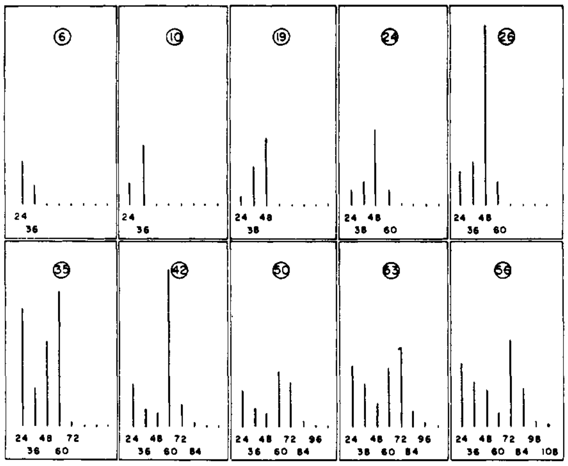
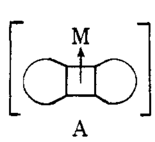


Figure 3. Mass spectra of the xylene-extractable portion of the metathesis product of cyclododecene after catalytic hydrogenation, at various stages of "distillation" in the mass spectrometer. Circled numbers denote the number of the spectrum recorded. The numbers on the bottom denote the number of carbon atoms in the ring. Only relative intensities of molecular ion peaks are given. Other fragments are very small and therefore omitted.

whenever pronounced changes in the spectrum were observed. Representative spectra at various stages of the fractionation are given in Figure 2. Upon following the continuous change of spectra, one could observe that at the beginning of the distillation only lower oligomers are distilled, followed by a gradual appearance of higher ones and a simultaneous disappearance of the lower ones. However, upon further distillation when still higher oligomers start to appear, the relative intensity of the molecular ion peaks of the lower oligomer region starts to reintensify markedly. We interpret this significant reintensification to be a result of fragmentation formed from cleavage of interlocked ring systems of various sizes present in the mixture.

Furthermore, a similar experiment was conducted as before, but now the xylene extractable mixture was catalytically fully hydrogenated under drastic conditions to yield a mixture of cycloparaffinic oligomers. Mass spectral examination of the product using the same technique as above indicated a similar behavior as was observed in the cyclopolyolefinic series. Representative spectra of the cycloparaffinic series are given in Figure 3. Here, in the saturated case, the molecular ion peaks of the C_{24} oligomer (m/e 336) and the C_{36} oligomer (m/e 504) were particularly rechecked (slower scanning and exact counting) toward the end of the distillation when the pronounced enhancement of the peaks occurred. The molecular ion peaks were still of the same m/e, *i.e.*, 336 and 504, corresponding to the *saturated* ring fragments of C_{24} and C_{36}. Similar reintensified fragments corresponding to monomers $C_{12}H_{24}$ in the saturated series or $C_{12}H_{22}$ in the cycloolefinic series were not observed. The obtention of *saturated* fragments of the lower oligomers and also the absence of monomeric fragments, since monomers of this size can by no means form catenanes, provide additional evidence for presence in the mixture of catenanes composed from rings of various sizes.

Intermediates containing a cyclobutane ring have so far not been identified in our present experiments or in the published[2a,4] work. A quasicyclobutane



complexed with a transition metal catalyst represented by A might be assumed as a transition state in the metathesis reaction. Finally, no evidence has been found for doubly charged ions when examined on the isolated cycloparaffinic or cyclopolyolefinic rings.

