Barriers to Internal Rotation in 1,3,5-Trineopentylbenzenes. VII.[1] Evidence for Attractive Steric Effects

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Abstract: ^1H and ^{13}C NMR spectra of symmetrically trisubstituted 1,3,5-trineopentylbenzenes may be consistently interpreted in terms of the predominance of a rotamer with all three neopentyl groups on the same side of the benzene ring, thus providing evidence for *attractive steric effects* among the neopentyl groups. A complete band shape analysis of the 100-MHz methylene proton spectrum of 2,4,6-tribromo-1,3,5-trineopentylbenzene has been carried out over a limited temperature interval with the aid of a computer program by means of which all possible rotamer interconversions could be taken into account. Solvent effects on the rotamer ratio in 2,4-dibromo-1,3,5-trineopentyl-6-nitrobenzene are described and discussed in terms of the existence of an "all cis" achiral rotamer and an enantiomeric pair of rotamers. For example, the predominance of the achiral rotamer in fluorobenzene solution is interpreted in terms of solute-solvent interactions involving mutual polarization of aromatic π-electron clouds, which is sterically favored in an "all cis" rotamer.

The importance of attractive steric effects in the determination of the equilibrium conformations of organic molecules has recently been reemphasized by Liberles, Greenburg, and Eilers[4] in terms of the partitioning of the total energy of a molecular system into components involving the kinetic energy of the electrons and the repulsive and attractive interactions among the nuclei and the electrons. Qualitatively similar conclusions may be reached by means of empirical force field molecular mechanics calculations,[5-8] employing appropriate non-bonded potential functions with inclusion of an attractive term, and allowing for relaxation of the input molecular geometry through bond stretching, bending, and torsional modes.

Most of the presently available *experimental* evidence for the operation of attractive steric effects emanates from interpretations of the conformational or rotational energetics of molecules containing adjacent electron pairs and/or polar bonds (for example, the "gauche effect"[9]). In saturated hydrocarbons and their derivatives, such evidence is not often encountered in the organic chemical literature, especially since traditional views of steric phenomena in these systems generally stress the "bulk repulsive approach".[10]

In this paper, we present results from our work on the 1,3,5-trineopentylbenzene system, which may be given a consistent interpretation in terms of *attractive steric effects* among the neopentyl groups, leading to the stabilization of a rotamer with all three neopentyls on the same side of the benzene ring.

Results and Discussion

In previous work,[11] the temperature-dependent methylene ^1H NMR spectrum of 2,4-dibromo-1,3,5-trineopentyl-6-nitrobenzene (I) was interpreted on the basis of interconversions among three rotamers, A, B, and C (see Figure 1; X = Y = Br, Z = NO_2), of which A and C form an enantiomeric pair and B is an achiral molecule. In principle, however, B may be replaced by a fourth rotamer, D, in the interconversion scheme since, in this case, we can not a priori determine which of these two rotamers is present by means of the NMR spectrum. The energy difference between rotamers B and D was roughly estimated to be 0.6 kcal/mol[11a] (with B at the lower energy) by a simple treatment involving a Lennard-Jones 6-12 nonbonded potential function,[12] without allowing for relaxation as referred to above. This was in line with our intuitive expectations (using the "bulk repulsive approach"), and we felt them further corroborated by the negative result of an investigation of the ^{13}C NMR spectrum[13] of compound I at −25°C, which showed no signals attributable to the presence of a fourth rotamer. In the light of subsequently obtained data, to be described in detail below, we now suggest that the achiral rotamer is in fact rotamer D, which is stabilized relative to B through attractive steric effects but destabilized relative to A and C due to a decrease in the resonance interaction between the nitro substituent and the aromatic ring, as discussed in the previous work[11] (with reference to rotamer B).

