mole fraction of OH attributable to **2** with respect to water (i.e., $\tau_x = \tau_w - CX$; see paragraph at end of this paper about Supplementary Material).

The solvents were obtained as commerical samples and were used as such without further purification. The proton spectra were recorded with either a Varian XL-100 or a Perkin-Elmer R32 spectrometer.

General Procedure for Hydrolysis of Acetylanthranil (1) in Organic Solvents. A sample of powdered **1** (0.04 g) was weighed into an NMR tube. Solvent (0.50 cm^3) was added by means of a microsyringe graduated into units of 0.01 cm^3 to produce a clear solution. A measured amount of water was then added by means of a microsyringe, graduated into units of 10^{-5} cm^3, and the initial time was noted. Tetramethylsilane (0.01 cm^3) was added as the internal reference and the first proton NMR spectrum was recorded immediately thereafter. The ratio [1]/[2] in the powdered sample taken for study and the ratio $[H_2O]/([1] + [2])$ were established from the relative integration values of τ for 1-CH_3, 2-CH_3, and active OH in this initial spectrum. Spectra were recorded periodically thereafter as needed to monitor the complete conversion of **1** to *o*-acetamidobenzoic acid (**2**). Usually the NMR tube was allowed to remain in the NMR probe (36 °C) during the first hour of hydrolysis or until hydrolysis was about 80% complete, whichever came first. Thereafter the NMR tube was stored at 22 °C until the next NMR spectrum was recorded.

The integration values for the sum of the methyl substituents 1-CH_3 and 2-CH_3 for each spectrum in the set of spectra recorded in order to monitor to completion the conversion of **1** to **2** were normalized to a common value of 50 units, which corresponded to 0.5 M with respect to solute (**1** + **2**) established gravimetrically. Accordingly, the units for concentration of unreacted **1** at time t were 0.01 of the corresponding integration value. Since the hydrolysis is known to be stoichiometric, the corresponding water concentration at time t was given by $[H_2O]_t = [H_2O]_0 - ([1]_0 - [1]_t)$. The values for log $[H_2O]/[1]$ were plotted as a function of t to establish the pseudo-second-order relationships shown in Figures 1 and 2 which were used to calculate k_b and k_a, the pseudo-second-order rate constants in L/mol·min before and after the observed point of inflection at t_i.

Registry No. 1, 525-76-8.

Supplementary Material Available: Detailed procedures for hydrolysis time studies using CD_3CN, $CDCl_3$, and benzene as solvents and the plots of the data obtained thereby (8 pages). Ordering information is given on any current masthead page.

ESR Study of Persistent Thioaminyls, *N*-(Arylthio)-3,5-di-*tert*-butylphenylaminyls[1,2]

Yozo Miura,* Akifumi Yamamoto, Yosuke Katsura, and Masayoshi Kinoshita

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan

Received February 5, 1980

N-(Arylthio)-3,5-di-*tert*-butylphenylaminyls (**2**) are generated by hydrogen-abstraction from *N*-(3,5-di-*tert*-butylphenyl)arenesulfenamides (**1**) and are investigated by means of ESR spectroscopy. When the sulfenamides were treated with lead dioxide in benzene, the solutions turn immediately dark blue or dark greenish blue (502–605 nm) and the colored solutions give a strong ESR signal due to **2**. The nitrogen hyperfine-splitting constants for **2** are in the range 9.52–9.64 G, and the *g* values are in the range 2.0057–2.0061. The spin densities in **2** are calculated by using the HMO and McLachlan HMO procedures, and the results are compared with the experimental results. The radicals **2** are very long-lived, even in the presence of oxygen, and can be isolated as hydrazine-type dimers (**3**) which dissociate into **2** at room temperature. The equilibrium constants for **3** $\rightleftarrows$ 2 **2** equilibria are measured in benzene, THF, chloroform, and acetone/benzene over a temperature range from 5 to 33 °C by means of ESR spectroscopy, and the following values are obtained: the equilibrium constants, 0.98×10^{-4}–4.59×10^{-4} M (in benzene at 27 °C); $\Delta H°$ and $\Delta S°$ for the equilibria, 13.3–13.8 kcal/mol and 29.0–29.2 eu (in benzene). These values are compared with literature values.

Although organic free radicals are generally recognized to be transient, there have been some exceptionally persistent free radicals.[3] For example, triarylmethyl radicals are in equilibrium with the isolable dimers in solution at room temperature,[4] and diphenylpicrylhydrazyl (DPPH),[5] nitroxides,[6] and verdazyls[7] can be isolated as pure crystals.

For the past few years, we have studied a type of thioaminyls, $R\dot{N}SR'$, by ESR spectroscopy.[1] Since the aminyls bear a divalent sulfur atom adjacent to the radical center, they are significantly stabilized by the resonance contributions $-\dot{N}-\ddot{S}- \leftrightarrow -\ddot{N}^{-}-\dot{S}^{+}-$. Thus, these radicals are fairly persistent when they have no active hydrogen atoms (e.g., β hydrogen atoms). For the purpose of isolating this class of radicals, we have prepared some sterically protected thioaminyls. It has been found that *N*-(arylthio)-3,5-di-*tert*-butylphenylaminyls (**2**) are quite persistent, even in the presence of oxygen, and can be isolated as dimers (**3**) which dissociate into **2** at room temperature.

In this report we describe the generation of **2** and their ESR parameters, the isolation of **3**, the equilibrium constants for **3** $\rightleftarrows$ 2 **2** equilibria, and the thermodynamic

---

(1) Part 14 of the series "ESR Studies of Nitrogen-Centered Free Radicals." For part 13 see Y. Miura and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **53**, 2395 (1980).

(2) For a preliminary report of this work see Y. Miura, Y. Katsura, and M. Kinoshita, *Chem. Lett.*, 409 (1977).

(3) For a review see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals", Academic Press, London and New York, 1968.

(4) M. Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

(5) S. Goldschmidt and K. Renn, *Chem. Ber.*, **55**, 628 (1922).