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Mass Spectral Evidence for Catenanes Formed *via* a "Möbius-Strip" Approach[1]

Sir:

We have interpreted the mass spectra of large carbocyclics as indicating the presence of interlocking rings (catenanes). The macrocyclics were obtained by the enlargement of cyclododecene using the olefin metathesis reaction[3a,b] as reported previously.[2,4] We had noted that the simple cyclic polyolefins thus obtained (I, in which only two of the many double bonds are shown) could undergo an additional metathesis which is intramolecular.[2] If, as shown in eq 1, a 360° twist had occurred in I prior to the metathesis

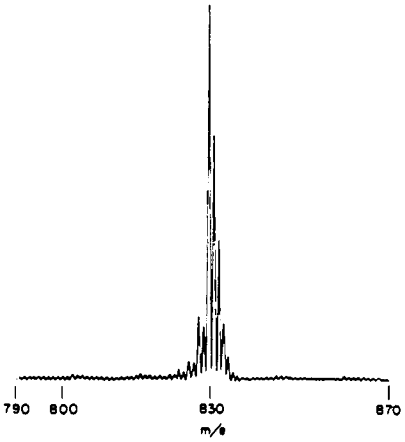

Figure 1. Part of a mass spectrum of a mixture of *cis–trans* isomers of cyclohexaconta-1,13,25,37,49-pentaene.

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[1] The work reported in this and the accompanying communication by R. Wolovsky (*J. Amer. Chem. Soc.*, **92**, 2132 (1970)) are similar but independent verifications of the suggestion that cyclic olefins should yield catenated systems under the metathesis conditions.[2]

[2] E. Wasserman, D. A. Ben-Efraim, and R. Wolovsky, *ibid.*, **90**, 3286 (1968).

[3] (a) N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Lett.*, **34**, 3327 (1967); (b) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).

[4] K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract L54, published in "Addition and Condensation Polymerization Processes," Advances in Chemistry Series, No. 91, American Chemical Society Publications, Washington, D. C., 1969; N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci., A-1*, **5**, 2209 (1967).

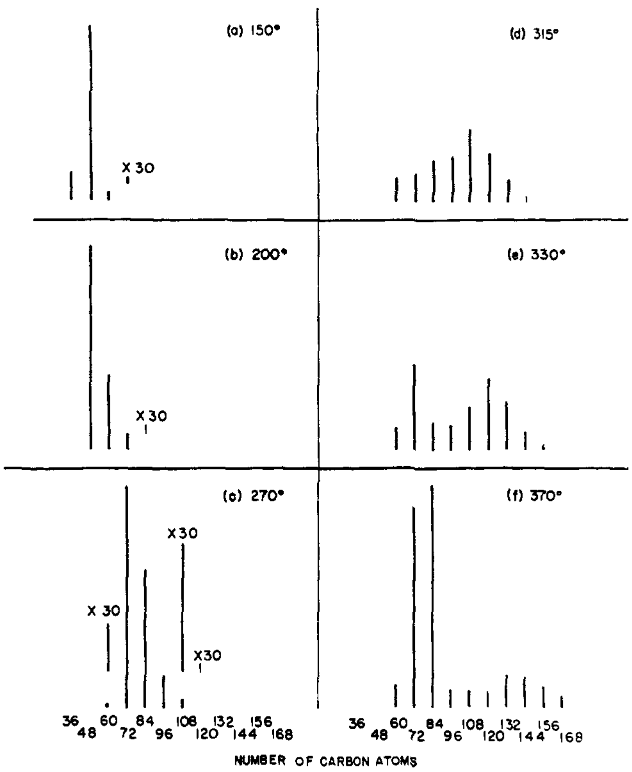
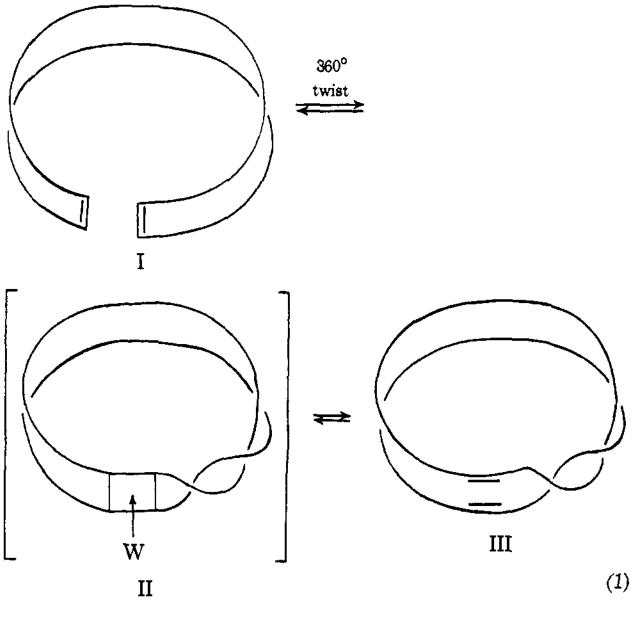