The first piece of positive evidence for the existence of rotamer D took the form of a 300-MHz ^1H NMR spectrum[14] of the methylene protons in 2,4,6-tribromo-1,3,5-trineopentylbenzene (II) at about −20°C (Figure 2a). In view of the symmetry properties of this molecule, there are only two possible rotamers (A = B = C, and D; cf. Figure 1, X = Y = Z = Br), the methylene protons of which should theoretically give rise to a singlet from rotamer D, along with a strongly coupled AB quartet and a singlet in the intensity ratio 2:1 from rotamers A, B, and C. The spectrum in Figure 2a shows no AB quartet, but the AB shift is hardly expected to be detectable[15] (see below); more interesting is the fact that the two upfield signals appear to have a 2:1 intensity ratio, and the area of the downfield signal is about three times that of the two upfield peaks together, as indicated by a simple curve-fitting procedure, assuming Lorentzian lines. These findings thus indicate not only the presence of rotamer D but its *predominance* in the rotamer mixture by a population ratio of ca. 3:1.[16] An analogous interpretation of the three signals (intensities ca. 9:2:1) in the ^{13}C NMR spectrum of the quaternary carbon atoms in the *tert*-butyl groups of the tribromo compound[13] may also be made, thus reversing the original assignments of Nilsson and Drakenberg.[13]

The *tert*-butyl region of the 300-MHz proton spectrum[14] of II at about −20°C consisted of two singlets with relative heights of 11:1. Assuming the smaller singlet to arise from one *tert*-butyl group in rotamers A, B, and C, and the larger from the three equivalent *tert*-butyl groups in D plus the remaining *tert*-butyl groups in A, B, and C, a population ratio of ca. 3:1 may also be estimated in this case.

We have performed a complete band shape analysis of the 100-MHz methylene proton spectrum of the tribromo compound at temperatures between −20 and +50°C in chloroform-*d* solution, using an "8-sites program"[19] by

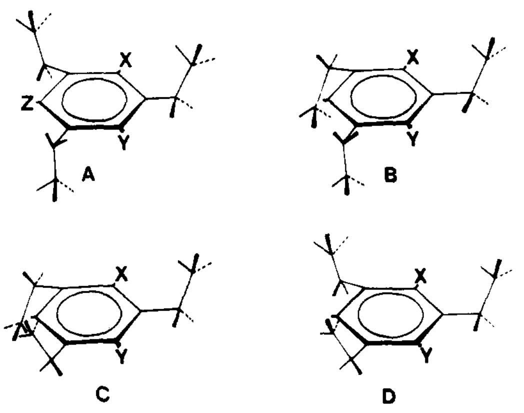

Figure 1. The four rotamers in a trisubstituted 1,3,5-trineopentylbenzene. Note that the wedges and the full or dashed lines denote methylene protons or *tert*-butyl methyl groups, as appropriate. The Z-substituent is omitted from rotamers B, C, and D for the sake of clarity.

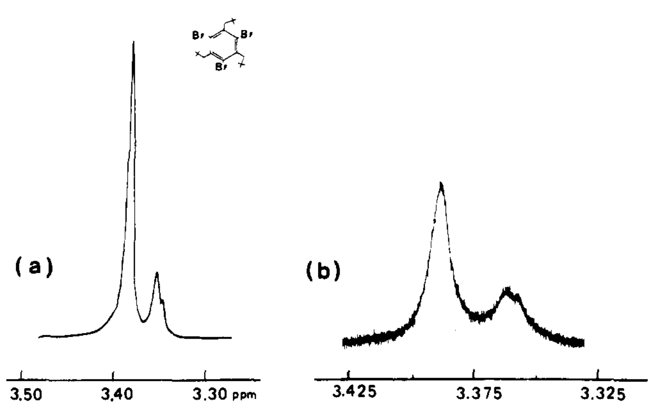

Figure 2. Methylene proton NMR spectrum of 2,4,6-tribromo-1,3,5-trineopentylbenzene at about −20°C in chloroform-*d* solution: (a) 300 MHz;[13] (b) 100 MHz.

means of which all of the four rotamers A, B, C, and D could be taken into account (see Figure 3). The population ratio was estimated to be 2.6_2 at −19.4°C, and ratios at higher temperatures were calculated assuming a temperature-independent $\Delta G°$ of 0.49 kcal/mol. The rather small chemical shift difference between the high- and low-field signals (2.8_5 Hz at −19.4°C; cf. Figure 2b), and the consequent difficulty in deriving rate constants over a sufficiently wide temperature interval, did not permit the accurate determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the interconversion process[21] but, by calculating $\Delta G^{\ddagger}$ at each temperature and plotting $\Delta G^{\ddagger}$ vs. T, satisfactorily reliable values for $\Delta G^{\ddagger}_{298\mathrm{K}}$ could be obtained: 17.0 ± 0.1 kcal/mol for the D → A, B, or C conversion, and 16.0 ± 0.1 kcal/mol for the A, B, or C → D conversion. The latter $\Delta G^{\ddagger}$ value, as might be expected, is in good agreement with the corresponding value for 2,6-dibromo-1,3,5-trineopentylbenzene[22] (16.2 ± 0.1 kcal/mol).

