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The Barrier to Internal Rotation in 2,4-Dichloro- and 2,4-Dibromo-1,3,5-trineopentylbenzene from Computer Treatment of Digitized NMR Lineshapes

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The title compounds have been prepared and the temperature dependence of the AB spectrum due to the restricted rotation of the 1- and 5-neopentyl groups has been studied by means of complete lineshape analysis of digitized NMR spectra. The activation parameters for the dichloro compound are $\Delta H^{\ddagger}=14.5\pm0.5$ kcal/mole and $\Delta S^{\ddagger}=0.6\pm2.3$ e.u., and for the dibromo compound $\Delta H^{\ddagger}=16.2\pm0.5$ kcal/mole and $\Delta S^{\ddagger}=-0.1\pm2.3$ e.u. A comparison of these data should reflect the relative effective sizes of the Cl and Br substituents. The internal rotation in these compounds is discussed in terms of a concerted disrotatory pathway which allows the bulky *t*-butyl groups to always be as far as possible from each other.

The observation of temperature-dependent AB-type NMR spectra for the $-CH_2$-protons in the 1- and 5-neopentyl groups of appropriately substituted 1,3,5-trineopentylbenzene derivatives (I) [1,2] prompted us to initiate an investigation of a series of such compounds in view of the possibility that the

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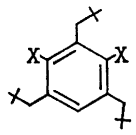
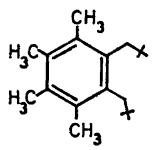


I
a X = Cl
b X = Br

major part of the barrier to internal rotation may be due to the steric effect of X, and thus a careful determination of the barrier heights for different X groups might give a quantitative measure of the relative effective size of each kind of substituent.

These compounds provide examples of hindered rotation about an sp^2—sp^3 carbon-carbon bond in relatively simple aromatic derivatives. The work of Dix *et al.*[3] on 1,2-dineopentyltetramethylbenzene (II) and that of Newsoroff



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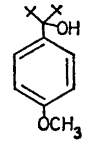

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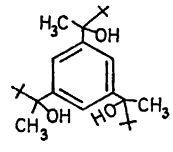

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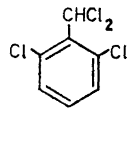
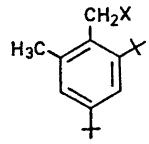


V

and Sternhell [4] on *p*-methoxyphenyl di-*t*-butylcarbinol (III) afforded the first two examples of this type of restricted rotation. From the data presented by Dix *et al.*[3] for II a value of 16 kcal/mole for $\Delta F^{\ddagger}$ at the collapse temperature may be estimated. Recently, the rotational barrier in 1,3,5-tris(1,2,2-trimethylpropan-1-ol)benzene (IV) was found [5] to be too high (>25 kcal/mole) for determination by the NMR kinetic method, and that in α,α,2,6-tetrachlorotoluene (V) was estimated to be 15±1 kcal/mole ($\Delta F_{25}^{\ddagger}$).[6]

Cupas *et al.*[7] have studied hindered rotation in 2,4-di-*t*-butyl-6-methylbenzyl halides (VI), and have determined the rotational barrier about the C_{Ar}—CH_2 bond by means of complete lineshape analysis. The barrier in this case is apparently a halogen-methyl barrier, and was found to be 11.3, 12.5, and 15.9 kcal/mole (E_a) for the chloride, bromide, and iodide, respectively.



VI
X = Cl, Br, I

In this paper, we report the results of complete lineshape analyses on digitized NMR spectra of the 2,4-dichloro and 2,4-dibromo compounds I*a* and *b*, carried out with the aid of a computer programmed to find the best fit of theoretically calculated lineshapes to those experimentally observed. Attempts to include the corresponding diiodo compound in this investigation were unsuccessful due to synthetic difficulties.[2]

METHODS AND RESULTS

Synthesis.[2] The dichloro compound (Ia) was synthesized by direct chlorination of 1,3,5-trineopentylbenzene with chlorine gas in dimethylformamide solution at 0°C. The dibromo compound (Ib) was originally prepared in two separate bromination steps. In the first, trineopentylbenzene was treated with excess bromine in dimethylformamide solution at room temperature, and in the second, monobromotrineopentylbenzene was further brominated in acetic acid:dioxane 5:1 (v/v) at room temperature in the presence of silver perchlorate or silver trifluoroacetate as catalyst. A direct route to the dibromo compound was found to be the reaction of trineopentylbenzene with excess bromine in the presence of iron powder in carbon tetrachloride solution at room temperature.

