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Thermal analysis of 'exploding' [*n*]rotanes

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Abstract

The thermal decomposition behavior of four different perspirocyclopropanated macrocyclic oligodiacetylenes, also known as 'exploding' [*n*]rotanes, was characterized by DSC and EGA.

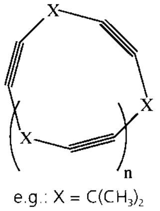
The influence of ring size, number of diethynylcyclopropane segments and permethylation of the cyclopropyl groups on the thermal decomposition is shown.

The heat of decomposition surpasses that of conventional explosives. For example, the heat of explosion of [6]rotane calculated by adiabatic thermodynamics is 3426±87 kJ/mol. The kinetic constants of the EGA profile of permethylated [6]rotane are reaction order $n=1$, activation energy $\Delta E_a=135.3\pm6.1$ kJ/mol and preexponential factor log $Z=12.82\pm1.04$. Besides quantities of soot, acetylene, methane and ethene were recorded as decomposition products, and tetramethylethene for permethylated [6]rotane, indicating that the first step in the thermal decomposition of 'exploding' [*n*]rotanes is the cleavage of the cyclopropane bond.

Keywords: Cyclopropyl groups; Oligodiacetylenes; Ring strain; Rotanes; Thermal decomposition

1. Introduction

The preparation and the properties of macrocyclic oligoalkynes **1** and oligoalkadiynes **2** have received much interest in organic chemistry because of the remarkably strong electronic interactions observed in these molecules [1–4].



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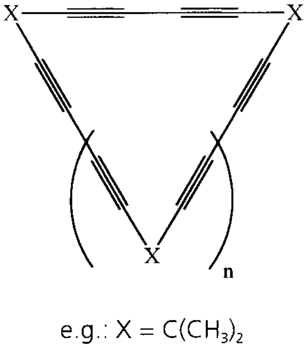

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Even stronger homoconjugative effects have been observed in the family of perspirocyclopropanated macrocyclic oligodiacetylenes or 'exploding'[*n*]

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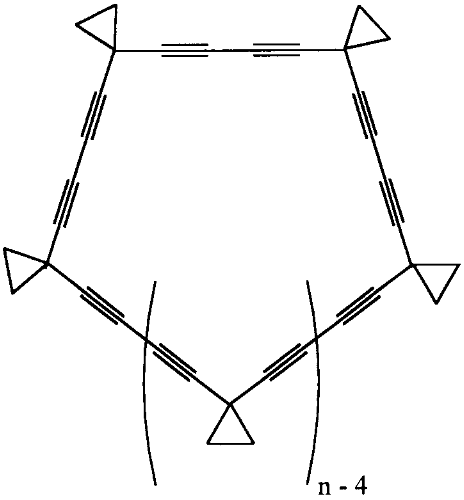
rotanes **3** caused by the closeness of the energy levels of the highest occupied HOMOs of the cyclopropane ring and the π-MOs of the acetylene unit [4,5].



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This family exhibits interesting properties. Besides the strong electronic interactions, they have an unusual high energy content and a high impact sensitivity. For example, when struck with a spatula they decompose spontaneously whereby a cloud of black soot is liberated. Responsible for the high energy content is the high strain energy incorporated in the carbocyclic three-membered rings, in combination with the high heat of formation of the acetylene units of the macrocyclic backbone. The high energy content and the high reactivity of this family led to the term 'exploding' [*n*]rotanes [5].

This work addresses the thermal properties of 'exploding' [*n*]rotanes and presents first results on the thermal decomposition behavior of the species listed in Table 1. The compounds selected differ in ring size (**4**, **5** and **7**) and in the permethylation of the cyclopropane moieties (**6**).

2. Experimental

The 'exploding' [*n*]rotanes were supplied by A. de Meijere, Institut für Organische Chemie, Georg-August Universität, Göttingen. The synthesis of the samples is described in the Refs. [4,5].

The thermal behavior of the samples was characterized by DSC and Evolved Gas Analysis.

For the DSC experiments, a TA Instruments MDSC 2920 system was used which was calibrated for a heating rate of 2 K/min. The samples weighing between 1.5 and 2.0 mg were analyzed in aluminum pans with pierced lids in an argon atmosphere. The argon flow rate was 50 ml/min. From the measured DSC curves, the (integral) heat of decomposition $\Delta H_{\mathrm{decomp}}$ was calculated based on a sigmoidal base line curvature.

