CH_3)_3$= 32.1, *o*-$CH_2C(CH_3)$=*p*-$CH_2C(CH_3)_3$=29.5
6	126.1	132.8	137.0	131.0	136.5	C-β=135.5, *trans*-C-γ=19.3, *cis*-C-γ=25.0, *o*-CH_2tBu=46.3, *p*-CH_2tBu=50.2, *o*-$CH_2C(CH_3)$=33.3, *p*-$CH_2C(CH_3)_3$=32.0, *o*-$CH_2(CH_3)_3$=*p*-$CH_2C(CH_3)_3$=29.7
7	192.1	136.0	129.5	128.8	134.3	—
8	192.5	135.4	141.2	130.3	143.6	*o*-CH_3=20.2, *p*-CH_3=21.4
9	192.3	130.2	147.7	127.7	149.8	*o*-CH_2CH_3=26.7, *p*-CH_2CH_3=28.8, *o*-CH_2CH_3=16.5, *p*-CH_2CH_3=14.4
10	194.7	130.3	150.2	121.5	153.5	*o*-$CH(CH_3)_2$=28.8, *p*-$CH(CH_3)_2$=34.7, *o*-$CH(CH_3)_2$=24.3, *p*-$CH(CH_3)_2$=23.8
11	194.4	136.1	141.2	133.4	142.8	*o*-CH_2tBu=44.4, *p*-CH_2tBu=50.1, *o*-$CH_2C(CH_3)_3$= 32.9, *p*-$CH_2C(CH_3)_3$=32.2, *o*-$CH_2C(CH_3)_3$=*p*-$CH_2C(CH_3)_3$=29.8
12	162.4	136.3	128.5	128.0	130.4	*N*-CH_3=48.1
13	162.4	135.6	137.3	129.1	138.6	*N*-CH_3=49.4, *o*-CH_3=20.7, *p*-CH_3=21.2
14	161.9	131.1	143.7	126.4	144.9	*N*-CH_3=49.1, *o*-CH_2CH_3=26.6, *p*-CH_2CH_3=28.0, *o*-CH_2CH_3=p-CH_2CH_3=15.7
15	162.7	131.6	146.8	120.7	149.3	*N*-CH_3=49.0, *o*-$CH(CH_3)_2$=29.5, *p*-$CH(CH_3)_2$=34.5, *o*-$CH(CH_3)_2$=*p*-$CH(CH_3)_2$=24.0
16	165.3	137.9	137.3	132.4	138.2	*N*-CH_3=50.5, *o*-CH_2tBu=45.2, *p*-CH_2tBu=50.1, *o*-$CH_2C(CH_3)_3$=33.2, *p*-$CH_2C(CH_3)_3$=32.2, *o*-$CH_2C(CH_3)_3$=*p*-$CH_2C(CH_3)_3$=29.5

[a] Solvent: acetone-d_6.

into the effects in the TNB systems, we have also included other alkyl groups in the series of 2,4,6-trialkylsubstituted styrenes, benzaldehydes and *N*-methylbenzaldimines. The following compounds were studied:

1 R=R′=R″=H
2 R=CH_3 R′=R″=H
3 R=CH_2CH_3 R′=R″=CH_3
4 R=$CH_2C(CH_3)_3$ R′=R″=H
5 " R′=CH_3 R″=H
6 " R′=R″=CH_3

7 R=H
8 R=CH_3
9 R=CH_2CH_3
10 R=$CH(CH_3)_2$
11 R=$CH_2C(CH_3)_3$

12 R=H
13 R=CH_3
14 R=CH_2CH_3
15 R=$CH(CH_3)_2$
16 R=$CH_2C(CH_3)_3$

Measurements and calculations. The ^{1}H NMR band shape method was used in the studies of compounds *3*–*6*, but only for compounds *3* and *6* could the barrier to internal rotation be estimated. For both of these cases a two-site exchange is applicable. For compound *6* the exchange is AB⇄BA and was treated as such, but for *3* the exchange is $ABX_3 \rightleftarrows BAY_3$ and was approximated as overlapping X⇄Y cases.

The ^{1}H NMR spectra were recorded on a JEOL MH 100 spectrometer, equipped with a JNM–VT–3C temperature control unit. The temperature was measured by means of a copper-constantan thermocouple, which was fixed near the receiver coil. The accuracy in these values has been found to be better than ±2 °C, and is reproducible within ±0.5 °C.[1b,e]

For all compounds, except for *3* and *6*, the ^{13}C relaxation times were measured on a JEOL FX 60 spectrometer operating in the Fourier transform mode at 15 MHz for ^{13}C. In all cases, the inversion-recovery pulse sequence was used.[4a–e]

Table 2. T_1 values ($T_{1\alpha}$, T_{1m} and T_{1p})[d], calculated correlation times (τ_α, τ_m and τ_i)[b] geometrical angles (β), angles of diffusion (θ) and calculated free energies of activation ($\Delta G^{\ddagger}_{301}$).

Compound	$T_{1\alpha}$/s	T_{1m}/s	T_{1p}/s	$\tau_\alpha/10^{-12}$ s	$\tau_m/10^{-12}$ s	β/°	θ/°	$\tau_i/10^{-12}$ s	$\Delta G^{\ddagger}_{301K}$ J$_{mol}^{-1}$	T_{1m}/T_{1p}
1	19.4 (1.0)	16.6 (0.5)	13.2 (0.6)	2.68 (0.14)	3.19 (0.10)	63	90	17.7–61.3	11.9–14.9	1.3 0.1
2	20.2 (1.0)	6.01 (0.20)	—	2.57 (0.14)	8.83 (0.29)	63	82–106	1.0	4.6	—
7	14.3 (0.6)	10.6 (0.4)	7.64 (0.5)	4.01 (0.19)	5.01 (0.20)	64.7	90	27.0–60.8	12.8–14.9	1.4 0.1
8	5.66 (0.35)	3.55 (0.23)	—	10.2 (0.7)	20.1 (1.9)	66.9	90	32.0–82.0	13.3–15.6	—
9	4.30 (0.24)	2.19 (0.10)	—	13.4 (0.7)	24.2 (1.2)	63.4	90	27.0–45.0	12.8–14.7	—
10	6.80 (0.50)	1.69 (0.07)	—	8.46 (0.72)	89.7 (3.7)	65.0	90	1.0–4.62	4.5–8.4	
11	1.43 (0.09)	0.59 (0.03)	—	40.2 (2.7)	90.0 (5.0)	65.6	90	47.0–85.0	14.2–15.7	—
12	7.45 (0.36)	6.98 (0.23)	4.60 0.33	7.72 (0.39)	7.60 (0.26)	64.7	90	[c]	[c]	1.5 0.3
13	8.79 (0.60)	3.65 (0.13)	—	6.54 (0.48)	14.5 (0.6)	66.9	90	8.2–14.5	9.9–11.3	—
14	7.70 (0.60)	2.40 (0.10)	—	7.47 (0.63)	22.1 (0.9)	63.4	90	3.6–8.5	7.8–10.0	—
15	3.80 (0.20)	1.36 (0.07)	—	15.1 (0.8)	39.1 (2.0)	65.0	90	12.6–23.0	10.9–12.4	
16	1.50 (0.20)	0.90 (0.06)	—	38.3 (5.8)	59.0 (5.7)	65.6	90	79.0–280.	15.5–18.7	—

[a] $T_{1\alpha}$, T_{1m} and T_{1p} refer to T_1 value for *α* carbon, aromatic *meta* and aromatic *para* carbon and the errors are all 3 (see text.) [b] τ_α, τ_m and τ_i are the correlation times for *α* carbon, molecular and internal correlation times resp. (se text). [c] Could not be estimated.

The 90° pulse length was 13 μs, and the time between sequences was $\geq 3 \times T_1$. All samples were degassed on a vacuum line, using three freeze-thaw cycles. The samples were prepared to 1 M concentration. The ^{13}C chemical shifts for all compounds are summarized in Table 1.

Relaxation times from ^{13}C NMR spectra were evaluated by fitting the peak intensities to an exponential function with three adjustable parameters, and are given in Table 2. The error limits found from these evaluations are 3σ, where σ is the "marginal" standard deviation as defined by Mayne *et al.*[5] For compounds *4* and *5* no reliable relaxation times could be obtained, due to severe overlap of the resonances of interest (Table 1).