Figure 2. Relative intensities of molecular ions from mass spectra of enriched samples of cyclododecene metathesis at (a) 150°, (b) 200°, (c) 270°, (d) 315°, (e) 330°, and (f) 370°. The intensities were obtained by subtracting the intensity of the repeating CH_2 patterns on the higher side of each molecular ion from the latter's intensity. The relative intensities at the different temperatures are not correlated.

reaction, then the postulated complexed intermediate (II) could collapse to a catenane (III).[2,5] A 180° twist would correspond to II being a Möbius strip,



which could only form a single large ring. A 540° twist would yield a trefoil knot, and a 720° twist a doubly threaded catenane. The twisting would occur statistically and for sufficiently large rings some twisted forms should occur. This statistical approach differs from that used in the earlier catenane synthesis.[6,7] There, one was concerned with the probability of a chain threading a flexible ring,[9] here, with the twisting of a large ring. Both are basically different from the directed synthesis of Schill and Lüttringhaus.[8]

The mixture of large cyclic polyolefins $(C_{12}H_{22})_n$ was prepared from cyclododecene as described previously.[2,4] Mass spectra of the product indicated the presence of rings up to C_{168}. Although lower polyene fractions have a single molecular weight, they were a mixture of *cis–trans* isomers.[2] The mass spectrum of such a *cis–trans* mixture, of a single molecular weight fraction, was dominated above $m/e = 200$ by a molecular ion (and the $M + 1$ due to ^{13}C), as is typical of cyclic systems (Figure 1). The high intensity of the parent ion, as opposed to its weakness in linear systems, follows from the need to break two C–C bonds to separate the ring into two fragments.

We have obtained mass spectral evidence similar to that described below, for unsaturated catenanes containing single C_{24}, C_{36}, and C_{48} rings in the reaction mixtures. Such observations have also been made by Wolovsky and these systems are discussed in detail in the accompanying report.[1] Here we concentrate on the higher molecular weight systems.

Since the yields of successive higher components in a metathesis mixture of a cyclic monoolefin decrease with ring size of the components,[2] we have enriched such a mixture with the higher components by column chromatography on Al_2O_3 Alcoa F-20. We thus obtained from the metathesis mixture of cyclododecene[10] a fraction in which the C_{12}–C_{36} components were absent and which by analytical vpc contained approximately 5% C_{48}, 3% C_{60}, and 3% C_{72}; the remainder were higher components.

This sample was examined by mass spectrometry (using an AEI MS-9 spectrometer[11]) at different temperatures. Spectra were obtained on the same sample by recording a spectrum at one probe temperature, then raising to a higher temperature and recording again, and so on (see Figure 2). Two features of these spectra are significant. (1) By raising the probe temperature from 315° (at which temperature we observed ions up to C_{144}) to 330° we observed not only

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(5) H. L. Frisch and E. Wasserman, *J. Amer. Chem. Soc.*, **83**, 3789 (1961).

(6) E. Wasserman, *ibid.*, **82**, 4433 (1960).

