An Analysis of the NMR Spectra of the $ABKLX_3Y_3$ System

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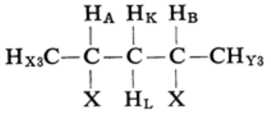
2, 4-Disubstituted pentane is often used as a model compound for vinyl-type polymers in investigating their physical and chemical properties. In the field of NMR, the analysis of the spectra of model compounds is of value in obtaining information concerning polymers. As disubstituted pentane has a much lower molecular weight than a polymer, the molecular motions are sufficient to give well-resolved spectra which permit unambiguous analysis. 2, 4-Disubstituted pentane has ten protons interacting with each other and belongs to the $ABKLX_3Y_3$ system. Analysis of the NMR spectra of this compound is simple in theory. However, the large number of included protons complicates the treatment. General formulas for NMR analysis are given for spin systems of three or less. For spin systems of four or more, the analysis is possible only in special cases or by numerical calculation. For the present analysis, the calculation was made by reducing the entire system to two six-spin systems and one four-spin system. The six-spin systems of the ABB'CC'D type[1] and the A_mBX_n type[2] were previously analysed, but the calculation of $AKLX_3$ type given below has not been previously reported.

The Analysis of $ABKLX_3Y_3$

2, 4-Disubstituted pentane has the following structure;



$$H_{X3}C-\overset{H_A}{\underset{X}{C}}-\overset{H_K}{\underset{H_L}{C}}-\overset{H_B}{\underset{X}{C}}-CH_{Y3}$$

Suffixes have been assigned to protons. Though these ten protons interact with each other, the spin-spin coupling constants between methylene protons and methyl protons are likely to be negligibly small compared with the others and with the chemical shifts (as is the usual case), and it is not always necessary to consider all the protons in the calculation at the same time. This makes it possible to reduce the system to several simple subgroups. The specra of methyl protons are quite simple because they interact with only one methine proton, either H_A or H_B, and are of the AX_3 or BX_3 type. Methylene protons interact with two methine protons. Since they are not necessarily they are analyzed as the KL part in the ABKL system. Methine protons give the most complicated spectra to be analyzed since they are coupled with two methylene protons and three methyl protons. Therefore, this system is expressed as $AKLX_3$ or $BKLY_3$; the transitions concerned merely with A or B are taken into account. The calculation procedure was the usual one; the results are shown in Tables I to IV. The present calculation is confined to the case where the spin-spin coupling constants between methine and methylene protons are small compared with the corresponding chemical shift. Therefore, the large off diagonal terms are $H_{3,4}$, $H_{8,9}$, $H_{12,13}$, $H_{16,17}$, $H_{20,22}$ $H_{24,25}$, $H_{28,29}$, $H_{31,32}$, $H_{35,36}$, $H_{37,38}$, $H_{41,42}$, $H_{44,45}$, $H_{48,49}$, $H_{51,52}$, $H_{55,56}$ and $H_{59,60}$. The diagonalization of the energy matrix is effected by solving sixteen 2×2 determinants. The absence of a spin-spin coupling between methyl and methylene protons simplifies the spectrum, since it makes the parameters R_a, R_c, S_a, and S_c all equal, and R_b, R_d, S_b, S_d all equal.

Discussion

The spectrum of the KL part has an asymmetric form; the effect of the sings of the coupling constants and chemical shifts will now be discussed in relation to this spectrum. The change in sign of the geminal coupling constants between two methylene protons leads to the same spectrum because the resonance frequency and the intensity of the lines reverse themselves at the same time, so that the resultant spectrum remains identical. If the sign of the vicinal coupling constant between methine and methylene protons is reversed, the parameters C and the resonance position interchange between 1 and 4, and between 2 and 3, and no change in the resultant spectrum occurs, although the line assignment becomes different. These considerations enable one to conclude that the spectrum of the KL

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[1] S. Fujiwara and H. Shimizu, *J. Chem. Phys.*, **32**, 1636 (1962).

[2] P. L. Corio, *J. Mol. Spectr.*, **8**, 193 (1962).

