

# Pyridine analogue of macrocyclic polyynes $C_{58}H_4N_2$ as a precursor to diazafullerene $C_{58}N_2$

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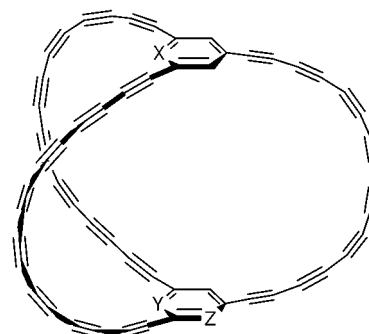
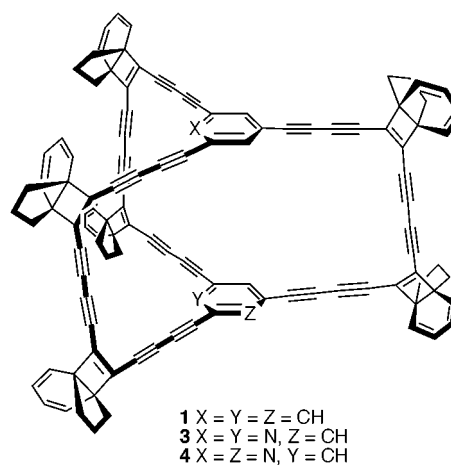
(1,3,5)Pyridinophanes having [4.3.2]propellatriene units were synthesized as precursors to macrocyclic polyynes  $C_{58}H_4N_2$ ; diazafullerene anion  $C_{58}N_2^-$  was detected in the laser desorption mass spectrum of the pyridinophanes.

Increasing interest has been focused on heterofullerenes, in which one or several carbon atoms of the fullerene cage are replaced by heteroatoms. Regarding azafullerenes, Wudl and Hirsch reported mass spectral detection of monoazafullerene cation  $C_{59}N^+$ , which was generated by the fragmentation of precursors manipulated from  $C_{60}$ .<sup>1</sup> Subsequently, isolation of its stable derivatives such as  $C_{59}NH$ ,  $C_{59}NR$  ( $R = CHPh_2$ , Ar) was reported from the same groups.<sup>2</sup> Rao reported the formation of azafullerenes  $C_{59}N$  to  $C_{56}N_4$  together with nitrogen-containing carbon clusters such as  $C_{70}N_2$ ,  $C_{59}N_6$ ,  $C_{59}N_4$  and  $C_{59}N_2$  in the soot produced by contact arc vaporization of graphite in the presence of  $N_2$  or  $NH_3$ .<sup>3</sup> The closed shell azafullerenes having an even number of nitrogen atoms,  $C_{60-n}N_n$  ( $n = 2, 4$  and  $6$ ), are isoelectronic with the di-, tetra- and hexa-anions of  $C_{60}$ , respectively, and are predicted to be reasonably stable.<sup>4</sup> However, selective formation of such azafullerenes has not been achieved so far experimentally.

Recently we synthesized (1,3,5)cyclophane **1** fused by [4.3.2]propellatriene units, as precursors to polyynes-bridged macrocycle  $C_{60}H_6$  **2**.<sup>5</sup> The laser-desorption mass spectra of **1** exhibited not only the negative ion corresponding to **2**<sup>-</sup> but also  $C_{60}$  ions in both positive and negative modes. Rubín obtained similar results using a cyclobutenedione derivative related to **1**.<sup>6</sup> The formation of  $C_{60}$  from **2** can be explained in terms of the zipping-up cyclization of the polyynes chain accompanying the loss of hydrogen atoms.<sup>7</sup> As an extension of this method to the synthesis of azafullerenes, we report here the synthesis of pyridinophane **3** and its regioisomer **4** which would serve as precursors to polyynes  $C_{58}H_4N_2$  **5** and **6**, respectively.<sup>8</sup> We detected the  $C_{58}N_2$  anion in the laser desorption mass spectrum of **3** and **4**.

