of the $(R^1/Et)_{1,3\text{-}p}$ interaction. The lower reactivity of dialkyl and alkyl aryl acrylonitriles compared to monosubstituted substrates is not unexpected considering the influence of the substituents on the electronic density at the double bond. This could also be responsible for the low reactivity of trisubstituted vinyl sulfoxide **8**, but the $(O/R^3)_{gauche}$ and $(Tol/R^3)_{gauche}$ interactions present when $R^3 \neq H$ can also be involved in the destabilization of both $\mathbf{TS_A}$ and $\mathbf{TS_B}$.

Desulfinylation of the amides **15**–**17** and **19** with Raney nickel afforded the corresponding enantiopure amides **21**–**24**, which were isolated in good yields (>70%, Scheme 3).[21]

In summary we have shown that the hydrocyanation of alkenyl sulfoxides with Et_2AlCN takes place in a completely stereoselective manner. Taking into account the chemical versatility of the cyano and sulfinyl groups, this reaction can be considered as the key step in a short sequence that allows the creation of optically pure molecules containing tertiary or quaternary chiral centers from terminal alkynes, as illustrated with the preparation of amides **21**–**24**.

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[17] After the reaction mixture was heated for 24 h at reflux, we isolated an unexpected compound (30% yield) which has not been identified yet.

[18] These conditions promote the conversion of sulfinyl nitriles into sulfinyl amides with inversion of the configuration at sulfur (see refs. [14c, 15]) The hydrolysis of nitrile **12** with KOH in refluxing *t*BuOH (J. H. Hall, M. Gisler, *J. Org. Chem.* **1976**, *41*, 3769) afforded diastereomer **18′**, an epimer at sulfur of **18**, because under these conditions neither the configuration at carbon or at sulfur is affected.

[19] Proper crystals of compunds **9**–**13** could not be obtained.

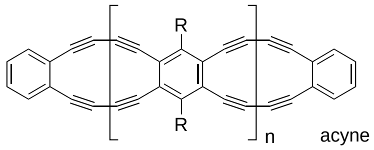
[20] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154583 (**16**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[21] As the optical purity of the amides could not be established by chiral shift reagents or chiral HPLC, the chemical correlation of **21** with commercially availale (*S*)-2-methylbutanoic acid was neccesary. The amides derived from (*S*)-2-methylbutanoic acid and from **21** by desulfurization exhibited a specific rotation of the same value and sign. Therefore, we can conclude that the configuration at C2 of **21** must be *S*, in complete agreement with the X-ray structure analysis.

Synthesis of a Remarkably Stable Dehydro[14]annulene[**]

Grant J. Palmer, Sean R. Parkin, and John E. Anthony[*]

Dehydroannulenes are a fascinating class of carbon-rich molecules which have been studied intensively.[1] With the development of improved synthetic methodologies, these macrocycles are now being exploited for their potential material properties. Recent applications employ such annulenes as conjugated scaffolds for nonlinear optical applications[2] and as precursors for carbon nanotube synthesis.[3] We are currently exploring the use of fused dehydroannulenes as components in conjugated ladder polymers (e.g. acynes **1** and rylynes **2**).



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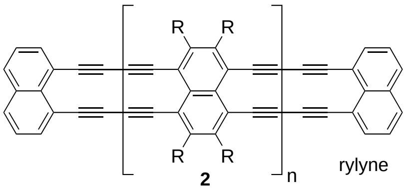

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While the phenyldiacetylene macrocycles that comprise **1** are well-known compounds,[4] the class of dehydroannulenes that make up the backbone of **2** is poorly understood. The parent compound **3** was prepared in 1968 by Mitchell and Sondheimer, who were unable to fully characterize this new

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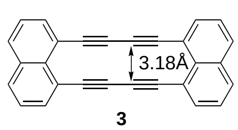

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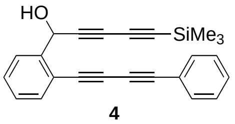

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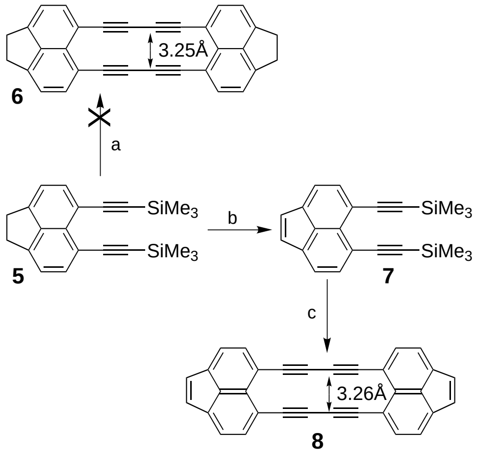
annulene because it decomposed rapidly, even in dilute solution.[5] They postulated that this instability arose from the proximity of the alkynes in the rigid macrocycle. Indeed, the high reactivity of this structural motif has been exploited in acyclic systems such as **4**, which undergo facile intramolecular cyclization to form extended aromatic structures.[6] Recently, several examples of unconjugated macrocyclic butadiynes have been shown to be stable at room temperature,[7] which has led us to revisit the chemistry of compounds based on **3**, the fundamental component of ladder polymer **2**.

