Barriers to Internal Rotation in Trineopentylbenzenes. III. Nitro-Substituted Compounds

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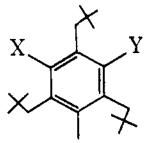
Received March 26, 1973

Abstract: The barriers to internal rotation of the 2-, 4-, and 6-neopentyl groups in 1,3-dibromo-2,4,6-trineopentyl-5-nitrobenzene have been determined by proton nuclear magnetic resonance complete line-shape studies at 100 MHz. At low temperatures, the methylene protons of the 4- and 6-neopentyl groups give rise to three different AB spectra, and the corresponding *tert*-butyl protons to three singlets, due to the presence of different rotamers (a chiral pair denoted A and C and an achiral species denoted B). The rotamers differ with respect to the positions of the various *tert*-butyl groups in relation to the plane of the aromatic ring. Their relative populations ($P^{A+C}:P^{B}$) were 2:0.55 at −30.4°, as determined by curve fitting of the *tert*-butyl signals. The barriers ($\Delta G^{\ddagger}{}_{298°}$) for the groups were found to be 14.6 ± 0.1 kcal/mol (A → B), 14.3 ± 0.1 kcal/mol (B → A), and 16.2 ± 0.1 kcal/mol ($A \rightleftarrows A'$). In connection with this analysis, the temperature dependence of the nmr spectra of the methylene protons in two other nitro-substituted 1,3,5-trineopentylbenzenes was also studied. The free energy of activation for the internal rotation of the 3-neopentyl group in 1,3,5-trineopentyl-2,4-dinitrobenzene ($\Delta G^{\ddagger}{}_{298°} = 12.9 \pm 0.1$ kcal/mol) was found to be lower than that for the 3-neopentyl group in 2-bromo-1,3,5-trineopentyl-4-nitrobenzene ($\Delta G^{\ddagger}{}_{298°} = 14.4 \pm 0.1$ kcal/mol), probably owing to a resonance effect of the second nitro group in the dinitro compound.

In previous work[3,4] we have studied the temperature dependence of the nmr line shape of the methylene protons in halogen-substituted 1,3,5-trineopentylbenzenes (Ia–e). The activation parameters for the neopentyl barriers in the unsymmetrically substituted compounds (Ic–e) could be interpreted on the basis of the suggestion[5] that in the slow exchange region the 3-neopentyl group induces magnetic nonequivalence in the 1- and 5-neopentyl groups, giving rise to three shifted AB quartets for the methylene protons, which collapsed at about the same temperature. In this paper we report the results of an investigation of 1,3-dibromo-2,4,6-trineopentyl-5-nitrobenzene (If), which in addition to the hindered rotation of the 2-neopentyl group is also expected to exhibit hindered rotation of the 4- and 6-neopentyl groups. At slow interconversion rates, the time-average symmetry of the molecule is destroyed, theoretically giving rise to four rotamers, in which the methylene protons of at least two of the neopentyl groups are anisochronous (see subsequent discussion). In order to facilitate the analysis of the complex spectra shown by the methylene protons in the dibromonitro compound (If), we also investigated the bromonitro and dinitro compounds Ih and Ig. This provided an opportunity for a study of the effects of an electron-attracting group on the internal rotational barriers.

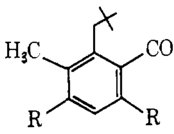


$$\left.\begin{array}{l}\text{Ia, } X = Cl;\ Y = Cl\\ \text{b, } X = Br;\ Y = Br\\ \text{c, } X = Cl;\ Y = I\\ \text{d, } X = Br;\ Y = I\\ \text{e, } X = Cl;\ Y = Br\end{array}\right\}\ Z = H$$

f, $X = Br;\ Y = Br;\ Z = NO_2$
g, $X = NO_2;\ Y = NO_2;\ Z = H$
h, $X = NO_2;\ Y = Br;\ Z = H$

The barrier to internal rotation of the 3-neopentyl group in the 2,4-dihalo-1,3,5-trineopentylbenzenes (Ia–e) is assumed to depend primarily on the steric interaction between a halogen and a *tert*-butyl group, with the smaller halogen determining the $\Delta G^{\ddagger}$ values in the unsymmetrically substituted cases. Resonance effects are expected to be of little importance in the determination of the height of the barrier, since the charge distribution between the halogen and the aromatic ring should be essentially the same in the initial and transition states. In compounds with substituent groups such as $-NO_2$, $-NH_2$, $-COR$, and $-CO_2R$, whose resonance effect depends on the magnitude of the dihedral angle between the ring plane and a plane through the substituent, it is reasonable to expect different degrees of resonance stabilization in the initial and transition states if the substituent is involved in steric interactions along the reaction path.

Results of Reuvers, *et al.*,[6] from nmr studies of compounds IIa and IIb, have been interpreted in terms of a



IIa, R = H
b, R = CH_3

rotation of the CO_2CH_3 group out of the ring plane. At −60° they found a decrease in the methylene AB proton shift values for compound IIb compared with IIa. The $\Delta G^{\ddagger}$ values depend on differences in both steric and resonance effects between initial and transi-

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[1] Organic Chemistry 2, Chemical Center.

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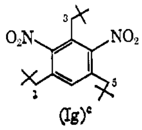
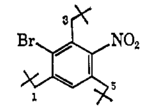
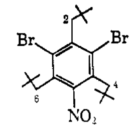
[3] R. E. Carter, J. Mårton, and K.-I. Dahlqvist, *Acta Chem. Scand.*, **24**, 195 (1970).

[4] B. Nilsson, R. E. Carter, K.-I. Dahlqvist, and J. Mårton, *Org. Magn. Resonance*, **4**, 95 (1972).

[5] P. Martinson, *Acta Chem. Scand.*, **26**, 3568 (1972).

[6] A. J. M. Reuvers, A. Sinnema, Th. J. Nieuwstad, F. van Rantwijk, and H. van Bekkum, *Tetrahedron*, **27**, 3713 (1971).

Table I. Chemical Shifts and Coupling Constants[a]

Trineopentylbenzene	Chemical shift (ppm) Methylene	Chemical shift (ppm) *tert*-Butyl	Chemical shift (ppm) Aryl	$\lvert J_{AB}\rvert$,[b] Hz
 (Ig)[c]	2.62 (1) 2.62 (5) 2.78 (3)	0.84 (1) 0.84 (5) 0.93 (3)	7.14	13.4 (1, 5)
 (Ih)[c]	2.87 (1) 2.51 (5) 3.05 (3)	0.95 (1) 0.90 (5) 1.00 (3)	7.03	13.0 (1) 13.9 (5) 14.25 (3)
 (If)[d]	3.03 (4) 3.03 (6) 3.45 (2)	0.97 (4) 0.97 (6) 1.09 (2)		14.6[e] (A4+C6+C′4+A′6) 14.6[e] (B4+B6+B′4+B′6) 14.75[e] (A6+C4+C′6+A′4)

[a] The numbers in parentheses refer to the different neopentyl groups. [b] In hertz at low temperature (∼ −30°) for each AB spectrum, determined on 100 Hz sweep width. [c] Chemical shifts in ppm downfield from internal TMS in *ca.* 6 mol % chloroform-*d* solutions, determined on 100 Hz sweep width at probe temperature. [d] Chemical shifts in ppm at +86.8°. [e] The letters in parentheses refer to the different rotamers in Figure 1. The larger coupling constant from the spectrum of methylenes A6+C4+C′6+A′4 refers to the neopentyl group on the same side of the ring as the 2-neopentyl group (see text).

