Experimental

All of the spectra were recorded with a Varian A60D spectrometer at an ambient probe temperature of 34 ± 2°C. The samples were dissolved in dimethyl-d_6 sulfoxide, and tetramethylsilane (TMS) was used as the internal reference for the chemical shifts, which could be measured to within 0.04 ppm. Assignments of spectral bands were made by comparing integrated line intensities, by observing the effect of substitution of deuterium for labile hydrogen, and by comparing the spectra of a series of related compounds.

With the exception of MHDN and 1,3,5-trinitro-1,3,5-triazapentane (TTP), the compounds were prepared according to procedures described in (*3*) and (*4*). Details of the identification and preparation of MHDN and TTP will be presented in a forthcoming publication.

Acknowledgment

We thank Louis Silberman for his suggestions and guidance in bringing this work to a successful conclusion.

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Received for review October 2, 1972. Accepted March 8, 1973. Financial support was provided by Picatinny Arsenal, Dover, N.J., under Contract No. DAAA21-68-C-0305.

Preparation and Spectra of Trimethylnaphthalene Isomers

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The collection of pure samples of 13 out of a possible 14 trimethylnaphthalene isomers and the measurement of reference spectral data on these compounds are described. Five isomers were synthesized, and five others were isolated from petroleum streams by the careful application of preparative scale, gas-liquid chromatographic techniques. Three isomers were obtained from outside sources. The only isomer that could not be obtained was 1,2,8-TMN. The properties of this isomer, however, can be predicted on the basis of the data collected for the other isomers. The nmr and ir spectra of the 13 isomers are also described. Portions of spectra from each isomer are shown along with correlation tables showing the important ir bands and nmr chemical shifts. The significance of each region of the spectrum is discussed in relationship to its usefulness in analytical identifications.

From 1964 through 1969 a major research effort of Sun Research and Development Co. was directed toward characterizing the C_{13}-alkylnaphthalenes and other dinuclear aromatics in catalytic gas oil streams. The major components of these streams were trimethylnaphthalenes (TMN) and methylethylnaphthalenes. Early in this research, it became apparent that the correct identification of individual components would depend upon the availability of adequate reference spectral data. A literature search was made to see what reference data were available at that time. Reference infrared spectra were available for seven of the 14 isomers. Three of these spectra were in the API Research Project 44 collection (*25*) and four spectra were in the Documentation of Molecular Spectroscopy (DMS) collection (*6*). Two nmr spectra were available, both in the API collection (*26*). Ultraviolet spectra for almost all of the isomers were available in scattered collections. Unfortunately, uv spectra are not extremely valuable for the characterization of compounds isolated from petroleum streams.

During this research, several more spectra became available. The DMS collection added all the ir spectra except that of 1,2,8-TMN. Yew et al. (*28, 29*) showed nmr spectra for eight of the TMN isomers and tabulated chemical shifts for two other isomers. Hume and Jenkins (*16*) published a bar chart correlation of the 8–15 μ ir region for seven TMN isomers. Two of these were from their own spectra, and the others were from Mosby (*18*) and DMS (*6*). One of the most complete spectral collections has been provided by Karr et al. (*17*). They show uv spectra for all 14 isomers and ir spectra for seven of the isomers.

Many investigators have reported spectra and other properties for TMN's thrroughout the last 30–40 years. Most of these spectra and properties resulted from the synthesis or isolation of TMN's from natural products. Although the spectra were sometimes not shown, these efforts will be reviewed to document the synthetic procedures. From 1929 through 1932, Ruzicka and coworkers (*20–24*) reported the isolation of trimethylnaphthalenes as dehydration products of sapogenins. To identify these TMN products, they undertook the synthesis of all the trimethylnaphthalenes from various known materials, by use of Freidel-Crafts acylations and other types of well-established synthetic methods. Most of these syntheses were laborious, but they did unequivocally establish the identities of the TMN products. They then obtained picrate and styphnate melting points of all the TMN isomers. Most of the data for trimethylnaphthalenes that are published in Elsevier (*9*) are that of Ruzicka.

Heilbronner et al. (*13*) published the uv spectra of all TMN's except the 1,6,7- and 2,3,6-isomers. The method of synthesizing these compounds was not given in the publication. In 1952 Mosby (*18*) reported the synthesis of four trimethylnaphthalenes by the Freidel-Crafts condensation of α-valerolactone with isomeric xylenes. Ir spec-

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tra were published in support of the TMN compound identifications.

The synthesis of seven TMN's was described by Reid and Bodem in 1958 (*19*). Chloromethylation of dimethylnaphthalene isomers followed by Zn dust reduction was the synthetic method used. The authors identified their products by melting point and picrate melting point. No spectra were given. Evans et al. (*10*) synthesized 1,3,5- and 1,4,5-TMN via the tetralones of 1,4-dimethylnaphthalene. Ir spectra of the TMN's were shown to confirm their identifications. Huckel and coworkers (*14, 15*) synthesized 1,2,4- and 1,2,5-TMN by reductive methylation of naphthalene and methylnaphthalene with Na and CH_3Br in liquid NH_4. They compared the ir spectra of the TMN's with other napthalene compounds. Various other investigators have synthesized one or two specific trimethylnaphthalenes throughout the years. References to these syntheses may be found in the TMN references in Heilbron (*5*) or Elsevier (*9*).