The mathematical model of London and Avitabile[6] involving free diffusion in a restricted range was used to calculate internal correlation times (τ_i) from relaxation times. The free energies of activation at ambient probe temperature ($\Delta G^{\ddagger}_{301}$) were then calculated from the τ_i by means of the Eyring equation[7] (Table 2).

The formula of London and Avitabile,[6] which has been used for the relaxation in methionine, relates the spin lattice relaxation time for a ^{13}C nucleus to spectral density terms $J(\omega)$ (eqn. 1). The spectral densities are calculated from an expression including matrices that describe the restricted motion. This model considers free internal diffusion over a restricted range (from $-\theta$ to $+\theta$) about an axis making an angle β with the relevant C–H relaxation vector.

$$T_{1\alpha}^{-1} = N_\alpha \gamma_C^2 \gamma_H^2 \hbar^2 (10 r_\alpha^6)^{-1} \times [J(\omega_C - \omega_H) + 3J(\omega_C) + 6J(\omega_C + \omega_H)] \quad (1)$$

$$J(\omega) = \sum_{a=-2}^{2} \sum_{n=0}^{\infty} |d_{ao}(\beta)|^2 \, |E(a,n)| \, \tau/(1+\omega^2\tau^2)$$

$$\tau = [6D_o + n^2\pi^2 D_i (4\theta^2)^{-1}]^{-1}$$

$$\text{With } E(a,0) = \frac{\sin a\theta}{a\theta}$$

$$E(a,n\neq 0) = 2^{-\frac{1}{2}} \left[\frac{\sin (a\theta - n\pi/2)}{a\theta - n\pi/2} + (-1)^n \frac{\sin (a\theta + n\pi/2)}{a\theta + n\pi/2} \right]$$

$$6D_o = \tau_m^{-1}; \; D_i = \tau_i^{-1}$$

$$\tau_\alpha^{-1} = \mu_o^2 (4\pi)^{-2} N_\alpha \gamma_C^2 \gamma_H^2 \hbar^2 r_\alpha^{-6} T_{1\alpha}$$

$$\tau_m^{-1} = \mu_o^2 (4\pi)^{-2} N_m \gamma_C^2 \gamma_H^2 \hbar^2 r_m^{-6} T_{1m}$$

$$\mu_o (4\pi)^{-1} = 10^{-7} (NA^{-2})$$

β was taken from the MM calculations. D_o is the isotropic diffusion coefficient and D_i is the internal diffusion coefficient. London and Avitabile[6] have pointed out that the relation between D_i and τ_i is somewhat arbitrary, but we set $D_i = \tau_i^{-1}$ in accord with the convention used in our calculations of the barriers to internal rotation in TNB.[1k] θ in equation *1* is half the jumping angle (from $-\theta$ to $+\theta$), ω_C and ω_H are the resonance frequencies for the ^{13}C nucleus and the proton (rads^{-1}); $d_{ao}(\beta)$ are the reduced second rank Wigner rotation matrices, and are given elsewhere.[8] τ_α and τ_m represent the correlation times for the vinyl, formyl or formimino group motion and the overall motion, respectively. N_α and N_m are the number of protons (one) bound to the α carbon in the vinyl, formyl or formimino group and the unsubstituted aromatic carbons (in the *meta* positions) with the relaxation times $T_{1\alpha}$ and T_{1m}, respectively. γ_C and γ_H are the gyromagnetic ratios for the ^{13}C nucleus and the proton. The r_α and r_m values (*i.e.*, the carbon-proton bond distances for the α and the *meta* carbons) could be taken from the MM calculations. However, Stark, Vold and Vold[9a] have advised a corrected value of 1.114 Å for the aromatic hydrogen bond length (r_m), instead of the normally accepted 1.09 Å, because effects of vibrational averaging must be taken into account.[9b,c] The value of r_α was then corrected in a similar manner (+0.024 Å). For the *N*-methylaldimines, the same r_a and r_m values were used as for the corresponding aldehydes.

The angle θ in equation *1* was set equal to 90° for compounds *1* and *7–16*, but for compound *2* it was varied. Eqn. (1) was solved iteratively by variation of τ_i until the equation was satisfied, and the parameter n in eqn. (1) was given the range (n=0,...100). The calculations were performed on the UNIVAC 1100/80 at the Lund University Computing Center.

The equation of London and Avitabile is based on the assumption that the overall motion is

isotropic and that a dipolar mechanism for the spin lattice relaxation of the ^{13}C nucleus is dominant, due to interaction with directly bonded protons.[4a] Measurements of the nuclear Overhauser effect[4a–c] (in compounds *1,2* and *7–16*) showed that the relaxation of the α (C-α) carbon and the aromatic C-3(5) carbons is completely dominated by dipolar relaxation.

The NMR relaxation times are affected by librational motions,[10a–g] so as to give T_1-values that are longer then they would be otherwise. This in turn leads to calculated correlation times (τ_i) that are too short, and rotational barriers that are too low. The extent to which librations influence estimated T_1-values is difficult to predict, and only a few papers have dealt with this problem.[10c–g] However, in general, the lower the rotational barrier the greater the effect of librational motions, especially if the initial state is a very shallow minimum on the potential curve.

The Allinger MMP1 program[11a–h] was used to calculate the total energy (E_{Total}) for different conformations on the potential surface for internal rotation of the vinyl or formyl group in compounds *1–11* (Table 3). However, the program does not have parameters suitable for calculations on aldimines. The calculations were performed for compounds *1, 2, 4, 5* and *7–11* by driving the vinyl of formyl group 180° (in increments of 5°), around the $C_{sp^2}-C_{sp^2}$(aryl) bond from the initial state, while all other groups in the molecule were free to relax. In the calculations on compounds *3* and *6*, where experimental evidence for restricted rotation was observed, the ortho alkyl group, toward which the vinyl group was rotated, was driven to give the conformation of lowest energy (for each rotation of the vinyl group). The other two alkyl groups in the ring were free to relax. The resulting rotational barriers are the differences between the highest and lowest points on the potential curves.

During the writing of this paper, a version of the Allinger MMP2 program became available to us.[12,13] This program, which employs a refinement of the force field used in the MMP1 program, uses smaller and softer hydrogens than MMP1. The expression defining the center of the hydrogen van der Waals sphere is 0.925 (C–H bond distance) in the MMP1 program, and 0.915 (C–H bond distance) in MMP2. Thus the reduction factor has been decreased by about 1.1 % in MMP2, and the hydrogens are in effect "smal-

Table 3. Calculated total energies (E_{Total}) for different conformations along the potential curve and calculated barriers to internal rotation (ΔE_{Total}).

Compound	E_{Total} [a]/kJ mol	E_{Total} [b]/kJ mol	E_{Total} [c]/kJ mol	ΔE_{Total}/kJ mol
1	48.4	—	58.7	10.3
2	65.8	—	91.7	25.9
3	95.8	98.1	159.8	64.0
4	113.1	127.5	164.5	51.4
5	115.1	127.3	175.9	60.8
6	117.8	126.2	195.0	77.2
7	36.7	—	55.9	19.2
8	53.8	—	62.0	8.2
9	79.9	—	82.3	2.4
10	105.2	—	116.7	11.5
11	108.0	—	115.1	7.1

[a] The most stable conformer for compounds (3)–(6), (9) and (11); the conformer with all three alkyl groups on one side of the ring plane and the vinyl (formyl) group on the other side of the ring plane. [b] The conformer with one *ortho* alkyl group and the vinyl group on one side of the ring plane and the other two alkyl groups the other side. [c] The conformer corresponding to the highest point on the potential curve (see text).

ler". The reduction factors used in the MMP2 program are the same as in the MM2 program.[13] The MMP2 program was used to calculate the energy for some conformations of compounds *1*, *4–6*.

RESULTS AND DISCUSSION

Systems with vinylic groups. Styrene *1* is an extensively studied molecule, and barriers to internal rotation found in the literature show considerable variation. NMR measurements[14a] give the barrier as 6.7 kJ mol^{-1}, while microwave spectroscopic methods[2d,14b–d] give 2.1–12.3 kJ mol^{-1}, and theoretical calculations give values between 6–19 kJ mol^{-1}, depending on the method of calculation.[2a,11e,14e]

MMP1 calculations on styrene *1* give the barrier 10.3 kJ mol^{-1} (Table 3). The lowest energy conformer is calculated to have the vinyl group 30° above (below) the ring plane, and the point of highest energy occurs when the vinyl group is perpendicular to the aromatic ring, as previously reported by Allinger and Sprague.[11e] The MMP1 calculations also show that the coplanar conformer lies 3.6 $kJmol^{-1}$ above the lowest point of energy. Calculations with the MMP2 program give the barrier 17.8 $kJ-mol^{-1}$ and the lowest energy conformer when the molecule is planar. The high energy conformer is the same as found from the MMP1 calculations. The MMP2 calculations are in agreement with microwave spectroscopic results[2d,e] which also provide evidence that the conjugated conformer is the most stable for styrene. Equation *1* should therefore be applicable, and the barrier estimated from relaxation time measurements is then 11.9–14.9 kJ mol^{-1} (Table 2).

