Composition of the Branched Paraffin-Cycloparaffin Portion of the Light Gas Oil Fraction

BEVERIDGE J. MAIR, NED C. KROUSKOP, and T. JACK MAYER
Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

THE RESEARCH included separation of the branched paraffin-cycloparaffin portion of the light gas oil fraction of petroleum into groups of closely related isomers and a study of their molecular structure by spectroscopic methods. Two isoprenoid type hydrocarbons, 2,6,10-trimethylundecane and 2,6,10-trimethyldodecane were isolated.

The reference petroleum was obtained from the Ponca, Okla., field (*6*). The branched paraffin-cycloparaffin portion was prepared from that portion of the original petroleum which boiled in the range from 230° to 305° C. by quantitatively removing the aromatic hydrocarbons by adsorption with silica gel (*5*) and by removing the greater part of the normal paraffin hydrocarbons by treatment with urea. The branched paraffin-cycloparaffin portion, 230° to 305° C., constituted 10.6% of the original petroleum.

PROCEDURE

The branched paraffin-cycloparaffin portion from the original distillate, 230° to 305° C, was distilled twice in columns of high separating efficiency at a pressure of 30 mm. Results of the distillation of that part of the material boiling in the range from 125° to 175° C. at 30 mm. (approximately from 230° to 285° C. at 760 mm.) are shown in Figure 1. In addition, 22 fractions from the distillate (Figure 1), were processed by preparative scale gas-liquid chromatography. Each distillate fraction was separated into four fractions, totaling 88 final fractions. All 88 fractions were examined by mass, most of them by nuclear magnetic resonance, and few by infrared spectroscopy. The data were correlated to provide information on the composition of the branched paraffin-cycloparaffin portion, C_{13} to C_{16}.

SEPARATION BY GAS-LIQUID CHROMATOGRAPHY

For the separation by gas-liquid chromatography (GLC), a Beckman Megachrom preparative scale instrument with two 24-foot columns connected in parallel was used. The column packing consisted of 20% butanediol succinate (Craig polyester succinate) on 42-60 mesh fire brick. The column was maintained at a temperature near 150° C. for distillate fractions 1 to 19 and near 180° C. for distillate fractions 20 to 22. Helium was used as the carrier gas at an inlet pressure of 20 p.s.i.g. and an outlet pressure of 1.8 p.s.i.g. Sample sizes were in the range from 0.7 to 1.0 ml. On each distillate fraction, the separation by gas-liquid chromatography was repeated (15 to 20 times) until approximately 1 ml. of the smallest final fraction was obtained. Each fraction was passed through a column of silica gel, 2 mm. in diameter, to remove small quantities of the partitioning liquid.

In Figure 2, the refractive index of each of the four final fractions, *A*, *B*, *C*, and *D*, is plotted with respect to its content in the original distillate Fraction 4.

Figure 3 gives the results of the mass spectral analyses of the four fractions.

ANALYSES BY MASS SPECTROMETRY(MS)

Type analyses were made by two laboratories using the method of Hood (*4*). Results for eight samples which were analysed by both laboratories were in excellent agreement. Table I gives the results for four of these samples. Also, as a partial check on the accuracy of the method, two distillate fractions were analysed before and after separation

Table I. Comparison of Mass Spectral Analyses

Fraction No.	Laboratory	Amount of Hydrocarbon Type, Volume % Paraffins	Monocycloparaffins	Bicycloparaffins	Tricycloparaffins
5A	A	97	2	1	0
5A	B	97	2	1	0
5B	A	8	87	5	0
5B	B	7	88	5	0
5C	A	0	9	88	3
5C	B	0	8	88	4
5D	A	0	15	60	25
5D	B	0	14	61	25

Table II. Hydrocarbon Types in Two Fractions

Distillate Fraction No.	Method	Amount of Hydrocarbon Type, Volume % Paraffins	Monocyclo-Paraffins	Bicyclo-paraffins	Tricyclo-paraffins	Tetracyclo-paraffins
9	Total distillate fraction	46.6	34.6	15.2	3.5	0.1
9	Four GLC fractions	48.3	35.1	13.8	2.7	0.1
18	Total distillate fraction	31.5	39.6	20.7	7.5	0.7
18	Four GLC fractions	30.1	40.4	21.6	7.4	0.5

into chromatographic cuts. Table II shows the good agreement of the analyses of the unseparated fractions with the values calculated from the analyses and chromatographic yields of the final fractions.

The hydrocarbon-type analyses of the 88 gas-liquid chromatographic fractions are given in Table III. From these analyses and from the chromatographic yield data, the percentage by volume of each hydrocarbon type was calculated for each of the 22 distillate fractions.

Figure 4 shows how the amounts of the different types of hydrocarbons vary throughout the range of distillate.

