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Intramolecular Reactions of Tethered Furan-based bis-(*p*-Quinodimethanes)

Douglas A. Klumpp *[a] Thomas M. Gilbert,[a] and Walter S. Trahanovsky,*[b]

Abstract: Tethered bis-2,5-dimethylene-2,5-dihydrofurans have been generated in the gas-phase by flash vacuum pyrolysis (FVP) of diester precursors. These furan-based bis-(*p*-quinodimethanes) are shown to undergo reactions leading to macrocycles. The observed products strongly support a mechanism involving cyclic diradical intermediates. Formation of the furan-based *p*-quinodimethane and the corresponding cyclization chemistry was studied by high-level *ab initio* calculations. The theoretical studies reveal the importance of the entropy-driven elimination steps in the high temperature FVP chemistry.

Introduction

p-Quinodimethanes are an important class of organic reactive intermediates. They are involved in reactions such as in the pyrolysis of organic compounds, cyclophane syntheses, and in polymerizations. This type of intermediate was first proposed by Szwarc in a report describing the pyrolysis of *p*-xylene.[1] At 1000°C, *p*-xylene leads to the formation of poly-*p*-xylylene, oligomers, and several cyclophane products. The conversions may be understood by formation of the parent *p*-quinodimethane reactive intermediate (*p*-xylylene, **1**, Scheme 1) via dehydrogenation of *p*-xylene. *p*-Xylylene (**1**) and its substituted derivatives have been studied extensively since Szwarc's initial report, in part due to the commercial importance of poly-*p*-xylylene macromolecules.[2,3] The unique electronic properties *p*-quinodimethanes have also been the subject of many theoretical investigations.[4] A variety of methods have been used to generate **1**, including pyrolysis of organomanganese substrates,[5] fluoride-induced silyl elimination,[6] Hofmann elimination,[7] photolysis of α,α'-dichloroxylenes,[8] thermal and photochemical dissociation of [2,2']paracyclophane,[9] electrochemical reactions,[10] dehydrohalogenation,[11] elimination with bis(sulfonium ion) salts,[12] *p*-Xylylene (**1**) has also been thoroughly characterized by spectroscopic methods.[13]

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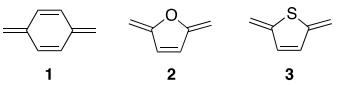
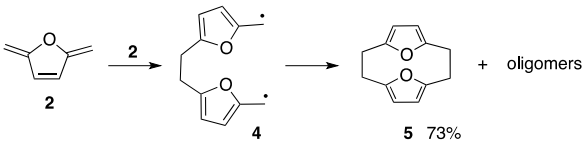


Scheme 1. *p*-Quinonedimethanes.

Both compounds **2** and **3** are well known heterocycle-based *p*-quinodimethanes. These heterocyclic systems have been generated by pyrolysis of varied precursors,[14] silyl-induced elimination reactions,[6a] and Hofmann elimination.[15] Both the furan- and thiophene-based *p*-quinodimethanes (**2** and **3**) have been characterized by spectroscopic methods.[14c] Like the *p*-xylylene (**1**), compounds **2** and **3** are known to form cyclophane products by intermolecular reactions. For example, the furan-based system (2,5-dimethylene-2,5-dihydrofuran, **2**) gives the dimeric cyclophane (**5**) in 73% yield (Scheme 2).[6a] The mechanism for this conversion is proposed to involve the diradical species (**4**), although the diradical intermediate could not be trapped by hydrogen atom donors or nitroxyl radical traps.[14a]



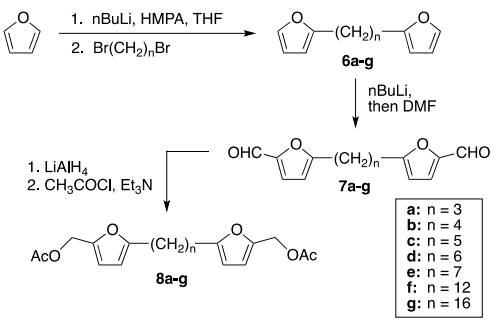
Scheme 2. Reaction of furan-based *p*-quinodimethane (**2**).

In the following manuscript, we describe a pyrolytic method of generating two furan-based *p*-quinodimethanes tethered by hydrocarbon chains of varying length. These furan-based bis(*p*-quinodimethanes) are shown to undergo several characteristic reactions of diradical species, including disproportionation, coupling, and cleavage processes – providing strong evidence for the role of diradicals in the chemistry of furan-based *p*-quinodimethanes. The reaction path involving diradical disproportionation provides a novel route to macrocyclic products having 15 to 22 carbons. The proposed mechanism is also studied by *ab initio* computational methods.

Results and Discussion

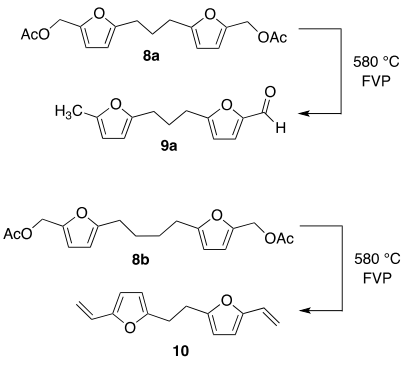
As described previously, the furan-based *p*-quinodimethane (**2**) may be generated by flash vacuum pyrolysis (FVP) of (5-methylfuran-2-yl)methyl benzoate and related esters.[14] The

conversion is thought to occur by a pair [3,3] sigmatropic bond migrations and β-elimination of benzoic acid.[14a] We sought to utilize this chemistry to generate a pair of furan-based *p*-quinodimethanes linked by a hydrocarbon chain or other tether. Thus, a series of precursors were synthesized with varied tether lengths between the furan rings (Scheme 3). 2-Furyllithium is prepared and reacts with the dibromoalkanes to give the di(2-furyl)alkanes (**6a-g**, 62-90% yields). Subsequent formylation (**7a-g**, 50-70% yields), reduction, and acylation, gives the FVP precursors (**8a-g**, two steps, 80-91% yields). Because these compounds were expected to be considerably less volatile than (5-methylfuran-2-yl)methyl benzoate, the acetate esters were prepared rather than the benzoate esters. In FVP experiments, both the acetate and benzoate esters have been shown to generate the desired 2,5-dimethylene-2,5-dihydrofuran **2**.[14]



Scheme 3. Synthesis of diester substrates **8a-g**.

