Journal of Mathematical Chemistry 13(1993)47–51

Real molecules as models for mathematical chemistry

I. Strategy for a synthesis of macromolecules with catenane subunits: A bifunctional catenane

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A [2]-catenane consisting of methylene groups and two additional acetylated aza groups has been synthesized in a multi-step sequence. After splitting off the acetyl bonds, the resulting secondary diamine should provide a good starting material for step-reaction (condensation or addition, respectively) polymerization.

The subject matter of this paper is the synthesis of a [2]-catenane with two acetylated amino groups, which – after deacetylation – should represent a good starting material for the directed synthesis of macromolecular compounds with catenane subunits.

The most convenient proof for the fact that the rings of undecomposably vaporized catenanes are combined – even in the gas phase – is the mass-spectrometric method. The idea that catenanes are stable interlocked molecules and not mixtures of separate rings was not self-evident up to 1967, i.e. when the first mass spectrum of a catenane was published [1]. In the beginning of the sixties at a seminar in Freiburg, a participant of the discussion called in question that catenanes can be stable as interlocked rings. He was influenced by the work of Rutherford at the beginning of this century, the famous scatter experiments of alpha particles at thin leaves of metal and the observed $\sin^4(\Theta/2)$ distribution of a few alpha particles scattered at the atom nuclei of the metal foil. Rutherford was impressed by the results of these experiments and concluded that materia is as vacant as the universe. In contrast, the existence of interlocked rings in the gas phase proven by mass spectrometry can only be explained by the fact that materia can penetrate each other only to some extent.

The basic mass spectrometric predictions confirmed by mass spectra of [2]-catenanes investigated so far (Vetter et al. [1,2]) are

- the molecular ion peak appears at a mass number which is equal to the sum of the molecular weights of the catenated macrocyclic compounds;

- the peaks corresponding to all those fragment ions of the macrocycles, which are formed without opening the rings, are shifted to higher mass numbers in the spectrum of the catenane, according to the molecular weight of the catenated partner;
- all those ions, which require opening of one of the rings, are registered at the same mass numbers as in the the spectra of the isolated macrocycles;
- the mass spectra of most of the functionalized catenanes investigated so far are distinguished by a dominant fragmentation process, which is initiated by the interannular transfer of a hydrogen atom to the functional group. Fragmentations caused by initial rupture of one of the macrocycles are less favoured.

Another striking feature for the fact that catenanes are interlocked rings is the crystal structure of these compounds, derived from X-ray analysis [3–6].

When comparing the ^{13}C NMR spectra, low field shifts of up to 1 ppm were noted in going from the molecular subunits to a [2]-catenane [7,8]. These shifts can be explained by van der Waals interactions between the two subunits. In the ^{1}H NMR spectra [7,8], high field as well as low field shifts can be observed, which are mainly caused by solvent effects.

An interesting phenomenon was noted when measuring, on the one hand, the carbon-13 longitudinal relaxation times T_1 of medium and large ring cycloalkanes, and on the other hand, of a catenane [8,9]. The T_1 value of the carbons of the methylene groups in a catenated ring is substantially reduced as compared with the corresponding value in the pure hydrocarbon. On the other hand, it is still considerably higher than in a rigid molecule. This can be taken as evidence that the motions in the catenane are restricted with regard to those in the free ring [9].

In comparing the infrared spectrum of a [2]-catenane with the infrared spectrum of a 1 : 1 mixture of the free molecular subunits, we did not find significant differences between these spectra [10]. Our infrared spectra of low molecular weight catenanes did not provide any proof for the presumption that the catenane structure could be regarded as a diathesis [11]; this means that the catenane structure cannot be considered as a characteristic group in infrared spectra. Our experiments with [2]-catenanes are in contrast to data published by Karagounis et al. [12], who postulated that in polymeric catena compounds the process of the interlocking of rings should result in the disappearance of some bands in the infrared spectra and in the formation of new bands which do not occur in the infrared spectra of the non-interlocked rings.

