

trum:⁵⁷ $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.2–8.2 (m, 8, aromatic and X part of ABX), 5.91, 5.63, 5.57, and 5.38 (8 lines, 2, AB portion of ABX). The entire product distribution is given in Table III.

11-Methoxymethyl-1,6-methanocyclodecapentaene (57). To a suspension of sodium hydride (139 mg, 5.8 mmol, 244 mg of 57% oil dispersion) in 5 ml of dry dimethylformamide was added 200 mg (1.16 mmol) of **28a** dissolved in 5 ml of the same solvent. After 1 hr, 825 mg (5.8 mmol) of methyl iodide was introduced *via* syringe, the mixture was allowed to stir for 20 hr, and subsequently pipetted over ice and pentane (40 ml). The pentane layer was washed with water (3 × 50 ml) and the individual water portions were extracted

(57) Sadtler spectrum no. 3566.

with pentane (3 × 30 ml). The combined organic layers were dried and evaporated, and the residue was recrystallized from hexane and sublimed (45°, 0.01 mm) to give a white solid: mp 54.2–55.5°; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.16–7.46 (m, 4), 6.74–7.08 (m, 4), 2.90 (s, OCH₃), 2.04 (d, $J = 6.9$ Hz, -CH₂O-), and -0.06 (t, $J = 6.9$ Hz, H₁₁).

Anal. Calcd for C₁₃H₁₄O: C, 83.83; H, 7.58; *m/e* 186.1045. Found: C, 83.68; H, 7.49; *m/e* 186.1047.

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Barriers to Internal Rotation in 1,3,5-Trineopentylbenzenes.

VI. Correlation between Barriers to Internal Rotation (ΔG^\ddagger) and Substituent Size

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Abstract: Relative "effective sizes" of the substituents H, F, Cl, Br, CH₃, and I in the 1,3,5-trineopentylbenzene system have been estimated from ΔG^\ddagger values obtained by dynamic nmr measurements of rotational barriers, ranging from 5.4 to 18.8 kcal/mol. An increase in barrier height with increasing substituent van der Waals volume was observed. The methyl group was found to be between chlorine and bromine in size in the trineopentylbenzene system. Linear free-energy relationships between the barriers for the trineopentylbenzenes and those for two other systems, in which the barriers arise from nonbonded interactions between an alkyl group and halogens, are presented.

At the molecular level, the significance of the term "size" when applied to a covalently bound atom or group is apparently not unequivocal. It may depend upon the molecular environment, especially in the case of atoms containing only a few electrons³ (H, F, etc.), and perhaps upon the geometry of the particular interaction used to measure the "size" in question, since bond polarizabilities are in general anisotropic,⁴ and the shape of a bound atom (or group) may be effectively nonspherical, as proposed by Nyburg and Szymański⁵ for the covalently bound fluorine atom. The careful determination of barriers to internal rotation in a series of molecules, in which a change in the substituent "size" is the most important factor in determining a change in barrier height, offers in principle a means of experimentally establishing the relative "effective sizes" of the substituents in the series. However, there are apparently few molecular systems which allow such a study over a sufficiently wide range of substituent "sizes" by the same method of measurement, and which have barriers whose relative heights are primarily determined by differences in effective substituent "sizes."

The nmr kinetic method has been extensively used for the measurement of barriers to internal rotation,⁶ and in some cases^{7–13} (see Discussion) it has been possible to determine the barrier as a function of substituent "size" for a limited number of substituents.

In the 1,3,5-trineopentylbenzene series **1**, we have available a molecular system in which barriers of the same group (*tert*-butyl) past the substituents H, F, Cl, Br, I, and CH₃ could be determined. We have previously reported the determination (by complete line-shape analysis) of barriers past chlorine,^{14,15} bro-

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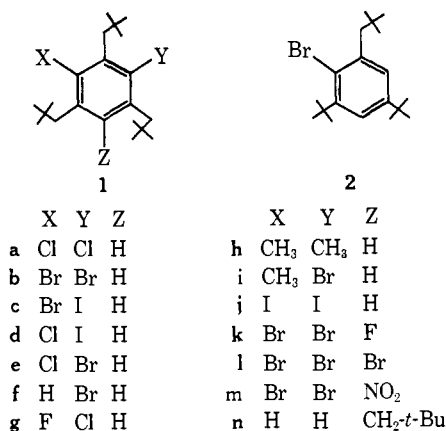
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mine,¹⁴⁻¹⁷ and a twisted nitro group¹⁶ and the estimation (by coalescence temperature measurement) of a barrier past fluorine.¹⁸ In the present paper, we report work on the refinement of the *tert*-butyl-fluorine barrier, the determination of barriers past a proton, a methyl group, and an iodine atom, and an attempt to utilize the series of barriers to gain some insight into the problem of steric effects and substituent "sizes."

Experimental Section

The syntheses of all compounds, except that of the diiodo compound **1j**, have been described elsewhere.¹⁸⁻²¹

2,4-Diiodo-1,3,5-trineopentylbenzene (1j). 1,3,5-Trineopentylbenzene²² (2.9 g, 10 mmol) was dissolved in 20 ml of acetic acid, and 7.6 g (30 mmol) of iodine and 14.3 g (60 mmol) of sodium peroxodisulfate were added.²³ The mixture was kept at 95° for 1 week and was then poured into water. The new mixture was extracted with cyclohexane. To remove excess iodine, the cyclohexane solution was washed with a solution of sodium sulfite in water and then with water. The organic solution was dried over magnesium sulfate and the solvent was distilled off. The product contained both 2-iodo-1,3,5-trineopentylbenzene²⁰ and **1j**, as well as some unidentified substances. Purification was effected by means of adsorption chromatography, once on aluminum oxide and once on silica gel; in both cases hexane was used as eluent. Recrystallization from nitromethane gave a product with mp 71-72°; yield 0.5 g (10%); mass spectrum *m/e* (% of base peak) 29 (17), 41 (26), 43 (22), 55 (6), 57 (100), 58 (5), 71 (9), 115 (9), 128 (6), 129 (5), 141 (6), 142 (5), 143 (7), 149 (13), 157 (5), 159 (5), 167 (6), 173 (9), 174 (7), 229 (14), 372 (78), 373 (8), 427 (5), 428 (46), 429 (7), 483 (7), 484 (35), 485 (7), 540 (21), 541 (5). The purpose of the synthesis was to obtain a sample of **1j** large enough to permit nmr measurements, and the reaction conditions were consequently not optimized.

