It was possible to separate PFP amino acid derivatives significantly faster than the corresponding TFA derivatives on both the liquid ureide and dipeptide phases while maintaining the same values for R/min.

Relative Utility of the Ureide and Dipeptide Phases. Since the ureide phase was proved useful for both amino acid derivatives and amines, a study was done to see if the dipeptide was useful for the separation of the enantiomers of amine derivatives. Table II shows that, while amine derivatives were strongly retained by the dipeptide phase, there was little or no selective interaction toward the enantiomers.

In addition, since the ureide and dipeptide phases were both useful for separating the enantiomers of amino acid derivatives, it was of interest to compare the speeds with which the two phases would perform a given separation. Table II shows the R/min values on the high-temperature solid ureide phase were approximately four times those on the dipeptide phase for the separation of the enantiomers of *N*-TFA-DL-alanine isopropyl ester. These results clearly indicated that the high-temperature solid ureide was capable of separating the enantiomers of some amino acid derivatives much faster than the dipeptide phase.

As noted previously (*2*), another characteristic of separations of both amine and amino acid derivatives on the solid ureide was much greater width of the peak for the more strongly retained enantiomer. Since this behavior was unexpected because of the great similarity of these two isomers, the greater width of the second peak might have been due to the presence of an unresolved component resulting from decomposition on the solid ureide.

Racemic mixtures of the enantiomers of *N*-TFA-2-aminooctane were placed on the column for additional 20- and 30-minute periods by shutting off the carrier gas flow. If a decomposition product was being formed, the longer exposure time should have formed more of that compound and should have caused the appearance of a separate peak or, at least, a change in the shape of the second peak. However, a third peak did not appear, nor did the shape or relative area of the second peak change. The only change was in the ratios of base peak-widths: 2.41, 2.37, and 2.24 for samples exposed to the solid ureide for an additional 0, 20, and 30 minutes, respectively. The decrease indicated that the first peak was spreading more rapidly than the second, as one would expect from a faster rate of diffusion for the less strongly retained isomer. Hence, the difference in peak widths was apparently due to accentuation of the differences in the interactions on sites of different energies on the surface of the solid.

DISCUSSION

The results obtained using the solid amino acid stationary phase and low-temperature solid ureide form clearly showed that the solid form of an optically active stationary phase is not necessarily better than the liquid form. Apparently, the solid phase must meet certain specific structural requirements, which are presently undefined, before a selective interaction can occur.

Since adsorption chromatography on the high-temperature solid ureide phase gave faster separations for the enantiomers of amino acid derivatives than the dipeptide phase, it should be preferred for many analytical applications. In addition, since the ureide phase can be used for separating the enantiomers of both amine and amino acid derivatives while the other commercially available phases cannot, it should be preferred for general use in many cases.

ACKNOWLEDGMENT

The authors wish to thank J. A. Nieman for his assistance with the DTA analyses.

RECEIVED for review June 19, 1970. Accepted September 3, 1970. This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1222.

Separation and Characterization of Methylethylnaphthalene Isomers by Chromatographic and Spectrometric Methods

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Thirteen out of a possible fourteen methylethylnaphthalene isomers were separated and characterized using instrumental methods of analysis. The sterically hindered 1-methyl-8-ethylnaphthalene was not found. Isomers were prepared by alkylating 1-methylnaphthalene and 2-methylnaphthalene. The individual components were separated and purified using preparative gas-liquid chromatography. Isomer structures were determined from infrared (IR) and nuclear magnetic resonance (NMR) spectra. Substitution positions on the naphthalene ring were assigned from the 10 to 15 micrometer IR band patterns and the NMR aromatic proton band patterns. NMR chemical shifts of the methyl and methylene protons were used to complete the assignment of the isomers.

