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Proton Magnetic Resonance Studies of 1,2-Bis(2,4,6-trineopentylphenyl)ethane and the Diastereomers of 2,3-Bis(2,4,6-trineopentylphenyl)butane

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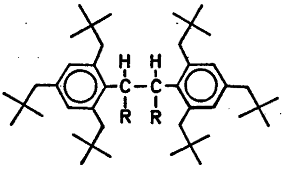
1,2-Bis(2,4,6-trineopentylphenyl)ethane, (±)-2,3-bis(2,4,6-trineopentylphenyl)butane and *meso*-2,3-bis(2,4,6-trineopentylphenyl)butane have been synthesized and studied by ^{1}H NMR to obtain information about free energies of internal rotation at the temperature of coalescence and about the conformations of the molecules.

The present work deals with the determination of barriers to internal rotation and conformations of 1,2-bis(2,4,6-trineopentylphenyl)ethane (*1*), *meso*-2,3-bis(2,4,6-trineopentylphenyl)butane (*2*) and (±)-2,3-bis(2,4,6-trineopentylphenyl)butane (*3*) by NMR studies, and also with the syntheses of these compounds by organolithium reactions.

RESULTS and DISCUSSION



1 : R = H

2, 3 : R = CH_3

Compounds *2* and *3* were synthesized by treating 2-(1-chloroethyl)-1,3,5-trineopentylbenzene[1] with methyllithium.[2] They were separated by means of liquid chromatography, and further purified by recrystallization. Compound 1 was synthesized by treating 2-chloromethyl-1,3,5-trineopentylbenzene[3] with methyllithium.

Compound 1. The NMR spectrum of 1,2-bis(2,4,6-trineopentylphenyl)ethane showed only singlets at ambient probe temperature (Table 1). By comparison with the NMR spectrum of 2-ethyl-1,3,5-trineopentylbenzene[1] it could be concluded that the four methylene protons that appeared at δ 2.34 belonged to the 4-neopentyls while the four methylene protons at δ 2.73 belonged to the ethane moiety. The other signals could be assigned by means of the chemical shifts and integrals. On cooling the sample in carbon disulfide to −70 °C the singlet at δ 2.41 (2- and 6-methylenes) disappeared and instead an AB pattern with $\Delta\nu_{AB} = 38$ Hz and $J_{AB} = 13$ Hz was formed (determined from 60 MHz spectra). On raising the temperature the AB pattern gradually broadened and coalesced at −46 °C, which corresponds to a barrier to internal rotation ($\Delta G^{\ddagger}$) of 46.1 kJ/mol.*

In 1,3,5-trineopentylbenzene all signals appear as singlets at −70 °C. The nonequivalence within the 2- and 6-methylene groups of *1* at low temperature can only be explained by restricted rotation about the aryl-methylene bonds of the ethane moiety. Below the tempera-

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* A complete bandshape analysis of this compound will be published separately.

Table 1. NMR data of compounds *1*, *2* and *3* determined from 100 MHz spectra (s = singlet, d = doublet and q = quartet).

	1	*3* (±)	*2* (*meso*)
tert-Butyl; 2,6	0.83s	0.62s	0.87s
		0.98s	0.99s
tert-Butyl; 4	0.88s	0.77s	0.89s
Methyl; 2,3		1.48[a]	0.93[b]
Methylene; 2,6	2.41s	1.51q	2.81q
J_{AB} (Hz)		14.1	13.7
$\Delta\nu_{AB}$ (Hz)		34.1	85.0
		2.75q	2.93
J_{AB} (Hz)		14.0	14.0
$\Delta\nu_{BA}$ (Hz)		43.7	68.2
Methylene; 4	2.34s	2.21s	2.38s
Methylene; 1,2	2.73s		
Methine; 2,3		3.31[c]	3.61[d]
Aryl H; 3,5	6.59s	6.22d	6.70d
		6.82d	6.92d
J (Hz)		1.9	1.8

[a] X_3X_3' part of $X_3AA'X_3'$ spectrum: $J_{AX} = 7.80(5)$ Hz, $J_{AX'} = -0.35(5)$ Hz (see text). [b] X_3X_3' part of $X_3AA'X_3'$ spectrum: $J_{AX} = 7.25(10)$ Hz, $J_{AX'} = -0.36(5)$ Hz (see text). [c] AA′ part of $X_3AA'X_3'$ spectrum: $J_{AA'} = 8.8(1)$ Hz. [d] AA′ part of $X_3AA'X_3'$ spectrum: $J_{AA'} = 12.0(2)$ Hz.