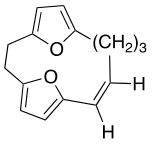
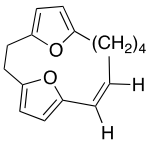
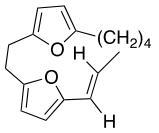
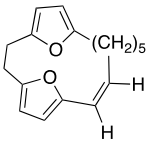
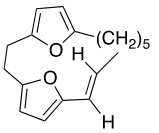
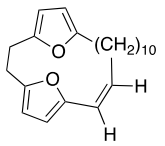
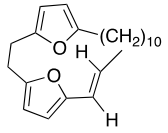
Compounds **8a-g** were subjected to FVP, using a procedure similar to that employed in the pyrolysis of the mono-ester (5-methylfuran-2-yl)methyl benzoate.[14] The substrates were place in a Pyrex sample chamber and the FVP apparatus evacuated to 10^{-5} Torr. With mild heating of the sample chamber (25–150 °C), the precursors were volatilized, passed through a heated quartz pyrolysis tube packed with quartz helices, and the products deposited in a liquid nitrogen-cooled trap. Chloroform was subsequently distilled into the trap for isolation of the products (see Supporting Information). The first compound in the series (**8a**) provides an unexpected fragmentation product **9a** in 33% yield from FVP as the only isolable major product (Scheme 4). It is unlikely that product **9b** is formed via the furan-based bis(*p*-quinodimethane). However, FVP of the butanediyl derivative **8b** gives product **10** as the only major product, though two other isomeric products could be detected by GCMS. The furan-based bis(*p*-quinodimethane) is likely involved in the formation of compound **10** (*vide infra*).



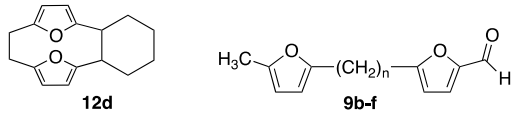
Scheme 4. Pyrolysis products from **8a-b**.

With FVP of larger substrates, macrocycles are formed in reasonable yields (Table 1). For example, compound **8c** gives compound **11c (cis)** as the only major product in 46% yield.

Table 1. FVP products and yields from diester substrates **8c-f**.

starting material	product	structure	yield[a]
8c	**11c (cis)**		46%
8d	**11d (cis)**		47%
	11d (trans)		11%
8e	**11e (cis)**		22%
	11e (trans)		17%
8f	**11f (cis)**		4%
	11f (trans)		19%

[a] Product yields determined by GC-FID analysis using diphenyl ether as an internal standard (see Supporting Information)



Scheme 5. FVP products.

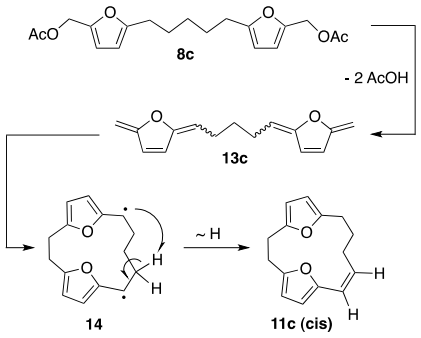
Based on ^{1}H NMR data, the alkene group can be assigned as having *cis* stereochemistry. Compound **8d** also gives macrocyclic products, both **11d (cis)** and **11d (trans)**, in 47% and 11% yields, respectively. In addition to these products, the ring-fused cyclophane **12d** is isolated in 4% yield (Scheme 5). Although ^{1}H NMR suggests a single stereoisomer is formed, we were not able to definitely assign the stereochemistry of the ring junction. Additionally, a small amount of compound **9d** could be detected by GCMS and observed in the NMR spectrum of the crude product mixture. This type of compound (i.e., **9b-f**) is observed as a minor product for all of the FVP experiments. Like diester **8d**, compound **8e** gives the *cis* and *trans* alkenes – **11e (cis)** and **11e (trans)** – as the major FVP products. The proportion of *trans* stereoisomer increases with ring size and this trend is also seen in the FVP of **8f**. These 22 carbon macrocycles – **11f (cis)** and **11f (trans)** – are formed in 23% overall yield with the *trans* stereoisomer being favored. Although **8g** was subjected FVP, this substrate primarily forms char and minor amounts of decomposition products. Presumably, the large diester **8g** is not sufficiently volatile for clean pyrolytic reactions and it decomposes in the FVP hot zone.

As noted above, the macrocyclic products are formed with a preference for the *cis* double bond for products **11c**, **11d**, and **11e**, but with a preference for the *trans* double bond for products **11f**. To determine if the alkene stereochemistry is controlled by a kinetic or thermodynamic effect, we evaluated the thermodynamic ratio of products **11e (cis)** and **11e (trans)** for comparison with the product mixture from FVP of **8e** (Table 2). The thermodynamic mixtures were obtained by isolation of purified **11e (cis)** and **11e (trans)** and subjecting these compounds to pyrolysis at ca. 750 °C. From both purified **11e (cis)** and **11e (trans)**, the observed product mixture consisted of an averaged 74:26 ratio of **11e (cis)**:**11e (trans)** – a value assumed to be the thermodynamic ratio. Since this ratio differs considerably from that obtained by FVP of **8e**, we conclude the product ratio is determined by kinetic control.

Table 2. Equilibration of **11e (cis)** and **11e (trans)** at ca. 750°C.

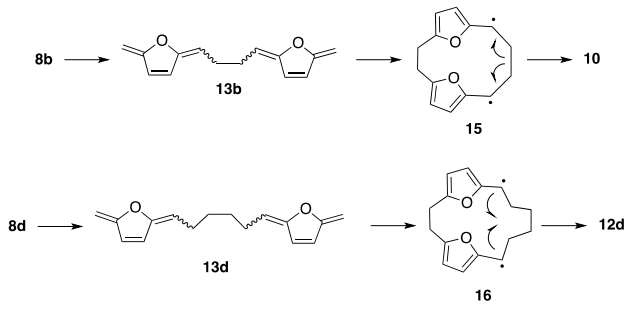
starting material		FVP temperature	product mixture	
11e (cis)	**11e (trans)**		**11e (cis)**	**11e (trans)**
98.0	2.0	753 °C	74.7	25.3
99.4	0.6	766 °C	74.6	25.4
6.2	93.8	753 °C	70.5	29.5
14.0	86.0	740 °C	76.8	23.2

The observed FVP chemistry is consistent with the formation of heterocyclic-based *p*-quinodimethanes linked by the carbon-chain tether. Product formation is in accord with previous work with heterocyclic-based *p*-quinodimethanes - that subsequent reaction steps involve diradical intermediates. Thus, elimination of two acetic acid molecules from **8c** leads to the bis(furan-based *p*-quinodimethane) **13c** (Scheme 6). Analogous to the intermolecular reactions of furan-based *p*-quinodimethanes, the initial cyclization reaction leads to the diradical **14**. The final macrocyclic product **11c (cis)** is formed by a transannular hydrogen atom abstraction involving the diradical **14**. The crude pyrolysis mixtures were isolated at low temperature and analyzed by NMR. No bis(furan-based *p*-quinodimethane) **13c** was observed in the product mixture – suggesting the cyclization and hydrogen migration occurs in the gas-phase. Although the heated zone of the FVP apparatus showed considerable amounts of charring, there were no dimers, trimers, or oligomers observed in the product mixture.



Scheme 6. Proposed mechanism for the fprmation of macrocycle **11c (cis)**.

The proposed general mechanism also explains some of the other observed products. For example, compound **8b** provides the bis(2-vinylfuranyl) product **10** from FVP. This product may arise by either of two routes involving the bis(furan-based *p*-quinodimethane) **13b** from **8b**, either an allowed 14-electron sigmatropic rearrangement or through 1,4-diradical **15** (Scheme 7). The cleavage of 1,4-diradicals is known to produce two alkenyl groups.[16] In the case of **8d**, the ring-fused cyclophane product **12d** was isolated. This product can be explained by formation of the corresponding bis(furan-based *p*-quinodimethane) **13d** from **8d** and closure to provide a 1,6-diradical **16**. Subsequent bond forming leads to cyclophane **12d** from the 1,6-diradical intermediate **16**.