The composition of the entire distillate boiling in the range from 125° to 175° C. at a pressure of 30 mm., obtained by determining the areas allocated to the several types in Figure 4, is as follows:

Type of Hydrocarbon	Volume, %
Normal paraffins	6.1
Branched paraffins	34.5
Monocycloparaffins	38.4
Bicycloparaffins	17.4
Tricycloparaffins	3.6
Total	100.0

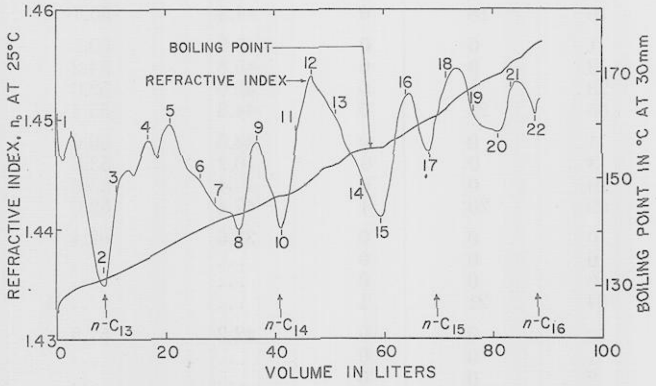


Figure 1. Results of distillation of the branched paraffin-cycloparaffin portion of the light gas oil fraction. The numbers show the positions of the fractions processed by gas-liquid chromatography

CARBON NUMBERS

The average carbon numbers for some of the fractions are recorded in Table III. These were obtained from the mass spectrometric parent ion peaks. For the paraffin hydrocarbons, the parent peak sensitivities decrease with increase in branching. Thus, for a mixture of paraffin

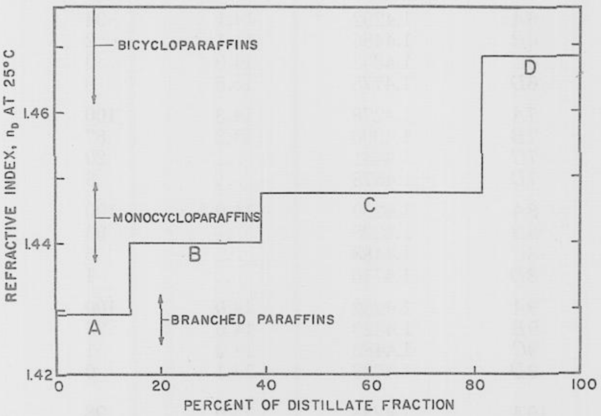


Figure 2. Refractive indices of Fractions *A*, *B*, *C*, and *D* plotted with respect to their per centage of the total fraction

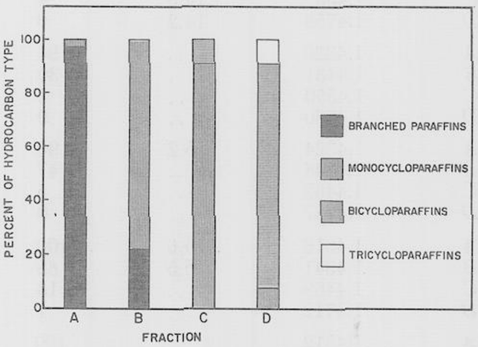


Figure 3. Results of the mass spectral analysis of Fractions *A*, *B*, *C*, and *D*

Table III. Properties of Fractions from GLC

Fraction No.	Refractive Index N_D at 25° C.	Carbon No.[a]	Amount of Hydrocarbon Type, Volume %					Hydrogen Distribution, Mole %	
			Paraffins	Monocycloparaffins	Bicycloparaffins	Tricycloparaffins	Tetracycloparaffins	Methyl	Nonmethyl
1*A*	1.4270	13.4	96	4	0	0	0	47.0	53.0
1*B*	1.4438	13.2	5	90	5	0	0	45.0	55.0
1*C*	1.4674	13.0	0	2	94	4	0	51.8	48.2
1*D*	1.4745	12.6	0	10	53	37	0	. . .	. . .
2*A*	1.4246	13.0	100	0	0	0	0	26.2[b]	73.8[b]
2*B*	1.4429	13.9	8	90	2	0	0	. . .	. . .
2*C*	1.4516	13.5	1	77	22	0	0	50.4	49.6
2*D*	1.4710	13.1	0	0	90	10	0	45.0	55.0
3*A*	1.4260	13.4	100	0	0	0	0	41.0	59.0
3*B*	1.4446	13.9	5	90	5	0	0	51.2	48.8
3*C*	1.4534	13.8	0	80	20	0	0	55.5	44.5
3*D*	1.4691	13.2	0	2	90	8	0	47.0	53.0
4*A*	1.4292	14.0	97	2	1	0	0	41.8	58.2
4*B*	1.4400	14.1	22	78	0	0	0	44.4	55.6
4*C*	1.4475	13.2	0	91	9	0	0	32.6	67.4
4*D*	1.4683	13.4	0	8	83	9	0	44.1	55.9
5*A*	1.4291	14.1	97	2	1	0	0	42.2	57.8
5*B*	1.4440	13.5	8	88	4	0	0	41.4	58.6
5*C*	1.4646	13.8	0	10	87	3	0	47.1	52.9
5*D*	1.4771	13.4	0	16	61	23	0	47.1	52.9

Table III. Properties of Fractions from GLC (*Continued*)

