

The results of ab initio calculations^{3b} indicate that the barrier of nitrogen inversion in HN=NH, CH₂=NH, and HN=C=NH is lower than the barrier to internal rotation.

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Natural-Abundance Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy. Electronic Effects in Benzenesulfonamides^{1a}

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The ¹⁵N chemical shifts of a number of benzenesulfonamides with different substituents at nitrogen have been measured in dimethyl sulfoxide solution and compared to those of similarly substituted benzenamines and ethanamides. The relative extent of phenyl-sulfur and nitrogen-sulfur p_x-d_x orbital overlap is discussed. Substitution of C₆H₅SO₂ for one benzyl group of *N,N*-dibenzylethanamide results in considerable lowering of the free energy of activation of the N-CO bond rotation.

Physical studies of sulfonamides have included analyses of the sulfur-oxygen and sulfur-nitrogen vibrational modes in the infrared spectrum²⁻⁴ and of X-ray⁵ and dipole moment⁶ data of selected species. The p*K*_a values of a few secondary arylsulfonamides also have been reported, and the effect of *N*-substituents on acidity has been discussed.⁷ A quantitative estimate of the electronic effect of the sulfamoyl group itself has been derived from the ¹⁹F chemical shifts of fluorobenzenesulfonamides⁸ and from the acidity constants⁹ of appropriately substituted benzoic acids and benzeneammonium ions.

This paper presents the results of an ¹⁵N NMR study of arylsulfonamides.

Results and Discussion

The ¹⁵N chemical shifts of a series of sulfonamides, measured as 9.0 mol % solutions in dimethyl sulfoxide at the natural-abundance level, are summarized in Table I together with one-bond N-H coupling constants.

Constraint of alkyl groups at nitrogen in *N,N*-dialkylbenzenesulfonamides through the formation of a five-membered ring (8 to 9) has no appreciable effect on the position of the ¹⁵N resonance, while ring expansion (9 to 11) causes only a small downfield shift (-1.1 ppm). The downfield shifts observed with increased alkyl substitution at nitrogen in benzenesulfonamides (2 to 4 to 13) are comparable to those observed for similar structural changes in ethanamides in the same solvent,¹⁰ as is the shift resulting from replacement of one hydrogen by an electron-withdrawing phenyl group (2 to 18, -26.2 and -29.9 ppm for the benzenesulfonamide and ethanamide systems, respectively). The effect of branching at an alkyl carbon atom α to nitrogen in the sulfonamides (3 to 5, -9.0 ppm) is identical in magnitude and direction with that in ethanamides (CH₃CONHC₂H₅ to CH₃CONHCH(CH₃)-C₂H₅, -8.9 ppm) despite the fact that the downfield shift resulting from β substitution (8 to 10) is only about one-tenth of that found for ethanamides and alkanamines. On the whole, the data demonstrate the similarity of substituent and steric effects at nitrogen in the *N*-alkylsulfonamides and ethanamides.

4-Substituted *N*-phenylbenzenesulfonamides with increasingly strong electron-withdrawing groups at the 4 posi-

tion of the *N*-aryl moiety exhibit progressively lower field shifts of the ¹⁵N resonance. These shifts only partially follow the trends in the corresponding p*K*_a values (Table II).

Exchange of the NH hydrogens was observed for the more acidic *N*-phenylbenzenesulfonamides. Thus, the doublets in the proton-coupled ¹⁵N spectra of 18-22 changed to a broad singlet with 4-CN (23) and to a sharp singlet with 4-NO₂ (24) as the result of proton exchange becoming fast on the NMR time scale.

The one-bond NH coupling constants appear to follow no definable trends except that their absolute magnitudes are consistently higher for secondary than for primary sulfonamides.

¹⁵N Shift Correlations with Substituent Parameters.