Scheme 7. Diradical reactions from **8b** and **8d**.

In order to further understand the mechanism of the conversions to macrocycles, the furan-based *p*-quinodimethanes were examined computationally. While multiple model

chemistries were employed, for simplicity only MN12SX/6-311+G(d,p) results are discussed hereafter (see Computational Methods section and Supporting Information for reasons behind this choice). Our initial studies examined the conversion of (5-methylfuran-2-yl)methyl acetate **19** to the furan-based *p*-quinodimethane (2,5-dimethylene-2,5-dihydrofuran, **2**. For comparison, energetics were determined at 0K (ZPE-corrected electronic energy), 298K, and 853K (experimental conditions) using the 0K-optimized structures. As described previously, the furan-based *p*-quinodimethane **2** is formed from the starting ester by a pair of [3,3] sigmatropic bond migrations and a β-elimination of the carboxylic acid (Figure 1).[14a] This chemistry leads to intermediates **20** and **21**, and in due course, to the product furan-based *p*-quinodimethane **2**. The computational results for this conversion are presented in Table 3 and Figure 1. The data show that the energetics are quite consistent regardless of temperature or thermodynamic parameter, save for the last step where the acetic acid molecule is eliminated. At all temperatures, formation of the first intermediate **20** is found to involve a significant barrier of *ca*. 190 kJ mol^{-1} (energies

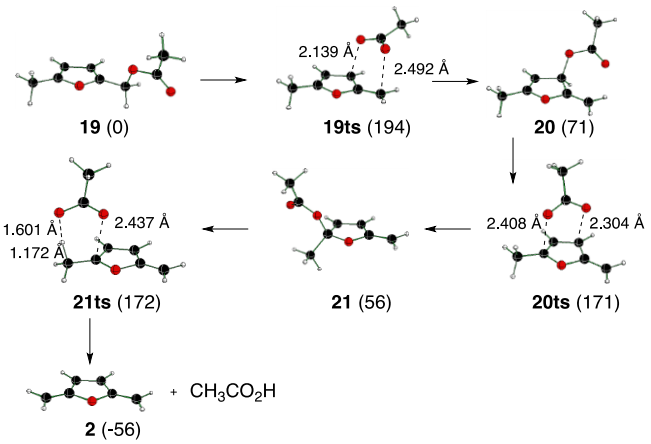


Figure 1. MN12SX/6-311+G(d,p) optimized structures for the conversion of **19** to **2 (**relative free energies at 580 °C/853 K, kJ mol^{-1}).

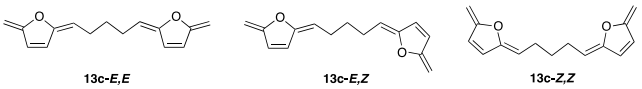
associated with **19ts**) and to be significantly endothermic/endergonic. This is clearly a consequence of the loss of aromatic stabilization within the furan ring. During this first [3,3]-sigmatropic bond migration, the incipient C–O bond forms from the carbonyl oxygen in **19** via the six-membered cyclic transition state **19ts**. The transferring acetate is poorly held by the molecular core, as exemplified by the long distance for the breaking C–O bond (2.492 Å). The potential energy surface around the transition state is quite flat, so this distance value is likely approximate. A degree of stabilization is achieved with the second sigmatropic bond shift to form intermediate **21** but the intermediate is still significantly less stable than the starting material **19**. Transition state **20ts** provides a slightly smaller barrier than does **19ts**. This may arise because transition state **20ts** is earlier (requires less breaking of the C–O bond) than is **19ts**, as suggested by the breaking C–O distances (2.304 vs 2.492 Å).

Table 3. Relative energies (kJ mol^{-1}, MN12SX/6-311+G(d,p)) for the conversion of **19** to **2** (plus CH_3CO_2H).

	19	**19ts**	**20**	**20ts**	**21**	**21ts**	**(2 + CH_3CO_2H)**
***E*, 0K**	0	182	58	163	38	164	74
ΔH_{298}	0	184	57	162	37	168	73
ΔG_{298}	0	188	63	166	44	169	28
ΔH_{853}	0	184	59	163	39	169	71
ΔG_{853}	0	194	71	171	56	172	–56

Finally, β-elimination through transition state **21ts** leads to the furan-based *p*-quinodimethane **2** and a molecule of acetic acid. As above, the potential energy surface around **21ts** is quite flat, so distances should be viewed with caution. It is plausible that two close stepwise transition states (one for breaking of the C–O bond and one for transfer of the hydrogen to the carbonyl oxygen/dissociation of acetic acid) are concatenated as a single concerted one here. While β-elimination is generally assumed to be a concerted reaction, Birney and coworkers have described a number of similar pseudopericyclic rearrangements and ester elimination reactions.[17] The same dynamics may be operating in the conversion to the furan-based *p*-quinodimethane **2**. The effects of temperature associated with formation of **2** are rather dramatic: at all temperatures, the β-elimination is endothermic; at 298K, it is modestly endergonic; at 853K, it is substantially exergonic. The comparison reflects the contribution and importance of entropy in the free energy of this conversion; one sees that enthalpies ΔH_{298} and ΔH_{853} differ little, denoting that differences in ΔG are engendered by entropy. Thus, the only overall calculated exergonic transformation (**19** → **2** + AcOH) is found at the FVP temperature. Since the steps prior to this exhibit high energy barriers and involve high-energy intermediates, this is consistent with the fact that no intermediates – such as **20** or **21** – have been observed from FVP experiments.[14]

The transformation of **8c** to **11c (cis)** was also studied computationally (Table 4 and Figures 2-3). As in the case of furan-based *p*-quinodimethane **2**, formation of the furan-based bis(*p*-quinodimethane) **13c** is found to be a strongly entropy-driven process. Of the three possible stereoisomers of **13c**, all were characterized as minima on the potential energy surface and geometry optimizations indicated that the **13c-*Z,Z*** stereoisomer (Scheme 8) is 10 kJ mol^{-1} more stable than **13c-*E,E*** and 13 kJ mol^{-1} more stable than the **13c-*E,Z***. Nevertheless, the three stereoisomers of **13c** are expected to rapidly interconvert at the pyrolysis temperature. The most stable stereoisomer, **13c-*Z,Z*,** is used in subsequent calculations and discussion.



Scheme 8. Isomers of furan-based bis(*p*-quinodimethane) **13**.

With elimination of two molecules of acetic acid at 853K, the furan-based bis(*p*-quinodimethane) intermediate **13c-*Z,Z*** forms in a highly exergonic process (ΔG_{853} = –192 kJ mol^{-1}), contrasted with the endothermicities predicted by the ΔE and ΔH values (*ca*. 90 kJ mol^{-1}at all temperatures) and the essentially neutral ΔG_{298} value. (Table 4). This value is notably greater than that for elimination of two molecules of acetic acid from two molecules of monoester **19** (ΔG_{853} = 2 x 56 = 112 kJ mol^{-1}) to give two molecules of the furan-based *p*-quinodimethane **2**.