Fraction No.	Refractive Index N_D at 25° C.	Carbon No.[a]	Amount of Hydrocarbon Type, Volume %					Hydrogen Distribution, Mole %	
			Paraffins	Monocyclo-paraffins	Bicyclo-paraffins	Tricyclo-paraffins	Tetracyclo-paraffins	Methyl	Nonmethyl
6*A*	1.4292	14.1	94	5	1	0	0	38.6	61.4
6*B*	1.4486	14.1	2	84	14	0	0	46.1	53.9
6*C*	1.4653	14.0	0	10	86	4	0	47.6	52.4
6*D*	1.4775	13.5	0	2	65	33	0	46.9	53.1
7*A*	1.4278	14.3	100	0	0	0	0	39.8	60.2
7*B*	1.4306	14.3	87	13	0	0	0	41.0	59.0
7*C*	1.4441	...	20	74	6	0	0	...	...
7*D*	1.4578	...	8	36	54	2	0	...	...
8*A*	1.4290	14.9	100	0	0	0	0	50.1	49.9
8*B*	1.4308	...	93	6	1	0	0	48.2	51.8
8*C*	1.4488	...	6	80	14	0	0	42.6	57.4
8*D*	1.4715	...	1	2	82	15	0	52.0	48.0
9*A*	1.4282	14.0	100	0	0	0	0	23.2[b]	76.8[b]
9*B*	1.4323	14.0	73	27	0	0	0	33.8	66.2
9*C*	1.4483	14.2	1	87	12	0	0	42.7	57.3
9*D*	1.4733	14.1	0	3	75	21	1	48.0	52.0
10*A*	1.4283	14.0	98	0	2	0	0	27.4[b]	72.6[b]
10*B*	1.4310	14.1	87	12	1	0	0	29.5[b]	70.5[b]
10*C*	1.4502	14.2	2	79	18	1	0	42.8	57.2
10*D*	1.4729	14.1	0	6	76	18	0	44.3	55.7
11*A*	1.4302	14.4	99	0	1	0	0	40.9	59.1
11*B*	1.4357	...	67	31	2	0	0	45.8	54.2
11*C*	1.4539	14.6	4	67	28	1	0	48.0	52.0
11*D*	1.4755	14.2	0	12	65	23	0	44.6	55.4
12*A*	1.4320	...	96	3	1	0	0	44.0	56.0
12*B*	1.4431	...	30	67	3	0	0	46.2	53.8
12*C*	1.4550	...	2	69	29	0	0	46.4	53.6
12*D*	1.4760	...	0	10	69	20	1	47.4	52.6
13*A*	1.4324	15.2	96	4	0	0	0	37.6	62.4
13*B*	1.4346	...	47	53	0	0	0	...	...
13*C*	1.4482	...	5	89	6	0	0	...	...
13*D*	1.4727	...	0	14	64	21	1	...	...
14*A*	1.4316	15.6	100	0	0	0	0	42.2	57.8
14*B*	1.4341	15.5	85	14	1	0	0	...	...
14*C*	1.4489	...	13	78	9	0	0	...	...
14*D*	1.4712	...	1	18	64	17	0	...	...
15*A*	1.4312	...	100	0	0	0	0	42.9	57.1
15*B*	1.4341	...	84	16	0	0	0	42.4	57.6
15*C*	1.4528	...	6	74	20	0	0	43.8	56.2
15*D*	1.4748	...	1	10	67	21	1	47.8	52.2
16*A*	1.4351	15.5	87	12	1	0	0	46.9	53.1
16*B*	1.4459	15.3	17	82	1	0	0	39.9	60.1
16*C*	1.4538	15.2	4	71	25	0	0	42.9	57.1
16*D*	1.4754	15.0	0	15	61	23	1	45.4	54.7
17*A*	1.4322	...	99	1	0	0	0	26.2[b]	73.8[b]
17*B*	1.4381	...	57	42	1	0	0	33.8	66.2
17*C*	1.4525	...	3	79	77	1	0	43.3	56.7
17*D*	1.4775	...	0	10	58	31	1	45.8	54.2
18*A*	1.4342	15.5	91	4	3	2	0	40.1	59.9
18*B*	1.4418	...	51	46	3	0	0	44.8	55.2
18*C*	1.4561	15.5	5	64	29	2	0	45.0	55.0
18*D*	1.4789	15.2	0	9	50	38	3	44.1	55.9
19*A*	1.4354	16.0	91	9	0	0	0	...	...
19*B*	1.4418	...	52	46	2	0	0	...	...
19*C*	1.4510	15.3	6	86	8	0	0	...	...
19*D*	1.4680	15.5	0	39	44	16	1	...	...
20*A*	1.4349	...	95	3	1	1	0	...	...
20*B*	1.4418	...	52	44	3	1	0	...	...
20*C*	1.4546	...	5	73	21	1	0	...	...
20*D*	1.4761	...	0	16	60	23	1	...	...
21*A*	1.4377	...	80	19	1	0	0	...	...
21*B*	1.4573	...	10	72	17	1	0	...	...
21*C*	1.4699	...	0	25	62	13	0	...	...
21*D*	1.4839	...	2	8	32	52	6	...	...
22*A*	1.4377	...	77	22	1	0	0	...	...
22*B*	1.4377	...	6	78	15	1	0	...	...
22*C*	1.4715	...	0	27	54	18	1	...	...
22*D*	1.4843	...	7	7	16	64	6	...	...

