formational equilibrium must be about the same in *sec*-butylamine and in isopentane, and hence explains the small difference observed in the shieldings of their γ carbon atoms.

In summary, the results presented show that C-13 nmr may be useful in studying rotational isomerism and make it possible to predict C-13 nmr spectra of unknown amines. In conjunction with mass spectral data it should be possible to perform unambiguous structure assignment on such unknowns, which will be an impressive achievement when it is recalled that, *e.g.*, the molecular formula $C_{21}H_{45}N$ corresponds[5] to over 38 million structural isomers.

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Carbon-13 Magnetic Resonance. XXIII.[1] The Methyldecalins

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Abstract: The proton-decoupled carbon-13 magnetic resonance (cmr) spectra have been obtained for *cis*- and *trans*-decalin, six of the possible ten monomethyldecaline, five available dimethyldecalins, and spiro[5.5]undecane. The resonance lines are assigned using previously developed methyl substituent parameter sets, with the aid of intensity arguments, and selective decoupling. A multiple regression analysis is executed on the data to develop a new and simpler set of substituent and conformational parameters applicable to aliphatic hydrocarbons in general.

Decahydronaphthalene (decalin) became a molecule of stereochemical interest shortly after the postulation of tetrahedral carbon,[2,3] Although it was thought for some time that only the cis isomer was possible, Sachse[4] predicted that cis and trans ring junctures were reasonable, and that several strain-free conformational isomerides would result from stable chair–boat combinations. Mohr created a controversy by proposing that, at ordinary temperatures, thermal energy was sufficient to interconvert chair and boat forms of cyclohexane, so that only two isomers of decalin would be isolable, as a result of the two kinds of ring junction.[5] He suggested that the chair–chair form of *trans*-decalin had the lowest energy, and that the boat–boat isomer of *cis*-decalin was most favorable. The Sachse–Mohr concept that *cis*-decalin exists primarily in a two-boat form was held for many years, until Bastiansen and Hassel used electron diffraction techniques to demonstrate that *cis*-decalin exists predominantly in a two-chair form.[6,7]

A comparison of models of the two decalin isomers reveals that *cis*-decalin has three steric interactions of the type found in the gauche conformation of *n*-butane which are not present in the trans compound. In previous papers in this series,[8,9] the evidence relative to the energetics of gauche interactions was discussed. It was concluded that the energy gained by a molecule for each gauche interaction is about 0.7–1.2 kcal/mol. Experimental measurements of the standard heats of combustion of *cis*- and *trans*-decalin have resulted in determination[10–12] of the standard heats of formation (in kcal/mol) as follows.

	Liquid	Gas
cis	-52.45 ± 0.22	-40.45 ± 0.22
trans	-55.14 ± 0.22	-43.54 ± 0.55
difference	2.69 ± 0.31	3.09 ± 0.59

These results are seen to be in agreement with the 0.7–1.2 kcal/mol of energy gained for each of the three gauche interactions. It is noted that the trans isomer is conformationally locked, while in the cis compound interconversion between equivalent chair–chair structures is possible.

The 9-methyldecalins are of biochemical interest, because they are commonly encountered as fragments of natural products. Measurement of thermodynamic properties[13] indicated standard free energies of formation of -58.31 ± 0.47 kcal/mol for *cis*-9-methyldecalin and -59.70 ± 0.44 kcal/mol for the *trans*-9-methyl isomer. The difference of 1.39 ± 0.64 kcal/mol is in agreement, within the limits of its uncertainty, with the postulated energy increment due to the one gauche interaction difference between the two compounds.

Methyl substitution on *cis*-decalin at positions other

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than the bridgehead carbons may produce steric interactions of the type found in skew pentane or the diaxial isomer of *cis*-1,3-dimethylcyclohexane. This conformation produces about 3.7 kcal/mol of steric energy.[14] Two unspecified isomers of 1-methyldecalin were isolated[15] as hydrogenation products of 1-methylnaphthalene in 1948. Few other studies are reported on the methyldecalins until Weitkamp and coworkers synthesized and characterized the eight isomers available from hydrogenation.[16-18] Subsequently, the 68 isomers of dimethyldecalin available from hydrogenation were obtained and identified.[18]

Among the cis compounds the parent and *cis*-9-methyldecalins are converting between two conformations of equal energy. At ordinary temperatures, thermal energies are sufficient to cause rapid inversion since the free energy of activation for flipping is 10–15 kcal/mol.[19,20] This conformational inversion reduces the number of lines in their decoupled, carbon-13 spectra. Although the proton spectra[17] of the other cis isomers studied indicate some averaging of the ring protons, the energy difference between conformers is sufficient that the carbon-13 spectra should not differ noticeably from those which would be produced by the lower energy conformers.