A PROGRAM TO SYSTEMATICALLY separate and identify all major dinuclear aromatic hydrocarbon constituents in a catalytic gas oil fraction has been in progress at this laboratory for some time. During the course of this investigation, it became apparent that little spectral and chromatographic reference data were available for the fourteen possible methylethylnaphthalene isomers. Mair and Mayer (*1*) reported the presence of three methylethylnaphthalenes in crude petroleum but could not completely identify their isomer structures. Chang and Karr (*2*) identified 2,6- and 2,7-methylethylnaphthalene in a low-temperature coal tar. They also reported finding methylethylnaphthalenes with 1,7- and 1,6-substitution but they too could not specify exact isomer structures. The IR spectra of 3-methyl-1-ethylnaphthalene and 1-methyl-7-ethylnaphthalene have been documented (*3*) and the IR spectrum of 3-

(1) B. J. Mair and T. J. Mayer, ANAL. CHEM., **36**, 351 (1964).
(2) T.-C. L. Chang, and C. Karr, Jr., *Anal. Chim. Acta*, **24**, 343 (1967).
(3) Documentation of Molecular Spectroscopy, Butterworth Publ., London, Serial Nos. 7250, 7519.

Table I. Gas–Liquid Chromatograph and Column Descriptions

Instrument	Column description					
	Substrate	Support	O.D. diameter, inch	Length, feet	Temp., °C	Flow rate, ml/min.
Preparative Chromatography						
F&M 775	25% LAC-728	30/60 Mesh Chromosorb P	3/4	10	180	250
Autoprep A-700	25% DEGS	45/60 Mesh Diatoport P	3/8	20	170	200
F&M 810 (Flame Ionization Detector)	10% Apiezon L	60/80 Mesh Chromosorb P	1/4	25	200	80
	10% DEGS	60/80 Mesh Chromosorb P	1/4	25	170	80
	10% Bentone −34+7% DOPC[a]	60/80 Mesh Chromosorb W AW-DMCS	1/4	5	170	80
	10% PPE-6[b]	60/80 Chromosorb P	1/4	25	230	80
Analytical Chromatography						
PE 226	PPE-7[c]		0.01 i.d.	150	130	(30 lbs. He pressure)
	PPE-6		0.01 i.d.	300	160	(40 lbs. He pressure)

[a] 2,6-dioctadecylparacresol.
[b] bis[*m*-(*m*-phenoxyphenoxy)phenyl]ether(polyphenylether 6 ring).
[c] *m*-bis[*m*-(*m*-phenoxyphenoxy)phenoxy]benzene(polyphenylether 7 ring).

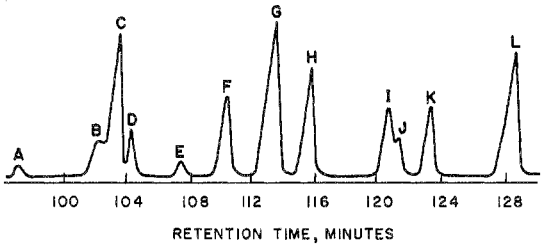


Figure 1. Capillary GLC chromatogram of Mixture A

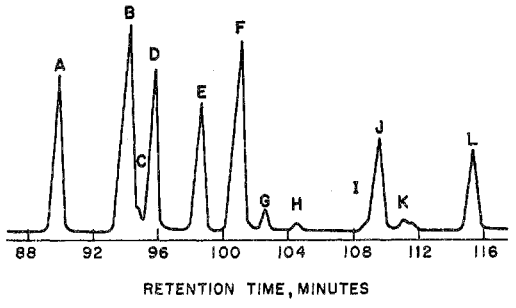


Figure 2. Capillary GLC chromatogram of Mixture B

methyl-1-ethylnaphthalene was also reported by Hume and Jenkins (*4*).

Reference compounds were needed for the chromatographic and spectrometric studies of the gas oil fraction. The synthesis of these reference compounds was simplified when another investigator found a convenient method of preparing mixtures of methylethylnaphthalenes by alkylating methylnaphthalenes (*5*). We decided to separate and characterize the isomers from the alkylation mixtures instead of attempting a synthesis of each individual methylethylnaphthalene.

EXPERIMENTAL

Equipment. Gas–liquid chromatographic separations were performed on four instruments using a variety of columns. The instruments and columns are described in Table I.

Low ionizing voltage MS analyses were performed on a CEC Model 21-103C mass spectrometer equipped with a MicroTek high temperature inlet system.

NMR spectra were measured on a Varian Model A-60 spectrometer equipped with a Varian C-1024 Time Averaging Computer. When possible the samples were run at concentrations of 5 wt % in carbon tetrachloride. The NMR spectra of the small samples collected from the 1/4-in. GLC columns were obtained with the Time Averaging Computer. In these cases 2 to 4 μl of collected material were diluted with carbon tetrachloride in standard NMR sample tubes to give concentrations of about 0.3 wt %.