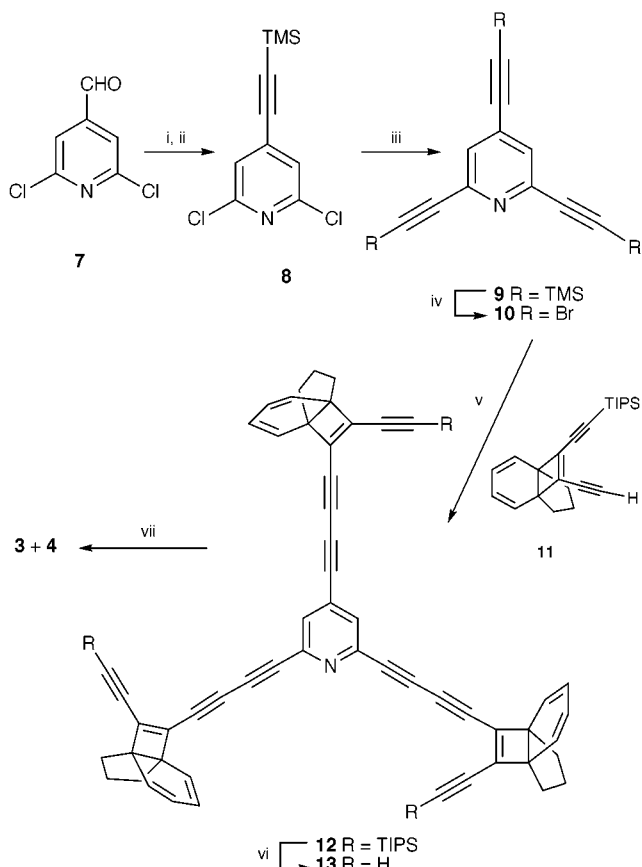
The Corey–Fuchs ethynylation<sup>9</sup> of dichloroformylpyridine **7**<sup>10</sup> afforded **8** which was converted to triethynylpyridine **9**<sup>†</sup> by the Sonogashira coupling<sup>11</sup> with trimethylsilylacetylene (Scheme 1). Tris(bromoethynyl)pyridine **10** derived from **9** by treatment with NBS and  $AgNO_3$  was coupled with mono-(triisopropylsilyl)-protected diethynyl[4.3.2]propellatriene **11**<sup>5</sup> using  $Pd^0$ – $Cu^I$  catalyst<sup>12</sup> to afford the tripod **12**.<sup>†</sup> After removal of the protective group, oxidative coupling of **13** under high-dilution conditions gave a mixture of pyridinophanes **3** and **4**<sup>†</sup> as a light-sensitive yellow solid.<sup>13</sup>

The positive mode laser desorption time-of-flight mass spectrum of **3** and **4** exhibited only indane fragments. Fig. 1 shows the negative mode laser desorption mass spectrum of **3** and **4**. The prominent peak due to **5**<sup>-</sup> and **6**<sup>-</sup>, i.e.  $C_{58}H_4N_2^-$ , was observed at  $m/z$  728 together with those of  $C_{58}H_4N_2$ (indane)<sup>-</sup> at  $m/z$  846 and  $C_{58}H_4N_2$ (indane)<sub>2</sub><sup>-</sup> at  $m/z$  964 formed by the successive loss of the indane fragments. More importantly, as shown in the inset of Fig. 1, the peak due to the  $C_{58}N_2$  anion was indeed observed at  $m/z$  724, albeit in relatively low

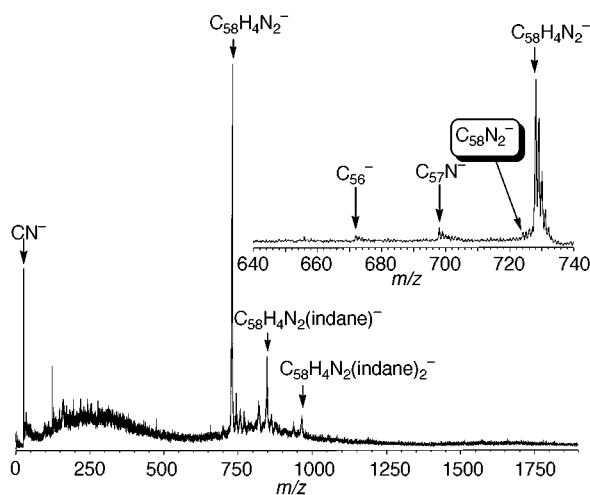


intensity, which represents the first observation of diazafullerene formed in a size selective manner. It seems likely that the conversion of  $C_{58}H_4N_2^-$  to  $C_{58}N_2^-$  takes place in a stepwise fashion, since intermediate species such as  $C_{58}H_3N_2^-$  and  $C_{58}H_2N_2^-$  were detected. Observation of such dehydrogenation from the aromatic pyridine derivative  $C_{58}H_4N_2^-$  manifests itself as the fullerene-like structure of the  $C_{58}N_2$  anion.<sup>14</sup>