NMR spectra. All spectra were run at 60 MHz on *ca.* 6 mole % chloroform-*d* solutions. The line width of internal TMS was adjusted to approximately the same value at each temperature in an attempt at maintaining the contribution of instrumental inhomogeneity, instability, *etc.* to the line width at a constant level. At least three (and in most cases five) spectra of the 1- and 5-CH_2-protons were recorded and digitized at each temperature. (For details, see the Experimental Section.)

Table 1. Chemical shifts[a] at probe temperature.

Trineopentylbenzene	δ, ± 0.003 ppm				
	1,5—*t*-Bu	3—*t*-Bu	1,5—CH_2—	3—CH_2—	Aryl H
2,4-Dichloro	0.965	1.017	2.719	3.112	6.894
2,4-Dibromo	0.981	1.049	2.802 [b]	3.346	6.930

[a] In ppm downfield from internal TMS in ~6 mole % chloroform-*d* solutions.
[b] Center of broadened AB quartet.

The chemical shifts determined at probe temperature are given in Table 1. These data are not abnormal and warrant no further comment, except to note that the peak for the aryl proton was broadened, most likely due to coupling with the —CH_2-groups. In the case of the dibromo compound, the low-temperature AB spectrum for the 1- and 5-CH_2-groups was slightly but reproducibly asymmetrical, perhaps as the result of *stereospecific* long-range coupling with the aromatic proton. A corresponding asymmetry in the spectrum

of the dichloro compound was not unequivocally discernible, in part due to some overlap between the 3-CH_2-peak and the low-field side of the low-temperature AB spectrum. In the calculation of the theoretical lineshapes the asymmetry in the spectra of the dibromo compound was explicitly taken into account (see below), whereas the spectra of the dichloro compound were assumed to be symmetrical but broadened by coupling with the aromatic proton.

Computer calculations. All calculations were performed on either a CDC-3200 or an IBM 360/75 computer.

The computer program for the calculation of theoretical lineshapes was based on the density matrix lineshape equations [8] for the coupled AB system.[9] The expression describing the absorption mode is the imaginary part v of the complete density matrix equation for the expectation value of the transverse component of the total magnetization, and is given [9] by

$$v = C\left\{\frac{r_+ b_+ - s a_+}{a_+^2 + b_+^2} + \frac{r_- b_- - s a_-}{a_-^2 + b_-^2}\right\}$$

where

$$a_\pm = [\omega_0 - \omega) \pm \tfrac{1}{2}J]^2 - (\tau^{-1} + T_2^{-1})^2 - \delta^2 - \tfrac{1}{4}J^2 + \tau^{-2}$$

$$b_\pm = 2[(\omega_0 - \omega) + \tfrac{1}{2}J](\tau^{-1} + T_2^{-1}) \mp J/\tau$$

$$r_\pm = (\omega_0 - \omega) \pm J$$

$$s = 2/\tau + T_2^{-1}$$

In these equations, $\omega_0 - \omega$ is the frequency separation between the center of the AB spectrum and the observing rf field rotating at frequency ω; J is the AB coupling constant; T_2 is the transverse relaxation time, related to the natural line width W (in Hz) by $W = (\pi T_2)^{-1}$; and $\pm\delta$ are the chemical shift parameters, defined by $2|\delta| = \pi(\delta\nu)$ where $\delta\nu$ is the AB chemical shift (in Hz) in the absence of exchange. The parameter τ denotes the mean lifetime of protons in sites A and B as obtained from the NMR experiment, and is equal to the average time between exchange events. The factor C does not affect the lineshape and was used in the program as a variable parameter to adjust the intensity of the theoretical spectrum to fit that of the experimental one.

