

1,2,5,6-TETRA-EXO-METHYLENOCYCLOOCTANE AND [2.2]-(2,3)- FURANOPHANE AS BIS-DIENE COMPONENTS IN DIELS-ALDER REACTIONS

Matthias Pollmann, Werner Wohlfarth, and Klaus Müllen*

Max-Planck-Institut für Polymerforschung,

Ackermannweg 10, D-6500 Mainz, FRG;

Johann Lex

Institut für Organische Chemie der Universität zu Köln,

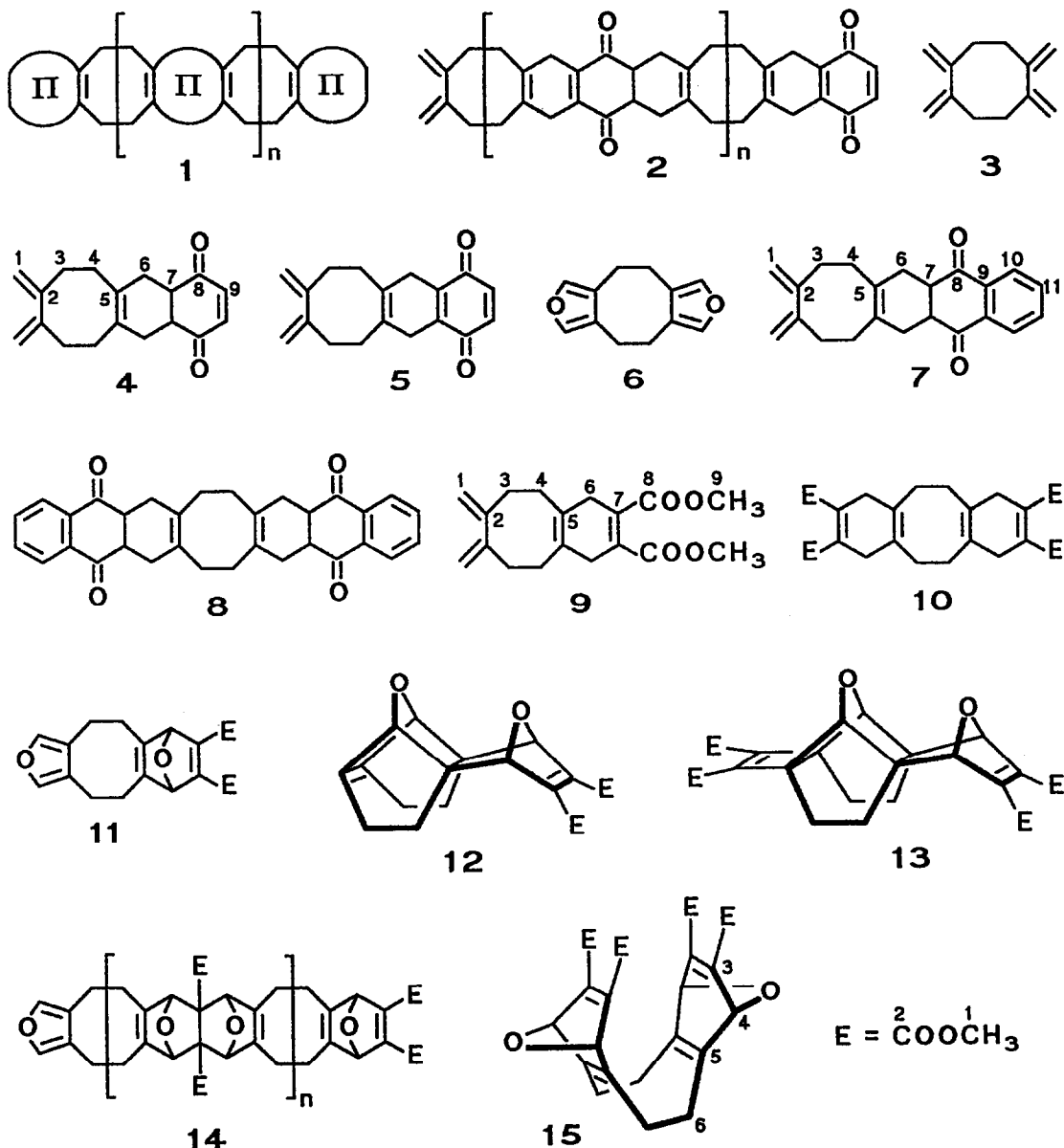
Greinstraße 4, D-5000 Köln 41, FRG

Abstract: Repetitive Diels-Alder reactions¹ of 1,2,5,6-tetra-*exo*-methylene-cyclooctane (3) and [2.2]-(2,3)-furanophane (6) provide novel band-type structures. 3 and 6 differ significantly in the relative rate of the first and second cycloaddition.