If the decomposition of **3** is in fact related to the proximity of the two parallel butadiyne units (calculated distance: 3.18 Å),[8] substituents which increase the separation between these units should stabilize the macrocycle. For example, it has been shown that changes in alkyne terminus separation of as small as 0.05 Å can have a significant effect on reactions such as the Bergman cycloaromatization.[9] According to ab initio calculations, the butadiyne units in acenaphthene derivative **6** are separated by 3.25 Å (Scheme 1), an increase of 0.07 Å compared to **3**. Thus, 5,6-diethynylacenaphthene[10] was subjected to oxidative cyclization under high-dilution conditions. Analysis of the resulting insoluble solid by high-resolution LD-MS (laser desorption mass spectrometry) showed only small amounts of both residual starting material and a dimerized, acyclic species. Compound **6** could not be detected, presumably as a result of the rapid decomposition of the macrocycle.



Scheme 1. Synthesis of macrocycle **8**. Reagents and conditions: a) 1. K_2CO_3 in MeOH/THF; 2. CuCl/TMEDA in CH_2Cl_2; b) DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone); c) 1. K_2CO_3 in MeOH/THF; 2. CuCl/TMEDA in CH_2Cl_2, 75%.

Examination of the π-bond topology of **3** reveals that the perimeter of that macrocycle is not fully conjugated, unlike other stable dehydroannulenes. The acenaphthylene-derived macrocycle **8** addresses this deficiency, leading to a fully-conjugated 28 π-electron macrocycle. Although this cycle is formally antiaromatic, numerous other antiaromatic dehydroannulenes have been shown to be stable.[11] To prepare **8**, diethynylacenaphthylene **7** was synthesized by the oxidation of acenaphthene **5**. Desilylation followed by oxidative cyclization led to a brilliant orange powder, which was sparingly soluble in dichloromethane.

The UV/Vis spectrum of this new compound (Figure 1) strongly resembles that reported for **3**, with two characteristic peaks at 455 and 485 nm (**3** shows absorbances at 502 and 540 nm). This stable compound survived recrystallization from *o*-dichlorobenzene (180 °C) without decomposition. High-resolution mass spectrometry and ^1H NMR spectroscopy support the structural assignment for **8**. Unfortunately, this compound proved to be too insoluble for further characterization.

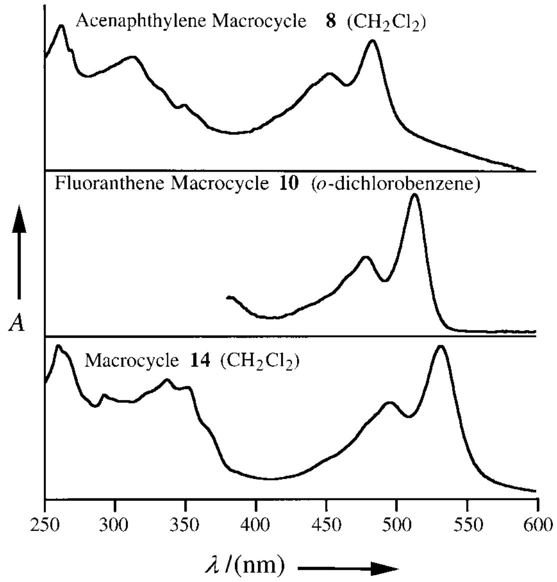
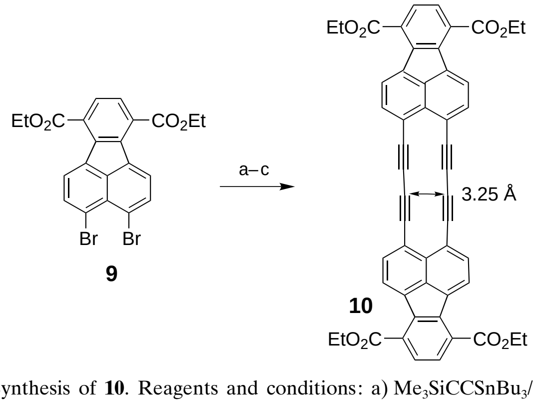


Figure 1. UV/Vis spectra of compounds **8**, **10**, and **14**.