The existence of interlocked rings in some polymers was already postulated by Mark [13], Frisch et al. [14], and Patat and Derst [15] at a time when there was no direct evidence for catenanes. According to the fact that monofunctional catenanes can be synthesized by directed synthesis [16,17], we used an analogous method for preparation of a bifunctional catenane with two aza groups in each of the cycles. In fig. 1, the most important steps of this reaction sequence are demonstrated.

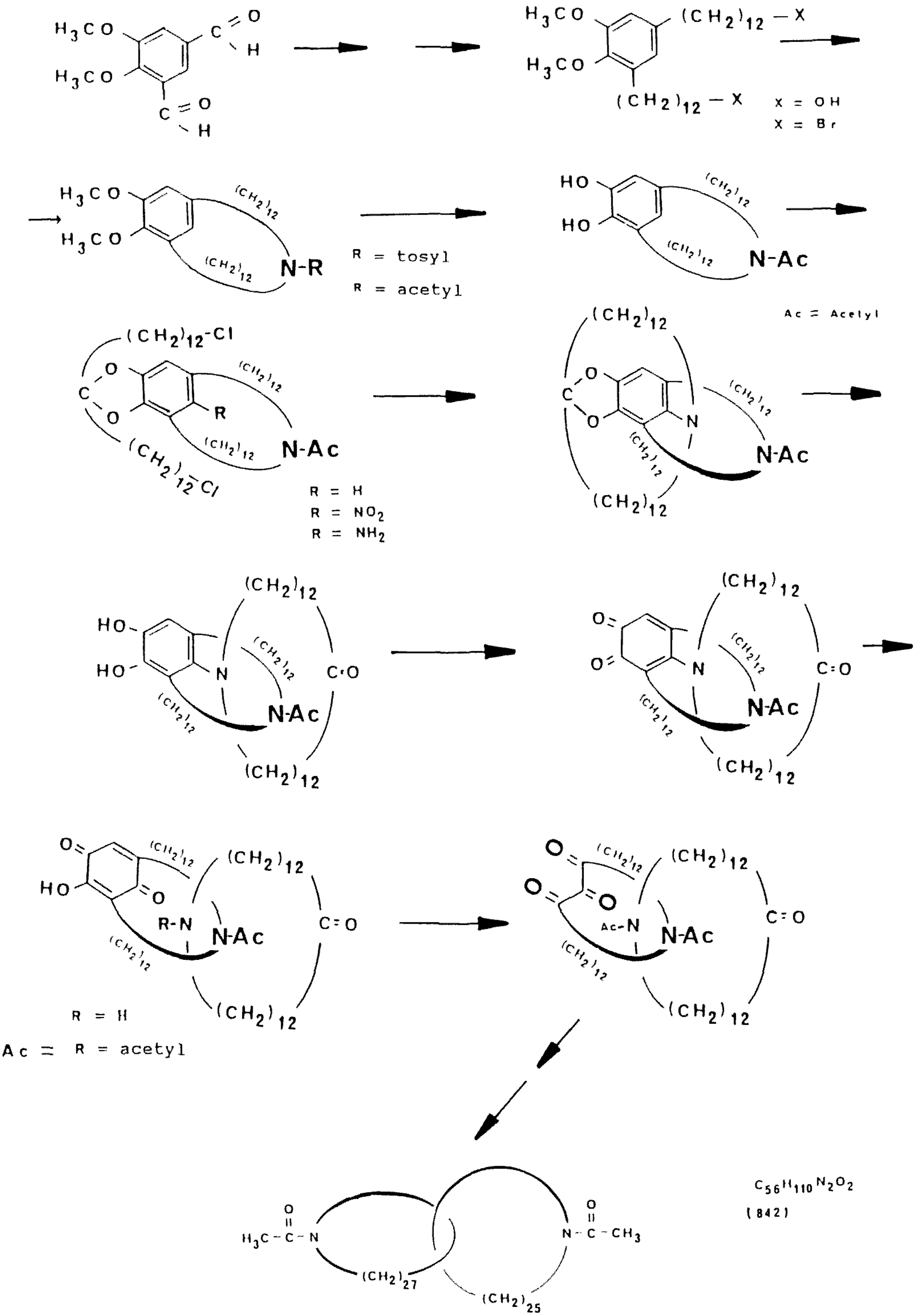

Fig. 1. The main steps of the synthesis of the [2]-[N-acetyl-azacyclooctacosane]-[N-acetyl-azacyclohexacosane]-catenane.