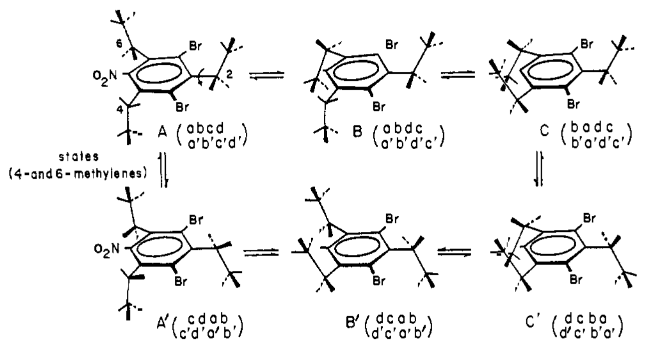


Figure 1. Different rotamers of compound If. For the sake of clarity, the NO_2 substituent is omitted in rotamers B, B′, C, and C′. The exchanges of the 4- and 6-methylene protons are also indicated.

tion states, which makes difficult an estimation of the resonance stabilization energy contribution from the CO_2CH_3 group in this case.

Experimental Section

The syntheses of 1,3,5-trineopentylbenzene and the three compounds studied in this work are described in ref 7–10.

Nmr Spectra. *Ca.* 6 mol % solutions of each of the three compounds, If–h, in chloroform-*d* containing tetramethylsilane (TMS) as internal reference, were prepared. All spectra were run on a Varian XL-100-15 spectrometer equipped with a variable-temperature probe and a Varian V-6040 temperature controller. The temperatures were measured by means of a precalibrated capillary containing an α-picoline–water mixture, which was concentrically held in the sample tube by means of two Teflon plugs. The temperature-dependent shift difference between the methyl and water protons had been calibrated in a separate experiment.[11,12] The temperatures measured in this way are believed to be accurate to within ±0.5°. All shifts were measured by use of a Varian frequency counter. The resolution was checked at each temperature by recording the signal from undeuterated chloroform, whose line width varied from 0.6 to 0.4 Hz over the temperature interval −30 to +100°. The assignment of the methylene peaks in compounds If and Ih was carried out at low temperatures by the indor technique.[13] The scale expansion and sweep rate for all spectra were 2 Hz/cm and 0.1 Hz/sec, respectively. All spectra were analyzed by visual curve fitting, using a Univac 1108 computer equipped with a Calcomp 563 plotter.

Results

The chemical shifts and coupling constants for the compounds investigated (If–h) are summarized in Table I. The assignment of the coupling constants for compound If refers to the different methylene groups in the rotamers discussed below (see Figure 1).

Compound If. At low temperature (∼ −30°) the 4- and 6-methylene protons in 1,3-dibromo-2,4,6-trineopentyl-5-nitrobenzene give rise to three partly overlapping AB quartets, and the corresponding *tert*-butyl groups to three singlets. This is assumed to be due to the presence of various rotamers of different energies. (*Cf.* Figure 1, which shows the complete cycle of rotamer interconversions *via* single neopentyl rotations, on which the nmr line-shape analysis is based.) Two of the three AB quartets are of equal intensity, and are assumed to arise from the 4- and 6-methylene protons in rotamers A and C (Figure 1), which form an enantiomeric pair. The third AB quartet, of lower intensity, is assigned to the 4- and 6-methylenes in an achiral rotamer (B). A theoretically possible fourth rotamer with all three neopentyl groups on the same side of the ring plane has been excluded from consideration for reasons presented in the Discussion.

At higher temperatures, the signals from the 4- and 6-methylenes and those from the *tert*-butyl groups collapse to single lines. The changes in the line shapes with temperature are shown in Figures 2 and 3, along with theoretically simulated spectra and the corresponding values of τ, the mean lifetime for a proton in a given site.

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(7) P. Martinson and J. Márton, *Acta Chem. Scand.*, **22**, 2382 (1968).

(8) P. Martinson, *Acta Chem. Scand.*, **23**, 751 (1969).

(9) K. Olsson, *Acta Chem. Scand.*, **26**, 3555 (1972).

(10) P. Martinson, *Acta Chem. Scand.*, submitted for publication.

(11) T. Drakenberg, K.-I. Dahlqvist, and S. Forsén, *Acta Chem. Scand.*, **24**, 694 (1970).

(12) R. E. Carter, *Acta Chem. Scand.*, **22**, 2643 (1968).

(13) V. J. Kowalewski, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 1 (1969).

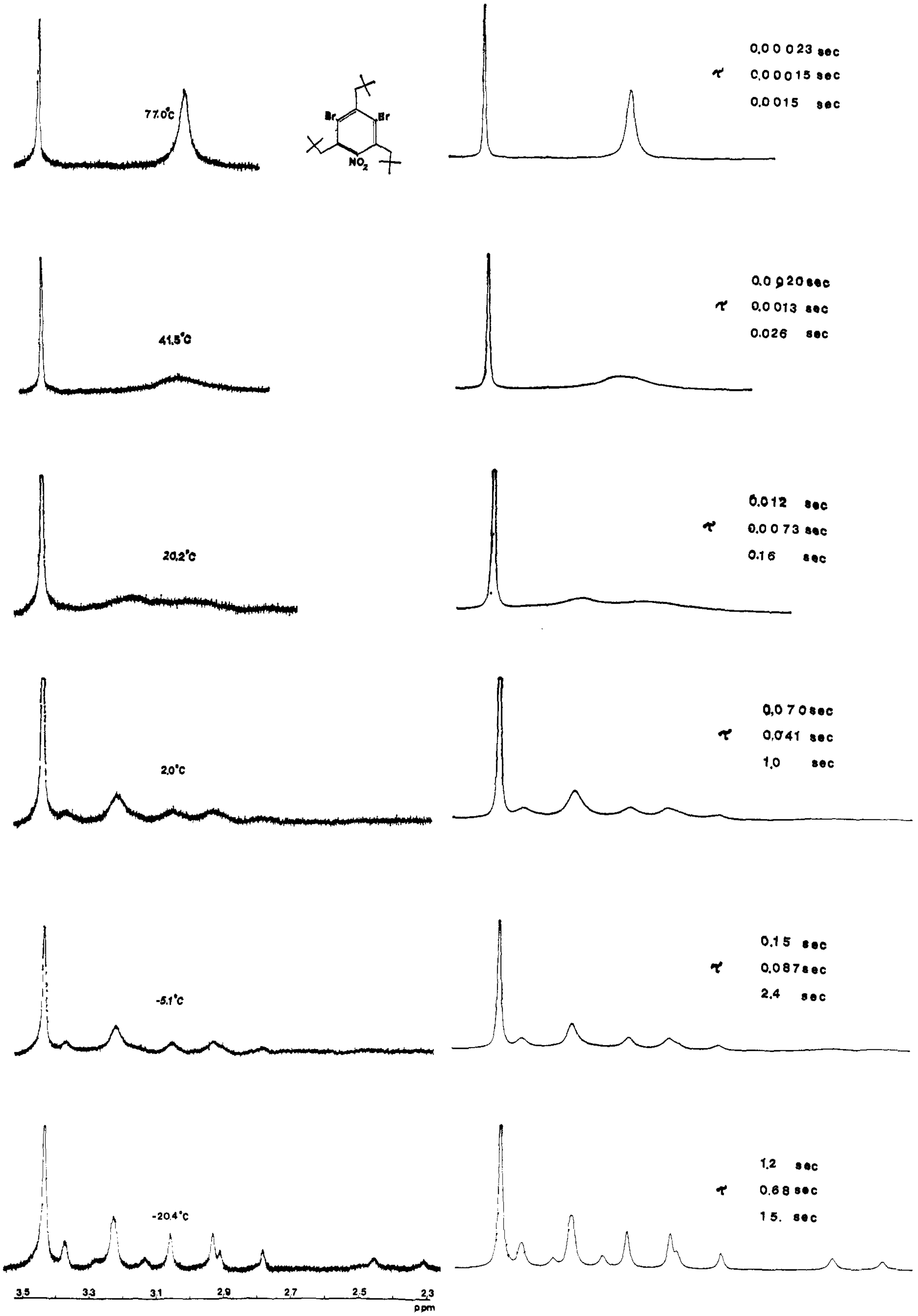

Figure 2. Experimental and calculated nmr spectra of the methylene protons in compound If at various temperatures. The experimental spectra were run at 100 MHz.

