

JOINT DISCUSSION*

MR. E. J. ROSENBAUM.¹—Does not the type of result discussed in these papers require instrumental resolution just about the limit of what is obtainable now?

MR. R. B. WILLIAMS (*author*).—We have been making analytical determinations such as these for about four years, during which time it has been possible steadily to improve the resolution. Certainly, better resolution does help. It helps in minimizing the overlap corrections one must make in quantitatively determining the two types of alkyl groups—groups alpha to the aromatic ring, and other alkyl groups further removed. Although we still do not have all of the potential resolution it is possible to get, better instrumental resolution at the frequency and field strength of present operation (30 Mc per sec and 7 kilogausses) would not help much since these groups in complex mixtures generally have rather broad absorption bands. In principle one would gain by operating at much higher frequency and field since the separation between the bands is proportional to the magnitudes of these factors.

MR. S. GROENNINGS.²—Mr. Williams states that the reliability is about 2 per cent—a very nice figure. This, I presume, is based on work with known mixtures. What is the reliability when working with a real distillate? If it is believed to be the same here, one would have another means of checking the *n*-d-M and similar carbon group analyses.

MR. WILLIAMS.—The paper by S. H. Hastings *et al*³ gives this information. It is possible to cross-check the various methods we have used. We substantiate our belief in the usefulness of the NMR method and in its accuracy by such cross-checks.

MR. J. M. McCREA.⁴—I would like some clarification of the statements concerning resolution of the instrument. I notice that all Mr. Williams' examples show traces taken with an older type recording system. Does he now have a newer system? Would anything be gained by the use of newer recording apparatus (and the associated field stabilizer accessory)?

MR. WILLIAMS.—Since installation of the new Varian Associates' field stabilizer one can scan spectra much more slowly and can take advantage of the larger chart, slower response, and more accurate types of recorders,

* This discussion is a joint discussion of the R. B. Williams paper, "Characterization of Hydrocarbons in Petroleum by Nuclear Magnetic Resonance Spectrometry," and the J. R. Zimmerman and J. A. Lasater paper, "The Influence of Intermolecular Interactions on Nuclear Magnetic Resonance Chemical Shift Measurements as Related to Certain High Molecular Weight Hydrocarbon Systems," (see pp. 168 and 195 of this symposium).

¹ Sun Oil Co., Marcus Hook, Pa.

² Shell Development Co., Emeryville, Calif.

³ S. H. Hastings, B. H. Johnson, H. E. Lumpkin, and R. B. Williams, "Comparison of Structural Group Analyses by Spectrometric and Physical Property Methods," see p. 250, this symposium.

⁴ M. W. Kellogg Co., Jersey City, N. J.

so that areas under the absorption bands may be more easily measured. However, the errors that we now get in measuring relative areas are greater than the errors inherent in the type of recorders that we use and in our technique of measurement. We stand to gain most by learning how to improve our spectrometry to get better absorption measurements. This probably means in part improving spectrometer instrumentation. Under conditions of very high resolution, when area measurements are required to measure absorptions, it is difficult to achieve better than 10 per cent relative accuracy.

MR. R. A. VAN NORDSTRAND.⁵—Does the relaxation time affect the problem in this type of analysis?

MR. WILLIAMS.—The relaxation time (actually there are two kinds, but for our purposes they may be considered equal in magnitude) affects the width of the absorption bands, and very short relaxation times do limit the ultimate resolution one gets in a particular sample. There is a particular relationship between the relaxation time and the amount of radio frequency power with which one irradiates the sample. One must obtain spectra under conditions of non-saturation by this power in order that the areas are accurately proportional to the number of hydrogen nuclei present. We must be careful at all times to insure that we are operating in the nonsaturation region. The difference in relaxation time between liquids and solids is quite substantial, and all high resolution work must be with liquids alone.

MR. VAN NORDSTRAND.—The asphaltenes are rather like solids.

MR. WILLIAMS.—The spectra of all

of our samples, including solids such as asphaltenes, were obtained on blends in liquid solvent. We use carbon disulfide most of the time since it is one of the best solvents and, most important, does not contain any hydrogen itself which would interfere with the desired spectrum.