Infrared spectra were recorded using a Perkin-Elmer Model 337B spectrophotometer. The samples were run as undiluted thin films on KBr plates.

Preparation of the Mixtures. 1-Methylnaphthalene was alkylated with ethylene over a solid phosphoric acid catalyst in a continuous flow reactor to produce Mixture A. The reaction was run in a 30% benzene solution with a liquid hourly space velocity (LHSV) equal to 2.0. Reaction conditions were 500 psig of ethylene at 275 to 300 °C. 2-Methylnaphthalene was alkylated under the same conditions in a 15% normal heptane solution to produce Mixture B. Mixture A was expected to contain only methylethylnaphthalene isomers with methyl groups in the alpha ring positions and Mixture B only isomers with methyl groups in the beta ring positions. This investigation later showed that some isomers were common to both mixtures.

(4) J. H. Hume and G. I. Jenkins, *Appl. Spectrosc.*, **18**, 161 (1964).
(5) G. Suld, Sun Oil Company, Marcus Hook, Pa., personal communication, 1970.

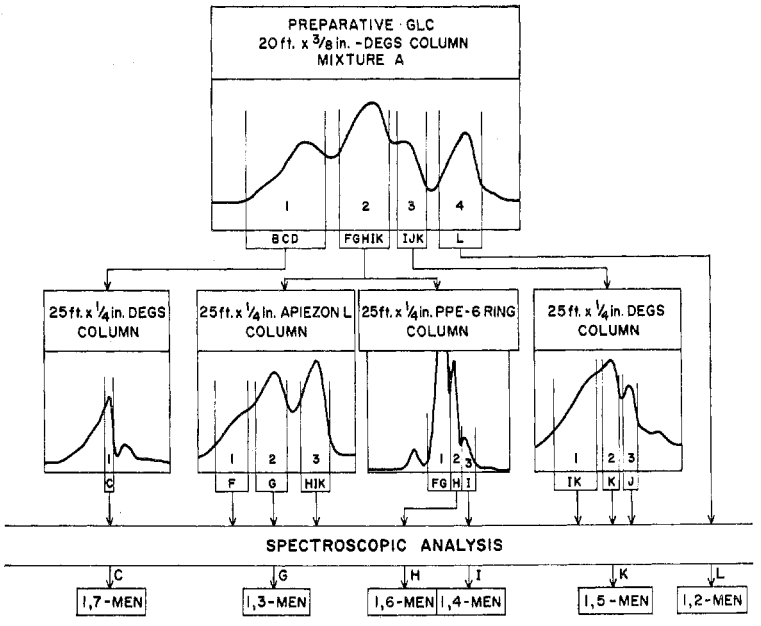


Figure 3. Chromatographic separations of Mixture A

Numbers indicate trapped fractions. Components that were identified in each fraction are indicated by letters. The letters correspond to capillary GLC peaks shown in Figure 1

Both Mixtures A and B were chromatographed through a 10-ft × $^{3}/_{4}$-in. GLC column to remove solvent, starting material, and high boiling byproducts.

The resulting Mixtures A and B were examined by low-voltage MS and shown to contain only C_{13}-alkylnaphthalenes.

RESULTS AND DISCUSSION

Separation of Methylethylnaphthalene Mixtures. Mixtures A and B were analyzed by capillary GLC in order to determine their complexity before further separations were attempted. The peaks were lettered for later reference so that the identified components could be correlated to the capillary GLC peaks. The capillary chromatograms are shown in Figures 1 and 2.

The steps involved in the separation of Mixture A are shown in Figure 3. The first preparative GLC separation, shown at the top of Figure 3, produced four fractions. Capillary GLC analyses of the trapped fractions showed that Fraction 4 contained only a single component and was pure enough for spectrometric analysis. Fractions 1, 2, and 3 required the additional separations shown in the lower portion of Figure 3. A center cut of Fraction 1 was collected to increase the purity of the major component. Fraction 2 required two different chromatographic separations to isolate all of the components. Components labelled F and G were isolated using the Apiezon L column whereas the PPE-6 column was needed to separate components H and I. Fraction 3 was also rechromatographed to separate components K and J. The remaining components, which were all β-methylethylnaphthalenes, were separated and identified in Mixture B.