In terms of the cycle of rotamer interconversions shown in Figure 1, there are two rotamer populations available from the nmr spectra: one pertaining to chiral molecules (rotamers A and C; equal populations), and the other pertaining to achiral ones (B). These populations were determined by visual curve

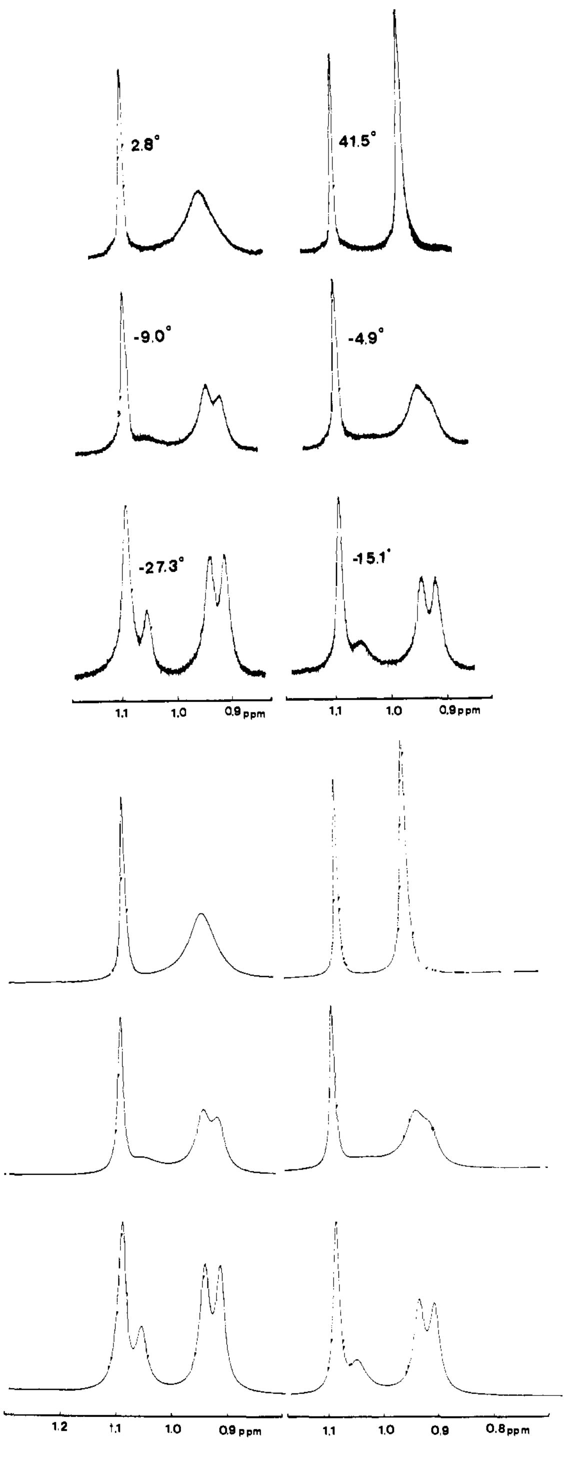

Figure 3. Experimental (top) and calculated (bottom) nmr spectra of the *tert*-butyl protons in compound If at various temperatures. The experimental spectra were run at 100 MHz.

fitting of the lines due to the *tert*-butyl groups over a temperature range of 20°. A slight increase in the population ratio, $P^B/P^A = P^B/P^C$, from 0.55_2 at 242.8°K to 0.57_7 at 264.2°K was found. If the temperature dependence of the population ratio is taken into account ($P^B/P^A = P^B/P^C = \exp(-\Delta G°/RT)$), $\Delta G°$ values of 287 and 289 cal/mol may be estimated at the above temperatures. Population values at higher temperatures could not be obtained with certainty from the *tert*-butyl spectra because the collapsing signal from the least populated rotamer (B) was hidden under the other signals. In the methylene proton spectra best curve fitting was obtained by assuming no change in the $\Delta G°$ values, and calculating populations at each temperature. In the temperature range of iteration (242.8–350.2°K), the population change under this assumption was 0.39–0.38 for the chiral molecules (A and C), and 0.22–0.24 for the achiral species (B).

The indor technique[13] was utilized to aid in the determination of the various AB chemical shift differences ($|\nu_A - \nu_B|$; "internal" chemical shift) and coupling constants for the 4- and 6-methylene protons. The internal shift differences for the three AB spectra were temperature independent, and the values are summarized in Table II. The remarkably large shift value (80 Hz) between the A and B protons in the spectrum due to the 4- and 6-methylene protons in rotamers B and B′ may be interpreted in terms of an increase in the dihedral angle between the nitro group and the aromatic ring (see subsequent discussion). Equations describing the (linear) dependence of $|\nu_A - \nu_B|$ or $(\nu_A + \nu_B)/2$ ("external" chemical shift) on temperature are also given in Table II. The shifts of the 4- and 6-*tert*-butyl groups, which were found to be temperature independent at slow exchange, are included in the same table.

The slightly temperature-dependent shift of the singlet from the 2-methylene protons was taken into account in the computer calculations (see Figure 2). The choice of appropriate values for the transverse relaxation times was difficult because in deuteriochloroform solution, sufficiently low temperatures to ensure that all lines were unaffected by exchange could not be reached. In the unsymmetrically halogen-substituted 1,3,5-trineopentylbenzenes, we observed[4] different T_2 values for the three methylene groups.[14] In principle, this should exclude the use of T_2 measurements on the signal from the 2-methylene protons in compound If at each temperature for obtaining a T_2 value for the 4- and 6-methylenes. Instead, we have calculated the difference in line width between the 2-methylene ($\Delta\nu_{1/2} = 0.6$ Hz) and the 4- and 6-methylene signals ($\Delta\nu_{1/2} = 2.1$ Hz) at high temperature (86.8°) and assumed that this contribution to the line width is constant throughout the whole temperature range. If we also assume that the three AB spectra have the same T_2 value, the T_2 parameter at each temperature may be determined. The errors at low temperatures are probably larger than those at higher temperatures because the 2-methylene protons should theoretically appear as one singlet and one strongly coupled AB quartet with intensities in the ratio $P^B/(P^A + P^C) = P^B/2P^A$, in which case exchange phenomena would increase the line width. A way of estimating the error in T_2 introduced at one temperature below the low temperature limit of rate determination (256.7°K) is to approximate the AB quartet by a single

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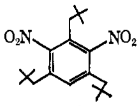
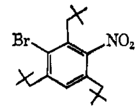
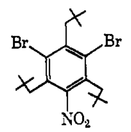
[14] In the original work[4] chloroform was used as solvent, which apparently did not allow sufficiently low temperatures to be reached before line broadening due to viscosity effects interfered with low-temperature T_2 determination. This is probably part of the explanation for the relatively large difference between the Eyring plots for the 1- and 5-methylenes and that for the 3-methylene protons in the chloroiodo compound (Ic); see Figure 3 of ref 4. We have recorded the spectrum of Ic in $CHClF_2$ (mp −135°), and the following T_2 parameters at −55° were obtained for the 1-, 3-, and 5-methylenes, respectively: 0.20, 0.25, and 0.20 sec. Using these values in conjunction with the high temperature T_2's previously determined,[4] new iterations at the high and low temperature ends of the ln $(1/\tau T)$ *vs.* $1/T$ plot were performed for the rotation of the 3-neopentyl groups. The results indicate that a complete line-shape analysis on the basis of the new T_2 values would certainly lead to a plot more closely approaching those for the 1- and 5-neopentyl groups.

