versity for the n.m.r. spectra and for assistance in the interpretation of the n.m.r. spectra.

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HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE SPECTRA OF VARIOUS POLYISOPRENES

Sir:

There has been some controversy recently as to whether hevea and balata (or gutta-percha) macromolecules comprise 100% 1,4 units, or whether they are predominantly *cis* and *trans* structures, respectively, with minor amounts of isopropenyl or 3,4 units. Binder[1] contends, on the basis of a small absorption peak at 11.25 μ in the infrared spectrum of each of these polymers, that the hevea and balata macromolecules contain 2.2 and 1.3% 3,4 units, respectively. This has been disputed by Fraga[2] who showed that there was no evidence for isopropenyl groups in the near infrared spectra; he therefore concluded that the natural polyisoprenes are essentially pure 1,4-type polymers. Another interesting question which has never been resolved is whether the 1,4 units in hevea (or balata) are exclusively *cis* (or *trans*) or whether these polymers contain a small amount of the opposite isomer as an impurity. Recent developments in high resolution n.m.r. work on polymers,[3] and in particular, the application of n.m.r. to an analysis of butadiene–isoprene copolymer compositions,[4] have prompted us to examine these questions with the aid of this tool. The present communication reports the results of an investigation of hevea and balata microstructure using a Varian high resolution 100 Mc. n.m.r. spectrometer as well as a Mnemotron Computer of Average Transients (C.A.T.) attached to a Varian A-60 spectrometer.

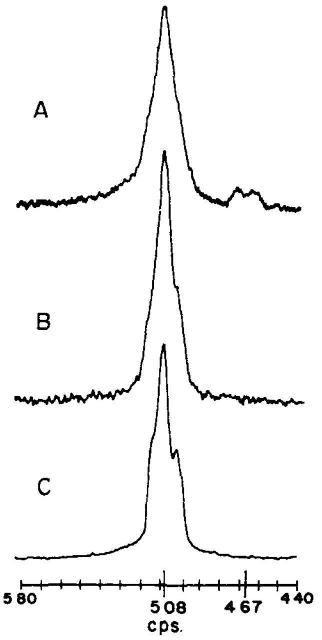

Fig. 1.—Proton n.m.r. spectra of various polyisoprenes at 100 Mc. in the olefinic proton region: (A) synthetic *cis;* (B) natural *cis* or hevea; and (C) natural *trans* or balata.

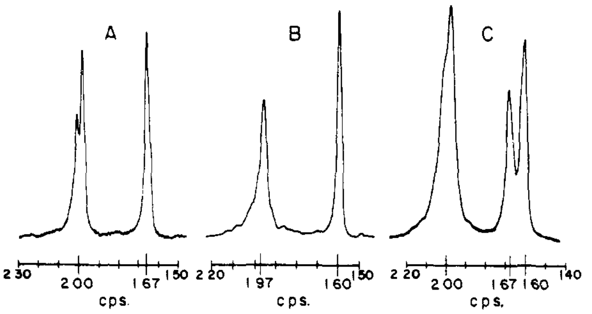

Fig. 2.—Proton n.m.r. spectra of natural *cis* (A) and natural *trans* (B) polyisoprenes and an isomerized polyisoprene (C) at 100 Mc. The peaks around 200 c.p.s. correspond to methylene protons while the 167 and 160 c.p.s. peaks correspond to methyl protons on *cis* and *trans* double bonds.

The broad resonance at 508 c.p.s. (4.92 τ) in the 100 Mc. spectra of hevea, balata and a synthetic *cis* polyisoprene[5,6] (Fig. 1) undoubtedly corresponds to —C(CH$_3$)=C*H*— protons while the doublet at 467 c.p.s. (5.33 τ) (Fig. 1A) corresponds to $>$C =C*H*$_2$ protons. The ratio of areas for these two kinds of protons in the synthetic polymer, *viz.*, 10.9, indicates that this polymer contains 4.4% 3,4 units, which agrees with the value from infrared analysis.[6] The important thing to note, however, is that there is no evidence for any 3,4 units in the n.m.r. spectra of the natural polyisoprenes (Figs. 1B and 1C). This was confirmed by detailed examination of the olefinic proton resonance obtained with the C.A.T.which afforded spectra with considerably greater signal-to-noise ratio than that shown in Fig. 1. Thus, from an analysis of the spectrum of a 9:1 balata-synthetic *cis* polyisoprene mixture, the minimum isopropenyl content which could be detected with the C.A.T. was found to be about 0.3% of the monomer units. Moreover, the corresponding spectra of hevea and balata showed even less than this amount. This finding thus corroborates the conclusions reached by Fraga.[2]

