Grenzfälle $\alpha = \beta$, $\alpha = \alpha^*$ sich in leicht durchschaubarer Art anschliessen, darf man behaupten, dass ein Kegelstumpf-Kegel, welcher der Bedingung $\beta < \alpha \leqslant \alpha^*$ genügt, nicht extremal sein kann[1].

Dasselbe gilt aber auch für irgendeinen zulässigen *Doppelkegelstumpf*, ist er doch Mitglied einer einparametrigen Körperschar mit den Randkörpern *Kegelstumpfkegel* und *Kegelstumpf* [vgl. Abb. 6 sowie (2)].

Schliesslich deformieren wir in passender Weise einen *Dreifachkegelstumpf* (Abb. 7). Wieder berechnet man:

$$a = \frac{\cos\beta}{1-\cos\beta} - 2\operatorname{cotg}\beta\ \frac{\sin\alpha}{1-\cos\alpha} + \frac{\cos\alpha}{1-\cos\alpha}\cdot \quad (3a)$$

Ist nun die Bedingung $\gamma < \beta < \alpha \leqslant \alpha^*$ erfüllt, wobei *zur* Berechnung von α^* in (4) β durch γ *zu* ersetzen ist, so ist nach früheren Ausführungen die ganze Körperschar nicht extremal.

Das Verfahren lässt sich sinngemäss auf Mehrfachkegelstümpfe mit beliebig vielen Gliedern anwenden, und man sieht, dass die ganze Klasse $\mathfrak{K}_1^{**}$ nicht extremal sein kann. Damit ist der Beweis fertig.

Es besteht die Vermutung, dass die Kegel in der vollen Klasse der konvexen Rotationskörper von fester Länge l extremal sind, das heisst, dass sie bei vorgegebenem M kleinstes F aufweisen. Wäre diese Eigenschaft gesichert, so würde man im Hauptproblem der konvexen Rotationskörper einen gehörigen Schritt vorankommen. Der Beweis der genannten Eigenschaft dürfte aber sehr schwierig sein.

H. BIERI

Bern, den 6. Januar 1953.

Summary

The problem is given to find those rotatory bodies of the fixed length l, which possess, for a given value of M, the least surface F. If we limit the admitted bodies to two well-defined subclasses $\mathfrak{K}_1^{*}$ and $\mathfrak{K}_1^{**}$, the quality mentioned belongs to the cones only. It is supposed that the cones in the whole class of the convex rotatory bodies of the fixed length l are extremal.

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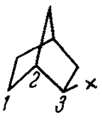
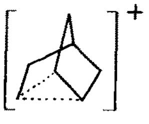
[1] Die Bedingung besagt anschaulich, dass aufeinanderfolgende Kantenwinkel nicht zu stark differieren dürfen!

The Driving Force for Formation of Non-Classical Ions

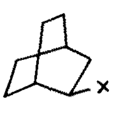
The elegant work of WINSTEIN and TRIFAN[1], and of ROBERTS and coworkers[2] on the solvolysis of norbornyl derivatives ($X = \mathrm{Br}$, Cl, $\mathrm{OSO_2C_6H_4Br}$-p) has demonstrated the existence of the nonclassical ion (II).



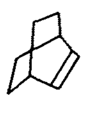
I



II

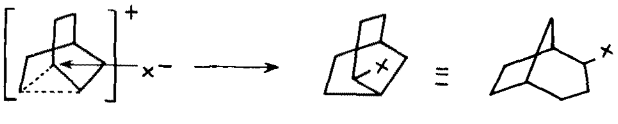


III



IV

This work prompted the investigation of the analogous bicyclo(2.2.2.)octane derivatives (III). This system was chosen because the geometry of the three carbon system is essentially identical with that of the norbornyl system; the critical difference between the two systems being that (I) is a strained molecule and (III) is strainless. This can readily be demonstrated by attempting to make a model of (I). The bicyclooctane system has a further advantage in that if rearrangement via a non-classical ion occurs, a different bicyclic system will be formed: bicyclo(1.2.3.)octane.



Attempts to demonstrate the existence or non-existence of the non-classical ion were undertaken in the following ways: by the addition of unsymmetrical reagents (HX, $X = \mathrm{Br}$, Cl, acetoxy, and thioacetoxy) to bicyclo(2.2.2.)octane-2 (IV), and by the solvolysis of (III) ($X = \mathrm{Br}$, Cl, and $\mathrm{OSO_2C_6H_4Br}$-p).

In all cases of addition, no rearrangement of the carbon skeleton was observed. The addition of hydrogen bromide in the presence of benzoylperoxyde gave the corresponding 2-bromobicyclo(2.2.2.)octane[1], the addition of gaseous hydrogen chloride yielded 2-chlorobicyclo(2.2.2.)octane, m.p. 110–112°.

Analysis: Cal*culated* for $\mathrm{C_8H_{13}Cl}$: C, 66·43; H, 9·05; Cl, 24·52. Found: C, 66·47; H, 9·04; Cl, 24·47.