(6) For a review see E. G. Rozantsev, "Free Nitroxide Radicals", translated from Russian by B. J. Hazzard, Plenum Press, New York and London, 1970.

(7) For a review see F. A. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 12, 455 (1973).

0022-3263/80/1945-3875$01.00/0

Table I. ESR Parameters and λ_{max} for 2 in Benzene[a,b]

radical	a_N	$a_{o\text{-H}}$[c]	$a_{p\text{-H}}$[c]	$a_{o\text{-H}}$[d]	$a_{m\text{-H}}$[d]	a_{other}	g	λ_{max}[e]
2a[f]	9.53	3.71	4.22	0.76	0.27	0.83 (*p*-H)[d]	2.0060	597
2b	9.52	3.73	4.23			10.34 (^{13}C), 5.44 (^{13}C), 4.62 (^{33}S)	2.0060	600
2c[f]	9.52	3.62	4.20	0.80	0.26	0.87 (CH_3)	2.0060	605
2d	9.58	3.70	4.42	0.75	*g*		2.0059	602
2e	9.56	3.71	4.38	0.77	0.22		2.0059	602
2f[f]	9.64	3.81	4.55	0.74	*g*		2.0057	502, 602
2g	9.59	3.85	4.55	0.68	*g*		2.0061	601
2h[f]	9.63	3.87	4.52	0.74		0.74 (*p*-H)[d]	2.0057	590
4[h]	9.59	3.70	4.18	0.78	0.27	1.26 (*m*-H),[c] 0.84 (*p*-H)[d]	2.0059	

[a] Hyperfine splitting constants are given in gauss. [b] At room temperature (23 °C). [c] *N*-Phenyl ring protons. [d] *S*-Phenyl ring protons. [e] Given in nanometers. [f] Determined by computer simulation. [g] Not resolved. [h] Reference 8.

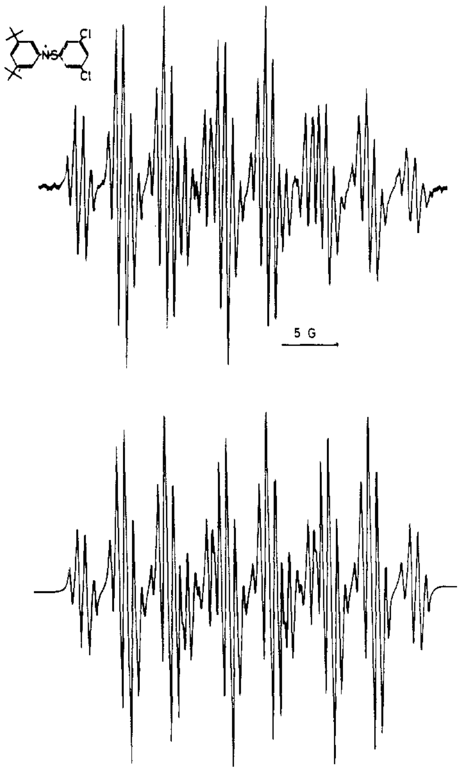


Figure 1. Experimental ESR spectrum of **2h** in benzene at 23 °C (upper) and computer-simulated spectrum using Lorentzian line shapes and a line width of 0.27 G (lower).

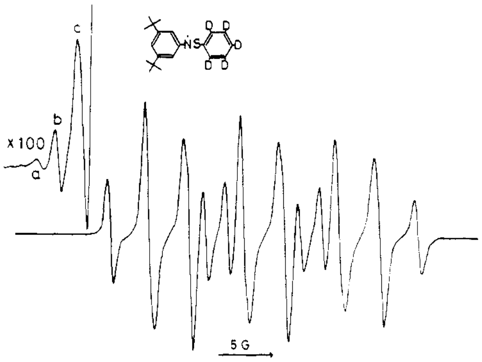
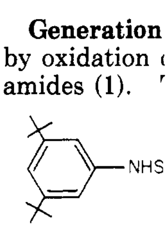


Figure 2. Experimental ESR spectrum of **2b** in benzene at 23 °C. Inset shows a part of the spectrum recorded under high gain (× 100); a, satellite due to ^{33}S in natural abundance, b and c, satellites due to ^{13}C in natural abundance.

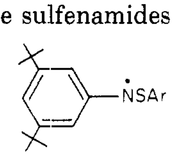
parameters ($\Delta H°$ and $\Delta S°$) for the equilibria.

Results and Discussion

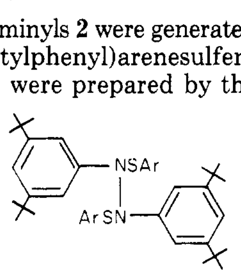
Generation of Radicals. The aminyls **2** were generated by oxidation of *N*-(3,5-di-*tert*-butylphenyl)arenesulfenamides (**1**). The sulfenamides **1** were prepared by the reaction of 3,5-di-*tert*-butylaniline with 1 equiv of arenesulfenyl chloride in the presence of triethylamine. When **1a–h** were treated in benzene with lead dioxide and potassium carbonate, the colorless (**1a–e**, **1g**, and **1h**) or light yellow solutions (**1f**) turned immediately dark blue (**2a–e**, **2g**, and **2h**) or dark greenish blue (**2f**) and the colored solutions gave strong ESR signals due to **2**. For example, an ESR spectrum recorded from the solution containing **2h** is illustrated in Figure 1. The signal is split into a 1:1:1 triplet (9.63 G), and each component of the triplet is further split into 1:3:3:1 quartets (0.74 G) of 1:2:1 triplets (3.87 G) of a 1:1 doublet (4.52 G). This spectrum is analyzed as follows: the 1:1:1 triplet is due to the central nitrogen nucleus, the 1:1 doublets and the 1:2:1 triplets are due to the para proton and the two ortho protons in the *N*-phenyl ring, respectively, and the 1:3:3:1 quartets are due to the magnetically almost equivalent three ortho and para protons in the *S*-phenyl ring. This assignment was performed with the aid of the deuterium-labeled aminyl **2b**. In the ESR spectrum of **2b** obtained on recording under high amplification (Figure 2), the satellite due to ^{33}S in natural abundance could be observed, together with the satellites due to ^{13}C in natural abundance. The hyperfine splitting (hfs) constants, *g* values, and λ_{max} obtained for **2** are summarized in Table I, together with those for the unsubstituted thioaminyl **4**, which was previously reported.[8] The aminyls **2** were also generated by hydrogen abstraction from **1** using *tert*-butoxyl radicals which were obtained on thermolysis of di-*tert*-butyl diperoxyoxalate or by photolysis of **1** using a high-pressure mercury lamp. However, the first procedure, the oxidation of **1** with lead dioxide, was found to be the most effective for generation