For both of the compounds studied, "coupling constant parameters" were included to take into consideration unresolved long-range coupling assumed to exist between the $-CH_2$-protons and the aromatic proton, which leads to deviation of the lineshape from a normal Lorentzian form, *i.e.* the shape in the absence of exchange is no longer characterized solely by the value of the relaxation parameter T_2. The spectrum of the $-CH_2$-protons is thus the AB-part of an ABX spectrum, which may be treated as two superimposed AB spectra. For the dichloro compound, the two AB spectra were given the same internal chemical shift and coupling constant, but were shifted slightly from each other by the value of the coupling constant $J_{AX} = J_{BX} = 0.34$ Hz, obtained by iteration at the high and low temperature limits of the exchange process. For the dibromo compound, the two AB spectra were given different internal shifts and shifted slightly from each other in order to reproduce the

asymmetry in the low-temperature spectra. This is equivalent to assuming $J_{AX} \neq J_{BX}$, the values of which were determined by iteration at the low temperature limit, and found to be 0.09 and 0.32 Hz. This treatment has been shown to be valid for the ABX case if the shift between the AB and X parts of the spectrum is large compared to J_{AX} and J_{BX}.[10,11] The "coupling constants" obtained in this work for Ia and b are not necessarily the true values, since magnetic field inhomogeneities might have a similar effect on the lineshape.

The lineshape program was coupled with an iterative program * by means of which the parameters describing the lineshape were varied until the "best fit" between calculated and experimental spectra was obtained.

Values of T_2 were obtained by iteration at the low and high temperature limits of the exchange process, where the lineshape becomes independent of the rate of exchange, and a value for each of the remaining experimental points was interpolated on a linear plot of the high and low temperature data. Although perhaps not entirely adequate, this seemed to us the only feasible

Table 2. The chemical shift parameter ($\delta\nu$) for the AB systems of I*a* and *b* as a function of temperature.

Trineopentylbenzene	T, °C	$\delta\nu$, Hz	
2,4-Dichloro (I*a*)	−25.2	22.76	Iterated values
	−10.4	21.66	
	− 4.7	21.42	
	− 0.6	21.18	
	1.4	21.08	
	7.8	20.78	
	11.4	20.56	Extrapolated values
	13.3	20.46	
	17.7	20.20	
	19.5	20.10	
	23.1	19.92	
	28.1	19.60	
	43.2	18.74	
2,4-Dibromo (I*b*)	− 8.4	26.76	Iterated values
	14.7	25.40	
	21.7	24.99	
	27.5	24.63	
	31.7	24.50	
	35.8	24.18	
	47.8	23.40	Extrapolated values
	51.6	23.18	
	55.9	22.94	
	60.2	22.68	
	65.3	22.44	
	68.3	22.20	

* This program is designated STUPID and contains the minimization subroutine STEPIT, copyright 1965, J. P. Chandler, Physics Department, Indiana University.

procedure by which we could take the temperature dependence of T_2 into consideration. Between the low and high temperature limits, the change in T_2 was from 0.17 to 0.26 sec for I*a* and from 0.23 to 0.25 sec for I*b*.

The temperature dependence of $\delta\nu$, the AB chemical shift in the absence of exchange, was taken into account by obtaining values for temperatures below coalescence by iteration, and then using extrapolation on a (linear) plot of $\delta\nu$ *vs.* T to estimate values in the region above the collapse temperature. The data obtained in this way are summarized in Table 2.

The coupling constant J obtained from the low-temperature spectra was assumed to be invariant, and thus the same value was used for calculations of theoretical spectra throughout the entire temperature range. The value of this parameter was 13.25 Hz for the dichloro compound, and 13.88 Hz for the dibromo compound.

The values of τ obtained from the computer calculations, and related to the first-order rate constant k by $k=1/\tau$, were used in conjunction with the Eyring equation [12] in the form

$$\ln(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(\mathbf{k}/\mathbf{h})$$

to calculate the activation parameters given in Table 3. The error limits

Table 3. Activation parameters for internal rotation in I*a* and *b*. The error limits are calculated assuming only random errors (see text.)