In the EGA experiments, the evolved gases during decomposition were investigated by monitoring online the gas phase in a controlled heatable optical cell by rapid scan FTIR spectroscopy (Nicolet 60 SX). The experimental set-up is described elsewhere [7]. The samples weighing ca. 5 mg were analyzed at 6 K/min in open aluminum pans in an argon atmosphere. Evolution profiles were calculated by plotting the intensity of a specific IR absorption band against temperature.

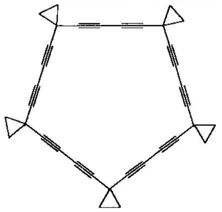
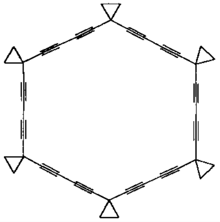
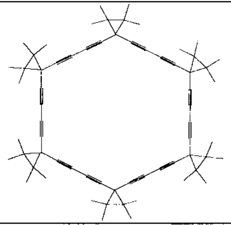
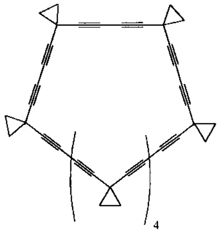
3. Results and discussion

The DSC curves are displayed in Fig. 1. The compounds decompose completely between 110° and 210°C as evidenced by strong exothermic peaks. (The endothermic peak at 93°C is caused by the evaporation of diethyl ether which is present in **4** as a solvent impurity).

As opposed to permethylated **6**, the peaks of (non-permethylated) **4**, **5** and **7** are centered at the low-temperature side of the decomposition interval, that of **7** being lowest. As apparent from Table 1, the macrocyclic backbone of **7** is composed of n=8 diethynylcyclopropane segments and, therefore, a high *n* seems to thermally destabilize the molecule. In contrast, permethylation thermally stabilizes the molecule as evidenced by the shift of the DSC peak to markedly higher temperatures.

The influence of *n* on the molar heat of decomposition is illustrated in Table 2 by the increase in $\Delta H_{\mathrm{decomp}}$ as more energetic diethynylcyclopropane segments are added to the macro ring. The dependence, however, is not linear. $\Delta H_{\mathrm{decomp}}$ is maximal for **5** and might reflect additional strain induced in the macro ring of this particular molecule.

Table 1
Type and specific parameters of the 'exploding' [*n*]rotanes investigated

sample	moleculare structure	sum formula	molecular weight	oxygen balance*
4 [5]rotane		$C_{35}H_{20}$	440.54 g/mol	- 291%
5 [6]rotane		$C_{42}H_{24}$	528.65 g/mol	- 291%
6 [6]rotane, permethylated		$C_{66}H_{72}$	865.29 g/mol	- 311%
7 [8]rotane		$C_{56}H_{32}$	704.87 g/mol	- 291%

Permethylation of the cyclopropyl groups, in contrast, stabilizes the molecule and causes $\Delta H_{\mathrm{decomp}}$ of **6** to drop by 40% with respect to that of the nonpermethylated analogue **5**.

The strong exothermicity of the $\Delta H_{\mathrm{decomp}}$ values listed in Table 2 is surprising, especially when compared to that of conventional explosives. For example, $\Delta H_{\mathrm{decomp}}$ of the well-known explosive hexogen (1,3,5-trinitro-1,3,5-triazacyclohexane; RDX) determined under similar experimental conditions measures 600 kJ/mol, which is less by half than that of **5**.

Moreover, the heat of explosion Q_{ex} of **5**, calculated by adiabatic thermodynamics [6], surpasses that of RDX, despite its extreme negative oxygen balance, as is expressed by the data summarized in Table 3. The main driving force for the high Q_{ex} is the remarkably high heat of formation $\Delta H_{\mathrm{f}}^{0}$ of **5** [5]. The latter is 24 times larger than that of RDX and illustrates best the large amount of energy stored in the 'exploding' rotane molecule.