1

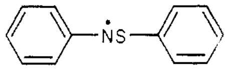


2



3

a, Ar = C_6H_5;
b, Ar = C_6D_5;
c, Ar = 4-$CH_3C_6H_4$;
d, Ar = 4-ClC_6H_4;
e, Ar = 4-BrC_6H_4;
f, Ar = 4-$NO_2C_6H_4$;
g, Ar = 2,4-di-ClC_6H_3;
h, Ar = 3,5-di-ClC_6H_3

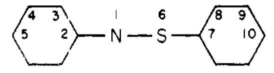


4

---

[8] Y. Miura and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50** 1142 (1977).

Table II. Observed and Calculated Spin Densities in 4



position	exptl hfs constant, G	spin density[a]	calcd spin density	
			HMO	McLachlan[b]
1	9.59	0.384	0.305	0.386
2			0.022	−0.017
3	3.70	0.137	0.124	0.154
4	1.26	0.047	0.003	−0.035
5	4.18	0.155	0.134	0.155
6	4.62[c]	0.140	0.187	0.189
7			0.005	−0.012
8	0.78	0.029	0.030	0.027
9	0.27	0.009	0.001	−0.009
10	0.84	0.031	0.032	0.025

[a] The spin densities were derived from the experimental hfs constants by use of the relationship $a = Q\rho$, with $a_N = 25\rho_N$, $a_H = 27\rho_C$, and $a_S = 33\rho_S$. [b] $\lambda = 0.7$. [c] The value observed for **2b** is described.

of **2**. For example, when a benzene solution of **1d** (0.37 mmol, 50 mL) was stirred for 10–15 min in the presence of lead dioxide (3 g) and potassium carbonate (3 g), the resultant solution contained **2d** in a concentration corresponding to ~10% of the **1d** used.

As can be seen in Table I, the magnitudes of the hfs constants of **2** are approximately constant and are very close to those for **4**. However, when the values are discussed in detail, we note that the magnitude of the nitrogen hfs constant is slightly increased when the substituent in the *S*-phenyl ring is electron-withdrawing. A similar tendency is also observed for the ortho and para protons in the *N*-phenyl ring. This can be interpreted in terms of an increase in the relative importance of the resonance form I.

$$-\dot{N}\underset{\text{I}}{-}\ddot{S}- \leftrightarrow -\ddot{N}^{-}\underset{\text{II}}{-}\dot{S}^{+}-$$

As can be seen from the hfs constants for **2**, in **2** the unpaired electron resides mainly on the central nitrogen atom and the *N*-phenyl ring. We calculated the spin densities in the aminyls by the HMO and McLachlan HMO procedures,[9] using the following parameters:[10] $\alpha_N = \alpha + 1.15\beta$, $\alpha_S = \alpha + 1.3\beta$, $\beta_{CN} = 1.2\beta$, $\beta_{NS} = 0.7\beta$, and $\beta_{CS} = 0.75\beta$. These parameters are chosen on the basis of the previously used values but are slightly varied to give the best fit with the experimental results. The experimental and calculated results are listed in Table II. For the estimation of the spin density on the sulfur atom, the value observed for **2b** [$a(^{33}S)$, 4.62 G] is used, and the spin density on the sulfur atom is derived by use of the relationship $a_S = 33\rho_s$.[11] As can be seen in Table II, better agreement between the experimental and theoretical values of the spin densities is obtained from the McLachlan HMO calculation, although there are some deviations between these values. The results in Table II reveal that the spin density on the centered nitrogen atom is ~38% and that on the sulfur atom is ~14%. The large *g* values observed for **2** and **4** for a nitrogen-centered free radical[12] are well-explained by this considerable delocalization of the unpaired electron onto the sulfur atom having a large spin-orbit-coupling parameter.[13]

We also measured the hfs constants and λ_{max} for **2** in various polar solvents in order to examine solvent effects on these values.[14] The obtained results are as follows (nitrogen hfs constant and λ_{max} for **2b**): 9.56 and 599 (chloroform), 9.56 and 598 (THF), 9.56 and 596 (acetone), 9.54 and 594 (acetonitrile), and 9.57 G and 596 nm (ethanol). These results indicate these values are almost constant. Similarly, the proton hfs constants were also almost constant. Thus, it is obvious that the spin distribution in **2** is almost independent of the polarity of the solvent.[15]

The aminyls **2** are quite persistent, even in the presence of oxygen. When degassed benzene solutions of **2** in concentrations of 2.3×10^{-4}–6.7×10^{-4} mM were allowed to stand for 1 day at 23 °C, 80–88% of **2** persisted under these conditions. In order to examine whether **2** are destroyed by oxygen or not, the same solutions were also allowed to stand under the same conditions as above, but in contact with atmosphere, and we obtained almost the same results as under the degassed conditions. It is well-known that nitrogen-centered free radicals generally react with oxygen and are converted into the corresponding nitroxides or decompose to diamagnetic species.[3] Therefore, this finding is very interesting. The present aminyls also persisted in acetone/benzene (9/1 (v/v), $\tau_{1/2}$ = 10 h at 27 °C) and THF ($\tau_{1/2}$ = 5 h at 27 °C) in the presence of oxygen but decomposed rapidly in chloroform ($\tau_{1/2}$ = 0.5 h at 27 °C).