ture of coalescence *1* will prefer to exist in a conformation in which the plane defined by the ethane bond and the bond between one of the aryl and methylene groups of the ethane moiety is approximately perpendicular to the plane of the mentioned aryl group. The 2- and 6-methylene groups are then enantiotopic due to the real or averaged symmetry of the molecule, the rotation around the ethane CC-bond still being rapid, but the hydrogens of the 2- and 6-methylene groups are diastereotopic. The hydrogens A and A′ (see Fig. 1) will then be equivalent and different from the equivalent hydrogens B and B′, and an AB pattern will be formed. Due to the symmetry properties of *1*, the nonequivalence between the two methylene protons of the 2- and 6-neopentyl groups, respectively, will remain even if these groups are free to rotate. According to Reuvers *et al.*[4] the spectrum of 1,2-bis(2,6-dimethylphenyl)ethane did not change on cooling to −60 °C. Even if the interannular bridge is locked in one position in this compound, the methyl groups will still give rise to a singlet, because the methyl hydrogens will not be diastereotopic.

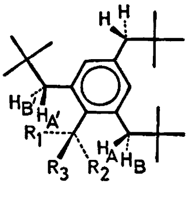

Fig. 1. *1*: $R_1 = R_2 = H$, $R_3 = -CH_2-R$. *2*, *3*: $R_1 = CH_3$, $R_2 = H$, $R_3 = -CH(CH_3)-R$. R = 2,4,6-trineopentylphenyl.

1,2-Bis(4-methylphenyl)ethane has been found[5] by X-ray crystallography to have an *anti* conformation with respect to the aryl groups. IR and Raman studies [6] of *p,p′*-disubstituted 1,2-diphenylethanes showed that these compounds exist in *anti* conformations in the solid state, but they also showed that in solution there was an equilibrium between *anti* and *gauche* conformers. The NMR data for *1* do not allow conclusions to be drawn concerning the preferred conformation of the compound at ambient temperature in solution.

*Compounds 2 (*meso*) and 3(±).* In several cases [4,7] a higher melting point has been reported for a *meso* compound than for a corresponding *racemic* mixture. This indicates that *2* (m.p. 232 – 233 °C) is a *meso* compound and that *3* (m.p. 155 – 156 °C) is a *racemic* mixture. In the following text, we will first discuss the case in which the above assignements are correct. Later in the text we will also discuss the case in which the high-melting compound is assumed to be the *racemic* mixture and the low-melting the *meso* compound.

At ambient probe temperature the aromatic protons of *2* and *3* in carbon disulfide solution both appeared as two *meta*-coupled doublets. This shows that the protons on one and the same aryl group are nonequivalent, but that the aryl groups are equivalent. The 2- and 6-methylene groups of both *2* and *3* formed two AB patterns, due to restricted rotation about the aryl-methine bonds and the chirality at carbons 2 and 3 of the butane moiety.

Compounds *2* and *3* each showed three *tert*-butyl resonances. On heating the sample of *3* in deuteriobromoform, two *tert*-butyl peaks (appearing at δ 0.62 and 0.98 in carbon disulfide) coalesced ($t_C = 185$ °C) to a singlet, which shows that they should be assigned to the 2- and 6-neopentyl groups. The aromatic protons of *3* also coalesced to a singlet at 185 °C. This corresponds to a barrier to internal rotation ($\Delta G^{\ddagger}$) of 96.3 kJ/mol for both measured coalescences. The two AB patterns of *3* broadened but did not coalesce completely even at 190 °C. The NMR spectrum of *2* was unchanged up to 190 °C ($\Delta G^{\ddagger} > 97$ kJ/mol).

The protons of the methine and methyl groups of the butane moieties of *2* and *3* gave rise to $X_3AA'X_3'$ patterns, which were analysed by a general method described by Anet [8] to obtain input data for the iterative computer program UEAITR.[9] Unfortunately, insufficient spectral detail was resolved to allow automatic iteration, and thus the search for the "best fit" of theoretical to experimental bandshape was performed manually. Analysis of the AA' part of the 100 MHz spectrum of *3* at ambient temperature in carbon disulfide solution gave, after considerable work with trial and error, $J_{AA'} = 8.8 \pm 0.1$ Hz. Analysis of the AA' part of the spectrum of *2* at ambient temperature in the same solvent gave $J_{AA'} = 12.0 \pm 0.2$ Hz The values of J_{AX} and $J_{AX'}$ were 7.80 ± 0.05 Hz and -0.35 ± 0.05 Hz for *3*, and 7.25 ± 0.10 Hz and -0.36 ± 0.05 Hz for *2*. Opposite signs for J_{AX} and $J_{AX'}$ were also found in most of the 2,3-disubstituted butanes studied by Anet [8] and Bothner-By and Naar-Colin.[10] $J_{XX'}$ was set equal to zero in all iterations.