MR. J. R. ZIMMERMAN (*author*).—There is one point which I would like to clarify related to Mr. Williams' remarks on the use of C¹³ for analytical characterization. In recent months a considerable amount of work has been done by Mr. Lauterbur of Mellon Institute on the study of C¹³ nuclear resonance spectra. He has demonstrated for a number of samples that there is sufficient sensitivity to make relatively accurate indirect spin-spin carbon-hydrogen coupling measurements.⁶

Large samples are used by Lauterbur in his C¹³ analysis. Carbon-hydrogen couplings are considerably greater than the more common hydrogen-hydrogen indirect couplings. Hence, within limits, large samples may be used at the expense of lower resolution (less magnetic field homogeneity over the sample). These early C¹³ nuclear resonance studies are very promising.

MR. WILLIAMS.—The paper by Lauterbur⁶ on determining the chemical shifts of C¹³ in natural abundance gives promise for extending the functional group characterizations of petroleum samples. I am able to detect C¹³ in natural abundance, but with the spectrometer I have to do this, the resolution is not sufficient to show differences in chemical shifts of different compounds.

The magnitude of the chemical shift as a function of the solvent can be used

⁵ Sinclair Research Laboratories, Harvey, Ill.

⁶ Lauterbur, *Journal Chemical Physics*, Vol. 26, pp. 217-218 (1957).

to study molecular association effects in a manner sufficiently different from other methods, that much new information is revealed. Many of the chemical structures which show a strong effect, such as those which undergo hydrogen bonding and some of the aromatic types, also show solvent dependent positions of the absorption bands in the infrared and ultraviolet regions. It might be possible, however, to systematically study all of these effects in the various spectral regions on the same systems and learn much more than by concentrating on one method of observation alone.

MR. ZIMMERMAN.—We have done quite a bit of work on hydrogen bonding of systems which are not hydrocarbons. Very large chemical shifts are observed, for instance, in ethyl alcohol; and many of the other alcohols exhibit very large chemical shifts for the OH hydrogens under "isolation" conditions.

The extent of "isolation" depends on the solvent, of course; and correspondingly, the chemical shift variation depends on the extent of "isolation". An important point arises—namely, what solvent should be used. We would like to think that the solvent used is inert—only then are "isolation" measurements possible. The difficulty in such experiments is to find an inert solvent. I would certainly like to have suggestions pertaining to possible inert solvents. We have not found one to date.

MR. ROSENBAUM.—Solvents are a matter of some importance if careful spectral measurements are to be made. What is coming to the fore is a real problem.

MR. VAN NORDSTRAND.—What about the gas phase? Is that a universal problem?

MR. ZIMMERMAN.—Nuclear magnetic resonance is not a micro-analysis tool. Under sufficiently high pressures, there is the possibility of certain isolation measurements. Also larger samples and better magnets in the future to maintain high resolution over the larger samples may improve the situation.

MR. G. L. BUC.⁷—I notice Mr. Zimmerman's work is done at about 24 C. Will there be any temperature effect at a high enough temperature?

MR. ZIMMERMAN.—If you mean that the external standard may be temperature dependent, the answer is "yes." If you are referring to the temperature dependence of the chemical shifts arising from isolations of aromatics, then such a shift is, at least to first order, independent of temperature. This type of chemical shift arises because of the combination of a magnetic anisotropy of the molecules and asymmetry of approach to the induced magnetic dipoles. Any molecular association which might possibly be related to this chemical shift phenomenon would, of course, be very small compared with association of hydrogen bonding in alcohols. Whereas the alcohol association is temperature dependent with respect to chemical shift values, we have observed no corresponding temperature dependence in aromatic isolation experiments within the accuracy of our chemical shift measurements. This apparent temperature independence suggests that the asymmetry of approach arises from molecular shape rather than association effects.

MR. ROSENBAUM.—In other words, keep the external standard.

MR. VAN NORDSTRAND.—Do mag-

⁷ Fisher Scientific Co., Pittsburgh, Pa.

netic fields change the density, due to association changes?

MR. ZIMMERMAN.—If you are asking whether this induced magnetic dipole can have any influence on the association of the molecules, then the answer is "no."

MR. VAN NORDSTRAND.—You were talking about a magnetic association which changed as you oriented the molecules.

MR. ZIMMERMAN.—A molecule, when placed in a magnetic field, will have certain diamagnetic properties. A molecule like benzene, for example, when placed in a magnetic field does not have the same average induced magnetic dipole values along its molecular axes. In benzene the induced magnetic dipole normal to the plane of the molecule is greater than that induced dipole along the two planar axes. Hence, we say benzene has a diamagnetic anisotropy normal to its plane.