[a] Carbon number of main hydrocarbon type in fraction. [b] Corrected for band overlap.

hydrocarbons, this method tends to give the average carbon number of the less highly branched components of the mixture.

INFRARED SPECTRA

The infrared spectra of eight paraffinic fractions were obtained using a cell 0.025 mm. in thickness. These spectra, in the range from 6 to 9 microns, are shown in Figure 5.

NUCLEAR MAGNETIC RESONANCE SPECTRA

The nuclear magnetic resonance (NMR) spectra were obtained at a frequency of 60 megacycles, a scan rate of 5 c.p.s./sec., and a radio frequency field, H_1 of 0.02 milligauss. The magnetic field of the instrument was proton controlled and was very stable over long intervals so that external referencing was automatic, and internal referencing was unnecessary. No solvent was used. The distribution of hydrogen atoms in methyl groups and in nonmethyl groups, determined by electronic integration of the spectra is recorded in Table III. Although NMR hydrogen distributions have been found to be accurate within ±4% of the methyl hydrogen present for pure normal or lightly branched paraffins, much higher errors have been observed for mixtures (by comparison with MS and GLC data). These errors are due principally to band overlap, and the uncorrected electronic integrals always give higher than the true values for the methyl content. Accordingly, for those fractions of high normal paraffin content, the distribution of hydrogen atoms was corrected for band overlap, insofar as is now possible by objective means. No correction was applied to the more highly branched paraffinic fractions or to the cycloparaffinic fractions, since in this case the error is less serious and the correction less certain.

Table IV. Relative Peak Heights in the Mass Spectra for Series C_nH_{2n+1}

Carbon atoms	Mass	Relative Peak Height Fraction 1*A* %	 Fraction 8*A* %
3	43	93.66	78.78
4	57	100.00	100.00
5	71	63.30	69.81
6	85	21.77	31.16
7	99	4.75	5.10
8	113	10.52	9.33
9	127	2.56	9.78
10	141	1.52	1.49
11	155	1.88	1.17
12	169	1.54	1.67
13	183	0.65	2.85
14	197	0.02	0.92
15	211	0	0

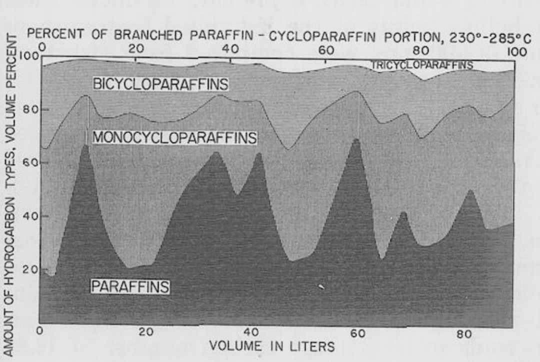
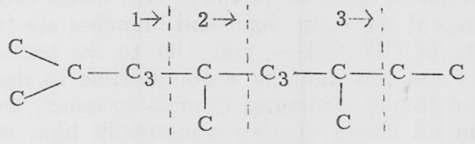


Figure 4. Results of the analysis of C_{13} to C_{16} portion

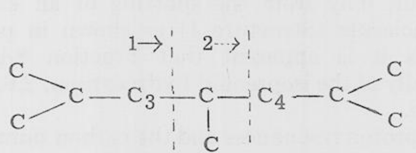
RESULTS FOR THE PARAFFINIC FRACTIONS

NMR spectra are shown for two paraffinic fractions, 2*A* and 8*A*, in Figure 6. These spectra may be compared with the spectra of three pure paraffins given in Figure 7. The spectrum of Fraction 2*A* closely resembles that of *n*-heptane and establishes that this fraction is composed largely of normal paraffins. (The MS data are in agreement with this conclusion). The spectrum of Fraction 8*A* closely resembles that of 2,7-dimethyloctane. The split in the spectrum of the methyl hydrogens, apparent for both Fraction 8*A* and for 2,7-dimethyloctane, occurs when a methyl group is attached to a carbon atom which carries a single hydrogen, that is with a $CH_3 \cdot CH <$ group, and is especially pronounced for isopropyl groups. Integrals of the proton resonances for Fraction 8*A* indicate that 50% of the hydrogen atoms are present in CH_3 groups (Table III). For a branched paraffin with the formula $C_{15}H_{32}$, this corresponds to 5.3 methyl groups per average molecule. The infrared spectrum of this fraction (Figure 5) shows a doublet with peaks at 7.225 and 7.320μ. This is additional evidence that some of the molecules in Fraction 8*A* contain methyl groups in the 2-position since other paraffin hydrocarbons with a few minor exceptions, such as those containing gem dimethyl groups, do not show this doublet. The foregoing indicates that this fraction is composed principally of C_{15} trimethyl paraffins with isopropyl group terminals on at least one end of the main chain.