Fig. 2 displays the EGA spectrum of **5** on heating at 6 K/min under argon atmosphere. Soot particles scattering the probing IR beam are responsible for the

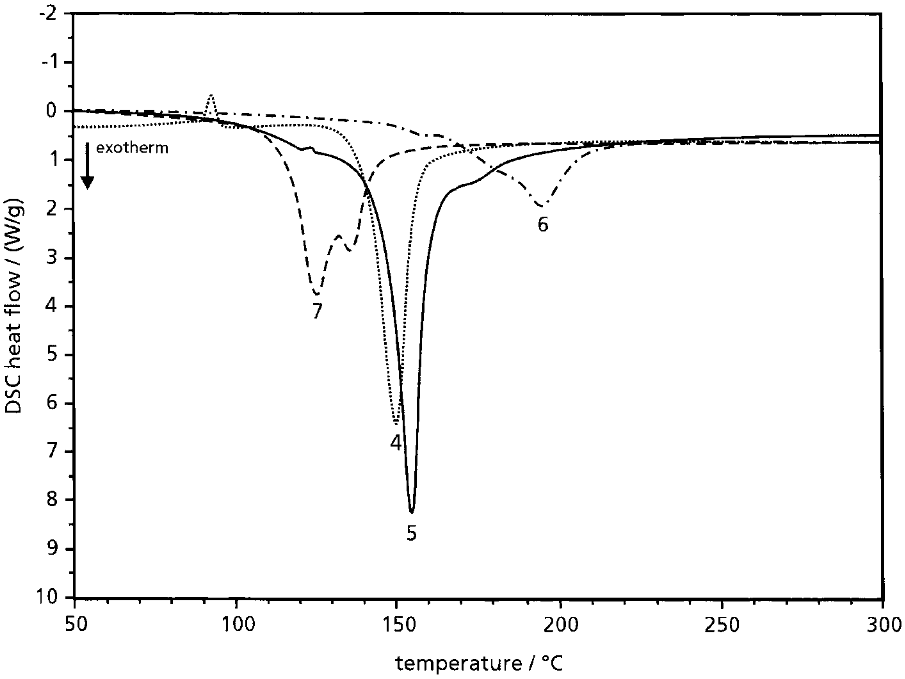


Fig. 1. DSC curves of the 'exploding' [*n*]rotanes **4**, **5**, **6** and **7** measured under argon atmosphere at 2 K/min.

Table 2
Integral molar heat of decomposition $\Delta H_{\mathrm{decomp}}$ of 'exploding' [*n*]rotanes calculated from the DSC curves measured at 2 K/min

[*n*]Rotane	Number of segments	Heat of decomposition $\Delta H_{\mathrm{decomp}}$/(kJ/mol)
4	n=5	870±60
5	n=6	2004±152
6	n=6, permethylated	1194±77
7	n=8	1501±94

'explosive' rise of the baseline at 147°C (and its slow fall during particle settling) and solid carbon is the main product in accordance with the strongly negative oxygen balance (−291%, c.f. Table 1). Besides soot, the products ethene, methane and acetylene were recorded. The intensity of the absorption bands was medium (CH_4, C_2H_2) or weak (C_2H_4) and the products appeared simultaneously with soot. Higher substituted acetylenes or cyclopropyl derivatives as a result of thermal decomposition were not found. (The further bands recorded were due to traces of the solvent diethyl ether and pentane coming from synthesis as well as cell impurities of water and carbon dioxide).

As summarized in Table 4, a similar EGA spectrum was recorded for **4**, with the onset of the 'explosive' baseline rise at 156°C. In contrast, only one product, besides solid carbon, was observed for **6** and **7**, namely tetramethyl ethene for (permethylated) **6** and ethene

Table 3
Comparison of the calculated heat of explosion Q_{ex} and related parameters of **5** ('exploding' [6]rotane) and the explosive RDX

Sample	Q_{ex}/(kJ/mol)	$\Delta H_{\mathrm{decomp}}$/(kJ/mol)	$\Delta H_{\mathrm{f}}^{0}$/(kJ/mol)	Oxgen balance%	Liberated gas volume/(ml/g)
5 [6]rotane	3426±87	2004±152	1710	−291	432
RDX	1250±35	600±28	70	−22	779