The 100-MHz ^{1}H NMR spectra of the analogous symmetrically substituted compounds 2,4,6-trichloro- and 2,4,6-trimethyl-1,3,5-trineopentylbenzene at low temperatures (between −20 and −50°C) in chloroform-*d* or carbon disulfide solutions could similarly be interpreted in terms of the predominance of rotamer D but, in these cases, the shift between the methylene signals became too small to be resolved. (The methylene proton band shapes were somewhat distorted, with a tendency toward the appearance of a shoulder.) However, in analogy with the case of the tribromo compound, the *tert*-butyl proton spectrum consisted of two signals separated by 3.2 and 4.0 Hz for the trichloro and trimethyl compounds, respectively, in carbon disulfide solution at −50°C. The corresponding intensity ratios (i.e., the ratios of the heights of the two *tert*-butyl signals) were 6.2:1 and 6.3:1. In the 100-MHz *tert*-butyl proton spectrum of the tribromo compound in carbon disulfide solution, the intensity ratio was 8.8:1. The shift data are collected in Table I, along with estimates of the relative populations of the rotamers, assuming that the smaller signal in all cases represents *one tert*-butyl group in rotamer A, B, or C.

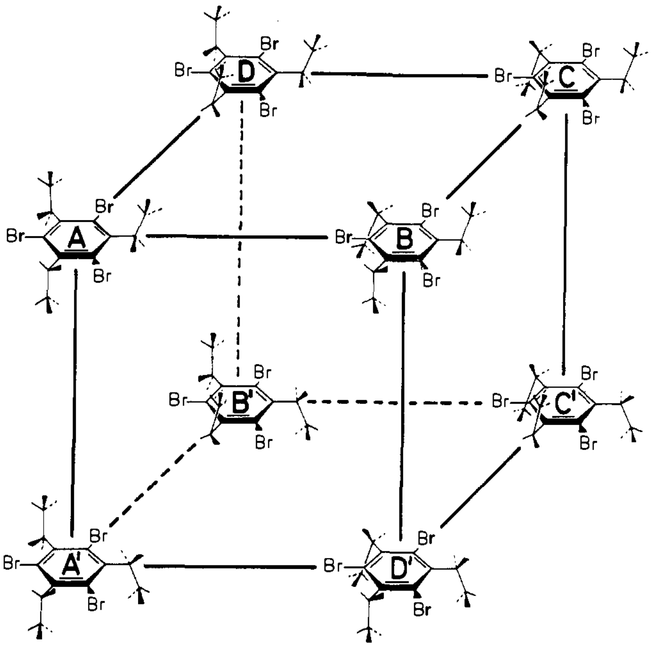

Figure 3. Rotamer interconversion scheme for 2,4,6-tribromo-1,3,5-trineopentylbenzene. Interconversions are assumed to occur via rotation of only one neopentyl group at a time. Note that the wedges and the full or dashed lines denote methylene protons or *tert*-butyl methyl groups, as appropriate.

Possible Origin of Chemical Shifts in Methylene Proton Region. In the symmetrically trisubstituted compounds, the difference in shift (at low temperature) between the methylene protons of the two "cis" neopentyl groups in rotamer A, B, or C and those of a given pair of neopentyl groups in rotamer D is primarily determined by the difference in the time average spatial orientation of the third neopentyl group. The *internal* shift in the theoretically expected AB quartet for the two "cis" neopentyls in A, B, or C is chiefly due to a differential effect of the spatial orientation of the remaining neopentyl group but, in view of the small magnitude of the shifts discussed above (at most a few hertz), this much smaller effect is (not surprisingly) undetectable.

