through the dark box with continuous mechanical stirring and bubbling of nitrogen through the solution. The resulting pale yellow precipitate of silver carbonate was filtered with suction on a Büchner funnel and rapidly washed successively with 1.5 1. of cold water, 1 1. of ethanol, and 1 1. of diethyl ether, all under an atmosphere of nitrogen. The product was dried *in vacuo* over P_2O_5 in the dark; yield 208 g. (91%) of a light yellow powder with no dark inclusions.

Long-Range Effect of an Asymmetric Grouping on the Magnetic Equivalence of Methylene Group Protons

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Nuclear magnetic resonance spectra of seventeen *ortho*- or *meta*-substituted N,N-dimethylbenzylamines indicated a long-range effect of an asymmetric group in the *ortho* or *meta* side chain on the magnetic equivalence of the methylene group protons in the amine side chain. The protons were magnetically equivalent in the nine cases for which a plane of molecular symmetry existed and were nonequivalent for the eight cases for which there was no symmetry plane. A limited temperature range study of two amines and an *ortho*-substituted benzyl alcohol indicated some reduction in the observed chemical shift differences of the two methylene group protons, but at the highest temperatures investigated a chemical shift difference persisted. The possible importance of the observed long-range effect in structural studies is discussed briefly.

Introduction

In a recent publication, Snyder[3] has given several examples and reviewed other cases in which an asymmetric atom or group affects magnetic nonequivalence in adjacent groups or atoms and has shown that the nonequivalence, as measured by the chemical shifts, is sensitive to the solvent used. Meyer, *et al.*,[4] have reported nonequivalence of O-methylene protons in derivatives of 10-carbethoxy-1,1-dimethyldecahydronaphthalene and postulated that steric interaction of the O-methylene group with the axial methyl group in the 1,1-dimethyl system gives rise to the observed magnetic nonequivalence. Gutowsky[5] has given a general treatment for the analysis of such systems and Pople[6] has discussed the type of spectrum that may appear for symmetrical and asymmetrical systems under various degrees of hindered rotation. In examining a number of substituted N,N-dimethylbenzylamines in this laboratory it was observed that magnetic nonequivalence of the benzylamine methylene protons, hereafter referred to as protons 1 and 2, was associated with the presence of an *ortho* or *meta* side chain bearing an asymmetric group. When the side chain had a plane of symmetry the 1,2-protons appeared equivalent. Since the chemical shift differences were small, only CCl_4, $CHCl=CCl_2$, and $CDCl_3$ solutions were investigated. Several compounds were examined over a convenient temperature interval as this can give some indication of the relative importance of conformation *vs.* intrinsic asymmetry to the observed magnetic nonequivalence. The nonequivalence, as evidenced by chemical shift differences, was reduced but not eliminated at the highest temperatures investigated. An increase in the number of cases investigated and a

more extended temperature study are indicated before unambiguous conclusions can be drawn concerning the origin of the observed nonequivalence but, as many investigators may work with systems at room temperature which contain an asymmetric group, it was felt the long-range effects here reported will be of interest.

Results

The n.m.r. spectral data reported in Tables I and II and the examples reproduced in Fig. 1, 2, and 3 are referenced to tetramethylsilane as an internal standard. For subsequent reference protons 1,2 have been previously designated; protons 3 and 4 refer to protons on the α-carbon of the side chain attached to either the *ortho* or *meta* position of the N,N-dimethylbenzylamine; proton 5 is on the β-carbon of the side chain. In order to eliminate the possible effect of the nitrogen quadrupole, an *ortho*-substituted benzyl alcohol was examined over a temperature interval and data for this and for compounds XII and XIII are recorded in Table II. Data in Table I refer to 32° unless otherwise noted. In both Tables I and II the chemical shift is given to the nearest cycle per second as this properly indicates the precision of the measured values for the data taken on the Varian A-60 instrument. Coupling constants and differences in chemical shift for components of an AB or ABX system are expressed to the nearest 0.1 c.p.s. as this precision was necessary in the AB and ABX calculations by which the values of $\nu_{1,2}$, $\delta_{1,2}$, $J_{1,2}$, etc., were determined. The error in a single observation is undoubtedly several tenths of a cycle per second.

In Tables I and II and in Fig. 1, 2, 3, and 4 the numbered compounds, using A for the $-CH_2N(CH_3)_2$ group, B for the $-C(C_6H_5)_2OH$ group, and D for the $-CC_6H_5HOH$ group, are shown in Scheme I.

