

# Unusual formation and X-ray crystal structure of stable anti-Bredt compounds by reaction of 3a,6a-diazapentalenes with dimethyl acetylenedicarboxylate

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The reaction of 1-aryl-2-aryl-3a,6a-diazapentalenes with dimethyl acetylenedicarboxylate affords, in an unusual fashion, stable anti-Bredt compounds possessing a 4,10-diazabicyclo[5.2.1]deca-1,3,5,8-tetraene skeleton, the structure of which is confirmed by X-ray crystal structure analysis as well as by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The chemistry of mesoionic heteropentalenes has attracted considerable attention because of their interesting chemical properties.<sup>1,2</sup> As early as 1965, Solomons *et al.* reported the preparation of 1-aryl-2-aryl-3a,6a-diazapentalenes.<sup>3</sup> These underwent [8 + 2] cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to give 2a,6b-diazacyclopenta[*cd*]pentalenes, a novel type of heterocycle, in the presence of Pd-C as described by Boeckelheide *et al.*<sup>4</sup> On the other hand, the synthesis of bridgehead alkenes has been attempted by many chemists since the original definition of the Bredt rule.<sup>5</sup> In spite of a large number of investigations that have been performed on the synthesis and properties of isocyclic systems of this structure variant,<sup>6</sup> heterocyclic anti-Bredt compounds are little known, although anti-Bredt enamines and enol ethers have been reported.<sup>7</sup> In particular, stable examples of such systems that have been characterized by X-ray crystallographic methods are very rare, with the exception of metal-complexed derivatives.<sup>8</sup> We now report the facile formation of novel and highly unsaturated anti-Bredt heterocycles, 4,10-diazabicyclo[5.2.1]deca-1,3,5,8-tetraenes **4**, in a one-pot reaction, as stable compounds with melting points above 100 °C. The structure of **4a** has been determined by X-ray crystallographic analysis.

The 1-benzoyl-2-phenyl-3a,6a-diazapentalene **1a**<sup>3</sup> upon reaction with 2 equiv. of DMAD gave a 1:2 adduct as an orange solid. Since modern NMR techniques such as HMBC, INADEQUATE and HSQC did not allow us to assign a reasonable structure for the product, we performed an X-ray analysis. The analysis was carried out at -50 °C, establishing that the compound had structure **4a**, which is consistent with the NMR data. Fig. 1 shows the ORTEP drawing of **4a** along with selected bond lengths and angles for the molecule. It is noteworthy that the bridgehead bonds [1.360(4) Å for C(1A)-C(2A) and 1.514 Å for C(7A)-C(8A)] are relatively long, indicating the large strain imposed on the bonds. This large strain is in agreement with the <sup>1</sup>J<sub>C(7A)-H(7A)</sub> coupling constant (154.0 Hz). This value† is close to that (155 Hz) of tetraprismane<sup>9</sup> (cubane) and is larger than that (148 Hz) of pentaprismane.<sup>9</sup> Furthermore, the alkenic carbon coupling