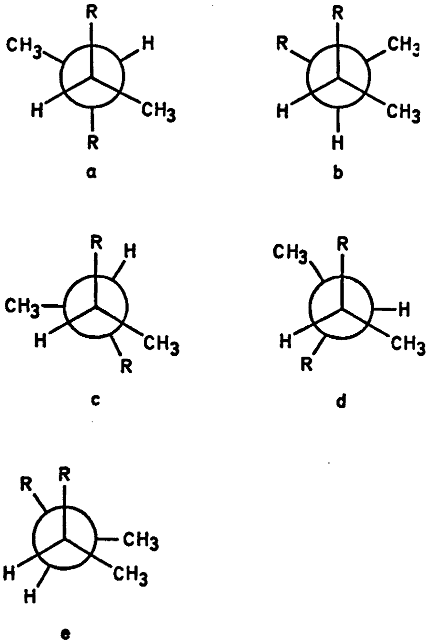

Fig. 2. Conformations of *meso*-2,3-bis(2,4,6-trineopentylphenyl)butane. R = 2,4,6-trineopentylphenyl.

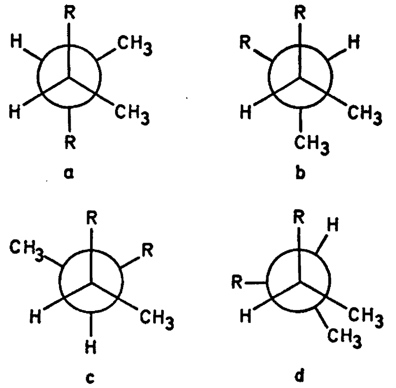

Fig. 3. Conformations of (+)- or (−)-2,3-bis(2,4,6-trineopentylphenyl)butane. R = 2,4,6-trineopentylphenyl.

In 2,3-diphenylbutane the coupling constants $J_{AA'}$ were found to be 7.0 and 9.9 Hz for the *racemic* mixture and the *meso* compound, respectively, in carbon disulfide solution.[10] In the corresponding isomers of 2,3-bis(2,6-dimethylphenyl)butane, $J_{AA'}$ was found [4] to be 9.5 and 12 Hz, and in 3,4-bis(2,6-dimethylphenyl)2,2,5,5-tetramethylhexane about 5 and 12 Hz, for the *racemic* mixture and the *meso* isomer, respectively, in carbon tetrachloride solution. The latter values were estimated from ^{13}C satellites.[4] A comparison of the chemical shift values of the isomers of 2,3-bis(2,6-dimethylphenyl)butane at ordinary and elevated temperatures led to the suggestion [4] that each of these isomers exists in only one conformation at ordinary temperatures. The *meso* isomer was proposed to exist in the conformation shown in Fig. 2a (with R = 2,6-dimethylphenyl) and the *racemic* mixture in a conformation resembling Fig. 3a (with R = 2,6-dimethylphenyl), with a distortion of 30 ° from the "ideal" H−H dihedral angle of 60 ° in this conformation. Studies of molecular models [4] indicated that the dihedral angle between the methyl groups was smaller than 60°. On the basis of the chemical shifts and coupling constants, it was proposed [4] that in the *meso* isomer of 3,4-bis(2,6-dimethylphenyl)2,2,5,5-

tetramethylhexane, the two *tert*-butyl groups, the two aryl groups and the two methine protons were pairwise *anti* to each other, and in the racemic isomer the *tert*-butyl groups were *anti*, while the methine protons were *gauche* to each other.

Due to the great steric hindrance and to the symmetry of the *meso* isomers of 2,3-bis(2,6-dimethylphenyl)butane and 3,4-bis(2,6-dimethylphenyl)2,2,5,5-tetramethylhexane, when the aryl groups are *anti* to each other, it seems reasonable to assume that a coupling constant of 12 Hz between the methine protons is very close to that for an "ideal" *anti* position of these protons. This conclusion is further strengthened by the fact that $J_{AA'}$ is 12.0 Hz in compound *2*.

Using the Karplus equation, $J_{AA'} = K \cos^2 \theta$,[11] with $K = 12$ Hz, the coupling constant can be calculated to be 3 Hz, if the dihedral angle between the methine protons is 60° as in a *gauche* conformation.