Several investigators have isolated and identified some of the trimethylnaphthalene isomers from petroleum and coal tar products. The most significant was the work of Karr and coworkers (*17*) described earlier. References to other TMN identifications in natural products may be found in the publications of Yew et al. (*28, 29*) and Duswalt and Mayer (*7*).

Preparation and Collection of Trimethylnaphthalene Isomers

Sufficient quantities of 13 out of the possible 14 trimethylnaphthalene isomers were obtained to permit adequate spectral characterization. Six isomers were synthesized in this laboratory, but only five were sufficiently pure to be used for further work. Five isomers were separated from petroleum streams, and three isomers were obtained from outside sources, two being "borrowed" and one purchased from a commercial supply house.

Isomers synthesized by chloromethylation of dimethylnaphthalenes. Six trimethylnaphthalene isomers were synthesized following the method of Reid and Bodem (*19*) as modified by Vanderwerff (*27*). This method involves the chloromethylation of a dimethylnaphthalene, followed by catalytic reduction to the trimethylnaphthalene. The general reaction scheme is as follows:

$$C_{10}H_6(CH_3)_2 + CH_2O + HCl \longrightarrow$$

$$C_{10}H_5(CH_3)_2CH_2Cl \xrightarrow[\substack{60\text{ psi }H_2\\ \text{ETOH}}]{\text{Pd on C}} C_{10}H_5(CH_3)_3$$

Chloromethylation on the naphthalene ring is directed to the alpha position, ortho- and/or para- to the existing methyl groups, and to the ring containing the most methyl groups. The chloromethylation of DMN's, therefore, will not produce all of the possible TMN isomers. Only seven of the possible 14 TMN's can be synthesized with DMN's as starting materials. Six of these isomers were synthesized at Sun with DMN starting materials. The remaining 1,4,5-TMN could have been synthesized from 1,8-DMN, but this starting material was not available in sufficient quantity. Fortunately, the 1,4,5-TMN isomer was obtained later from another source.

The experimental procedures for the chloromethylation and catalytic hydrogenation reactions were developed by Vanderwerff (*27*) following the method of Reid and Bodem (*19*). Table I shows the starting materials, the essential reaction conditions, and the products obtained for the synthetic reactions performed in the authors' laboratories. Additional details about the synthesis, and especially the separation procedures, are described for each separate isomer synthesis, as follows:

1,2,6-Trimethylnaphthalene. *Hydrogenation.* The chloromethylated product was hydrogenated in five batches by use of a small Parr bomb. Each batch was monitored by glc after the hydrogenation. Reducing the amount of palladium catalyst improved the trimethylnaphthalene yield by reducing the amounts of decalins and tetralins that were formed.

Separation. Initially, separation of the final TMN product was attempted on a Varian A-700 Auto-Prep glc instrument with a 10-ft × 3/8-in. SE-54 column. The products from this separation, however, were contaminated with lower boiling materials. Better results were obtained with a homemade prep glc instrument equipped with a 6-

Table I. Synthesis of Trimethylnaphthalenes by Chloromethylation
Summary of starting materials, reaction conditions, and products

Expt no.	Starting material[a]	Chloromethylation product	Hydrogenation method	Crude product		Separation method[b]	Final product		
				State	TMN, %		Isomer	Amount,[c] g	Purity[d]
1	2,6-DMN	3 phases: white and yellow liquids and white solid	Parr bomb, 5 batches	. . .	50	Prep glc[e]	1,2,6-TMN	0.7	99+
2	2,3-DMN	Orange liquid	Parr bomb, 5 batches	Liquid–solid mixture	80–90	Prep glc	1,2,3-TMN	0.5	99+
3	1,2-DMN	Green solid	Parr bomb, 5 batches	Green solid	50	Distillation–crystallization	1,2,4-TMN	0.9	99+
4	2,7-DMN	Yellow–green solid	1 l. Rocker bomb	Yellow viscous oil	80–90	Prep glc	1,2,7-TMN	0.8	99+
5	1,6-DMN	Yellow oil	1 l. Rocker bomb	Dark, golden oil	. . .	Distillation–prep glc	1,4,6-TMN	0.5	99+

[a] 33 grams (0.25 mole) of starting material used in every synthesis. All starting materials were 99+% pure by ir. [b] Details of separation procedures given in text. [c] When final product was separated by prep glc, only enough crude product was processed to give 0.5–1.0 gram of trapped final product. [d] Purity determined by capillary glc. [e] Trap products were percolated through silica gel to remove column bleed materials.

ft × 1/2-in. column packed with 25% DEGS on 45/60 mesh Chromosorb W.

1,2,3-Trimethylnaphthalene. *Separation.* Attempts to purify this TMN product by crystallization failed; the by-products also crystallized along with the desired product. The separation by preparative glc with the same instrument and column as above was more successful.