The symbols used in Tables I and II have the following meanings: $\nu_{1,2}$ are the chemical shifts of the 1,2-protons in the amine side chain—in case these are an AB system the two calculated values are shown,

(1) Tennessee Eastman Fellow, Duke University.
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(3) E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963).
(4) W. L. Meyer, A. S. Levinson, D. L. Davis, and V. L. Sawin, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 85Q.
(5) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).
(6) J. A. Pople, *Mol. Phys.*, **1**, 3 (1958).

TABLE I[a]

N.M.R. DATA FOR 32° AND 60 Mc.

Compound	$\nu_{1,2}$		$\delta_{1,2}$	$J_{1,2}$	$\nu_{3,4}$		$\delta_{3,4}$	$J_{3,4}$	ν_5	$J_{3,5}$	$J_{4,5}$	ν_6
I	−190	−182	7.8	12.5	−360(3)							−125
II	−176											−124
III	−200	−192	7.9	13.0	−344(3)							−127
IV	−195											−124
V	−193											−122
VI	−184	−146	38.1	12.0								−123
VII	−190											−127
VIII	−214	−176	38.0	12.0	−175	−165	10	12.0	−280	4.0	8.0	−132
IX	−206	−193	13.0	13.0	−170	−160	10.6	12.0	−279	4.0	8.0	−136
X	−197				−212(3,4)							−129
XI	(−194)[b]	−163	31.5	12.2	−370(3)							−140
XII[c]	−223	−175	47.8	12.3	−280(3)				−304	9.1		−135
XIII[d]	−187	−169	18.7	13.0	−314(3)				−299	7.0		−125
XIV	−194				−219(3,4)							−128
XV	−271	−255	16.5	11.9	−176	−174	2.4	12.5	−280	8.4	4.2	
XVI	−202											−131
XVII	−204											−135
XVIII	−200											−112

[a] See text for meaning of symbols; CCl₄ was used as solvent except for XI (CDCl₃) and XV (CHCl₂CHCl₂); TMS was used as an internal reference; data are in c.p.s. and were obtained with a Varian A-60 spectrometer. [b] This value is rather uncertain as half of the AB system spectrum was diffused. [c] This measurement was made at 34°. [d] This measurement was made at 33°.

whereas for an A_2 system the single observed frequency is recorded; $\delta_{1,2}$ is the difference in the 1,2-proton chemical shifts used in calculating the coupling constants $J_{1,2}$ and the chemical shifts $\nu_{1,2}$; $\nu_{3,4}$, $\delta_{3,4}$, and $J_{3,4}$ refer to the 3,4-protons on the α-carbon of the
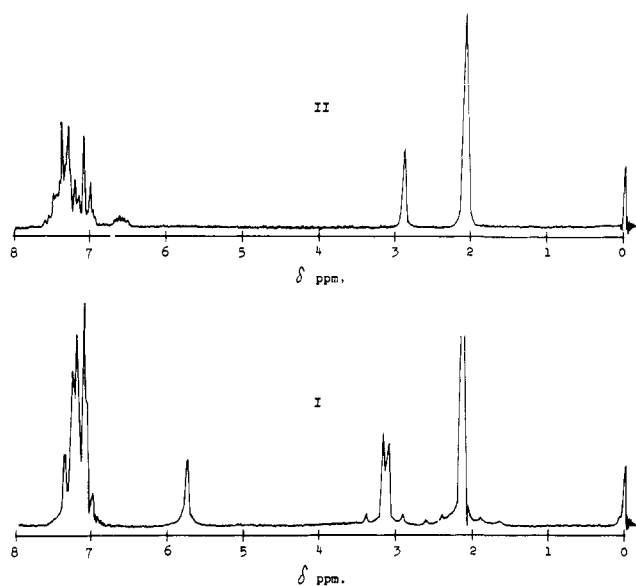

Fig. 1.—N.m.r. spectra of compounds I and II at 32° and 60 Mc.

side chain—when a single value is recorded it is followed by (3) or (3,4) to show the value is for a single proton or for two protons; ν_5 is the chemical shift for the proton on the β-carbon of the side chain; $J_{3,5}$ and $J_{4,5}$ are the applicable coupling constants; ν_6 is the observed chemical shift for the CH₃ groups in the N,N-dimethyl group of the A side chain. Calculations for AB and ABX systems were made in the usual[7] manner.