(7) E. Wasserman, *Sci. Amer.*, 207 (5), 94 (1962). There has been some misunderstanding[8] concerning this article. Near the end of p 96 a threading probability of 1% is indicated as 1 mg of the acyloin ring is threaded out of 100 mg formed. This value is the same as that given in ref 6. The figure we now prefer is 0.7%. On p 97 a yield of isolated catenane of 0.0001% is given. While ambiguous as stated there, this figure refers to the overall conversion of the C_{10} diacid to the purified catenane and includes the large excess of hydrocarbon ring used as solvent. The characterization of the product (the acyloin was converted to acetate for the separation) was based on its chromatographic properties, a comparison of its infrared spectrum with an equimolar mixture of the constituent rings, and on cleavage of partially purified catenane, containing some 30–40% of acyloin acetate, to C_{34} diacid and deuterated hydrocarbon (with L. Barash). A closely related threading process is found in an unpublished experiment of Dr. I. T. Harrison in which he prepares his hooplane[9] in solution without the solid support. After correcting for dilution he finds a threading probability of 1.0% with a C_{30} ring; thus he has a larger probability with a smaller ring using a different reaction. We are grateful to Dr. Harrison for permission to quote his result prior to publication.

(8) G. Schill and A. Lüttringhaus, *Angew. Chem., Intern. Engl. Ed.*, 3, 546 (1964).

(9) See also I. T. Harrison and S. Harrison, *J. Amer. Chem. Soc.*, **89**, 5723 (1967). The C_{30} ring is threaded by a C_{10} chain.

(10) Yields in the cyclododecene metathesis were approximately: C_{12} 11%, C_{24} 4%, C_{36} 3%, C_{48} 2%, C_{60} 1%, and C_{72} 0.7%.

(11) Many of the mass spectrometric analyses were kindly performed by Dr. J. Wright.

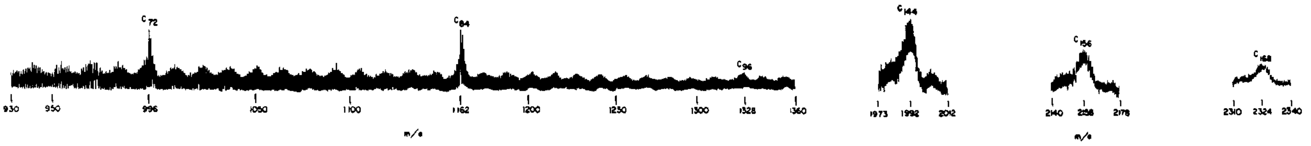

Figure 3. Mass spectrum of enriched sample of cyclododecene metathesis at 370° (Figure 2f). The C_{144}, C_{156}, and C_{168} peaks were traced at a 9-fold higher sensitivity relative to the C_{72}–C_{96} peaks.

the enhancement of the C_{144} and appearance of the C_{156} molecular peaks, but also a sudden increase in the C_{72} molecular peak over its C_{60} and C_{84} neighbors. By raising the temperature from 330 to 370° we then observed not only the appearance of the C_{168} molecular peak but also an increase in the intensity of the C_{84} peak to equal that of the C_{72} peak, both being stronger than their neighboring C_{60} and C_{96} peaks. (2) At 370° the C_{60} and C_{96} are only slightly stronger than the background fragmentation patterns on both sides (Figure 3).

We ascribe the above observations to the presence of catenanes composed of $C_{72} + C_{72}$, $C_{72} + C_{84}$, and $C_{84} + C_{84}$ in the sample. The sudden appearance of the enhanced C_{72} and C_{84} peaks is due to the cleavage of one ring of a catenane in the mass spectrometer, followed by the separation from the remaining ring. We speculate that this separation should occur rapidly as compared to the movement of the ions out of the source.[12] The individual components should now appear in the spectrum. The rising temperature of the probe effectively performed a fractional distillation, so that the C_{72} and C_{84} simple rings were already reduced substantially by the time the C_{144} and higher systems were beginning to appear. The rise in temperature from 270 to 315° shows an increase in the intensity ratio C_{60}:C_{72}, which may also be due to catenanes containing a C_{60} ring. However, the absence in Figure 2d of a bimodal intensity distribution, which we take as characteristic of catenanes, makes us give less weight to this contention.