1,2,4-Trimethylnaphthalene. *Separation.* The separation of the final product from this synthesis presented some problems. Separation by prep-glc methods failed because the product aerosoled and could not be collected in the trap. Recrystallization was tried with no success, because the higher boiling by-products crystallized along with the desired TMN. Separation of the isomer from its by-products was finally effected by distillation with a "Mini-Lab" apparatus. First, a packed column 8 in. high by 1-in. i.d. was tried, but this did not work because the material was too viscous. The packing was removed, and the distillation was accomplished under a vacuum of about 100 mm Hg. A heart cut was taken at constant boiling point. Recrystallization of this distillate fraction from the ethanol gave pure 1,2,4-TMN.

1,2,7-Trimethylnaphthalene. *Separation.* This isomer was separated routinely on the Auto-Prep A-700 with a 10-ft × 3/8-in. SE-54 column on Chromosorb W, 45/60 mesh. The collected trap product was 99+% pure.

1,2,5- and 1,4,6-Trimethylnaphthalenes. *Separation.* First attempts to separate these products by glc on the Auto-Prep A-700 went smoothly until the injection port plugged after about 5–10 injections. A new column was made, and the same problems were experienced. Examination of the first part of this column showed a deposit of black carbonaceous material. Apparently, the high boiling products were carbonizing in the injection port. The crude product was then distilled in the "Mini-Lab" apparatus described above, to remove the TMN's from the higher boiling by-products. The resulting distillate fraction was then rechromatographed successfully on the Auto-Prep with a 20-ft. × 5/8-in. o.d., 25% DEGS on 45/60 Chromosorb P column. The 1,4,6-isomer was collected pure, but the 1,2,5- product contained impurities.

Isomers separated from petroleum. Four TMN isomers, including the 1,2,5-TMN which was not synthesized in good purity, were collected during the characterization studies of catalytic gas oil fractions (7). Some of the compounds had already been isolated in sufficient purity and quantity to permit direct spectral characterization, but in a few instances, additional glc collections had to be performed to either increase the purity or volume of the material. Table II shows the TMN isomers that were collected and the purity of the final products, along with the source fractions and the chromatographic conditions that were used to isolate the pure materials. Additional details about these separations and the glc chromatograms may be found in the original publication (7).

One isomer, 2,3,6-TMN, was separated from the catalytic gas oil by fractional crystallization. Two recrystallizations from ethanol produced 2,3,6-TMN in about 99% purity as determined by capillary glc.

Isomers obtained from outside sources. 1,6,7-TMN (2,3,5-TMN) was purchased from Aldrich Chemical Co. Although the source of this compound was not specified, it presumably came from coal tar.

Two isomers, 1,3,8- and 1,4,5-TMN, were obtained on loan from API Research Project No. 58A. These isomers were synthesized and purified by Eisenbraun and coworkers (*8*). A Freidel-Crafts acylation of *m*- or *p*-xylene with γ-valerolactone was followed by cyclization and reduction to produce the trimethylnaphthalene.

All three of these isomers were examined by capillary glc and were 99+ pure.

Nmr and Ir Spectra of Trimethylnaphthalenes

Reference nmr and ir data were obtained for the 13 available trimethylnaphthalene isomers. The spectroscopic data were subsequently used to identify the trimethylnaphthalene isomers in petroleum fractions (7). The nmr spectra of the trimethylnaphthalenes are relatively simple. The proton signals occur in two regions, the 7–8 ppm δ region for the aromatic protons and the 2–3 ppm δ region for the methyl group protons. These two regions will be described in more detail below.

The infrared spectra of the isomers are much more complex owing to the many vibrational modes of the trisubstituted two-ring systems. These spectra are characteristic for each TMN isomer. Specific ir regions can

Table II. Glc Separation of TMN Isomers from Petroleum Fractions

TMN isomer	Source petroleum fraction		Glc column description, packing and dimensions		Purity of collected materials,[a] wt %	
	Bp, °C	Ref	1st Collection	2nd Collection	1st Collection	2nd Collection
1,3,5-TMN	286–287	Figure 12 (7)	25% DEGS, 45/60 mesh Diataport P; 20 ft × 3/8 in.	10% Bentone-34 + 7% DOPC 60/80 mesh Chrom. W; 5 ft × 1/4 in.	60	95
1,3,6-TMN	286–287	Figure 12 (7)	Same	10% FFAP, 60/80 mesh Chrom. P; 15 ft × 1/4 in.	80	97
1,3,7-TMN	283	Figure 11 (7)	4% Bentone-34 + 15% QF-1, 40/60 mesh Chrom. W; 20 ft × 1/4 in.	10% PPE-6 ring, 60/80 mesh Chrom. P; 25 ft × 1/4 in.	86	99+
1,2,5-TMN	289–291	Figure 16 (7)	20% LAC-278 Prep-5% Grade; 80 in. × 3/4 in.	5% OV-225, 60/80 mesh Chrom. P; 25 ft × 1/4 in. plus 8 in. × 1/4 in. after column to absorb column bleed	40	93[b]

[a] Purity determined by capillary glc. [b] Impurities were mainly OV-225 column bleed.

also be used in the characterization of the higher trisubstituted alkyl homologs (*29*). The infrared spectra will be divided into three regions for the discussion in this paper, the 5-6, the 11-14, and 15-34 μ regions. The significance of each region will be discussed below.