It is seen in Fig. 2 that the methyl proton resonances in the *cis* and *trans* polyisoprenes occur at

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[1] J. L. Binder, *Rubber Chem. and Technol.*, **35**, 57 (1962); J. L. Binder and H. C. Ransaw, *Anal. Chem.*, **29**, 503 (1957).

[2] D. W. Fraga, *J. Polymer Sci.*, **41**, 522 (1959).

[3] F. A. Bovey and G. V. D. Tiers, paper presented at the 142nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962, Polymer Division Preprint Booklet, p. 115*, and references therein.

[4] H. Y. Chen, *Anal. Chem.*, **34**, 1134 (1962).

[5] The spectra in Figs. 1 and 2 were obtained at room temperature on CCl$_4$ solutions containing 1% tetramethylsilane as internal standard. The polymer concentrations ranged from about 2% in the high *cis* solutions to about 10% in the high *trans* solutions.

[6] Hevea and balata were obtained through the courtesy of J. J. Shipman, The B. F. Goodrich Company Research Center, Brecksville, Ohio. The synthetic polyisoprene was obtained from Shell Chemicals Company, Torrance, California, and was considered to have 4.7% 3,4 content based on infrared analysis.

167 and 160 c.p.s. (8.33 and 8.40 τ), respectively.[7] The corresponding peaks in a "copolymer"[8] of *cis* and *trans* $-\mathrm{C(CH_3)}=\mathrm{CH}-$ units are clearly separated. This immediately suggests a new method for determining the *cis/trans* ratio in any synthetic polyisoprene by measuring the relative areas of the two peaks; this method has been found to be more accurate than the methods based on infrared analysis.[10] Thus, for example, the "copolymer" shown in Fig. 2C has a *cis/trans* ratio of 47/53 which is certainly a more reliable value than that reported previously[9] (50/50 to 60/40) for this type of polymer.

Careful examination of the 100 Mc. spectra of various synthetic mixtures of polyisoprene in the methyl region showed that the minimum detectable *cis* content in an otherwise all-*trans* polyisoprene, and *vice versa*, was about 1%. It was thus possible to ascertain that hevea and balata both contained less than this amount of the opposite isomeric form. Thus, not only are the natural polyisoprenes essentially 100% 1,4 structures but also the double bonds in hevea and balata are at least 99% *cis* or 99% *trans*, respectively. It is important to point out that this last conclusion could not have been obtained from infrared since there is no way of knowing *a priori* what the spectrum of a truly 100% *cis* or 100% *trans* polyisoprene would look like.

The authors wish to express their thanks to Mr. W. R. Anderson, Jr., who ran the Varian HR-60 n.m.r. spectra of the various polyisoprenes, which suggested corresponding work at 100 Mc.

[7] Similarly, in the n.m.r. spectrum of squalene the resonance of the terminal *cis* methyls occurs at 167 c.p.s. and that of both the terminal and internal *trans* methyls occurs at 160 c.p.s., which is at higher field due to shielding by an additional adjacent methylene in the latter case.

[8] A sample of Shell *cis*-polyisoprene which was isomerized with selenium to an equilibrium *cis–trans* structure according to the method of Golub.[9]

[9] M. A. Golub, *J. Polymer Sci.*, **36**, 523 (1959).