Reduction of the chloride with sodium and alcohol produced bicyclo(2.2.2.)octane, m.p. 166–168° identical with a sample obtained by hydrogenation of (IV). Thioacetic acid[2] gave the thioacetate, b.p. 101–102° at 2 mm, n_D^{24} 1·5209.

Analysis: Calculated for $\mathrm{C_{10}H_{16}OS}$: C, 65·2; H, 8·8. Found: C, 64·8; H, 8·4.

Desulfurization of the thioacetate with Raney-nickel gave saturated (IV), m.p. 168–171°. The addition of acetic acid in the presence of p-toluenesulfonic acid yielded the corresponding acetoxy compound, which was reduced with lithium aluminum hydride to the known alcohol[3], m.p. 212–214°, phenylurethane, m.p. 135–137°, p-nitrobenzoate, m.p. 97–98°.

Analysis: Calculated for $\mathrm{C_{16}H_{17}O_4N}$: C, 65·43; H, 6·22; N, 5·08. Found: C, 65·47; H, 6·24; N, 5·11.

p-Bromobenzenesulphonate, m.p. 80–82°.

Analysis: Calculated for $\mathrm{C_{14}H_{17}O_3SBr}$: C, 48·66; H, 4·96; S, 9·28. Found: C, 48·50; H, 4·96; S, 9·28.

The p-bromobenzenesulphonate ester was reduced with lithium aluminum hydride to yield bicyclo(2.2.2.)octane, m.p. 160–162°[4].

It has, therefore, been demonstrated that whether the addition goes by way of a free radical mechanism (HBr and thioacetic acid) or by an ionic mechanism (HCl and acetic acid) the reactions proceed without rearrangement of the carbon skeleton.

When III ($X = \mathrm{Cl}$, Br, and $\mathrm{OSO_2C_6H_4Br}$-p) was subjected to solvolysis by treatment with aqueous lithium carbonate, the product isolated was bicyclo(2.2.2.)octane-2-ol, m.p. 212–214°. DOERING[5] has shown

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[1] S. WINSTEIN and D. TRIFAN, J. Amer. Chem. Soc. *74*, 1147 (1952).

[2] J. D. ROBERTS *et al.*, J. Amer. Chem. Soc. *72*, 3116, 3329 (1950); *73*, 5009 (1951).

[1] W. VON DOERING and M. FARBER, J. Amer. Chem. Soc. *71*, 1514 (1949).

[2] H. BADER, L. C. CROSS, I. HEILBRON, and E. R. H. JONES, J. Chem. Soc. *1949*, 621.

[3] G. KOMMPA, Ber. dtsch. chem. Ges. *68*, 1267 (1935).

[4] The low m.p. is probably due to a slight impurity, since these substances have large cryoscopic constants. See: M. S. NEWMAN and Y. T. YU, J. Amer. Chem. Soc. *74*, 507 (1952).

[5] Private communication from Prof. W. VON DOERING.

that treatment of 2-aminobicyclo(2.2.2.)octane with nitrous acid also gives the same alcohol[2].

It seems, therefore, that the formation of a non-classical ion which leads to rearrangement is unique to systems which are strained. Since the geometry of both systems is essentially identical, the only difference being that (I) is strained and (III) is strainless, the driving force for the formation of the non-classical ion would seem to be mainly due to the relief of strain in going to the ion.

Although Newman[3] in the hydration of (IV) obtained the rearranged alcohol, bicyclo(1.2.3.)octan-2-ol, and Doering[4] the bicyclo(1.2.3.)octan-2-bromide by treating (III) (X = Br) with silver bromide, it should be pointed out that in the cases reported here, the ion has a short lifetime. Apparently, when the ion has a longer lifetime, as in the cases of Newman and Doering, rearrangement will occur. However, under the identical solvolysis conditions that were employed here, the norbornyl derivatives underwent rearrangement[5].

The rate of solvolysis of bicyclo(2.2.2.)octyl-2-p-bromobenzenesulfonate, and its comparison with cyclohexyl p-bromobenzenesulfonate, will give quantitative measure of the driving force and determine the amount, if any, of carbon participation. These experiments will shortly be undertaken in these laboratories.

H. M. Walborsky[6]

Department of Chemistry of the Florida State University Tallahassee, Fla., March 16, 1953.

Zusammenfassung

Es wird vorgeschlagen, dass die Bildung nicht-klassischer Ionen ein Merkmal gespannter Systeme darstellt. Nach dieser Auffassung stellt die Entspannung, welche die Bildung des Ions begleitet, die treibende Kraft seiner Bildung dar.

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[2] K. Alder and G. Stein, Ann. Chem. *514*, 211 (1934).

[3] The low m.p. is probably due to a slight impurity, since these substances have large cryoscopic constants. See: M. S. Newman and Y. T. Yu, J. Amer. Chem. Soc. *74*, 507 (1952).