Discussion

In Fig. 1 the AB system found for the 1,2-protons of compound I is contrasted with the A_2 system found for these same protons in compound II. Compounds

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

I and II differ in that I has an asymmetric group in the *ortho* position, whereas in compound II there is a

SCHEME I
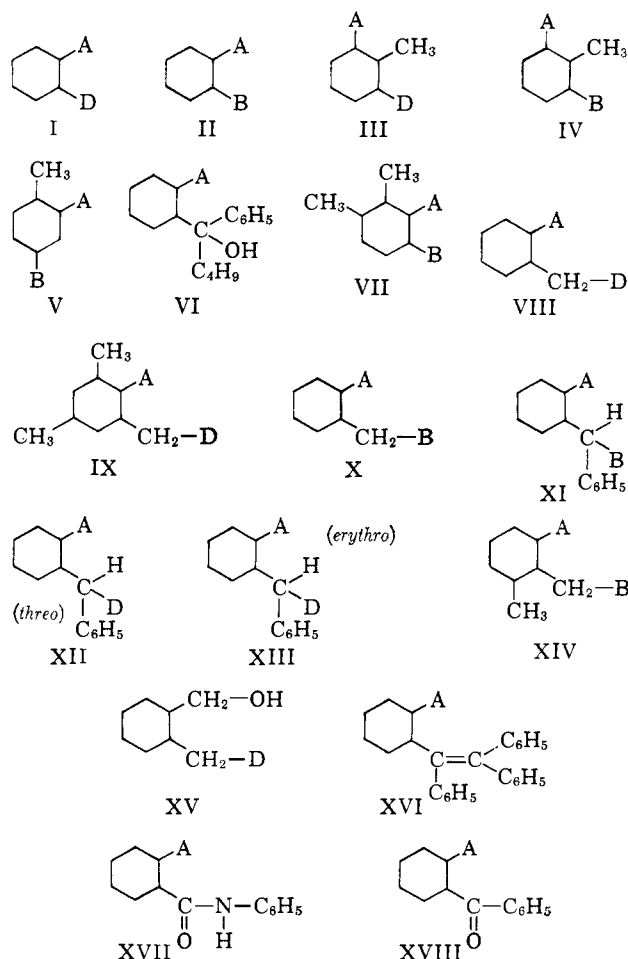
molecular plane of symmetry. In both compounds there could be considerable steric hindrance as well as some restraint due to bond character so the observed nonequivalence of protons 1 and 2 could arise from a relatively high population of any, necessarily unsym-

TABLE II[a]

TEMPERATURE EFFECT ON N.M.R. SPECTRA

Compd.	T, °C.	ν1,2		δ1,2	J1,2	ν3,4		δ3,4	J3,4	ν5	δ3,5	J3,5	J4,5
XV	32	−271	−255	16.5	11.9	−176	−174	2.4	12.5	−280		8.4	4.2
	67	−274	−260	13.5	11.6	−179	−177	2.0	12.5	−283		8.4	4.2
	85	−275	−264	10.8	11.8	−180	−179	1.0	12.5	−286		8.6	4.3
	103	−277	−267	9.3	11.9	−182	−181	0.8	12.5	−289		8.8	4.4
	123	−276	−269	7.6	11.9	−183	−182	.8	12.5	−289		9.0	4.5
	129	−276	−269	7.3	12.5	−184	−183	.7	12.5	−291		8.8	4.4
	138	−278	−271	6.2	12.1	−185	−184	.6	12.5	−292		8.6	4.3
	143	−279	−272	6.7	11.6	−186	−185	.6	12.5	−293		9.0	4.5
	152	−279	−272	5.9	12.0	−186	−185	.6	12.5	−294		8.8	4.4
XII	32	−236	−177	58.8	12.7	−284(3)				−309	25.0	9.8	
	52	−232	−179	52.5	12.8	−287(3)				−311	23.8	9.4	
	77	−227	−181	45.8	12.5	−288(3)				−312	23.7	9.7	
	93	−223	−183	40.7	12.7	−292(3)				−315	23.5	9.0	
	114	−221	−185	36.1	13.0	−297(3)				−317	20.1	9.0	
XIII	34	−192	−172	20.1	12.2	−306(3)				−321	14.8	7.1	
	56	−192	−174	18.5	13.0	−307(3)				−321	14.5	7.2	
	75	−192	−175	16.3	12.5	−306(3)				−321	14.3	7.2	
	89	−192	−176	15.4	12.8	−307(3)				−321	14.0	7.1	

[a] Spectra referred to TMS internal reference using Varian A-60 spectrometer with trichloroethylene as the solvent.