Table 4. Relative energies (kJ mol^{-1}, MN12SX/6-311+G(d,p)) for the conversion of **8c** to **11c** (plus CH_3CO_2H).

	8c	13c-*Z,Z*	14 +2 CH_3CO_2H	14ts	11c (cis)
***E*, 0K**	0	89	104	153	–42
ΔH_{298}	0	89	107	155	–47
ΔG_{298}	0	–10	31	82	–123
ΔH_{853}	0	84	99	144	–59
ΔG_{853}	0	–192	–106	–47	–257

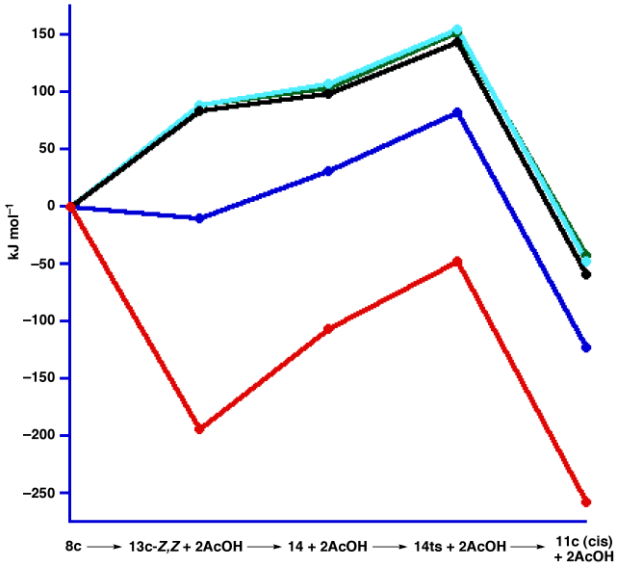


Figure 2. Graphical representation of relative energies (MN12SX/6-311+G(d,p) level, kJ mol^{-1}).

Following generation of the furan-based bis(*p*-quinodimethane) intermediate **13c–*Z,Z***, cyclization gives the singlet diradical intermediate **14**. Calculations reveal this to be an energetically unfavorable step at all temperatures, despite the formation of two aromatic furan rings (Figure 2). At 853K, the free energy change for the step is +86 kJ mol^{-1}, which can be partitioned as +15 kJ mol^{-1} of enthalpic change (Table 4, ΔH_{853} values) and +71 kJ mol^{-1} of entropic change, corresponding to an entropy loss of –83 J/mol • K. The unfavorable enthalpy change appears to arise mostly from the formation of an open-shell diradical. It is conceivable that formation of the cyclophane structure in **14** might prevent efficient stabilization of the benzylic radical centers (contributing to the unfavorable enthalpy change); however, this does not seem to be the case. The optimized structure of **14** exhibits C(ring)–C(ring)–C(ring)–C(radical) torsion angles > 175°, while the C(ring)–C(ring)–C(radical)–C(methylene) torsion angles are > 170°. Moreover, the H-C-C-H bonds are effectively staggered throughout the structure. The energetically dominant entropic change presumably arises mostly from loss of degrees of freedom associated with cyclization, including the torsion angles mentioned. Despite residing in a significant potential energy well, none of the furan-based bis(*p*-quinodimethane) intermediates, such as **13c-*Z,Z***, were observed (low temperature NMR) and oligomeric by-products were not found in the product mixtures. This suggests the subsequent reaction steps occur rapidly in the gas-phase.

The final reaction step leads to the formation of **11c (cis)** by transannular hydrogen atom abstraction. The transition state **14ts** for this process was located through a combination of potential energy surface scans and optimizations and it exhibits "folding" of the macrocycle to lessen the distance the hydrogen atom travels (Figure 3). Specifically, the optimized structure of

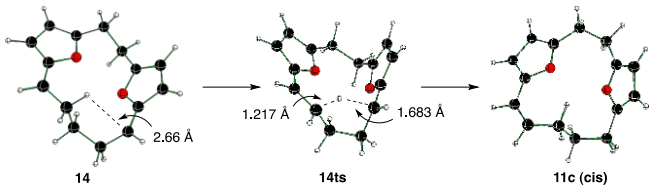


Figure 3. Optimized structures for the transformation of diradical **14** to the alkene **11c (cis)** via transition state **14ts** (UMN12SX/6-311+G(d,p) level).

14 shows a distance of 2.66 Å between the radical center and the reactive hydrogen – well beyond the sum of covalent atomic radii (1.04 Å) but within the sum of van der Waals radii (2.9 Å). Folding the ring (and stretching the C–H bond) to reach the transition state shortens this to 1.68 Å. The pairing of folding and hydrogen transfer motions makes it difficult to characterize the transition state as early or late from a dynamic perspective; that said, one sees that the breaking carbon-hydrogen bond is 1.217 Å at the transition state, elongated by only ca. 0.1 Å from the equilibrium value. Employing the methodology of Manz and Sholl,[18] we find y = 0.20, characteristic of an early transition state. The barrier for this step is predicted to remain in the range of 50–60 kJ mol^{-1} (Table 4) as the reaction temperature increases from 0-853 K. These represent only modest additional energy inputs compared to those required to form **14** (Figure 2).

The hydrogen atom abstraction leads to a pair of new, stable bonds, a C-H σ-bond and C-C π-bond. As such, this contributes to a strongly exergonic step (ΔG_{853} = –294 kJ mol^{-1}) from the diradical **14**. Overall, the formation of **11c (cis)** from **8c** is favorable by 269 kJ mol^{-1}, much of which is due to the elimination of two acetic acid molecules at the elevated pyrolysis temperature. The conversion of **8c** to **11c (cis)** occurs by a total

of eight independent reaction steps: the elimination of each acetic acid to generate the furan-based *p*-quinodimethanes involves three steps each and the cyclization is a two-step process proceeding through the macrocyclic diradical.

The transformation of **8b** to **10** was also examined by DFT calculations. This study sought to compare the viability of a mechanism involving the furan-based bis(*p*-quinodimethane) **13b** and an allowed 14-electron sigmatropic rearrangement versus one proceeding through the 1,4-singlet diradical **15** (Schemes 7 and 9). As above, the furan-based bis(*p*-quinodimethane) **13b-*Z,Z*** proved 5-6 kJ mol^{-1} more stable than the **(*E,E*)** and **(*E,Z*)** stereoisomers. Scans of the potential energy surfaces associated with cyclizing the three stereoisomers of **13b** suggested several possible transition state structures. Energetic and wavefunction stability considerations suggested plausible diradical *and* sigmatropic pathways. These are shown in Scheme 9, along with E(0 K) data. The top process is the sigmatropic rearrangement, while the bottom one is the biradical process. Complete energetic data appear in Table 5 while a full description of the computational methods is found in the Supporting Information section.

Scheme 9. The 14 electron sigmatropic and singlet diradical pathways for the formation of **10** from the furan-based bis(*p*-quinodimethane) **13b**.

