Synthesis of Molecular Lines, Rigid Linear Molecules with Nanometer Scale Dimensions

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The synthesis of molecular 3.06, 5.28, and 7.50 nm lines, composed of polyacenequinone units, *via* repetitive Diels–Alder reactions is reported.

We report the synthesis of several linear molecules of unusual length and constitution. Repetitive Diels–Alder reactions have been used in a convergent synthesis leading to molecules which have accurately defined lengths up to 7.5 nm. Until now, to our knowledge, the only linear structures of this length are polymers which have mixed lengths.

Structures with well defined dimensions in the range of 5—10 nm and defined chemical constitution provide a new field of study with potential applications in areas including electronics. Currently, the production of semiconductor-based microelectronic devices relies on selective etching and lithographic processes. These have good spacial resolution on the micron and even submicron scale. Molecular synthesis is an alternative method, which has been dreamed of for more than twenty-five years.[1] Synthesis is attractive because it could lead to nanometer scale devices, but synthesizing complex surface structures with appropriate electronic properties is obviously a challenging, long-term task. As a first step, we set out to prepare simple structures on the 1–10 nm scale, using sequential addition of rigid building blocks to control precisely the size and shape.

In this paper we report that repetitive Diels–Alder reactions lead to the simplest structures of this type, which we have termed molecular lines. We also report that our previously developed approach to solubilize a nonacene triquinone[2] imparts some solubility even on the longest of these lines. We believe that soluble (therefore, purifiable) compounds of this type will be useful for the surface synthesis we plan, and will be of interest as conductive molecular wires and as rigid spacers for other scientific studies.

Polyacenequinones were chosen as building blocks for these lines for reasons that have been presented elsewhere.[2,3] In the present case these building blocks were linked together by imides since they retain the linear structure and have certain synthetic advantages. Beginning from the bis-diene (**1**), we have used a two-step elongation sequence of Diels–Alder addition, followed by aromatization with conc. H_2SO_4. This is illustrated (Scheme 1) by preparation of (**4**) from (**1**) in 61% yield.† Compound (**4**) is 3.1 nm long.

A key development was the preparation of the unsymmetrical monoadduct (**3**). In preliminary studies,† it was found that Diels–Alder adducts from (**1**) were always *endo*. *N*-Methylmaleimide, for example, formed a mono-*endo* adduct with a *syn*; and *anti*- pair of bis-*endo* products. The first