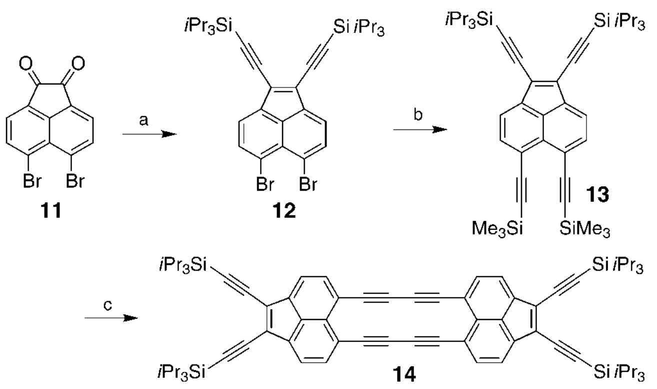
In an attempt to synthesize a more characterizable macrocycle, fluoranthene **9** was prepared[12] and alkynylated (Scheme 2). Desilylation followed by oxidative cyclization again led to a stable orange powder, which exhibited characteristic absorbances at 480 and 515 nm. Surprisingly, this compound was significantly less soluble than the ace-



Scheme 2. Synthesis of **10**. Reagents and conditions: a) $Me_3SiCCSnBu_3$/$[(Ph_3P)_2PdCl_2]$; b) K_2CO_3 in EtOH/THF; c) CuCl/TMEDA in CH_2Cl_2.

naphthylene derivative **8**. Although the high-resolution mass spectrum and UV/Vis absorption spectrum supported the assignment of macrocyclic structure **10**, a species soluble enough for more thorough characterization was still required.

A more aggressive solubilization strategy was utilized in the preparation of **14** (Scheme 3). Beginning with quinone **11**, treatment with a Grignard reagent followed by reductive deoxygenation led to the very soluble enediyne **12**.[13] Alkynylation by Stille coupling[14] led to tetrayne **13**, which was selectively desilylated and oxidatively coupled to yield a deep red solution of macrocycle **14**. This soluble material shows remarkable thermal and photochemical stability. Solutions of **14** were heated at > 190 °C for several hours, or left in direct sunlight for a period of several weeks, without noticeable decomposition. Examination of the ^{1}H NMR spectrum shows a slight paratropic shift of all of the aromatic protons of the macrocycle with respect to the acyclic starting material. The FTIR, ^{13}C NMR, and mass spectral analyses all support the structural assignment of **14**.



Scheme 3. Synthesis of **14**. Reagents and conditions: a) 1. iPr$_3$SiCCMgBr; 2. AcOH/SnCl$_2$, 80 %; b) Me$_3$SiCCSnBu$_3$, [(Ph$_3$P)$_2$PdCl$_2$], 60 %; c) 1. K$_2$CO$_3$ in MeOH/THF; 2. CuCl/TMEDA in acetone, 88 %.

Slow evaporation of a 1,2-dichloroethane solution of compound **14** led to dark purple crystals with a golden metallic luster. The structure was determined by X-ray crystallographic analysis (Figure 2).[15] Consistent with calculations, the central carbon atoms of the two butadiyne units (C14–C1) are indeed splayed outward, separated by a distance of 3.23 Å. Even with this distortion, the butadiyne units are nearly linear, with the most extreme variation from linearity a mere 7°. As expected, the annulene backbone is planar to within 0.05 Å.

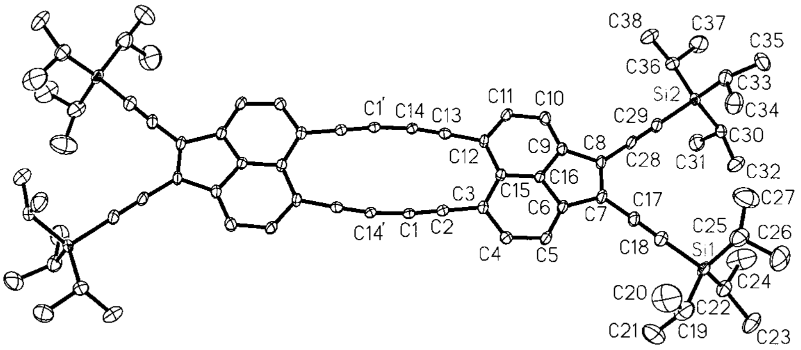


Figure 2. Molecular structure of **14** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: C1′-C14 1.371(3), C14-C13 1.201(3), C13-C12 1.430(3), C12-C15 1.441(3), C15-C3 1.439(3), C3-C2 1.428(3), C2-C1 1.202(3), C1-C14′ 1.371(3), C12-C11 1.389(3), C11-C10 1.407(3), C10-C9 1.370(3), C9-C8 1.474(3), C8-C7 1.379(3), C7-C6 1.472(3), C6-C5 1.369(3), C5-C4 1.402, C4-C3 1.398(3), C15-C16 1.394(3), C9-C16 1.411(3), C16-C6 1.413(3); C1′-C14-C13 173.6(2), C14-C13-C12 176.3(2), C13-C12-C15 121.34(19), C12-C15-C3 129.65(18), C15-C3-C2 123.26(19), C3-C2-C1 178.0(2), C2-C1-C14′ 172.7(2).