TABLE I. BASIC PRODUCT FUNCTIONS AND DIAGONAL MATRIX ELEMENTS FOR $AKLX_3$

n	ϕ_n	F_z	Symmetry	H_{nn}									
				$\frac{\nu_A}{2}$	$\frac{\nu_K}{2}$	$\frac{\nu_L}{2}$	$\frac{\nu_X}{2}$	$\frac{J_{AK}}{4}$	$\frac{J_{AL}}{4}$	$\frac{J_{AX}}{4}$	$\frac{J_{KL}}{4}$	$\frac{J_{KX}}{4}$	$\frac{J_{LX}}{4}$
1	$\alpha\alpha\alpha\alpha\alpha\alpha$	3	a_3	+	+	+	+3	+	+	+3	+	+3	+3
2	$\beta\alpha\alpha\alpha\alpha\alpha$	2	a_2	−	+	+	+3	−	−	−3	+	+3	+3
3	$\alpha\beta\alpha\alpha\alpha\alpha$	2	a_2	+	−	+	+3	−	+	+3	−	−3	+3
4	$\alpha\alpha\beta\alpha\alpha\alpha$	2	a_2	+	+	−	+3	+	−	+3	−	+3	−3
5	$\alpha\alpha\alpha(\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta)/\sqrt{3}$	2	a_2	+	+	+	+	+	+	+	+	+	+
6	$\alpha\alpha\alpha(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	2	e_2	+	+	+	+	+	+	+	+	+	+
7	$\alpha\alpha\alpha(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	2	e_2	+	+	+	+	+	+	+	+	+	+
8	$\beta\beta\alpha\alpha\alpha\alpha$	1	a_1	−	−	+	+3	+	−	−3	−	−3	+3
9	$\beta\alpha\beta\alpha\alpha\alpha$	1	a_1	−	+	−	+3	−	+	−3	−	+3	−3
10	$\alpha\beta\beta\alpha\alpha\alpha$	1	a_1	+	−	−	+3	−	−	+3	+	−3	−3
11	$\beta\alpha\alpha(\beta\alpha\alpha+\alpha\beta\beta+\alpha\alpha\beta)/\sqrt{3}$	1	a_1	−	+	+	+	−	−	−	+	+	+
12	$\alpha\beta\alpha(\beta\alpha\alpha+\alpha\beta\beta+\alpha\alpha\beta)/\sqrt{3}$	1	a_1	+	−	+	+	−	+	+	−	−	+
13	$\alpha\alpha\beta(\beta\alpha\alpha+\alpha\beta\beta+\alpha\alpha\beta)/\sqrt{3}$	1	a_1	+	+	−	+	+	−	+	−	+	−
14	$\alpha\alpha\alpha(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	1	a_1	+	+	+	−	+	+	−	+	−	−
15	$\beta\alpha\alpha(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	1	e_1	−	+	+	+	−	−	−	+	+	+
16	$\alpha\beta\alpha(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	1	e_1	+	−	+	+	−	+	+	−	−	+
17	$\alpha\alpha\beta(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	1	e_1	+	+	−	+	+	−	+	−	+	−
18	$\alpha\alpha\alpha(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	1	e_1	+	+	+	−	+	+	−	+	−	−
19	$\beta\alpha\alpha(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	1	e_1	−	+	+	+	−	−	−	+	+	+
20	$\alpha\beta\alpha(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	1	e_1	+	−	+	+	−	+	+	−	−	+
21	$\alpha\alpha\beta(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	1	e_1	+	+	−	+	+	−	+	−	+	−
22	$\alpha\alpha\alpha(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	1	e_1	+	+	+	−	+	+	−	+	−	−
23	$\beta\beta\beta\alpha\alpha\alpha$	0	a_0	−	−	−	+3	+	+	−3	+	−3	−3
24	$\beta\beta\alpha(\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta)/\sqrt{3}$	0	a_0	−	−	+	+	+	−	−	−	−	+
25	$\beta\alpha\beta(\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta)/\sqrt{3}$	0	a_0	−	+	−	+	−	+	−	−	+	−
26	$\alpha\beta\beta(\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta)/\sqrt{3}$	0	a_0	+	−	−	+	−	−	+	+	−	−