Redox polymers with separate electrophores (= electroactive groups) are of fundamental and practical significance.² A unique example is the polymeric band-type structure 1 in which acene subunits are linked with the formation of ortho-cyclophanes. We have recently prepared polymer 2 which constitutes a suitable precursor for a band structure with ortho-anthracenophane moieties.³ The method of synthesis is the Diels-Alder reaction between the bis-diene 1,2,5,6-tetra-*exo*-methylene-cyclooctane (3) and a bis-dienophile such as para-benzoquinone. The initial 1:1-Diels-Alder adduct 4 can readily be dehydrogenated to 5 which is prone to undergoing a poly-reaction.³ Crucial to this approach is the relative rate of the first and second Diels-Alder addition to 3. This will control not only the mechanism of the polymer forming reaction, but also the eventual access to oligomeric model compounds.

We investigate here the stepwise Diels-Alder reaction of 3 by kinetic analysis and by identification of the resulting oligomers. Since a twist within the butadiene units of 3 and 5 is expected to influence the ease of the Diels-Alder reaction, the present study also includes furanophane⁴ 6 in which both butadiene moieties are coplanar.

A straightforward kinetic analysis of the Diels-Alder reactions of 3 requires the use of a monofunctional dienophile such as 1,4-naphthoquinone (NQ). While 3 and NQ readily react at room temperature with formation of monoadduct 7 (3 : NQ = 1 : 0.8, CDCl₃, 25°C, k₁ = 2.2 · 10⁻³ l/mol·s, yield 80%³), compound 7 does not undergo further Diels-Alder reaction under these

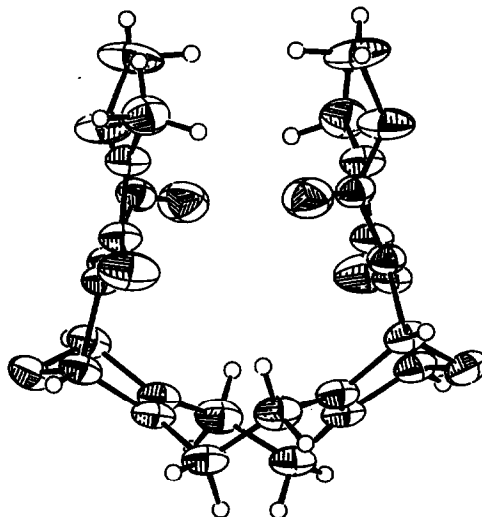


conditions. Diadduct **8** is only formed at elevated temperatures (100°C, toluene, 70%). A related result appears from the reaction of **3** with dimethyl acetylenedicarboxylate (DMAD), since even a twofold excess of DMAD only gives monoadduct **9** (CDCl₃, 25°C, $k_1 = 4.1 \cdot 10^{-4}$ l/m·s, 85 %). However, compound **9** can be transformed into the related diadduct **10** by heating with one equivalent of DMAD (70°C, CCl₄, 18 h, 82 %).

The reluctance of **7** and **9** to undergo a second Diels-Alder reaction must be ascribed to the geometry of the remaining butadiene moiety. The crystal structure of monoadduct **9**⁵ reveals a large angle of torsion about the central C-C-bond of the butadiene unit ($\varphi = 102^\circ$). A comparison of the ¹H-NMR spectra

of 3, 7 and 9 shows that this is also the case in solution.⁶ It appears that the signals of the exo-methylene protons suffer from a shielding effect when the twist of the butadiene unit increases.

The crystal structure of 15.



Diels-Alder adducts of furan and benzoquinone are known to undergo a ready retro-reaction.⁷ The present comparison of bis-dienes 3 and 6 is therefore restricted to the cycloaddition with DMAD.

Bisfuran 6 differs from 3 in that its reaction with one equivalent of DMAD does not afford the expected monoadduct 11. Instead, several products are obtained due to the competition of intra- and intermolecular⁸ Diels-Alder reactions (see below). One product, namely cage type compound 13, could be identified by a crystal-structure analysis.⁵ It can be readily deduced that an intramolecular cycloaddition of 11 produces the reactive intermediate 12 which is subsequently stabilized by a [2+2]cycloaddition with DMAD to give 13.

The oxonorbornadiene structure of monoadduct 11 possesses a terminal double bond which due to the ring strain acquires an increased dienophilic character. Accordingly, the bifunctional intermediate 11 constitutes a monomer which is capable of undergoing a poly-Diels-Alder reaction. Indeed, upon chromatographic work-up products are isolated which exhibit strongly broadened ¹H-NMR signals of furan, oxanorbornadiene and oxanorbornene subunits as would be expected for structure 14. The preparation and characterization of band-type structure 14 will be dealt with elsewhere.⁹

The reaction of DMAD with 3 and 6, respectively, reveals that the diene subunit of intermediate 11 is more reactive than that of 9. Nevertheless, the poly-reaction of 11 can be suppressed by treating 6 with an excess of DMAD which affords bis-adduct 15. A crystal structure of 15 points toward a syn-arrangement of the oxygen bridges.⁵

In view of the complex reactivity of 11 the Diels-Alder reaction between

bis-dienophile **15** and bis-furan **6** could be an interesting alternative for the formation of band-type structures.

It appears that **5** and **9** are less susceptible to a Diels-Alder reaction than **11**. Even in the presence of Lewis acids and at elevated temperatures monoadduct **9** cannot be polymerized. On the other hand, the use of adduct **10** as bis-dienophile is inhibited by its pronounced tendency toward aromatization.