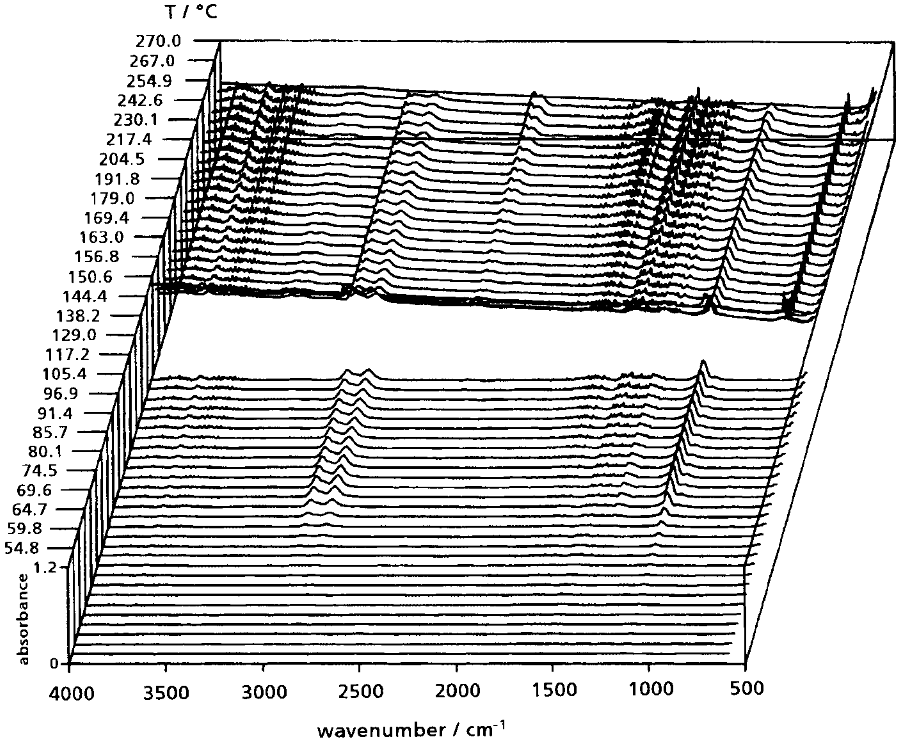


Fig. 2. EGA curves of **5** measured under argon atmosphere at 6 K/min.

for (non-permethylated) **7**. In addition, an 'explosive' baseline rise as present in the spectra of **4** and **5** was not observed.

The mechanistic origin is apparent on comparing the onset and the steepness of the evolution profiles plotted in Fig. 3. Because of the weakness of the IR bands, the profiles appear noisy but they all exhibit a defined onset and a rise without intermediate stages. For **4** and **5** the profile steepness is discontinuous and it resembles that of the soot formation. Such profiles result from uncontrolled sample selfheating which causes decomposition to occur at considerably higher temperatures than indicated by the thermoanalytical measurement.

Decomposition products generated at high temperatures under equilibrium conditions were determined by adiabatic thermodynamics [8] and Table 5 summarizes the products calculated for **5** at freeze-out under isochoric and isobaric conditions. On comparing with Table 4, the same products are noted in the EGA experiment (the formation of hydrogen could not be confirmed since hydrogen is IR-inactive and remained undetected). Therefore, the gases generated represent a hazardous mixture which, in view of the high $\Delta H_{\mathrm{decomp}}$ of the parent molecule, can potentially self-ignite.

From the curve structure in Fig. 1, the decomposition appears as a superposition of two reaction steps. Whereas **4** exhibits a single band of narrow width (8 K), **5** displays a narrow band of similar width with a shoulder located at higher temperature and **7** a broad band with two maxima. The order is reversed for permethylated **6** in that a shoulder is situated at the low-temperature side of the DSC band. The separation of the maxima ranges between 9 and 15 K. The positions of the maxima and/or shoulders are listed in Table 6 and compared with the onset temperatures of the EGA profiles.