In the light of these observations, it is worthwhile considering the origin of the AB shifts in the 1- and 5-methylene proton spectra of the corresponding 2,4-disubstituted 1,3,5-trineopentylbenzenes.[22] In these compounds (at sufficiently low temperatures), AB patterns were observed for the methylene protons of the rapidly rotating 1- and 5-neopentyl groups due to the presence of the slowly rotating 3-neopentyl group.[23] (The AB shifts were 21.7, 26.8, and 31.0 Hz at about −10°C in chloroform-*d* solution for the dichloro, dibromo, and dimethyl compounds, respectively.) If the 1- and 5-neopentyl groups are assumed to rotate completely independently of each other, the AB shifts would be determined solely by the differential effect of the spatial orientation of the 3-neopentyl group, which would be roughly of the same order of magnitude as in the trisubstituted analogs, *i.e.*, most likely difficult or impossible to resolve at 100 MHz. However, since all of the possible relative orientations of the 1- and 5-neopentyl groups are not

Table I. Proton Chemical Shifts and Population Ratios for 2,4,6-Trisubstituted 1,3,5-Trineopentylbenzenes

Substituents	Temp, °C	Solvent	Chemical shifts, δ^a			Population ratio[b]
			tert-Butyl	Methylene	Methyl	
2,4,6-Trichloro	−50	CS_2	0.947 (A, B, C "trans") 0.979 (D; A, B, C "cis")	3.010 (A, B, C, D)		1.4[c]
2,4,6-Trichloro	−20	$CDCl_3$	0.985 (A, B, C, "trans") 1.029 (D; A, B, C "cis")	3.099		2.1[c]
2,4,6-Tribromo	−10	CS_2	1.000 (A, B, C "trans") 1.034 (D; A, B, C "cis")	3.309 (A, B, C) 3.334 (D)		2.0[c]
2,4,6-Tribromo	−10	$CDCl_3$	1.020 (A, B, C "trans") 1.065 (D; A, B, C "cis")	3.362 (A, B, C) 3.388 (D)		2.5 (2.3)[d]
2,4,6-Trimethyl	−50	CS_2	0.848 (A, B, C "trans") 0.888 (D; A, B, C "cis")	2.658 (A, B, C, D)	2.194 (A, B, C, D)	1.4[c]
2,4,6-Trimethyl	−40	$CDCl_3$	0.897 (A, B, C "trans") 0.947 (D; A, B, C "cis")	2.811 (A, B, C, D)	2.300 (A, B, C) 2.324 (A, B, C, D)	3.2 (3.1)[e]

[a] Assignments to rotamers in parentheses; cf. Figure 1. [b] Relative populations (D/A, B, C) were estimated by a straightforward curve-fitting procedure, assuming Lorentzian line shapes. [c] From *tert*-butyl signals. [d] From band shape analysis of methylene proton signals; ratio from *tert*-butyl signals in parentheses. [e] From *tert*-butyl signals and (in parentheses) from aryl methyl signals.

Table II. ^{13}C NMR Chemical Shifts at Approximately −30° in Chloroform-*d* Solution

Substituents	*tert*-Butyl		Chemical shifts, ppm from Me_4Si^a		
	CH_3-	$-\overset{|}{\underset{|}{C}}-$	Methylene	Methyl	Aryl
2,4,6-Trichloro	34.9 (D; A, B, C "cis") 35.4 (A, B, C "trans")	40.4, 40.7 (A, B, C) 40.8 (D)	50.1 (A, B, C, D)		135.5, 136.5
2,4,6-Tribromo[b]	30.6 (D; A, B, C "cis") 31.1 (A, B, C "trans")	34.5, 34.9 (A, B, C) 35.2 (D)	49.3 (A, B, C, D)		139.4, 139.7
2,4,6-Trimethyl	30.4 (D; A, B, C "cis") 30.9 (A, B, C "trans")	34.3, 34.5 (A, B, C) 34.8 (D)	41.0 (A, B, C, D)	20.4	134.7, 135.1

[a] Rotamer assignments in parentheses; cf. Figure 1. [b] From ref 12; rotamer assignments revised (see text).

energetically equal, one methylene proton in a given methylene group spends more time oriented toward the aromatic proton (or toward the substituent) than does the other, and the AB shift becomes easily detectable.

^{13}C NMR Spectra. The ^{13}C NMR spectra of the neopentyl carbons in the trichloro and trimethyl compounds at low temperatures (ca. −30°C) exhibited features similar to those previously observed in the tribromo case[13] and may be interpreted in the same way as described above. The ^{13}C chemical shift data are summarized in Table II. In this connection, it should be noted that the ^{13}C NMR spectrum of trineopentylbenzene itself shows only one signal from the quaternary carbon atoms at temperatures as low as ca. −160°C. An interpretation of this observation consistent with the other data reported in this paper may of course be made in terms of the strong predominance of rotamer D.