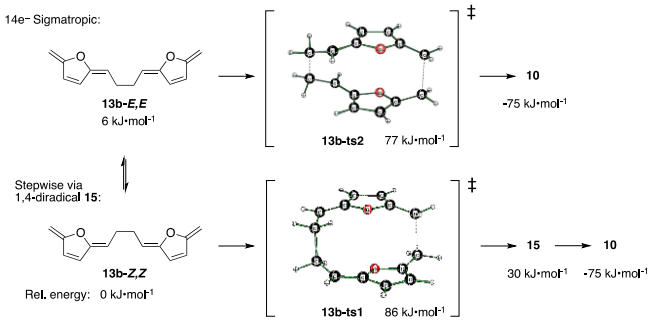


Table 5. Relative energies (kJ mol^{-1}, MN12SX/6-311+G(d,p)) for the two pathways for conversion of **13b** to **10**.

	13b-*Z,Z*	**13b-ts1**	**15**	**13b-*E,E***	**13b-ts2**	**10**
***E*, 0K**	0	86	30	6	77	–75
ΔH_{298}	0	81	25	6	71	–76
ΔG_{298}	0	109	51	14	103	–61
ΔH_{853}	0	77	23	6	66	–78
ΔG_{853}	0	163	101	29	167	–33

Based on the calculated E (0K) and ΔH values, the sigmatropic rearrangement is somewhat favored kinetically, as gauged by the 10 kJ mol^{-1} greater stability for concerted transition state (**13b-ts2**) versus the stepwise transition state (**13b-ts1**). However with entropy considered, the diradical pathway becomes more favorable at increasing temperature. The stepwise, diradical pathway (via **13b-ts1**) is slightly favored at the experimental temperature of 853 K. Nevertheless, the ΔG_{853} values for the transition states differ so little as to be indistinguishable. As all other steps are exothermic/exergonic, the computational modeling does not allow differentiation between the two mechanisms. Consequently, DFT calculations suggest both mechanistic pathways are viable for conversion of furan-based bis(*p*-quinodimethane) **13b** to the observed product **10**.

Regarding products **9a-f**, it is not exactly clear how these compounds are formed from the starting diesters. In most cases, they are observed as minor byproducts, but with **9a** it is the dominant product (formed in 33% isolated yield from **8a**). It is plausible that they arise from radical homolysis and/or disproportionation reactions.

Conclusions

In summary, we showed that furan-based bis(*p*-quinodimethane) structures may be generated by FVP of suitable heterocyclic esters. The furan-based bis(*p*-quinodimethanes) are shown to form macrocyclic products by reaction of the tethered furan-based *p*-quinodimethanes. This represents a rare example of macrocyclic synthesis based on gas-phase chemistry. In accord with previous studies involving *p*-quinodimethanes, the observed products are consistent with formation of diradical intermediates. Theoretical studies have demonstrated a strong thermodynamic driving force for elimination of the carboxylic acid molecule (to form the *p*-quinodimethane) at elevated temperatures as the key driving force for the reactions. It is also shown that formation of the macrocyclic diradical is an energy intensive step, but radical disproportionation leads to a sizable stabilization of the system, providing the final macrocyclic product. Additionally, minor products were observed in most of the FVP experiments – acyclic aldehydes **9a-f** – which appear to be formed by a novel bond homolysis cascade.[19]

Experimental Section

Some general methods have been described previously.[14c] Gas chromatographic analysis was performed on a gas chromatograph (GC), employing a 30 meter DB-1 capillary column, helium carrier gas, and flame ionization detector (FID). Elemental analyses were done by a commercial analytical lab and accurate mass MS data was obtained from a time-of-flight MS instrument operating in EI mode. For the FVP product mixtures, yield percentages were calculated from GC integration by comparison to an internal standard. Phenyl ether was used as the internal standard and the FID detector response factor was previously determined by preparing a solution of measured amounts of phenyl ether and **11c (cis)**. The isolated yield of **11c (cis)** was found to be comparable to the yield calculated from GC analysis. When flash chromatography was used to purify products, standard methods were used with 230-400 mesh silica gel.[20]

Computational Methods. Reactants, intermediates, and products were fully optimized without constraints initially at either the HF/6-31+G(d,p) level or the M06-2X/6-31+G(d,p) level, and confirmed to be minima (no imaginary frequencies) or transition states (1 imaginary frequency) using the *Gaussian 09* suite.[21] When appropriate, wavefunctions were tested for stability with respect to diradical behaviour using the Stable keyword. Singlet diradicals were treated using the "broken symmetry" approach, which employs unrestricted "mixed" wavefunctions for singlets. Test optimizations indicated that this approach gave structures with SCF energies within a few kJ mol^{-1} of those from more demanding CASSCF(6,6) calculations, so the approach was considered appropriate. Structures were further optimized at the (u)M06-2X/6-311+G(d,p) and (u)MN12SX/6-311+G(d,p) DFT levels,[22,23] with frequency analyses performed at the former level to provide more accurate thermal corrections and to confirm that the structures remained minima after inclusion of DFT-based correlation. We employed multiple model chemistries (see Supporting Information) to provide thorough analyses of the structures and to provide a measure of computational variance. We report here only results from the MN12SX model for clarity and because it has been shown to perform exceptionally for a range of test sets encompassing molecules and solid-state materials.[24] Electronic energies for all structures were corrected for zero point energy using data from the HF/6-31+G(d,p) frequency calculations with the zero point energies scaled by a factor of 0.93.[25] Enthalpies and free energies were corrected using unscaled thermal corrections from the (u)M06-2X/6-311+G(d,p) frequency calculations. Complete details are available as Supporting Information.

General procedure for the preparation of α,ω-di(2-acetoxymethyl-5-furyl)alkanes (8a-g). (**6a-g**) are prepared using a published procedure for the alkylation of furans.[26] To a stirred solution at -78 °C containing furan (2.0 g, 29 mmol) in THF (18 mL) and HMPA (2 mL), 11.6 mL BuLi (2.5 M, 29 mmol) is added slowly. The solution is stirred at -78 °C for 1 h, then the α,ω-dibromoalkane (13 mmol, in 5 mL THF) is added and the mixture is allowed to warm (3 h, -78 to 20 °C). The dark solution is then quenched with 20 mL 1.0 M HCl, and this mixture is poured into a separatory funnel containing 50 mL of diethyl ether and 30 mL of 1.0 M HCl. Acidic extraction is followed by washes with saturated $NaHCO_3$, brine, and drying with anhydrous $MgSO_4$. Filtration and removal of ether provides the α,ω-di(2-furyl)alkanes which is purified by distillation or by flash chromatography using 9:1 hexanes:ethyl acetate. Typical yields for this step are 62 to 90%.

(**7a-g**) were prepared using a published procedure for the formylation of furans.[27] To a solution at -78 °C containing the α,ω-di(2-furyl)alkane (10 mmol) in THF (9 mL) and HMPA (1 mL), 8.4 mL of butyllithium (2.5 M, 21 mmol) is added slowly. The solution is stirred at -78 °C for 1 h, DMF (0.73 g, 0.1 mol) is then added and it is allowed to warm (3 h, -78 °C to 20 °C). This solution is stirred for 12 h, then quenched with enough 10% HCl to produce a solution of about pH 7, and added to a separatory funnel containing 50 mL of diethyl ether and 30 mL of 10% HCl. Acidic extraction is followed by washes with saturated $NaHCO_3$, brine, and drying with anhydrous MgS04. Filtration and removal of the ether provides the which is purified by flash chromatography using 3:2 hexanes:ethyl acetate. The α,ω-di(2-formyl-5-furyl)alkanes are yellow solids obtained in 50-70% yields.