MR. S. S. KURTZ.⁸—Going back to some of the early literature on magnetic effects, I recollect a statement which may or may not be considered correct now. I think it was said that if you had a diamagnetic material put in a strong magnetic field you always got an expansion.

MR. J. MAURIN.⁹—Is the equipment for nuclear magnetic resonance commercially available? What is the size and cost, and possible makes?

MR. WILLIAMS.—It is available commercially from Varian Associates and from Nuclear Magnetics Corp. The latter has not marketed a high resolution instrument. Specifications and prices may be obtained from these companies.

MR. J. K. FOGO.¹⁰—Mr. Williams'

naphthenicity-BI correlation is apparently independent of the *n*-paraffin - isoparaffin ratio of the samples analyzed. What are the reasons for this and what is the reliability of assuming this to be true for all samples?

MR. WILLIAMS.—The beauty of any correlation is that one may use it without understanding it. However, the reason for the validity of the present correlation is probably because the paraffins consist mostly of normal paraffins and lightly branched isoparaffins, and most of the branching (concentration of methyl groups) is on the naphthenes. The other possibility is that when naphthenes exist in high concentration the isoparaffin concentration is also very high. There seems to be no strong evidence for the latter. However, it is known from individual component analyses in the gasoline range that naphthenes do tend to be highly methylated and the concentration of branchy isoparaffins—for example the trimethylpentanes—is low in comparison with other isomers.

MR. F. P. HOCHGESANG.¹¹—Is there any possibility that the NMR technique may be able to determine olefins at the concentration at which they may be present in crude petroleum?

MR. WILLIAMS.—Very little. What we examined was a very highly concentrated fraction. For a 1 per cent concentration of a C₂₀ olefin the concentration of olefinic hydrogen would be only about 0.05 per cent of the total. Roughly 10 per cent of olefin would be required for detection by present high resolution techniques.

MR. H. F. HITCHCOX.¹²—For waxes

⁸ Sun Oil Co., Marcus Hook, Pa.
⁹ Brookhaven National Laboratory, Upton, L. I., N. Y.

¹⁰ Union Oil Company of California, Brea, Calif.

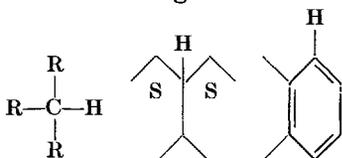
¹¹ Socony Mobil Oil Co., Inc., Research and Development Laboratories, Paulsboro, N. J.

¹² Esso Research and Engineering Co., Linden, N. J.

from residual fractions (assume it contains only paraffins, isoparaffins, and both single and condensed ring naphthenes), can analysis by NMR be made satisfactorily on the whole wax? If not, what type separations are recommended?

MR. WILLIAMS.—I believe the branchiness index correlation should hold for waxes also. In the few we have examined those which were hard, probably because of a preponderance of normal paraffins had lower branchiness indices than those which were soft. In fact, for any series of saturate fractions of comparable molecular weight, the branchiness index correlates with the fluidity. Of course, physical separations of the component types will always provide additional information. The thermal diffusion method is perhaps one of the better ones for this separation

MR. S. MIRON.¹³—Is NMR able to differentiate between tertiary hydrogen atoms attached to alkyl carbon atoms and ring carbon atoms? Specifically, can NMR differentiate between the following:



MR. WILLIAMS.—In a completely aliphatic system the tertiary hydrogen is always in such low concentration relative to the other types that its characteristic location, if there is one, is masked by the large overlap of the methyl and methylene bands. The exact position may also be sensitive to the types of neighboring groups. When the tertiary group is attached to an aromatic ring, an olefinic group,

or a hetero atom, however, it is shifted in position and there is a characteristic hyperfine splitting which identifies the group provided the contribution from interfering bands of other aliphatic groups is not too great.

MR. J. HERMAN.¹⁴—If I understand correctly, one NMR paper indicated that naphthenic hydrocarbons in petroleum are highly branched, whereas the paper on mass spectrometry indicated a long paraffin chain with the ring structure at one end of the chain. Is there a basic difference in these two interpretations?

MR. E. G. CARLSON.¹⁵—The simplified picture which we have suggested is based on mass spectral observations made over a long period of time. The evidence is based to a considerable extent on our experience with aromatics. Although the picture seems most clear for aromatics, we feel that it holds reasonably well for naphthenes, especially those having a small number of rings per molecule. For naphthenes containing a larger number of rings, we have had to lean heavily on what we found for the aromatic rings. This is because there just are not enough calibration compounds of the polycyclic saturate types.