Solvent Effects on the Population Ratio in the Dibromonitro Compound. We reasoned that, if the nature of the solvent were changed from "aliphatic" to "aromatic", allowing for some form of weak solute-solvent interaction involving mutual polarization of solute and solvent π-electron clouds, we might be able to increase the relative amount of the achiral rotamer (D or B), in which the nitro group is thought to be essentially perpendicular to the ring plane. A solute-solvent interaction of this type would be expected to be favored for rotamer D, in which one side of the aromatic ring plane is essentially entirely free from steric hindrance. Furthermore, the energy gain associated with such a solute-solvent interaction, in conjunction with the increase in attractive non-bonded interactions among the *tert*-butyl groups on going from rotamer A, B, or C to rotamer D, could counterbalance the energy loss due to decreased resonance between the nitro group and the ring in rotamer D.

The data are summarized in Table III and show that our expectations were fulfilled in the sense that a change in solvent from, e.g., carbon disulfide to carbon disulfide-hexafluorobenzene 25:75 (v/v) leads to a 43% increase in the relative amount of the achiral rotamer. In monofluorobenzene solution, the achiral rotamer is the dominant species (population ratio = 1.12). These data do not allow us to unequivocally distinguish between rotamers B and D in the dibromonitro system, but our preference is for D in the light of the results for the symmetrically trisubstituted compounds.

Table III. Solvent Effects on the Rotamer Population Ratio in 2,4-Dibromo-1,3,5-trineopentyl-6-nitrobenzene (I)

Solvent	Ratio of rotamer D to A or C[a] at ca. −25°C
$CHCl_2F$	0.44
CS_2	0.51
$CS_2-C_6F_6$ 50:50	0.61
$CS_2-C_6F_6$ 25:75[b]	0.73
Pyridine	0.93
C_6H_5F	1.12

[a] Cf. Figure 1; rotamer B is excluded from consideration for reasons given in the text..The population ratios were estimated by a straightforward curve-fitting procedure, assuming Lorentzian line shapes. [b] Spectra could not be obtained in C_6F_6 in the absence of CS_2 due to solubility difficulties.

Estimation of the Resonance Effect of the Nitro Group in Compound I. The energy of stabilization due to the resonance between the nitro group and the aromatic ring on going from the tribromo to the dibromonitro compound may be roughly estimated as follows: rotamer A, B, or C in the tribromo system lies 0.49 kcal/mol higher in free energy than rotamer D at a concentration of ca. 6 mol % in chloroform-*d* solution at −19.4°C (data from band shape analysis); the corresponding difference for the dibromonitro compound (excluding rotamer B from consideration) at comparable concentration and temperature in chloroform-*d* solution[11a] is −0.3 kcal/mol (i.e., rotamers A and C at the lower energy). Thus the replacement of a bromine by a nitro group leads to a stabilization of the A/C rotamers by about 0.8 kcal/mol. If the greater part of this stabilization energy may be attributed to the resonance interaction between the nitro group and the aromatic ring, and the total energy of this interaction is of the order of 3.0 ± 1.5 kcal/mol,[24] we may derive a lower limit value for the nitro group–aromatic ring dihedral angle of ca. 58°, assuming a $\cos^2$ (dihedral angle) dependence. This may be compared with a dihedral angle of 66° in 2,6-dimethylnitrobenzene, estimated from UV data by Wepster.[25]

Experimental Section

The syntheses of 2,4-dibromo-1,3,5-trineopentyl-6-nitrobenzene and 2,4,6-trichloro-1,3,5-trineopentylbenzene have been described previously.[26,27] The original sample of 2,4,6-tribromo-1,3,5-trineopentylbenzene was a gift from Dr. Per Martinson, Göteborg.