The extent of nitrogen lone-pair delocalization into the 4-*X*-substituted phenyl ring in the general system, Q-NH-C₆H₅-4-*X*, can be evaluated reasonably well from a linear correlation of ¹⁵N shifts with the Taft dual substituent parameters⁸ according to eq 1,

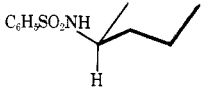
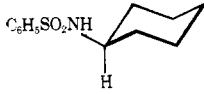
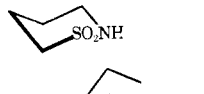
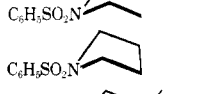
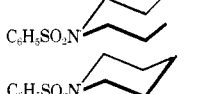
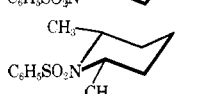
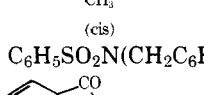
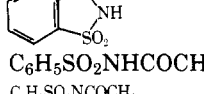
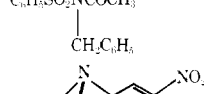
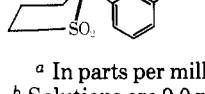
$$\delta(^{15}\text{N})_{\text{X}=\text{X}} = \rho_{\text{I}}\sigma_{\text{I}} + \rho_{\text{R}}\sigma_{\text{R}}^{-} + \delta(^{15}\text{N})_{\text{X}=\text{H}} \quad (1)$$

where σ_I and σ_R⁻ are the inductive and resonance (benzenamine-type) parameters, respectively, for the substituent, X, while the coefficients ρ_I and ρ_R reflect the sensitivity of the ¹⁵N shifts to these substituent effects. Because the nitrogens of *N*-phenylbenzenesulfonamides are expected to be electronically similar to those of benzenamines and *N*-phenylamides, it seemed likely that correlations based on σ_I and σ_R⁻ might be possible for each of these kinds of systems.

The substituted benzenamine shifts, taken from Axenrod's study¹¹ (¹⁵N shifts relative to internal benzenamine, 1 M in dimethyl sulfoxide) and referenced to external HNO₃, are listed in Table III. The ¹⁵N shifts of *N*-phenylethanamides are also taken from the literature.¹⁰ The constants ρ_I and ρ_R are given in Table IV together with the correlation coefficient *r*, the root mean square error (rms), and the number of data points (*n*) for each correlation.

It is apparent that the sensitivity of the ¹⁵N shifts to electronic substituent effects in *N*-C₆H₄-4-*X* decreases markedly in the series: benzenamines > *N*-phenylbenzenesulfonamides > *N*-phenylethanamides. That this may be due to increased delocalization of the electron pair on nitrogen into Q of Q-

Table I. ^{15}N Shifts^a and One-Bond ^{15}N -H Coupling Constants of Benzenesulfonamides in Dimethyl Sulfoxide

compd	no.	$\delta(^{15}\text{N})^b$	$^1J_{^{15}\text{N}\text{H}}$, Hz
4-NH ₂ C ₆ H ₄ SO ₂ NH ₂	1	278.1	78.7
C ₆ H ₅ SO ₂ NH ₂	2	279.7	80.8
C ₆ H ₅ SO ₂ NHC ₂ H ₅	3	275.4	84.2
C ₆ H ₅ SO ₂ NHCH ₂ C ₆ H ₅	4	277.2	85.1
	5	266.4	86.8
	6	266.0	86.0
	7	278.2	
	8	274.0	
	9	273.8	
	10	276.7	
	11	272.7	
	12	270.0	
(cis) C ₆ H ₅ SO ₂ N(CH ₂ C ₆ H ₅) ₂	13	273.1	
	14	215.4	c
C ₆ H ₅ SO ₂ NHCOCH ₃	15	204.6	c
C ₆ H ₅ SO ₂ NCOCH ₃ CH ₂ C ₆ H ₄	16	209.9	c
	17	255.5	

^a In parts per million upfield from external 1 M H¹⁵NO₃ in D₂O.
^b Solutions are 9.0 mol % in dimethyl sulfoxide. ^c Averaged signal because of fast proton exchange.