metrical, conformer in compound I. Similar observations apply to compounds VIII and X shown in Fig. 2. In compounds III and IV, shown in Fig. 3, the steric hindrance is essentially removed yet the AB system appears for compound III and not for IV. It is of interest that in both compounds III and VIII the asym-
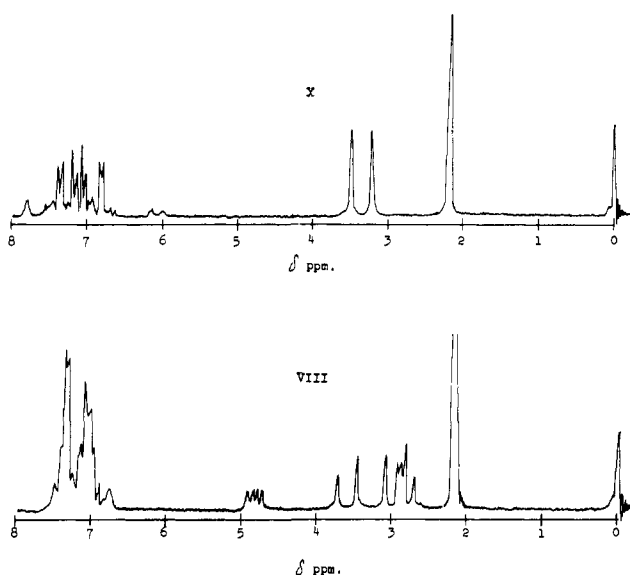

Fig. 2.—N.m.r. spectra of compounds VIII and X at 32° and 60 Mc.

metric group is five bonds removed from the 1,2-protons. Figure 4 reproduces the spectrum of compound XI as, in this case, the analysis of the AB system for protons 1 and 2 is complicated by an apparent coupling of one of the protons with another atom or group in the molecule. The diffuse nature of one-half of the AB system makes assignment of the chemical shift uncertain. Since area measurements confirm the assignment of one proton each to the diffuse and to the sharp portions of the spectrum, the conclusion that it was an AB system seems justified.

Referring to Table I it is seen that, at 32°, every compound investigated that has an asymmetric group exhibits magnetic nonequivalence of the 1,2-protons and that when there is a molecular plane of symmetry

the 1,2-protons appear as an A₂ system. The occurrence of an AB system in the 3,4-protons adjacent to an asymmetric grouping, as shown in compounds VIII,
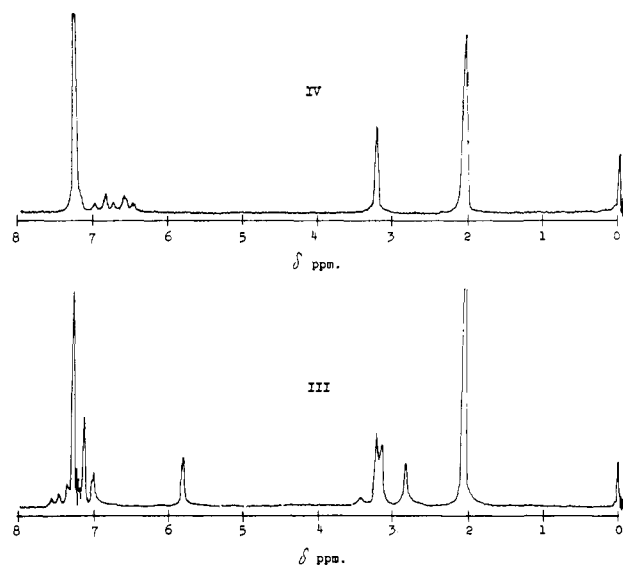

Fig. 3.—N.m.r. spectra of compounds III and IV at 32° and 60 Mc.
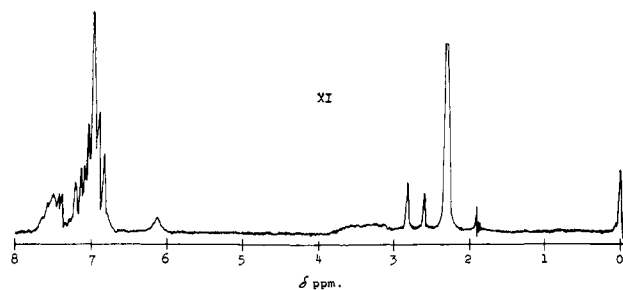

Fig. 4.—N.m.r. spectrum of compound XI showing the diffuse character of one-half of the AB system.

IX, and XV, has been observed by many investigators,[3] but the long-range effect noted for protons 1 and 2 does not seem to have been reported.