MR. WILLIAMS.—I had the impression that the mass spectrometer data did not rule out the possibility of branchy naphthenes, but just the contrary. The definition of branchiness we use is essentially the ratio of methyl to methylene hydrogens. It is possible for a naphthene ring to be highly substituted with methyl groups plus also a single long chain and still have a high branchiness index.

¹⁴ Socony Mobil Oil Co., Inc., Paulsboro, N. J.

¹⁵ Shell Oil Co., Houston Research Laboratory, Houston, Tex.

¹³ American Oil Co., Texas City, Tex.

MR. F. W. MELPOLDER.¹⁶—I would like to clarify one angle here. We have talked about molecular structures of the naphthenes without adequately defining the type of fraction in terms of wax or oil. I can visualize that both arguments can be correct.

For example, waxes can have a naphthenic content as high as 15 per cent. In order to have a high melting point, the naphthenes must have long straight chains. Likewise, oils with low pour points might well contain naphthenes with highly branched chains.

MR. KURTZ.—On this whole problem of the length of side-chains and the amount of short chain in these complex molecules, I think that it is only going to be a short time—a few years at least—before a study of viscosity will straighten us out. I think if we have some good work on viscosity in relation to molecular weight and number of rings we will very soon find out which molecules have long chains, and which ones have a multiplicity of short chains, because I am sure the viscosity characteristics will be different.

MR. B. A. ORKIN.¹⁷—My comments will refer to aromatics. We spent very little time with the non-aromatics or the saturate portion of the oil. To refer to Mr. Carlson's comments, he said he has the feeling that aromatics contain only 1 long chain and several very short chains. We have some evidence that does not agree with that.

I refer to the fraction 5 or the least aromatic portion. That had an average carbon number of 30. It was for the most part 1 and 2 ring structures. If you take a maximum of 10 for the

rings, 20 remaining carbon atoms are in the side chains. If there is only one long side chain, as Mr. Carlson states, then it would have 14 to 17 carbon atoms. From pure compound data, we would expect a viscosity index greater than 100. Actually, we found a viscosity index of only 60.

We feel that that fraction was composed of benzene ring and maybe tetralin or indane with several side chains of 5, 6, or 7 carbons.

Another comment by Mr. Carlson was the feeling that aromatics did not contain any rings that were not fused. In our fraction 2, (the most polar) the mass spectrometer analysis showed a sizeable -6 class. Because of the separation we believe there could not have been any alkyl benzene as such in that fraction; they must have been in the mass spectrometer as fragments.

MR. WILLIAMS.—We are not too concerned about whether the aromatic nuclei are joined directly to each other or are separated by aliphatic chains, since we make calculations based on both possibilities and the total rings per molecule from the two calculations deviate by no more than 10 per cent for the heaviest petroleum fractions (asphalt) and much less for the lighter ones. We do know that aromatic rings are rather highly substituted, to the extent of about 40 to 50 per cent in most virgin stocks. In materials where side chains are expected to be removed by processing, such as in catalytic cycle stocks produced in catalytic cracking, we find that the substitution drops to about 30 per cent for this particular example.

MR. CARLSON.—I think that differences of opinion are generally healthy; however, the discrepancy be-

¹⁶ The Atlantic Refining Co., Philadelphia, Pa.

¹⁷ Socony Mobil Oil Co., Inc., Paulsboro, N. J.

tween mass spectrometry and nuclear magnetic resonance is more apparent than real. Since the term "highly branched" refers to the methyl-methylene ratio or branchiness index of NMR, the NMR data can be interpreted as being consistent with the following structure suggested by mass spectrometry. The typical naphthene nucleus appears to contain a number of methyl (and possibly ethyl) side chains. These account for the high degree of substitution and for the large number of methyl groups found by NMR. From mass spectral evidence, one chain however contains the necessary methylene

groups required to bring the structure up to the observed molecular weight. Further information will be needed to establish the nature of this long chain—for example, the extent of branching along the chain. Perhaps physical property correlations may help here when pure compounds become available.

MR. ROSENBAUM.—It is interesting to me that this symposium, which presumably is dealing with the limit of our knowledge of the composition of petroleum oils, has touched closely on the limit of our knowledge of the actual phenomena taking place in this process of nuclear magnetic resonance.