When the *ortho* protons are replaced by methyl groups, as in the case of vinylmesitylene *2*, a very low barrier to internal rotation of the vinyl group of 4.6 kJ mol^{-1} (Table 2) is found from relaxation data. In the calculations, τ_i in eqn. (1) was set equal to 10^{-12} s as a lower limit, because lowering the τ_i value below 10^{-12} s for a fixed diffusion angle θ will only have negligible effects on calculated T_1-values. θ in eqn. (1) was then varied until the equation was satisfied. The measurements show that the internal rotation in compound *2* is essentially free.

MMP1 calculations on vinylmesitylene give a barrier to internal rotation as high as 25.9 kJ mol^{-1} (Table 3), which is probably somewhat too high (*cf.* calculations on compounds *4* and *5*). The potential curve shows that the transition and initial states for vinylmesitylene *2* are not the same as for styrene *1*. For vinylmesitylene the initial state conformation occurs when the vinyl group is perpendicular to the ring plane, and the transition state when the vinyl group lies in the ring plane.

Compounds 4 *and* 5. The ^1H NMR spectra of compounds *4* and *5* in $CDCl_3$ solution at ambient temperature (28 °C) show in each case only two singlets in the ratio 2:1 (from low field) in the methylene region. The substances were therefore dissolved in $CHCl_2F$ and the temperature was lowered as far as possible (−135 °C for compound *4* and −128 °C for compound *5*). No temperature effect on the methylene region could be observed in either case.

Attempts to make use of the ASIS effect (Aromatic Solvent Induced Shift)[15] by use of *o*-dichlorobenzene *4* and hexafluorobenzene *5* gave no visible effects in the corresponding 100 MHz ^1H NMR spectra, indicating either chemical shift equivalence or low barriers to internal rotation.

As mentioned earlier, no useful information could be obtained from relaxation data on substances *4* and *5*. In the ^{13}C NMR spectrum of compounds *4* and *5*, the vinylic α carbon signal overlaps with the vinyl-substituted aromatic carbon and with the *p*-aromatic carbon signal (Table 1).

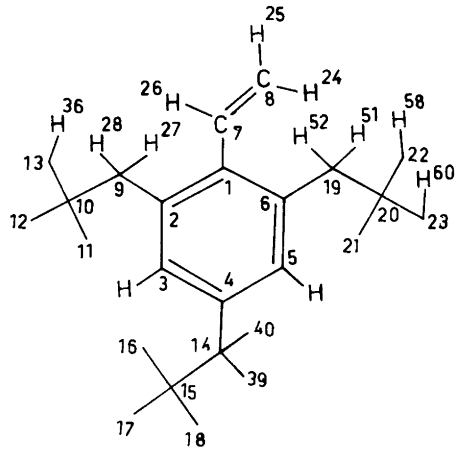


Fig. 1. Numbering in the molecular system of compound *4*.

The barriers calculated by the MMP1 program are 51.4 *4* and 60.8 *5* kJ mol^{-1} (see Table 3). The calculations show in both cases that the initial state conformation occurs when all neopentyl groups are on the same side of the ring plane (perpendicular to the ring) and the vinyl group is on the other side and perpendicular to the ring plane. The transition state conformation occurs in both cases when the vinyl group lies in the ring plane. In this conformation, one of the ortho neopentyls (in Fig. 1 the one defined by carbons 19–23) has twisted so the dihedral angle 1–6–19–20 is 85°, while the other two neopentyls remain essentially in their initial-state positions.

The barriers calculated for compounds *4* and *5* are in striking contrast to experimental results, since barriers as high as 50–60 kJ mol^{-1} would easily be observable by ^{1}H NMR (as restricted internal rotation), unless shift equivalence occurs. However, for sterically strained systems the MMP1 program has been shown to give barriers that are too high.[1m] Consequently, initial and transition states for compounds *4* and *5* were recalculated with the MMP2 program. The calculated barriers are 23.9 *4* and 18.4 *5* kJ mol^{-1}. The lower barrier for compound *5* is a result of a more strained initial state. Energy contributions ($\Delta E_x = E_x$ (transition state) − E_x (initial state)) to the calculated barrier in compound *4* are shown in Table 4 for the two programs. Table 4 shows that the greatest differences occur in the bending and the van der Waals terms (see Table 5).

Table 4. Energy contributions ($\Delta E_x = E_x$ (TS) − E_x(IS), in kJ mol^{-1}) to the barrier in compound (4) calculated by the MMP1 and MMP2 programs.

ΔE_x	MMP1	MMP2
$\Delta E_{Compress}$	6.1	4.4
$\Delta E_{Bending}$	36.8	22.9
$\Delta E_{Stretch\text{-}bend}$	1.0	0.9
$\Delta E_{van\ der\ Waals}$	28.3	20.8
$\Delta E_{Torsion}$	−20.3	−25.1
$\Delta E_{Torsion\text{-}bend}$	−0.5	[a]
ΔE_{Dipole}	0	0
ΔE_{Total}	51.4	23.9

[a] The torsion-bend term does not exist in the MMP2 program.

The differences in the van der Waals energies (Table 4) is, as pointed out above, a result of the different reduction factors for the C–H bond length (see above) used in the two programs.

Compounds 3 *and* 6. When the *cis*-*β*-vinylic proton in compound *5* is replaced by a methyl group, the methylene region in the ^{1}H NMR spectrum at ambient probe temperature consists of an AB quartet from the *o*-methylene groups superimposed on a singlet from the *p*-methylene group (Fig. 2; compound *6*). As the temperature was increased, the AB quartet broadened and coalesced at about 90 °C, and at 180 °C the methylene region consisted of two sharp singlets in the ratio 2:1. The width of the singlet due to

Table 5. Expressions and parameters used by the MMP1 and MMP2 programs in the calculations of the bending energies in compound (4).

MMP1: $E_{Bending} = 4.187\ 0.02191 k_B (\theta - \theta_o)^2 (1 - 0.006(\theta - \theta_o))$ kJ mol^{-1}
MMP2: $E_{Bending} = 4.187\ 0.02191 k_B (\theta - \theta_o)^2 [1 + 0.007 \cdot 10^{-5} (\theta - \theta_o)^4]$ kJ mol^{-1}

Angle	MMP1 θ_o(°)	MMP1 k_B(mdyn Å rad^{-2})	MMP2 θ_o(°)	MMP2 k_B(mdyn Å rad^{-2})
C_{sp^2}–C_{sp^2}–C_{sp^2}	120.0	0.60	120.0	0.43
C_{sp^2}–C_{sp^2}–H	120.0	0.24	120.0	0.36
out of plane	0.0	0.05	0.0	0.05
C_{sp^2}–C_{sp^3}–C_{sp^3}	110.2	0.38	109.5	0.45
C_{sp^2}–C_{sp^2}–C_{sp^3}	121.7	0.38	120.0	0.55
C_{sp^2}–C_{sp^3}–H	108.5	0.24	109.4	0.36
C_{sp^3}–C_{sp^3}–C_{sp^3}	109.5	0.38	109.5	0.45
C_{sp^3}–C_{sp^3}–H	108.5	0.24	110.0	0.36
H–C_{sp^3}–H	110.8	0.19	109.4	0.32