Experimental Section

Sample Preparation. The two parent decalins were obtained from standard commercial sources, and the two 9-methyl isomers were synthesized in this laboratory using previously published methods.[21] The *cis-syn*-2-methyldecalin was synthesized by hydrogenation over Ru/C catalyst as previously described.[9] Prior to hydrogenation, the 2-methylnaphthalene was refluxed several hours in ether with Raney nickel to remove sulfur-containing impurities. The two principal hydrogenation products, 6-methyltetralin (46%) and *cis-syn*-2-methyldecalin (36%), were separated on a spinning band distillation apparatus, and were identified by their ^{13}C and proton spectra.[16] The remaining methyldecalins studied were obtained from Weitkamp.[22]

All of the compounds studied herein are liquids at room temperature and were put in 10-mm o.d. ground glass tubes with about 10% by volume TMS (tetramethylsilane) added as reference.

Instrumentation. Proton spectra were obtained on a Varian A-56/60 spectrometer. The proton-decoupled carbon-13 data were obtained using a Varian AFS-60 spectrometer operating at 15.1 MHz as previously described.[9] It was necessary to accumulate some spectra on a Varian C-1024 time-averaging device.

Assignments and Factor Analysis

The carbon-13 chemical shift data for the methyldecalins which were available for study and for spiro[5.5]undecane are listed in Table I. Although the resonance frequencies were measured relative to that of internal TMS, the chemical shifts are also given with respect to neat benzene, so that they might be compared with previous papers in this series. The factor of 128.82 ppm was used to convert from TMS to benzene scale. The previously used chemical shift between TMS and benzene (128.54 ppm) was the difference between the shifts of 100% C_6H_6 and 100% TMS as determined through a proton-decoupling experiment in which both shifts were related back to the benzene and TMS proton lines. With greater sensitivity now available the shifts are related to low concentration internal ^{13}C standards.

Items 1 and 33 of Table I may be assigned solely on the basis of their unique intensities. The selective decoupling technique[9] was used to identify all resonances resulting from methyl groups, enabling items 14, 24, 29, 46, 57, 64, 71, and 77 to be unequivocally assigned. The resonance lines resulting from the remaining pairs of methyl groups (items 88, 89, 100, 101, and 112, 113) are unambiguously identified by use of the methyl parameters of Table V of ref 9, utilizing the additional assumption that a vicinal methylene is equivalent to a vicinal methyl.

Items 26, 28, 59, 60, and 66, 67 may be associated with pairs of bridgehead carbons in their respective compounds on the basis of intensity differences, but further assignment must be done using parameters such as those derived from the methylcyclohexanes.[9] Application of the methyl substitution parameters of Table IV of ref 9 is somewhat ambiguous for the bridgehead carbons of *cis*- and *trans*-9-methyldecalin, due to their simultaneous presence in two rings, but the resulting assignments (items 26, 28, and 58, 60) are clearly not interchangeable. The assignments given items 66, 67 are tentative, due to the proximity of the two lines, but their assignment is consistent with the small upfield shift often noted for δ_e carbons.[23]

All other assignments of resonance lines to specific carbon positions must be made parametrically. In order to use the methyl substituent parameters of Table IV of ref 9, it is first necessary to assign the chemical shifts of the parent compounds. This is a fairly simple task for the trans isomer. The bridgeheads, C-9, 10, have been assigned because of their unique intensities. Carbons 2, 3, 6, and 7 of *trans*-decalin should be very cyclohexane-like in character, since they have only γ_e and δ_e substituents in their respective six-membered rings. The 101.65-ppm value of item 35 meets this criterion perfectly (predicted = 101.70 ppm), leaving item 34 to be assigned to C-1,4,5,8, by default.

For *cis*-decalin C-9,10 was assigned by its unique intensity. The remaining two resonance lines, items 2 and 3, represent average environments of sets of equivalent pairs of carbons. They may be assigned by comparison of the predicted and low temperature spectra,[19] as is done in Table II.

Also included in Table II are the low temperature experimental and calculated results for *cis*-9-methyldecalin, for which some difficulties in applying the methyl parameters are found because of the substitution at the bridgehead, which belongs to both rings. It will be noted that differences greater than 1.0 ppm occur

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(22) The authors are indebted to Dr. A. W. Weitkamp and the American Oil Co. for supplying these compounds.

