Pergamon

Tetrahedron Letters 42 (2001) 3559–3562

TETRAHEDRON LETTERS

Synthesis and characterization of [3,3]- and [3,4]-perinophane†

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Received 21 March 2001; accepted 28 March 2001

Abstract—Synthesis of [3,3]- and [3,4]-perinophanes is described via a novel route which will permit the synthesis of both symmetrical and unsymmetrical perinophanes and related cyclophane structures.

Since Cram's pioneering studies of cyclophanes,[1] interest in these molecules has continued unabated.[2] On the one hand the studies have been concerned with classical motifs such as structural-strain effects on reactivity, transannular effects, and calculational work aimed at providing a theoretical basis for the wealth of chemistry exhibited by these molecules. More recently, however, other motifs are being explored which take advantage of the proximity between sub-units offered by the cyclophane structure, a feature that is also present in supramolecular assemblies.[3a,c] This complementarity with supramolecular chemistry has undoubtedly contributed heavily to the burgeoning activity recently witnessed in cyclophane chemistry.

We wish to report the synthesis of two new perinophanes, extended cyclophane structures, and a general route leading to both symmetrical and unsymmetrical perinophanes. The first perinophane to be synthesized and characterized was the [8,8]-perinophane, **5**, which was designed by Lehn and co-workers in 1987 as a cyclobisintercaland receptor.[3b] Their method of preparation followed the classical technique of joining two aromatic residues, at two junctions, via a bifunctional coupling reagent under high dilution conditions (Scheme 1). While Lehn's system (a supramolecular intercalate displaying face-to-face complementarity),[3b] was designed specifically to ensure a large cavity so as to observe inclusion phenomena involving neutral molecules such as nitrobenzene, we were interested in perinophanes with shorter bridges, both symmetrical and unsymmetrical, so as to modulate their electronic properties. The overall aim was to examine the resulting perinophanes as possible novel organic photoreceptor devices.

We report herein the first synthesis of an unsymmetrically bridged perinophane. The present approach, involving the sequential bridging of perinone chromophores, should permit ready preparation of a range of novel unsymmetrical cyclophanes.

Our general route to perinophanes features two steps, as shown in Scheme 1. Starting with 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride (NTDA, **1**),[4] reaction with 4 equivalents of base yielded the potassium tetracarboxylate which was converted into the monoanhydride on acidification to pH 6.5 with 3 equivalents of H_3PO_4. The monoanhydride was condensed under reflux with the first diamine, $H_2N(CH_2)_nNH_2$ in this case, to give 1,3-bis(1,8-naphthalene-tetracarboxylic-monoimide-4,5-monohydrido)-alkane **2** in 85% yield after heating with acetic anhydride. In the second step,[5] reaction of the precursor **2** with the second diamine under conditions of high dilution in DMF at 100°C, in the presence of 1,4-diaza[2.2.2]bicyclooctane (DABCO) as proton transfer catalyst, gave the desired perinophanes **3** and **4** in 2–3% yield, with polymeric material being formed as the major product. The high yield of **2** that was precursor to **3** and **4** combined with the low yield of the perinophanes suggests that polymerization is more facile than the clipping together of **2** even under high dilution conditions.

Keywords: cyclophanes; perinophanes; unsymmetrical; synthesis.

