

**STRUCTURES OF LIQUID-LIKE SYSTEMS:
X-RAY DIFFRACTION OF MODEL ORGANIC HYDROCARBONS.**

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Introduction

Since the work of T. F. Yen in 1961 (1), there has been much effort in the determination of the structure of petroleum heavy ends. Although x-ray diffraction shows broad lines, indicative of correlation lengths of $\sim 10\text{-}30$ A, the d values of the peaks have been associated with specific organic functionality: 4.5-4.8 A (aliphatic), 3.4-3.8 (aromatic stacking), and 2.1 A (aromatic diameter).

In two previous papers (2,3), we have performed x-ray diffraction on the liquid phases of model organic hydrocarbons to obtain additional insights into these assignments. In contrast to earlier work (1), we found that the " γ -band" at 4.6 A was related to intermolecular interference among paraffins, but not to interference among naphthenes, which we found to appear at 5.3 to 5.4 A (2,3). Although the "(002) band" at 3.4 to 3.6 A presumably does arise from the approximately parallel stacking of planar aromatic molecules, we found evidence for (00L) peaks at lower values of 2θ , arising from the small stack height of the aromatic clusters. The true identity period became the stack height itself, thereby giving rise to lines at "d value" greater than that of the "(002) band." The above inferences indicated that the x-ray diffraction-based method of determining fractional aromaticity, by comparing areas of the γ -band and (002) band, fails for a number of reasons.

In the present paper, we extend our work on the x-ray diffraction of liquid-phase organic hydrocarbons. Analysis of the patterns of the methyl-branched paraffins pristane and phytol shows an intermolecular interference maximum at 4.7 to 4.8 A, slightly higher than that found for n-paraffins, but significantly lower than that found for naphthenes. Diffraction of quinoline shows two (00L) peaks, exactly the behavior exhibited by 1-methyl naphthalene (2,3). When a given molecule contains both sp^2 and sp^3 hybridized carbon, as in tetralin or tetrahydroquinoline, broadening of the lines results, although when one carbon type predominates (as in n-heptadecyl benzene), that carbon type will dominate the diffraction pattern.

Experimental details

Diffraction experiments on liquids were carried out as described previously (2,3). A cell with Be windows was mounted on a Siemens Type F diffractometer, equipped with a divergent 1° slit and a receiving 0.1° slit. Copper radiation was used.

Quinoline (99%) was obtained from Aldrich. The methyl branched paraffins pristane (2,6,10,14 tetramethyl pentadecane, 99%) and phytol (3,7,11,15 tetramethyl-2-hexadecen-1-ol, 70%) were obtained respectively from Wiley Organics and Aldrich. The purity of the quinoline and pristane was verified by GC/MS; the MS pattern of the major component of the phytol showed peaks at m/e of 71 ($I=100$), 55 ($I=56$), 57 ($I=52$), and 81 ($I=33$), with the highest detected $m/e=278$, reflecting a loss of water from the pure phytol (molecular weight = 296.5). A high resolution C-13 NMR pattern of the pristane showed resonances at 19.8 δ (the methyl groups on the 6 and 10 carbons), 22.7 δ (the four equivalent "terminal" methyl groups), 24.6 δ (the central, 8, methylene carbon), 24.9 δ (the 4 and 12 methylene carbons), 28.1 δ (the 2 and 14 methylene carbons), 32.9 δ (the 6 and 10 methylene carbons), 37.5 δ (the 7 and 9 methylene carbons), and 39.5 δ (the 3 and 13 methylene carbons). The reader should note that the spectrum of this isoprenoid carbon skeleton is quite distinct from that of an n-paraffin (e.g., internal methylenes at 29.8 δ , terminal methyl groups at 14.2 δ). The remarkable finding reported here is that branched paraffins and normal paraffins show different patterns in liquid-phase x-ray diffraction, because of differences in intermolecular packing.

Results and Discussion

The diffraction patterns of the liquids pristane, phytol, and quinoline are given in Figure 1. The "d value" of the single observed interference maximum is 4.8 A for pristane and 4.7 A for phytol, measurably higher than the 4.6 A that we have found for n-paraffins. This increase is presumably related to the presence of the methyl groups, and confirms the identification of the " γ -band" as an intermolecular interference peak of paraffins (2,3).