*α,ω-Di(2-acetoxymethyl-5-furyl)alkanes (**8a-g**).* The general procedure used to convert the dialdehydes to the diacetates is based on published procedures.[28] A stirred mixture of $LiAlH_4$ (0.57 g, 15 mmol) in THF (25 mL) is cooled to 0 °C, and to it is slowly added a solution of the α,ω-di-(2-formylfuryl-5)alkane (10 mmol) in THF (10 mL). The ice bath is then removed and the mixture was stirred for 1 h at 25 °C. The mixture is cooled to 0 °C and 0.6 mL of H_2O is slowly added, followed by 0.6 mL of 15% NaOH, and then 1.8 mL of H_2O. The mixture is stirred at 25 °C for an additional 20 min. and ~2 g of $MgSO_4$ is then added to the solution. Vacuum filtration removes the precipitated salts, the reaction flask is then rinsed with 20 mL of ethyl acetate, and this solution is poured through the filtered salts. Removal of the solvent then provides crude diol.

The resulting diol is not isolated/purified, but dissolved in THF (20 mL). To the diol (10 mmol) solution, triethylamine (3.5 mL, 25 mmol) and acetyl chloride (1.8 mL, 25 mmol) is added and the solution stirred at 25 °C. The mixture is allowed to react for at least 5 h, during which the triethylammonium chloride precipitates. The progress of the reaction is monitored by thin layer chromatography (eluent, 4:1 hexanes:ethyl acetate). Upon completion of the reaction, the product mixture is poured into a separatory funnel containing 50 mL of 1.0 M HCl and 25 mL of ethyl ether. The acidic extraction was then followed by extraction with saturated $NaHCO_3$ and saturated NaCl. Drying with $MgSO_4$ and removal of the solvent gave the crude diacetate **8.** The diacetate is then purified by flash chromatography using 9:1 hexanes:ethyl acetate as the eluent. From the α,ω-di(2-formyl-5-furyl)alkanes (**7**), typical yields of diacetates **8a-g** are 80-91%.

1,3-Di(2-acetoxymethyl-5-furyl)propane (8a). Clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ, 6.28 (d, *J*= 3.1 Hz, 2H), 5.96 (d, *J*= 3.0 Hz, 2H), 4.98 (s, 4H), 2.65 (t, *J*= 7.5 Hz, 4H), 2.06 (s, 6H), 1.99 (p, *J*= 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 170.08, 156.94, 147.14, 110.89, 105.62, 57.73, 26.89, 25.90, 20.40. IR (thin film, cm^{-1}) 2949, 2872, 1732, 1560, 1437, 1375, 1227, 1022, 972, 791, 752. High-resolution mass spectrum, calcd. for $C_{17}H_{20}O_6$ 320.1260, found 320.1254.

1,4-Di(2-acetoxymethyl-5-furyl)butane (8b). White solid, mp 99-101°C (ether:hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ, 6.29 (d, *J* = 3.1 Hz, 2H), 5.95 (d. *J* = 3.1 Hz, 2H), 4.99 (s, 4H), 2.69-2.60 (m, 4H), 2.08 (s, 6H), 1. 73-1.67 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 170.64, 157.04, 147.60, 111.45, 105.88, 58.29, 27.77, 27.36, 20.93. IR (thin film, cm^{-1}) 2941, 2864, 1734, 1560, 1437, 1375, 1215, 1018, 974, 957, 791. Anal. calcd. for $C_{18}H_{22}O_6$: C 64.66, H 6.63. Found: C 64.70, H, 6.56.

1,5-Di(2-acetoxymethyl-5-furyl)pentane (8c). Clear oil. ^{1}H NMR (C_6D_6, 300 MHz) δ, 6.15 (d, *J*= 3.1 Hz, 2H), 5.74 (d, *J*= 3.1 Hz, 2H), 4.94 (s, 4H), 2.34 (t, *J*= 7.5 Hz, 4H), 1.59 (s, 6H), 1.41–1.32 (m, 4H), 1.12–1.07 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 170.75, 157.37, 147.53, 111.48, 105.79, 58.38, 28.71, 27.98, 27.59, 21.01. IR (thin film, cm^{-1}) 2937, 2862, 1742, 1560, 1435, 1375, 1236, 1018, 974, 795. Anal. calcd. for $C_{19}H_{24}O_6$: C 65.50, H 6.94. Found: C 66.75, H, 7.42.

1,6-Di(2-acetoxymethyl-5-furyl)hexane (8d). Clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ, 6.25 (d, *J* = 3.0 Hz, 2H), 5.90 (d. *J* = 3.0 Hz, 2H), 4.95 (s, 4H), 2.56 (t, *J* = 7.6 Hz, 4H), 2.03 (s, 6H), 1.62–1.55 (m, 4H), 1.37–1.30 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 170.70, 157.48, 147.46, 111.46, 105.71, 58.34, 28.82, 28.00, 27.73, 20.95. IR (thin film, cm^{-1}) 2934, 2860, 1745, 1560, 1437, 1375, 1360, 1238, 1018, 974, 798. Anal. calcd. for $C_{20}H_{26}O_6$: C 66.28, H 7.23. Found: C 67.60, H, 8.22.

1,7-Di(2-acetoxymethyl-5-furyl)heptane (8e). Clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ, 6.24 (d, *J*= 3.1 Hz, 2H), 5.89 (d, *J*= 3.1 Hz, 2H), 4.95 (s, 4H), 2.56 (t, *J*= 7.6 Hz, 4H), 2.03 (s, 6H), 1.64–1.52 (m, 4H), 1.30 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 170.68, 157.57, 147.44, 111.43, 105.66, 58.34, 29.04, 28.99, 28.04, 27.81, 20.95. IR (thin film, cm^{-1}) 2932, 2858, 1744, 1560, 1437, 1375, 1360, 1236, 1018, 972, 798. Anal. calcd. for $C_{21}H_{28}O_6$: C 67.00, H 7.50. Found: C 68.09, H, 8.03.

1,12-Di(2-acetoxymethyl-5-furyl)dodecane (8f). White solid, mp 43-46 °C (ether:hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ, 6.29 (d, *J*= 3.1 Hz,

2H), 5.93 (d, *J*= 3.1 Hz, 2H), 4.99 (s, 4H), 2.60 (t, *J*= 7.7 Hz, 4H), 2.07 (s, 6H), 1.67–1.59 (m, 4H), 1.39–1.23 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, 171.71, 157.72, 147.40, 111.43, 105.61, 58.37, 29.59, 29.53, 29.34, 29.20, 28.09, 27.88. IR (thin film, cm^{-1}) 2920, 2853, 1736, 1562, 1472, 1379, 1246, 1204, 1028, 937, 798. Anal. calcd. for $C_{26}H_{38}O_6$: C, 69.93, H, 8.58. Found: C, 70.02, H, 8.66.