(23) The substitution parameter notation of ref 9 will be used in this work.

Table I. Carbon-13 Chemical Shift Data for the Methyldecalins

Item	Compd	Carbon assigned[a]	δ ^{13}C experimental[b]		δ ^{13}C predicted[b,c]	
			From TMS	From benzene	Methyl parameters	Hydrocarbon parameters
1	*cis*-Decalin[j]	9, 10	36.93	91.89	*d*	92.02
2		1, 4, 5, 8	29.78	99.04	*d*	98.60
3		2, 3, 6, 7	24.62	104.20	*d*	104.32
4	*cis-syn*-1-Methyldecalin[e]	9	42.98	85.84	86.29	87.03
5		10	38.70	90.12	90.27	90.12
6		1	37.18	91.64	92.44	91.61
7		5	33.55	95.27	95.49	95.14
8		2	29.54	99.28	98.74	98.11
9		3	27.42	101.40	100.81	102.04
10		7	27.42	101.40	100.86	102.04
11		4	25.77	103.05	102.53	102.06
12		6	21.89	106.93	106.97	106.60
13		8	20.04	108.78	108.68	106.62
14		CH_3	19.78	109.04	108.52	109.54
15	*cis-syn*-2-Methyldecalin[e]	9	36.98	91.84	91.84	92.02
16		10	36.47	92.35	92.11	92.02
17		1	35.63	93.19	93.28	93.57
18		2	34.22	94.60	94.90	95.02
19		4	33.22	95.60	95.44	95.14
20		8	33.22	95.60	95.49	95.14
21		3	30.33	98.49	97.94	98.11
22		6	27.63	101.19	100.86	102.04
23		5	26.37	102.45	102.31	102.06
24		CH_3	23.16	105.66	105.70	104.98
25		7	21.43	107.39	106.97	106.60
26	*cis*-9-Methyldecalin[c]	10	41.76	87.06	88.39[f]	87.03
27		1, 8	36.39	92.43	92.95	91.86
28		9	32.93	95.89	94.46[f]	95.10
29		CH_3	28.22	100.60	100.02	101.18
30		4, 5	28.10	100.72	100.04	100.88
31		3, 6	24.48	104.34	104.06	104.32
32		2, 7	22.81	106.01	105.09	106.60
33	*trans*-Decalin[j]	9, 10	44.22	84.60	*d*	85.03
34		1, 4, 5, 8	34.74	94.08	*d*	93.55
35		2, 3, 6, 7	27.17	101.65	*d*	102.04
36	*trans-anti*-1-Methyldecalin	9	50.60	78.22	78.02	80.04
37		10	44.05	84.77	84.55	85.03
38		1	38.42	90.40	90.57	90.02
39		2	37.12	91.70	92.62	93.55
40		4	35.39	93.43	94.30	93.55
41		5	35.29	93.53	94.30	93.55
42		8	31.02	97.80	100.45 (96.90)[g]	98.11
43		3	27.45	101.37	101.60	102.04
44		6	27.16	101.66	101.65	102.04
45		7	26.82	102.00	101.87	102.04
46		CH_3	19.74	109.08	108.52	109.54
47	*trans-syn*-2-Methyldecalin	9	43.49	85.33	84.55	85.03
48		10	43.39	85.43	84.82	85.03
49		1	43.31	85.51	85.05	85.07
50		3	35.66	93.16	92.62	93.55
51		4	34.30	94.52	94.03	93.55
52		5	34.30	94.52	94.08	93.55
53		8	34.15	94.67	94.30	93.55
54		2	33.06	95.76	95.69	95.01
55		6	27.02	101.80	101.65	102.04
56		7	27.02	101.80	101.65	102.04
57		CH_3	22.85	105.97	105.70	104.98
58	*trans*-9-Methyldecalin	10	46.17	82.65	83.37	83.54
59		1, 8	42.44	86.38	88.37	86.65
60		9	34.78	94.04	90.43	95.22
61		4, 5	29.36	99.46	99.23	98.11
62		3, 6	27.42	101.40	101.71	102.04
63		2, 7	22.24	106.58	106.00	106.60
64		CH_3	15.75	113.07	117.41	113.51
65	*trans-syn*-2-*syn*-7-Dimethyldecalin	1, 8	43.05	85.77	85.27	85.07
66		9	42.84	85.98	84.50	85.03
67		10	42.60	86.22	85.04	85.03
68		3, 6	35.60	93.22	92.62	93.55
69		4, 5	34.05	94.77	94.03	93.55
70		2, 7	32.89	95.93	95.69	95.01
71		CH_3	23.00	105.82	105.70	104.98