Nmr Spectra. The monobromo compounds **1f** and **2** and the fluorine compounds **1g** and **1k** were dissolved in dichlorodifluoromethane and the solutions were carefully degassed on a vacuum line. A small amount of dichloromethane was used as a standard of resolution. The solutions were as dilute as practicable (<1 mol %) in order to avoid the precipitation of the compounds at the extremely low temperatures necessary to obtain exchange-broadened spectra. The methyl and iodo compounds were dissolved in deuteriochloroform and deuteriobromoform, respectively, in concentrations of *ca.* 6 mol %.

All spectra were run on a Varian XL-100-15 spectrometer

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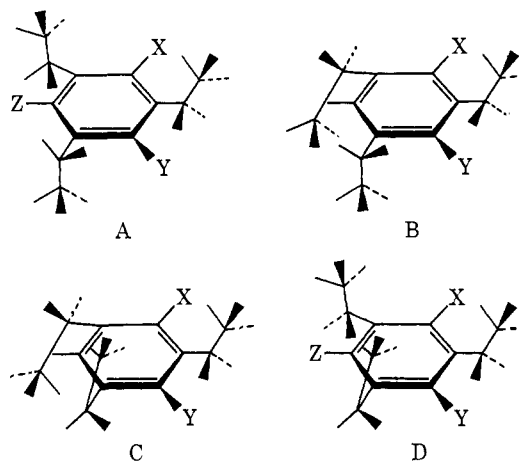
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equipped with a variable temperature probe and a V 6040 temperature controller. TMS was added to the solutions before the tubes were sealed off and was used as internal lock. The shifts were measured by use of a Varian frequency counter. The nmr spectra treated in the line-shape analysis were recorded with a sweep rate of 0.1 Hz/sec and sweep width of 2 Hz/cm. The temperatures in all runs except those in the investigation of the methyl compounds were obtained by use of a copper-constantan thermocouple, which was directly fixed in a 12-mm insert. A few temperatures at the lower end of the temperature range were checked against a thermocouple placed inside an nmr tube (nonspinning) and were found to differ by at most 2° (at -112°). In the investigation of the dimethyl and bromomethyl compounds, the temperatures were determined by means of a capillary containing α -picoline-water. The temperatures determined from the temperature-dependent shift between the methyl proton resonance in α -picoline and that of the protons in water had been calibrated in a separate experiment.²⁴ Spectra were analyzed by visual curve fitting using a Univac 1108 computer equipped with a Calcomp plotter.

Results

Theoretical Predictions of Low-Temperature Spectra.

The results of recent investigations^{17,25} of 2,4,6-tribromo-1,3,5-trineopentylbenzene (**1l**) may be used to predict the low-temperature nmr spectra of compounds that exhibit slow rotation of all three neopentyl groups. In the ¹³C nmr spectrum of **1l** at *ca.* -30°, the quaternary carbon atoms in the *tert*-butyl groups exhibit three singlets of unequal intensity, which may be interpreted in terms of the existence of different rotamers¹⁶ (*cf.* A, B, C, and D). In the case of **1l**, rotamers A, B,



and C are identical molecules ($X = Y = Z = \text{Br}$)²⁶ whose quaternary *tert*-butyl carbons would give rise to singlets with a (theoretical) intensity ratio 2:1. The remaining singlet is ascribed to rotamer D, in which all three neopentyl groups are on the same side of the aromatic ring. In a previous study of 1,3-dibromo-2,4,6-trineopentyl-5-nitrobenzene (**1m**),¹⁶ in chloroform-*d* solution, rotamer D could not be detected. In this case, rotamers A and C form an enantiomeric pair, and rotamer B is an achiral molecule.

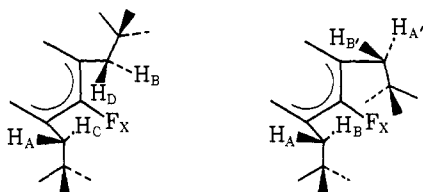
The 1- and 3-methylene proton spectrum of 2-bromo-1,3,5-trineopentylbenzene (**1f**) and the 1- and 5-methylene proton spectrum of 2,4-dibromo-6-fluoro-1,3,5-trineopentylbenzene (**1k**, fluorine decoupled) would thus be expected to appear as four AB quartets (at sufficiently low temperature), due to the presence of the different rotamers. Without fluorine decoupling, the

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(26) The ¹H nmr line-shape analysis is based on single rotations from rotamer to rotamer.¹⁶

^1H nmr spectrum of **1k** is expected to be quite complex. If we assume rotamers of types A, B, C, and D, exchanges occur between the ABCD (rotamers A and C) and AA'BB' (rotamers B or D) parts of ABCDX and AA'BB'X spectra for the 1- and 5-methylene protons



when the rotation past the aromatic fluorine is slow. At somewhat higher temperatures, the slow rotation of the 3-neopentyl group should still cause magnetic non-equivalence of the 1- and 5-methylene protons, and the spectrum is assumed to change to the AA'BB' part of an AA'BB'X spectrum.

In view of the expected complexity of the low-temperature methylene proton spectrum of **1f**, from which a *tert*-butyl proton barrier could in principle be obtained, we have chosen instead to determine the barrier to rotation of the 1-neopentyl group past the aromatic proton in 2-bromo-3,5-di-*tert*-butylneopentylbenzene (**2**), which only exhibits one AB spectrum for the methylene protons.

The determination of a *tert*-butyl-fluorine barrier in the chlorofluoro compound **1g** is not entirely straightforward. In analogy with the previously studied¹⁵ unsymmetrically substituted dihalotrineopentylbenzenes **1c-e**, the fluorine-decoupled ^1H spectrum of the methylene protons in **1g** would appear as three AB quartets in a temperature range where the passage of the 1- and 5-neopentyl groups past the aromatic proton is fast on the nmr time scale. However, at the low temperatures¹⁸ necessary in this case to reach the slow exchange limit, where the rotation of the 1- and 5-neopentyl groups becomes slow, the spectrum may be predicted to consist of as many as twelve overlapping AB quartets (*cf.* A-D), making a complete line-shape analysis a rather formidable task. To circumvent these difficulties, we have determined ΔG^\ddagger at several temperatures, as described below.