Trineopentylbenzene	$\Delta F^{\ddagger}$ 298°K kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u.	E_a kcal/mole
2,4-Dichloro (I*a*)	14.3±0.2	14.5±0.2	0.6±0.6	15.0±0.2
2,4-Dibromo (I*b*)	16.2±0.1	16.2±0.1	−0.1±0.7	16.8±0.1

reported in Table 3 were calculated assuming only random errors, and are almost certainly too low. More realistic error limits [13] are ±0.5 kcal/mole in $\Delta H^{\ddagger}$ and E_a, and ±2.3 e.u. in $\Delta S^{\ddagger}$ (based on the errors in $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$). The τ values obtained near the low and high temperature limits were not included in this calculation since the lineshape becomes fairly insensitive to changes in τ under these conditions. A plot of $\ln(1/\tau T)$ *vs.* $1/T$ for compounds I*a* and *b* is shown in Fig. 1. The τ values at the low and high temperature ends of the plot showed a maximum deviation of the order of ±5 % for five values at a given temperature, while those at or near the collapse temperature had ±1−2 % maximum deviation.

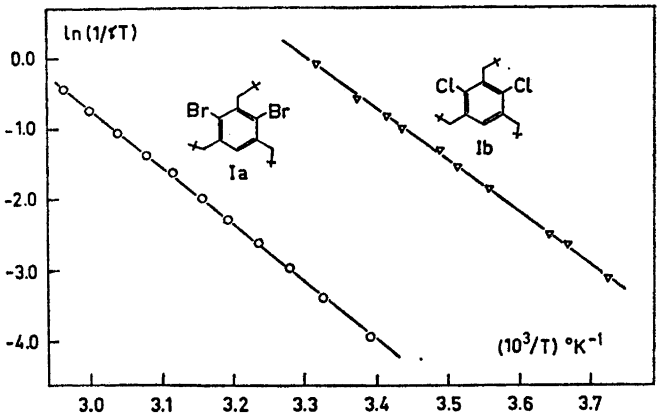
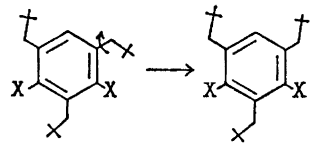


Fig. 1. Plots of $\ln(1/\tau T)$ *vs.* $1/T$ for I*a* (○) and I*b* (▽).

DISCUSSION

If an initial "alternate" configuration of the bulky *t*-butyl groups is assumed (*cf.* I), with appropriate angles of twist around the aryl—CH_2 bonds to minimize steric interactions among the *t*-butyl groups and between these groups and the ring, it is then possible to bring about an interchange of the —CH_2- protons by rotation about the aryl—CH_2 bonds. A stepwise path in which the rotation of one neopentyl group precedes that of the other is regarded as implausible since it implicates an "intermediate" in which the *t*-butyl groups must assume sterically unfavorable "nonalternate" positions.



Two possible concerted paths for rotation will be considered. One path is visualized as involving *conrotatory* movement of the neopentyl groups, while the other would involve *disrotatory* movement of the neopentyl groups, one toward a halogen atom and one toward the aromatic hydrogen. The disrotatory path is considered the most reasonable choice since only one of the *t*-butyl groups passes halogen along this path whereas both pass halogen along the conrotatory pathway. Furthermore, it is possible for the two *t*-butyl groups to always maintain a comfortable distance from each other along the disrotatory pathway. (See Fig. 2a.)

It is interesting to note that the spectra of the corresponding monohalo compounds show only general broadening down to about —100°C in dichloromethane solution. This indicates that the internal rotation in these compounds

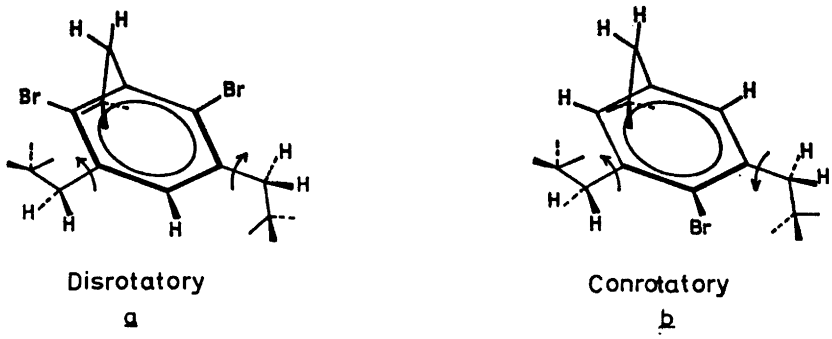


Fig. 2. (a) Disrotatory and (b) conrotatory modes of rotation for neopentyl groups in di- and monohalotrineopentylbenzenes, respectively. The methyls in the *t*-butyl groups have been omitted for the sake of clarity.