Table I (*Continued*)

			δ ^{13}C experimental[b]		δ ^{13}C predicted[b,c]	
Item	Compd	Carbon assigned[a]	From TMS	From benzene	Methyl parameters	Hydrocarbon parameters
72	*trans-syn*-2-*syn*-3-	9, 10	44.18	84.64	84.77	85.03
73	Dimethyldecalin	1, 4	44.18	84.64	85.00	85.07
74		2, 3	39.78	89.04	89.11	90.02
75		5, 8	34.32	94.50	94.30	93.55
76		6, 7	27.14	101.68	101.65	102.04
77		CH_3	20.30	108.52	108.52	109.51
78	*trans-anti*-1-*syn*-8-	9	52.42	76.40	75.52	75.05
79	Dimethyldecalin[i]	10	36.84	91.98	91.77	89.59
80		2	35.60	93.22	92.68	93.55
81		4	35.48	93.34	94.36	93.55
82		5	35.37	93.45	94.36	93.55
83		7	34.59	94.23	94.67	94.58 (1)
84		1	34.04	94.78	96.94	95.18 (7)
85		3	28.54	100.28	101.60	101.57 (3)
86		8	26.60	102.22	102.48 (98.93)[g]	102.48 (8)
87		6	20.95	107.87	108.02	106.60
88		CH_3 (1)	19.19	109.63	108.52	109.54
89		CH_3 (8)	12.50	116.32	116.76	117.05
90	*trans-anti*-1-*syn*-3-	9	49.44	79.38	78.24	80.04
91	Dimethyldecalin	2	45.42	83.40	83.59	85.07
92		10	43.67	85.15	84.50	85.03
93		4	42.99	85.83	85.27	85.07
94		1	37.71	91.11	90.52	90.02
95		5	34.63	94.19	94.52	93.55
96		3	32.44	96.38	95.64	95.01
97		8	30.63	98.19	100.45 (96.90)[g]	98.11
98		6	27.16	101.66	101.65	102.04
99		7	26.91	101.91	101.87	102.04
100		CH_3 (3)	22.84	105.98	105.70	104.98
101		CH_3 (1)	19.74	109.08	108.52	109.54
102	*trans-anti*-1-*syn*-2-	9	49.36	79.46	77.97	80.04
103	Dimethyldecalin	1	44.34	84.48	83.99	85.03
104		10	43.30	85.52	84.77	85.03
105		2	39.27	89.55	89.11	90.02
106		3	35.82	93.00	92.57	93.55
107		4	34.80	94.02	94.25	93.55
108		5	34.51	94.31	94.30	93.55
109		8	30.96	97.86	100.45 (96.90)[g]	98.11
110		6	27.14	101.68	101.65	102.04
111		7	26.58	102.24	101.87	102.04
112		CH_3 (2)	20.94	107.88	108.52	109.54
113		CH_3 (1)	16.10	112.72	111.27	114.10
114	Spiro[5.5]undecane	1, 5, 7, 11	37.61	91.21	92.65	92.81
115		6	32.71	96.11	*h*	95.22
116		3, 9	27.50	101.32	101.98	102.04
117		2, 4, 8, 10	22.02	106.80	106.00	106.60

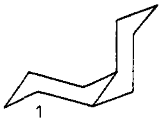
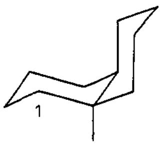
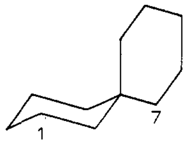
[a] Number in parentheses indicates methyl position. [b] In parts per million. [c] The predicted values on the left were calculated using the parameters from Tables IV and V of ref 9, with *cis*- and *trans*-decalin as the basis compounds. The other predicted values were calculated using the hydrocarbon parameters given in this work. [d] See text for discussion of assignments in these compounds. [e] The chemical shift values obtained from the low-temperature spectrum were used for the parent values (see Table II). [f] Direct application of the parameters was ambiguous, so averages of the appropriate values were used. [g] If C-8 is viewed as a *vic*-methyl, the lower value obtains. It apparently represents an intermediate case (see ref 9). [h] Direct application of the methyl parameters could not be made unambiguously. [i] An equally appropriate name is *trans-syn*-1-*anti*-8. [j] Similar results have been reported for these compounds by E. Lippmaa and T. Pehk, *Eesti NSV Tead. Akad. Toim. Keem. Geol.*, **17**, 287 (1968).

between a few of the experimental and predicted values, probably as a result of a need for correction parameters to account for butressing effects, such as those discussed in ref 9. Similar observations may be made for spiro[5.5]undecane.

