

# 1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Dianhydride: A Close Approach to a Neutral Homoaromatic Semibullvalene

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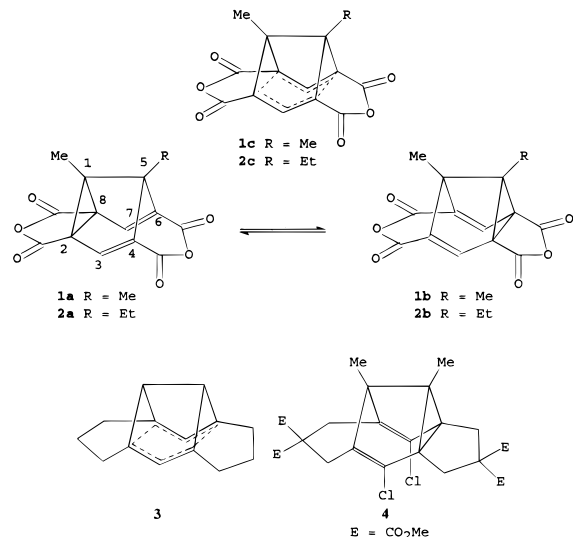
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We report in this paper the syntheses and the results of an investigation of the structure (delocalized homoaromatic or localized Cope system) of 1,5-dimethyl-2,4,6,8-semibullvalenetetracarboxylic dianhydride **1** and the 5-ethyl analog **2**. Although many homoaromatic cationic species are known, there is to date no well-accepted example of an electrically neutral homoaromatic molecule.<sup>1</sup>

The semibullvalenes have long been recognized as the system most closely approaching neutral homoaromaticity.<sup>1,2</sup> The Cope rearrangements of semibullvalenes (e.g. **1a** ⇌ **1b**) proceed through the homoaromatic transition state (e.g. **1c**) often with very low activation barriers.<sup>1,3</sup> A number of attempts to design semibullvalenes having homoaromatic ground states have been considered.<sup>1</sup> One suggestion, by Paquette, is that the bisannelated semibullvalene (**3**) might be such a system since the “breathing motion” of the Cope process would be inhibited.<sup>4</sup> Semiempirical<sup>5,6</sup> and *ab initio*<sup>7</sup> quantum mechanical calculations on other bisannelated semibullvalenes support this hypothesis. Müllen *et al.* subsequently prepared the first example<sup>8</sup> (**4**) of a bisannelated semibullvalene and demonstrated that its Cope rearrangement is rapid on the NMR time scale even at -160 °C.<sup>10</sup> Similarly, our theoretical studies predict the bisanhydride **1** to have a single minimum potential energy surface with a homoaromatic ground state.<sup>6</sup>

The known<sup>11</sup> tetraester **5** was viewed as an ideal precursor to bisanhydride **1**. Grohmann's route<sup>11</sup> to **5** (Scheme 1A) was modified to give this tetraester more easily and in improved



yield (Scheme 1B). The tetraester **5** was converted to the desired anhydride **1** *via* the tetraacid **7** (Scheme 1B).

**1** proved to be remarkably stable; it can be purified by sublimation (200 °C at ambient pressure) and only undergoes slight hydrolysis of one of the anhydride moieties upon prolonged exposure to the atmosphere. This is in contrast with other semibullvalenes, which frequently yield cyclooctatetraene upon *mild* thermolysis<sup>12</sup> and react more or less readily with oxygen.<sup>10,13</sup>

The anhydride **1** crystallizes in space group *Cc* or *C2/c*, which are crystallographically indistinguishable. In the latter, the molecule uses a crystallographic 2-fold axis, while in the former no symmetry is imposed on the molecule. Data were all taken on the same crystal with Mo K $\alpha$  radiation to  $2\theta_{\max}$  of 70° at 293, 243, 163, 148, and 123 K. For the three higher temperatures the refinement of coordinates was straightforward in *C2/c* (Figure 1a) but not in *Cc* where the ratio of shifts with respect to error remained high, even though the *R*-factor was somewhat lower in *Cc* than in *C2/c* (0.045 and 0.055, respectively). The difference in *R*-factors is not significant, because the number of parameters in *Cc* is twice that in *C2/c*. An analysis of the thermal ellipsoids in *C2/c* at room temperature (Figure 1a) did not agree with rigid body motion. The weighted agreement between observed and calculated components of the thermal ellipsoids is 0.22, while for a rigid motion this is expected to be less than 0.10.<sup>14</sup> Even a visual inspection of Figure 1a (compare atoms C(2) and C(3)) indicates that the apparent thermal ellipsoids are not due to rigid body motion. Therefore, at the three higher temperatures, a dynamic disorder between **1a** and **1b** is occurring and the homoaromatic species is not present. At the two lower temperatures, the results are quite different. The refinement proceeds smoothly in *Cc* (Figure 1b) and the weighted *R*-values at these temperatures are significantly lower than for *C2/c* (at 148 K, 0.12 for *C2/c* and 0.05 for *Cc*; at 123 K, 0.16 for *C2/c* and 0.04 for *Cc*). This result clearly shows that, at the lower temperatures also, the homoaromatic species does not prevail. Instead, one form (**1a** or **1b**), which does not have a 2-fold axis, dominates. The thermal ellipsoids indicate a certain degree of disorder between **1a** and **1b**. The