[4] W. von Doering and M. Farber, J. Amer. Chem. Soc. *71*, 1514 (1949).

[5] J. D. Roberts *et al.*, loc. cit.

[6] Present address: Institute for organic Chemistry, University of Basle.

Isolated Chromosomes and Casual Contaminants in Electron Microscopy[1]

Chromosomes, bacterial cells, and fungal filaments may often display similar size and shape and banded or helical internal structure. Careful controls are therefore needed to assure their clear discrimination in the electron microscope. This need has recently been emphasized by the publication of some micrographs[2] identified as isolated chromosomes but resembling certain casual contaminants.

Such internal structure in a contaminant is beautifully illustrated by the object encountered several years ago by Robley C. Williams (Fig. 1), determined to be a bacterial contaminant of distilled water. This measures 1/6 by $3{\cdot}8\ \mu$ and shows a helical pitch of $1/6\ \mu$ per gyre. Rather similar and smaller structures have been reported for some soaps and greases[1].

Against this background, one of us (A.R.T.D.), interested in the identity of isolated chromosomes[2], was concerned by the cited figures reportedly representing whole isolated chromosomes of the turtle *Clemmys japonica* (Fig. 1–4 of reference[3]), of carp (Fig. 7 *f* of reference[4]), and, subsequently, of carp, triton, and rabbit[5]. Moreover, a stalked «isolated chromosome» in this last paper[5] reminded one of *Caulobacter* as figured by Houwink and Van Iterson[6]. Such objects had not been encountered by this worker as chromosomal isolates from other materials. However, we had encountered some generally similar forms as casual contaminants on rare occasions (Fig. 2); on the basis of form and size these were presumed to be bacterial. The illustrated contaminant measures $^3/_4 \times 6{\cdot}8\ \mu$, the periods *ca.* $0{\cdot}8\ \mu$.

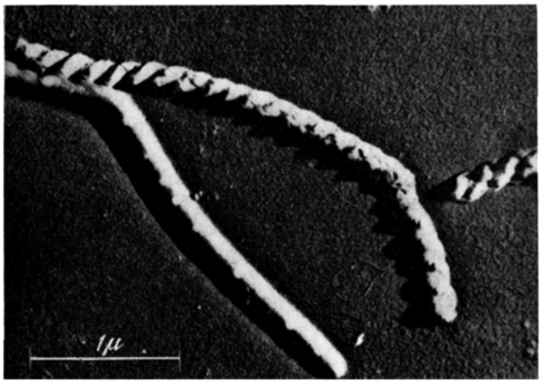

Fig. 1.—Helically organized bacterial contaminant of distilled water. Reproduced with the kind permission of Professor Robley C. Williams, now of the Virus Laboratory, the University of California.

Investigation disclosed that helical structures had also been encountered by others. Some unidentified

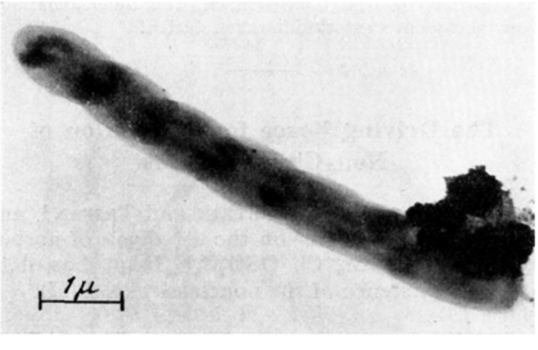

Fig. 2.—Relatively rare, structured casual contaminant from distilled water controls.

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[1] This work by an Alfred P. Sloan Foundation Fellow (A.R.T.D.) was supported by grants from the National Cancer Institute of the National Institutes of Health, Public Health Service, from the Damon Runyon Memorial Fund, and from the American Cancer Society.

[2] G. Yasuzumi, Chromosoma *4*, 222 (1951). – G. Yasuzumi, G. Miyao, Y. Yamamoto, and J. Yokoyama, Chromosoma *4*, 359 (1951). – G. Yasuzumi, T. Yamanaka, S. Morita, Y. Yamamoto, and J. Yokoyama, Exper. *8*, 218 (1952).

[1] A. Y. Mottlau, J. Appl. Phys. *20*, 1055 (1949). – S. G. Ellis, Electron Microscopy, II. Oil Industry Uses: Petroleum Refiner *27*, 487 (September 1948).

[2] A. R. T. Denues, Exp. Cell Res. *3*, 540 (1952); in press, *ibidem*.

[3] G. Yasuzumi, G. Miyao, Y. Yamamoto, and J. Yokoyama, Chromosoma *4*, 359 (1951).

[4] G. Yasuzumi, Chromosoma *4*, 222 (1951).

[5] G. Yasuzumi, T. Yamanaka, S. Morita, Y. Yamamoto, and J. Yokoyama, Exper. *8*, 218 (1952).

[6] A. L. Houwink and W. van Iterson, Biochim. Biophys. Acta *5*, 10 (1950) (fig. 16, p. 31).