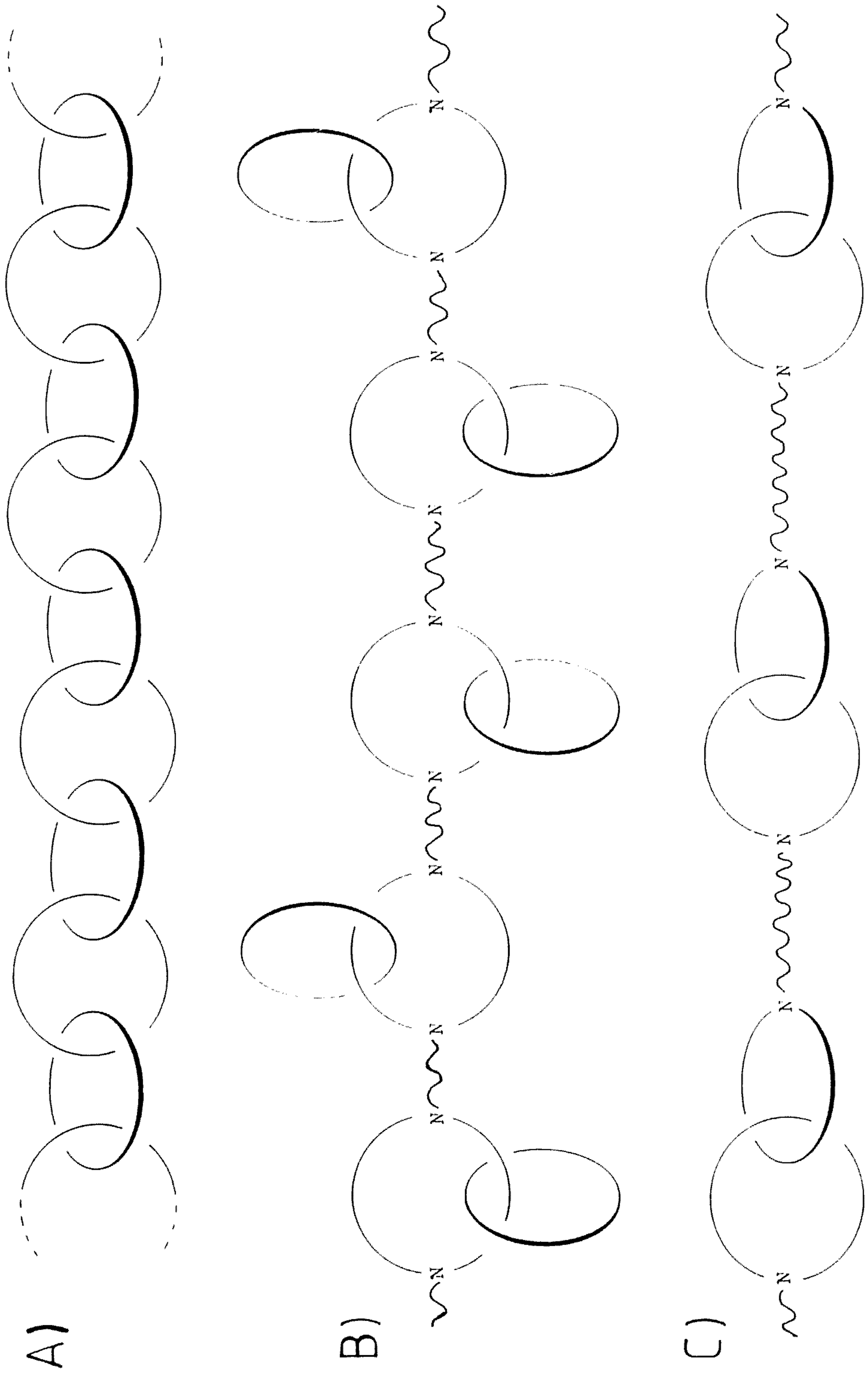

Fig. 2. Different types of macromolecules with catenane subunits.