Nuclear magnetic resonance spectra. Nmr spectra were measured on a Varian Model A-60 spectrometer. The hydrocarbon samples were run at concentrations of 5 wt % in carbon tetrachloride, except the 1,2,5-isomer which was run at a concentration of about 0.4 wt % with the aid of the Varian C-1024 time-averaging computer. All chemical shifts are expressed in ppm δ from TMS.

The 7-8 ppm δ region. The band patterns in the 7-8 ppm region are characteristic for the type of substitution on the naphthalene ring (*29*). Replacement of a methyl group by another alkyl group does not significantly alter this pattern. In the case of steric effects some changes in the patterns may be expected. The patterns in the 7-8 ppm region for the 13 isomers are shown in Figure 1. In each case the patterns show some characteristic differences which can be used to identify specific trimethylnaphthalenes and also help in determining the substitution of unknown trisubstituted alkylnaphthalenes.

The 2-3 ppm δ region. The proton signals in the 2-3 ppm region originate from the three methyl groups. In general, the proton signals of methyl groups in any of the four beta positions of the naphthalene ring occur upfield from signals of methyl groups in the four alpha positions of the ring.

Yew and coworkers (*28*) developed an empirical equation for determining the chemical shifts of methyl groups in polymethylnaphthalene compounds. The equation for the chemical shift value depends upon the number of adjacent methyl groups and to a lesser extent, on the number of methyl groups in the same ring and in the neighboring ring. Predicted and measured values for six TMN isomers are listed in the reference.

The measured TMN chemical shift values for alpha and beta methyl groups obtained in this work are listed in Table III in order of location of neighboring methyl groups. The trends in effects of neighboring methyl groups can be seen from the data presentation in this table. The chemical shift for the center beta methyl groups in the 1,2,3-isomer had the lowest value, highest upfield signal, as Mair's equation predicted for two adjacent groups. The next three columns of beta methyl groups have overlapping chemical shift values. The last column of beta values was generally higher, but there is some overlap with the preceding column. The chemical shift values for the alpha methyl group show the same general trends. Alpha methyl groups in C-1 and C-8 ring positions are shifted more downfield because of steric effects. This is observed in the chemical shift data for the 1,3,8- and 1,4,5-isomers in Table III. Polymethylnaphthalenes with methyl groups in the C-1 and C-8 positions can be readily identified in a mixture by their characteristic downfield signals near 2.8 ppm.

The data in Table III also show that in some instances chemical shift values for beta and alpha methyl groups can overlap. Figure 2 shows the 2-3 ppm region for the various isomers. The 1,2,4- and 1,2,5-isomers are very similar as one would expect. The 1,3,6- and 1,3,7- pair of isomers also show some similarity, as expected. In contrast to this, the 1,2,6- and 1,2,7-isomers do not have similar patterns. In fact, without authentic reference material and careful examination of the data, one might incorrectly assign the structure of the 1,2,7-isomer. In the case of the 1,2,7-isomer, the chemical shift value for the beta methyl group with two groups in the neighboring ring overlaps the alpha methyl group with one adjacent group and one group in the other ring. Precautions must therefore be taken in using chemical shift data to assign methyl groups to alpha and beta-ring positions in trisubstituted or higher alkyl naphthalenes.

Infrared spectra. Infrared spectra were recorded on three different instruments: a Perkin-Elmer Model 337B spectrophotometer, a Perkin-Elmer Model 21, and a Perkin-Elmer Model 221 equipped with a cesium bromide in-