Isolation of Dimers. When toluene solutions of **2** were cooled to −78 °C, the characteristic blue color of **2** rapidly faded and, on raising to room temperature, the color due to **2** reappeared and this cycle was completely reversible. From this observation, **2** were found to be in equilibrium with a dimer in solution. This finding prompted us to try to isolate the dimers. The sulfenamides **1a–e** and **1g** were treated with lead dioxide and potassium carbonate in benzene for 10–15 min. After the resultant blue colored reaction mixtures were filtered, the solvent was removed by freeze-drying to afford light green powders, which were recrystallized from hexane or benzene–hexane, providing colorless or slightly blue colored crystals in 15–54% yields. In the cases of **1f** and **1h**, the corresponding crystals could not be isolated in pure form. On ESR measurement, the crystals were found to be essentially diamagnetic. The IR spectra of the crystals were very similar to those of the corresponding **1**, but the strong NH absorptions at 3330–3350 cm^{-1}, which are clearly observed in the spectra of **1**, disappeared completely. The crystals were highly soluble in benzene, THF, chloroform, and DMF, providing dark blue solutions which gave strong ESR signals due to **2**. The λ_{max} of the benzene solutions were identical with the values shown in Table I. On the other hand, hexane, acetone, acetonitrile, and ethanol were poor solvents for the crystals. The elemental analyses of the crystals were

---

[9] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[10] (a) E. T. Strom and G. A. Russell, *J. Am. Chem. Soc.*, **87**, 3326 (1965); (b) P. D. Sullivan, *ibid.*, **90**, 3618 (1968); (c) C. L. Kwan, M. Carmack, and J. K. Kochi, *J. Phys. Chem.*, **80**, 1786 (1976); (d) R. C. Haddon, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, **100**, 1235 (1978).

[11] F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, **100**, 4612 (1978).

[12] E.g., the *g* values for diarylaminyls have been reported to be in the range from 2.0031 to 2.0036: F. A. Neugebauer and S. Bamberger, *Chem. Ber.*, **107**, 2362 (1974).

[13] Sulfur spin orbit coupling parameter has been reported to be 382 cm^{-1}: D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

[14] The ESR samples were obtained by method C (see Experimental Section).

[15] The nitrogen hfs constant for nitroxide is largely dependent upon the polarity of solvent. For example, the nitrogen hfs constant for diphenyl nitroxide has been reported to be increased by 2.3 G in changing from cyclohexane to water: Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **35**, 260 (1962).

Table III. Equilibrium Constants for $3 \rightleftarrows 2\ 2$ Equilibria in Solution

dimer	temp, °C	solvent	$K \times 10^4$, M
3a	27	benzene	3.45 ± 0.15
3c	5	benzene	0.79
3c	17	benzene	2.08
3c	27	benzene	4.59 ± 0.14
3c	33	benzene	7.22
3c	27	THF	12.3 ± 0.3
3c	27	$CHCl_3$	20
3c	27	acetone/benzene[a]	5.22 ± 0.10
3d	5	benzene	0.39
3d	17	benzene	1.11
3d	27	benzene	2.45 ± 0.10
3d	33	benzene	3.86
3d	27	THF	5.88 ± 0.09
3d	27	$CHCl_3$	9
3e	27	benzene	2.38 ± 0.06
3g	27	benzene	0.98 ± 0.08

[a] Acetone/benzene 9/1 (v/v).

in good agreement with those calculated for the dimers **3**. The average molecular weight of **3d** (482) in benzene at 33 °C, which was obtained with a vapor-pressure osmometer, was in relatively good agreement with the value (521) calculated on the basis of the equilibrium constant of **3d** in benzene at 33 °C. From these results we assigned the isolated crystals as the dimers **3**.

Equilibrium Constants and Thermodynamic Parameters. As described above, the dimers **3** dissociate into **2** in solution even at room temperature. The equilibrium constants for $3 \rightleftarrows 2\ 2$ equilibria were measured in benzene, THF, chloroform, and acetone/benzene (9/1 v/v) in a temperature range from 5 to 33 °C. The results are summarized in Table III.

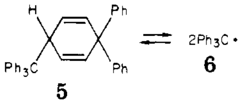
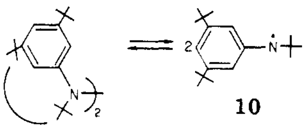
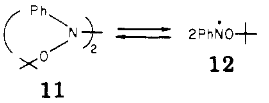
$$\text{dimer} \rightleftarrows 2 \text{ radicals}$$

$$K = \frac{[\text{radical}]^2}{[\text{dimer}]}$$

The thermodynamic parameters, $\Delta H°$ and $\Delta S°$, for the equilibria were calculated from the plot of the equilibrium constants vs. $1/T$, using the equation $\ln K = -(\Delta H°/R)(1/T) + (\Delta S°/R)$.[16] The values thus obtained are 13.3 kcal/mol ($\Delta H°$) and 29.0 eu ($\Delta S°$) for $\mathbf{3c} \rightleftarrows 2\ \mathbf{2c}$ equilibrium and 13.8 kcal/mol ($\Delta H°$) and 29.2 eu ($\Delta S°$) for $\mathbf{3d} \rightleftarrows 2\ \mathbf{2d}$ equilibrium. In Table IV these values are compared with literature values.