Three other possibilities should be eliminated before we can assign the mass spectral features mentioned above to catenanes. (1) Cyclobutanes if produced in the metathesis reaction could give a spectrum which mimics the results. However, there has been no evidence of the formation of cyclobutanes.[2–4] Since they are considerably more stable than a pair of ethylenes,[13] they should accumulate if they were produced at all. Most likely, their appearance as II in eq 1 is only as transient complexed intermediates.[3b] (2) Doubly charged ions are another possibility. These are excluded by the absence of any C_{78} peak which would originate from C_{156} (Figure 3). (3) Finally thermal cracking of large single rings by the high temperature of the probe could yield C_{72} and C_{84} fragments. Such a concentration in these two masses would imply some association with the position of the olefinic groups; these positions are known not to migrate.[3] However, either side of a double bond is likely to have the same probability of cleavage. We thus expect additional strong peaks 2 or 4 carbon units from C_{72} and C_{84} as well as fragments about C_{60} and C_{96}. In fact, however, these are not enhanced over the regular background pattern involving groups of peaks spaced 14 mass units (CH_2) apart from a parent peak (Figure 3).

The mass spectral analysis of a catenane by Vetter and Schill[14] indicated cleavage of the ring at substantially lower temperatures and a substantial amount of an M + 1 ion from a ring fragment. The larger variety of functional groups in their system may be responsible for the difference.

Assuming our fractionation has not removed substantial amounts of other C_{144} and higher catenanes, the predominance of interlocked systems composed of two rings of approximately equal size indicates that the large rings do not have random conformations before internal metathesis. It is possible that because they are only slightly soluble, they collapse in solution to mimic the cigar-shaped conformation in the crystal.[15,16] Intramolecular metathesis might then take place after twisting and folding, preferentially at the more accesssible ends as in I. Such packing of smaller alkane chains in solution has been observed by X-ray scattering of haloalkanes.[17]

The demonstration of catenanes of such high molecular weight increases the probability that the higher molecular weight polymer which is also produced in the metathesis reaction with cyclic olefins[4] contains substantial amounts of interlocked simple and knotted rings. Such interlocking may serve as a significant means of bonding in the system. See the Note Added in Proof.[17a]

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[12] This statement is based on the assumption that at least for some configurations in the gas phase van der Waals interactions between the two partners of the catenane are not large enough to overcome the random motion which would separate the ion and the neutral partner; see also ref 14.

[13] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1969.

[14] W. Vetter and G. Schill, *Tetrahedron*, **23**, 3079 (1967).

[15] H. F. Kay and B. A. Newman, *Acta Crystallogr.*, **B24**, 615 (1968); B. A. Newman and H. F. Kay, *J. Appl. Phys.*, **38**, 4105 (1967).

[16] Were the large rings open (and not collapsed), there would then seem to be little steric barrier to a 360° twist which could form catenanes composed of two rings of very different sizes.

[17] G. W. Brady, E. Wasserman, and J. Wellendorf, *J. Chem. Phys.*, **47**, 855 (1967).

[17a] NOTE ADDED IN PROOF (with M. L. Kaplan). Similar experiments, increasing the temperature of the sample in the mass spectrometer, have been performed with the polymer remaining after exhaustive extraction of the reaction mixture with refluxing xylene. At 500° the mass spectrum shows the presence of C_{24}, C_{36}, C_{48}, and C_{60} fragments. These are the only peaks in this range above the repeating CH_2 background. We take these observations as indicating that the polymer contains a network of interlocking rings which are thermally cleaved at 500°. The physical properties of the polymer and a statistical analysis of the metathesis reaction for cyclic systems are consistent with this suggestion of an extensive multicatenated structure.

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