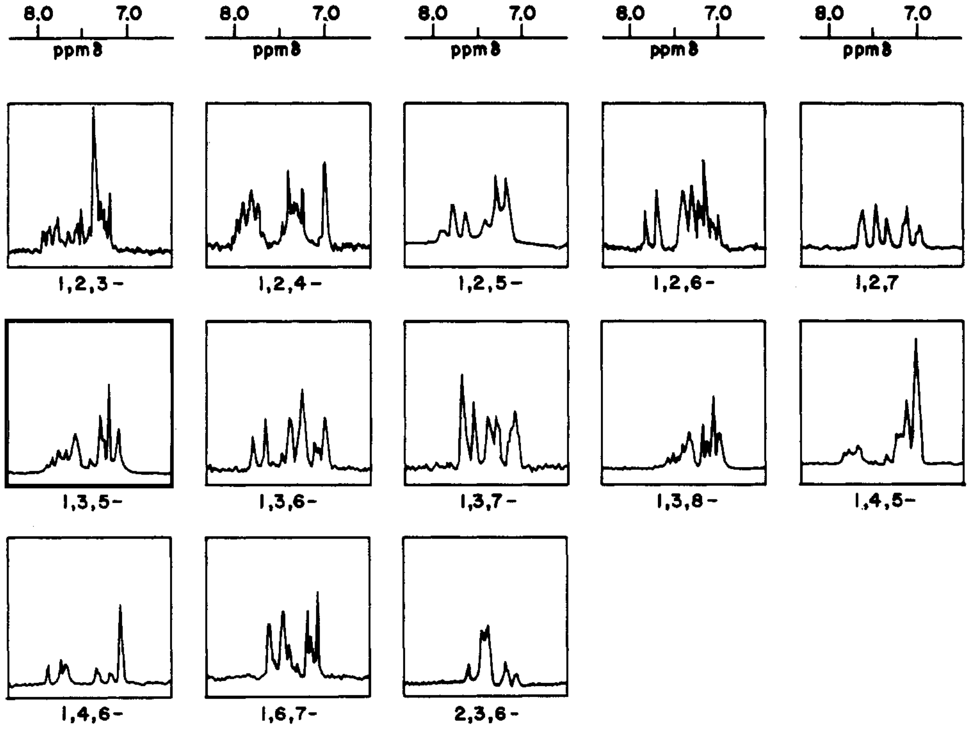

Figure 1. Characteristic nmr patterns of aromatic proton signals in 7-8 ppm δ region for trimethylnaphthalenes

terchange. Liquid samples were run undiluted, and solids were run as nujol mulls or in carbon tetrachloride solution. The wavelength values that are listed in Table IV were recorded with the Perkin-Elmer Model 21.

The 5–6 μ region. The 5–6 μ region has been used extensively in the benzene series to determine the substitution on the ring. The absorption bands in this region are due to overtone and combination bands. Benzene derivative studies show that each type of ring substitution has a distinct pattern and that these patterns remain fairly constant for different substituents (*3*).

For the naphthalene system, Bellamy (*1*) suggested that the complexity of the patterns resulting from the combined effects of two rings, each differently substituted, would invalidate the use of this region for identifications. Data for mono- and disubstituted naphthalenes were reported (*11, 12*), and their patterns are much more complex than those for substituted benzenes. Figure 3 shows the observed ir bands in the 5–6 μ region for the 13 trimethylnaphthalenes. The patterns for naphthalenes with an unsubstituted ring have a band at a lower wavelength (5.17 μ), which is not present in the other isomers. This may be used to identify an unsubstituted ring (*11*). For symmetrical structures the patterns are similar and simpler. As more groups are substituted on the rings, the patterns become less complex and more distinct. Cox and coworkers (*4*) showed that the patterns for monosubstituted naphthalenes are altered by different

Table III. Chemical Shifts of Methyl Protons in Trimethylnaphthalenes

	Beta methyl group, ppm δ					Alpha methyl group, ppm δ				
	Neighboring methyl groups									
Trimethyl-naphthalene isomer	2-Adj	1-Adj, 1-same ring	1-Adj, 1-other ring	1-Same, 1-other ring	2-other ring	1-Adj, 1-same ring	1-Adj, 1-other ring	2-Same ring	1-Same, 1-other ring	2-Other ring
1,2,3-	2.28	2.36	...	...	...	2.52	...	...	...	...
1,2,4-	...	2.38	...	...	...	2.50	...	2.57	...	...
1,2,5-	...	...	2.42	...	...	...	2.52	...	...	2.62
1,2,6-	...	...	2.39	...	2.44	...	2.49	...	...	...
1,2,7-	...	...	2.40	...	2.48	...	2.48	...	...	...
1,3,5-	...	...	...	2.45	...	...	...	...	2.60	2.60
1,3,6-	...	...	...	2.40	2.45	...	...	...	2.57	...
1,3,7-	...	...	...	2.43	2.50	...	...	...	2.61	...
1,3,8-	...	...	...	2.36	...	...	...	...	2.82	2.82
1,4,5-	...	...	...	...	...	...	...	...	2.57	...
									2.81	2.81
1,4,6-	...	...	...	...	2.51	...	...	...	2.59	2.59
1,6,7-	...	...	2.36	...	...	...	...	...	...	2.60
			2.38							
2,3,6-	...	...	2.35	...	2.44	...	...	...	...	...
			2.35							