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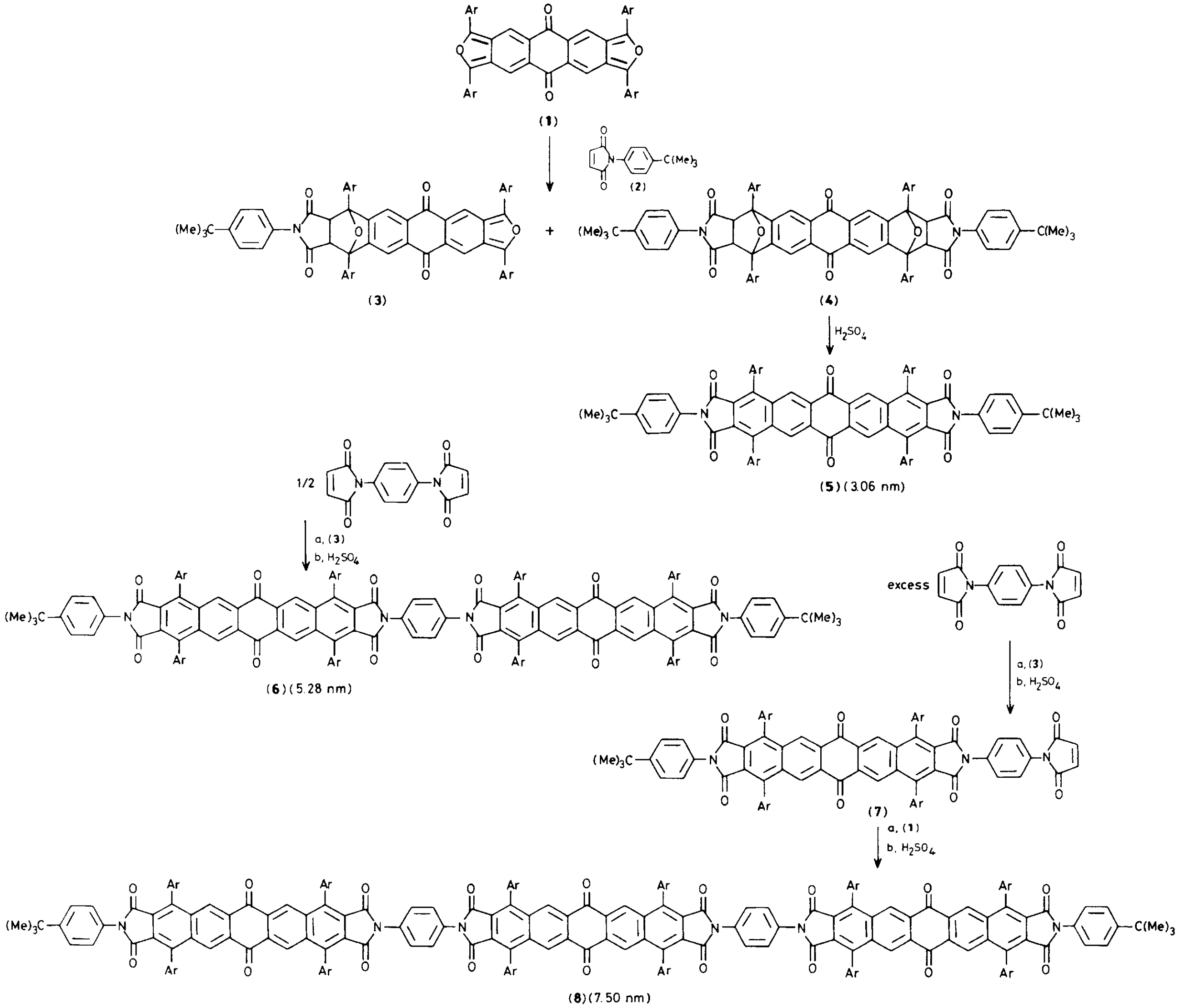
† Compounds (**1**)—(**8**) were characterized by ^1H n.m.r. i.r., and fast-atom bombardment m.s. *e.g.* (**5**): ^1H n.m.r. δ 8.99 (s, 4H), 7.58 (d, *J* 8.4 Hz, 8H), 7.41 (d, *J* 8.4 Hz, 8H), 7.40 (d, *J* 8.6 Hz, 4H), 7.24 (d, *J* 8.6 Hz), 1.42 (s, 36H), 1.26 (s, 18H); ^{13}C n.m.r. 182.0 (no H), 165.6 (no H), 152.1 (no H), 151.5 (no H), 142.0 (no H), 138.4 (no H), 131.7 (no H), 130.4 (no H), 130.1 (no H), 129.8 (1 H), 128.6 (no H), 126.48 (no H), 126.45 (1 H), 125.9 (1 H), 125.4 (1 H), 34.9 (no H), 34.7 (no H), 31.4 (3 H), 31.2 (3 H); i.r. (KBr) 1772, 1724, 1688 cm^{-1}; m.s. (f.a.b.) (*m*-nitrobenzyl alcohol) calc. for ($M + 1$) $C_{86}H_{83}N_2O_6$ 1239.6251; found 1239.6277. (**8**) ^1H n.m.r. ($CDCl_3$) δ 8.97 (s), 8.926 (s), 8.919 (s), 7.60—7.55 (m), 7.45 (s), 7.42—7.35 (m), 7.24 (d, *J* 9), 1.42 (s), 1.41 (s), 1.25 (s). i.r. (KBr) 1772, 1727, 1685 cm^{-1}; m.s. (f.a.b.) (*m*-nitrobenzyl alcohol) exact mass average molecular weight from centroid of isotopic peaks calc. 3338.155; found 3337.958 (unit resolution not achieved).



Scheme 1. Ar = p-$Me_3CC_6H_4$.

addition of *N*-methylmaleimide was only four times faster than the second, so that isolation of the monoadduct was not practical. Formation of the mono-*endo* adduct from the longer dienophile (**2**), however, sterically prevented formation of the *syn*-bis-*endo* adduct, and this slowed the rate of bis-adduct formation just enough so that reaction of (**1**) with one equivalent of (**2**) allowed isolation and purification of (**3**) in 54% yield.

Reaction of (**3**) with one-half equivalent of bis-maleimidobenzene, followed by dehydrative aromatization gave (**6**) which is 5.3 nm long. Compound (**6**) was soluble in usual organic solvents.

The preparation of (**8**) involved reaction of (**3**) with excess bis-maleimidobenzene, followed by treatment with sulphuric acid to give (**7**) (60%), which was fully characterized. Reaction of (**7**) with (**1**) gave a bis-adduct which was taken on to (**8**) (63%). Compound (**8**) 7.5 nm long, was sparingly soluble in solvents like $CDCl_3$.

The structures (**5**), (**6**), (**7**) and (**8**)† are interesting not only because they are so long and monodisperse, but also because manipulation of the quinone functions provides the future possibility of manipulating the properties. The solubility of these lines is remarkable, since linear quinones as small as an undecacenepentaquinone[4] are totally insoluble. For the future, this synthetic approach involving repetitive Diels–Alder reactions will be amplified by imide coupling reactions to produce three dimensional 5—10 nm scale structures.

This work was supported by the Office of Naval Research. We thank Dr. E. Larka for the mass spectra.

Received, 21st August 1987; Com. 1236

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