If the population of the *anti* conformation is denoted X_{anti}, and rapid interconversion is assumed, the following relation can easily be obtained

$$X_{anti} = (J_{AA'} - J_g)/(J_a - J_g)$$

where J_g and J_a are the expected coupling constants 3 and 12 Hz for the *gauche* and *anti* positions of the methine protons, respectively).

On the basis of the iterated value of $J_{AA'}$ for *2* (12.0 Hz), this compound is found to exist essentially in the *anti* conformation shown in Fig. 2a. The chemical shift differences between the 2- and 6- methylene groups (0.12 ppm), the 2- and 6-*tert*-butyl groups (0.12 ppm) and the aromatic protons (0.22 ppm) on each aryl group of *2*, can be explained by their location near centers of chirality.

For *3*, an *anti:gauche* ratio of 64:36 may be obtained on the basis of the iterated value of $J_{AA'}$ (8.8 Hz) if it is assumed that an equilibrium exists between the conformations. On the other hand, a single intermediate conformation may also be assumed. By means of the Karplus equation,[11] with $K = 12$ Hz, the dihedral angle between the methine protons is found to be either 30 or 150° for *3*. In conformations 3a and 3c (with an H – H dihedral angle of 30°), the 2- and 3-methyl groups will be located in the shielding zone of the neighboring aryl group, which would result in an upfield shift of these protons, contrary to the observed behavior (δ 1.48 for these protons, while the corresponding protons of *2* appear at δ 0.93). A dihedral angle of 150° is thus more reasonable. This is nearly consistent with conformation 3b. The fact that the methine protons of *3* are shifted 0.30 ppm upfield with respect to those of *2* indicates that the former protons are in the shielding zone of the neighboring aryl group, and that the aryl groups of *3* are thus forced apart from each other. With an H – H dihedral angle of 150° the dihedral angle between the aryl groups will, in this case, be 90° (see Fig. 3d), and the large upfield shift of one of the 2- or 6-methylene groups, one of the 2- or 6-*tert-butyl*-groups and one of the aromatic protons on each aryl group (1.24, 0.36 and 0.60 ppm with respect to the downfield shifted groups, respectively) can be explained by their location in the shielding zone of the other aryl group, while the downfield shifts of the 2-and 3-methyl groups (0.55 ppm with respect to those of *2*) can be explained by their location in deshielding zones of the aryl groups. The racemic mixture thus seems to prefer to exist in conformation 3d in carbon disulfide solution at ambient temperature.

A comparison between the chemical shifts of *2* and *3* and those of 1,3,5-trineopentylbenzene, which shows *tert*-butyl, methylene and aromatic resonances at δ 0.86, 2.37 and 6.61, respectively, in carbon disulfide solution, indicates that the above assignments are correct, and we prefer the single conformation 3d to an *anti/gauche* mixture as the explanation of the iterated value of $J_{AA'}$.

Contrary to the above assignment, we can assume that the low-melting isomer *3* is the *meso* compound. An H – H dihedral angle of 150° is in accord with conformations 2c and 2d. In these conformations the methyl groups will be expected to have different chemical shifts. Furthermore, the chemical shift difference between the 2- and 6-methylene groups, the 2- and 6-*tert*-butyl groups and the aromatic protons, respectively, on each aryl group will be expected to be small, which is not the case (see Table 1). An H – H dihedral angle of 30° is in accord with conformation 2e. Perhaps the small chemical shift difference, in this conformation, between the methyl groups is not resolved due to instrumental limitations.

In that case, all the chemical shift values can be explained by means of the same arguments that were used above when *3* was assumed to be the *racemic* mixture. However, if *3* is the meso compound, the high-melting compound *2* must be the *racemic* mixture. In *2* there is an H – H dihedral angle of 0 or 180°. Assuming that *2* is the *racemic* mixture the value 180° is consistent with conformation 3b. In this conformation the methyl groups would be expected to be shifted downfield to about the same extent as those of *3* (compare 2e and 3b), which is not the case. A larger chemical shift difference than is found between the 2- and 6-methylene groups, the 2- and 6-*tert*-butyl groups and the aromatic protons, respectively, on each aryl group would also be expected. In a conformation with an H – H dihedral angle of 0°, both the aryl groups eclipse a methyl group. Although this conformation cannot be rejected on the basis of the chemical shift values, it seems unreasonable that it should be the lowest energy conformation of the compound.