1,16-Di(2-acetoxymethyl-5-furyl)hexadecane (8g). White solid, mp 56-57°C (ether:hexane). ^{1}H NMR ($CDCl_3$, 300 MHz) δ, $CDCl_3$ 6.25 (d, *J*= 3.1 Hz, 2H), 5.90 (d, *J*= 3.1 Hz, 2H), 4.90 (s, 4H), 2.56 (t, *J*= 7.6 Hz, 4H), 2.04 (s, 6H), 1.63–1.54 (m, 4H), 1.34–1.20 (m, 24H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ, $CDCl_3$ 171.70, 157.71, 147.36, 111.43, 105.61, 58.38, 29.67, 29.58, 29.36, 29.23, 28.11, 27.90. IR (thin film, cm^{-1}) 2916, 2851, 1730, 1558, 1472, 1377, 1236, 1207, 1020, 966, 800. Anal. calcd. for $C_{30}H_{46}O_6$: C 71.68, H, 9.22. Found: C 71.61, H, 9.32.

General procedure for FVP of the diester substrates 8a-g. The FVP apparatus is based on a published design.[14a] The heated zone is first allowed to equilibrate to the desired FVP temperature. The appropriate diester (ca. 0.1-0.3 g) is placed in the sample chamber (see Supporting Information) and the apparatus evacuated to 10^{-5} to 10^{-6} Torr. The FVP trap is cooled with liquid nitrogen (-196 °C) and the sample chamber is then heated. Products deposit in the trap as white or yellow solids. Upon complete vaporization of the sample (some residue may remain), dry $CHCl_3$ or $CDCl_3$ (ca. 10 mL) is distilled into the trap from the side inlet. The FVP apparatus is filled with argon gas and the trap is removed. The trap is allowed to warm and anhydrous Na_2CO_3 (0.5 g) is added to the product mixture. The mixture is then filtered and the products are isolated.

FVP of 8a. FVP required heating the starting material **8a** to 70 °C for volatilization. Product composition was somewhat variable, but one major product was observed by GCMS to have m/z of 218. This product was isolated and identified as **9a. 1-(2-Methyl-5-furyl)-3-(2-formyl-5-furyl)propane (9a).** Clear oil, 33% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.50 (s, 1H), 7.15 (d, *J*= 3.5, 1H), 6.23 (d, *J*= 3.5 Hz, 1H), 5.85 (s, 1H), 5.82 (s, 1H), 2.75 (t, *J*= 7.6, 2H), 2.62 (t, *J*= 7.3, 2H), 2.23 (s, 3H), 2.01 (p, *J* = 7.5, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 176.8, 163.2, 152.9, 151.7, 150.4, 123.2, 108.8, 105.9, 105.7, 27.5, 27.2, 26.0, 13.4. IR (thin film, cm^{-1}) 2950, 1677, 1516, 1020, 784. MS (EI) 218 (M+), 123, 122, 109, 108, 107, 96, 95, 81, 53. High-resolution mass spectrum, calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0943.

FVP of 8b. FVP required heating the starting material **8b** to 90 °C for volatilization. The crude mixture contained four products in a 43:10:4:1 ratio and GCMS indicated respective *m/z* values of 214, 232, 214, and 214. The most abundant product was isolated and identified as 1,2-di(2-vinylfuryl-5)ethane (**10**), the second most abundant product was thought to be **9b**, and the two minor products could not be isolated and identified. **1,2-Di(2-vInyl-5-furyl)ethane (10)**. Clear oil, 10% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.40 (dd, J= 11.3, 17.5 Hz, 2H), 6.10 (d, J= 3.2, 2H), 5.96 (d, J= 3.2 Hz, 2H), 5.54 (dd, J= 1.2, 17.5 Hz, 2H), 5.04 (dd, J = 1.3, 11.3 Hz, 2H), 2.95 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5, 151.8, 125.0, 110.9, 109.0, 108.9, 107.1, 26.9. IR (thin film, cm^{-1}) 2918, 1678, 1639, 1585, 1528, 1254, 1032, 1018, 897, 785. MS (EI) 214 (M+), 108, 107, 77, 55. High-resolution mass spectrum, calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0997.

FVP of 8c. FVP required heating the starting material **11c** to 100°C for volatilization. The crude mixture contained three products in a 17:2:1 ratio and GCMS indicated respective m/z values of 228, 228, and 246. The most abundant product was isolated and identified as **11c (cis)**, the product of m/z 246 was thought to be **9c**, while the other product could not be isolated/identified. ***cis*–1,2-Dehydro[5,2](2,5)furanophane, 11c (cis).** White solid, mp 96-97 °C (ether:hexane), 46% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.99 (d, J = 11.6 Hz, lH), 5.92 (d, J = 3.1 Hz, lH), 5.88 (d, J= 2.9, lH), 5.84 (d, J= 2.9 Hz, lH), 5.79 (d, J= 3.2 Hz, lH), 5.48 (dt, J= 8.8, 11.6 Hz, lH), 2.60-2.51 (m, 6H), 2.42-2.35 (m, 2H). 1.87–1.75 (m, 2H). ^{13}C NMR (C_6D_6, 75 MHz) δ 155.6, 154.6, 153.8, 153.4, 129.1, 118.2, 110.4, 107.9, 107.2, 105.9, 30.2, 28.7, 28.5, 27.7, 27.6. IR 2924, 2854, 1560, 1456, 1423, 1396, 1169, 1018, 789. MS (EI) 228 (M+), 134, 133, 121, 107. High-resolution mass spectrum, calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1148.

FVP of 8d. FVP required heating the starting material **11d** to 105°C for volatilization. The crude mixture contained four products in a 18:4:2: 1 ratio and GCMS indicated respective m/z values of 242, 242, 242, and 260. The three most abundant products were isolated and identified as **11d (cis), 11d (trans), and 12d,** while one product could not be isolated but presumably was product **9d. *cis*–1,2-Dehydro[6.2](2,5)furanophane, 11d (cis).** Clear oil, 47% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.99 (d, *J*= 3.3 Hz, lH), 5.97 (d, *J*= 3.2 Hz, lH), 5.89 (d, *J*= 11.7, lH), 5.80 (d, *J*= 2.9 Hz, lH), 5.75 (d, *J*= 2.9 Hz, lH), 5.42 (dt, *J*= 8.3, 11.6 Hz, lH), 3.07-2.98 (m, 2H), 2.81-2.75 (m, 2H), 2.62 (t, *J* = 6.3, 2H), 2.30-2.20 (m, 2H), 1. 78- 1.65 (m, 2H), 1.28–1.20 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.2, 154.1, 152.4, 152.1, 129.8, 117.0, 110.3, 106.9, 106.9, 106.4, 29.3, 28.9, 27.9, 27.5, 27.4, 27.0. IR (thin film, cm^{-1}) 2930, 2860, 1568, 1435, 1213, 1132, 1015, 984, 783. MS m/e (EI) 242 (M+), 135, 120, 107, 94. High-resolution mass spectrum, calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1309. **trans–1,2-Dehydro[6.2](2,5)furanophane, 11d (trans).** Clear oil, 11% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.02 (d, *J*= 3.0 Hz, lH), 5.97 (d, *J*= 15.9 Hz, lH), 5.96 (d, *J*= 3.0, lH), 5.91 (d, *J*= 3.0 Hz, lH), 5.84 (d, *J*= 2.9 Hz, lH), 5.56 (dt, *J*= 7.1, 15.9 Hz, lH), 2.84 (s, 4H), 2.57-2.50 (m, 2H), 2.12-2.03 (m, 2H), 1.67–1.50 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.1, 154.0, 153.0, 149.5, 132.2, 118.3, 107.5, 106.2, 105.4, 105.4, 31.0, 29.2, 28.7, 28.1, 25.8, 23.5. MS (EI) 242 (M+), 135, 120, 107, 77. High-resolution mass spectrum, calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1306. **[1:2]Butano[2.2](2,5)furanophane (12d).** Clear oil, 4% yield. IR (thin film, cm^{-1}) 2918, 2853, 1547, 1447, 1190, 1157, 1016, 1007, 787. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.10 (d, *J*= 3.0 Hz, 2H), 6.03 (d, *J*= 3.0 Hz, 2H), 2.82 (d, *J*= 9.4, 2H), 2.61 (d, *J* = 9.6, 2H), 2.43-2.37 (m, 2H), 1.95–1.84 (m, 2H), 1.70–1.55 (m, 2H), 1.43–1.33 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 156.0, 107.9, 105.3, 48.7, 30.7, 28.4, 26.0. IR (thin film, cm^{-1}) 2918, 2853, 1547, 1447, 1190, 1157, 1016, 1007, 787. MS (EI) 242 (M+), 135, 120, 107, 94. High-resolution mass spectrum, calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1311.