27	$\beta\alpha\alpha(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	0	a_0	−	+	+	−	−	−	+	+	−	−
28	$\alpha\beta\alpha(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	0	a_0	+	−	+	−	−	+	−	−	+	−
29	$\alpha\alpha\beta(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	0	a_0	+	+	−	−	+	−	−	−	−	+
30	$\alpha\alpha\alpha\beta\beta\beta$	0	a_0	+	+	+	−3	+	+	−3	+	−3	−3
31	$\beta\beta\alpha(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	0	e_0	−	−	+	+	+	−	−	−	−	+
32	$\beta\alpha\beta(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	0	e_0	−	+	−	+	−	+	−	−	+	−
33	$\alpha\beta\beta(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	0	e_0	+	−	−	+	−	−	+	+	−	−
34	$\beta\alpha\alpha(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	0	e_0	−	+	+	−	−	−	+	+	−	−
35	$\alpha\beta\alpha(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	0	e_0	+	−	+	−	−	+	−	−	+	−
36	$\alpha\alpha\beta(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	0	e_0	+	+	−	−	+	−	−	−	−	+
37	$\beta\beta\alpha(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	0	e_0	−	−	+	+	+	−	−	−	−	+
38	$\beta\alpha\beta(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	0	e_0	−	+	−	+	−	+	−	−	+	−
39	$\alpha\beta\beta(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	0	e_0	+	−	−	+	−	−	+	+	−	−
40	$\beta\alpha\alpha(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	0	e_0	−	+	+	−	−	−	+	+	−	−
41	$\alpha\beta\alpha(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	0	e_0	+	−	+	−	−	+	−	−	+	−
42	$\alpha\alpha\beta(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	0	e_0	+	+	−	−	+	−	−	−	−	+
43	$\beta\beta\beta(\beta\alpha\alpha+\alpha\beta\alpha+\alpha\alpha\beta)/\sqrt{3}$	−1	a_{-1}	−	−	−	+	+	+	−	+	−	−
44	$\beta\beta\alpha(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	−1	a_{-1}	−	−	+	−	+	−	+	−	+	−
45	$\beta\alpha\beta(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	−1	a_{-1}	−	+	−	−	−	+	+	−	−	+
46	$\alpha\beta\beta(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	−1	a_{-1}	+	−	−	−	−	−	−	+	+	+
47	$\beta\alpha\alpha\beta\beta\beta$	−1	a_{-1}	−	+	+	−3	−	−	+3	+	−3	−3
48	$\alpha\beta\alpha\beta\beta\beta$	−1	a_{-1}	+	−	+	−3	−	+	−3	−	+3	−3
49	$\alpha\alpha\beta\beta\beta\beta$	−1	a_{-1}	+	+	−	−3	+	−	−3	−	−3	+3
50	$\beta\beta\beta(\beta\alpha\alpha+\alpha\beta\alpha-2\alpha\alpha\beta)/\sqrt{6}$	−1	e_{-1}	−	−	−	+	+	+	−	+	−	−
51	$\beta\beta\alpha(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	−1	e_{-1}	−	−	+	−	+	−	+	−	+	−
52	$\beta\alpha\beta(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	−1	e_{-1}	−	+	−	−	−	+	+	−	−	+
53	$\alpha\beta\beta(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{6}$	−1	e_{-1}	+	−	−	−	−	−	−	+	+	+