The spectra of the remaining compounds, in which barriers past a methyl group (**1h,i**) and an iodine (**1j**) could be determined, presented no unusual features and were treated in accordance with our previous work¹⁴⁻¹⁶ on analogous compounds.

Spectra. The shifts at probe temperature and the coupling constants (J_{AB}) between the methylene protons at slow exchange for the compounds studied are given in Table I. The assignments are based on an assumed additivity of substituent effects.

Compounds 2 and 1f. At -155° the spectrum of the methylene protons in the di-*tert*-butyl compound **2** had the appearance of a collapsed AB quartet, but no resolvable spectrum was observed at lower temperatures, down to about -170° . (Part of the AB spectrum was hidden under the 3-*tert*-butyl signal.) This collapsed spectrum is assumed to represent the slow passage of a neopentyl group past an aromatic proton, and using the shift and coupling constant obtained from the dibromo compound **1b**,¹⁴ we have calculated a free energy of activation of 5.4 kcal/mol. Simulation of the spectrum at -155° (3-*tert*-butyl signal included)

Table I. Chemical Shifts and Coupling Constants^a

Compd	Chemical shifts, ^b ppm				$ J_{\text{AB}} $, ^c Hz
	Methylene	<i>tert</i> -Butyl	Aryl	Methyl	
2	2.92 (1)	0.99 (1) 1.31 (5)	7.10 ($J_{\text{H-H}} = 2.6$)		
1f	2.92 (1,3) 2.42 (5)	0.97 (1,3) 0.92 (5)	7.38 6.75		
1g	2.74 (1) ($J_{\text{H-F}} = 0$) ^d	0.97 (1) ($J_{\text{H-F}} = 0$) ^d			14.0 (1)
	2.85 (3) ($J_{\text{H-F}} = 3.1$)	0.99 (3) 1.5	6.86 ($J_{\text{H-F}} = 8.0$)		<i>e</i> (3)
	2.51 (5) ($J_{\text{H-F}} = 2.0$)	0.95 (5) ($J_{\text{H-F}} = 1.0$)			13.0 (5)
1h	2.79 (3) 2.57 (1,5)	0.93 (1,3,5)	6.75	2.26	13.7 (1,5)
1i	2.82 (1) 3.10 (3) 2.56 (5)	1.00 (3) 0.95 (5) 0.99 (1)	6.86	2.32	13.0 (1) 14.0 (3) 14.0 (5)
1j	2.89 (1,5) 3.68 (3)	1.00 (1,5) 1.06 (3)	6.86		13.4 (1,5)
1k	3.34 (3) ($J_{\text{H-F}} = 0$) ^d	1.06 (3) ($J_{\text{H-F}} = 0$) ^d			13.0 (1,5)
	2.92 (1,5) ($J_{\text{H-F}} = 3.6$) ^f	1.02 (1,5) 1.7			

^a The numbers in parentheses refer to the different alkyl groups. Solvents are given in the text. ^b Chemical shifts were determined on 100-Hz sweep width at probe temperature, except for **1i** and **1j**, for which the shifts were measured at higher temperatures. In appropriate cases coupling constants in hertz to an aromatic proton or fluorine are given. ^c Iterated values from low-temperature spectra were used in the line-shape analysis. In the case of **1g**, the lines were exchange broadened, and thus it was not possible to obtain as accurate values as in the other cases. ^d No resolvable lines were observed, but the width of the lines decreased in a decoupling experiment. ^e Not obtainable. ^f These methylene protons showed stereospecific fluorine coupling at low temperature; see text.

showed that the spectrum was nearly unaffected by a 20% change in the AB shift value, and consequently the ΔG^\ddagger value was unchanged. At these extremely low temperatures the accuracy in the free energy value is to a large extent determined by the accuracy in the temperature measurements. An error of $\pm 2^\circ$ resulted in an error of ± 0.1 kcal/mol in ΔG^\ddagger . Realistic error limits for the ΔG^\ddagger value for **2** are assumed to be ± 0.2 kcal/mol.

The signal due to the 3-*tert*-butyl (adjacent to the bromine), and that of the *tert*-butyl moiety of the 1-neopentyl group, broadened much faster with decreasing temperature than did the 5-*tert*-butyl signal, but no resolution into separate peaks could be detected. In the case of the 3-*tert*-butyl group, the broadening may in part be due to hindered rotation. A rationalization of the broadening of the signal due to the *tert*-butyl moiety of the 1-neopentyl group solely on the basis of T_2 relaxation effects does not seem adequate, since the extent of the broadening is considerably greater than that of the 5-*tert*-butyl signal; the width at half-height ($\Delta\nu_{1/2}$) of the former is 17.0 Hz at -141° , while that of the latter is 7.0 Hz at the same temperature. (The width of the 3-*tert*-butyl signal is 11.5 Hz at -141° .)

A broad spectrum ($\Delta\nu_{1/2} \approx 50$ Hz) from the 1- and 3-methylene protons (2.92 ppm) in the monobromo

Table II. Activation Parameters (or ΔG^\ddagger near the Collapse Temperature for **2** and **1g**) for Internal Rotation in Neopentylbenzenes

Compd	ΔG^\ddagger , kcal/mol	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/(mol °K)
2	5.4 ± 0.2		
1g	9.0 ± 0.1	<i>a</i>	<i>a</i>
1a^b	14.3 ± 0.1	14.5 ± 0.2	0.6 ± 0.6
1b^b	16.2 ± 0.1	16.2 ± 0.1	-0.1 ± 0.7
1i	15.5 ± 0.1	16.0 ± 0.2	1.6 ± 0.8
1h	15.0 ± 0.1	15.3 ± 0.2	1.1 ± 0.7
1j	18.4 ± 0.1	17.5 ± 0.3	-3.1 ± 0.8

^a Not calculated; see text. ^b Activation parameters obtained from ref 14.

compound **1f** was observed at -158° , which was partly overlapped by a singlet ($\Delta\nu_{1/2} \approx 20$ Hz) from the 5-methylenes (2.42 ppm). This spectrum is more difficult to analyze than that of the di-*tert*-butyl compound, but the drastic change in the line shape between -152 and -158° is most probably caused by restricted rotation of the neopentyl groups.