Up to now, we have isolated a few milligrams of the acetylated diamine: [2]-[N-acetyl-azacyclooctacosane]-[N-acetyl-azacyclohexacosane]-catenane. Its structure has been proven by mass spectrometry. The mass spectrum has been published [2]. The molecular ion peak appears at the mass number *m/e* 842, which is equal to the sum of the masses of the macrocycles (435 + 407). The mass line at *m/e* 421 is associated with the doubly charged molecular ion, as indicated by its isotope peak at *m/e* 421.5. The fragment ions at *m/e* 436 and *m/e* 408 are associated with the protonated acetylated aza rings.

It seems obvious that by splitting off the acetyl groups of the catenane as described above it should be possible to synthesize macromolecules (type C); see fig. 2 depicting catenane subunits according to standard methods of step-reaction (condensation or addition, respectively) polymerization [18,19].

References

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

[2] W. Vetter, E. Logemann and G. Schill, Org. Mass Spectr. 12(1977)351.

[3] M. Cesario, C.O. Dietrich-Buchecker, J. Guilhem, C. Pascard and J.P. Sauvage, J. Chem. Soc. Chem. Commun. (1985)244.

[4] C.O. Dietrich-Buchecker, J. Guilhem, A.K. Khemiss, J.P. Kintzinger, C. Pascard and J.P. Sauvage, Angew. Chem. 99(1987)711 [Angew. Chem. Int. Ed. 26(1987)661].

[5] P.R. Ashton, T.T. Goodnow, A.E. Kaifer, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent and D.J. Williams, Angew. Chem. 101(1989)1404 [Angew. Chem. Int. Ed. 28(1989)1396].

[6] W. Littke and E. Logemann, J. Math. Chem., this volume.

[7] H. Fritz, E. Logemann, G. Schill and T. Winkler, Chem. Ber. 109(1976)1258.

[8] G. Schill, N. Schweickert, H. Fritz and W. Vetter, Chem. Ber. 121(1988)961.

[9] H. Fritz, P. Hug, H. Sauter and E. Logemann, J. Magn. Reson. 21(1976)373.

[10] E. Logemann, Thesis, University of Freiburg/Brsg. (1976).

[11] G. Dijkstra and W.G. de Ruig, Z. Anal. Chem. 264(1973)204.

[12] G. Karagounis, J. Pandi-Agathokli and E. Kondaraki, Chimika Chronika, New Series 1(1972)130; Chem. Abstr. 77(1972)140576g.

[13] H. Mark, Monatsh. Chem. 83(1952)545.

[14] H. Frisch, I. Martin and H. Mark, Monatsh. Chem. 84(1953)250.

[15] F. Patat and P. Derst, Angew. Chem. 71(1959)105.

[16] G. Schill and A. Lüttringhaus, Angew. Chem. 76(1964)567 [Angew. Chem. Int. Ed. 3(1964)546].

[17] G. Schill, E. Logemann and W. Vetter, Angew. Chem. 84(1972)1144 [Angew. Chem. Int. Ed. 11(1972)1089].

[18] *Houben-Weyl, Methoden der Organischen Chemie*, 4th Ed., Vol. XIV, Makromolekulare Stoffe (1963) and Vol. E20, Makromolekulare Stoffe, ed. H. Bartl and J. Falbe (Thieme, Stuttgart, 1987).

[19] F.W. Billmeyer, Jr., *Textbook of Polymer Science* (Wiley-Interscience, New York, 1966) pp. 237–261.