[10] In addition to the infrared method of Binder and Ransaw,[1] there are also those of J. I. Cunneen, G. M. C. Higgins and W. F. Watson, *ibid.*, **40**, 1 (1959), and of P. J. Corish, *Spectrochim. Acta*, **11**, 598 (1959). The agreement obtained between the measured *cis* (or *trans*) content in various synthetic mixtures of hevea and balata and the predetermined values for the isomer composition of these mixtures was better with the n.m.r. method than with those based on infrared. The former method also could be followed with the 60 Mc. spectrometer, but the separation of the peaks is not as good as with the 100 Mc. instrument.

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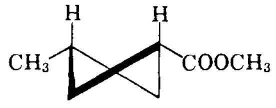
CONFORMATIONAL ANALYSIS. XXXVI. SOME CONSEQUENCES OF THE NON-PLANARITY OF CYCLOBUTANE AND CYCLOBUTANONE RINGS[1,2]

Sir:

While three-membered rings are necessarily planar, every larger saturated carbocyclic ring so far studied appears to be non-planar. Spectroscopic and thermodynamic studies have shown that cyclobutane itself is non-planar,[3] and a similar suggestion has been made regarding cyclobutanone.[4] The objects of the present work were to ascertain whether or not cyclobutanone actually showed a significant deviation from planarity, and second to determine whether unexpected physical and chemical properties might result from the non-planarity of cyclobutane and cyclobutanone systems.

The implication of non-planarity with regard to its effects on the relative stabilities of geometric isomers of the saturated ring system was considered first. If the cyclobutane ring were planar, it seems reasonable that a 1,3-disubstituted derivative would be more stable in the *trans* form than in the *cis*. A puckered structure (I), on the other hand, would suggest that a *cis* isomer would be more nearly "diequatorial," and might well be thermodynamically more stable, particularly if the substituents are different (so as not to cause an entropy loss in the *cis* form from symmetry) and at least one is non-polar.



I

Methyl 3-methylcyclobutane carboxylate (I) was prepared from the reaction of malonic ester with 1-chloro-3-bromo-2-methylpropane, and was obtained as a mixture of two isomers, b.p. 146–147°, which showed two peaks on vapor phase chromatography on Tide (retention times 36 and 40 minutes at 44°). Equilibration of the ester with sodium methoxide in methanol (65°) gave an equilibrium constant of 1.6 ± 0.2 favoring the *cis* isomer. The *cis* isomer was prepared independently from the cyclic anhydride of *cis*-1,3-cyclobutanedicarboxylic acid[5,6] by ring opening with methanol[7] to give the half acid ester, then diborane reduction[8] to give methyl 3-hydroxymethylcyclobutanecarboxylate. The latter was treated with phosphorus tribromide[9] to yield the bromo-ester, which was reduced to I with zinc and water. This compound gave one peak on gas chromatography identical in retention time with the major peak found in the equilibrium mixture. Assignments of structure by the application of von Auwers' rule[10] to cyclobutane derivatives (such as made earlier for the 1,3-dimethylcyclobutanes[11]) therefore become questionable. The Conformational Rule[12] cannot be applied with

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[1] Paper XXXV, N. L. Allinger, M. A. DaRooge, M. A. Miller, and B. Waegell, *J. Org. Chem.*, **28**, in press (1963).

[2] This research was supported in part by the U. S. Army Research Office.

[3] (a) J. D. Dunitz and V. Schomaker, *J. Chem. Phys.*, **20**, 1703 (1952); (b) G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn, and K. S. Pitzer, *J. Am. Chem. Soc.*, **75**, 5634 (1953); (c) A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

[4] R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1215 (1960).

[5] D. H. Deutsch and E. R. Buchman, Abstracts, 119th Meeting of the American Chemical Society, Boston, 1951, p. 35-M.

[6] The authors are indebted to Dr. E. R. Buchman and Dr. K. Wiberg for samples of this compound and helpful correspondence regarding its preparation.

[7] J. Cason, "Organic Syntheses," Col. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 169.

[8] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

[9] A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955).

[10] K. von Auwers, *Ann.*, **420**, 84 (1920).

[11] A. Kazanskii and M. Y. Lukina, *Doklady Akad. Nauk. S.S.S.R.*, **65**, 693 (1949); *C. A.*, **45**, 2878 (1951).