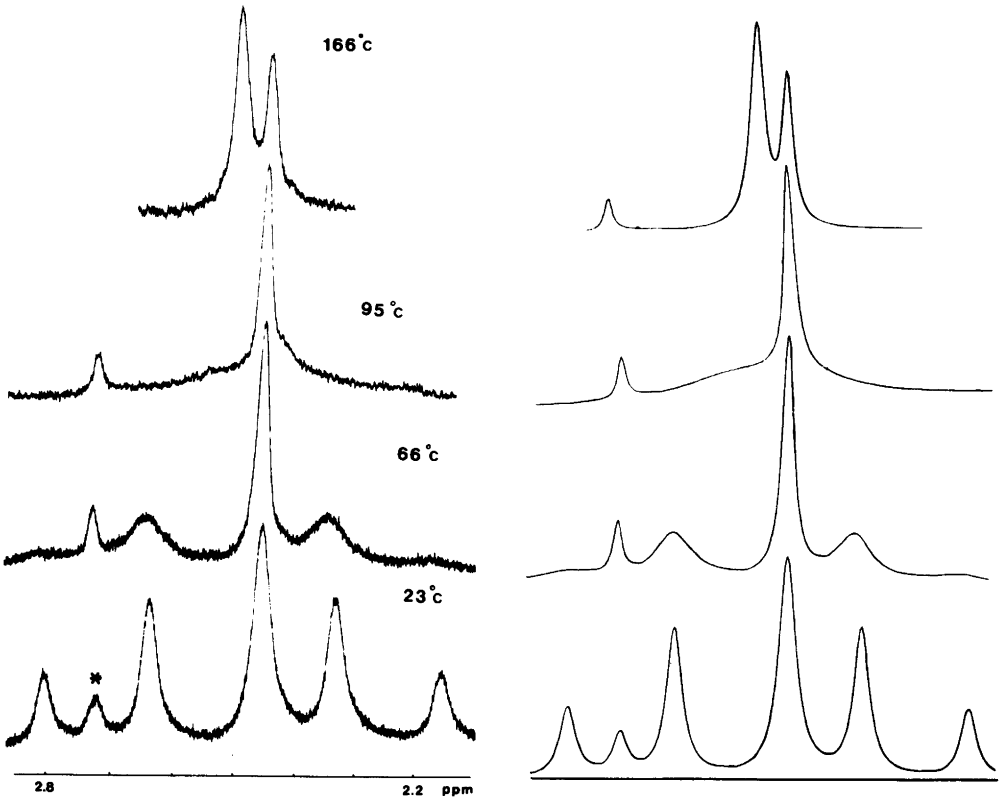


Fig. 2. Temperature dependence of the methylene region in the ^{1}H NMR spectrum of compound *6* in bromoform-d solution (left). The small extra peak (*) is due to an impurity and is included in the calculated spectra (right).

the *p*-CH_2 group was found to be independent of temperature, and a complete band shape analysis was performed (see Fig. 2), in which the *p*-CH_2 group was used as internal resolution standard. A free energy of activation $\Delta G^{\ddagger}_{298}=74\pm2$ kJ mol^{-1} could be estimated. (Statistical error, estimated from linear regression).

If the *t*-butyls in compound *6* are replaced by methyls (to give compound *3*), the methylene region will be further complicated due to spin couplings to the methyl protons. The ^{1}H NMR spectrum of compound *3* in $CDCl_3$ solution at −16 °C could be interpreted as a quartet from the *p*-methylene and a second one from the *o*-methylenes, which was further split due to the nonequivalence of the *o*-methylene protons (Fig. 3).

On increasing the temperature, peaks due to the AB part of the spectrum coalesced, and above 40 °C the methylene proton region consisted of two quartets, one from the methylene protons in the *o*-ethyl groups and the other from the methylene protons in the *p*-ethyl group. It was not feasible to decouple the methylene resonances, since this requires that two methyl resonances must be simultaneously irradiated. In order to get a reasonable estimate of the rate constant (τ^{-1}), the central peaks in the different AB spectra (denoted 1 and 2 in Fig. 3) were used for band shape analysis, involving a two-site simulation. Due to serious overlap between signals, only an approximate rate constant could be estimated (τ=0.3 s at 29 °C) which gives $\Delta G^{\ddagger}_{302}=66\pm3$* kJ mol^{-1}. (Statistical error, estimated from linear regression). MMP1 calculations on compounds *3* and *6* show the same initial state conformation as found for compounds *4* and *5*. The transition state for compounds *3* and *6*

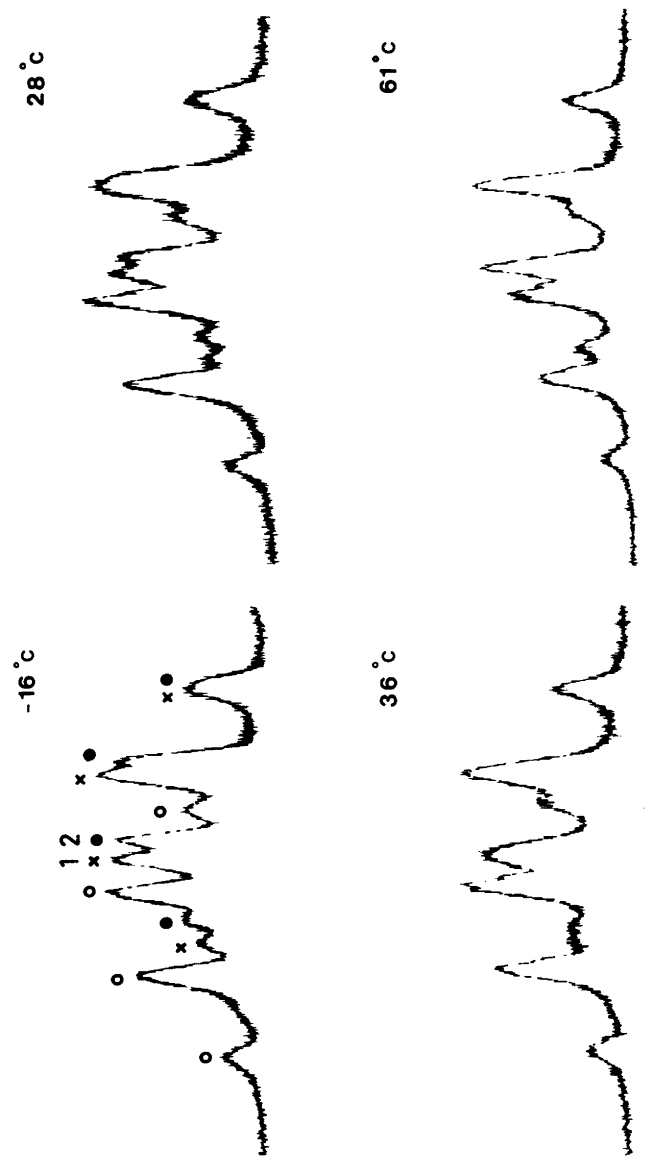


Fig. 3. The methylene region in the ^{1}H NMR spectrum of compound *3* in chloroform-d solution at different temperatures. Peaks belonging to the different AB quartets are marked (○, ●, ×) and peaks numbered 1 and 2 were used for bandshape analysis.

occurs when the vinyl group lies in the ring plane and the *ortho* alkyl, toward which the vinyl rotates, had rotated 90° from its initial state. (The 1–6–19–20 angle in Fig. 1 is 180°). Tables 3 and 6 show that there is good agreement between measured and calculated (MMP1) barriers. Initial and transition states for compound *6* were recalculated with the MMP2 program for comparison in this system, for which the MMP1 calculations are in good agreement with experimental data. The calculated barrier is 76.2 $kJmol^{-1}$ (MMP2), which is in good agreement with measurements and with the MMP1 calculations. Thus the MMP2 program leads to results that are more realistic than those obtained with MMP1, at least for hydrocarbons (*cf.* results for compounds *4* and *5*, above).

Systems with formyl groups. In performing calculations based on results from ^{13}C spin lattice relaxation measurements on compounds *7–16* (Table 2), the maximum diffusion range of the formyl group was restricted from −90° to +90° [*i.e.* θ=90° in eqn. (1)]. Barriers calculated with the MMP1 program are collected in Table 3 (Fig. 4).