Table II. ^{15}N Shifts^a and One-Bond ^{15}N -H Coupling Constants of 4-Substituted *N*-Phenylbenzenesulfonamides in Dimethyl Sulfoxide

C ₆ H ₅ SO ₂ NHC ₆ H ₄ -4-X		pK _a ^b	$\delta(^{15}\text{N})^c$	$^1J_{^{15}\text{N}\text{H}}$, Hz
X	no.			
OCH ₃	18	10.52	256.8	84.2
F	19	10.00	255.2	84.2
CH ₃	20	10.44	255.0	84.2
Br	21	9.54	253.5	82.5
H	22	10.26	253.5	82.5
CN	23		248.3	d
NO ₂	24		247.1	d

^a In parts per million upfield from external 1 M H¹⁵NO₃ in D₂O.
^b Reference 6. ^c Solutions are 9.0 mol % in dimethyl sulfoxide.
^d Averaged signal because of fast proton exchange.

NH-C₆H₄-4-X and not just the result of differing -I effects of Q is indicated by the different order of σ_1 constants of Q: H (0.0); COCH₃ (0.28); SO₂C₆H₅ (ca. SO₂CH₃, +0.59).

The reduced *N*-aryl resonance in the *N*-phenylbenzenesulfonamides relative to benzenamines is also reflected in the downfield shift of the ¹⁵N resonance of the 4-CN group of

Table III. ^{15}N Chemical Shifts of 4-Substituted Benzenamines as 1 M Solutions in Dimethyl Sulfoxide

X	$\delta(^{15}\text{N})^a$	X	$\delta(^{15}\text{N})^a$
NO ₂ ^d	295.8 ^b	Cl	314.8 ^c
CN ^d	302.4 ^b	H ^d	315.1 ^b
SO ₂ NH ₂	307.4 ^{b,e}	CH ₃	317.7 ^c
I	313.7 ^c	F	318.4 ^c
Br	314.1 ^c	CH ₃ O	320.9 ^c

^a In parts per million upfield from external HNO₃. ^b This study.
^c Reference 11. ^d Registry no.: X = NO₂, 100-01-6; X = CN, 873-74-5; X = H, 62-53-3. ^e $^1J_{\text{NH}} = 86.4$ Hz.

N-4-cyanophenylbenzenesulfonamide (**23**; 118.0 ppm) relative to its position in 4-cyanobenzenamine (122.5 ppm).

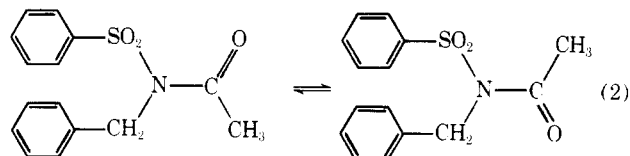
From the correlation line of the benzenamines and the ¹⁵N shift of the 4-amino nitrogen of 4-aminobenzenesulfonamide (307.4 ppm), a value of 0.11 can be derived for σ_{R}^- of the SO₂NH₂ group using $\sigma_{\text{I}} = +0.44$.¹² This is only slightly larger than the σ_{R} value of +0.05 previously reported¹² for this substituent.

From these results, it appears that the extent of p_{π} - d_{π} overlap between the sulfur d orbitals of the sulfamoyl group and the p orbital system of an attached phenyl ring is not very large when substituents are present that enhance the electron density of the ring. This is in considerable contrast to what has been reported⁹ for the methylsulfonyl group with σ_{R} and σ_{R}^- values of +0.12¹² and +0.38,¹² respectively. The lower values of both of the σ_{I} and σ_{R}^- parameters of SO₂NH₂ relative to SO₂CH₃ can be attributed to p_{π} - d_{π} orbital overlap between sulfur and nitrogen in the former, an interaction expected to reduce the positive charge at sulfur much more effectively than the hyperconjugation of the methyl group in SO₂CH₃.

¹³C NMR Studies. A possible way to gauge the extent of aryl-SO₂ resonance in benzenesulfonamides would be through the ¹³C shifts of the 4 carbons of the benzene rings (Table V). The variation in this shift seems to support this idea in being quite small for *N*-alkylbenzenesulfonamides but larger for substituents on nitrogen which possess varying electron-delocalizing power such as H (**2**), C₆H₅ (**22**), and COCH₃ (**15**).

The alkyl group at nitrogen in the sulfonethanamide **16** appears to favor nitrogen electron pair delocalization into the acyl group to a greater extent than the hydrogen of **15**, as suggested by the greater deshielding of the carbonyl and methyl carbon ¹³C resonances in **16** relative to **15** associated with differences in anisotropy of the carbonyl group¹³ in the two sulfonethanamides. The lower carbonyl stretching frequency in the infrared spectrum of **16** (1705 cm⁻¹) relative to that of **15** (1720 cm⁻¹) is in accord with this interpretation.