The proper assignments having been made for the parent compounds, all chemical shifts in Table I remaining unassigned may be characterized with relative simplicity by use of the methyl parameters of Table IV of ref 9, with the exception of a few proximate resonance lines. These assignments are bracketed to indicate that a degree of uncertainty remains in the result. In the case of the *anti*-1-*syn*-8 compound there is considerable ambiguity, which is probably indicative of greater than normal molecular distortion in this strained molecule.

It is possible to increase the accuracy of fitting the chemical shifts obtained in this study by adding or deleting parameters as necessary to accommodate new geometrical features existing in the methyldecalins but not found in the methylcyclohexanes. However, this process is of questionable merit because the regression technique fails to provide a criterion of uniqueness. Any linearly independent combination of parameters would

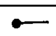
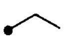
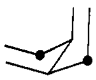
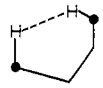
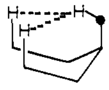
Table II. Comparison of Experimental and Predicted ^{13}C Chemical Shift Values[a] for Low-Temperature Spectra of *cis*-Decalin, *cis*-9-Methyldecalin, and Spiro[5.5]undecane

			Predicted parameters	
	Carbon	Exptl	Methyl substituent	Hydrocarbon
 1	9, 10	91.89[b]	*d*	92.02
	4, 8	95.49	94.67	95.14
	2, 6	100.86	101.71	102.04
	1, 5	102.31	103.75	102.06
	3, 7	106.97	106.90	106.60
	Averages			
	1, 4, 5, 8	99.04[c]	99.21	98.60
	2, 3, 6, 7	104.20[c]	104.30	104.32
 1	8	86.50	87.73	86.65
	10	87.06[b]	*d*	87.03
	9	95.77	*d*	95.10
	1	98.46	98.17	97.07
	4	100.41	99.84	99.70
	CH_3	100.52	*d*	101.18
	5	100.76	100.24	102.06
	6	101.04	101.08	102.04
	2	105.99	104.90	106.60
	7	105.99	105.21	106.60
	3	107.01	107.03	106.60
	Averages			
	1, 8	92.43[c]	92.95	91.86
	4, 5	100.60[c]	100.04	100.88
	3, 6	104.34[c]	104.06	104.32
	2, 7	106.01[c]	105.06	106.60
	1, 7	86.07	88.53	88.56
 1 7	6	96.11[b]	*d*	95.22
	5, 11	96.82	96.78	97.07
	3, 9	101.18	101.98	102.04
	2, 10	106.78	106.00	106.60
	4, 8	106.78	106.00	106.60
	Averages			
	1, 5, 7, 11	91.21[c]	92.65	92.81
	2, 4, 8, 10	106.80[c]	106.00	106.60

[a] In parts per million. [b] Used as internal reference in the low-temperature measurement. [c] Determined from room temperature spectra with internal TMS reference rather than from arithmetic averages. Some small temperature dependence is apparent in the chemical shifts. [d] Direct application of methyl parameters is unreliable in these cases due to uncertainty as to which parameters pertain. [e] Parameters are given in ref 9; since neither the γ_a nor axial parameters strictly apply here, an average value of 5.14 ppm was used for γ_a.

yield an identical fit. Thus, a smaller parameter set was sought where the correspondence between a given structural feature and each term in the regressional analysis may be intuitively perceived. A general and simplified parameter set provides a conceptually preferable division of the shift parameter. Use of a limited parameter set is expected to be somewhat less accurate as subtle molecular distortions cannot be characterized. This disadvantage is offset to some degree by greater ease with which tentative assignments can be made. The structural parameters can always be refined further by adding additional parameters which accommodate the unique geometrical and positional features found in a given class of compounds. In some cases expansion of the parameter set may not be justified because the parameters become so refined as to be less than the experimental uncertainties due to instrumental limitations, solvent variations, etc. In general, it has been found that only questionable significance can be attached to the absolute assignment of resonance lines to better than a few tenths ppm. Thus, this technique is not reliable for assigning lines separated by only a few Hz. When the demands of the experiment requires unequivocal assignment of such lines, other techniques are required. The simplified hydrocarbon parameter set is presented in Table III along with the statistical results of the analysis. Included in the stepwise linear regression analysis were the chemical shifts of the simple hydrocarbons for which conformation is not a problem: methane, ethane, propane, isobutane, neopentane, and cyclohexane.[8,24]