TABLE I (contnd.)

n	ϕ_n	F_z	Sym-metry	H_{nn}									
				$\frac{\nu_{\mathrm{A}}}{2}$	$\frac{\nu_{\mathrm{K}}}{2}$	$\frac{\nu_{\mathrm{L}}}{2}$	$\frac{\nu_{\mathrm{X}}}{2}$	$\frac{J_{\mathrm{AK}}}{4}$	$\frac{J_{\mathrm{AL}}}{4}$	$\frac{J_{\mathrm{AX}}}{4}$	$\frac{J_{\mathrm{KL}}}{4}$	$\frac{J_{\mathrm{KX}}}{4}$	$\frac{J_{\mathrm{LX}}}{4}$
54	$\beta\beta\beta(\beta\alpha\alpha-\alpha\beta\alpha)/\sqrt{2}$	-1	e_{-1}	$-$	$-$	$-$	$+$	$+$	$+$	$-$	$+$	$-$	$-$
55	$\beta\beta\alpha(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	-1	e_{-1}	$-$	$-$	$+$	$-$	$+$	$-$	$+$	$-$	$+$	$-$
56	$\beta\alpha\beta(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	-1	e_{-1}	$-$	$+$	$-$	$-$	$-$	$+$	$+$	$-$	$-$	$+$
57	$\alpha\beta\beta(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	-1	e_{-1}	$+$	$-$	$-$	$-$	$-$	$-$	$-$	$+$	$+$	$+$
58	$\beta\beta\beta(\beta\beta\alpha+\beta\alpha\beta+\alpha\beta\beta)/\sqrt{3}$	-2	a_{-2}	$-$	$-$	$-$	$-$	$+$	$+$	$+$	$+$	$+$	$+$
59	$\beta\beta\alpha\beta\beta\beta$	-2	a_{-2}	$-$	$-$	$+$	-3	$+$	$-$	$+3$	$-$	$+3$	-3
60	$\beta\alpha\beta\beta\beta\beta$	-2	a_{-2}	$-$	$+$	$-$	-3	$-$	$+$	-3	$-$	-3	$+3$
61	$\alpha\beta\beta\beta\beta\beta$	-2	a_{-2}	$+$	$-$	$-$	-3	$-$	$-$	-3	$+$	$+3$	$+3$
62	$\beta\beta\beta(\beta\beta\alpha+\beta\alpha\beta-2\alpha\beta\beta)/\sqrt{3}$	-2	e_{-2}	$-$	$-$	$-$	$-$	$+$	$+$	$+$	$+$	$+$	$+$
63	$\beta\beta\beta(\beta\beta\alpha-\beta\alpha\beta)/\sqrt{2}$	-2	e_{-2}	$-$	$-$	$-$	$-$	$+$	$+$	$+$	$+$	$+$	$+$
64	$\beta\beta\beta\beta\beta\beta$	-3	e_{-3}	$-$	$-$	$-$	-3	$+$	$+$	$+3$	$+$	$+3$	$+3$