Compounds 1g and 1k. The fluorine-decoupled methylene proton spectrum of 2-chloro-4-fluoro-1,3,5-trineopentylbenzene (**1g**) was composed of three overlapping AB patterns at *ca.* -100° . The expected complexities at still lower temperatures (see above), and the difficulties associated with recording nmr spectra at very low temperatures, discouraged us from making a complete line-shape analysis on this compound. We have instead obtained rate constants at temperatures where only the rotation of the 3-neopentyl group is expected to be slow. The T_2 parameter, which at temperatures where all lines are considerably exchange broadened gives relatively small contributions to the line width, was determined from one high-temperature spectrum (-66°) and was then held constant throughout the entire temperature range. Values of ΔH^\ddagger and ΔS^\ddagger are quite uncertain when determined over narrow temperature intervals, and consequently we have determined the more accurate parameter, ΔG^\ddagger , at each temperature. The mean value obtained in this way is given in Table II.

A previous study of the dibromofluoro compound²¹ **1k** in CDCl_3 at 100 MHz, at temperatures where the rotation of only the 3-neopentyl group is slow, did not allow the observation of magnetic nonequivalence in the 1- and 5-methylene groups. At 220 MHz a poorly resolved pattern of two closely spaced lines resulted, but the spectrum was not further analyzed. In the present study, in the solvent CCl_2F_2 [containing $(\text{CD}_3)_2\text{CO}$ as lock signal], the 1- and 5-methylene signal was resolved into a strongly coupled AB pattern at -39° when the fluorine was decoupled. Unfortunately, this pattern did not split further into several AB patterns below -90° , which is an estimated temperature of collapse for the rotation of a neopentyl group past a fluorine (predicted from **1g**). This lack of splitting may be due to accidental shift equivalence between AB spectra from rotamers of types A, B, C, and D.

The study of both the decoupled and undecoupled proton nmr spectra of the 1- and 5-methylene protons of **1k** at -39° (see Figure 1) offered an opportunity to determine (with the aid of LAOCN 3²⁷ analysis) the

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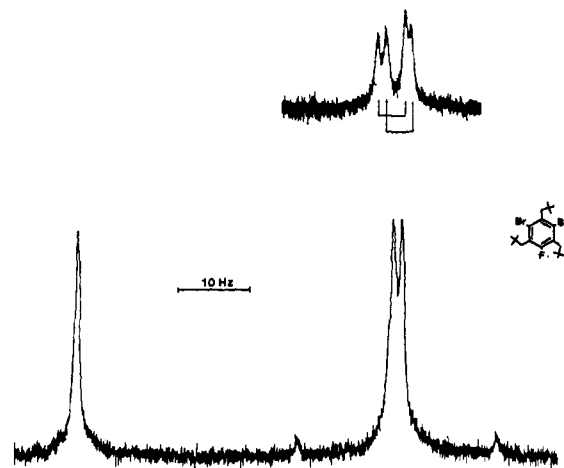
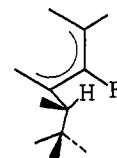


Figure 1. Fluorine-decoupled (below) and undecoupled spectra at -39° of the methylene protons in 2,4-dibromo-6-fluoro-1,3,5-trineopentylbenzene (**1k**).

stereospecific proton-fluorine coupling constants $^4J_{AF} = -4.0$ Hz and $^4J_{BF} = -3.3$ Hz. (J_{AB} is assumed to be negative.) In line with the results of an investigation of the stereospecificity of $|^4J(\alpha, F)|$ coupling constants in fluoro derivatives of benzal chloride by Schaefer and coworkers,²⁸ we assign the smaller coupling constant in our compound to the cisoid arrange-



ment of one methylene proton and the aromatic fluorine.

Compounds 1h and 1i. The bromomethyl compound **1i** gave rise to three overlapping AB quartets for the 1- and 5-methylene protons in the temperature range -30 to $+20^\circ$ where the rotation of the 3-neopentyl group was slow. In approximately the same temperature range the dimethyl compound **1h** showed an AB pattern for the 1- and 5-methylene protons (centered at 2.57 ppm), which was partly overlapped by the 3-methylene singlet (at 2.79 ppm). Unresolved long-range coupling between the aromatic proton and the methylene protons and between the aromatic proton and the methyl protons was observed. The analysis was simplified by decoupling the aromatic proton in all the runs. Due to instrumental limitations, it was not possible to simultaneously decouple the methyl protons. (The shift between the methyl resonance and the most upfield half of the methylene AB quartet was only 16.0 Hz at -5.9° .) It should be noted, however, that the lines in both halves of the AB quartet have the same width (2.4 Hz at -5.9° ; aromatic proton decoupled).

A complete line-shape analysis of both compounds has been carried out, and the parameters describing the line shape were obtained in the usual way.^{14,15} A minor impurity was observed in the spectrum of **1i**, but this did not disturb the line-shape analysis. Plots of $\ln(1/\tau T)$ vs. $1/T$ are shown in Figure 2. The activation

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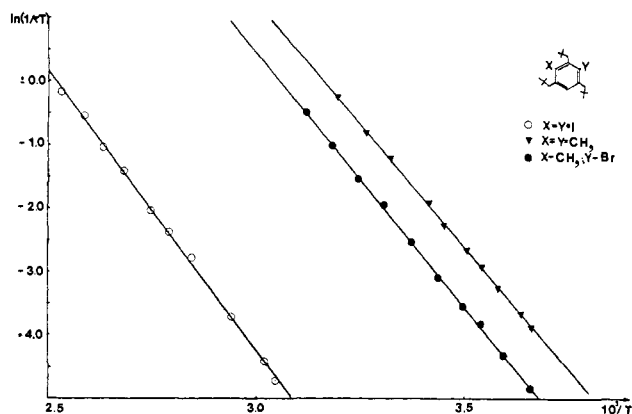


Figure 2. Plots of $\ln(1/T)$ vs. $1/T$ for compounds **1h**, **1i**, and **1j**.

parameters were calculated according to the Eyring equation²⁹ and are summarized in Table II.