The close correspondence noted in Table 6 between the position of the first DSC maximum and/or shoulder and the evolution onset shows that the formation of the gaseous products is an early event in the

Table 4
Thermal decomposition products of the 'exploding' [*n*]rotanes as detected by FTIR spectroscopy in the EGA experiment at 6 K/min under argon atmosphere

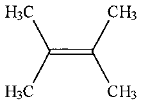
[n]rotanes	thermal decomposition products	IR absorption bands of gaseous decomposition products / cm^{-1}
4 [5]rotane	C_s (soot) CH_4 C_2H_4 (traces) C_2H_2	 3015, 1305 950 3311, 3254, 731
5 [6]rotane	C_s (soot) CH_4 C_2H_4 (traces) C_2H_2	 3015, 1304 950 3308, 3256, 730
6 [6]rotane, permethylated	C_s (soot) tetramethyl ethylene 	3015, 2928, 1136
7 [8]rotane	C_s (soot) C_2H_4	 950

Table 5
Thermal decomposition products calculated by adiabatic thermodynamics for **5** at freeze-out under isochoric and isobaric conditions

Reaction products at freeze-out	Mass% under isochoric conditions (1500 K, 540 bar)	Mass% under isobaric conditions (1500 K, 1 bar)
C_s (solid)	89.365	95.357
H_2	2.544	4.553
CH_4	8.076	0.089
C_2H_2	0.000	0.001
C_2H_4	0.015	0.000

decomposition history of the macromolecule. Fig. 4 presents a kinetic analysis by a least-squares fit to the tetramethyl ethene profile of **6** assuming simple kinetics of first-order decay [9]. The kinetic constants determined were activation energy $\Delta E_a=135.3\pm 6.1$ kJ/mol and preexponential factor log $Z=12.82\pm 1.04$. The bond strength calculated for cyclopropane is 210 kJ/mol [10]. Assuming the bond strength to be substantially lower in the highly strained cyclopropane moiety (note that cyclopropane bonds are severely altered on perspirocyclopropanation [5]) then the closeness of the two values suggests that the

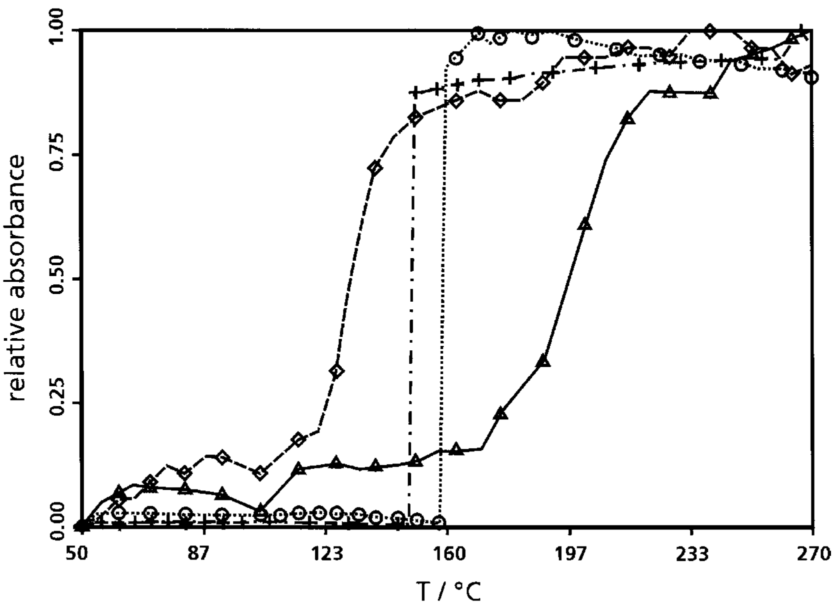


Fig. 3. EGA profiles of the decomposition products of **4** (acetylene: 728–734 cm^{-1}; +), **5** (methane: 3013–3017 cm^{-1}; ○), **7** (ethene: 946–952 cm^{-1}; ◆) and **6** (tetramethyl ethene: 2930–2940 cm^{-1}; △) obtained at 6 K/min under argon atmosphere.

