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* —C(CH_3)=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.

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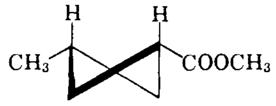
CONFORMATIONAL ANALYSIS. XXXVI. SOME CONSEQUENCES OF THE NON-PLANARITY OF CYCLOBUTANE AND CYCLOBUTANONE RINGS[1,2]

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).

any degree of certainty to such systems, so that other methods are required for the establishment of geometric relationships.

The question of planarity is less obvious *a priori* in the case of cyclobutanone. Here, compared to the saturated hydrocarbon, the planar form is more stable since the number of eclipsed ethane structures is only two instead of four, and the non-planar form is destabilized by the increased angular strain brought about by the presence of a trigonal ring atom. The result of these effects was examined by an investigation of 2-bromocyclobutanone, obtained by bromination of cyclobutanone. The 2-bromo ketones are a well-studied class of compounds against which all kinds of physical techniques have been brought to bear.[13,14] One of the most useful of such measurements has been dipole moments,[13] which was also employed here. From the known group moments of the carbonyl[15] and the C–Br bond,[16] the moment of 2-bromo-cyclobutanone was calculated assuming a planar ring[17] as 3.43 *D*. The experimental moment in heptane was 3.21 *D*, indicating that the bromine was a little more axial-like than predicted for a planar form. If it is assumed that this moment corresponds to a single axial conformation,[18] the angle between the dipoles can be calculated to be 101°. This fixes also the angle between the dipoles for the corresponding equatorial conformation at 69°, and gives a calculated moment for the latter of 3.85 *D*.

If the bromine is in fact very largely axial in heptane, it would be expected that some of the equatorial form could be detected as the solvent polarity was increased.[19] The observed moment was in fact greater in benzene (3.23 *D*) and in dioxane (3.45 *D*), indicating a mole fraction of the equatorial form which increases to about 0.4 in dioxane.[20] It seemed likely that confirmation of these values could be found in the ultraviolet and infrared spectra, and such was found to be the case (Table I). The increases of the carbonyl stretching frequency were from 3 to 21 cm.$^{-1}$ as the solvent was changed from cyclohexane to dimethyl sulfoxide, which may be compared to +4 cm.$^{-1}$ for an axial and +15 cm.$^{-1}$ for an equatorial halogen in the 2-bromo-4-*t*-butyl-cyclohexanones.[21] Similarly, the shifts of the ultraviolet maxima range from +36 to +21 mμ in cyclohexane and ethanol, compared to about +25 to +20 mμ in the six-membered ring. The extinction coefficients in the ultraviolet are quite large in each case (120 to 180), indicating the presence of a substantial amount of axial form even in the polar solvents.

TABLE I

CARBONYL SHIFTS IN THE INFRARED AND ULTRAVIOLET OF 2-BROMOCYCLOBUTANONE RELATIVE TO CYCLOBUTANONE

Solvent	Infrared $+\Delta_{C=O}$ (cm.$^{-1}$)	$+\Delta\lambda$ (mμ)	$+\Delta$
Cyclohexane	3[a]	36	170
Dioxane	18	20	120
Alcohol[b]	20	21	180
Dimethyl sulfoxide	21	..	..
Neat	20	..	..

[a] Determined at a concentration of about 0.5%; if 10% concentration used, Δ was 13 cm.$^{-1}$. [b] Methanol was used for the infrared measurements, ethanol for the ultraviolet.

A cursory glance was given to the feasibility of calculating the equilibrium point of the ring bending, but using ordinary values for bending and torsional constants[22]; this did not seem possible. The difficulty appeared to be in the fact that the bending constants acceptable for small degrees of angular distortion are poor approximations for an ordinary planar cyclobutane ring, and are useless for predicting how such a structure will further bend.

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(12) (a) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957); (b) H. van Bekkum, A. VanVeen, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **80**, 1310 (1961).

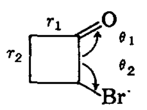
(13) For a compilation of leading references, see N. L. Allinger and H. M. Blatter, *J. Org. Chem.*, **27**, 1523 (1962).

(14) For a chemical and spectroscopic study of the halogenated cyclobutanones in general, see J. M. Conia and J. L. Ripoll, *Bull. Soc. Chim. France*, in press.

(15) R. Arndt, H. H. Günthard and T. Gäumann, *Helv. Chim. Acta*, **41**, 2213 (1958).

(16) The resultant moments calculated here employ as bond noments for C=O and C–Br, 2.76 and 2.24 *D*, except for the equatorial orm where 2.63 and 2.04 *D* were used to allow for induction (ref. 17).

(17) The structure assumed was



θ_1 132.5°
θ_2 113.2°
r_1 1.50 Å.
r_2 1.545 Å.

(18) This seems like a good approximation from the infrared data in Table I.

(19) J. Allinger, and N. L. Allinger *Tetrahedron*, **2**, 64 (1958).

(20) The change in dipole moment with solvent found here is similar to that found in the 2-bromocyclopentanones and 2-bromocyclohexanones (see W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956)).

(21) N. L. Allinger and J. Allinger, *ibid.*, **80**, 5476 (1958).

(22) F. H. Westheimer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

(23) Correspondence should be directed to this author.

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PHOTOSENSITIZED *CIS-TRANS* ISOMERIZATION OF THE STILBENES[1]

Sir:

The *cis-trans* isomerization of the stilbenes under the influence of ultraviolet light has been studied by several groups.[2,3,4,5,6] The results are confusing to say the least. The quantum yields for both the *cis-trans* and *trans-cis* processes are close to temperature independent at moderate temperatures but become strongly temperature dependent below about −70°.[3,4] A corresponding temperature effect is observed on the relative yield of fluores-

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(1) Mechanism of Photoreactions in Solution. XII. Part XI is N. J. Turro and G. S. Hammond, *J. Am. Chem. Soc.*, **84**, 2841 (1962).

(2) G. N. Lewis, T. T. Magel and D. Lipkin, *ibid.*, **62** 2973 (1940).

(3) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(4) S. Malkin and E. Fischer, "Symposium on Reversible Photochemical Processes," Durham, N. C., April, 1962, symposium papers, p. 281.

(5) D. Schulte-Frohlinde, *ibid.*, p. 295.

(6) H. Stegemeyer, *J. Phys. Chem.*, to be published.