Compound 1j. At probe temperature, the 1- and 5-methylene protons of the diiodo compound **1j** appeared as an AB quartet with slightly unequal intensities of the signals due to the A and B protons. This is most likely the result of stereospecific long-range coupling between the methylene protons and the aromatic proton, an observation also made in the case of the symmetrically substituted dichloro and dibromo compounds.¹⁴ Interestingly enough, a similar effect was not detected in the spectra of the unsymmetrically disubstituted compounds.¹⁵

No effect on the line width of the signals in the downfield half of the AB quartet in the spectrum of **1j** was observed in an experiment in which the aromatic proton was decoupled, and consequently we assume that $^4J_{AX} = 0.0$ Hz. A value for the coupling constant to the other proton, the line width of which decreased in the decoupling experiment, was estimated by iterative lineshape fitting from spectra at slow interconversion. The value obtained in this way ($^4J_{BX} = 0.35$ Hz; X = aryl H) was assumed to be temperature independent. The line shape of the methylene protons was studied up to 125°, at which temperature discoloration of the sample due to decomposition was not yet evident. This temperature was, however, not sufficiently high to neglect broadening due to exchange. A test of the stability of the compound showed that rapid decomposition took place at temperatures around 180°. Consequently, the high temperature T_2 value could not be obtained in the manner previously described.^{14,15} Instead we have calculated the difference between the line width of the 3-methylene proton signal and that of the 1- and 5-methylene protons at several temperatures below probe temperature. This contribution to the line width is then assumed to be constant throughout the temperature region investigated and the T_2 parameter is thus obtained at each temperature from the line width¹⁶ of the 3-methylene protons. A plot of $\ln(1/\tau T)$ vs. $1/T$ is shown in Figure 2, and the activation parameters for the hindered rotation of the 3-neopentyl group are summarized in Table II.

Discussion

The barriers to rotation in the trineopentylbenzene series are predominantly "steric" in nature. By this

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

we mean that the substituent effect on the barrier is not transmitted *via* the bonds, but rather occurs through a change in the potential energy of nonbonded interaction, taking into account bond stretching (or compression), interbond angle bending, as well as torsional energies. A given barrier apparently almost solely depends on the "size" of the *smallest* of the two substituents ortho to the neopentyl group in question,^{15,18} thus making for a rather straightforward interpretation of the observed barrier height in terms of a particular *tert*-butyl substituent interaction.

The Effective "Size" of the Methyl Group. The order of substituent "size" estimated by the order of the barriers (ΔG^\ddagger in Table III) is $H < F < Cl < CH_3 <$

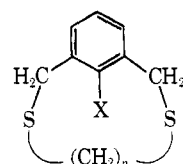
Table III. Data Used in Correlation between van der Waals Volumes (V_w)^a and Rotational Barriers in 1,3,5-Trineopentylbenzenes (TNB) and Ethanes (E)

Substituent	ΔG^\ddagger_{TNB} , kcal/mol	ΔG^\ddagger_E , kcal/mol	V_{wTNB} , cm ³ /mol	V_{wE} , cm ³ /mol
H	5.4 ^b	7.0	3.32 ^c	3.45 ^c
F	9.0	8.0	5.80	5.72
Cl	14.7	10.4	12.00	11.62
Br	16.6	10.7	15.12	14.40
I	18.8	11.1	19.64	19.18
CH ₃	15.4		13.67	

^a See ref 38. ^b ΔG^\ddagger values obtained at one temperature. ^c Estimated van der Waals volume.

$Br < I$, which places the CH₃ group between Cl and Br. The same order for CH₃ and Br substituents in the trineopentylbenzene system has been deduced from comparisons of deuterium kinetic isotope effects in the nitration of methyl- and bromo-substituted 1,3,5-trineopentylbenzenes.¹⁹

Work as early as 1932 on the configurational inversion of two series of biphenyls by Adams and co-workers²⁰ allowed the establishment of "relative interference effects" in the order $Cl < CH_3 < Br$. In a comparison of the steric requirements of Cl, Br, and CH₃ substituents in dithiametacyclophanes (**3**), Vögtle¹²

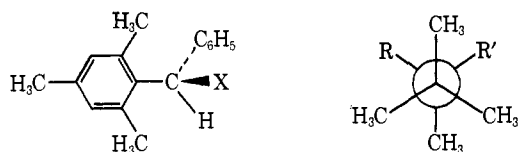


3, $n = 8, 9$; X = Cl, Br, CH₃

also found the order $Cl < CH_3 < Br$, while Mannschreck and Ernst,^{11a} in a study of an extensive series of substituted benzylmesitylenes (*cf.* **4**), report barriers (ΔG^\ddagger) to rotation in the order $CH_3 \approx Cl < Br$. The same order for ΔG^\ddagger , but with a much larger difference between CH₃ and Cl, was reported by Roberts and co-workers¹⁰ in a study of halogenated methylbutanes (**5**). Finally, Taft's steric substituent constants³¹ (E_s) indicate the order $Cl < Br \approx CH_3$. Thus, the placement of CH₃ in relation to Cl and Br is apparently not independent of the molecular system studied (or perhaps of

(30) R. W. Stoughton and R. Adams, *J. Amer. Chem. Soc.*, **54**, 4426 (1932); H. C. Yuan and R. Adams, *ibid.*, **54**, 4434 (1932); see also R. L. Shriner, R. Adams, and C. S. Marvel in "Organic Chemistry," H. Gilman, Ed., Wiley, New York and London, 1944, p 362.

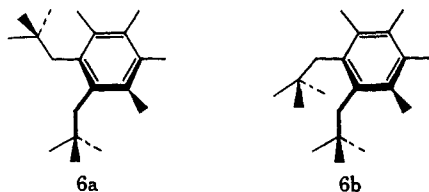
(31) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York and London, 1956, p 598.



4, X = Cl, Br, CH₃, CN, SH, OH, OCH₃ 5, R = Cl; R' = CH₃, Cl, Br

the physical method used). One of the reasons for this is almost certainly that the halogens and the CH₃ group are not strictly comparable. The comparison involves the tacit assumption that the CH₃ group is a more or less cylindrically symmetrical or pear-shaped substituent, thus not taking cognizance of the actual "three-pronged" nature of CH₃ and its consequent tendency to become involved in "gear effects."^{10,32} This qualitative difference between the halogens and the CH₃ group should be borne in mind when comparisons between them are made (see below).