Table II. Equations for the Chemical Shift Parameters ($\nu_A - \nu_B$) and ($\nu_A + \nu_B$)/2 as Functions of Temperature[a] (t, °C) Determined at 100 MHz

Trineopentylbenzene		$\nu_A - \nu_B$[b]	$(\nu_A + \nu_B)/2$
 (Ig)		$-0.10t + 36.0$ (1,5) $r = 0.945$	261.5 (1,5)
 (Ih)		$-0.11t + 30.7$ (1) $r = 0.999$ 36.1 (3) $-0.08t + 35.6$ (5) $r = 0.967$	286.7 (1) 304.9 (3) 251.2 (5)
 (If)	Methylene protons	28.0 (A4+C6+C′4+A′6)	$-0.024t + 315.2$ $r = 0.993$
		80.0 (B4+B6+B′4+B′6)	$+0.018t + 281.5$ ($r = 0.862$)
		40.8 (A6+C4+C′6+A′4)	309.1
	tert-Butyl protons		94.1[c] (A6+C4+C′6+A′4)
			105.6 (B4+B6+B′4+B′6)
			91.5[c] (A4+C6+C′4+A′6)

[a] The temperature-independent values are the means of about six points. [b] The different methylene groups in compounds Ig and Ih are identified in parentheses; in the case of If, the notation in parentheses refers to the 4- and 6-neopentyl groups of the various rotamers shown in Figure 1. The correlation coefficient r is also given; the plots consisted of five–six points. [c] This assignment should be regarded as tentative.

line and calculate a theoretical T_2 value from eq 1[15]

$$1/T_2' = P_1/T_{21} + P_2/T_{22} + P_1^2P_2^2(\omega_1 - \omega_2)^2(\tau_1 + \tau_2) \quad (1)$$

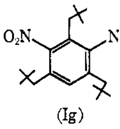
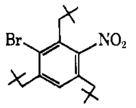
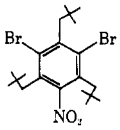
using the values 0.22 and 0.78 for the two populations involved. T_2' is the effective transverse relaxation time and P_1 and P_2 are the appropriate populations for the two lines. If $T_{21} = T_{22}$ and the peak separation is chosen as $(\omega_1 - \omega_2) = 2\pi 0.25$ radian/sec, a T_2 value of about 10% greater than that measured from the line width of the 2-methylene signal is obtained at the lowest temperature of iteration. The relaxation time varied from 0.21 to 0.32 sec in the temperature range under consideration if the broadening due to exchange at 256.7°K is taken into account.

Another way of estimating T_2 is to measure the line width of one signal from the 4- and 6-methylene protons in the dibromonitro compound (If) at low temperature, and then use the slope of the $1/T_2$ *vs.* temperature plot for the 2-bromo-4-nitro compound (Ih) to obtain values of T_2 at higher temperatures. In the same temperature region as that used in the above method, T_2 varied from 0.23 to 0.32 sec. The fact that the T_2 variation in both methods is essentially the same is probably fortuitous.

The T_2 parameters for the 4- and 6-*tert*-butyl protons were obtained from the line widths at both high and low temperatues, and are collected in Table III. We have assumed the same T_2 parameter at slow exchange for the three lines due to the 4- and 6-*tert*-butyl groups in all rotamers.

Compounds Ig and Ih. In the slow exchange limit, the spectrum of the 1- and 5-methylene protons in the dinitro compound (Ig) showed an AB pattern centered at 2.62 ppm from TMS, which was partly overlapped by the singlet from the 3-methylene protons at 2.78 ppm. The bromonitro compound (Ih) gave rise to three shifted AB methylene proton spectra at low temperature which collapsed to three singlets at higher temperatures.

Table III. Spin–Spin Relaxation Times (T_2) at Low and High Temperatures[a]

Trineopentyl-benzene	T_2, sec	Temp, °C	T_2, sec	Temp, °C
 (Ig)	0.10 (1) (5)	−55.0[b]	0.27 (1) (5)	51.8
 (Ih)	0.14 (1) 0.16 (5) 0.16 (3)	−23.0	0.29 (1) 0.26 (5) 0.26 (3)	93.0
 (If)	0.16[c] (4) (6)	−27.0	0.32[c] (4) (6)	86.8
	0.21–0.23[d] (4) (6)	−27.0	0.32[d] (4) (6)	86.8

[a] The numbers in parentheses refer to the different neopentyl groups. [b] A small amount of CH_2Cl_2 was used as resolution standard. [c] T_2 values from the spectra of the *tert*-butyl groups. [d] T_2 values from the spectra of the methylene protons (see text). The values given at low temperature refer to the two different T_2 measurements.

Curve fitting was performed by superposition of experimental and calculated spectra, and the parameters describing the line shape were determined as described below. The AB-shift parameters ($\nu_A - \nu_B$) and coupling constants for the methylene protons in the two compounds were calculated at several temperatures below the slow exchange limit of iteration. The temperature-dependent shift values were extrapolated to higher temperatures on linear plots, the equations of which are given in Table II.

As decoupling of the aromatic proton produced no significant effect on the line width of the methylene proton signal, the transverse relaxation times (T_2) were determined from the line width at both high and low temperatures. The values obtained in this way are given in Table III. A general broadening of all lines in

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(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 222.

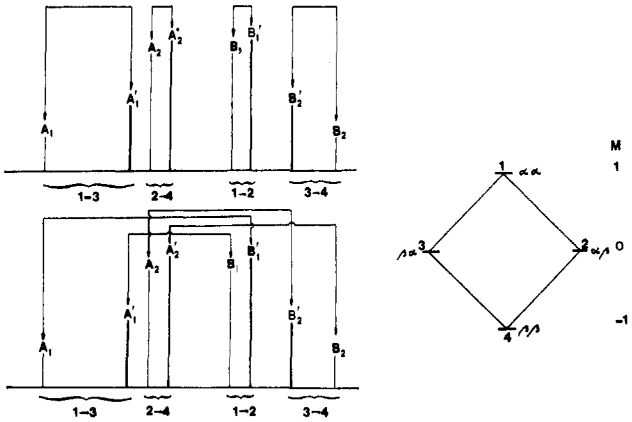

Figure 4. Different modes of exchange between two AB spectra. The various AB transitions are also indicated.

the dinitro compound, observed at temperatures below −60°, may be rationalized in terms of solvent viscosity effects.[4,14]

Computer Calculations. The computer program for calculation of spectra of the two compounds Ig and Ih was the same as that previously described.[4] The singlet from the 3-methylene protons in the 2,4-dinitro compound was taken into account by treating it as an AB spectrum with a shift parameter equal to zero. The temperature-dependent spectra of the methylene protons in compound If were more complex, and can theoretically be described by six coupled AB cases, assuming that the population of rotamers with all neopentyl groups on the same side of the ring is negligible (see subsequent discussion).