2,4,6-Trimethyl-1,3,5-trineopentylbenzene was obtained via chloromethylation of 2,4-dimethyl-1,3,5-trineopentylbenzene[26] and subsequent reduction of the product. 2,4-Dimethyl-1,3,5-trineopentylbenzene[26] (640 mg, 2 mmol) was dissolved in 5 ml of carbon disulfide, and 0.12 ml (1 mmol) of tin(IV) chloride, 1.4 ml (12 mmol) of silicon tetrachloride, and 3.8 ml (50 mmol) of chloromethyl methyl ether were added. The reaction mixture was maintained at 50°C, and the reaction was followed by gas chromatographic analysis of aliquots drawn from the mixture. After 4 weeks, no starting material remained. Water was added to the reaction mixture, and the new mixture was extracted with water and dried with magnesium sulfate. After evaporation of the solvent, the product was directly reduced with lithium tetrahydridoaluminate, as described for the reduction of 2-chloromethyl-1,3,5-trineopentylbenzene.[26] After recrystallization from nitromethane, 365 mg (55% overall yield) of a colorless product, mp 114–115°C, was obtained: mass spectrum *m/e* (% of base peak) 29 (11), 41 (26), 43 (10), 57 (43), 71 (10), 161 (23), 217 (20), 273 (100), 274 (36), 330 (10).

NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped with a 12-mm variable temperature probe and a Varian V-6040 temperature controller. Temperatures were determined by means of a copper–constantan thermocouple fixed near the receiver coil. The ^{13}C NMR spectra were obtained in the Fourier transform (FT) mode on ca. 2 *M* solutions in chloroform-*d* at temperatures from ambient to −30°C. Some of the proton spectra were also recorded on a Jeol JNM-MH-100 instrument.

The band shape analysis of the spectrum of the tribromo compound was carried out on an approximately 6 mol % sample in chloroform-*d* solution, containing a small amount of methylene chloride as a standard of resolution, and sealed off on a vacuum line after degassing by the freeze–thaw technique. The spectra were recorded in the continuous wave (CW) mode on the XL-100 spectrometer, at a scale expansion of 0.5 Hz/cm and with a sweep rate of 0.1 Hz/sec. The rf field was always chosen sufficiently low to avoid saturation effects.

Computer Calculations. The computer program utilized to simulate band shapes for the tribromo compound was based on the McConnell equation[28] written in matrix form. Exchanges among eight sites could be taken into account (see Figure 3).[19] The computer calculations were carried out on a Univac 1108 computer equipped with a Calcomp plotter. Simulated spectra obtained from the plotter were visually fitted to experimental ones. Rotameric populations and chemical shifts were obtained from iterations of spectra run at low temperatures. A temperature-independent $\Delta G°$ was assumed to calculate populations at higher temperatures. The low-temperature chemical shifts were used in the calculations at all higher temperatures, as it was not feasible to determine the temperature dependence of the shifts over a suitably wide temperature interval. Values for the linewidth parameter, T_2, were determined in the usual way[11a,29] at the slow and fast exchange limits of the exchange process, and were assumed to vary linearly with temperature. The rate constants extracted from spectra in a narrow temperature interval (13–48°C) were then used in conjunction with the Eyring equation[30] to obtain the activation parameters.

The curve-fitting procedure employed to estimate the relative rotamer populations in Tables I and III (except for that obtained from the band shape analysis of the spectrum of the tribromo compound) assumed Lorentzian line shapes and was performed on a Hewlett-Packard desk calculator Model 9820A, equipped with a Model 9862A plotter.

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(14) This spectrum was obtained through the kindness of Dr. J. Shoolery, Varian Associates, Palo Alto, Calif. Dr. Shoolery also suggested the predominance of rotamer D as the most likely interpretation of the spectrum.
(15) The putative AB shift of the methylene protons in the 3-neopentyl group in compound I is also undetectable, as mentioned in ref 11a.

(16) Empirical force field calculations on the corresponding two rotamers in trineopentylbenzene itself, using the STRAIN program developed at Princeton University,[7,8,17] gave values of −1.05 and −0.14 kcal/mol for rotamers D and A, B and C, respectively. The difference of 0.91 kcal/mol is of interest in comparison with the $\Delta G°$ value of 0.49 kcal/mol estimated in connection with a band shape analysis of the methylene proton spectrum of the tribromo compound at 100 MHz (see subsequent text). The details of the molecular mechanics calculations will be described in a later paper.[18]
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Steric Effects. IV. E1 and E2 Eliminations

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Abstract: Rate constants for E2 elimination of β-substituted 'onium compounds and orientation data for E2 and E1 eliminations taken from the literature give significant correlations in nine out of ten sets studied with the modified Taft equation, $Q_{\mathrm{X}} = \psi v_{\mathrm{X}} + h$. The effect of β-alkyl groups on rates and orientation in E2 elimination reactions and on orientation in E1 elimination reactions can be quantitatively described by steric effects.