The *meso* configuration can thus be assigned to the high-melting compound *2*, while the low-melting *3* is the *racemic* mixture.

EXPERIMENTAL

Gas chromatographic (GLC) analyses were carried out on a Perkin-Elmer 900 gas chromatograph fitted with a flame ionization detector (column: 2 m × 2 mm 3 % SE-30 silicon gum on Gaschrom 100 – 200 mesh).

The IR spectra were recorded on a Beckman IR 9 spectrophotometer using potassium bromide pellets. The absorption maxima are reported in cm^{-1}, and the intensities are characterized as weak (w), medium (m), strong (s), or very strong (vs).

The mass spectra were determined (at the Department of Medical Biochemistry, University of Göteborg) on an AEI MS 902 mass spectrometer with the following conditions: electron energy 70 eV, accelerating voltage 8 kV and emission 100 μA. The intensities of the peaks are reported in parentheses as percentages of the base peak. Only the most abundant peaks are reported, together with the parent peaks and the isotope peaks corresponding to the latter.

The melting points were determined on a Kofler micro hot stage.

The NMR spectra were recorded on Varian A 60, XL-100, and/or JEOL JNM-MH-100 spectrometers. About 10 % by weight solutions in carbon disulfide were used for identification of the compounds at a probe temperature of 38 °C. The chemical shifts are reported in ppm downfield from tetramethylsilane as internal standard. For the variable temperature studies, the same concentrations as mentioned above were used, but *2* and *3* were dissolved in deuteriobromoform. The temperatures were measured by methanol or 1,2-ethanediol shifts with separate NMR tubes. The accuracy of the temperature is estimated to be within ± 5 °C. The $\Delta G^{\ddagger}$ values were calculated as described by Mannschreck *et al.*[12]

(±)-2,3-Bis(2,4,6-trineopentylphenyl)butane (3) and meso*-2,3-bis(2,4,6-trineopentylphenyl)-butane (2).* A solution of 250 mg (0.71 mmol) of 2-(1-chloroethyl)1,3,5-trineopentylbenzene[1] in dry ether was added to a solution of 25 mmol of methyllithium[2] in 20 ml of diethyl ether under nitrogen. The reaction mixture was then stirred overnight at room temperature, after which the excess of methyllithium was destroyed with water, and the mixture was neutralized with 6 M hydrochloric acid. The aqueous layer was then extracted several times with diethyl ether, and the combined ethereal layers were dried over magnesium sulfate. Compounds *2* and *3* were separated on a column of silica gel (< 0.08 mm) by elution with hexane, and further purified by repeated recrystallization from ethanol. Compounds *2* and *3* were identified as *meso*-2,3-bis(2,4,6-trineopentylphenyl)butane and (±)-2,3-bis(2,4,-6-trineopentylphenyl)butane from their spectral characteristics (see the above discussion). The yields of *2* and *3* were 90 mg (40 %) and 69 mg (31 %), respectively.

Data for *3* were: M.p., 155 – 156 °C. IR, 2950vs, 290w, 2865 m, 1608m, 1568w, 1475vs, 1390s, 1378w, 1362vs, 1238s, 1200 m, 1135 w, 1048m, 878m, 750w, 604w. MS, 29(4),41(10), 43(18), 57(27), 69(24), 71(27), 315(100), 316(27), 630(0.127), 631(0.058).

Data for *2* were: M.p. 232 – 233 °C. IR, 2960vs, 2910w, 2865m, 1610m, 1569m, 1480vs, 1392s, 1378w, 1365vs, 1338w, 1240s, 1200m, 1168w, 1060m, 1000m, 883s, 793m, 751w, 633m. MS, 29(5), 41(10), 43(21), 57(33), 69(32), 71(33), 145(6), 146(6), 315(100), 316(19), 630(0.091), 631(0.049).

1,2-Bis(2,4,6-trineopentylphenyl)ethane (1). To a solution of 15 mmol of methyllithium[2] in 12 ml of diethyl ether, under nitrogen, 500 mg (1.5 mmol) of 2-chloromethyl-1,3,5-trineopentylbenzene[3] was added. The reaction mixture was stirred at room temperature, and at regular time intervals small aliquots were withdrawn and analyzed by GLC. After 20 h a main product had been formed in 80 % yield. The work-up procedure described above for *2* and *3* was then applied, and the main product was purified by repeated recrystallization from ethanol. Its physical properties were identical with those previously reported[1] for 1,2-bis(2,4,6-trineopentylphenyl)ethane and the yield was 334 mg (74 %).

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