Rotational Barrier of the Sulfonethanamide **16.** Some idea of the magnitude of the electronic effect of the benzenesulfonyl group may be gained from a study of the *cis*-*trans* interconversion rate of an amide in which the nitrogen bears this substituent, such as **16**. Both the electrostatic -I effect of C₆H₅SO₂ as well as any p_{π} - d_{π} orbital overlap between nitrogen and sulfur are expected to reduce the degree of double-bond character of the N-CO bond, thereby lowering the energy barrier to rotation (eq 2).





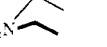


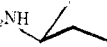
The proton NMR spectrum of **16** in sulfonyl chloride fluoride exhibits broadening of both the methylene and methyl resonances below -40 °C. Splitting of the methyl peak into

Table IV. Correlation of ^{15}N Shifts of 4-Substituted Benzenamines, *N*-Phenylbenzenesulfonamides, and *N*-Phenylethanamides with the DSP Equation (Eq 1)

compd	ρ_I	ρ_R	r^a	rms ^b	n^c
$\text{NH}_2\text{C}_6\text{H}_4\text{-4-X}$	-12.106	-21.642	0.9950	0.76	9
$\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_6\text{H}_4\text{-4-X}$	-4.416	-8.606	0.9983	0.20	7
$\text{CH}_3\text{CONHC}_6\text{H}_4\text{-4-X}$	-0.613	-5.271	0.9967	0.14	5

^a Correlation coefficient. ^b Root mean square error (parts per million). ^c Number of points in the correlation.

Table V. ^{13}C Shifts^a of $\text{C}_6\text{H}_5\text{SO}_2\text{N}<$ in Dimethyl-*d*₆ Sulfoxide

compd	no.	C-1	C-4	C-2	C-3 ^b
	11	137.1	134.2	130.6	128.7
$\text{C}_6\text{H}_5\text{SO}_2(\text{C}_6\text{H}_5)$	10	137.1	134.2	130.6	128.7
	9	137.7	134.2	130.6	128.6
	8	141.3	133.9	130.6	128.0
	12	142.8	133.5	130.5	127.6
$\text{C}_6\text{H}_5\text{SO}_2\text{NHCH}_2\text{C}_6\text{H}_5$	4	142.2	133.6	130.4	
$\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_2\text{H}_5$	3	142.1	133.6	130.5	127.8
	6	143.8	133.3	130.3	127.6
	5	143.6	133.3	130.3	127.7
$\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$	2	145.5	133.1	130.2	127.0
$\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_6\text{H}_5$	22	141.0	134.1	130.4	128.0
$\text{C}_6\text{H}_5\text{SO}_2\text{NHCOCH}_3^c$	15	140.8	134.9	130.4	128.8
$\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{COCH}_3^d$	16	140.5	135.3	130.7	

^a In parts per million downfield from Me_4Si . ^b Shifts for C-2 and C-3 may be reversed. ^c C=O, 170.1 ppm; CH_3 , 24.5 ppm. ^d C=O, 171.5 ppm; CH_3 , 25.6 ppm.

a doublet occurs below -91°C , and the rotation is frozen at -110°C with approximately equal populations of *Z* and *E* isomers. Line-shape analysis of the spectra in Figure 1 gave a value of 9.2 kcal/mol for the free energy of activation (ΔG^\ddagger) for the rotational process. The corresponding ΔG^\ddagger for **16** in dichlorofluoromethane is 9.4 kcal/mol. These values are considerably lower than that for the geometrically similar *N,N*-diphenylmethylethanamide (18.0 kcal/mol in CH_2Br_2),¹⁴ and they approach those for systems having substituents at nitrogen with large $-I$ and/or $-R$ effects (13.4 and 13.3 kcal/mol for $\text{CH}_3\text{CON}(\text{CH}_3)\text{CH}=\text{CH}_2$ (neat)¹⁵ and $\text{CH}_3\text{CON}(\text{CH}_3)\text{OCOCH}_3$ in CDCl_3 ,¹⁶ respectively). In the related *N*-arenesulfenylurethanes, $\text{ArSN}(\text{CH}_2\text{C}_6\text{H}_5)\text{CO}_2\text{CH}_3$, the barrier to amide rotation (~ 12 kcal/mol in toluene)¹⁷ has been shown to be insensitive to substituent polar effects in the *S*-phenyl moiety.