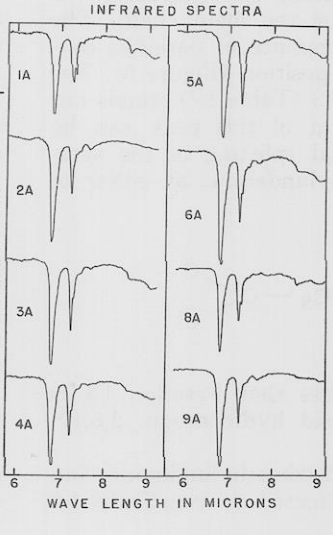
Values for the relative peak heights for the series C_nH_{2n+1}in the mass spectra of Fractions 1*A* and 8*A* are given in Table IV. For Fraction 8*A*, peaks at masses 113 and 127, corresponding to C_8 and C_9 fragment ions, stand out strikingly above any base line which might be drawn. The exceptional heights of these peaks can be accounted for by the preferential splitting of either of the following trimethyldodecanes at positions 1 or 2.



(1)



(2)



←

Figure 5. Infrared spectra of eight paraffinic fractions

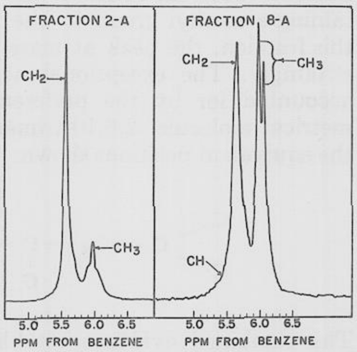


Figure 6. Nuclear magnetic resonance spectra of Fractions 2*A* and 8*A*

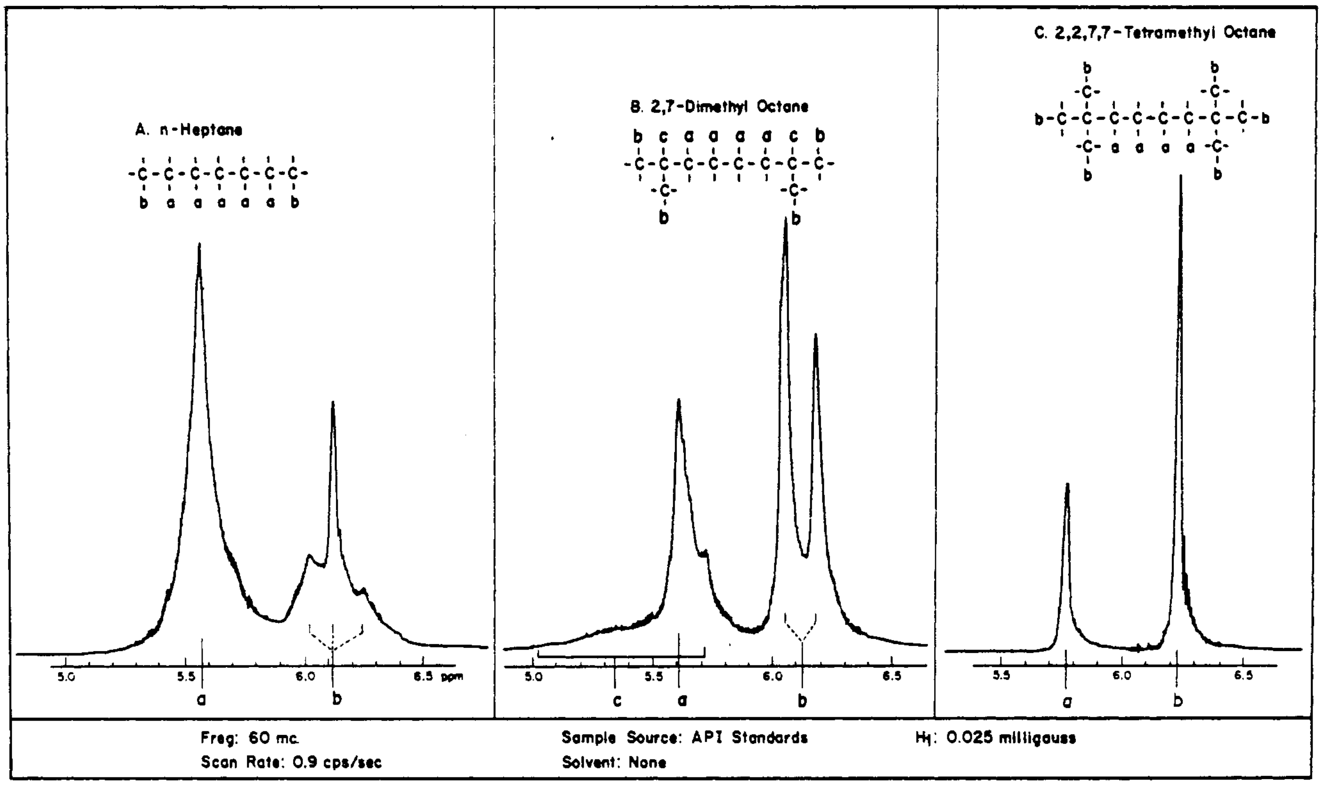
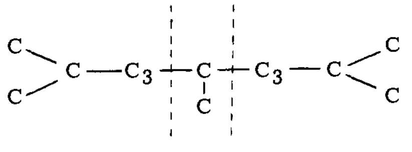


Figure 7. Nuclear magnetic resonance spectra of three paraffin hydrocarbons

When these molecules split at position 1, C_9 fragment ions result; when at position 2, C_8 fragment ions are produced.