The barrier past a methyl group in **1h** or **1i** ($\Delta G^\ddagger = 15.4 \pm 0.1$ kcal/mol, with the statistical factor $RT \ln 2$ added to the value of **1h**) is of especial interest in comparison with what we believe³³ to be another *tert*-butyl-methyl barrier in 1,2,3,4-tetramethyl-5,6-dineopentylbenzene (**6**), studied by Dix, Fraenkel, Karnes, and



Newman³⁴ almost 10 years ago. These authors reported an Arrhenius activation energy of 11.5 ± 0.6 kcal/mol, which together with an assumed collapse temperature of 52° may be used to estimate ΔG^\ddagger and ΔS^\ddagger values of 16.2 kcal/mol and -16 cal/(mol °K), respectively. The ΔS^\ddagger values for the trineopentylbenzenes in our work cover a very narrow range near zero and indeed in essentially all cases are indistinguishable from zero, if a realistic error of $\sim \pm 3$ cal/(mol °K) is assumed. We feel that a comparison between **1h** and **6** is valid because the nonbonded interactions occurring in the initial and transition states (for rotation of one neopentyl group past a methyl) are similar in the two compounds, if the methylene group in the second neopentyl group in **6** is regarded as a "frozen" methyl.

We have carried out a reinvestigation³⁵ of the temperature-dependent line shape of the methylene protons in **6** in chloroform-*d* solution, which confirms the work of Dix, *et al.*³⁴ (whose measurements were made in carbon tetrachloride solution), and leads to the following thermodynamic activation parameters at 298°K: $\Delta G^\ddagger = 16.3 \pm 0.1$ kcal/mol, $\Delta H^\ddagger = 12.9 \pm 0.6$ kcal/mol, and $\Delta S^\ddagger = -11.5 \pm 2.1$ cal/(mol °K). Thus, a large

(32) (a) C. Roussel, Thesis, Université de Provence, Marseille, France, 1973; (b) C. Roussel, M. Chanon, and J. Metzger, *Tetrahedron Lett.*, 1861 (1971).

(33) See ref 18. Experimental support for this opinion was obtained by Dr. R. J. M. Reuvers, Delft Institute of Technology, The Netherlands, who observed no sign of hindered rotation in the nmr spectrum of 1,2-dineopentylbenzene down to -90° (private communication).

(34) D. T. Dix, G. Fraenkel, H. A. Karnes, and M. S. Newman, *Tetrahedron Lett.*, 517 (1966).

(35) The sample of **6** was kindly provided by Professor M. S. Newman, Ohio State University.

negative ΔS^\ddagger for the internal rotation in compound **6** seems to have a rather firm experimental basis.

The rotation of each neopentyl group by π rad is a prerequisite for the exchange of methylene proton environments in **6**, and Dix, *et al.*,³⁴ visualize the exchange as taking place "by concerted rotations of the neopentyl groups about the C_{AR}-CH₂ bonds, one conrotatory with respect to the other. . . ." If the concertedness of the rotations implies a transition state in which both neopentyl groups are simultaneously passing methyl groups, with each such passage analogous to the situation in 2,4-dimethyl-1,3,5-trineopentylbenzene (**1h**), a barrier as high as 30.8 (= 2×15.4) kcal/mol would not be inconceivable. The interpretation of the much lower observed barrier in terms of nonconcerted rotations¹⁸ implies taking into account the possible existence of a rotamer with both neopentyl groups on the same side of the benzene ring. However, no evidence for the presence of more than one rotamer was obtained from proton-decoupled ¹³C nmr spectra at low temperature (*ca.* -25°), in which a low rotamer population might be more easily detectable than in the corresponding ¹H spectra.

Nonetheless, it is intriguing to speculate about the possible consequences of the existence of a putative rotamer of relatively high energy. This would, for example, imply a reaction path passing through two identical transition states, symmetrically disposed with respect to a "dip" in the energy profile corresponding to the high energy rotamer. Consequently, one-half of the high energy rotamers would continue on to "products" (exchange of methylene protons) and one-half would revert to the initial state. This statistical factor of $1/2$ is, however, counteracted by the presence of two identical neopentyl groups in the initial state of **6**, either of which may begin to pass a methyl group to give the high energy rotamer, and thus the rotation of one neopentyl group past a methyl group would be well represented by the activation parameters given above.

The difference between the ΔS^\ddagger value for **6** and those for our compounds may be explained by a loss of rotational degrees of freedom within the neopentyl groups in a crowded transition state (different from those referred to above), in which one neopentyl group has already passed a methyl group and has pushed the other neopentyl group from its initial position. The contribution to the entropy of activation from the complete loss of rotation of a methyl group may be estimated to be -3.6 cal/(mol °K), while that from the loss of the $-\text{CH}_2-\text{C}\leftarrow$ rotation of a neopentyl group is *ca.* -7.0 cal/(mol °K).³⁶

Another compound of interest in this connection is 1,2,3,5-tetraneopentylbenzene (**1n**),¹⁸ in which two neopentyl groups are situated ortho to each other, as in **6**. The main difference between these two compounds is that only *one* neopentyl group (in the 2 position) in **1n** is restricted in its rotation at reasonably high tempera-

(36) The values were calculated (by Professor Lars Melander, University of Göteborg) from the expression for the entropy $S = R[\ln Q - (1/QT)(\partial Q/\partial(1/T))]$, where $Q = (8\pi^3kT)^{3/2}/nh$. Q is the partition function for free rotation of a rigid rotor, I is the moment of inertia, n is the symmetry number, and T is 298°K. (See, for example, D. Malcolm, "Introduction to Statistical Thermodynamics," Prentice-Hall, New York, N. Y., 1954, p 170 ff.) As pointed out by one of the referees, this calculation assumes freely rotating methyl groups in the ground state, admittedly an unlikely possibility, but the calculation nevertheless provides an "order-of-magnitude estimation" of the importance of the effect.