Table III. Factor Analysis Results for the Methyldecalins

Symbol	Parameter	Value, ppm	No. of occurrences	F test of variance
α		-9.94 ± 0.25	133	1523.8
β		-8.49 ± 0.12	129	4913.9
T		2.91 ± 0.31	33	90.3
Q		9.04 ± 0.67	4	184.4
V_g		3.50 ± 0.10	112	1165.5
$\beta_g\gamma_t$		-1.91 ± 0.25	11	57.9
γ_{HH}		4.56 ± 0.18	38	621.3
γ_{2HH}		3.95 ± 0.31	11	162.5

No. of observations: 134
No. of independent variables: 8
Multiple correlation coeff: 0.9957
Chemical shift range: 52.6 ppm
Constant term: 131.89 ppm
Standard deviation of fit: 0.88 ppm

Discussion

The α and β parameters of Table III are seen to be large and negative, while most other parameters are smaller and positive. It has been asserted[25] that the ^{13}C chemical shift resulting from α substitution is smaller than anticipated because a large, negative paramagnetic contribution is greatly reduced by a large diamagnetic shift produced by substituting carbon for directly bonded hydrogen. If this assertion is correct, then contrary to the suppositions of many workers in the field, it is the small α shift rather than a large β effect which is anomalous relative to expected attenuation of chemical shift effects with chain length. Changes at the α carbon in both the paramagnetic and diamagnetic term are probably of an inductive nature.

The β shift probably arises from a relatively small variation in the localized paramagnetic term for which there are no corresponding, canceling diamagnetic effects. Relatively small perturbations are, of course,

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(24) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964).

(25) J. Mason, *J. Chem. Soc. A*, 1038 (1971).

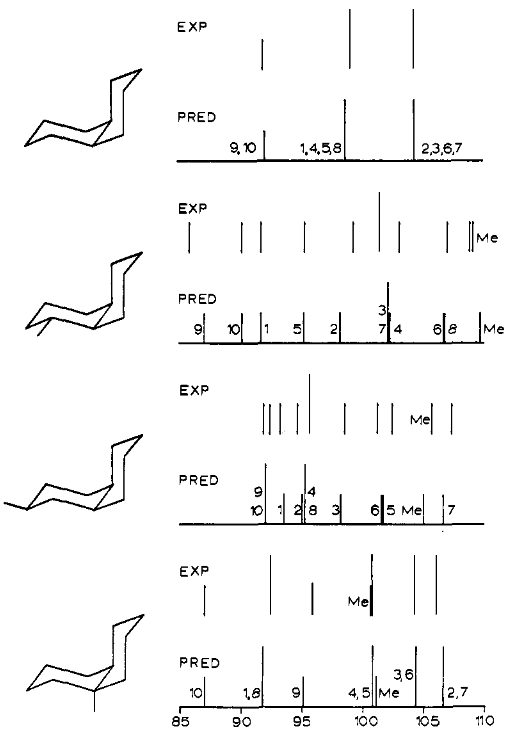

Figure 1. Comparison of experimental and predicted carbon-13 spectra for the parent and *cis*-methyldecalins. The chemical shifts were predicted by use of Table III.

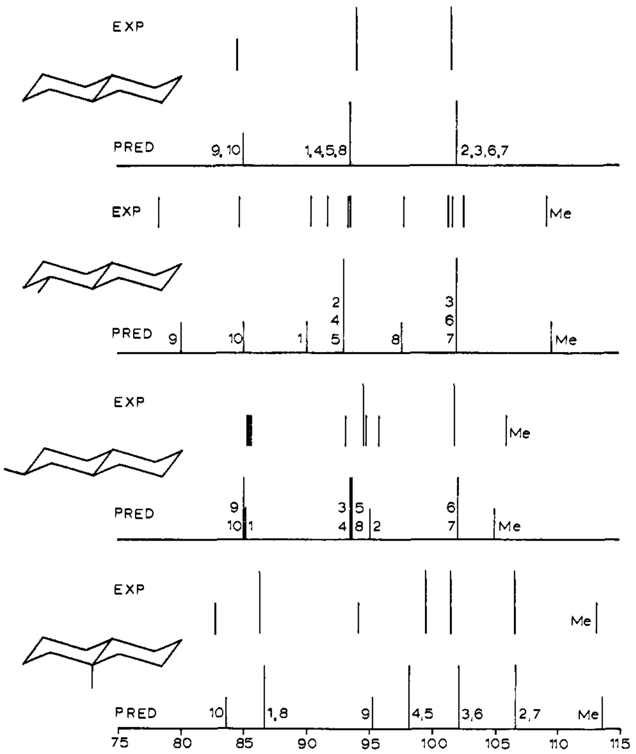

Figure 2. Comparison of experimental and predicted carbon-13 spectra for the parent and *trans*-methyldecalins, as in Figure 1.

difficult to delineate, but it is assumed that the β effect is inductive in origin. If Mason's position is valid, then a -9-ppm β effect represents chain attenuation in the paramagnetic term from the approximately -37-ppm paramagnetic term at the α position which is required to yield a -9-ppm overall α shift when combined with the $+28$-ppm diamagnetic term calculated by Mason.