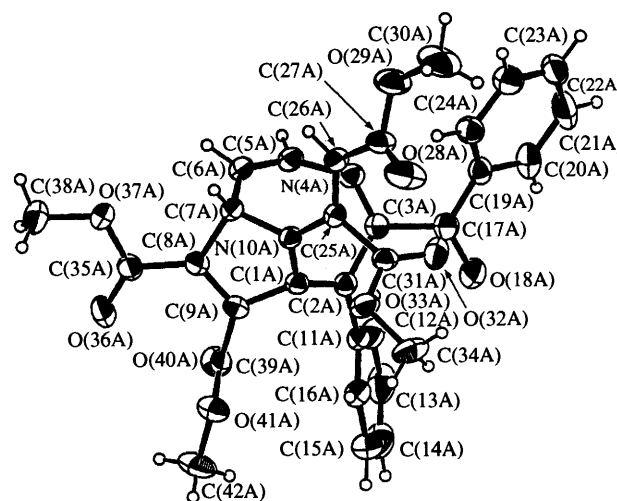


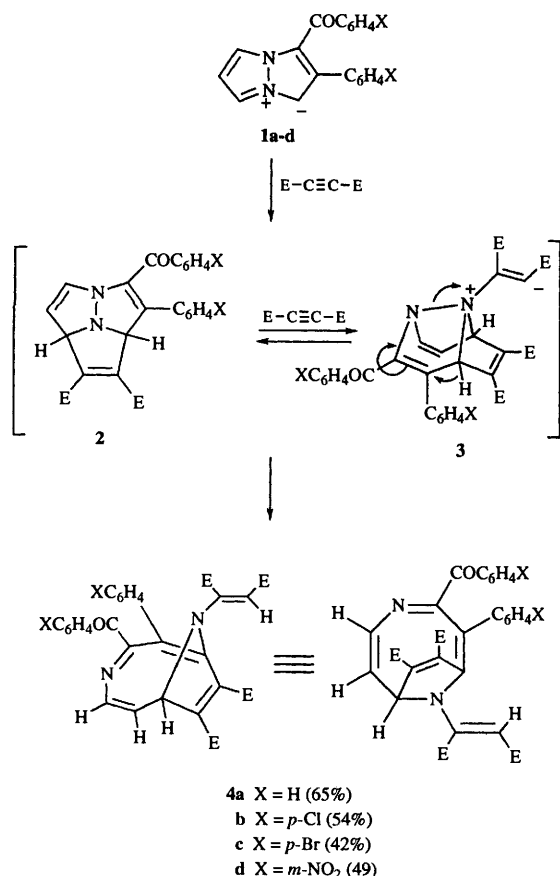
Fig. 1 An ORTEP drawing of **4a** showing 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): C(1A)-C(2A) 1.360(3), C(7A)-N(10A) 1.465(3), C(6A)-C(7A) 1.498(4), C(1A)-C(9A) 1.466(4), C(7A)-C(8A) 1.514(4), C(8A)-C(9A) 1.349(3), C(1A)-N(10A) 1.405(3), C(1A)-C(2A)-C(3A) 116.0(2), C(1A)-C(2A)-C(11A) 120.7(2), C(3A)-C(2A)-C(11A) 122.7(2), C(2A)-C(1A)-C(9A) 130.6(2), C(2A)-C(1A)-N(10A) 120.9(2), C(6A)-C(7A)-N(10A) 107.3(2), C(7A)-C(8A)-C(9A) 109.4(2), C(8A)-C(9A)-C(1A) 107.1(2), C(8A)-C(7A)-N(10A) 99.6(2), C(9A)-C(1A)-N(10A) 104.4(2), C(8A)-C(7A)-N(10A) 99.6(2), C(6A)-C(7A)-C(8A) 109.9(2).

constants (<sup>1</sup>J<sub>C(6A)-H(6A)</sub> = 165.5 Hz and <sup>1</sup>J<sub>C(5A)-H(5A)</sub> = 176.2 Hz) are found to be larger than those of cyclopentene (161 Hz) and norbornene (165 Hz). Apparently, bending of the formally trisected sp<sup>2</sup> system is not energetically prohibitive; thus, in the remarkable compound **4a**, in-plane distortion (*s*-strain) leads to reduced sp<sup>2</sup> endocyclic angles of 116.0(2)° [C(1A)-C(2A)-C(3A)] and 104.4(2)° [C(9A)-C(1A)-N(10A)], while the exocyclic angle is increased to 130.6(2)° for C(2A)-C(1A)-C(9A).

The similar products **4b-d** were obtained in fair yields from the reactions of 1-(4-chlorophenyl)-2-(4-chlorobenzoyl)-3a,6a-diazapentalene **1b**, 1-(4-bromophenyl)-2-(4-bromobenzoyl)-3a,6a-diazapentalene **1c** and 1-(3-nitrophenyl)-2-(3-nitrobenzoyl)-3a,6a-diazapentalene **1d** with DMAD, respectively.