TABLE II. TRANSITIONS OF A PART IN $AKLX_3$

Transition	Frequency	Relative intensity
$1-2$	$\nu_{\mathrm{A}}+1/2(J_{\mathrm{AK}}+J_{\mathrm{AL}}+3J_{\mathrm{AX}})$	1
$5-11$, $6-15$, $7-19$	$\nu_{\mathrm{A}}+1/2(J_{\mathrm{AK}}+J_{\mathrm{AL}}+J_{\mathrm{AX}})$	3
$14-27$, $18-34$, $22-40$	$\nu_{\mathrm{A}}+1/2(J_{\mathrm{AK}}+J_{\mathrm{AL}}-J_{\mathrm{AX}})$	3
$30-47$	$\nu_{\mathrm{A}}+1/2(J_{\mathrm{AK}}+J_{\mathrm{AL}}-3J_{\mathrm{AX}})$	1
$10-23$	$\nu_{\mathrm{A}}+1/2(-J_{\mathrm{AK}}-J_{\mathrm{AL}}+3J_{\mathrm{AX}})$	1
$26-43$, $33-50$, $39-54$	$\nu_{\mathrm{A}}+1/2(-J_{\mathrm{AK}}-J_{\mathrm{AL}}+J_{\mathrm{AX}})$	3
$46-58$, $53-62$, $57-63$	$\nu_{\mathrm{A}}+1/2(-J_{\mathrm{AK}}-J_{\mathrm{AL}}-J_{\mathrm{AX}})$	3
$61-64$	$\nu_{\mathrm{A}}+1/2(-J_{\mathrm{AK}}-J_{\mathrm{AL}}-3J_{\mathrm{AX}})$	1
$3'-8'$	$\nu_{\mathrm{A}}+3/2J_{\mathrm{AX}}+R_{\mathrm{a}}-R_{\mathrm{b}}$	$\cos^2(\theta R_{\mathrm{a}}-\theta R_{\mathrm{b}})$
$12'-24'$, $16'-31'$, $20'-37'$	$\nu_{\mathrm{A}}+1/2J_{\mathrm{AX}}+S_{\mathrm{a}}-S_{\mathrm{b}}$	$3\cos^2(\theta S_{\mathrm{a}}-\theta S_{\mathrm{b}})$
$28'-44'$, $35'-51'$, $41'-55'$	$\nu_{\mathrm{A}}-1/2J_{\mathrm{AX}}+S_{\mathrm{c}}-S_{\mathrm{d}}$	$3\cos^2(\theta S_{\mathrm{c}}-\theta S_{\mathrm{d}})$
$48'-59'$	$\nu_{\mathrm{A}}-3/2J_{\mathrm{AX}}+R_{\mathrm{c}}-R_{\mathrm{d}}$	$\cos^2(\theta R_{\mathrm{c}}-\theta R_{\mathrm{d}})$
$4'-8'$	$\nu_{\mathrm{A}}+3/2J_{\mathrm{AX}}-R_{\mathrm{a}}-R_{\mathrm{b}}$	$\sin^2(\theta R_{\mathrm{a}}-\theta R_{\mathrm{b}})$
$12'-24'$, $17'-31'$, $21'-37'$	$\nu_{\mathrm{A}}+1/2J_{\mathrm{AX}}-S_{\mathrm{a}}-S_{\mathrm{b}}$	$3\sin^2(\theta S_{\mathrm{a}}-\theta S_{\mathrm{b}})$
$29'-44'$, $36'-51'$, $42'-55'$	$\nu_{\mathrm{A}}-1/2J_{\mathrm{AX}}-S_{\mathrm{c}}-S_{\mathrm{d}}$	$3\sin^2(\theta S_{\mathrm{c}}-\theta S_{\mathrm{d}})$
$49'-59'$	$\nu_{\mathrm{A}}-3/2J_{\mathrm{AX}}-R_{\mathrm{c}}-R_{\mathrm{d}}$	$\sin^2(\theta R_{\mathrm{c}}-\theta R_{\mathrm{d}})$
$3'-9'$	$\nu_{\mathrm{A}}+3/2J_{\mathrm{AX}}+R_{\mathrm{a}}+R_{\mathrm{b}}$	$\sin^2(\theta R_{\mathrm{a}}-\theta R_{\mathrm{b}})$
$12'-25'$, $16'-32'$, $20'-38'$	$\nu_{\mathrm{A}}+1/2J_{\mathrm{AX}}+S_{\mathrm{a}}+S_{\mathrm{b}}$	$3\sin^2(\theta S_{\mathrm{a}}-\theta S_{\mathrm{b}})$
$28'-45'$, $35'-52'$, $41'-56'$	$\nu_{\mathrm{A}}-1/2J_{\mathrm{AX}}+S_{\mathrm{c}}+S_{\mathrm{d}}$	$3\sin^2(\theta S_{\mathrm{c}}-\theta S_{\mathrm{d}})$
$48'-60'$	$\nu_{\mathrm{A}}-3/2J_{\mathrm{AX}}+R_{\mathrm{c}}+R_{\mathrm{d}}$	$\sin^2(\theta R_{\mathrm{c}}-\theta R_{\mathrm{d}})$
$4'-9'$	$\nu_{\mathrm{A}}+3/2J_{\mathrm{AX}}-R_{\mathrm{a}}+R_{\mathrm{b}}$	$\cos^2(\theta R_{\mathrm{a}}-\theta R_{\mathrm{d}})$
$13'-25'$, $17'-32'$, $21'-38'$	$\nu_{\mathrm{A}}+1/2J_{\mathrm{AX}}-S_{\mathrm{a}}+S_{\mathrm{b}}$	$3\cos^2(\theta S_{\mathrm{a}}-\theta S_{\mathrm{b}})$
$29'-45'$, $36'-52'$, $42'-56'$	$\nu_{\mathrm{A}}-1/2J_{\mathrm{AX}}-S_{\mathrm{c}}+S_{\mathrm{d}}$	$3\cos^2(\theta S_{\mathrm{c}}-\theta S_{\mathrm{d}})$
$49'-60'$	$\nu_{\mathrm{A}}-3/2J_{\mathrm{AX}}-R_{\mathrm{c}}+R_{\mathrm{d}}$	$\cos^2(\theta R_{\mathrm{c}}-\theta R_{\mathrm{d}})$