For this fraction the NMR spectrum shows that the approximate relative amounts of the groups which constitute the endings of the main chain and branches are from 0 to 20 parts of $CH_3 \cdot CH_2-$ and 100 to 80 parts of $CH_3 \cdot CH <$. From this data, it is not possible to decide which of the molecular structures (1 or 2) to select. However, Fraction 8*A* shows another abnormally high mass spectral peak at mass 183 corresponding to a C_{13} fragment ion. This can result only from the splitting of an ethyl group from the molecule (Structure 1) as shown in position 3. From this it is apparent that Fraction 8*A* is composed principally of the isoprenoid hydrocarbon, 2,6,10-trimethyldodecane.

Integrals of the proton resonances and the carbon number (Table III) establish that Fraction 1*A* is composed principally of C_{14} trimethyl paraffins. The NMR spectrum is very similar to that of Fraction 8*A* indicating the presence of isopropyl terminals on the main chain. The infrared spectrum confirms the presence of paraffins containing a methyl group in the 2-position (Figure 5). For this fraction, the peak at mass 113 (Table IV) stands out strikingly. The exceptional height of this peak can be accounted for by the preferential splitting of the symmetrical molecule, 2,6,10-trimethylundecane, at either of the equivalent positions shown:



The combined evidence establishes that Fraction 1*A* is composed largely of the isoprenoid hydrocarbon, 2,6,10-trimethylundecane.

The two hydrocarbons, 2,6,10-trimethylundecane and 2,6,10-trimethyldodecane are estimated to constitute 1.2 and 2.5% by volume respectively, of the branched paraffin-cycloparaffin portion, 230° to 285° C. Corresponding values for the amounts in the total crude are 0.08 and 0.17% by volume. It is possible that additional 2,6,10-trimethylundecane will be found in the fraction boiling immediately below that covered in the present investigation so that the value for the amount of this compound in the total crude may need to be adjusted upward.

In addition to Fractions 1*A* and 8*A*, several other fractions, 3*A*, 4*A*, 5*A*, and 6*A*, show one main peak in the infrared at 7.225μ and a shoulder at 7.320μ (Figure 5). These fractions also contain paraffins with 2-methyl groupings, though in much smaller amounts.

The lower part of Figure 8 gives a plot of the number of methyl groups per molecule for the paraffinic fractions (the *A* fractions) with respect to the volume of distillate of the original branched paraffin-cycloparaffin portion. The upper part of the figure gives a plot, on the same basis, of the average carbon numbers of these fractions. At the top of the figure the range of distillate is shown in which the normal, monomethyl, dimethyl, and trimethyl paraffins, C_{13} to C_{15}, would occur, if present. To obtain these ranges, the boiling points of the individual hydrocarbons at a pressure of 760 mm. were computed from structural parameters (*1*) and converted to boiling points at 30 mm. (*3*).

Consider the fractions listed in Figure 8 and proceed consecutively from Fraction 1*A* to the higher numbered fractions. As already discussed, Fraction 1*A* is composed mainly of the isoprenoid hydrocarbon, 2,6,10-trimethyllundecane. The boiling point is in accord with this supposition. The main impurity is the slightly higher boiling normal tridecane. On the basis of 4.5 methyl groups per molecule, it is computed that this fraction contains 93% 2,6,10-trimethylundecane and 17% C_{13} normal paraffins. This leads to an average carbon number of 13.83 compared with the value 13.4 actually found. However, as already discussed, the MS method tends to give the carbon number of the less highly branched component of the mixture, in this case normal tridecane. Fraction 2*A* is composed principally of normal tridecane which was incompletely removed in the processing with urea. Fractions 3*A*, 4*A*, and 5*A* are composed chiefly of C_{14} dimethyl paraffins together with small amounts of more highly branched components. The curve for methyl group content shows a minimum in the vicinity of Fraction 6*A*, attributable to the presence of C_{14} monomethyl paraffins which boil in this region. As noted, Fraction 8*A* is composed largely of 2,6,10-trimethyldodecane. The boiling point is in accord with this conclusion. Fractions 9*A* and 10*A* are rich in normal tetradecane. Fraction 12*A* contains C_{15} dimethyl- and trimethyl paraffins. In the region near Fraction 13*A*, in the boiling point range of the C_{15} monomethyl paraffins, the curve for methyl group content shows another minimum. Fractions 15*A* and 16*A* are rich in C_{16} trimethyl paraffins, and Fraction 17*A* in the normal paraffin, pentadecane.