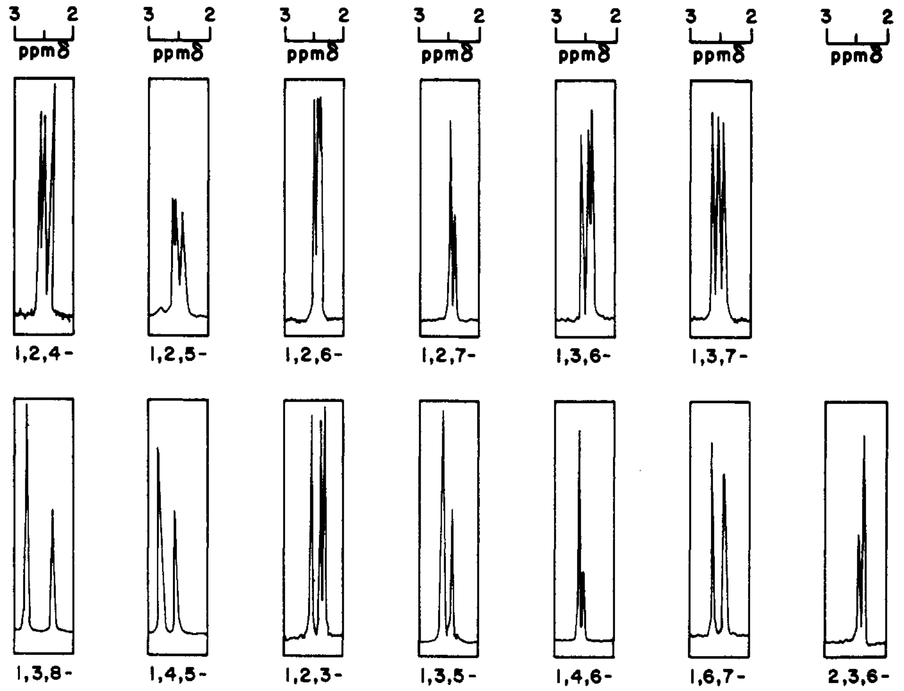

Figure 2. Methyl group proton nmr signals in 2–3 ppm δ region for trimethylnaphthalenes

functional groups on the ring. The bands in the 5-6 μ region, therefore, cannot be used with the same confidence for the identification of naphthalenes as for the identification of benzene derivatives. As more data become available for additional naphthalene derivatives, this region may be more useful.

The 11-14 μ region. This is the region for the out-of-plane hydrogen bending vibrations or umbrella vibrations. These vibrations give rise to intense absorption bands which are characteristic for the type of substitution on the ring. They have been extensively studied in benzene and naphthalene compounds (*1, 3, 12*). Replacement of methyl groups by alkyl groups does not significantly change the patterns, but substitution of electronegative groups does change the patterns. Most of the infrared identifications and characterizations of aromatics are done in this region.

Figure 4 shows the band patterns in the 11-14 μ region for the 13 trimethylnaphthalenes. Each isomer in Figure 4 has a distinct pattern in this region, which can be readily used to identify the type of substitution on the ring. The substitution positions of any unknown trialkylnaph-

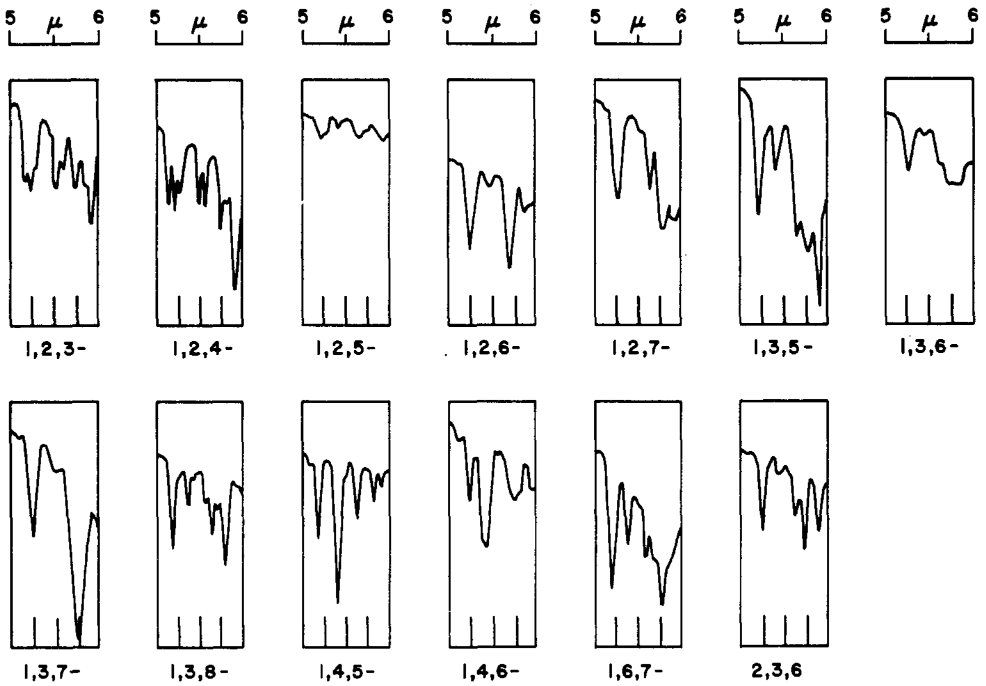

Figure 3. Characteristic patterns of overtone and combination ir bands in 5-6 μ region for trimethylnaphthalenes