Benzaldehyde *7* is the most extensively studied

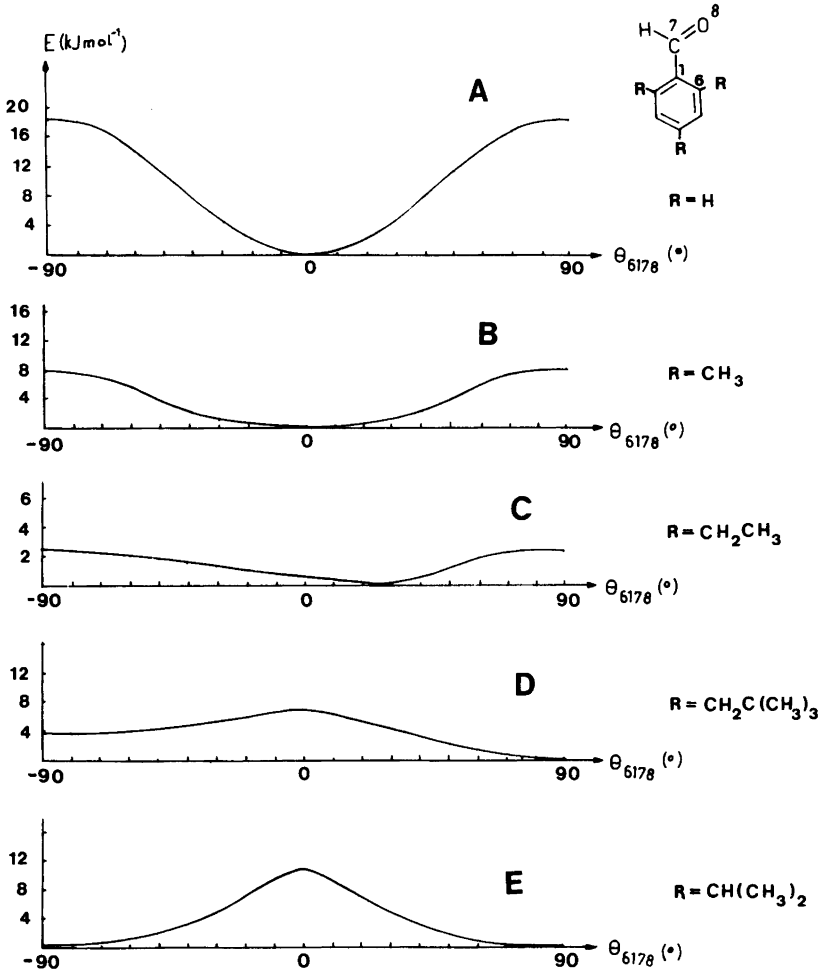


Fig. 4. Calculated potential curves for formyl group rotation in A: benzaldehyde, B: 2,4,6-trimethylbenzaldehyde, C: 2,4,6-triethylbenzaldehyde, D: 2,4,6-trineopentylbenzaldehyde and E: 2,4,6-triisopropylbenzaldehyde (for further details, see text). The dihedral angle θ_{6178} is defined so that for θ_{6178}=0° the formyl group is in the ring plane.

molecule of the aldehydes *7–11*, and the literature contains a considerable range of estimated barriers to internal rotation, depending on the method used. Microwave and infrared measurements[16a] give values in the range 19.5–20.6 kJ mol^{-1}, NMR methods[16b–d] give 31.8–33.0 kJ mol^{-1}, and calculations[2a,14e] 19.3–27.6 kJ mol^{-1}, depending on the method of calculation. The value calculated in this work for benzaldehyde (19.3 kJ mol^{-1}) is consistent with lower limit of those found in the literature, but the value estimated from ^{13}C spin lattice relaxation measurements (12.8–14.9 kJ mol^{-1}) is somewhat low.

As pointed out above, librational effects tend to increase the T_1-values, which will result in estimated barriers that are too small.[10a–d] Although the exact magnitude of the librational effect in benzaldehyde is not known, its influence will be demonstrated. Suppose we allow a librational angle of 20° (i.e. θ_{6178} in Fig. 4A varies in the range ±20°). According to Fig. 4A, an angle of 20° corresponds to an energy of 2.5 kJ mol^{-1} (equal to RT, the thermal energy avilable at room temperature, T=300 K). Inserting this angle into eqn. (1) and assuming free libration (τ_i=10^{-12} s) gives a new T_{1m} value (T_{1m}corr=11.90 s). If T_{1m}^{corr} and θ=90° are inserted into eqn. (1), a new τ_i value (=82.5 10^{-12} s) can be calculated for the absence of librational effects. The barrier to internal rotation in benzaldehyde will then be 15.6 kJ mol^{-1}, which is still low compared to other experimental estimates. The choice of a librational angle of 20° gives a decrease in rotational barrier of 12 %, which is reasonable in view of the results of Johnson,[10d] who calculated an increase of 10 % in the methyl barrier in solids in the absence of these motions. Apparently, librational motions must be taken into account when relaxation data are used to calculate rotational barriers.

Measured barriers for compounds *7–9* show no differences (within error limits), but the calculated barriers show a decrease as the *ortho* substituents change from H to Me to Et (Tables 2 and 3). MMP1 calculations show the energy profiles of benzaldehyde *7* and mesitaldehyde *8* to be rather similar in shape (curves A and B in Fig. 4). For both compounds, the initial state was calculated to be conjugated, and the rotamers with the formyl group perpendicular to the ring plane were found to be the corresponding transition states. 2,4,6-Triethylbenzaldehyde *9* also has the same transition state conformation as compounds *7* and *8*, according to the calculations, but the formyl and the three ethyl groups are on the opposite sides of the ring plane (curve C in Fig. 4). The minimum on the potential curve occurs when the formyl group is 25° above the ring plane and all three ethyl groups are on the other side of the ring plane.

The barrier to internal formyl rotation estimated for 2,4,6-triisopropylbenzaldehyde *10* is only half of that found for 2,4,6-trineopentylbenzaldehyde *11* (Table 2). However, MMP1 calculations show the opposite order (Table 3, curves D and E in Fig. 4). The order of barriers calculated may be a result of the "hard hydrogens" used in the MMP1 program. As shown earlier (compounds *4* and *5*), the MMP1 program may give barriers that are too high for sterically strained systems, and molecule *10* is the more strained since it has six benzylic methyls, while *11* only has three t-butyls. Unfortunately, the MMP2 program does not yet have suitable parameters for calculations of aromatic aldehydes.[17]

The calculations show that the initial state conformation of compound *10* occurs when the formyl group is perpendicular to the ring plane and all isopropyl groups have their methine hydrogens in the ring plane. The methine hydrogens of the two *ortho* isopropyl groups are both facing the formyl group. Calculations (MMP1) made by Ito *et al.*[18] on 2,4,6-triisopropylbenzophenone showed the same initial state, which is also in agreement with X-ray results on this compound in the solid state. Conformations in which one or none of the *ortho* methine hydrogens (still in the ring plane) faces the carbonyl group were calculated to be higher in energy by 7.9 and 9.6 kJ mol^{-1}, respectively.

The transition state for compound *10* occurs when the formyl group is conjugated with the ring and the two *ortho* isopropyls are twisted so that their methine hydrogens are on opposite sides of the ring plane. One of the methine hydrogens is 20° above the ring plane while the other is 20° below the plane.

In the initial state of compound *10*, where only the methine proton in one of the two isopropyls is facing the carbonyl group (which is perpendicular to the ring plane), there are two possible modes of formyl rotation. One involves rotation so that

the carbonyl oxygen passes a methine hydrogen, the other so that the oxygen passes two methyl groups in the other *ortho* isopropyl. Both modes of rotation are calculated to give higher barriers (18.3 and 20.2 kJ mol^{-1}, respectively) than found above.

For 2,4,6-trineopentylbenzaldehyde *11*, MM calculations show the initial state conformation to be one with the formyl group perpendicular to the ring plane, while the three neopentyl groups are on the opposite side, all perpendicular to the ring plane. The transition state conformation occurs when the formyl group lies in the ring plane, and all three neopentyl groups are on the same side of the plane as in the initial state.

Lunazzi *et al.*[2b] have studied the rotational barrier of the formyl group in a series of *ortho* monoalkyl substituted benzaldehydes, where the *ortho* substituent was H, Me, Et, iPr or tBu. For the first four of these compounds, the rotational barrier was found to decrease from 32.2 to 27.1 to 26.9 to 24.7 kJ mol^{-1}. This trend was explained by Lunazzi *et al.*[2b] as follows: when the *ortho* substituent increases in size, the initial state deviates more and more from the planar conformation, while the transition state is unchanged, which makes the barriers decrease.

Our relaxation data (Table 2) on the aldehydes *7–10* show essentially the same trend. The trend found by Lunazzi *et al.* shows greater differences than our relaxation data, but their measurements were performed by ^1H NMR band shape at low temperatures (<−130 °C) and in another solvent (CHF_2Cl). The value of the barrier measured for 2,4,6-trineopentylbenzaldehyde *11* is very close to that of its triethylsubstituted analogue *9*, which seems reasonable since ^1H NMR measurements on the vinylic compounds *3* and *6* show that the barrier to internal rotation increases only moderately when the *ortho* ethyl groups are replaced by neopentyl groups.