As can be seen in Table III, the equilibrium constants for $3 \rightleftarrows 2\ 2$ equilibria are considerably large (e.g., 0.98×10^{-4}–4.59×10^{-4} M in benzene at 27 °C) compared with the related nitrogen-centered free radicals.[17-21] These large values are interpreted in terms of the great ability of divalent sulfur to donate electrons. That is, the dipolar repulsion between the nitrogen atoms in **3** should be more enhanced by this ability of sulfur[22] compared with those in **8** and **10**. In fact, the nitrogen–nitrogen bond strengths of **3c** and **3d** are only 13.3 and 13.8 kcal/mol, as shown in Table IV, and these values are considerably smaller than those of **8** and **10** and are similar to that of **12**, which is isoelectronic with **3**.[21] The dipolar repulsion between the nitrogen atoms in hydrazines is also enhanced by the introduction of an electron-donating substituent, as has been shown in many reports, with respect to arylaminyls.[3,22,23] The order in magnitude of the equilibrium constants observed for a series of **3**, **3c** > **3a** > **3d** ≳ **3e** > **3g**, can be explained by this substituent effect. As can be seen in Table III, the magnitude of the equilibrium constant is largely dependent upon the polarity of the solvent used. The value obtained in acetone/benzene is similar to that in benzene, while the value in THF is 2.6 times larger than that in benzene and that in chloroform is 4.0 times larger than that in benzene. This large solvent effect on the equilibrium constant is of interest. We assume that in THF and chloroform, **2** are more stabilized than in benzene or acetone/benzene, leading to the large equilibrium constant in these solvents. Further investigation on this point is in progress.

Table IV. Comparison of Thermodynamic Parameters for Some Dimer ⇄ 2 Radical Equilibria

equilibria	$\Delta H°$, kcal/mol	$\Delta S°$, eu	ref
 **5** **6**	10.8	24.5	18
$(Ph_2N)_2 \rightleftarrows 2Ph_2N\cdot$ **7** **8**	30.5		19
 **9** **10**	31.2	73.6	20
 **11** **12**	12.5	21	21
3c $\rightleftarrows$ 2 **2c**	13.3	29.0	this work
3d $\rightleftarrows$ 2 **2d**	13.8	29.2	this work

Experimental Section

General. Melting points were taken on a Yamaco Model MP micro melting point apparatus and are uncorrected. IR spectra were run on a JASCO Model IR-G spectrometer and visible spectra were recorded with a Hitachi recording spectrometer, Model EST-3T. NMR spectra were obtained with a Hitachi Perkin-Elmer R-20 spectrometer, using tetramethylsilane (δ = 0 ppm) as an internal standard. The molecular weight of **3d** in benzene at 33 °C was measured with a Knauer vapor-pressure osmometer. ESR spectra were recorded at 23 °C on a JES-ME-3X spectrometer with an x-band microwave unit and 100-kHz field modulation. Hyperfine splitting (hfs) constants and g values were determined by comparison with the nitrogen hfs constant (13.09 G) and the g value (2.0057) of Fremy's salt. Computer simulation of the ESR spectra and the spin density calculations were performed on a FACOM 230-60, equipped with a FACOM F6201D plotter.

Materials. Benzenethiol, 4-methyl-, 4-chloro-, and 4-nitrobenzenethiols were obtained commercially. 4-Bromo-,[24,25] 2,4-

---

[16] The values of $\Delta H°$ and $\Delta S°$ were calculated by the least-squares method (γ > 0.999).

[17] E.g., the equilibrium constant for $\mathbf{9} \rightleftarrows 2\ \mathbf{10}$ equilibrium has been reported to be 6.00×10^{-6} M (in methylcyclohexane at 44.7 °C); see ref 20.

[18] F. S. Diachkovskii, N. N. Bubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **122**, 629 (1958).

[19] L. G. Cole and E. C. Gilbert, *J. Am. Chem. Soc.*, **73**, 5423 (1951).

[20] S. F. Nelsen and R. T. Landis II, *J. Am. Chem. Soc.*, **95**, 8707 (1973).

[21] R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 7375 (1976).

[22] S. F. Nelsen, "Free Radicals", J. K. Kochi, Ed., John Wiley, New York and London, 1972, Vol. 2, Chapter 21.

[23] W. C. Danen and F. A. Neugebauer, *Angew. Chem., Int. Ed. Engl.*, 14, 783 (1975).

dichloro-,[26] and 3,5-dichlorobenzenethiols,[26] benzene-*2,3,4,5,6-d_5*-thiol,[8] 3,5-di-*tert*-butylaniline,[27] and di-*tert*-butyl diperoxyoxalate[28] were prepared by the reported methods. Lead dioxide, purchased from Hayashi Pure Chem. Indust. Co. Ltd., was purified as follows. Lead dioxide (250 g) was refluxed in a 2 N NaOH solution (300 mL) for 2 h, washed several times with water by decantation, then refluxed in a 2 N HNO_3 solution (300 mL), washed well with water by decantation, and dried over P_2O_5. Arenesulfenyl chlorides were prepared by the usual method. Into a solution of arenethiol (21–40 mmol) in chloroform (30–100 mL) was bubbled chlorine at 0–3 °C for 0.5–2 h, and solvent was removed under reduced pressure. Benzenesulfenyl chloride (bp 56–57 °C (3 torr)), benzene-*2,3,4,5,6-d_5*-sulfenyl chloride (bp 73–75 °C (8 torr)), and 4-methylphenylsulfenyl chloride (75–78 °C (3 torr)) were purified by distillation, and other sulfenyl chlorides were used in the following step without any purification. 1,3,5-Triphenylverdazyl was prepared by the reaction of 1,3,5-triphenylformazan with 37% formalin and recrystallized from methanol; mp 142–143 °C (lit.[29] mp 142–143 °C).

General Procedure for Preparation of 1. Arenesulfenyl chloride (21 mmol) in dry ether (50 mL) was added dropwise to a solution of 3,5-di-*tert*-butylaniline (25 mmol) and triethylamine (25 mmol) in dry ether (200 mL) at 0–5 °C with stirring. After being stirred for 1 h at 0–5 °C, the reaction mixture was filtered and solvent was removed under reduced pressure, giving a crystalline residue, which was chromatographed on an alumina column (E. Merck, Art 1097; eluant benzene; 50 × 250 mm) in order to remove polar byproducts and then recrystallized from an appropriate solvent.