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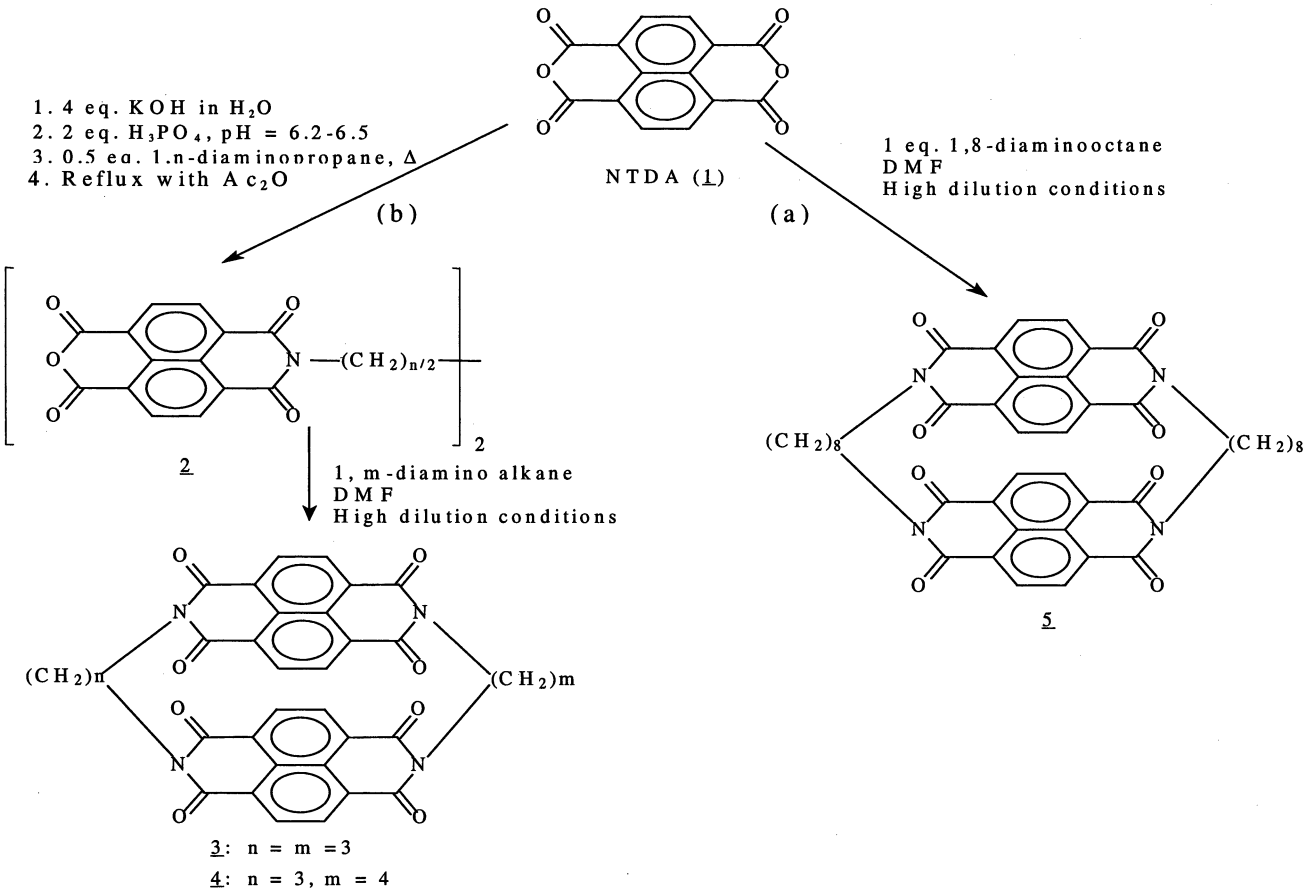
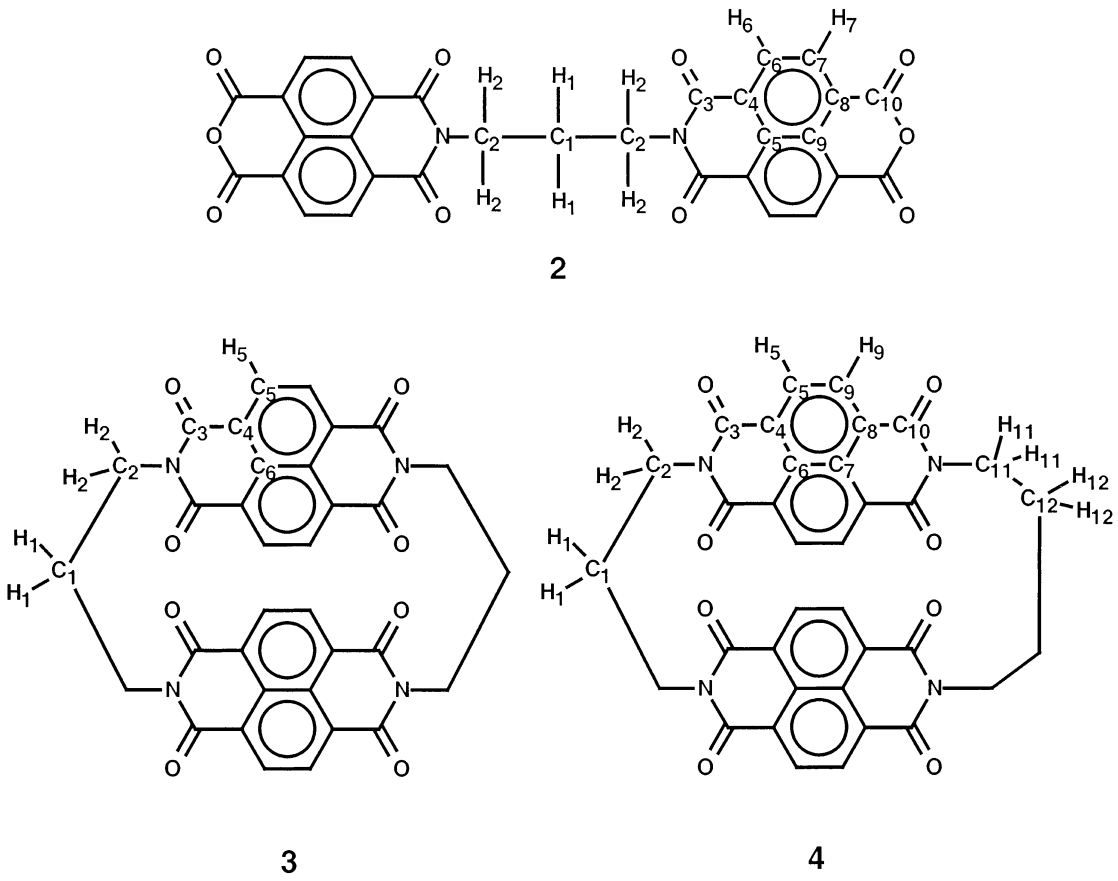
† This paper is in memory of Professor Ray Lemieux, a great organic chemist.