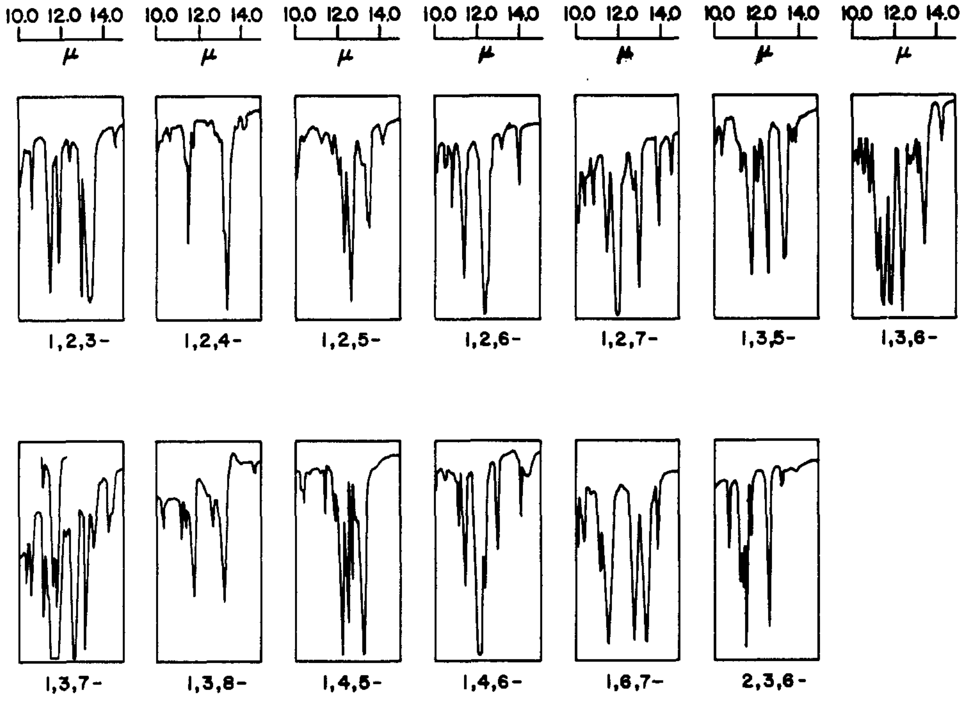

Figure 4. Characteristic ir band patterns in 11-14 μ "fingerprint" region for trimethylnaphthalenes

thalene can be found by matching the pattern of the unknown to one of those shown in Figure 4.

The wavelengths of the trimethylnaphthalene bands in the 11–14 μ region are listed in Table IV. This table is arranged by the number of adjacent hydrogens according to the correlations of Colthup et al. (3). The hydrogen patterns of each side of the naphthalene ring are considered separately, and hydrogen positions are given the lowest numbers, as opposed to the conventional numbering system where substituents are given the lowest numbers. The second and third columns in Table IV list the hydrogen patterns for each ring, A and B, separately. The next five columns give the wavelength assignments of bands for each isomer according to the number of adjacent hydrogens. In most cases, the wavelength values for the bands fall in the ranges specified by Colthup et al. For 1,2,4-hydrogen patterns for 2-adjacent hydrogens, the wavelengths for some of the isomers occurred at slightly higher values. This range probably should be extended to 12.55 μ.

Colthup and coworkers (3) reported an additional band in the 3- and 4-adjacent hydrogen regions which they attributed to a ring-bending mode. In four of the trimethylnaphthalene isomers, an extra band was observed between 13.1–13.5 μ. Each of these four isomers had in common a 1,2,4-hydrogen pattern in the B-ring, but in two other cases of a 1,2,4-pattern, the band was absent. The extra band occurred in the region of 4-adjacent hydrogens and probably was due to the ring-bending mode.

The 15–30 μ region. The skeletal, out-of-plane, and torsional bending modes of vibrations are observed in the region above 15 μ. The absorption band data for nine of the trimethylnaphthalenes are summarized in Table V. Figure 5 shows a bar chart of the trimethylnaphthalenes which is useful as a quick reference for matching bands in this region. During the last part of our experimental work, the Perkin-Elmer 221 with the cesium bromide interchange was not available; therefore, four of the isomers could not be run in this region.

Bentley and Wolfarth (2) studied many compounds in this region. They looked at aromatic hydrocarbons, including alkylnaphthalenes, and found that the spectra of 1-alkylnaphthalenes were much more complex than those for 2-alkylnaphthalenes. They also reported the presence of a strong band near 23–24.9 μ in 1-alkylnaphthalenes which was shifted to shorter wavelengths by larger and branched alkyl groups.

Of the nine trimethylnaphthalenes measured, six showed an intense band in the 23.5–24.1 μ region. The exceptions, the 1,4,5- and 2,3,6-isomers, had a medium to weak band in this region, and the 1,2,5-isomers had a weak band shifted to 22.8 μ.

All the measured isomers showed bands in the 15–16 μ region of weak to strong intensity. Intense bands also occurred in the vicinity of 18.5–20.7 μ for five of the isomers. The 2,3,6- and 1,2,6-isomers have strong absorption bands at longer wavelengths, 28.9 and 29.6 μ respectively, which can be used for quantitative analyses.

Use of TMN spectral data in analytical characterizations. The spectral data compiled in this report can be used to characterize trialkylnaphthalenes in petroleum fractions, other natural products, or synthetic mixtures.