***N*-(3,5-Di-*tert*-butylphenyl)benzenesulfenamide (1a)**: colorless prisms; mp 136–138 °C (hexane); yield 51%; IR (KBr) 3340 (NH), 2950–2850 (CH), 1600, 1587, 1486, 1430, 1367, 1310, 1250, 1030, 1000, 990, 858, 744, 710, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (s, *t*-Bu, 18 H), 5.08 (br s, NH, 1 H), 6.88–7.26 (m, aromatic, 8 H).

Anal. Calcd for $C_{20}H_{27}NS$: C, 76.62; H, 8.68; N, 4.47. Found: C, 76.45; H, 8.67; N, 4.39.

***N*-(3,5-Di-*tert*-butylphenyl)benzene-*2,3,4,5,6-d_5*-sulfenamide (1b)**: colorless prisms; mp 117–118 °C (hexane); yield 52%; IR (KBr) 3340 (NH), 2950–2850 (CH), 1590, 1540, 1485, 1425, 1390, 1360, 1335, 1305, 1243, 1028, 998, 982, 853, 705, 565, 545 cm^{-1}; NMR ($CDCl_3$) 1.26 (s, *t*-Bu, 18 H), 5.02 (br s, NH, 1 H), 6.75–7.10 (m, aromatic, 3 H).

Anal. Calcd for $C_{20}H_{22}D_5NS$: C, 75.41; H, 8.54; N, 4.40. Found: C, 75.07; H, 8.58; N, 4.11.

***N*-(3,5-Di-*tert*-butylphenyl)-4-methylbenzenesulfenamide (1c)**: colorless prisms; mp 124–126 °C (hexane); yield 62%; IR (KBr) 3350 (NH), 2950–2850 (CH), 1600, 1500, 1440, 1368, 1325, 1310, 1250, 1225, 1210, 980, 860, 805, 715, 495 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 2.28 (s, CH_3, 3 H), 5.10 (br s, NH, 1 H), 6.89–7.15 (m, aromatic, 7 H).

Anal. Calcd for $C_{21}H_{29}NS$: C, 77.01; H, 8.92; N, 4.28. Found: C, 77.04; H, 9.22; N, 4.06.

***N*-(3,5-Di-*tert*-butylphenyl)-4-chlorobenzenesulfenamide (1d)**: colorless plates; mp 150–151 °C (hexane); yield 51%; IR (KBr) 3330 (NH), 2950–2850 (CH), 1585, 1480, 1465, 1420, 1385, 1355, 1300, 1240, 1090, 1010, 980, 860, 852, 820, 703, 490 cm^{-1}; NMR($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 5.12 (br s, NH, 1 H), 6.88–7.25 (m, aromatic, 7 H).

Anal. Calcd for $C_{20}H_{26}ClNS$: C, 69.03; H, 7.53; N, 4.03. Found: C, 68.91; H, 7.44; N, 3.91.

***N*-(3,5-Di-*tert*-butylphenyl)-4-bromobenzenesulfenamide (1e)**: colorless plates; mp 137–138 °C (hexane); yield 45%; IR (KBr) 3330 (NH), 2950–2850 (CH), 1585, 1480, 1460, 1420, 1355, 1300, 1240, 1075, 1005, 980, 860, 853, 818, 800, 700, 480 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 5.08 (br s, NH, 1 H), 6.82–7.45 (m, aromatic, 7 H).

Anal. Calcd for $C_{20}H_{26}BrNS$: C, 61.22; H, 6.68; N, 3.57. Found: C, 61.50; H, 6.50; N, 3.62.

***N*-(3,5-Di-*tert*-butylphenyl)-4-nitrobenzenesulfenamide (1f)**: yellow prisms; mp 160–162 °C (benzene–hexane); yield 35%; IR (KBr) 3330 (NH), 2950–2850 (CH), 1580, 1560, 1490, 1460, 1415, 1350, 1320, 1290, 1235, 1105, 1075, 970, 850, 833, 736, 695, 530, 520 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 5.17 (br s, NH, 1 H), 6.92–7.00 (m, C_6H_3, 3 H), 7.32 and 8.12 (d, $J = 9$ Hz, C_6H_4, 4 H).

Anal. Calcd for $C_{20}H_{26}N_2O_2S$: C, 67.01; H, 7.31; N, 7.82. Found: C, 66.85; H, 7.14; N, 7.75.

***N*-(3,5-Di-*tert*-butylphenyl)-2,4-dichlorobenzenesulfenamide (1g)**: colorless prisms; mp 150–152 °C (hexane); yield 47%; IR (KBr) 3330 (NH), 2950–2850 (CH), 1590, 1490, 1450, 1430, 1380, 1365, 1306, 1245, 1210, 1145, 1125, 1100, 1038, 1000, 980, 860, 805, 710 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 5.00 (br s, NH, 1 H), 6.84–7.34 (m, aromatic, 6 H).

Anal. Calcd for $C_{20}H_{25}Cl_2NS$: C, 62.82; H, 6.59; N, 3.66. Found: C, 62.59; H, 6.50; N, 3.51.

***N*-(3,5-Di-*tert*-butylphenyl)-3,5-dichlorobenzenesulfenamide (1h)**: colorless plates; mp 96–98 °C (hexane); yield 35%; IR (KBr) 3340 (NH), 2950–2850 (CH), 1600, 1570–1560, 1490, 1430, 1420, 1408, 1360, 1307, 1250, 1160, 1110, 980, 858, 845, 792, 708, 666 cm^{-1}; NMR ($CDCl_3$) 1.28 (s, *t*-Bu, 18 H), 5.03 (br s, NH, 1 H), 6.80–7.09 (m, aromatic, 6 H).

Anal. Calcd for $C_{20}H_{25}Cl_2NS$: C, 62.82; H, 6.59; N, 3.66. Found: 62.63; H, 6.55; N, 3.74.

General Procedure for Preparation of 3. Sulfenamide 1 (0.37 mmol) in benzene (50 mL) was stirred for 10–15 min at room temperature in the presence of lead dioxide (3.0 g) and potassium carbonate (3.0 g). After filtration, solvent was removed by freeze-drying to afford a light green crystalline powder which was recrystallized from hexane or benzene–hexane.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis(phenylthio)hydrazine (3a)**: colorless prisms; mp 110–112 °C; yield 22%; IR (KBr) 2950–2850 (CH), 1580, 1475, 1420, 1355, 1295, 1240, 1195, 1020, 980, 850, 730, 703, 680 cm^{-1}.