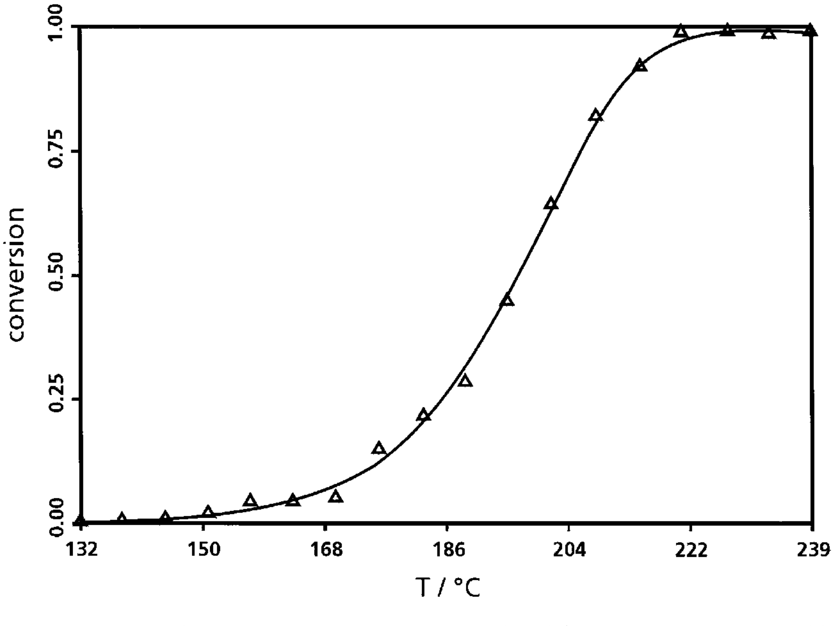


Fig. 4. Kinetic analysis by a least-squares fit to the tetramethyl ethene EGA profile of **6** assuming simple kinetics of first-order (n=1) decay: activation energy ΔE_a=135.3±6.1 kJ/mol and preexponential factor log Z=12.82±1.04.

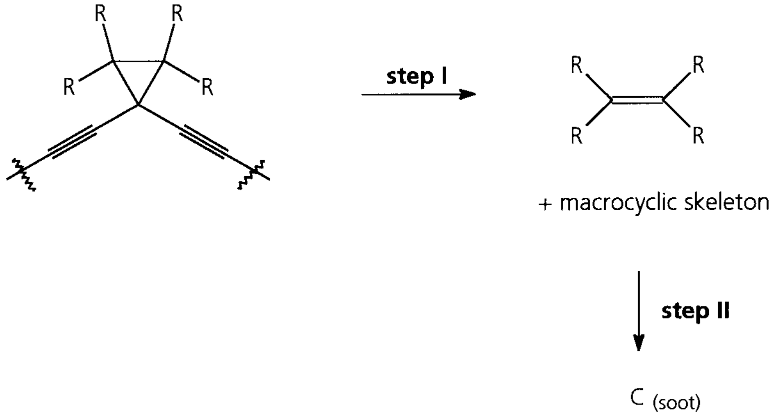


Fig. 5. Scheme of assumed mechanism of the thermal decomposition of 'exploding' [*n*]rotanes.

Table 6
Temperature of the DSC maxima and/or shoulders (sh) and of the onset of the EGA evolution profiles

[*n*]Rotane	T_{max} (DSC)/°C	T_{onset} (EGA)/°C
4 [5]rotane	149	149
5 [6]rotane	154 169 (sh)	157
6 [6]rotane permethylated	186 (sh) 195	189
7 [8]rotane	125 136	126

breaking of the cyclopropane bond could be the first step in the thermal decomposition.

Fig. 5 summarizes schematically the mechanism of the decomposition. The breaking of the cyclopropane bond is followed by the decomposition of the remaining macro ring skeleton whereby soot is formed. For **4** (and the most part of **5**) decomposition of the macro ring skeleton must be fast, causing the two mechanistic steps to superimpose, giving rise to a strong, narrow and structureless DSC band. For **6** and **7**, in contrast, the two steps are kinetically separated leading to a broad band carrying two distinct maxima. A high *n* as present in **7**, or permethylation of the propane ring as in **6** seem to kinetically retard step 2.

Both mechanistic steps are exothermic and their contribution to the overall thermal reaction can be judged for **6** and **7** from their DSC curves in Fig. 1. For **7**, step 1 is more exothermic, i.e. on decomposition the energy released by the highly strained spirocyclopropane moieties surpasses that released by the butadiyne units of the macro ring. For **6** the order is reversed and step 1 is less exothermic, which is direct evidence for thermal stabilization of the molecule by permethylation. The kinetic evidence for this event is given in Fig. 3 by the less steep evolution profile of **6** with respect to that of **7**. Note that permethylated macrocyclic oligodiynes are less sensitive to impact and do not explode on shock like the nonpermethylated analogues [5].

Acknowledgements

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