Systems with formimino groups. The restricted diffusion model was used to treat ^{13}C spin lattice relaxation data on compounds *12–16* with the boundary condition $\theta=90°$. (Table 2). The trend in $\Delta G^{\ddagger}_{301}$ values for the formimino group rotation in the aldimines *12–16* is expected to be the same as that found for the corresponding aldehydes. The aldimines *14* and *15* show an order opposite to that found for the corresponding aldehydes *9* and *10*, but the difference in $\Delta G^{\ddagger}$ between *14* and *15* is very small.

Ortho substituted benzaldimines have rarely been studied, but Boyd *et al.*[19] studied the restricted $C_{sp^2}-C_{sp^2}$(aryl) bond rotation in *ortho*-substituted imines $Ar(Me)C=NCHMe_2$, where $Ar=o\text{-}X-C_6H_4$ (X=Me, C_6H_5, NO_2, OCH_3). Their results show that the barrier decreases as the size of the *ortho* substituent increases from methyl to the larger phenyl.

Comparisons between systems. Results from the three different groups of compounds above are most easily compared if two counteracting effects are considered, one due to *steric* effects and the other due to effects of *conjugation.*

The effect of conjugation when a vinyl group is attached to an aromatic ring is very small. MMP1 calculations show the initial state to be when the vinyl group is slightly twisted out of the ring plane, due to steric effects from the *o*-hydrogens, but MMP2 calculations show the initial state to be planar. Recently, as mentioned above, experimental evidence for a planar initial state for styrene has been adduced.[2d,e] If the substituent is a formyl group (benzaldehyde). MMP1 calculations show that the effect on conjugation completely dominates the steric effect, as a result of the strongly electronegative character of oxygen. The initial state is calculated to be when the carbonyl group lies in the ring plane.

When the *o*-hydrogens in styrene are replaced by methyls and groups of larger size (compounds *2* and *4*), the steric effects dominate, and the MMP1 calculations show in these cases the initial state to be when the vinyl group is perpendicular to the ring plane. If the *o*-hydrogens in benzaldehyde are replaced by methyl groups, the conjugative effect still dominates, and MMP1 calculations show the conjugated conformer to be the initial state. When the *ortho* substituents are ethyl and groups of larger size, steric effects are calculated to outweigh the conjugative effect.

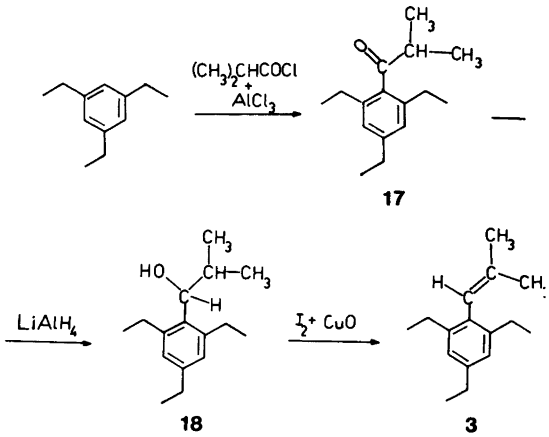
The barrier to internal rotation in 2,4,6-triisopropylbenzaldehyde *10* is calculated to be greater than that for 2,4,6-tri-neopentylbenzaldehyde *11*. The relaxation time measurements show the opposite order, although the differences are small, and these experimental results are in accord with those of Lunazzi *et al.*[2b,16d] on *o*-monosubstituted benzaldehydes. The anomalous order calculated by the MMP1 program may be an effect of the "hard hydrogens" used in the program.

The effects of different *ortho* substituents in

N-methylbenzaldimines will be very similar to those for the corresponding aldehydes, since nitrogen is only slightly less electronegative than oxygen.

It is interesting to compare the above results for the benzaldehydes with those found when the formyl proton is replaced by a methyl group. In the case of acetophenone, on the basis of ^{1}H NMR and dipole measurements, the initial state is suggested to be when the carbonyl group lies in the ring plane, due to the dominance of the effects of conjugation.[2a,3a,c] On the other hand, when acetophenone is substituted with *o*-methyl groups (acetylmesitylene), ^{1}H NMR chemical shifts and dipole moment measurements strongly indicate that the acetyl group is twisted 45° out of the ring plane.[3a-c] When the *ortho* substituents are neopentyl groups, Dahlberg *et al.*[1i] found evidence for restricted internal rotation, and a barrier of 46 kJ mol^{-1} was esimated for 2-acetylTNB. The proposed initial state for 2-acetylTNB is a conformation with the carbonyl group perpendicular to the ring plane and on the side opposite to that of the three neopentyl groups (similar to that calculated for 2,4,6-trineopentylbenzaldehyde and 2,4,6-trineopentylstyrene). If the *α* methyl is replaced by a *t*-butyl group, Dahlberg *et al.*[1i] estimated a barrier >96 kJ mol^{-1} for 2 pivaloylTNB. When the substituents in TNB are vinyl or formyl groups, the barriers to internal rotation are very low (see Table 4 for compound *4* and Tables 2 and 3 for compound *11*). The introduction of a trans-*β*-methyl group in compound *4* does not affect the low barrier (compound *5*), but introduction of a *cis*-*β*-methyl group leads to restricted internal rotation (similar to that observed by Dahlberg *et al.*[1i] in 2-alkyl and 2-acylTNB:s), and a barrier of 74 kJ mol^{-1} could be estimated (compound *6*).

Synthetic aspects. The syntheses of *2–6* all follow the general pattern shown for the synthesis of compound *3*. The syntheses involve acylation of a 1,3,5-trialkylsubstituted aryl compound with an appropriate acyl halide under Friedel-Crafts conditions. The resulting 2-acyl-1,3,5-trialkylbenzene (structure *17*) was then reduced with lithium aluminium hydride to the corresponding 2-(1-hydroxyalkyl)-1,3,5-trialkylbenzene (structure *18*), which in turn was dehydrated to the desired 2,4,6-trialkylstyrene (compound *3*).



In the case of 2,4,6-trimethylstyrene (vinylmesitylene *2*), phosphorous oxychloride in pyridine was used as dehydrating agent in the last step.[20]

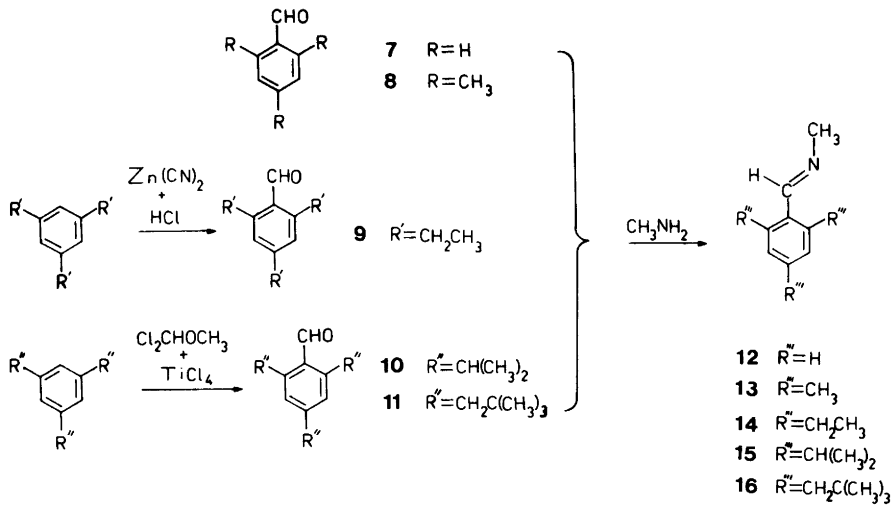
The compounds 2-(2-methylvinyl)-1,3,5-trineopentylbenzene *5* and 2-(2,2-dimethylvinyl)-1,3,5-trineopentylbenzene *6* were synthesized at the University of Gothenburg by Dr. E. Dahlberg, who kindly supplied them to us.

Benzaldehyde *7* and 2,4,6-trimethylbenzaldehyde *8* were commercially available. 2,4,6-Triethylbenzaldehyde *9* was synthesized from 1,3,5-triethylbenzene *via* a Gattermann reaction involving reaction with zinc cyanide and hydrogen chloride.[21a] 2,4,6-Triisopropylbenzaldehyde *10* and 2,4,6-trineopentylbenzaldehyde *11* were prepared from 1,3,5-triisopropylbenzene and 1,3,5-trineopentylbenzene, respectively, by reaction with dichloromethyl methyl ether and titanium tetrachloride.[21b,c]

The *N*-methylbenzaldimines *12–16* were synthesized by reaction between methylamine and the corresponding aldehydes in an autoclave.[22]

Summary and Conclusions. It is clear from the results reported here that ^{13}C spin lattice relaxation times can not be used directly to calculate rotational barriers with the same degree of reliability as those from NMR band shape analyses, since detailed information about librational motions is generally not available.