The separation of Mixture B is shown in Figure 4. The initial preparative GLC separation produced five fractions. Capillary GLC analyses showed that Fractions 3, 4, and 5 were pure enough for spectrometric analysis. Fractions 1 and 2 were separated further using two different GLC columns.

Identification of Methylethylnaphthalene Isomers. The structure of each isomer was assigned from its infrared and NMR spectra. The identifications were made using: the infrared band patterns in the 10 to 15 micrometer region; the NMR band pattern for the aromatic protons; and the NMR chemical shifts of the methylene and methyl groups attached to the aromatic ring.

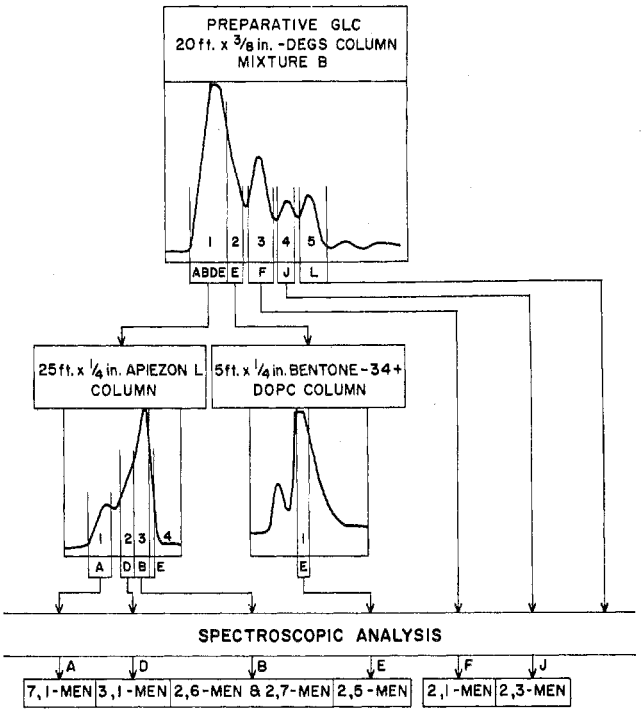


Figure 4. Chromatographic separations of Mixture B

Numbers indicate trapped fractions. Components that were identified in each fraction are indicated by letters. The letters correspond to capillary GLC peaks shown in Figure 2

The IR identifications were based on the strong bands in the 10 to 15 micrometer region which are due to the out-of-plane vibrations of the aromatic protons in the naphthalene ring. These band patterns are characteristic for the type of substitution on the naphthalene ring (*4*, *6–8*). Since the replacement

(6) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, 1964, p 230.
(7) W. Cocker, J. O. Hopkins, J. Mabrouk, and H. B. H. McMurray, *J. Chem. Soc.*, **1960**, 2230.
(8) J. C. Hawkins, E. R. Ward, and D. H. Whiffen, *Spectrochim. Acta*, **10**, 105 (1957).

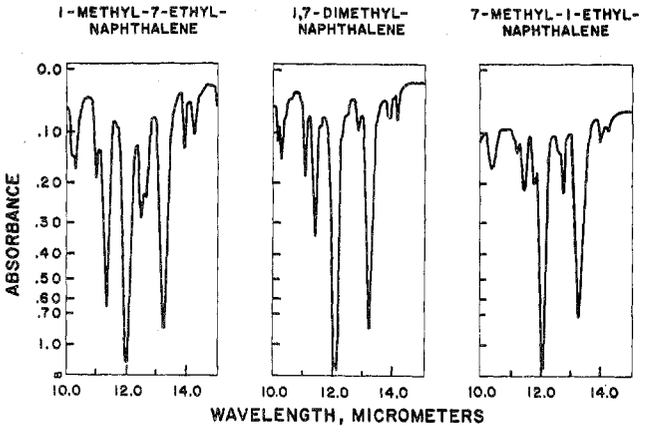


Figure 5. Infrared spectra (10- to 15-micrometer region) of three [1,7] disubstituted alkylnaphthalenes