A relatively high yield of  $C_{60}^-$  was reported for the transformation of  $C_{60}H_6$  to  $C_{60}$ .<sup>5,6</sup> The relatively inefficient conversion of  $C_{58}H_4N_2$  to  $C_{58}N_2$  in the present work is ascribed to the thermodynamic and kinetic lability of diazafullerene.<sup>4</sup> Indeed, Fig. 1 shows a strong peak due to  $CN^-$  which must be extruded from  $C_{58}N_2$  or its precursors. Moreover, anions  $C_{57}N^-$  and  $C_{56}^-$  formed by the loss of neutral CN from  $C_{58}N_2^-$  are detected as shown in the inset of Fig. 1, even though it is well-documented that the internal temperature of negative ions is relatively low.<sup>15</sup>



**Scheme 1** Reagents and conditions: i,  $\text{CBr}_4$ ,  $\text{PPh}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $0^\circ\text{C}$ , 76%; ii, LDA, THF,  $0^\circ\text{C}$ , then  $\text{Me}_3\text{SiCl}$ , 89%; iii, trimethylsilylacetylene,  $\text{Pd}(\text{PPh}_3)_4$ , CuI,  $\text{Pr}_2\text{NH}$ , THF, 73%; iv, NBS,  $\text{AgNO}_3$ , acetone, 77%; v,  $\text{Pd}(\text{dba})_3$ ,  $\text{CHCl}_3$ , CuI, pentamethylpiperidine, benzene, 61%; vi,  $\text{Bu}_4\text{NF}$ , AcOH, THF; vii,  $\text{Cu}(\text{OAc})_2$ , pyridine, 12%.



**Fig. 1** Negative mode laser desorption time-of-flight mass spectrum of **3** + **4**. Liquid paraffin was used as a matrix and the third harmonic of a Nd:YAG laser (355 nm, typically  $3 \text{ MW cm}^{-2}$  with a 7 ns duration) was employed for simultaneous desorption and ionization.

In summary, we synthesized pyridinophanes **3** and **4** which served as precursors to polyynes **6** and **7** and detected

diazafullerene anion  $\text{C}_{58}\text{N}_2^-$  in the laser desorption mass spectrum of **3** and **4**.

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## Notes and references

† Selected data for **9**: mp  $78\text{--}80^\circ\text{C}$ ;  $\nu(\text{KBr})/\text{cm}^{-1}$  2163;  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  0.24 (27H, s), 7.40 (2H, s);  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$   $-0.44, -0.40, 96.1, 100.6, 101.5, 102.6, 128.3, 132.0, 143.3$ . For **10**: decomp.  $159^\circ\text{C}$ ;  $\nu(\text{KBr})/\text{cm}^{-1}$  2195;  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  7.37;  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  53.7, 58.2, 76.3, 78.5, 128.8, 132.0, 143.2. For **12**: mp  $97\text{--}99^\circ\text{C}$ ;  $\nu(\text{KBr})/\text{cm}^{-1}$  2201, 2136, 2124;  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  1.09 (63H, br s), 1.18–1.33 (6H, m), 1.41–1.53 (3H, m), 1.55–1.67 (3H, m), 1.93–2.01 (6H, m), 5.78–5.92 (12H, m), 7.41 (2H, s);  $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3)$  11.2, 18.6, 18.7, 32.8, 33.0, 56.3, 56.7, 56.9, 75.4, 75.8, 77.2, 77.7, 78.4, 80.2, 80.7, 98.3, 98.4, 101.0, 101.4, 122.0, 122.1, 128.1, 128.2, 129.2, 129.5, 131.2, 138.2, 138.7, 143.1. For **3** + **4**: decomp.  $128^\circ\text{C}$ ;  $\nu(\text{KBr})/\text{cm}^{-1}$  2205;  $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3)$  1.19–1.34 (12H, m), 1.38–1.52 (6H, m), 1.59–1.62 (6H, m), 1.90–2.01 (12H, m), 5.90–5.92 (12H, m), 7.36–7.41 (4H, m);  $\lambda_{\text{max}}(\text{benzene})/\text{nm}$  (log  $\epsilon$ ) 369 (4.85), 393 (4.82), 428 (4.65).

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- There are many possible isomers for **3** and **4** due to the orientation of the propellane units. Only one of the isomers of **3** and **4** are depicted in this paper for clarity.
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- There are so many possible isomers for the oxidative coupling product of **13** that it is not possible to determine the ratio of **3** and **4** nor even confirm whether it is indeed a mixture of the two by spectroscopic and chromatographic techniques.
- Only one isomer, 1,49-diazafullerene, would result from the  $\text{C}_{58}\text{N}_2$  isomer **5**, while two isomers, 1,49- and 1,60-diaza derivatives, would be formed from **6**, provided that the cyclization of the polyynes takes place without bond breaking through a transition state with minimal bond angles of the alkyne chains as depicted in ref. 7.
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