Table IV. Ir Absorption Bands of Trimethylnaphthalenes in 11–14 μ Region

Trimethylnaphthalene isomer	Hydrogen pattern in ring		Wavelength, μ				
	A	B	Isolated H	2-Adj H	3-Adj H	Extra band	4-Adj H
1,2,3-	1	1,2,3,4	11.48 s[a] (11.90 m)[b]	...	...	...	13.48 s 13.00 s
1,2,4-	2	1,2,3,4	11.48 m	...	...	...	13.35 s 13.20 m
1,2,5-	1,2	1,2,3	...	12.4 m	12.7 s 13.5 m	...	...
1,2,6-	1,2	1,2,4	11.42 m	12.37 s (12.5) side shoulder	...	...	...
1,2,7-	1,2	1,2,4	11.54 m	12.1 s	...	13.10 m	...
1,3,5-	1,3	1,2,3	11.77 s 11.37 w	...	12.58 s 13.43 s	12.15 w[c]	...
1,3,6-	1,3	1,2,4	11.24 m 11.50 s 11.88 s	12.40 s	...	13.47 m	...
1,3,7-	1,3	1,2,4	11.52 s 11.70 s	12.55 s	...	13.10 m	...
1,3,8-	1,3	1,2,3	11.75 s 11.22 w	...	12.70 w 13.20 s	...	...
1,4,5-	2,3	1,2,3		12.23 s	12.50 m 12.74 m 13.24 s	...	...
1,4,6-	2,3	1,2,4	11.50 m	12.16 s (12.40) side shoulder	...	13.04 m	...
1,6,7-	1,4	1,2,3	11.55 s 11.28 m	...	12.76 s 13.35 s	...	...
2,3,6-	1,4	1,2,4	11.10 m 11.25 m 11.40 s	12.53 s	...	...	...

[a] Band intensity rating: s, strong. [b] m, medium. [c] w, weak.

Table V. Ir Absorption Bands of Trimethylnaphthalenes in 15-30 μ Region

Trimethyl-naphthalene isomer	Wavelength, μ											
	15	16	17	18	19	20	21	22	23	24	28	29
1,2,3-	15.6 m[a]	...	...	18.6 s[b]	19.1 s	...	...	22.8 m	...	...	...	...
1,2,4-	15.6 m	...	17.3 m	...	...	...	21.1 m	...	23.6 s	...	28.2 m	...
1,2,6-	15.7 s	...	...	18.3 m	19.6 m	...	21.0 m	...	...	24.1 s	...	29.6 s
1,2,7-	15.6 w[c]	...	...	18.0 w 18.5 m	19.1 s	20.8 m	...	...	23.7 s	...	...	...
1,3,6-	15.1 w	16.0 w	...	18.4 m 18.7 s	...	20.3 w 20.9 m	21.8 m	...	23.2 s	...	...	...
1,4,5-	15.9 m	16.4 w	...	18.1 m	19.3 w	...	21.5 m	22.0 m	23.8 w	...	...	...
1,4,6-	15.7 s	...	17.3 w	...	19.0 w 19.7 w	20.2 s	21.5 w	22.7 w	...	24.1 s	...	...
1,6,7-	15.2 m	...	...	18.3 m	19.1 m	20.9 w	21.6 m	...	23.7 s	...	...	...
2,3,6-	15.2 m	16.7 w	17.8 m	...	...	20.7 s	...	22.8 m	23.7 m	...	28.9 s	...

[a] Band intensity rating: m, medium. [b] s, strong. [c] w, weak.

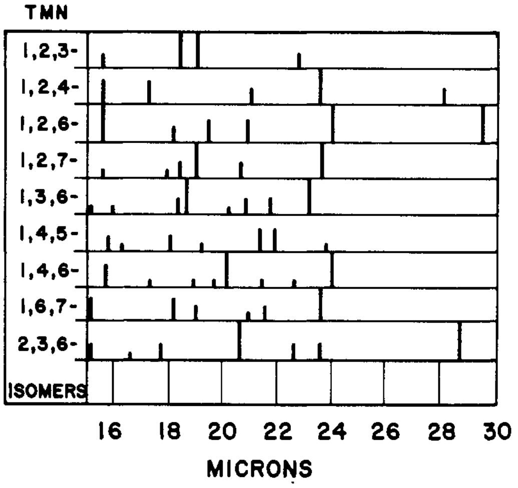

Figure 5. Ir bar chart of 15-30 μ region for nine trimethylnaphthalenes

The 5-6 and 11-14 μ regions of the infrared, along with the 7-8 ppm region of the nmr, show the substitution positions on the naphthalene ring. Chemical shift correlations for the alkyl groups in the 2-3 ppm nmr region can be used to further pinpoint the location of these groups in either the alpha or beta-ring positions.

Examples of the application of these correlations for the identification of trimethylnaphthalenes in petroleum fractions were reported by Duswalt and Mayer (*7*) and Yew and Mair (*29*).

Acknowledgment

The authors acknowledge C. T. Armes, E. L. Armstrong, R. E. Bingeman, R. M. Fratantoni, C. F. Mahoney, T. C. Werner, and H. C. Williamson for their technical assistance. We also thank E. J. Eisenbraun for supplying the two TMN isomers.

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Received for review October 16, 1972. Accepted March 15, 1973.