where

$R_{\mathrm{a}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}-1/2J_{\mathrm{AK}}+1/2J_{\mathrm{AL}}-3/2J_{\mathrm{KX}}+3/2J_{\mathrm{LX}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta R_{\mathrm{a}}=1/2\sin^{-1}J_{\mathrm{AB}}/2R_{\mathrm{a}}$
$R_{\mathrm{b}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}+1/2J_{\mathrm{AK}}-1/2J_{\mathrm{AL}}-3/2J_{\mathrm{KX}}+3/2J_{\mathrm{LX}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta R_{\mathrm{b}}=1/2\sin^{-1}J_{\mathrm{AB}}/2R_{\mathrm{b}}$
$R_{\mathrm{c}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}-1/2J_{\mathrm{AK}}+1/2J_{\mathrm{AL}}+3/2J_{\mathrm{KX}}-3/2J_{\mathrm{LX}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta R_{\mathrm{c}}=1/2\sin^{-1}J_{\mathrm{AB}}/2R_{\mathrm{c}}$
$R_{\mathrm{d}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}+1/2J_{\mathrm{AK}}-1/2J_{\mathrm{AL}}+3/2J_{\mathrm{KX}}-3/2J_{\mathrm{LX}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta R_{\mathrm{d}}=1/2\sin^{-1}J_{\mathrm{AB}}/2R_{\mathrm{d}}$
$S_{\mathrm{a}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}-1/2J_{\mathrm{AK}}+1/2J_{\mathrm{AL}}-1/2J_{\mathrm{KX}}+1/2J_{\mathrm{LK}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta S_{\mathrm{a}}=1/2\sin^{-1}J_{\mathrm{AB}}/2S_{\mathrm{a}}$
$S_{\mathrm{b}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}+1/2J_{\mathrm{AK}}-1/2J_{\mathrm{AL}}-1/2J_{\mathrm{KX}}+1/2J_{\mathrm{LK}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta S_{\mathrm{b}}=1/2\sin^{-1}J_{\mathrm{AB}}/2S_{\mathrm{b}}$
$S_{\mathrm{c}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}-1/2J_{\mathrm{AK}}+1/2J_{\mathrm{AL}}+1/2J_{\mathrm{KX}}-1/2J_{\mathrm{LK}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta S_{\mathrm{c}}=1/2\sin^{-1}J_{\mathrm{AB}}/2S_{\mathrm{c}}$
$S_{\mathrm{d}}=1/2[(\nu_{\mathrm{L}}-\nu_{\mathrm{K}}+1/2J_{\mathrm{AK}}-1/2J_{\mathrm{AL}}+1/2J_{\mathrm{KX}}-1/2J_{\mathrm{LK}})^2+J^2{}_{\mathrm{KL}}]^{1/2}$ $\theta S_{\mathrm{d}}=1/2\sin^{-1}J_{\mathrm{AB}}/2S_{\mathrm{d}}$