Nonetheless, the fact that the *N*-C(O) barrier of **16** is 3 kcal less than that of the *N*-arenesulfenylurethanes despite the effect of the OCH_3 in lowering the barriers of urethanes relative to amides suggests that the electrical effect of the $-\text{SO}_2-$ group on the barrier of **16** is substantial. The rough similarity in ΔG^\ddagger values of the sulfonethanamide **16** (σ_I of $\text{C}_6\text{H}_5\text{SO}_2$, +0.59) and ethanoylmethylazanyl ethanoate (σ_I of CH_3CO_2 , +0.39) may signify that the $-I$ effect of the benzenesulfonyl group is more important than delocalization of the nitrogen lone pair of the sulfonyl group in causing the low barrier of **16** relative to amides in general.

Below -99°C , the methylene resonance of **16** is split into five very broad peaks of unequal areas (see Figure 1), a possible consequence of the additional slowing of the rotation about the sulfur-nitrogen bond.

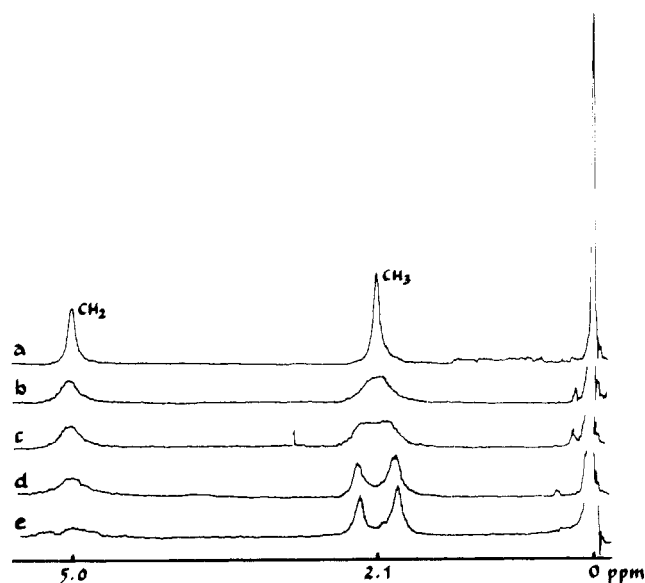


Figure 1. ^1H NMR spectra of benzene-*N*-(phenylmethyl)sulfonethanamide (**16**) in sulfolane: a, -75.0°C ; b, -87.5°C ; c, -91.0°C ; d, -96.8°C ; e, -109.5°C .

Experimental Section

Nitrogen-15 chemical shifts were measured at the natural-abundance level with a Bruker WH-180 FT-NMR spectrometer operating at 18.25 MHz, using techniques previously described.¹⁸ Spectra were obtained for 9.0 mol % solutions in dimethyl sulfoxide at temperatures

between 19 and 27 °C, using an external reference of 1 M H^{15}NO_3 in D_2O . Chemical shifts, corrected to 25 °C, are reported upfield of this reference in parts per million.

Proton noise-decoupled ^{13}C spectra were obtained at 15.09 MHz with our Brukerian DFS-60 pulse Fourier transform modified spectrometer¹⁹ on 1 M solutions in dimethyl- d_6 sulfoxide. Shifts were measured relative to internal cyclohexane (2.5% by volume) and referenced to Me_4Si .

Low-temperature proton spectra were recorded with a Varian A-56/60 spectrometer, using about a 0.5 M solution of sulfonethanamide 16 in sulfonyl chloride fluoride and in dichlorofluoromethane. Temperatures were measured before and after recording each spectrum by replacing the sample tube in the probe with a tube containing a thermometer in carbon disulfide precooled in dry ice-acetone.

The sulfonamides were synthesized by standard techniques^{7,20} and purified by recrystallization from 70% aqueous isopropyl alcohol. Dimethyl sulfoxide was dried over calcium hydride and distilled prior to use.