According to Kaplan[16,17] and Alexander,[18] the equation for the time-dependent density matrix, ρ, of an AB system of nuclear spins may be written

$$\mathrm{d}\rho/\mathrm{d}t = i[\rho,\mathcal{H}] - \rho/T_2 + (R\rho R^{-1} - \rho)/\tau_{\mathrm{AB}} \quad (2)$$

where $[\rho,\mathcal{H}]$ denotes the commutator of the spin density matrix and the Hamiltonian of the spin system, and R is an exchange operator. When eigenfunction representation is used, the elements of R are complicated functions of the different nmr parameters, but if basis functions are used instead, R becomes a permutation matrix symmetric about the diagonal, with all terms either 0 or 1.[19] In the rotating frame the nuclear spin Hamiltonian for an AB system takes the form[18]

$$\mathcal{H} = \omega_0(I_z^{\mathrm{A}} + I_z^{\mathrm{B}}) + \delta(I_z^{\mathrm{A}} - I_z^{\mathrm{B}}) + J_{\mathrm{AB}}(\mathbf{I}^{\mathrm{A}}\cdot\mathbf{I}^{\mathrm{B}}) \quad (3)$$

where $\omega_0 = \gamma H_0$, $2|\delta|$ is the chemical shift in frequency units between the A and B protons, and $\mathbf{I}^{\mathrm{A}}$ and $\mathbf{I}^{\mathrm{B}}$ are the nuclear spin vector operators. The last term in eq 2, which represents the exchange, may be alternatively expressed as $1/\tau_{\mathrm{AB}}[\rho$ (after exchange) $-$ ρ (before exchange)].

The 4- and 6-methylene protons in the rotamers shown in Figure 1 undergo several mutual exchanges and exist in various environments on going through an exchange cycle. Different terms of ρ (after exchange) are obtained depending on which methylene group is under consideration. A method developed by Kaplan and Fraenkel[19] simplifies the evaluation of ρ (after exchange) even in rather complicated exchanges. If the rows and columns of the density matrix ρ^k, where k denotes the kth rotamer, are labeled by the basis functions, $abcd$, $a'b'c'd'$ (as done for the 4- and 6-methylenes in Figure 1), the ρ^k (after exchange) for the 4- as well as the 6-methylene protons can be evaluated. A general expression for the kth rotamer exchange may be obtained if three different environments $l \rightleftarrows k \rightleftarrows m$ are considered, with rate constants of the type $1/\tau_{kl}$ (from k to l). The two different results for the exchange terms in the case of rotamer A are for 6- (eq 4) and 4-methylene (eq 5)

$$\rho^{\mathrm{B}}{}_{dc,d'c'}/\tau_{\mathrm{BA}} + \rho^{\mathrm{A}'}{}_{ab,a'b'}/\tau_{\mathrm{A'A}} - \rho^{\mathrm{A}}{}_{cd,c'd'}/\tau_{\mathrm{A}}{}^{\mathrm{red}} \quad (4)$$

$$\rho^{\mathrm{B}}{}_{ab,a'b'}/\tau_{\mathrm{BA}} + \rho^{\mathrm{A}'}{}_{cd,c'd'}/\tau_{\mathrm{A'A}} - \rho^{\mathrm{A}}{}_{ab,a'b'}/\tau_{\mathrm{A}}{}^{\mathrm{red}} \quad (5)$$

where $1/\tau_{\mathrm{A}}{}^{\mathrm{red}} = 1/\tau_{\mathrm{AB}} + 1/\tau_{\mathrm{AA'}}$. Different line shapes are obtained in the solution of the density matrix equation for the two cases. If the 4-methylene protons in rotamers A and B are considered (Figure 1), one can see that the protons have not changed places but each has acquired a slightly modified environment. This can be understood as a case in which corresponding lines exchange in the subspectrum from each AB environment.

A way of tackling the exchange problem is to modify the equation given by Sutherland[20] in his recent comprehensive review on nmr kinetics. All exchange terms are taken to be of the type in expression 5, and the cyclic exchanges are distinguished in the computer calculations by choosing different signs of the chemical shift parameter, δ, in the following way. A single AB spectrum is symmetric about the frequency, ω_0, and the resonance frequencies for the two nuclei can be defined as $\omega_{\mathrm{A}} = \omega_0 + \delta$ and $\omega_{\mathrm{B}} = \omega_0 - \delta$, where $2|\delta| = |\omega_{\mathrm{A}} - \omega_{\mathrm{B}}|$ is the chemical shift. It is evident that a sign change of δ permutes the A and B frequencies. The result on the basis functions ($\psi_1 = \alpha(\mathrm{A})\alpha(\mathrm{B})$, $\psi_2 = \alpha(\mathrm{A})\beta(\mathrm{B})$, $\psi_3 = \beta(\mathrm{A})\alpha(\mathrm{B})$, and $\psi_4 = \beta(\mathrm{A})\beta(\mathrm{B})$) is an interchange of the ψ_2 and ψ_3 levels, and the influence on the transitions is that 1 → 2 changes to 1 → 3 and 2 → 4 changes to 3 → 4 (*cf.* Figure 4). For a single exchanging AB system the labeling is invariant, but for two (or more) exchanging AB systems, it is of utmost importance to know if, for example, a 1 → 2 line in one system exchanges with a 1 → 2 or a 1 → 3 line in the other AB system, *i.e.*, if A exchanges with A′ or with B′ (Figure 4). By choosing different signs of δ each case may be represented. Equation 2 can be expressed in explicit form for each exchange, taking into account the population (p^k) in each environment.

The equations for the kth rotamer are

$$\mathrm{d}\rho^k{}_{12}/\mathrm{d}t = 1/2i\cdot J^k\cdot\rho^k{}_{13} + p^k\cdot i\cdot C + i\left(\delta^k - \frac{1}{2}J^k - \omega^k{}_0 + \omega\right)\rho^k{}_{12} - \rho^k{}_{12}/T^k{}_{2\mathrm{B}} - \rho^k{}_{12}/\tau_k{}^{\mathrm{red}} + \rho^l{}_{12}/\tau_{lk} + \rho^m{}_{12}/\tau_{mk} \quad (6)$$

$$\mathrm{d}\rho^k{}_{13}/\mathrm{d}t = \frac{1}{2}\,i\cdot J^k\cdot\rho^k{}_{12} + p^k\cdot i\cdot C - i\left(\delta^k + \frac{1}{2}J^k + \omega_0{}^k - \omega\right) \times \rho^k{}_{13} - \rho^k{}_{13}/T^k{}_{2\mathrm{A}} - \rho^k{}_{13}/\tau_k{}^{\mathrm{red}} + \rho^l{}_{13}/\tau_{lk} + \rho^m{}_{13}/\tau_{mk} \quad (7)$$

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(16) J. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958).

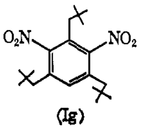
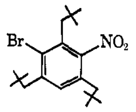
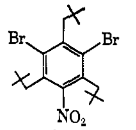
(17) J. Kaplan, *J. Chem. Phys.*, **29**, 462 (1958).

(18) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962).

(19) J. Kaplan and G. Fraenkel, *J. Amer. Chem. Soc.*, **94**, 2907 (1972).

(20) I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, **4**, 97 (1971).