The effects associated with the T, Q, and V_g parameters are identified with steric factors and attributed to bond deformation as a result of steric crowding. Changes of less than 0.01 Å are reasonable in such systems, and these changes could explain the shifts noted. The $\beta_g\gamma_t$ effect probably results from geometrical distortion; it may in fact be peculiar only to the cyclic paraffins and may not be a general parameter which is useful in continuous hydrocarbons.

The γ_{HH} and γ_{2HH} parameters result from a well-characterized steric effect. The second interaction γ_{2HH} is not twice the value of γ_{HH}, however, indicating the importance of using more than one parameter to fit the variety of such interactions discussed in ref 9. There is evidence[26] that more crowded steric interactions between methyls such as found in the skew pentane configuration result in even smaller upfield shifts than anticipated for these sterically proximate carbons. Significant molecular distortions probably nullify the large upfield shifts expected in these highly strained systems.

By use of the parameters of Table III the ^{13}C chemical shift assignments for a rather large array of data can be accomplished in a relatively straightforward manner with a high degree of reliability. In Figures

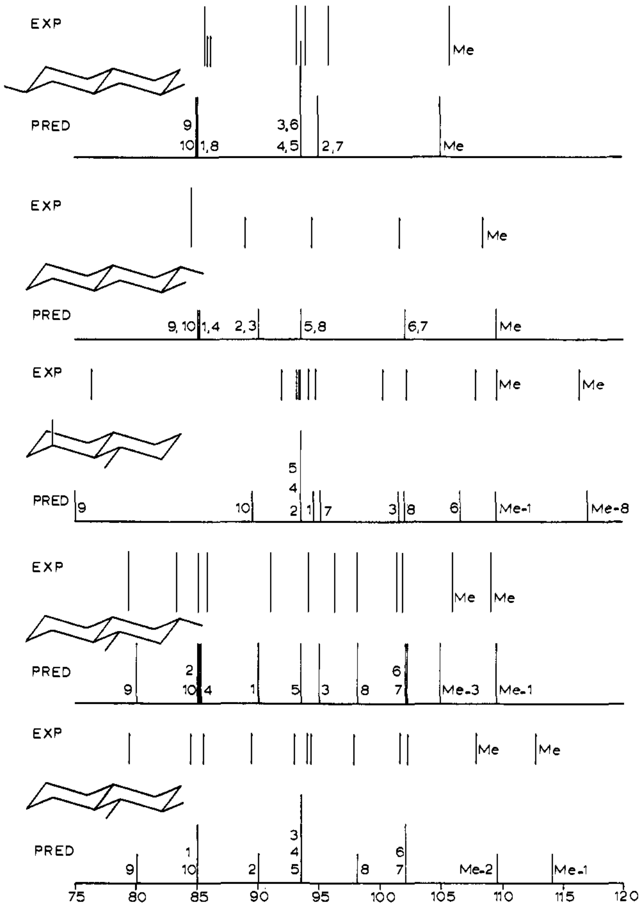

Figure 3. Comparison of experimental and predicted carbon-13 spectra for the *trans*-dimethyldecalins, as in Figure 1.

1–3 the experimental and predicted chemical shifts are compared. In every case the agreement between ex-

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[26] (a) D. K. Dalling and D. M. Grant, unpublished observations; (b) J. Stothers, private communication.

perimental and predicted spectra of a given isomer is clearly much greater than that between the experimental spectrum of one isomer with the predicted spectrum of any other isomer. The rather close agreement between observed and calculated spectra for *cis*- and *trans*-decalin is taken as additional evidence that these compounds do have all chair ground states.

The parameters in Table III will greatly facilitate ^{13}C chemical shift assignments of the spectra of other isomers of this series and of other compounds of this general type. For example, the many isomers produced by hydrogenation of polycyclic aromatic hydrocarbons should be readily identified by this technique. It is anticipated that the parameters developed in this work will provide a basis for conformational identification of systems which otherwise are not readily characterized. Furthermore, the parameter set provides a reasonable basis for estimating the shifts of the parent hydrocarbons for such important systems as the steroids, thereby providing a basis for elucidating other substituent parameters important in these systems.