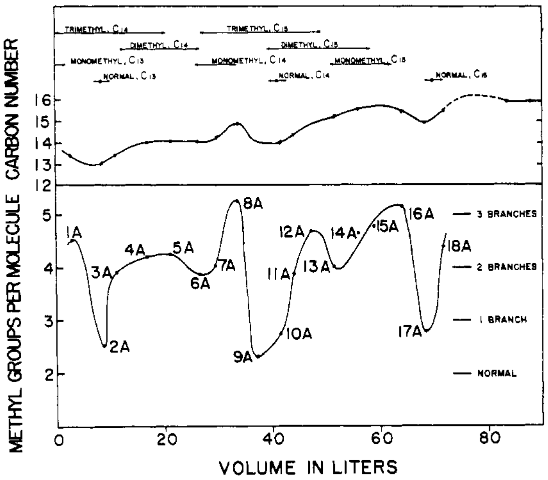
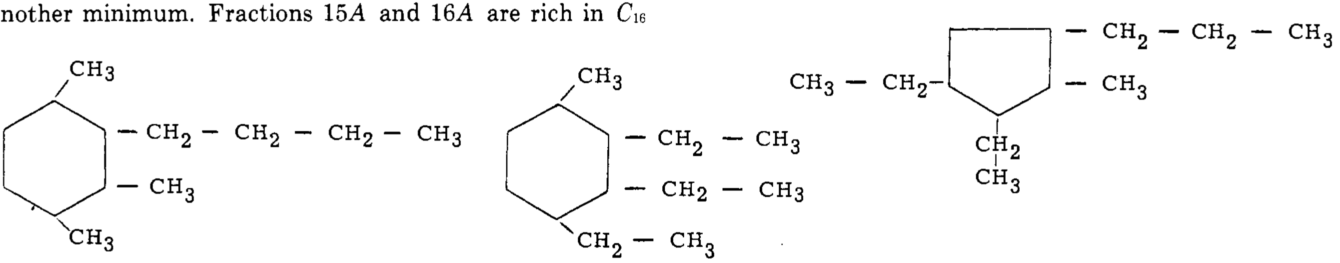


Figure 8. The lower part gives the methyl content of the paraffinic (*A*) fractions plotted with respect to the volume of the original distillate; the upper part gives average carbon numbers; the top of the figure gives the distillate ranges in which the normal, monomethyl-dimethyl-, and trimethylparaffins can occur.

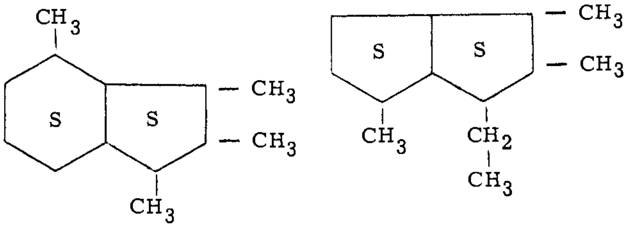
The NMR, carbon number, and boiling point data correlate well on the supposition that these fractions are composed of normal, monomethyl-, dimethyl-, and trimethyl paraffins. These appear to be the principal components, though more highly branched paraffins and paraffins with longer branches are probably also present in small amounts.

RESULTS FOR THE CYCLOPARAFFINIC FRACTIONS

The nuclear magnetic resonance spectrum for a monocycloparaffin concentrate, Fraction 1*B* (5% paraffin, 90% monocycloparaffin, 5% bicycloparaffin) is given together with the spectrum of *n*-decylcyclohexane in Figure 9. The much higher methyl content of the fraction from petroleum (45 mole % hydrogen in methyl groups) is readily apparent. Making the logical assumption that the paraffinic impurities in this fraction have the same distribution of hydrogen atoms as those in Fraction 1*A*, and the bicycloparaffin impurities the same distribution as those in Fraction 1*C*, a corrected value of 44.5 mole % is obtained for hydrogen in methyl groups for the monocycloparaffins in Fraction 1*B*. On the basis of a carbon number of 13, this results in a value of 3.9 methyl groups per molecule for the monocycloparaffins in Fraction 1*B*. On the assumption that the number of methyl groups in branches on side chains is negligible (this is in accord with the finding of Project 6 for monocycloparaffins in the lower boiling fractions) there are, on the average, 3.9 side chains per monocycloparaffin molecule. Three of the many arrangements of molecular structure which account for four side chains are shown.



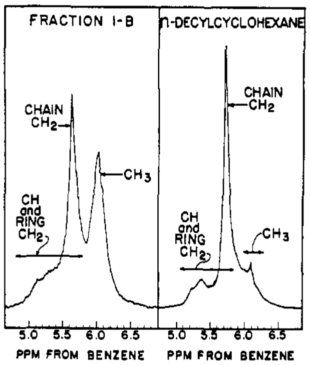
The NMR spectrum for a bicycloparaffin concentrate, Fraction 1*C* (2% monocycloparaffin, 94% bicycloparaffin, 4% tricycloparaffin) and that of a mixture of the isomers of monoamyldecahydronaphthalene are compared in Figure 10. Using 51.8 for the percentage of hydrogen in methyl groups and a carbon number of 13, a value of 4.1 methyl groups per molecule is obtained. It is not possible to accommodate four side chain carbon atoms in a C_{13} alkyldecahydronaphthalene. However, many other structures are possible; two are shown.