A *cis*-*β*-methyl substituent on 2,4,6-trineopentylstyrene leads to a high barrier (74 kJ mol^{-1}) to vinyl group rotation. In contrast, the compound with a *trans*-*β*-methyl group has a barrier (<20 kJ mol^{-1}) of similar magnitude to that of 2,4,6-trineopentylstyrene itself. Calculations with the



MMP1 program do not clearly reproduce this large difference in barrier height, whereas MMP2 was found to give quite satisfactory results. This is attributed to the effectively "smaller" hydrogens in the MMP2 force field, which apparently provides an adequate representation of sterically strained hydrocarbon conformations.

For the 2,4,6-trialkyl substituted benzaldehydes and *N*-methyl benzaldimines studied in this work, the barrier to internal rotation of the aldehyde or aldimine group was estimated from ^{13}C spin lattice relaxation time measurements. In all cases, the barrier was less than 20 kJ mol^{-1}. A model involving free diffusion in a restricted range was found suitable for the calculation of correlation times for internal motion from the T_1 data. The trend in the experimental barriers for the aldehydes was well represented by calculations with the MMP1 program.

Our molecular mechanics calculations have shown that while MMP1 reproduces the trend for the aldehydes, the results for the pure hydrogens are mimicked much more satisfactorily by MMP2.

EXPERIMENTAL

^1H NMR spectra for identifications were run on a JEOL JNM 60 spectrometer, and in a few cases on a JEOL MH 100 spectrometer. The chemical shifts are reported in ppm downfield from tetramethylsilane. The multiplicities of the peaks are designated as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m).

The IR spectra were recorded on a Perkin Elmer 257 Grating Infrared spectrometer using cells of sodium chloride.

The mass spectra were determined on an LKB MS 9000 mass spectrometer operating with 70 eV electron energy, at the University of Lund.

Melting points were obtained on a Kofler hot stage and are uncorrected.

Elementary analyses were performed by the Analytical Service Laboratory at the University of Lund.

The gas chromatographic (GLC) analyses were carried out on a Varian 1400 Aerograph gas chromatograph. The column had 1/8 inch outer diameter and a length of 2 m. The stationary phase was 3 % SE 30, silicon gum rubber on Chromosorb G, and the flow rate of nitrogen was 25 ml/min. The analyses on compound *3* and its precursors were performed on the Varian 1400 Aerograph operating with temperature programming (4 °C/min). The column used was a capillary column with OV-17 as the stationary phase, operating at a nitrogen flow rate of 5 ml/min.

2-Acetyl-1,3,5-trimethylbenzene 19 was prepared according to Ref. 23a; b.p. 125–126 °C/23 Torr, n_D^{20}=1.5176. (Lit. b.p. 240 °C/735 Torr n_D^{20}=1.5175).[23b]

2(1-Hydroxyethyl)-1,3,5-trimethylbenzene 20 was prepared according to Klages *et al.*[23b]; b.p. 140–141 °C/22 Torr. (Lit. b.p. 141 °C/24 Torr, 248 °C/760 Torr).[23b]

2,4,6-Trimethylstyrene (Vinylmesitylene 2) was prepared from compound *20* by the dehydration method described by Butenandt *et al.*[20]; b.p. 86–87 °C/11 Torr, n_D^{25}=1.5290. (Lit. b.p. 92 °C/14 Torr, n_D^{25}=1.5296.[23c] ^1H NMR ($CDCl_3$): δ 2.22 (9H, s, CH_3), 5.20 (1H, q, CH trans to ring,

J=16 Hz), 5.48 (1H, q, CH *cis* to ring, J=12 Hz), 6.69 (1H, q, CH=), 6.84 (2H, s, arom. H).

2(2-Methylpropanyl)-1,3,5-triethylbenzene 17. Aluminium chloride (33.9 g 0.25 mol) was covered with 100 ml of dry carbon disulfide in a three-necked flask. Isobutyryl chloride (28.6 g, 0.25 mol) was added with cooling and the mixture was stirred for 15 min. 1,3,5-Triethylbenzene (25.6 g, 0.16 mol) dissolved in 40 ml of dry carbon disulfide was added slowly, with cooling. The temperature was then allowed to rise and the reaction mixture was stirred at ca. 40 °C. After 2 h, GLC showed the reaction to be complete (99 % had reacted). The reaction mixture was hydrolysed with 50 ml of water, the carbon disulphide evaporated and the aqueous phase extracted with five 30 ml portions of hexane. The organic phases were collected, washed with 15 ml of a 10 % solution of sodium chloride, and 15 ml of water, dried ($MgSO_4$) and the solvent evaporated. An oily colourless residue was left, which was chromatographed on a column of silica with methylene chloride as eluent. Evaporation of the solvent left 29.9 g of an colourless oil, which was pure according to GLC; yield 82 %. (Found: C 82.6; H 10.4. Calc. for $C_{16}H_{24}O$: C 82.69; H 10.42.) ^{1}H NMR (100 MHz $CDCl_3$): δ 1.09 (3H, d, CH_3), 1.15 (3H, t, CH_3, J=11 Hz), 1.17 (6H, t, CH_3, J=11 Hz), 1.38 (3H, d, J=7 Hz), 2.56 (4H, q, CH_2, J=11 Hz), 2.58 (2H, q, CH_2: J=11 Hz), 2.91 (1H, m, CH, J=7 Hz), 6.83 (2H, s, arom. H). IR (ν_{max} CCl_4): 1700 cm^{-1} (C=O str.). MS[*m/e* (%)]: 232 (3, M), 189 (100, M−iPr), 161 (3, M−CO−iPr).

2-(1-Hydroxy-2-methylpropyl)-1,3,5-triethylbenzene 18. Lithium aluminium hydride (19.6 g, 0.52 mol) was covered with 100 ml of dry ether in a three-necked flask. Compound *17* (19.8 g, 0.11 mol), dissolved in 50 ml of dry ether, was added dropwise with cooling and stirring. The mixture was then refluxed. After 15 h GLC showed the reaction to be complete (99 % had reacted). The reaction mixture was cooled, hydrolysed consecutively with 20 ml of ethyl acetate, 20 ml of water and 10 ml of a 10 % solution of sodium hydroxide. The organic and aqueous phases were separated, and the aqueous phase was extracted with 15 ml of cyclohexane. The organic phases were collected, dried ($MgSO_4$) and the solvent evaporated, leaving a light yellow viscous residue, which was chromatographed on a column of silica with methylene chloride as eluent. Evaporated of the solvent left 18.0 g of a colourless liquid, which was pure according to GLC; yield 91 %. (Found: C 81.8; H 10.9. Calc. for $C_{16}H_{26}O$: C 81.98; H 11.19.) ^{1}H NMR (100 MHz $CDCl_3$): δ 0.64 (3H, d, CH_3, J=7 Hz), 1.12 (3H, d, CH_3, J=7 Hz), 1.17 (6H, t, CH_3, J=11 Hz), 1.26 (3H, t, CH_3, J=11 Hz), 1.79 (1H, s, OH), 1.9−2.4 (1H, m, CH), 2.61 (2H, q, CH_2, J=11 Hz), 2.73 (4H, q, CH_2, J=11 Hz), 4.56 (1H, d, CH, J=11 Hz), 6.75 (2H, s, arom. H). IR ($\nu_{max}CCl_4$): 3495 cm^{-1} (OH str.), 1390 cm^{-1} (C−O str.). MS [*m/e* (%)]: 234 (6, M), 191 (100, M−iPr), 161 (7, M−iPr−CHOH).