There is considerable controversy in the literature regarding the explanation of the effect of alkyl groups on reaction rates and orientation in E1 and E2 eliminations.[1] In the case of E2 eliminations, Banthorpe, Hughes, and Ingold[2] made the statement that, "the inductive and electromeric effects dominate the picture of eliminations down to the simplest examples of Hofmann and Saytzeff". These authors regard steric effects as insignificant except in the case of very large alkyl groups. Brown and his coworkers,[3] on the other hand, have proposed that steric effects are the cause of the observed effect of alkyl groups on the orientation in both E1 and E2 reactions. It seemed of interest to examine the available data quantitatively by means of correlations with the modified Taft equation

$$Q_{\mathrm{X}} = \psi v_{\mathrm{X}} + h \tag{1}$$

where Q is the quantity to be correlated, and v is the steric parameter we have defined in the first paper of this series,[4] from the esterification of carboxylic acids. Some of the data have been correlated with the equation

$$Q_{\mathrm{X}} = \alpha\sigma_{\mathrm{IX}} + \beta\sigma_{\mathrm{RX}} + \psi v_{\mathrm{X}} + h \tag{2}$$

to detect the presence of significant electrical effects. In this equation, σ_{I} and σ_{R} are substituent constants representative of the localized and delocalized electrical effects, respectively. Values of σ_{I} are taken from our compilation,[5] values of σ_{R} are from the equation

$$\sigma_{\mathrm{R}} = \sigma_{\mathrm{p}} - \sigma_{\mathrm{I}} \tag{3}$$

The σ_{p} values are taken from the compilation of McDaniel and Brown.[6] The data were also correlated with the equation

$$Q_{\mathrm{X}} = \psi' v'_{\mathrm{X}} + h \tag{4}$$

where v' represents the steric parameter defined from nucleophilic substitution of substituted alkyl bromides as described in the third paper of this series.[7]

The data sets studied fall into two groups, rate constants for the E2 elimination reactions of 'onium ions bearing β-alkyl substituents (sets 1-4) and ratios of percent 1-olefin formed to percent 2-olefin formed, or similar quantities, for elimination reactions involving compounds that can produce more than one elimination product (sets 5-10). When two or more products are formed, the overall rate constant k_{T} is given by

$$k_{\mathrm{T}} = k_1 + k_2 + \ldots + k_n \tag{5}$$

where $k_1, k_2, \ldots k_n$ are the rate constants for the formation of products 1, 2, ... n. For these rate constants, we may write

$$k_1 = p_1 k_{\mathrm{T}}, k_2 = p_2 k_{\mathrm{T}}, \ldots k_n = p_n k_{\mathrm{T}} \tag{6}$$

where $p_1, p_2, \ldots p_n$ denote the percents formed of products, 1, 2, ... n. Thus, applying the modified Taft equation we may obtain

$$\log k_1 = \log p_1 k_{\mathrm{T}} = \psi_1 v_{\mathrm{X}} + h_1 \tag{7}$$

$$\log k_2 = \log p_2 k_{\mathrm{T}} = \psi_2 v_{\mathrm{X}} + h_2 \tag{8}$$

$$\log p_1 k_{\mathrm{T}} - \log p_2 k_{\mathrm{T}} = \log (p_1/p_2) = \psi_1 v_{\mathrm{X}} + h_1 - (\psi_2 v_{\mathrm{X}} + h_2) = \log r_{12} \tag{9}$$

$$\log r_{12} = \psi_{12} v_{\mathrm{X}} + h_{12} \tag{10}$$

The data for sets 5-10 were also correlated with the equation

$$\log r_{12} = \psi_{v12} v'_{\mathrm{X}} + h'_{12} \tag{11}$$

The data used in the correlations are presented in Table I.

Results

The results of the correlation of sets 1-4 (sets labeled A) with eq 2 are set forth in Table II. Only set 2 gave significant results. In this set, the values of α and β were not significant, whereas the value of ψ was significant, as deter-