Registry No.—1, 63-74-1; 2, 98-10-2; 3, 5339-67-3; 4, 837-18-3; 5, 67723-08-4; 6, 3237-31-8; 7, 37441-50-2; 8, 1709-50-8; 9, 5033-22-7; 10, 28859-91-8; 11, 5033-23-8; 12, 67723-09-5; 13, 67723-10-8; 14, 81-07-2; 15, 5661-14-3; 16, 67723-11-9; 17, 67723-12-0; 18, 7471-26-3; 19, 312-63-0; 20, 6311-65-5; 21, 16468-97-6; 22, 1678-25-7; 23, 67723-13-1; 24, 1829-81-8.

References and Notes

- (1) (a) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072 from the Division of General

- Medical Sciences. (b) On sabbatical leave from The Pennsylvania State University, Ogontz Campus. (c) National Research Center, Sherif Pasha St., Cairo, Egypt.
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$^3J_{\text{CH}}$ Coupling Constants in Oxiranes, Thiiranes, and Cyclopropanes

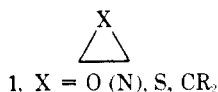
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Three-bond coupling constants are reported between carbon and hydrogen in oxiranes, thiiranes, and cyclopropanes, plus limited data on aziridines. These coupling constants appear to be sufficiently regular to aid in assigning stereochemistry, although substantial differences occur with change in heteroatom. The increase in $^3J_{\text{CH}}$ in the order O, N, S, and CX_2 parallels the increase in bond length of the ring C-C bond. No effect of hybridization of the coupling carbon is evident.

In recent years, the NMR spectra of small ring compounds have attracted increasing interest.¹ The ^{13}C spectra of azirines,^{1e} oxaziridines,^{1d} oxiranes,² and aziridines³ have been reported, as well as ^{13}C coupling constants for certain nitrogen heterocycles.^{4,5} The importance of the orientation of the lone pair on nitrogen on the magnitude of various types of coupling constants has been elucidated.⁴ A number of ^1H -NMR studies of small rings of general structure 1 have



appeared.⁶⁻¹⁴ In particular, Manatt, Brois, and Elleman reported that vicinal ^1H coupling constants increased in the order X = O, N, S, CR_2 , although thiiranes (X = S) rather poorly obeyed attempted correlations with electronegativity.¹⁵ Two- and three-bond coupling constants are of the same sign in oxiranes and aziridines, but of opposite sign in thiiranes and cyclopropanes.¹⁵

On the other hand, Ohtsura and Tori found that ^1H coupling constants were of larger magnitude in thiirane 1-oxides (and 1,1-dioxides) than in thiiranes. The results were interpreted in terms of the Pople-Bothner-By model for spin

coupling.¹⁷ However, the larger 3J values for 1 (X = SO) were ascribed to greater electronegativity of the SO.

The present study emphasizes coupling constants between carbon and hydrogen. The purpose of this work was to determine whether a geometric dependence of $^3J_{\text{CH}}$ was present in three-membered rings and whether this dependence was sufficiently regular to be of use in predicting or substantiating configuration.¹⁸ Scheme I illustrates the coupling constant data for certain oxiranes and thiiranes having a similar substitution pattern. The $^3J_{\text{CH}}$ values for *cis*- CH_3 and -H ring substituents are substantially larger than for trans substituents, where at best the coupling is barely observable. The data in Scheme I show that carbon-hydrogen coupling constants are rather similar to hydrogen-hydrogen coupling constants in their geometric dependence. Chertkov and Sergeyev,¹⁹ as well as Perlin *et al.*,²⁰ have studied the geometric dependence of $^3J_{\text{CH}}$, and the general indications are that a Karplus relationship is obeyed for carbon-hydrogen nuclei.²¹ However, Lemieux and co-workers have expressed reservations.²² In 2-4 *cis*- CH_3 and -H exhibit $^3J_{\text{CH}}$ values from 2-3 Hz whereas *trans* nuclei show values of 0.5-1.8 Hz in fair agreement with expectations. Thus, the dihedral angle between *cis* nuclei is 0°, whereas the dihedral angle between *trans* nuclei is ca. 120°.