2(2,2-Dimethylvinyl)-1,3,5-triethylbenzene 3. (Compound *18* (1.0 g, 4.0 mmol) was mixed with copper oxide (0.05 g) in 10 ml of cyclohexane. Iodine (4.0 g, 15.9 mmol) dissolved in 500 ml of cyclohexane was added and the reaction mixture was refluxed. After 20 h, GLC showed the reaction to be complete. The reaction mixture was cooled, decolourised by shaking with 100 ml of a 10 % solution of sodium sulfite and then with 50 ml of water. The organic phase was separated, dried ($MgSO_4$), the solvent evaporated, and the oily residue was chromatographed on a column of alumina with hexane as eluent. Evaporation of the solvent left 0.91 g of an oily colourless substance, which was pure acording to GLC; yield 98 %. (Found: C 88.8 H 11.2. Calc. for $C_{16}H_{24}$: C 88.81; H 11.18.) ^{1}H NMR (100 MHz $CDCl_3$): δ 1.26 (6H, t, CH_3 in *ortho* ethyls, J=7 Hz), 1.45 (3H, t, CH_3 in para ethyl, J=7 Hz), 1.63 (3H, d, *cis*-CH_3 to H in vinyl, J=0.2 Hz), 2.17 (3H, d, trans-CH_3 to H in vinyl, J=0.5 Hz), 2.83 (4H, m, CH_2 in *ortho* ethyls, J=7 Hz), 2.99 (2H, q, CH_2 in para ethyl, J=7 Hz) 6.91 (1H, m, CH, J=0.5 Hz), 7.81 (2H, s, arom. H). IR (ν_{max} CCl_4): 3050 cm^{-1} (C−H str.), 1615 cm^{-1} (C=C str.). MS [*m/e* (%)]:216 (65, M), 201 (100, M−CH_3), 187 (45, M−C_2H_5).

2,4,6-Trineopentylstyrene 4 was prepared according to Dahlberg *et al.*[1i], except that iodine and copper oxide were used in the dehydration step. All spectroscopic data are in accordance with those published.

2,4,6-Triethylbenzaldehyde 9. The general procedure for the synthesis of mesitaldehyde *8* given in Ref. 21a was followed, yield 79 %, b.p. 91−92 °C/1 Torr n_D^{25}=1.5331. (Lit. b.p. 146−149 °C/21 Torr).[21a] ^{1}H NMR ($CDCl_3$): δ 1.23 (9H, t, CH_3, J=7.5 Hz), 2.62 (2H, q, CH_2, J=7.5 Hz), 2.95 (4H, q, CH_2, J=7.5 Hz), 6.92 (2H, s, arom. H), 10.54 (1H, s, CHO).

2,4,6-Triisopropylbenzaldehyde 10. 1,3,5-Triisopropylbenzene (15.0 g, 62.5 mmol) dissolved in 150 ml of methylene chloride was mixed with titanium tetrachloride (39.8 g, 212 mmol) and dichloromethyl methyl ether (15.0 g, 137 mmol) was added according to the procedure described by Rieche *et al.*[21c] for the synthesis of mesitaldehyde (8). The reaction was followed by GLC and was found to be complete (99 % had reacted) after 12 h. After work up,[24b] the product was distilled in vacuum to give 12.5 g of an oil,

yield 86 %, b.p. 96–97 °C/0.2–0.3 Torr, n_D^{21}= 1.5151. (Lit. b.p. 85 °C/0.08 Torr. n_D^{20}= 1.5141–1.5150, b.p. 123–125 °C/4 Torr).[24c] ^{1}H NMR ($CDCl_3$): δ 1.00 (18H, d, CH_3, J=7 Hz), 2.64 (1H, m, CH, J=7 Hz), 3.35 (2H, m, CH, J=7 Hz), 6.90 (2H, s, arom. H), 10.42 (1H, s, CHO).

2,4,6-Trineopentylbenzaldehyde 11 was prepared from 1,3,5-trineopentylbenzene by the method described for the synthesis of compound *10*. After 40 h reaction time GLC showed the reaction to be complete (99 % had reacted). The reaction mixture was hydrolysed with 40 ml of water, the organic phase separated and the aqueous phase extracted with two 25 ml portions of methylene chloride. The organic phases were combined, washed with 15 ml of a saturated solution of sodium chloride and with 10 ml of water, and dried ($MgSO_4$). The solvent was evaporated and the solid black residue was sublimed at 120–125 °C/0.08 Torr, giving a white crystalline product, yield 96 %, m.p. 54–55 °C. (Found: C 83.3; H 11.7. Calc. for $C_{22}H_{36}O$: C 83.47; H 11.48.) ^{1}H NMR ($CDCl_3$): δ 0.90 (18H, s, $C(CH_3)_3$), 0.92 (9H, s, $C(CH_3)_3$) 2.46 (2H, s, CH_2), 2.92 (4H, s, CH_2), 6.76 (2H, s, arom. H), 10.47 (1H, s, CHO). IR (ν_{max} CCl_4): 1695 cm^{-1} (C=O str.), 1400 cm^{-1} (C=C str.). MS [*m/e* (%)]: 316 (15, M), 301 (15, M–CH_3), 259 (13, M–*t*Bu).

General method for N-*methylaldimines*. The procedure of Kindler[22] was followed. The aldehyde was mixed with a threefold excess of methylamine in an autoclave, which was heated to 85 °C for 5 h with agitation.

N-*Methylbenzaldimine 12*. Yield 89 %, b.p. 90–91 °C/30 Torr, n^{23}=1.5519. (Lit. b.p. 90–91 °C/30 Torr, n_D^{20}=1.5540).[22]

N-*Methyl-2,4,6-trimethylbenzaldimine (*N-*methylmesitaldimine 13)*. Reaction time 15 h, yield 91 %, b.p. 118–119 °C/14 Torr. (Found: C 82.3; H 8.33; N 8.68. Calc. for $C_{11}H_{13}N$: C 82.47; H 8.23; N 8.80) ^{1}H NMR ($CDCl_3$): δ 2.22 (3H, s, CH_3), 2.34 (6H, s, CH_3), 3.47 (3H, s, =NCH_3), 6.73 (2H, s, arom. H), 8.53 (1H, s, CH=N). IR (ν_{max} CCl_4): 1645 cm^{-1} (C=N str.). MS [*m/e* (%)]: 161 (33, M), 146 (100, M–CH_3), 132 (37, M–NCH_3).

N-*Methyl-2,4,6-triethylbenzaldimine 14*. Reaction time 15 h, yield 95 %, b.p. 92–93 °C/1 Torr (Found: C 82.3; H 10.4; N 6.57. Calc. for $C_{14}H_{21}N$: C 82.67; H 10.45; N 6.88.) ^{1}H NMR ($CDCl_3$): δ 1.14 (9H, m, CH_3, J=7 Hz), 2.66 (6H, m, CH_2, J=7 Hz), 3.84 (3H, s, NCH_3), 6.79 (2H, s, arom. H), 8.54 (1H, s, N=CH). IR (ν_{max} CCl_4): 1650 cm^{-1} (C=N str.). MS [*m/e* (%)]: 203 (21, M), 188 (100, M–CH_3), 174 (20, M–NCH_3).

N-*Methyl-2,4,6-triisopropylbenzaldimine 15*. Reaction time 15 h at 95 °C, yield 98 %, b.p. 95–96 °C/0.2 Torr. (Found: C 83.2; H 11.1; N 5.86. Calc. for $C_{17}H_{27}N$: C 83.17; H 11.10; N 5.73) ^{1}H NMR ($CDCl_3$): δ 0.94 (12H, d, CH_3, J=7 Hz), 0.96 (6H, d, CH_3, J=7 Hz), 2.58 (1H, m, CH, J=7 Hz), 2.97 (2H, m, CH, J=7 Hz), 3.20 (3H, s, NCH_3), 6.67 (2H, s, arom. H), 8.31 (1H, s, CH=N). IR (ν_{max} CCl_4): 1655 cm^{-1} (C=N str.). MS [*m/e* (%)]: 245 (13, M), 230 (100, M–CH_3), 215 (27, M–NCH_3).

N-*Methyl-2,4,6-trineopentylbenzaldimine 16*. Reaction time 24 h at 95 °C. After work up the product was chromatographed on a column of alumina with methylene chloride as eluent. Evaporation of the solvent left a white crystalline residue, yield 98 %, m.p. 56–57 °C. (Found: C 83.9; H 11.8; N 4.38. Calc. for $C_{23}H_{39}N$: C 83.83; H 11.93; N 4.24.) ^{1}H NMR ($CDCl_3$): δ 0.88 (18H, s, $C(CH_3)_3$), 0.95 (9H, s, $C(CH_3)_3$), 2.43 (2H, s, CH_2), 2.75 (4H, s, CH_2), 3.49 (3H, s, NCH_3), 6.74 (2H, s, arom. H), 8.52 (1H, s, N=CH). IR ν_{max} CCl_4): 1690 cm^{-1} (C=N str.). MS [*m/e* (%)]: 329 (14, M), 314 (100, M–CH_3), 300 (7, M–NCH_3).

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