In contrast to the paraffins, the diffraction pattern of liquid quinoline contains two peaks in the region $10 - 45^\circ 2\theta$. The larger peak is at 3.9 A, with a shoulder at 5.1 to 5.4 A. This behavior is analogous to that previously reported for 1-methyl naphthalene, and confirms our suggestion of the presence of high d value (OOL) lines in aromatic clusters of stack height 15 - 25 A (2,3).

To see the origin of these lines, one may make an analogy between aromatic clusters and the intramolecular order of n-paraffins. In the infinite n-paraffin, polyethylene, the fundamental intramolecular repeat distance is that between the first and third carbons, a distance of about 2.5 Å. As one goes to finite-sized n-paraffins, as n-C₁₀ or n-C₁₂, the fundamental intramolecular repeat distance is the length of the paraffin, and one observes a family of high d value lines obeying the relation $d(L) = \text{constant}/(L)$, in which the constant is either the length of the paraffin or twice the length of the paraffin (2,3). Exactly the same situation exists for our aromatic clusters. For the infinite aromatic stack, graphite, the fundamental stacking repeat distance in an ABAB... arrangement is the AB distance, which is 6.7 Å in graphite, and the most intense observed line is the (002) at 3.35 Å. As one goes to clusters of small stack height, one can observe lines obeying the relation $d(L) = \text{constant}/(L)$, just as in the case of intramolecular order of paraffins. If one insists on indexing the line near 3.4 to 3.6 Å as a "(002)" line, one finds that the values of L for the other lines can be either integers or rational numbers (2,3).

In the diffraction of liquids, the major peaks observed are those arising from intermolecular interference. In the case of paraffins, the single peak observed is the γ -band, arising from interference between approximately parallel paraffin groupings. Ironically, although most discussions of the γ -band occur in the context of petroleum materials, the γ -band obtained its name from a study of coal materials (4). Of course, most coals show a dominant (002) band, arising from the intermolecular interference between aromatic molecules (5).

X-ray diffraction can, of course, be used for liquids more complex than simple paraffins or aromatics. The narrowest diffraction lines, representing the longest correlation lengths, seem to occur with spherically symmetric molecules, such as 1, 3 di-methyl adamantane (2,3) or (+)-longifolene (Aldrich 23,517-2), whose pattern is given in Figure 2. The one dimensional order of aromatic stacking can be seen even for the single ring compound, hexafluoro benzene, as seen in Figure 2. Here, the scattered intensity is increased relative to that of benzene by virtue of the fluorine atoms which are co-planar with the carbon atoms. This "assistance" does not extend to perfluoro decalin, in which case the scattering arising from carbon-carbon, carbon-fluorine, and fluorine-fluorine intermolecular distances is more complex.

What happens when one has molecules containing both sp² and sp³-hybridized carbon? In tetralin, with six aromatic

and four aliphatic carbons, one observes only a broad diffraction envelope, but in n-heptadecyl benzene (six aromatic, seventeen aliphatic) one sees a γ -band much as in liquid n-paraffins (3).

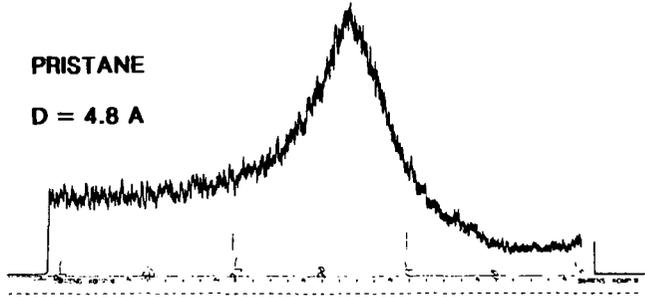
To more systematically study these mixed systems, we have performed reductive alkylation on model aromatic hydrocarbons (6). In the case of perylene, for which we found a potassium consumption of two moles K per mole perylene (7), we quenched with methyl iodide (CD₃I) and actually obtained a crystalline product of di-methyl di-hydro perylene, as illustrated in Figure 3. GC/MS analysis of this product showed 72% to be a single isomer of di-methyl di-hydro perylene (parent peak m/e = 288.2), with perylene itself, a second isomer of di-methyl di-hydro perylene, and a small amount of tri-methyl di-hydro perylene also present. It is likely that the crystallinity of our product is correlated with the dominance of one isomer of di-methyl di-hydro perylene.