FVP of 8e. FVP required heating the starting material **11e** to 105 °C for volatilization. The crude mixture contained three products in a 25:18:1 ratio and GCMS indicated respective m/z values of 256, 256, and 274. The two most abundant products were isolated and identified as **11e (trans),** and **11e (cis),** while the minor product could not be isolated, but was likely **9e. *cis*–1,2-Dehydro[7.2](2,5)furanophane, 11e (cis).** Clear oil, 22% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.02 (d. *J* = 3.1 Hz, lH), 6.00 (d, *J* = 3.1 Hz, lH), 5.92 (d. *J* = 11.7 Hz, lH), 5.89 (d, *J*= 11.7, lH), 5.76 (d. *J* = 2.9 Hz, lH), 5.71 (d, J = 2.8 Hz, lH), 5.29 (dt, *J* = 8.1, 11.7 Hz, lH), 3.01-2.93 (m, 2H), 2.85-2.79 (m, 2H), 2.56 (t, *J*= 6.0 Hz, 2H), 2.32 (dd, *J*= 6.9, 6.9, 2H), 1.69–1.57 (m, 2H). 1.42–1.31 (m, 4H). ^{13}C NMR ($CDCl_3$. 75 MHz) δ 155.0, 152.4, 152.0, 130.0, 117.9, 110.3, 106.4, 106.3, 105.7, 29.3, 28.2, 28.0, 28.0, 27.8, 27.3, 27.0. IR (thin film, cm^{-1}) 2920, 2857, 1585, 1429, 1013, 980, 779. MS m/e (EI) 256 (M+), 120, 107, 94, 91. High-resolution mass spectrum, calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1463. ***trans*–1,2-Dehydro[7.2](2,5)furanophane**, **11e (trans).** Clear oil, 17% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.96 to 5.87 (m, 5H), 5.83 (d, *J*= 3.0 Hz, lH), 2.94- 35 2.83 (m, 4H), 2.54 (t, *J* = 6.1 Hz, 2H), 2.10 (dd, *J* = 6.0, 5. 7 Hz, 2H), 1. 70–1.61 (m, 2H), 1.49–1.41 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.1, 153.9, 129.9, 117.9, 106.5, 106.1, 105.8, 105.5, 31.1, 27.9, 27.7, 27.2, 27.0, 26.5, 24.6. IR (thin film, cm^{-1})

2920, 2857, 1585, 1429, 1013, 980, 779. MS (EI) 256 (M+), 120, 107, 94, 91. High-resolution mass spectrum, calcd for $C_{17}H_{20}O_2$ 256.1463, found 256.1467.

FVP of 8f. FVP required heating the starting material **8f** to 130 °C for volatilization. The crude mixture contained two major products in a 4:1 ratio and GCMS indicated respective m/z values of 326 and 326. The most abundant product was isolated and identified as **11f (trans),** while a partial characterization of the other product suggested its identity as **11f (cis).** In addition, a minor product was observed by GCMS which had a m/*z* value of 344. This product was thought to be **9f.** ***trans*–1,2-Dehydro[12.2](2,5)furanophane**, **11f (trans).** Clear oil, 19% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.05 (d, *J* = 16.1, lH), 5.96-5.86 (m, 3H), 5.80 (d. *J* = 3.0 Hz, lH), 5. 75 (d, *J* = 2.9 Hz, lH), 2.99-2.84 (m, 4H), 2.47 (t, *J*= 7.1 Hz, 2H), 2.14 (dd, *J*= 6.0, 5.7 Hz, 2H), 1.53–1.12 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.6, 153.7, 152.6, 151.7, 128.6, 119.2, 106.8, 106.5, 105.7, 105.1, 31.1, 28.0, 27.6, 27.5, 27.2, 27.2, 26.6, 26.1. MS (EI) 326 (M+), 121, 108, 107, 95. IR (thin film, cm^{-1}) 2926, 2854, 1568, 1533, 1460, 1437, 1281, 1092, 1015, 960, 800, 775. High-resolution mass spectrum, calcd for $C_{22}H_{30}O_2$ 326.2247, found 326.2246. ***cis*–1,2-Dehydro[12.2](2,5)furanophane, 11f (cis).** Clear oil, ~ 4% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.05-5.95 (m), 5.86 (d), 5.86-5.75 (m), 2.92 (s), 2.55 (t), 2.23 (d), 1.30 (s). MS (EI) 326 (M+), 133, 121, 108, 107, 95, 94, 55.

FVP of 8g. FVP required heating the starting material **8g** to 150°C for volatilization. The crude mixture contained no products such as **11g** or **9g.** The GCMS data suggested that considerable fragmentation occurred during FVP.

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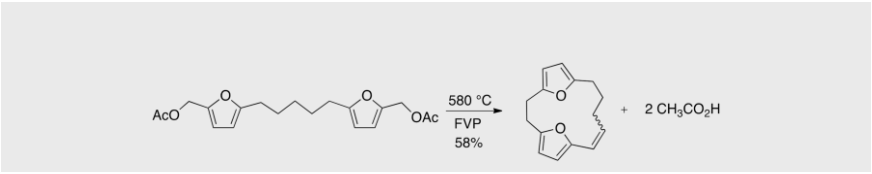

Flash vacuum pyrolysis (FVP) is used to generate furan-based bis-(*p*-quinodimethanes and a gas-phase macrocyclization occurs to give cyclophane products. A mechanism is proposed involving cyclization of the furan-based bis-(*p*-quinodimethane, formation of cyclic diradicals, and transannular hydrogen atom migration. The chemistry is also studied by computational methods, revealing the importance of entropy effects in the high-temperature, gas-phase chemistry.

Reactive Intermediates

Douglas A. Klumpp, Thomas M. Gilbert, and Walter S. Trahanovsky**

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Intramolecular Reactions of Tethered Furan-based bis-(*p*-Quinodimethanes)