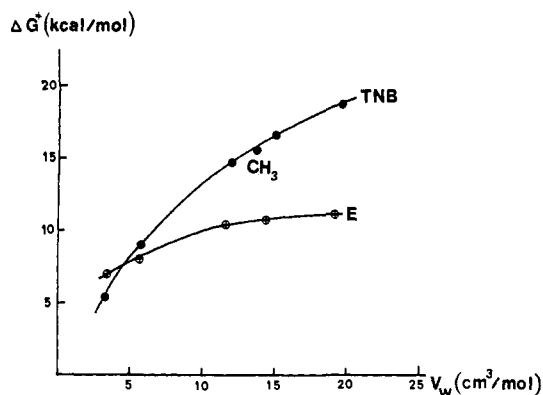
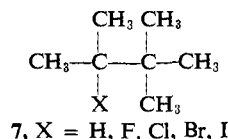


Figure 3. Plots of ΔG^\ddagger values vs. van der Waals volume for halogen- and/or methyl-substituted 1,3,5-trineopentylbenzenes. A corresponding plot for halogen-substituted ethanes^{8a} is also included.

tures. A recent complete line-shape analysis³⁷ of this compound yields a value of -3.1 ± 2.1 cal/(mol °K) for ΔS^\ddagger , along with values of 16.7 ± 0.7 and 17.6 ± 0.2 kcal/mol for ΔH^\ddagger and ΔG^\ddagger , respectively (at 298°K). The barrier in **1n** is assumed to be due to steric interactions between the *tert*-butyl moiety of the 2-neopentyl group and either the 1- or 3-methylene group. The difference in ΔG^\ddagger values between **1n** and **1h** may be the result of the 1- and 3-methylene groups in **1n** behaving as "frozen" methyl groups, thus being unable to participate in cogwheeling ("gear effect") during the passage of the 2-neopentyl group.

Correlations. We have attempted to correlate our barriers with some more or less obvious measure of the "size" of the substituent, such as the van der Waals volume, V_w , estimated by Bondi.³⁸ (See Table III.) A plot of ΔG^\ddagger vs. V_w is shown in Figure 3 and is seen to give a smooth curve³⁹ passing through the points for H, F, Cl, Br, and I. Note that the point for CH_3 deviates somewhat from the curve, perhaps a reflection of the previously mentioned qualitative difference between the CH_3 group and the other substituents. In the same figure we have plotted the recent nmr data of Anderson and Pearson^{8a} on barriers to rotation in substituted ethanes **7**, covering the same range of sub-



stituents (except for the methyl group) as in the trineopentylbenzene series. In these ethanes, the factors other than "steric" responsible for the barriers, while perhaps not constant, are at least *comparable* from molecule to molecule in the series, and thus it is of interest to compare these data with ours. From Figure 3 it is obvious, for example, that the barriers measured by Anderson and Pearson^{8a} are, as expected, much less

(37) E. Dahlberg, B. Nilsson, K. Olsson, and P. Martinson, to be submitted to *Acta Chem. Scand.*

(38) A rough estimate of the van der Waals volume of an aromatic or aliphatic proton was obtained from the data in Tables 14.4 and 14.1 in A. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses," Wiley, New York, N. Y., 1968, p 456.

(39) Interestingly, a plot of ΔG^\ddagger vs. $\ln V_w$ gave an excellent straight line ($r = 0.999$). The physical significance of this plot (if any) is, however, far from clear.

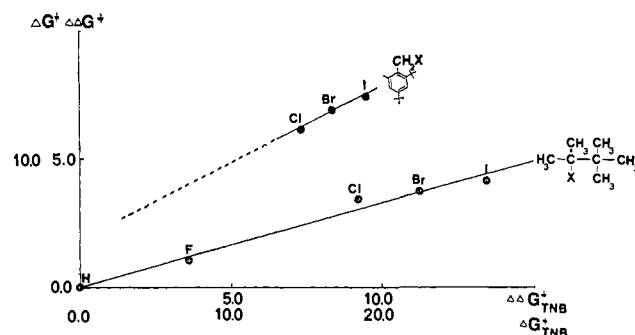


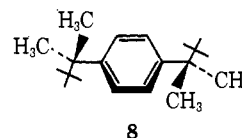
Figure 4. Linear free energy relationships between barriers (ΔG^\ddagger or $\Delta\Delta G^\ddagger$, see text) in the 1,3,5-trineopentylbenzene series (reference system) and barriers in either halogen-substituted ethanes^{8a} ($\Delta\Delta G^\ddagger = \Delta G_{\text{X}}^\ddagger - \Delta G_{\text{H}}^\ddagger$) or benzyl halides⁷ (ΔG^\ddagger).

sensitive to changes in the van der Waals volume than are the barriers in the trineopentylbenzenes.

A more direct comparison between our data and those of Anderson and Pearson^{8a} is shown in Figure 4, which is a plot of the $\Delta\Delta G^\ddagger$ values for the ethanes **7** vs. $\Delta\Delta G^\ddagger$ values for trineopentylbenzenes with the same substituents, with $\Delta\Delta G^\ddagger = \Delta G_{\text{X}}^\ddagger - \Delta G_{\text{H}}^\ddagger$, X = F, Cl, Br, I. This is a linear free-energy relationship of the form

$$\Delta\Delta G^\ddagger_{\text{E}} = \gamma \Delta\Delta G^\ddagger_{\text{TNB}}$$

which has been discussed in some detail by Wells⁴⁰ and by Pryor and Smith.⁴¹ The subscripts E and TNB refer to the ethanes and to our trineopentylbenzenes, respectively. One of the conditions under which such a linear free-energy relationship is applicable is that the reaction series be isoentropic. (For details and further discussion, see Pryor and Smith.⁴¹) In the case of the trineopentylbenzenes, we have been able to establish experimentally that the series is most likely isoentropic: $\Delta S^\ddagger = 0 \pm 3$ cal/(mol °K) for all the compounds in our series for which we were able to perform complete line-shape analyses. For the ethanes of Anderson and Pearson,^{8a} data are available at only one temperature for each compound, and consequently no values of ΔS^\ddagger have been determined for this series. However, in this context we may note that a value of $\Delta S^\ddagger = -2.8 \pm 0.7$ cal/(mol °K) (random error) has been derived⁴² for the internal rotation of the *tert*-butyl groups about the ethane bonds in *p*-ditriptylbenzene (**8**). (The ΔG^\ddagger_{298}



and ΔH^\ddagger values for this process are 9.3 ± 0.1 and 8.4 ± 0.1 kcal/mol, respectively.)