Anal. Calcd for $C_{40}H_{52}N_2S_2$: C, 76.87; H, 8.39; N, 4.48. Found: C, 76.57; H, 8.50; N, 4.48.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis(phenylthio-*2,3,4,5,6-d_5*)hydrazine (3b)**: colorless prisms; mp 126–128 °C; yield 15%; IR (KBr) 2950–2850 (CH), 1580, 1470, 1420, 1350, 1295, 1240, 1025, 1010, 983, 850, 702 cm^{-1}.

Anal. Calcd for $C_{40}H_{42}D_{10}N_2S_2$: C, 75.65; H, 8.25; N, 4.41. Found: C, 75,38; H, 8.41; N, 4.44.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis[(4-methylphenyl)thio]hydrazine (3c)**: colorless prisms; mp 127–129 °C; yield 54%; IR (KBr) 2950–2850 (CH), 1590, 1495, 1430, 1360, 1305, 1250, 1205, 980, 855, 800, 710, 490 cm^{-1}.

Anal. Calcd for $C_{42}H_{56}N_2S_2$: C, 77.24; H, 8.64; N, 4.29. Found: C, 76.97; H, 8.82; N, 4.25.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis[(4-chlorophenyl)thio]hydrazine (3d)**: light blue prisms; mp 135–137 °C; yield 50%; IR (KBr) 2950–2850 (CH), 1600, 1485, 1435, 1369, 1312, 1097, 1015, 993, 860, 820, 810, 710, 490 cm^{-1}.

Anal. Calcd for $C_{40}H_{50}Cl_2N_2S_2$: C, 69.23; H, 7.26; N, 4.04. Found: C, 69.28; H, 7.43; N, 3.92.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis[(4-bromophenyl)thio]hydrazine (3e)**: light blue prisms; mp 136–138 °C; yield 54%; IR (KBr) 2950–2850 (CH), 1590, 1470, 1430, 1365, 1300, 1245, 1075, 1005, 988, 853, 800, 700, 480 cm^{-1}.

Anal. Calcd for $C_{40}H_{50}Br_2N_2S_2$: C, 61.37; H, 6.44; N, 3.58. Found: C, 61.64; H, 6.51; N, 3.43.

***N*,*N'*-Bis(3,5-di-*tert*-butylphenyl)-*N*,*N'*-bis[(2,4-dichlorophenyl)thio]hydrazine (3g)**: light blue prisms; mp 156–158 °C; yield 50%; IR (KBr) 2950–2850 (CH), 1585, 1447, 1300, 1242, 1090, 1028, 980, 853, 810, 800, 705 cm^{-1}.

Anal. Calcd for $C_{40}H_{48}Cl_4N_2S_2$: C, 62.98; H, 6.34; N, 3.67. Found: C, 62.71; H, 6.39; N, 3.46.

ESR Samples. (A) Sulfenamide 1 (0.03 mmol) was stirred in benzene (20 mL) for 0.5–1 min in the presence of lead dioxide (0.5 g) and potassium carbonate (0.5 g). After filtration, 0.40 mL of the filtrate was placed in an ESR cell, and the solution was

---

[24] R. Adams and C. S. Marvel, "Organic Syntheses", Collect. Vol. I, John Wiley, New York, 1941, p 504.

[25] H. F. Wilson and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 5200 (1950).

[26] (a) M. B. Sparke, J. L. Cameron, and N. Kharasch, *J. Am. Chem. Soc.*, **75**, 4907 (1953); (b) Y. Miura, Y. Makita, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 482 (1977).

[27] N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *J. Am. Chem. Soc.*, **88**, 2999 (1966).

[28] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82** 1762 (1960).

[29] R. Kuhn and H. Trischmann, *Monatsh. Chem.*, **95**, 457 (1964).

degassed by three freeze–pump–thaw cycles and then sealed. (B) **1** (0.01 mmol), di-*tert*-butyl diperoxyoxalate (0.01 mmol), and benzene (0.40 mL) were placed in an ESR cell, and the solution was degassed as above and then sealed. (C) Dimer **3** (0.01–0.03 mmol) and solvent (0.40 mL) were placed in an ESR cell, and the solution was degassed as above and then sealed.

Measurement of Equilibrium Constants. Dimer **3** (0.64×10^{-2}–2.51×10^{-2} mmol) was dissolved in solvent (total volume 10 mL). The solution (0.20 mL) was placed in an ESR cell and integrated signals were recorded on the ESR instrument equipped with a JES-ID-2 integrator. Areas under the integrated curves were determined by their weights. Calibration curves were obtained as follows: 0.20 mL of 1,3,5-triphenylverdazyl solutions (0.20–1.00 mM) was placed in the same cell used for the dimer solutions, and integrated signals were recorded with the same instrument settings.

Registry No. 1a, 74282-58-9; **1b**, 74282-59-0; **1c**, 74282-60-3; **1d**, 74282-61-4; **1e**, 74282-62-5; **1f**, 74282-63-6; **1g**, 74282-64-7; **1h**, 74282-65-8; **2a**, 74282-66-9; **2b**, 74282-67-0; **2c**, 74282-68-1; **2d**, 62991-69-9; **2e**, 62991-70-2; **2f**, 74282-69-2; **2g**, 74282-70-5; **2h**, 62991-71-3; **3a**, 74282-71-6; **3b**, 74282-72-7; **3c**, 74282-73-8; **3d**, 74282-74-9; **3e**, 74282-75-0; **3g**, 74282-76-1; **4**, 62991-73-5; 3,5-di-*tert*-butylaniline, 2380-36-1; benzenesulfenyl chloride, 931-59-9; benzene-*2,3,4,5,6-*d_5-sulfenyl chloride, 74282-77-2; 4-methylphenylsulfenyl chloride, 933-00-6; 4-chlorophenylsulfenyl chloride, 933-01-7; 4-bromophenylsulfenyl chloride, 1762-76-1; 4-nitrophenylsulfenyl chloride, 937-32-6; 2,4-dichlorophenylsulfenyl chloride, 38064-02-7; 3,5-dichlorophenylsulfenyl chloride, 74282-78-3.