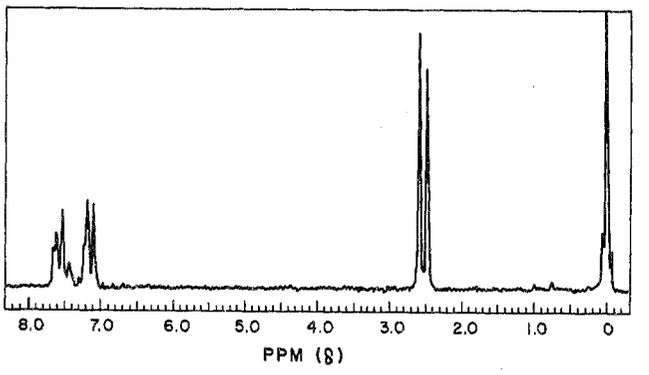
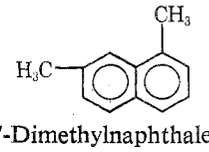


Figure 6. NMR spectrum of 1,7-dimethylnaphthalene

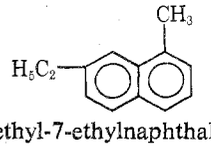
of a methyl group by an ethyl group on the naphthalene ring does not significantly change these bands, the IR patterns for the methylethylnaphthalenes are very similar to the patterns of the corresponding dimethylnaphthalenes.

There are fourteen methylethylnaphthalene isomers. Eight of these (four pair) result from interchanging the methyl and ethyl groups in the alpha and beta positions of the ring. For example:

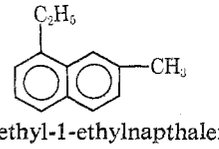
1,7-Disubstituted Naphthalenes



1,7-Dimethylnaphthalene



1-Methyl-7-ethylnaphthalene



7-Methyl-1-ethylnapthalene

The remaining six isomers are symmetrical so that interchanging the methyl and ethyl substituents has no effect on the molecule. The IR band pattern for any methylethylnaphthalene should therefore correspond to one of the ten dimethylnaphthalene band patterns.

Figure 5 illustrates the close similarity of the bands in the 10- to 15-micrometer region for 1,7-dimethylnaphthalene and the two methylethylnaphthalene isomers with the same ring substitution. The comparison of band patterns served to tentatively identify five of the symmetrical isomers and showed

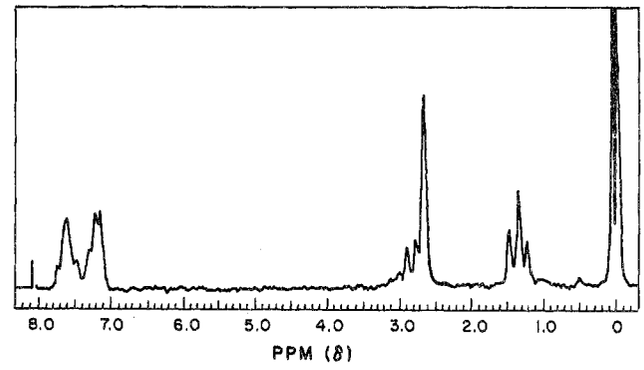


Figure 7. NMR spectrum of 1-methyl-7-ethylnaphthalene

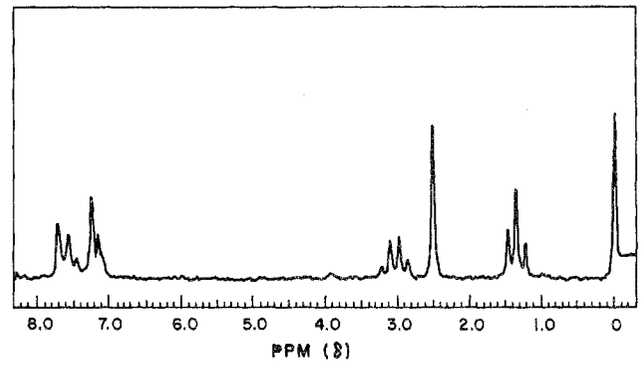


Figure 8. NMR spectrum of 7-methyl-1-ethylnaphthalene

the ring substitution positions for the other eight isomers. Final identifications of the latter eight isomers were made using the NMR results. NMR was also used to confirm the structures of the five symmetrical isomers.