TABLE III. BASIC PRODUCT FUNCTIONS FOR ABKL SYSTEM

No.	ϕ_n				F_z	H_{nn}									
	K	L	A	B		$\frac{\nu_K}{2}$	$\frac{\nu_L}{2}$	$\frac{\nu_A}{2}$	$\frac{\nu_B}{2}$	$\frac{J_{KL}}{4}$	$\frac{J_{AK}}{4}$	$\frac{J_{BK}}{4}$	$\frac{J_{AL}}{4}$	$\frac{J_{BL}}{4}$	$\frac{J_{AB}}{4}$
1	α	α	α	α	2	+	+	+	+	+	+	+	+	+	+
2	β	α	α	α	1	−	+	+	+	−	−	−	+	+	+
3	α	β	α	α	1	+	−	+	+	−	+	+	−	−	+
4	α	α	β	α	1	+	+	−	+	+	−	+	−	+	−
5	α	α	α	β	1	+	+	+	−	+	+	−	+	−	−
6	β	β	α	α	0	−	−	+	+	+	−	−	−	−	+
7	β	α	β	α	0	−	+	−	+	−	+	−	−	+	−
8	α	β	β	α	0	+	−	−	+	−	−	+	+	−	−
9	β	α	α	β	0	−	+	+	−	−	−	+	+	−	−
10	α	β	α	β	0	+	−	+	−	−	+	−	−	+	−
11	α	α	β	β	0	+	+	−	−	+	−	−	−	−	+
12	β	β	β	α	−1	−	−	−	+	+	+	−	+	−	−
13	β	β	α	β	−1	−	−	+	−	+	−	+	−	+	−
14	β	α	β	β	−1	−	+	−	−	−	+	+	−	−	+
15	α	β	β	β	−1	+	−	−	−	−	−	−	+	+	+
16	β	β	β	β	−2	−	−	−	−	+	+	+	+	+	+

TABLE IV. FREQUENCIES AND INTENSITIES OF KL SPECTRUM FOR ABKL SYSTEM

Transition	Frequency relative to $(\nu_K+\nu_L)/2$						Relative intensity
	$\frac{J_{AK}}{4}$	$\frac{J_{AL}}{4}$	$\frac{J_{BK}}{4}$	$\frac{J_{BL}}{4}$	$\frac{J_{KL}}{2}$		
1 − 2	+	+	+	+	+	$-C_1$	$1+\sin 2\theta_1$
1 − 3′	+	+	+	+	+	$+C_1$	$1-\sin 2\theta_1$
2′ − 6	+	+	+	+	−	$+C_1$	$1+\sin 2\theta_1$
3′ − 6	+	+	+	+	−	$-C_1$	$1-\sin 2\theta_1$
4 − 7′	−	−	+	+	+	$-C_2$	$1+\sin 2\theta_2$
4 − 8′	−	−	+	+	+	$+C_2$	$1-\sin 2\theta_2$
7′ − 12	−	−	+	+	−	$+C_2$	$1+\sin 2\theta_2$
8′ − 12	−	−	+	+	−	$-C_2$	$1-\sin 2\theta_2$
5 − 9′	+	+	−	−	+	$-C_3$	$1+\sin 2\theta_3$
5 − 10′	+	+	−	−	+	$+C_3$	$1-\sin 2\theta_3$
9′ − 12	−	−	+	+	−	$+C_3$	$1+\sin 2\theta_3$
10′ − 12	−	−	+	+	−	$-C_3$	$1-\sin 2\theta_3$
11 − 14′	−	−	−	−	+	$-C_4$	$1+\sin 2\theta_4$
11 − 15′	−	−	−	−	+	$+C_4$	$1-\sin 2\theta_4$
14′ − 16	−	−	−	−	−	$+C_4$	$1+\sin 2\theta_4$
15′ − 16	−	−	−	−	−	$-C_4$	$1-\sin 2\theta_4$

$C_1=1/2[(\nu_{LK}-1/2J_{AK}-1/2J_{BK}+1/2J_{AL}+1/2J_{BL})^2+J^2_{KL}]^{1/2}$ $\theta_1=1/2\sin^{-1}J_{KL}/2C_1$

$C_2=1/2[(\nu_{LK}+1/2J_{AK}-1/2J_{BK}-1/2J_{AL}+1/2J_{BL})^2+J^2_{KL}]^{1/2}$ $\theta_2=1/2\sin^{-1}J_{KL}/2C_2$

$C_3=1/2[(\nu_{LK}-1/2J_{AK}+1/2J_{BK}+1/2J_{AL}-1/2J_{BL})^2+J^2_{KL}]^{1/2}$ $\theta_3=1/2\sin^{-1}J_{KL}/2C_4$

$C_4=1/2[(\nu_{LK}+1/2J_{AK}+1/2J_{BK}-1/2J_{AL}-1/2J_{BL})^2+J^2_{KL}]^{1/2}$ $\theta_4=1/2\sin^{-1}J_{KL}/2C_4$

part does not contribute to the determination of the sign of the coupling constants through an approximation of this kind.