The formation of the product **4** could arise from the [8 + 2] cycloaddition of DMAD with **1** to form the primary 1:1 adduct **2**, which could react reversibly with the central atom to give a betaine **3** in which the N-N bond is highly polarized. This could break down to **4** via intra- or inter-molecular hydrogen

† The value can be compared with that (134.9 Hz) of dodecahedrane.<sup>13</sup>



Scheme 1

transfer (Scheme 1). The driving force for the selective elimination of one of the two bridgehead protons would be relief of strain between the large groups on C(2A) and C(3A) as C(2A)–C(3A) becomes a single bond and twisting is permitted.‡

In contrast with the above result, a novel ring cleavage of a diazacyclopentene ring has been reported in the reaction of the 1,3,4,6-tetraazapentalene and DMAD, giving the 1-azacyclo[3.2.2]azine system rather than an anti-Bredt compound.<sup>10</sup>

## Experimental

### General procedure for reaction of 1-aryl-2-aryl-3a,6a-diazapentalenes 1 with DMAD

A mixture of 1 (10 mmol) and DMAD (20 mmol) in dry benzene (30 ml) was stirred at room temperature for 12 h. After evaporation of the solvent under vacuum, the residue was triturated with ethanol, heated until dissolved, then left to stand at room temperature overnight. The orange crystals that precipitated were collected by filtration, giving the 4,10-diazabicyclo[5.2.1]deca-1,3,5,8-tetraenes 4.

### Dimethyl 3-benzoyl-10-[1,2-bis(methoxycarbonyl)viny]-2-phenyl-4,10-diazabicyclo[5.2.1]deca-1,3,5,8-tetraene-8,9-dicarboxylate 4a

Mp 152–153 °C;  $\delta_{\text{H}}$ (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 3.35 (3 H, s), 3.57 (3 H, s), 3.65 (3 H, s), 3.72 (3 H, s), 4.74 (1 H, d, *J* 3.0§), 5.32 (1 H, s), 5.78 (1 H, dd, *J* 10.2, 3.0), 7.06 (1 H, d, *J* 10.2), 7.02–8.03 (10 H, m);  $\delta_{\text{C}}$ (CD<sub>2</sub>Cl<sub>2</sub>) 51.6 (q), 52.9 (q), 52.9 (q), 53.1 (q), 62.0 (d), 95.4 (d), 118.5 (d), 127.8 (d), 128.1 (d), 128.9 (d), 129.5 (d), 130.9

(d), 132.8 (d), 134.3 (s), 136.4 (s), 136.5 (d), 138.3 (s), 140.6 (s), 144.4 (d), 146.5 (s), 146.8 (s), 161.7 (s), 161.8 (s), 163.6 (s), 163.7 (s), 166.8 (s), 189.8 (s) (Found: C, 65.1; H, 4.5; N, 4.8. C<sub>31</sub>H<sub>26</sub>O<sub>9</sub>N<sub>2</sub> requires C, 65.3; H, 4.6; N, 4.9%).

### Crystal structure determination for compound 4a

Data were collected at  $T = -50$  °C on a RIGAKU RAXIS-CS diffractometer using imaging plates; C<sub>31</sub>H<sub>26</sub>N<sub>2</sub>O<sub>9</sub>,  $M$  570.54, dimensions 0.30 × 0.20 × 0.10 mm, monoclinic, space group  $P2_1/a$ ,  $a = 16.103(2)$ ,  $b = 26.015(5)$ ,  $c = 20.411(4)$  Å,  $\beta = 104.567(11)^\circ$ ,  $U = 8276(3)$  Å<sup>3</sup>,  $F(000) = 3576$ ,  $Z = 12$ ,  $D_c = 1.374$  g cm<sup>-3</sup>, Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu(\text{Mo-K}\alpha) = 0.102$  mm<sup>-1</sup>,  $\theta = 1.29$ – $27.64^\circ$ , 27 222 reflections were collected on 20 multi-layer Weissenberg photographs ( $\Delta\phi = 100.5^\circ$ ) and 15 227 unique reflections ( $R_{\text{int}} = 0.0507$ ) were used in the refinement. The structure was solved by direct methods using SIR92<sup>11</sup> and refined anisotropically by full-matrix least-squares on  $F^2$  using SHELXL-93.<sup>12</sup> Final  $R$  indices were  $R(F) = 0.0593$  for 8016 reflections  $F^2 > 2\sigma(F^2)$  and  $wR(F^2) = 0.1276$  for all data. Three independent molecules form a column along the  $b$  axis. As they have essentially the same geometry, only one of them (labelled A) is shown in Fig. 1. The H atom positions were calculated geometrically. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/51.

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§  $J$  Values in Hz.

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