NMR identifications were made from the characteristic patterns for the aromatic proton signals and the chemical shifts of the methylene and methyl protons attached to the ring. Since the coupling constants for the aromatic ring protons in alkylnaphthalenes do not change appreciably when methyl groups are replaced by ethyl groups (*9*, *10*), the pattern of the NMR signals for aromatic protons is characteristic for the type of substitution on the ring. The spectrum of a methylethylnaphthalene should be similar to the spectrum of a dimethylnaphthalene, but as with IR analysis, the problem of isolating two fractions with the same aromatic proton patterns also occurs. Figures 6 to 8 show the NMR spectra of 1,7-dimethylnaphthalene, 1-methyl-7-ethylnaphthalene, and 7-methyl-1-ethylnaphthalene. Note the similarity of the band structure in the 7.0 to 8.0 ppm δ regions. This similarity of aromatic proton patterns between the dimethyl and methylethyl compounds was observed for all of the isomers isolated, and substantiated the IR assignments.

The isomer pairs exhibiting similar IR and NMR aromatic band patterns were all substituted in both the alpha and beta positions on the naphthalene ring. Fortunately, the NMR chemical shifts for methyl and methylene groups in alpha and beta positions on the naphthalene ring are different, thereby making it possible to complete the structural identification of each isomer.

(9) F. Fu-Hsie Yew, R. J. Kurland, and B. J. Mair, ANAL. CHEM., **36**, 843 (1964).
(10) F. Fu-Hsie Yew and B. J. Mair, *ibid.*, **38**, 231 (1966).

Table II. Summary of Isomer Identification

Capillary GLC peak	Naphthalene ring substitution determined by NMR	Naphthalene ring substitution determined by IR	Position of alkyl group determined by chemical shift: Methyl	Position of alkyl group determined by chemical shift: Methylene	Naphthalene isomer identification
Mixture A					
A		Identified in Mixture B			7-Me-1-EtN
B		Identified in Mixture B			2-Me-6-EtN / 2-Me-7-EtN
C	1,7	1,7	alpha	beta	1-Me-7-EtN
D		Identified in Mixture B			3-Me-1-EtN
E		Identified in Mixture B			2-Me-5-EtN
F		Identified in Mixture B			2-Me-1-EtN
G	1,3	1,3	alpha	beta	1-Me-3-EtN
H	1,6	1,6	alpha	beta	1-Me-6-EtN
I	1,4	1,4	alpha	alpha	1-Me-4-EtN
J		Identified in Mixture B			2-Me-3-EtN
K	1,5	1,5	alpha	alpha	1-Me-5-EtN
L	1,2	1,2	alpha	beta	1-Me-2-EtN
Mixture B					
A	1,7	1,7	beta	alpha	7-Me-1-EtN
B	2,6 / 2,7	2,6 / 2,7	beta	beta	2-Me-6-EtN / 2-Me-7-EtN
C		Identified in Mixture A			1-Me-7-EtN
D	1,3	1,3	beta	alpha	3-Me-1-EtN
E	1,6	1,6	beta	alpha	2-Me-5-EtN
F	1,2	1,2	beta	alpha	2-Me-1-EtN
G		Identified in Mixture A			1-Me-3-EtN
H		Identified in Mixture A			1-Me-6-EtN
I		Identified in Mixture A			1-Me-4-EtN
J	2,3	2,3	beta	beta	2-Me-3-EtN
K		Identified in Mixture A			1-Me-5-EtN
L		Identified in Mixture A			1-Me-2-EtN

Table III. Characteristic IR Bands for Disubstituted Naphthalenes

Naphthalene isomer	Wavelength, micrometers								
1,2-DMN						12.4	12.9		13.5
1,2-MEN					12.2		12.8		13.4
2,1-MEN					12.3		12.7		13.4
1,3-DMN		11.6	11.8				12.9		13.4
1,3-MEN		11.5					12.9		13.4
3,1-MEN		11.5	11.8				12.7		13.4
1,4-DMN					12.1			13.3	
1,4-MEN					12.0			13.2	
1,5-DMN							12.7		
1,5-MEN							12.7		
1,6-DMN		11.5			12.3		12.7		13.4
1,6-MEN		11.4			12.2		12.7	13.2	
2,5-MEN		11.4			12.2	12.5		13.3	
1,7-DMN		11.4			12.1			13.2	
1,7-MEN		11.4			12.0			13.3	
7,1-MEN		11.4			12.1			13.3	
2,3-DMN		11.4							13.5
2,3-MEN		11.4							13.4
2,6-DMN		11.2			12.1				
2,6-MEN		11.3			12.2				
2,7-DMN	10.9		11.9						
2,7-MEN		11.1	11.9						