Alkane Stereodynamics: Nuclear Magnetic Resonance and Empirical Force Field Studies of 2,2,3,3-Tetramethylpentane and 3,3,4,4-Tetramethylhexane

C. Hackett Bushweller,*[1a] Warren G. Anderson,[1a] Martin J. Goldberg,[1a] Mona W. Gabriel,[1a]
Laura R. Gilliom,[1b] and Kurt Mislow*[1b]

Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, and Princeton University, Princeton, New Jersey 08544

Received February 27, 1980

The two title compounds have been studied by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by empirical force field calculations using Allinger's 1971, Allinger's MM2, and Bartell's MUB-2 force fields. The experimental work on 2,2,3,3-tetramethylpentane shows restricted *tert*-butyl rotation with $\Delta G^{\ddagger} = 9.4$ kcal/mol. 3,3,4,4-Tetramethylhexane exists as a statistical mixture of gauche and anti conformers, with rotation about the central bond requiring $\Delta G^{\ddagger} = 10.4$ kcal/mol. The calculated barriers are critically compared with the experimentally determined values. In conjunction with this work, the barrier to central-bond rotation in hexamethylethane has been estimated at 8.4–8.8 kcal/mol.

Studies in static and dynamic stereochemistry which combine experimental measurements with empirical force field (EFF) calculations[2] are finding increasing use in the conformational analysis of substituted alkanes. Experimental work has confirmed the theoretical predictions of ground-state structures in symmetrically substituted tetraalkylethanes,[3,4] tetraarylethanes,[5] and related systems.[6-9a] The barrier to rotation about the central bond calculated by the EFF method has been experimentally verified for many of these systems,[3b,6a,9b] usually by dynamic NMR (DNMR) studies.[10]

Table I. EFF Minima for TMP and TMH from ALL-71

	descriptor[a]	symmetry[b]	steric energy[c]
TMP	(a)	C_s	6.1
	(+)	C_s	7.8
TMH	G(a)(a)	C_2	9.1
	G(+)(+)	C_2	12.7
	G(−)(−)	C_2	12.8
	A(a)(a)	C_{2h}	9.2
	A(+)(−)	C_i	12.7
	A(−)(−)	C_2	13.0
	A(+)(+)	C_2	12.4

[a] A implies an anti conformation with respect to $\phi = C_{Et}-C-C-C_{Et}$. G implies a gauche conformation. We define torsion angle δ such that for TMP δ = C2–C3–C4–C5 and for TMH δ = C1–C2–C3–C4 or (equivalently) δ = C3–C4–C5–C6. The three descriptors +, −, and a (for anti) refer to $0° < \delta < 120°$, $-120° < \delta < 0°$, and $|\delta| \geqslant 120°$, respectively. [b] Refers to symmetry of input structure. [c] In kcal/mol.

Hexamethylethane (HME), a key compound in studies of carbon–carbon single bond rotation, is not amenable to analysis by the DNMR approach for reasons of symmetry. We have therefore examined two structurally similar but less symmetric systems, 2,2,3,3-tetramethylpentane (TMP) and 3,3,4,4-tetramethylhexane (TMH), by this technique and have compared the results with the predictions of EFF calculations.

Results and Discussion

2,2,3,3-Tetramethylpentane (TMP). Three different EFF's were employed in a study of TMP: Allinger's 1971[11]

---

(1) (a) University of Vermont. (b) Princeton University.

(2) For recent reviews of the EFF method, see: (a) Dunitz, J. D.; Bürgi, H. B. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1976**, 81; Ermer, O. *Struct. Bonding (Berlin)* **1976**, *27*, 161; (b) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1; Altona C.; Faber, D. H. *Fortschr. Chem. Forsch.* **1974**, *45*, 1. See also: *Comput. Chem.* **1977**, *1*, 139.

(3) (a) Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736. (b) Ōsawa, E.; Shirahama, H.; Matsumoto, T. *J. Am. Chem. Soc.* **1979**, *101*, 4824 and references therein.

(4) Baxter, S. G.; Fritz, H.; Hellmann, G.; Kitschke, B.; Lindner, H. J.; Mislow, K.; Rüchardt, C.; Weiner, S. *J. Am. Chem. Soc.* **1979**, *101*, 4493.

(5) Finocchiaro, P.; Gust, D.; Hounshell, W. D.; Hummel, J. P.; Maravigna, P.; Mislow, K. *J. Am. Chem. Soc.* **1976**, *98*, 4945. Dougherty, D. A.; Mislow, K.; Blount, J. F.; Wooten, J. B.; Jacobus, J. *Ibid.* **1977**, *99*, 6149. Dougherty, D. A.; Llort, F. M.; Mislow, K.; Blount, J. F. *Tetrahedron* **1978**, *34*, 1301.

(6) (a) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795. (b) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(7) Ardebili, M. H. P.; Dougherty, D. A.; Mislow, K.; Schwartz, L. H.; White, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 7994.

(8) Beckhaus, H.-D.; McCullough, K. J.; Fritz, H.; Rüchardt, C.; Kitschke, B.; Lindner, H. J.; Dougherty, D. A.; Mislow, K. *Chem. Ber.* **1980**, *113*, 1867.

(9) (a) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. *J. Chem. Soc., Chem. Commun.* **1974**, 426. (b) Brunelle, J. A.; Bushweller, C. H.; English, A. D. *J. Phys. Chem.* **1976**, *80*, 2598.

(10) Jackman, L. M.; Cotton, F. A., Eds.; "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1975.

(11) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637.

0022-3263/80/1945-3880$01.00/0