does not involve *t*-butyl-halogen barriers and suggests a conrotatory movement of the 1- and 5-neopentyl groups which allows both *t*-butyl groups to pass aromatic hydrogen atoms. (See Fig. 2b).

It is not unreasonable to suggest that the increase in $\Delta H^{\ddagger}$ between the dichloro and dibromo compounds primarily reflects the greater effective size of the bromo substituent. (Bondi [14] reports van der Waals volumes for aromatic chlorine and bromine as 12.0 and 15.12 cm^3/mole, respectively.) Inductive and resonance effects are not expected to be of any great significance in determining the height of the rotational barrier, since the charge distribution in the sp^2-sp^3 bond about which rotation occurs, and thus electronic interactions between this bond and the halo substituent, should be essentially the same in the initial and transition states. In any case, judging from the similarity of the Hammett substituent constants for chlorine and bromine,[15] *differences* in inductive and resonance effects between these two substituents may safely be neglected for our purposes. $\Delta S^{\ddagger}$ is equal to zero within the experimental error, which according to Binsch [16] is expected for hindered internal rotation. It is worth noting in this connection that Dix *et al.* report $E_a = 11.5$ kcal/mole for the rotation of the neopentyl groups in II. Together with the $\Delta G^{\ddagger}$ value of the kcal/mole estimated from their data, this implies that $\Delta S^{\ddagger}$ is roughly of the order of -16 e. u. in this case.

EXPERIMENTAL

NMR spectra were obtained on a Varian A 60 A instrument. Calibration of spectra and sweep was performed using sidebands from internal TMS generated by a Hewlett-Packard model 200 CD wide-range oscillator or model 3300 A function generator. The sideband frequency was measured with a Hewlett-Packard model 3734 A electronic counter.

Most of the spectra were recorded on a sweep width of 2 Hz/cm, at a sweep rate of 0.2 Hz/sec. The relatively sharp collapsed signal at high temperatures was in most cases recorded on a sweep width of 1 Hz/cm, at a sweep rate of 0.1 or 0.05 Hz/sec. The amplitude of the radiofrequency field was always maintained below the level at which saturation effects could be observed.

Digitization of NMR spectra. The NMR signal level was measured by a Solartron digital voltmeter, model LM 1420.2, equipped with a Solartron binary-coded decimal fan out unit (EX 1418) and activated to register once per second by a Hewlett-Packard model 202 A low frequency function generator using the square wave function set at exactly 1 Hz and monitored by a Hewlett-Packard model 5512 A electronic frecuency counter. The voltmeter was connected *via* the fan-out unit to an Addo paper tape punch, which thus recorded one point per second from the NMR spectrum. The punched tape obtained in this way could be fed directly to the computer.

Temperature measurements were made by the concentric capillary technique,[13,17] using a narrow capillary held in place by teflon plugs. The capillary used for the dichloro compound contained a mixture of methylene chloride, tetradeuteriomethanol, and concentrated aq. hydrochloric acid,[18] while that for the dibromo compound contained a mixture of pyridine and water (5:1). The temperature was obtained by determining the shift between the CH_2Cl_2 and OH peaks or between one of the signals due to the γ-H in pyridine and the OH of water. The capillaries had been calibrated with a copper-constantan thermocouple as previously described.[13,19] The temperature could be estimated to within about ± 0.5°C by this method.[13] Runs during which the temperature changed by more than ± 1°C were rejected if the temperature in question was in the region used for the determination of τ-values.

It should be noted that the calibration curve for the type of capillary used for the dichloro compound may change considerably (undergo a parallel displacement) if the capillary is exposed to high temperatures for a prolonged period of time.

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