Although the transition state geometries in the two series are certainly quite different, a reasonably good correlation ($r = 0.991$) between the $\Delta\Delta G^\ddagger$ values is obtained (Figure 4). It should be pointed out, however, that this is in fact a log-log plot, and such plots are well known to often be insensitive to subtle changes in the variables.⁴¹

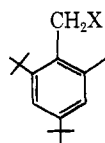
It may be illuminating to consider another linear free-energy relationship of the same type, in which molecules

(40) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(41) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 2731 (1970).

(42) R. Sikkar, B. Nilsson, and P. Martinson, unpublished results.

with more analogous transition state geometries are compared. Cupas, *et al.*,⁷ studied the rotation about the $C_{Ar}-CH_2$ bond in 2,4-di-*tert*-butyl-6-methylbenzyl halides (**9**) and determined halogen-methyl barriers for



9, X = Cl, Br, I

the series **9**. From their data, we have calculated ΔG^\ddagger values at 298°K and have plotted them in Figure 4 against the values for the corresponding trineopentylbenzenes. The slope of this plot (only three points, however) is closer to unity than that obtained with the data on the ethanes, which is not surprising since the molecules studied by Cupas, *et al.*,⁷ are more comparable to the trineopentylbenzenes than are the ethanes.

Steric Substituent Constants. The steric substituent constants of Taft,³¹ defined as

$$\log(k/k_0) = E_s$$

are based on rate constants for the acidic hydrolysis of ortho-substituted benzoates or aliphatic esters, with the CH_3 group as the standard of comparison (*i.e.*, $k_0 = k_{CH_3}$). Values for F, Cl, Br, and I substituents have been derived from data for ortho-substituted benzoates, and we have attempted to correlate our $\Delta\Delta G^\ddagger$ values (in this case, $\Delta\Delta G^\ddagger = \Delta G^\ddagger_X - \Delta G^\ddagger_{CH_3}$) with these parameters, but with poor results, since the line does not pass through the origin, as it should theoretically. (It lies almost a factor of 10 outside the experimental error limits.) This may simply be another reflection of the qualitative difference between the standard of comparison, the CH_3 group, and the halogen substituents.

Charton⁴³ has presented a statistical analysis of the composition of the E_s values in terms of parameters for field and/or inductive effects (σ_I), resonance effects (σ_R), and van der Waals radius. He comes to the remarkable conclusion that the E_s values derived from ortho-substituted benzoates "are completely independent of the van der Waals radii and may be completely accounted for (with the exception of the Ph group) in terms of electrical effect parameters."^{43a} It should be pointed out in this connection that a plot of the E_s values for the halogens⁴⁴ *vs.* van der Waals volumes gives an excellent straight line ($r = 0.999$), indicating internal consistency in the halogen E_s values³¹ and a relationship between these values and van der Waals parameter.

Conclusions

The barriers measured in our work on trineopentyl-

(43) (a) M. Charton, *J. Amer. Chem. Soc.*, **91**, 615 (1969); (b) M. Charton, *Progr. Phys. Org. Chem.*, **8**, 247 (1971).

(44) Serendipitously, the E_s value for Br is also 0.0, as is, by definition, that for CH_3 , thus allowing the standard of comparison for the halogens to be another halogen, rather than a methyl group.

benzenes range from 5.4 to 18.8 kcal/mol, which is (to our knowledge) the widest range of barriers ever determined on the same basic molecular system by one and the same method of measurement. This provides us with a set of "internally consistent" quantitative data, which places comparisons of substituent "size," such as $Cl < CH_3 < Br$, on a firm foundation in the trineopentylbenzene system. Obviously, "size" is not an unequivocal concept at the molecular level, since the relative position of CH_3 with respect to Cl and Br apparently depends on the molecular system studied. Furthermore, CH_3 and the halogens are not strictly comparable; *e.g.*, "gear effects" may be operative in the case of the methyl group. This situation is probably also mirrored in the poor results of the attempt to correlate our data with Taft's steric substituent constants³¹ for the halogens, with CH_3 as standard.

The use of free-energy relationships (assumed to be linear) allows a comparison to be made between the data for the trineopentylbenzenes and the data for different series of barrier measurements in which the same substituents are involved. Data for such disparate molecular systems as ethanes and benzyl halides correlate almost equally well with the trineopentylbenzene data, but the slopes in the two correlations are quite different. An interpretation in terms of more closely analogous transition states in the case of benzyl halides *vs.* trineopentylbenzenes seems quite obvious. It should be possible to obtain information on the detailed transition state geometries in these various systems by means of semiempirical energy calculations of the Westheimer type,⁴⁵ as refined and modified by later authors.⁴⁶ It is encouraging to note the positive results obtained by, *e.g.*, Mannschreck and Ernst^{11a} and by Peeling, *et al.*,⁴⁷ with such calculations on aromatic molecules exhibiting restricted rotation about an sp^2-sp^3 bond.

Acknowledgments. We wish to express our thanks to Dr. Christian Roussel, Université de Provence, Marseilles, for many stimulating discussions. We gratefully acknowledge our indebtedness to Professor Lars Melander, University of Göteborg, for his active interest in this work and for comments on the manuscript. One of the authors (R. E. C.) wishes to thank Professor Melvin S. Newman and especially Professor Gideon Fraenkel for their hospitality during the tenure of a visiting professorship at Ohio State University (1972-1973). This work was supported by the Swedish Natural Science Research Council and a grant from Stiftelsen Bengt Lundquists Minne (to B. N.). The XL-109-15 spectrometer used in this work was purchased with the aid of a grant from the Knut and Alice Wallenberg Foundation.

(45) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York and London, 1956, p 523.

(46) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968), and references cited therein.

(47) J. Peeling, L. Ernst, and T. Schaefer, *Can. J. Chem.*, submitted for publication. We wish to thank Dr. Schaefer for sending us a copy of the manuscript prior to publication.