References:

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2. R.W. Murray in "Electroanalytical Chemistry", A.J.M. Bard, ed., Dekker, New York, **1984**, *13*, 191.
3. M. Wagner, W. Wohlfarth, K. Müllen, *Chim.* **1988**, *42*, 377.
4. P.J. Garratt, S.B. Neoh, *J. Org. Chem.* **1979**, *44*, 2667.
5. **Some spectroscopic data of novel compounds:**
4: $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz): δ_{C} 194.4 (C-8), 146.3 (C-2), 133.9 (C-9), 123.2 (C-5), 105.6 (C-1), 41.4 (C-7), 32.9 (C-6), 26.7/23.4 (C-3/C-4); $^1\text{H-NMR}$ (CDCl_3 , 200 MHz): δ_{H} 6.60 (2H, s), 4.72 (2H, d), 4.57 (2H, d), 3.09 (2H, t), 2.46 - 1.96 (12H, m); MS (70 eV) m/z 268 (M^+), 240 (M^+-CO), 212 (M^+-CO , -2 CH_2).
7: $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ_{C} 198 (C-8), 151.7 (C-2), 134.1 (C-9/11), 128.7 (C-5), 126.8 (C-10), 110.9 (C-1), 47.1 (C-7), 38.2 (C-6), 32.1 (C-3), 28.9 (C-4); $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ_{H} 8.03/7.73 (4H, m), 4.76 (2H, d), 4.63 (2H, d), 3.29 (2H, t), 2.55 - 1.98 (12H, m); MS (70 eV) m/z 318 (M^+ , 100%), 290 ($\text{M}^+-2 \text{CH}_2$), 262 ($\text{M}^+-2 \text{CH}_2$, -CO); IR (KBr) 3095, 2945 - 2840, 1695, 1442, 920, 910; m.p. 109°C.
9: $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ_{C} 168.2 (C-8), 151.5 (C-5), 132.6 (C-7), 126.6 (C-5), 111.0 (C-1), 52.0 (C-9), 37.8 (C-6), 32.2/31.1 (C-3/C-4); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ_{H} 4.78 (2H, d), 4.62 (2H, d), 3.75 (6H, s), 2.93 (4H, s), 2.27/2.16 (8H); MS (70 eV) m/z 302 (M^+), 274 ($\text{M}^+-2 \text{CH}_2$), 271 (M^+-OCH_3); m.p. 54°C.
 Crystal structure of **9**: $\text{C}_{18}\text{H}_{22}\text{O}_4$, $M = 302.37$. The compound crystallizes in the triclinic space group P1 with cell dimensions of $a = 8.149(2)$, $b = 9.779(2)$, $c = 11.048(3)$ Å, $\alpha = 69.35(2)^\circ$, $\beta = 88.67(2)^\circ$, $\gamma = 79.16(2)^\circ$; $V = 808.18$ Å³, $Z = 2$, $D(\text{calcd}) = 1.242$ g cm⁻³. 2513 reflections with $I \geq 2 \sigma(I)$ were taken as observed. Final $R = 0.040$.
 Crystal structure of **13**: $\text{C}_{24}\text{H}_{24}\text{O}_{10} \cdot 2 \text{H}_2\text{O}$, $M = 508.48$, monoclinic, space group P2₁/n, cell dimensions: $a = 15.426(3)$, $b = 9.565(2)$, $c = 16.384(3)$ Å, $\beta = 90.21(2)^\circ$; $V = 2417.42$ Å³, $Z = 4$, $D(\text{calcd}) = 1.397$ g cm⁻³; 2016 reflections, $R = 0.049$.
15: $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): δ_{C} 163.2 (C-2), 152.34 (C-3), 146.97 (C-5), 90.07 (C-4), 52.09 (C-1), 25.57 (C-6); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ_{H} 5.24 (4H, s), 3.80 (12H, s), 2.62 (8H, m); MS (70 eV) m/z 411 ($\text{M}^+-\text{COOCH}_3$), 352.1 ($\text{M}^+-2 \text{COOCH}_3$); m.p. 170°C.
 Crystal structure of **15**: $\text{C}_{24}\text{H}_{24}\text{O}_{10}$, $M = 472.45$, monoclinic, space group C2/c, cell dimensions: $a = 18.928(4)$, $b = 9.717(2)$, $c = 15.537(3)$ Å, $\beta = 129.50(2)^\circ$; $V = 2204.78$ Å³, $Z = 4$, $D(\text{calcd}) = 1.423$ g cm⁻³; 1311 reflections, $R = 0.051$.
 Intensity measurements on an Enraf-Nonius CAD-4 four-cycle diffractometer, room temperature, graphite-monochromated MoK α -radiation, ω -2 θ scan mode; structure solution by direct methods, hydrogen atoms from difference fourier maps, full-matrix least squares refinement with anisotropic thermal parameters for all non-hydrogen and isotropic for hydrogen atoms. Lists of the atomic coordinates, bond distances and angles, torsion angles, have been deposited at the Cambridge Crystallographic Data Centre, U.K., as Supplementary Material.
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