DISCUSSION

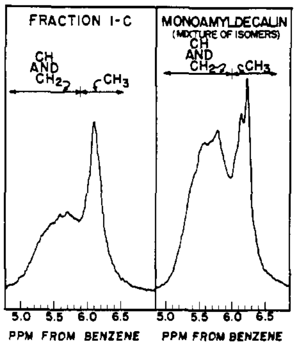
The isolation of the isoprenoid hydrocarbon, 2,6,10,14-tetramethylpentadecane, from several petroleums has recently been accomplished by Bendoraitis, Brown, and Hepner (2). They have also tentatively identified 2,6,10,14-tetramethylhexadecane as a constituent. The isolation in the present investigation of the two isoprenoid hydrocarbons, 2,6,10-trimethylundecane and 2,6,10-trimethyldodecane establishes that an entire series of isoprenoid hydrocarbons with the regular condensed sequence of isoprene units are important constituents of petroleum.

A correlation of boiling point data with data obtained from mass and nuclear magnetic resonance spectroscopy can yield considerable information concerning the types of isomers present in wellseparated paraffinic fractions. The information obtained concerning the structures of the cycloparaffin molecules was less extensive. In part, this was due to the greater difficulty in obtaining monocycloparaffin and bicycloparaffin fractions which were essentially free from other types of hydrocarbons. In addition, there



←
Figure 9. Nuclear magnetic resonance spectra for Fractions 1B and for n-decylcyclohexane.

→
Figure 10. Nuclear magnetic resonance spectra for Fraction 1C and for a mixture of monoamyldecalins.



is a need for spectral data on individual cycloparaffins which have a high proportion of short chains attached to the ring system.

ACKNOWLEDGMENT

The authors are grateful to Nugent F. Chamberlain of the Humble Oil and Refining Co. for the examination by nuclear magnetic resonance spectroscopy, for supplying Figure 7, and for assistance in interpreting the data; to George F. Crable of the Gulf Research and Development Co., and to Archie Hood of the Shell Development Co. for the mass spectral analyses. In addition, Archie Hood suggested that two of the fractions contained isoprenoid type hydrocarbons and provided the mass spectral data which confirmed this supposition.

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, Selected Values of Properties of Hydrocarbons and Related Substances, Tables 61aa and 62aa, October 1957.
(2) Bendoraitis, J.G., Brown, B.L., Hepner, L.S., *Anal. Chem.* **34**, 49 (1962).
(3) Camin, D.L., Sun Oil, Co., Marcus Hook, Pa., unpublished data.
(4) Hood, Archie, Shell Development Co., Houston, Tex., unpublished data.
(5) Mair, B.J., Sweetman, A.J., Rossini, F.D., *Ind. Eng. Chem.* 41, 2224 (1949).
(6) Rossini, F.D., Mair, B.J., Streiff, A.J., "Hydrocarbons in Petroleum," Reinhold, p. 400, New York, 1953.

RECEIVED for review October 26, 1961. Accepted February 16, 1962. Investigation performed as part of the work of the API Research Project 6. Division of Petroleum Chemistry, 141st Meeting, ACS, Washington, D. C., March 1962.

Nitroglycerine Migration in Ethylcellulose

MARTIN H. KAUFMAN
Propulsion Development Department, U. S. Naval Ordnance Test Station, China Lake, Calif.

A STUDY has been made of the effect of changing ethoxy content of ethylcellulose on the migration of nitroglycerin from a standard double-base propellant containing as the volatile constituents nitrogylcerine and diethyl phthalate. Migration decreased in samples having either higher or lower ethoxy content than the usual commercially available materials. Since some of these ethylcelluloses are more difficult to work, as they require high temperatures, they were plasticized to various degrees. The effect of this plasticization on the migration of nitroglycerine was also investigated.

Each anhydroglucose unit in cellulose has three hydroxy groups, any or all of which may react to form derivatives of various degrees of substitution. In the formation of ethylcellulose from alkali cellulose and ethyl chloride complete substitution would give a material containing 54.88% ethoxy. This polymer is known to be weak and brittle and to be a nonthermoplastic having very limited solubility.

An ethylcellulose having approximately 54% ethoxy content picked up no discernible quantity of nitroglycerine. A polymer was desired which picked up very little (ideally no) nitroglycerine, was easily available and capable of being worked, and had acceptable physical properties.

EXPERIMENTAL

Materials. The Dow Chemical Co., Midland, Mich. and the Hercules Powder Co., Wilmington, Del. supplied ethylcellulose samples covering a wide range of degree of substitution. It was found that reproducible results could be obtained using a double-base propellant as the nitroglycerine source. This method, which is safer than using pure nitroglycerine, was applied to all experiments reported here. The propellant, which contained only diethyl phthalate and nitroglycerine as the volatile constituents, was pressed into a billet and subsequently turned into shavings on a lathe to provide a large surface area. 1,1,4,4-Tetramethylbutylphenylether (P-1099) was supplied by the Dow Chemical Co.

Sample Preparation. For initial migration studies a 10% solution of ethylcellulose in toluene or 80% toluene-20% ethanol (more toluene was needed with increasing ethoxy content of the ethylcellulose) was poured within a stainless