References

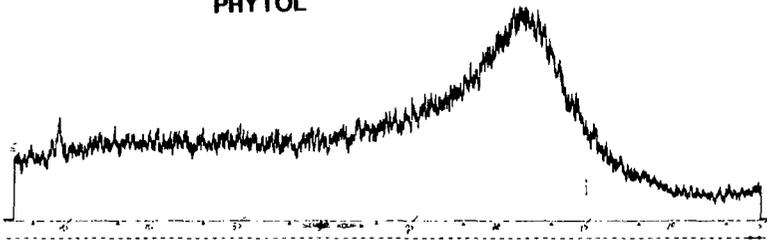
- (1). T. F. Yen, J. G. Erdman, and S. S. Pollack, *Anal. Chem.*, 33, 1587 (1961).
- (2). L. B. Ebert, J. C. Scanlon, and D. R. Mills, *Preprints, Petroleum Division of the American Chemical Society*, 28, 1353 (1983).
- (3). L. B. Ebert, J. C. Scanlon, and D. R. Mills, *Liq. Fuels Tech.*, 2, 257 (1984).
- (4). H. E. Blayden, J. Gibson, and H. L. Riley, *Proceedings of the Conference on the Ultra-fine Structure of Coals and Carbons*, p. 176 (1944).
- (5). P. B. Hirsch, *Proc. Roy. Soc. A*, 226, 143 (1954).
- (6). L. B. Ebert, "Reductive Chemistry of Aromatic Hydrocarbons," in Chemistry of Engine Combustion Deposits, pp. 303-376, Plenum, 1985.
- (7). L. B. Ebert, submitted to Fuel, April, 1985.

PRISTANE

D = 4.8 A



PHYTOL



QUINOLINE

**NOTE THE PRESENCE OF TWO PEAKS
AT 3.9 AND 5.1 A**

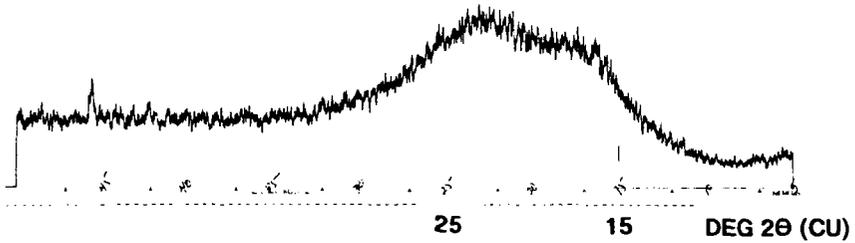


FIGURE 1. XRD OF LIQUIDS.

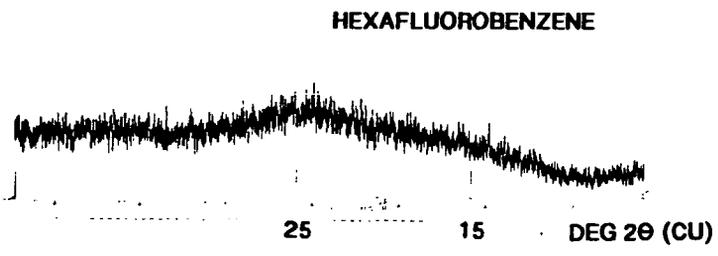
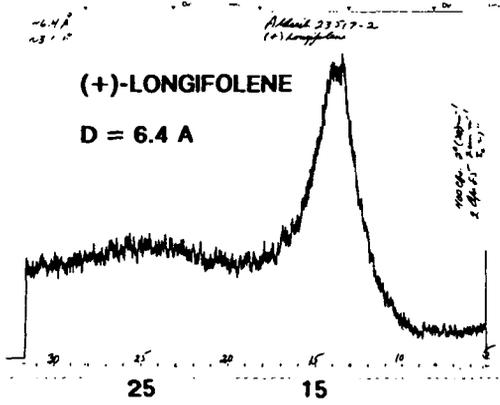
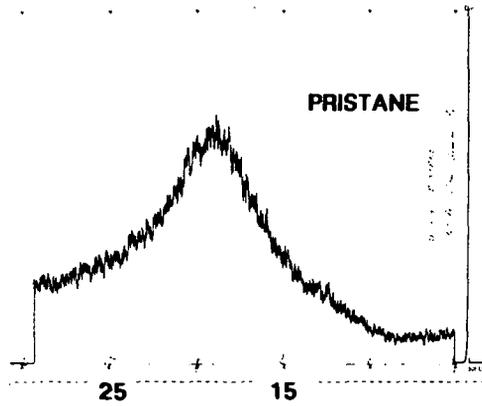


FIGURE 2. XRD OF LIQUIDS.