We have demonstrated that with proper functionalization, the preparation of stable naphthalene diacetylene macrocycles is possible. The distance between butadiyne units in these systems has been found to be less important to stability than conjugation. We are currently exploring the incorporation of these stabilized macrocycles into new carbon ladder polymers based on **2**.

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$I > 2\sigma(I)$), $R_1 = 0.0768$, $wR_2 = 0.1153$ (for all data); data-to-parameter ratio 16.52; residual electron density $+0.302/-0.260$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158650. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

IR-UV Double-Resonance Photodissociation of Nitric Acid ($HONO_2$) Viewed as Molecular Information Processing**

Thomas Witte, Christine Bucher, Françoise Remacle, Detlev Proch, Karl L. Kompa, and R. D. Levine*

One route to nanoscale computing is to make single molecules that can mimic the function of conventional components of electronic logic circuits, such as switches or wires. There is therefore increasing activity in producing molecules that can conduct electrical current or can be instructed to turn it on or off when placed within a suitable support. This field of activity, sometimes known as molecular electronics[1] or molecular scale electronics,[2] is a major current research area. Now that several groups[2–4] have demonstrated that a molecule can act as a switch,[5] it is possible to begin thinking about replacing transistors by single molecules within larger digital devices. The chemical pumping of molecules in solution that induces changes that can be optically detected has also been been studied for some time[6–8] as a possible route to logic gates. More generally, the progress in supramolecular chemistry towards the construction of molecular machines[9, 10] opens up many possibilities for an induced response.

An alternative to the approach in which a molecule acts as a single switch is a scheme where the function of an entire logic circuit is performed by a single isolated molecule.[11, 12] A particular molecular coordinate, which could be a reactive one, acts as the bus for information transfer. This alternative route has the distant goal of incorporating the logic capabilities of a complete integrated circuit on a single molecule. A more modest goal is the experimental demonstration of a circuit containing several connected logic gates as a (logic) equivalent of the intramolecular dynamics of a single molecule. The experimental demonstration of such a scheme is presented herein.

A molecule in a molecular logic gate scheme[11] becomes a vehicle for information processing, where the input is optical excitation. In the experiment discussed below the resonance requirement is paramount, and an intramolecular motion is essential for the logic action. We discuss time-resolved measurements because one advantage of our gates is that they can be ultrafast, as reported for a number of other systems.[11] With our device we get the output as an optical signal. However, the recent experiments of Crim and co-workers[13] suggest that the logic of the present approach can be probed by chemical means.

A conventional logic circuit is built from connected switches. The advantage of the approach we follow is that by operating a single molecule as a logic circuit one avoids the need to connect switches. The circuit reported here is already equivalent to several switches, and this, we hope, is only the beginning. The logic gate that we describe is completely irreversible since the molecule is destroyed. This dissociation is not an essential aspect and we have discussed[11] other molecules where this need not be the case, and where the initial state can be recovered as quickly as one picosecond.

The power of organic synthesis to design molecules should not be overlooked. What one wants is a circuit that is operable over many cycles. The first step is the need to regenerate the ground state. In some systems, for example, the photoinduced keto–enol tautomerism, this requirement is inherently satisfied. In other systems, such as electrocyclic ring openings, the photoprocess generates more than one possible product, and this can be used to advantage. In essence what we look for is a prompt intramolecular response to an optical excitation. Typically, such a response involves a rotation of part of a molecule relative to another to bring about a recoupling of the electronic orbitals.

Since the 1970s great advances have been made possible by combining laser spectroscopy and reaction dynamics. The double-resonance experiment that we discuss falls into this class. The principles[14–16] are understood and the application to the $HONO_2$ system has been previously studied.[17, 18] What is new and interesting is the hitherto unknown effect determined by the order of the two ultrafast UV and IR pulses. Still, it can be asked if what we are discussing is little more than a semantic rephrasing of an experiment. What we actually do is to explore the implications of a spectroscopic experiment from a new point of view, which opens up options and possibilities that are not evident without it. It also raises new questions of principle. For the moment, however, we just want to highlight a cross-disciplinary study involving modern chemical physics and Boolean logic. We are aware that one can carry our ideas into the non-Boolean (that is, quantal) regime, but for now we will view the experiment in chemical kinetic, that is, classical, terms.

To introduce the subject we begin with the IR-UV double-resonance experiment of Crim and co-workers (Figure 1).[14, 17–19] An IR photon generates a vibrationally excited state (OH stretch overtone) of the ground electronic state of

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