0040-4039/01/$ - see front matter
PII: S0040-4039(01)00528-7



Scheme 1. Strategy in synthesis of perinophanes: (a) Lehn's route (3b); (b) this work.



Structural identification of the synthesized perinophanes followed a variety of techniques (FT-IR, NMR, high resolution MS). High resolution MS was possible using the EI method at high temperatures which gave the molecular mass parent ions at 613 and 627 m/z, respectively, within +3 ppm of the theoretical values.[5] The observed ^{1}H NMR upfield shift of the aromatic protons by 0.8–1 ppm in the formation of **3** and **4** from the shift found for the comparable peak in **2** is characteristic of small cyclophane structures and can be attributed to the close mutual proximity of the shielding cones of the joined π-systems.[6]

We anticipate that the general method we have outlined will be applicable to the synthesis of a variety of cyclophane structures, such as perylenophanes, with novel electronic properties. The first synthesis of unsymmetrical perinophanes is significant because unsymmetrical cyclophanes provide a unique opportunity for systematically changing the chromophore orientation. This is important since pigment orientation in the solid state is responsible for crystallochromy,[7] that is color changes associated with different forms of crystal packing and for their electronic properties.[8]

Further work will refine the synthetic procedure to improve the yield and minimize polymeric side products. Also, other cyclophanes with architecturally interesting structures will be investigated. The ring strain that is expected to be present in such short-bridged molecules as **3** and **4** will be probed by means of a full range of spectroscopic and theoretical methods.[9] The study of host–guest interactions of the perinophanes, and comparisons with other hosts, would be of further interest.[10]

Acknowledgements

Funding of this research by the Natural Sciences and Engineering Research Council of Canada via a research grant (E.B.) is gratefully acknowledged.