Table IV. Parameters for Internal Rotation in If–h[a]

Trineopentylbenzene		$\Delta G^{\ddagger}_{298\,°\mathrm{K}}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$ cal/(mol deg)
 (Ig)		12.9 ± 0.1 (1) (5)	12.7 ± 0.2 (1) (5)	−0.8 ± 0.7 (1) (5)
 (Ih)		14.4 ± 0.1 (1) 14.4 ± 0.1 (3) 14.4 ± 0.1 (5)	13.3 ± 0.6 (1) 13.8 ± 0.6 (3) 13.7 ± 0.7 (5)	−3.7 ± 1.9 (1) −2.0 ± 2.1 (3) −2.3 ± 2.3 (5)
 (If)	Methylene protons	14.6 ± 0.1 (A → B) 14.3 ± 0.1 (B → C) 16.2 ± 0.1 (A ⇄ A′)	15.2 ± 0.3 (A → B) 14.4 ± 0.3 (B → C) 16.8 ± 0.2 (A ⇄ A′)	2.1 ± 1.2 (A → B) 2.3 ± 1.2 (B → C) 2.1 ± 0.5 (A ⇄ A′)
	Methylene protons[b]	14.5 ± 0.2 (A → B) 14.2 ± 0.2 (B → C)	16.5 ± 0.8 (A → B) 16.3 ± 0.8 (B → C)	6.8 ± 2.9 (A → B) 6.9 ± 2.9 (B → C)
	tert-Butyl protons[c]	14.4 ± 0.2 (A → B) 14.1 ± 0.2 (B → C)	16.7 ± 0.8 (A → B) 16.7 ± 0.8 (B → C)	7.8 ± 3.1 (A → B) 8.9 ± 2.9 (B → C)

[a] The error limits are only random errors from the least-squares treatment. The numbers in parentheses refer to the different neopentyl groups. [b] Activation parameters obtained with values included from the ends of the Eyring plots (see Figure 6). [c] Activation parameters obtained from a limited temperature region (seven points between 252 and 287 °K).

where the subscripts of ρ refer to the different transitions. Using the steady-state approximation, $d\rho^k/dt = 0$, eq 6 and 7 were expressed for each rotamer and the ρ values were obtained from a 12th-order equation system. Evaluation of the expressions for ρ^k_{24} and ρ^k_{34} gives two more equations with the same coefficients, except that the sign before the coupling constant is reversed. The theoretical absorption intensity of the spectrum is given by a summation of the imaginary parts of all 24 ρ values. It is obvious that a reverse sign of δ in either (6) or (7), accompanied by a permutation of the subscripts, converts one equation into the other.

The AB spectra due to the 4- and 6-methylenes in the chiral rotamers A and C have iterated chemical shifts ($|\nu_A - \nu_B|$) of 40.8 and 28.0 Hz at −30.4°. If the larger shift is assigned to the protons of the 6-methylene group in rotamer A (magnetically equivalent with the 4-methylene group of rotamer C; Figure 1), and the shift parameter (δ) for one proton in this methylene group is given with a positive sign, we may follow the sign changes in this parameter through a cycle of exchanges, diagramatically expressing the sign changes as

$$\begin{tikzcd}
 & B+ \arrow[dr] & \\
A+ \arrow[ur] & & C- \arrow[d] \\
A'+ \arrow[u] & & C'- \arrow[dl] \\
 & B'- \arrow[ul] &
\end{tikzcd}$$

The alternative is to instead consider the 4-methylene group in rotamer A (magnetically equivalent with the 6-methylene group in rotamer C) through an exchange cycle, whereupon another sign combination results

$$\begin{tikzcd}
 & B- \arrow[dr] & \\
A+ \arrow[ur] & & C- \arrow[d] \\
A'+ \arrow[u] & & C'- \arrow[dl] \\
 & B'+ \arrow[ul] &
\end{tikzcd}$$

If the assignment is reversed, *i.e.*, the larger AB shift assigned to the protons of the 4-methylene group in rotamer A, the sign combinations for the 4- and 6-methylenes on going through an exchange cycle will, of course, be different from those given above. It is possible to distinguish these sign combinations from a complete line-shape analysis. However, the effective temperature range of iteration is too small for a visual observation of the exchange because of the low population of achiral rotamers (B). A theoretical shift parameter can, however, be obtained by summing the AB shifts with the same sign, multiplied by the appropriate population for each rotamer, and subtracting those with opposite sign. In our case three AB spectra collapse to a broadened AB pattern, which at higher temperature becomes a singlet. The shift between the A and B protons at 20.2° in this broadened AB quartet may be calculated to be 23.4 and 14.0 Hz for the sign combinations considering the 6- and 4-methylene groups, respectively. The nmr spectra at temperatures around 20° show that a shift value as high as 23.4 Hz is not very plausible, and curve fitting was unsuccessful with the sign combination obtained from the 6-methylene group in Figure 1.

The activation parameters were calculated from the Eyring[21] equation assuming a transmission coefficient of unity. Three different rate constants describing two independent processes were calculated from both *tert*-butyl and methylene proton spectra. The rate constants refer to the rotations of the 6- and 4-neopentyl groups, *e.g.*, A → B and B → C, and that of the 2-neopentyl group, *e.g.*, C ⇄ C′, which leads to a mutual exchange of the 4- and 6-methylene proton environments. The τ values obtained from the methylene signals in the spectrum of the bromonitro compound (Ih) and from the 6- and 4-*tert*-butyl group rotations were used as input in the calculation of rate constants from the

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(21) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, p 195 f.

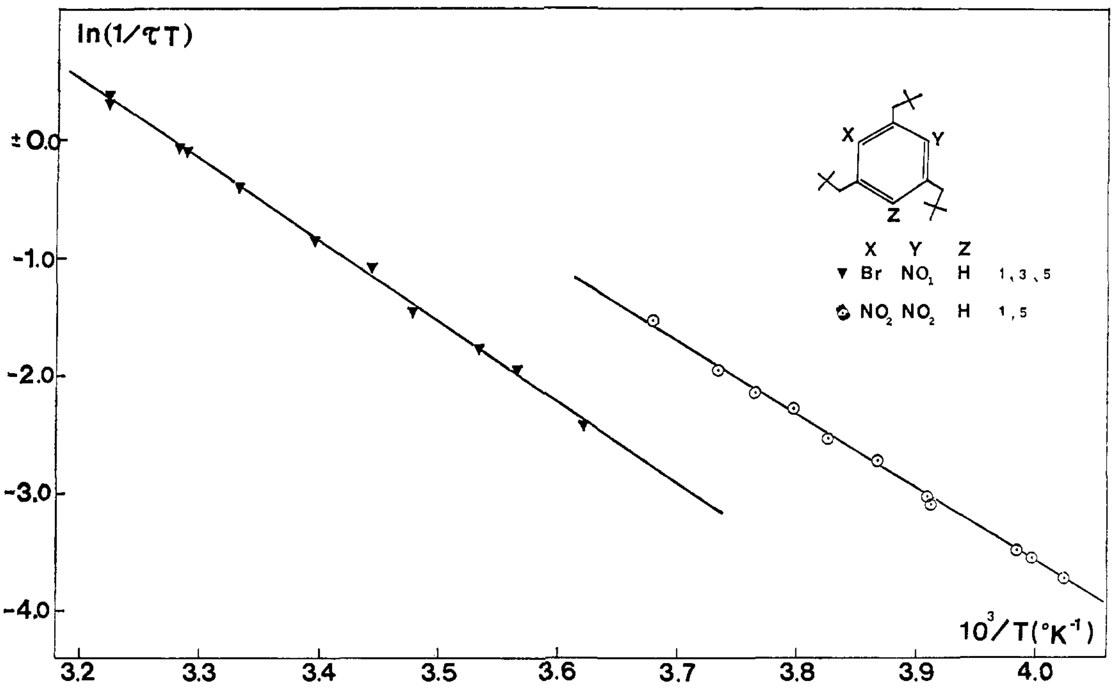

Figure 5. Plots of ln $(1/\tau T)$ *vs.* $1/T$ for Ig (⊙) and Ih (▼).