The sign of the chemical shift between K and L in a methylene group is determined when the relative magnitude of two vicinal coupling constants between methine and methylene protons are determined; i. e., the relative magnitude of the coupling constants decides the sign of the chemical shift. The change of the sign of the chemical shift results in an interchange of parameters between C_1 and C_4 and between C_2 and C_3, but the relative resonance positions are not altered, therefore the asymmetric spectrum is reversed against the field direction.

Another point of interest is that the present approximation makes the calculation fairly simple, though the application is limited to cases where the coupling constants between methine and methylene protons are not very large compared with chemical shift. The perturbation method can be used in cases where the coupling constants are not very small but are still considerably smaller than the chemical shift. If the coupling constants are larger, a secular equation which includes determinants higher than 2×2 must be solved.

The present treatment may be applied to pentanes substituted by electronegative atoms or groups, such as halogens and OH, but it is not suitable for those groups which do not affect the electron density or the magnetic state surrounding methine hydrogen.

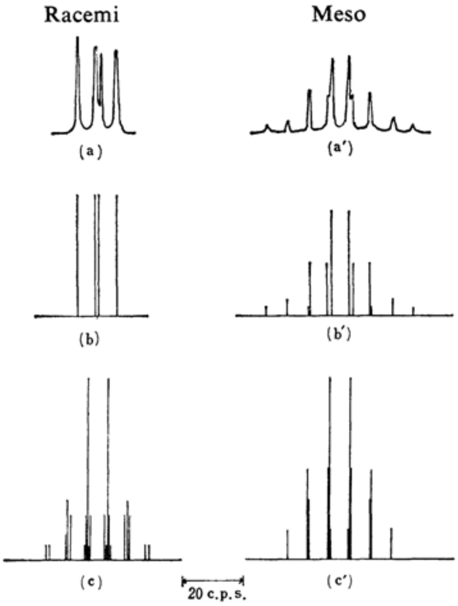

Fig. 1. NMR Spectra of 2,4-dichloropentane.

(a) and (a′) : methylene spectra observed at 60 Mc.[3]

(b) and (b′) : calculated methylene spectra

(c) and (c′) : calculated methine spectra.

Example

The NMR spectra of 2,4-dichloropentane were analysed using the spin-decoupling technique[3]. This compound has two isomers (racemic and meso) and shows two corresponding spectra. The spectra of methylene protons and the results of analysis are shown in Fig. 1 and Table V respectively, where chemical shifts between methylene protons are estimated from the decoupled pattern with the assumption that the spin coupling constants between methylene protons are the same for both isomers.

The calculated spectra with the values in Table V are compared with the observed ones in Fig. 1.

TABLE V. CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 2,4,-DICHLOROPENTANE

	Chemical shift ν_{LK}, c.p.s.	Coupling constant c.p.s.		
		CH_3-CH	CH_2	CH_2-CH
Racemi	0	6.7	14.5	5.8 7.1
Meso	15.6	6.7	14.5	7.0

The agreement of the methylene spectra is quite satisfactory. L=K for racemic compound and K≠L for meso one. The calculated spectrum of the methine proton in the racemic compound is more complicated than the simple sextet which appears for the meso compound. This is also in good agreement with the experimental results reported.[3] Another example of K≠L will be given in a succeeding paper.[4]

Added in Proof: Calculated spectrum of Fig. 1b was constructed from the values in Table V. Same spectrum can be obtained by using another set of parameters, $\nu_{LK}=0$, $J_{AK}=J_{BL}=10.8$ and $J_{AL}=J_{BK}=2.2$. In the latter case, Fig. 1c, should be replaced with a figure of different shape, that is also a complex sextet. The set seems to be a more plausible one.

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[3] S. Sato, R. Chujo and E. Nagai, Proceedings of 3rd Simposium on NMR, Osaka, (1963) p. 51.

[4] Y. Fujiwara and S. Fujiwara, This Bulletin., 37, 8450 (1964).