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4. *Synthesis of 1,4,5,8-tetracarboxylic-naphthalene-1,8-anhydro-4,5-imidoalkanes (**2**)*—NTDA (Aldrich, 10 g) was added to a solution of KOH (13 g) in 2 L water with stirring and the resulting brown solution was acidified with phosphoric acid to pH 6.2–6.4. The 1,*n*-diaminoalkane (0.5 equiv.) was added which caused the pH to rise to 7.2 but this was adjusted to 6.2–6.4 with further addition of phosphoric acid. The yellow solution was then heated and maintained at reflux for 24 h when a cloudy solution resulted. After cooling to ambient temperature the solution was filtered and the filtrate treated with acetic acid until the pH was brought to 5.0, whereupon a yellowish precipitate formed and was filtered and subsequently dried under vacuum to yield the free tetracarboxylic-acid. The latter was triturated with boiling acetic anhydride (200 ml) which after cooling, filtration and drying under vacuum yielded 9.5 g (85%) of **2** ($n=3$), mp 356.5–358°C.
2 ($n=3$): ^{1}H NMR (200.1 MHz) $CDCl_3$–TFA-*d*: δ 9.30 (s, 8H, $H_{5,6}$) 4.88 (t, $J=5.9$ Hz, 4H, H_2), 2.74 (m, 2H, H_1). ^{13}C NMR (50.3 MHz) JMOD $CDCl_3$–TFA-*d*: δ 165.3 (4′, C_3) 160.5 (4′, C_{10}), 133.9 (3′, C_6), 132.2 (3′, C_7), 129.3 (4′, C_5), 127.5 (4′, C_4), 122.7 (4′, C_8), 122.1 (4′, C_9), 40.0 (2′, C_2), 27.5 (2′, C_1). FT-IR (cm^{-1}): 1781, 1744 (C=O carbonyl stretch sym, *anti*-sym of anhydride), 1707, 1671 (C=O carbonyl stretch sym, *anti*-sym of imide). Calcd for $C_{31}H_{14}N_2O_{10}$: C, 64.81; H, 2.45; N, 4.87. Found: C, 64.29; H, 2.66; N, 5.23. MS (CI): M^+ 574.1; calcd: 574.43.
5. *Preparation and characterization of perinophanes **3** and **4***—The intermediate **2** (2 mmol) in 100 ml of *N*-methyl pyrrolidinone (NMP) and an equivalent solution of (1,*m*)-diaminoalkane ($m=3$, 4) were injected by means of an automated syringe pump into a solution of DABCO (10 g) in anhydrous DMF (1 L) contained in a Morton flask over 48 h while heating to 100°C and stirring. After a further 6 h reaction time, the solution was allowed to cool to rt and then left standing for 48 h before concentrating to 100 ml. The reddish reaction mixture was poured into aq HCl (1 L, 5% v/v) and the dark precipitate was filtered, freeze-dried and Soxhlet extracted for 3 days with 250 ml of $CHCl_3$. The red extract was concentrated to 20 ml, loaded onto a silica gel column and eluted with ethyl acetate–methylene chloride (20:80 v/v). Compounds **3** and **4** were obtained as yellowish solids in 2.0 and 2.7% yield, respectively, mp darken at 385°C.
3: ^{1}H NMR (200.1 MHz) $CDCl_3$–TFA-*d*: δ 8.27 (s, 8H, H_5), 4.38 (m, 8H, H_2), 2.40 (m, 4H, H_1). ^{13}C NMR (50.3

MHz) JMOD $CDCl_3$–TFA-*d*: δ 164.4 (4′, C_3), 131.5 (3′, C_5), 126.6 (4′, C_4), 39.8 (2′, C_2), 29.1 (2′, C_1). FT-IR (cm^{-1}): 1702, 1661 cm^{-1} (C=O carbonyl stretch sym, *anti*-sym). MS (EI): 612.130 (calcd 612.128).

4: ^1H NMR (200.1 MHz) $CDCl_3$–TFA-*d*: δ 8.46 (s, 8H, $H_{5,9}$), 4.63 (t, 4H, H_2), 4.27 (m, 4H, H_{11}), 2.80 (m, 2H, H_1), 2.28 (m, 4H, H_{12}). ^{13}C NMR (50.3 MHz) JMOD $CDCl_3$–TFA-*d*: δ 164.5 (4′, $C_{3,10}$), 133.0 (3′, C_5). 132.3 (3′, C_9), 126.5 (4′, C_4), 126.3 (4′, C_8), 43.1 (2′, C_2), 41.5 (2′, C_{11}), 31.2 (2′, C_1), 29.4 (2′, C_{12}). FT-IR (cm^{-1}): 1710, 1667 cm^{-1} (C=O carbonyl stretch sym, *anti*-sym). MS (EI): 626.143 (calcd 626.141).

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