The temperature studies of compounds XII, XIII, and XV recorded in Table II were undertaken to in-

vestigate, in a preliminary way, the contributions of conformer populations *vs.* intrinsic asymmetry to the observed magnetic nonequivalence of protons 1 and 2. Although the temperature range was small, there was no evidence of change in the details in the chemical shift difference for the 1,2-protons. Thus it could be reasonably concluded that either there was a predominant conformer whose contribution to the asymmetry was reduced slowly throughout the temperature range investigated or that the system was in reasonably "rapid" rotation even at the lowest temperatures and the change with temperature is that appropriate to a system subjected to an averaging process that changes slowly with temperature.[8]

The observed magnetic nonequivalence of the 1,2-protons in the compounds investigated which have an asymmetric grouping in the molecule and the parallel observation of the apparent equivalence of these protons in molecules which have a plane of symmetry clearly demonstrate a longer range effect of the asymmetric system than might be expected from results previously reported in the literature. While the origin of this effect is not now clear, one might have to con-

(8) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

sider not only the field effects through space, such as for conformers, but also the possible influence of asymmetry introduced in the electronic system of the molecule by the asymmetric group. The observed effect would seem to have considerable potential importance in problems involving structural elucidation.

Experimental

(9) F. N. Jones, R. L. Vaulx, and C. R. Hauser, *J. Org. Chem.*, **28**, 3461 (1963); I, II, VI, XVII, XVIII.

(10) R. L. Vaulx, F. N. Jones, and C. R. Hauser, *ibid.*, **29**, 1387 (1964); VIII, X, XI, XIV, XVI.

(11) R. L. Vaulx, G. C. Jones, and C. R. Hauser, *ibid.*, **27**, 4385 (1962); III, IV.

(12) J. C. Randall, R. L. Vaulx, M. E. Hobbs, and C. R. Hauser, to be published; XII, XIII.

(13) K. P. Klein, R. L. Vaulx, and C. R. Hauser, to be published; V, VII.

Vibrational Assignment for *cis*- and *trans*-1,2-Dichloro-1-fluoroethylenes: FClC=CClH and FClC=CClD

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Infrared, Raman, and proton nuclear magnetic resonance spectra are presented for *cis*- and *trans*-FClC=CClH and FClC=CClD. Assignments of vibration frequencies are obtained for the twelve fundamentals of the *cis* species and for eleven fundamentals of the *trans* species. The assignments for the nine planar modes in each species are supported by normal coordinate calculations. In determining the isomeric configurations, advantage is taken of the significantly greater splitting between the two carbon–chlorine stretching frequencies for the *cis* isomer than for the *trans* isomer. The dynamic origin of this generally useful splitting rule is explored.

The substituted ethylenes are interesting molecules. As *cis–trans* isomers, they provide pairs of distinct chemical species with minimal structural differences. Their well-defined geometry provides a useful basis for studying the energetics of configurational stability.[1] Although in many cases it has been found that the configuration of lower energy is the *trans* isomer, in several halogenated ethylenes it appears to be the *cis*.[2-4] It, however, generally remains to be shown that these are differences in electronic energy and are not merely due to differences in heat capacity or zero-point vibrational energy. For this reason, a careful study of the vibrational and rotational energy levels of *cis–trans* isomeric pairs is desirable. The chlorofluoroethylenes are well suited to such a study because within the series we find an interesting range of relative stabilities. Moreover, they are tractable from a spectroscopic viewpoint. As a fundamental part of this study, it is our intention to examine the vibrational spectra of a number of chlorofluoroethylenes.

In the present paper we have used normal coordinate analysis primarily to confirm the vibrational assignment. We hope that when all of the spectroscopic data are in hand, it will also be possible to determine reliable force constants for this series of molecules and to establish where there are, in fact, differences in force constants between the *cis* and *trans* configurations which can be related to differences in electronic energy. In addition, for the particular case of an unsymmetrically substituted ethylene such as FClC=CClH, there are problems in the assignment of configuration, for the well-recognized differences between the infrared and Raman spectra of two symmetrically substituted isomers are no longer useful.[5] In the present paper, the utility of the frequency difference between the two carbon–halogen stretching modes in *cis–trans* isomer pairs is brought out.

cis–trans fluorinated olefins have also proved to be of considerable interest in n.m.r. studies where the greater magnitude of the *trans* coupling constant, compared with the *cis* coupling constant, appears to be well established experimentally, but not fully understood.[6,7]

(1) E. B. Wilson, Jr., paper presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 1963.

(2) R. E. Wood and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 1650 (1941); K. S. Pitzer and J. L. Hollenberg, *ibid.*, **76**, 1493 (1954).

(3) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, pp. 44–49.