Mair and coworkers (*9*) have shown that proton signals of methyl groups in any of the four beta positions of the naphthalene ring will appear upfield from the signals of methyl protons in the four alpha positions of the ring. Since this chemical shift difference also applies to other alkyl groups, the relative positions of these proton signals can be used to assign the methyl and ethyl groups to the correct ring positions. For example, in Figures 7 and 8, 7-methyl-1-ethylnaphthalene can be readily distinguished from 1-methyl-7-ethylnaphthalene by the relative positions of the methylene quartet and methyl singlet. For the 7,1- isomer the beta methyl signal is upfield and the alpha methylene signal is downfield. The reverse occurs for the 1,7- isomer which results in the overlapping of the signals. Similar differences were also observed in the spectra of the other isomer pairs.

Dilution effects were found to be small and did not interfere with the assignment of methyl and methylene positions using chemical shifts. Mair and coworkers (*9*) also reported observing small dilution effects with these compounds.

All of the isomer structures were unequivocally assigned from the IR and NMR spectrometric data. The results are shown in Table II.

Table IV. NMR Chemical Shifts for Methyl and Methylene Groups Adjacent to Naphthalene Ring

Naphthalene isomer	Proton chemical shifts, δ ppm from TMS: Methyl group singlet naphthalene ring position		Methylene group quartet naphthalene ring position	
	alpha	beta	alpha	beta
1,2-DMN	2.52	2.43	...	...
1,2-MEN	2.56	...	...	2.78
2,1-MEN	...	2.46	3.04	...
1,3-DMN	2.59	2.43	...	...
1,3-MEN	2.64	...	...	~2.8[a]
3,1-MEN	...	2.43	3.03	...
1,4-DMN	2.60	...	...	...
1,4-MEN	2.64	...	3.07	...
1,5-DMN	2.62	...	...	...
1,5-MEN	2.68	...	3.08	...
1,6-DMN	2.62	2.47	...	...
1,6-MEN	2.65	...	...	2.80
2,5-MEN	...	2.49	3.06	...
1,7-DMN	2.58	2.48	...	...
1,7-MEN	2.65	...	...	2.80
7,1-MEN	...	2.52	3.05	...
2,3-DMN	...	2.36	...	...
2,3-MEN	...	2.38	...	2.70
2,6-DMN	...	2.43	...	...
2,6-MEN	...	2.44	...	2.75
2,7-DMN	...	2.43	...	...
2,7-MEN	...	2.44	...	2.75

[a] Methylene quartet was not resolved from the methyl singlet.

Compilation of Data. The IR band positions in the 10- to 15-micrometer region for the thirteen methylethylnaphthalene isomers characterized in this work are compiled in Table III. The dimethylnaphthalenes are included in this Table in order to show the close comparison of the band values.

The NMR chemical shifts for the methylene and methyl groups attached to the naphthalene ring are summarized in Table IV. The dimethylnaphthalenes are also listed in Table IV to show their correlative value. Copies of the complete IR and NMR spectra can be supplied upon request to the authors.

Physical properties could not be obtained for the individual methylethylnaphthalenes because of the small amounts that were isolated, usually 0.1 milliliter or less. Most of these physical properties are tabulated in the literature however (*11*, *12*).

CONCLUSIONS

Thirteen of the fourteen possible methylethylnaphthalene isomers were characterized in the two synthetic mixtures. The sterically hindered 1-methyl-8-ethylnaphthalene was not found. The IR and NMR spectral data and the GLC retention times obtained in this investigation have been used to characterize the methylethylnaphthalenes in petroleum fractions. An application of the data to the analysis of an aromatic concentrate from catalytic gas oil will be reported separately.

This approach to isomer identification should be applicable to other disubstituted alkylnaphthalenes, higher substituted naphthalenes, and other complex aromatic systems.

ACKNOWLEDGMENT

The authors wish to thank George Suld for synthesizing the methylethylnaphthalene isomer mixtures.

RECEIVED for review July 2, 1970. Accepted September 3, 1970. Presented before the Division of Petroleum Chemistry, 160th National Meeting, ACS, Chicago, Ill., September 15, 1970.

(11) "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Texas A&M University, College Station, Texas, 1967, Table 23-2-(33.5211)-a.
(12) I. Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford Press, New York, N. Y., 1965, p 1397.