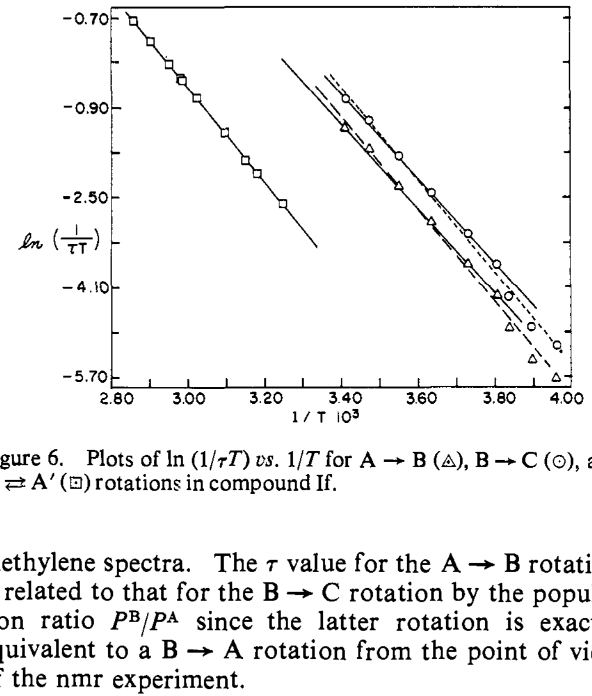

Figure 6. Plots of ln $(1/\tau T)$ *vs.* $1/T$ for A → B (△), B → C (⊙), and A ⇄ A′ (⊡) rotations in compound If.

methylene spectra. The τ value for the A → B rotation is related to that for the B → C rotation by the population ratio P^B/P^A since the latter rotation is exactly equivalent to a B → A rotation from the point of view of the nmr experiment.

The free energies, enthalpies, and entropies of activation for the three compounds are summarized in Table IV, where reported error limits are random errors[22] from the least-squares treatment of the rate data. Plots of ln $(1/\tau T)$ *vs.* $1/T$ for Ig and Ih are shown in Figure 5. In the case of If, the points at the low-temperature end of the Eyring plot for the A → B and B → C rotations proved to be relatively insensitive to the value of τ. We have calculated activation parameters including three such values (see Figure 6), which may be compared to the parameters obtained if these values are excluded. The τ values for A ⇄ A′ rotations at the low-temperature end of the Eyring plot and those for A → B rotations in the same temperature interval are interdependent, and a change in the A → B τ value by +10% could be compensated by a larger change in the other (−50%). Similarly, at the high-temperature end of the A → B Eyring plot interdependent τ values are also expected. Consequently, the ends of the Eyring plots are most uncertain, which affects the $\Delta S^{\neq}$ values. The accuracy in $\Delta S^{\neq}$ for an A ⇄ A′ rotation is probably less than that for an A → B rotation, as many of the parameters describing the line shape are extrapolated over a larger temperature interval in the former case than in the latter. The temperature dependence of the *tert*-butyl proton signals due to rotation of the 4- and 6-neopentyl groups could only be studied in a limited temperature region due to the interdependence of the two rate processes, and the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values from these spectra given in Table IV are necessarily uncertain.

To estimate the error in $\Delta S^{\neq}$ for compounds Ig and Ih, we have used an equation developed by Taft and coworkers.[23] If k and Δk are the rate constant and its corresponding error for the internal rotation, the error can be calculated from eq 8. Here T_1 and T_2 are the

$$\Delta(\Delta S^{\neq}) = \pm R/(T_2 - T_1)[(T_2\Delta k_2/k_2)^2 + (T_1\Delta k_1/k_2)^2]^{1/2} \quad (8)$$

temperatures at the ends of the Eyring plot with corresponding rate constants, k_1 and k_2. The errors were calculated to be 1.1 and 2.2 cal/(mol deg) for compounds Ig and Ih with a 10% error in the τ values.

Discussion

In the symmetrically 2,4-disubstituted compounds (Ia,b,g) we assume the initial state to be a time-average

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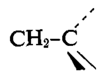
[22] The error limits in $\Delta G^{\neq}{}_{298°}$ were obtained directly from a least-squares treatment of ln $(1/\tau T)$ *vs.* $1/T$. In previous work[4] the error limits in $\Delta G^{\neq}$ were based on the least-squares errors in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ which resulted in unrealistically large random errors. Treatment of the previous data[4] with the least-squares program used in the present work gave error limits in $\Delta G^{\neq}{}_{298°}$ lower than 0.1 kcal/mol.

[23] E. L. Purlee, R. W. Taft, Jr., and C. A. De Fazio, *J. Amer. Chem. Soc.*, 77, 837 (1955).

conformation in which a plane through the 3-neopentyl group is perpendicular to the ring plane, whereas in the unsymmetrically disubstituted compounds this plane is not necessarily perpendicular to the ring due to differences in the nonbonded repulsions between the neopentyl group and the ortho substituents. In the trisubstituted compound If, the initial state for the rotation of the 4- and 6-neopentyl groups is analogous to that in the unsymmetrically disubstituted compounds. This is also the case for the 2-neopentyl group in the chiral rotamers A and C, since the nonbonded interactions between *tert*-butyl groups on the same side of the ring may be expected to lead to a twist of the 2-neopentyl group about the C_{aryl}–C-bond axis. On the other hand, the initial state of the 2-neopentyl group in rotamer B is quite analogous to that in the symmetrically disubstituted compounds. In both the disubstituted compounds and in compound If we define the transition state as a conformation in which the



CH_2–C

bond of one neopentyl group is in the plane of the ring.

The results of the study of compounds Ig and Ih are nicely accounted for by an interpretation in terms of induced magnetic nonequivalence, as previously suggested[4,5] for 2,4-dihalo-1,3,5-trineopentylbenzenes. It is interesting to note that the barrriers for the dihalo compounds are apparently independent of the nonbonded repulsions between the 3-methylene group and the larger halogen. Thus the dibromo and bromoiodo compounds gave essentially the same $\Delta G^{\ddagger}$ value (16.6 and 16.7 kcal/mol) for rotation past a bromine.[3,4]

The three partly overlapping AB quartets in the spectrum of 2-bromo-1,3,5-trineopentyl-4-nitrobenzene (Ih) collapsed at about the same temperature and gave a $\Delta G^{\ddagger}$ value of 14.4 ± 0.1 kcal/mol. Let us first assume that the 3-neopentyl group rotations are solely past the nitro group. If only the symmetry factor $RT \ln 2$ is taken into account, a free energy of activation of around 14.0 kcal/mol at 298°K would be expected for 1,3,5-trineopentyl-2,4-dinitrobenzene (Ig). However, $\Delta G^{\ddagger}$ was found to be only 12.9 kcal/mol (see Table IV). A plausible explanation for this observation may be made in terms of an increased resonance stabilization of the transition state by *one* nitro group for the rotation of the 3-neopentyl group past the other nitro group. The resonance effect from the cylindrically symmetric bromine in the bromonitro compound is assumed to be the same in both initial and transition states. As mentioned above, the steric interactions between the bromine and the methylene group apparently have a negligible effect on the height of the barrier.

Hitherto, we have only considered the rotation past the nitro group in the bromonitro compound. However, it is possible that the nitro group can lower the barrier in a rotation past the *bromine* by increased resonance interaction with the aromatic ring in the transition state as the result of a decrease in the NO_2-ring dihedral angle. In order to obtain a value for a nitro-*tert*-butyl barrier, we performed a complete line-shape analysis[24] of the temperature-dependent nmr spectrum of 2-iodo-1,3,5-trineopentyl-4-nitrobenzene. Within the combined limits of error, the $\Delta G^{\ddagger}$ value (14.4 ± 0.1 kcal/mol) was found to be equal to that for the bromonitro compound, which may be taken as an indication—but not a proof—that the rotations in both compounds are past the nitro group.

The observation of three AB patterns due to the 4- and 6-methylene protons in 1,3-dibromo-2,4,6-trineopentyl-5-nitrobenzene at slow interconversion rates may be readily understood in terms of the scheme of rotamers in Figure 1. The rotamers A ($\equiv$A′) and C ($\equiv$C′) are chiral and are related to each other by mirror-image symmetry; rotamer B ($\equiv$B′) is achiral. The interconversions A $\rightleftarrows$ A′ and C $\rightleftarrows$ C′ are of course degenerate, but detectable from the point of view of the nmr experiment, since the 4- and 6-methylene protons switch environments during these interconversions.