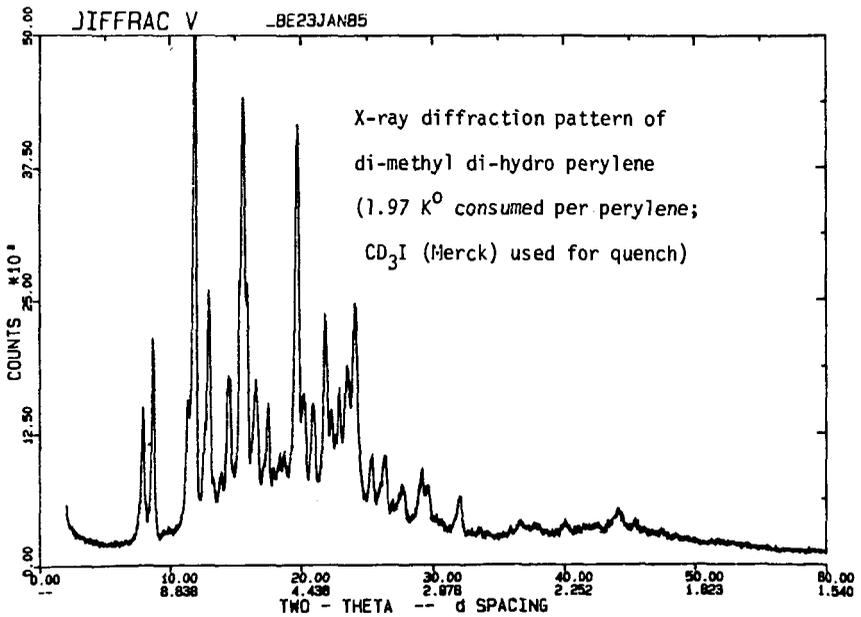
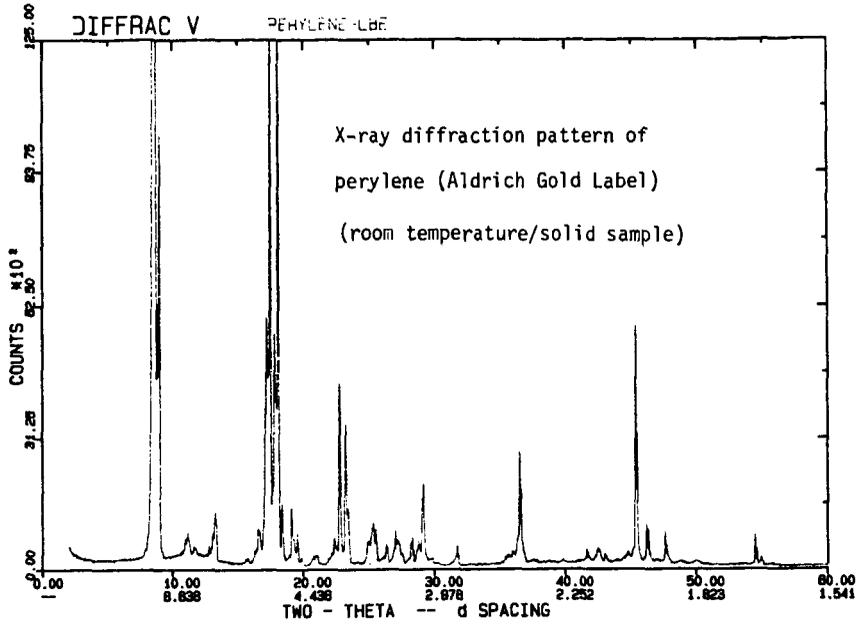


FIGURE 3. XRD OF PERYLENE PRODUCT.