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pH-Dependent Nuclear Magnetic Resonance Spectra of ^{15}N-Enriched Glycine. Line Shape and Relaxation Studies[1a]

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Abstract: The influence of pH on the line shapes, chemical shifts, and relaxation times of the ^{15}N resonances in aqueous solutions of 95%-enriched ^{15}N glycine is discussed. Below pH 6.4, the observed ^{15}N and ^{1}H spectra of glycine clearly reflect chemical-exchange modulation of the $^{15}N-^{1}H$ scalar interaction. The observed increase in the scalar relaxation, as well as the concomitant decrease in the nuclear Overhauser enhancement of the ^{15}N resonance as the pH increases, can also be explained on the basis of chemical exchange. A comparative study of ^{15}N-enriched glycine and ethyl glycinate shows that the ^{15}N chemical-shift changes found for glycine in the acid region reflect the electronic changes at the carbonyl function. Furthermore, the observed differences in the line shapes for the two compounds correlate well with the differences in pK_a's for the $^{+}NH_3$ group. The changes in line shape for both the decoupled and undecoupled ^{15}N spectra of glycine and its ethyl ester above pH 6.4 suggest that ^{15}N chemical-shift averaging occurs as the result of exchange between the protonated and deprotonated forms.

The question of the effects of chemical exchange on ^{15}N nmr spectra is of special importance to the use of ^{15}N resonances in the study of biological systems. In an earlier paper,[2] the nuclear Overhauser enhancement of ammonium-^{15}N chloride resulting from irradiation of the protons was shown to be pH dependent, as expected for chemical exchange. In addition, it was noted that the proton-decoupled ^{15}N signals of ammonium chloride disappeared in basic solution in an apparently anomalous way. Other reports have shown that both chemical shifts[3] and $^{1}J_{^{15}NH}$ splittings[4] are pH dependent as the result of chemical exchange. Surprisingly, the reported[5] ^{15}N relaxation studies have ignored the possible contributions of chemical exchange to the total spin–lattice relaxation time. The purpose of this paper is to delineate the effects of chemical exchange on ^{15}N resonances through the pH dependence of the line shapes, chemical shifts, nuclear Overhauser enhancements, and nuclear relaxation rates of ^{15}N-enriched glycine.

Experimental Section

Glycine-^{15}N. Glycine, enriched to 99% with ^{15}N (Bio Rad), was used, for the most part, without further purification. For relaxation studies, the amino acid was passed through a column packed with Dowex IA chelating resin to remove paramagnetic ions that might be present. The T_1's obtained before and after this treatment were identical. The samples were thoroughly degassed with N_2 before the spectra were taken.

Ethyl Glycinate-^{15}N Hydrochloride. Glycine, enriched in ^{15}N (0.069 g), was added to 3.0 ml of absolute ethanol in a 5-ml pear-shaped flask fitted with a reflux condenser. Gaseous hydrogen chloride was bubbled slowly into the solution. The temperature rose quickly and the glycine dissolved. The flow of hydrogen chloride was continued for an additional 20 min. The reaction mixture was then poured into a petri dish and the solvent removed under reduced pressure at room temperature. The yield was 0.11 g (87%) and the melting point was 142–144° (lit.[6] 144°).

Procedures. The pH measurements were made with a Radiometer Model 26 pH meter and a combined glass reference electrode (Radiometer Copenhagen). Hydrochloric acid and potassium hydroxide were used to adjust the pH.

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(1) (a) Supported by the Public Health Service, Research Grant No. GM-11072 from the Division of General Medical Sciences, and the National Science Foundation; (b) National Institutes of Health Postdoctoral Fellow, 1971–1972.

(2) R. L. Lichter and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3200 (1971).

(3) R. L. Lichter, "Determination of Organic Structures by Physical Methods," Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N. Y., 1971, Chapter 4.

(4) R. L. Lichter and J. D. Roberts, *Spectrochim. Acta, Part A*, **26**, 1813 (1970).

(5) T. Saluvere and E. Lippmaa, *Eesti NSV Tead. Akad. Tiom., Fuus., Mat.*, **20**, 91 (1971); E. Lippmaa, T. Saluvere, and S. Laisaar, *Chem. Phys. Lett.*, **11**, 120 (1971).

(6) T. Curtius and F. Goebel, *J. Prakt. Chem.*, [2] **37**, 157 (1888).