The deviation of the population ratio $P^{A+C}:P^{B}$ (found to be 3.6:1 at −30.4° by curve fitting) from the statistically expected 2:1 may be rationalized in terms of a difference in the time-average value of the dihedral angle between the plane of the nitro group and that of the aromatic ring. The spatial orientations of the 4- and 6-methylene groups in rotamers A and C allow the nitro group to twist further toward the ring plane than in rotamer B, leading to a more effective nitro-ring resonance interaction in the former rotamers.

Supporting evidence for this interpretation may be obtained from consideration of the chemical shifts of the protons in the various methylene groups. Yamaguchi[25] has reported a regular dependence of *o*-methyl shifts on the rotational angle of the nitro group in aromatic compounds, which has been attributed to magnetic anisotropy. The contribution of the mesomeric effect of the nitro group to the methyl shift is assumed to change negligibly with the dihedral angle between the nitro group and the aromatic ring.[25] Both calculations and results on polymethyl nitrobenzenes as well as on methyl nitronaphthalenes[26,27] show that the contribution to the *o*-methyl shift changes sign when the nitro group moves from planar to perpendicular to the aromatic ring. In view of these results, it is quite reasonable to suggest that in compound If the protons nearest the nitro group in all rotamers are most upfield. The upfield shift value (2.41 ppm at −30.4°) for the 4- and 6-methylene protons nearest the nitro group in the achiral rotamer (B) compared to those of rotamers A and C (2.89 and 3.01 ppm) is due to an *increase* in the dihedral angle.

The possibility of establishing the details of the exchanges between the three AB spectra by a complete line-shape analysis offers a way of determining the effect of the position of the 2-neopentyl group on the 6- and 4-methylene proton shift. A larger AB shift value for the 6- and 4-methylene protons (A6, C4, C′6, A′4; $\nu_A - \nu_B = 40.0$ Hz) is obtained for the neopentyl group on the same side of the ring as the 2-neopentyl group. The increased shift may be plausibly explained in terms of a change in the average distance between one methylene proton and the nitro group due to nonbonded repulsions between the two *tert*-butyl groups.

Theoretically, a fourth rotamer with all neopentyl groups on the same side of the ring exists. The energy difference between such a rotamer and those in Figure 1

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[24] B. Nilsson, P. Martinson, K. Olsson, and R. E. Carter, unpublished results.

[25] I. Yamaguchi, *Mol. Phys.*, 6, 105 (1963).

[26] P. R. Wells and P. G. E. Alcorn, *Aust. J. Chem.*, 16, 1108 (1963).

[27] P. R. Wells, *Aust. J. Chem.*, 17, 967 (1964).

is probably too large to allow its detection by the nmr technique. We have estimated the difference in nonbonded repulsions between such a rotamer and rotamer B by employing a Lennard–Jones 6–12 potential function.[28] Idealized geometries, with the nitro group perpendicular to the ring plane in the two rotamers, were assumed, and only atom–atom distances smaller than about 7 Å were taken into account. The coefficient for the r^{-6} term in each potential equation was determined by using the Slater–Kirkwood equation[28,29] and that for the r^{-12} term was obtained by minimizing the energy for a distance equal to the sum of the van der Waals radii of the interacting atoms. The methyl groups were treated as "extended atoms."[28] In this way we obtained an energy difference between the two rotamers of 565 cal/mol, and the populations at 298°K of all four rotamers may be calculated to be $P^{A+C}:P^{B}:P^{X} = 0.70:0.22:0.08$, where P^X is the population of the rotamer with all neopentyl groups on the same side of the ring.

Acknowledgments. We wish to express our thanks to Dr. Torbjörn Drakenberg for stimulating discussions and for help with the computer program. We are grateful to Dr. Peter Stilbs for providing us with the least-squares program for treatment of rate data, and to Professor Lars Melander for illuminating comments on the manuscript. This work was supported by the Swedish Natural Sciences Research Council and a grant from Stiftelsen Bengt Lundquists Minne (to B. N.).

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[28] H. A. Scheraga, *Advan. Phys. Org. Chem.*, **6**, 103 (1968).

[29] R. E. Carter and J. Sandström, *J. Phys. Chem.*, **76**, 642 (1972).

The Regioselectivity of Concerted Cycloadditions

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Received December 15, 1972

Abstract: Perturbation theory can be used to predict the preferred orientation (regioselectivity) of concerted cycloadditions. In many, but not all, cases, 2 + 2 thermal cyclodimerizations are expected to occur in a head-to-tail manner and 2 + 2 photodimerizations in a head-to-head manner, if the reactions are concerted. In the same sense, 4 + 2 thermal semipolar photocycloadditions are expected to occur with "meta" orientation and 4 + 2 semipolar photocycloadditions with "para" or "ortho" orientation, if the reactions are concerted. These predictions are compared with experimental evidence, and the mechanistic implications are discussed.

While the stereoselectivity of pericyclic reactions has been the topic of numerous theoretical investigations,[1–8] the regioselectivity of pericyclic reactions has only recently received attention from theoretical chemists.[9] We shall use perturbation theory[10] in order to derive rules concerning the regioselectivity of nonpolar *concerted* 2 + 2 and 4 + 2 cycloadditions.

2 + 2 Dimerizations. We first consider the thermal dimerization of propylene and inquire which of the two possible regiochemical modes of union of the cycloaddends will be preferred. The two distinct regiochemical modes of union are the head-to-head (HH) and the head-to-tail (HT) modes of cycloaddend union. Figure 1a shows the principal MO interactions in the concerted $2_s + 2_a$ thermal dimerization of propylene. The stabilization energy due to orbital interaction for each of the two regiochemical modes is given by

$$\mathrm{SE(HH)} = [4_\gamma{}^2/(E_1 - E_2)](C_{11}C_{21} + C_{12}C_{22})^2 \quad (1)$$

$$\mathrm{SE(HT)} = [4_\gamma{}^2/(E_1 - E_2)](C_{11}C_{22} + C_{12}C_{21})^2 \quad (2)$$

In the expression above, E_1 and E_2 are the energies of the frontier MO's of propylene, γ is the resonance integral of the uniting p atomic orbitals, and C's are AO coefficients with the first index denoting the appropriate MO and the second index denoting the appropriate carbon atom. It becomes clear that regioselectivity will depend on the magnitude of the coefficient terms of eq 1 and 2, and it is easy to show that the coefficient term of eq 2 is greater than the one of eq 1. Calculations show that $C_{12} \simeq C_{21} > C_{11} \simeq C_{22}$. If one makes the substitutions $C_{12} \simeq C_{21} = a$ and $C_{11} \simeq C_{22} = b$, eq 1 and 2 become

$$\mathrm{SE(HH)} = K(2ab)^2 \quad (3)$$

$$\mathrm{SE(HT)} = K(a^2 + b^2)^2 \quad (4)$$

where K equals $4_\gamma{}^2/(E_1 - E_2)$. The inequality $a^2 + b^2 > 2ab$ holds for all positive values of a and b, except $a = b \geq 0$. The conclusion is then reached that SE(HT) > SE(HH) and, accordingly, a concerted thermal dimerization of propylene is predicted to occur in a

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[1] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

[2] M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

[3] H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

[4] K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

[5] L. Salem, *J. Amer. Chem. Soc.*, **90**, 543, 553 (1968).

[6] C. Trindle, *J. Amer. Chem. Soc.*, **92**, 3251, 3255 (1970); T. F. George and J. Ross, *J. Chem. Phys.*, **55**, 3851 (1971).

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