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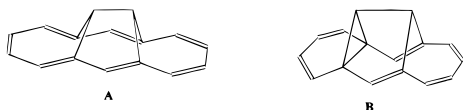
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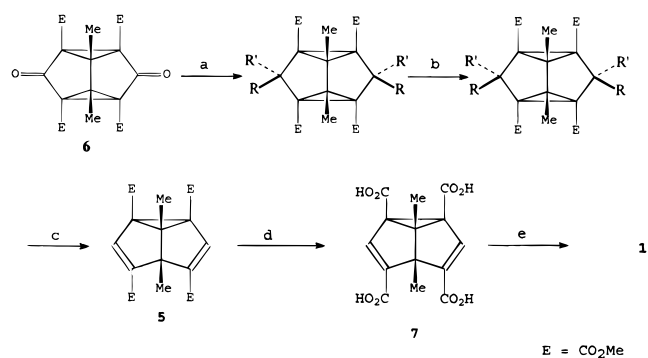
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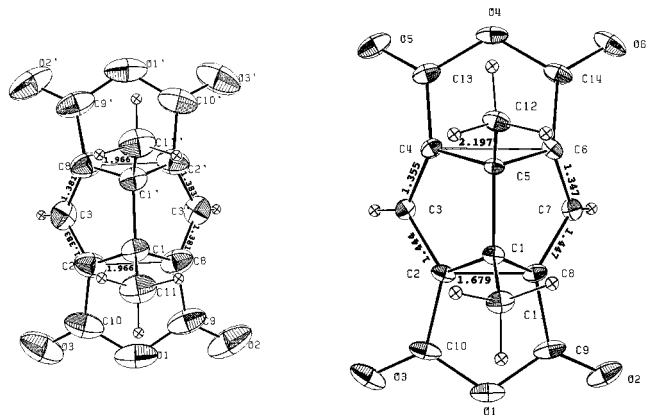
(12) For example, tetraester **5** thermolyzes at 78 °C to give the corresponding cyclooctatetraene;<sup>11</sup> 2,6-dicyano-1,5-dimethyl-4,8-diphenylsemibullvalene undergoes a similar thermolysis at temperatures > 30 °C.<sup>13b</sup>

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Scheme 1<sup>a</sup>

<sup>a</sup> (A) (a) <sup>t</sup>Bu<sub>3</sub>Al, toluene, ambient, 4 h. R = OH, R' = H (76%). (b) MsCl, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 5 °C → ambient, 40 h. R = OMs, R' = H (83%). (c) NaI, acetone, reflux, 3.5 h (63%). (B) (a) NaBH<sub>4</sub>, THF, H<sub>2</sub>O, <0 °C, 5 h. R = H, R' = OH (82%). (b) PBr<sub>3</sub>, benzene, H<sub>2</sub>O, 48 °C, 48 h. R = Br, R' = H (81%). (c) NaI, acetone, reflux, 5 h (85%). (d) NaOH, H<sub>2</sub>O, ambient, 18 h (88%). (e) TFAA, ambient, 24 h (79%).

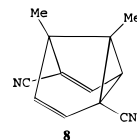


**Figure 1.** ORTEP plots of **1** at (a) 293 K and (b) 123 K.

observed distances for C(2)–C(8), 1.726(6) Å at 148 K and 1.679(4) Å at 123 K, and for C(4)–C(6), 2.160(6) Å at 148 K and 2.197(4) Å at 123 K, indicate that the proportion of the dominant valence tautomer increases with decreasing temperature. At even lower temperatures (15 K), the observed C(2)–C(8) distance would probably be even shorter (corresponding with a “full single bond”) and bonding between C(4) and C(6) would be absent.

The solid phase <sup>13</sup>C CP-MAS NMR spectra of **1** are temperature independent over the range 293–223 K and consistent with the interpretation of the X-ray data. Apart from small splittings of 1.50 and 0.84 ppm of the C(2,4,6,8) and the carbonyl carbon resonances, respectively, these spectra correspond to a “symmetrical” system. The small splittings are reminiscent of those observed in the CP-MAS spectra of the pseudo-C<sub>2</sub> dinitrile **8**<sup>15</sup> and support the contention that, in the crystalline state, **1** consists of the equilibrating valence tautomers, **1a** and **1b**, which are nearly degenerate with the enthalpy difference between them ( $\Delta H$ ) close to zero. Larger values of  $\Delta H$  are found for **8** and related systems.<sup>15,16</sup>

The solution phase <sup>13</sup>C NMR spectra (75 MHz) of the bisanhydride **1** correspond to either the homoaromatic species



or rapidly exchanging valence tautomers. The C(2,4,6,8) signal exhibits no line broadening attributable to exchange at 190 K (the solubility limit of **1**). Using a predicted chemical shift difference of ~100 ppm between C(2,8) and C(4,6) in **1a** (based on data for semibullvalenes in which the Cope rearrangement can be frozen out<sup>3,15</sup>) and a limit of observable broadening due to exchange of 0.5 Hz, we estimate  $\Delta G^\ddagger$  (190 K) < 17 kJ mol<sup>-1</sup> for the latter process.

In order to further probe the solution structure of **1**, we have used a modification of the Saunders' isotopic perturbation method<sup>17</sup> introduced by Gompper<sup>18</sup> for studying semibullvalenes. The unsymmetrical derivative **2** was prepared in a similar manner to the preparation of **1**. The solution phase <sup>13</sup>C NMR spectra of **2** showed a small but significant, equilibration-driven, tracking of the C(2,8) and C(4,6) chemical shifts with temperature. The shifts were measured relative to the C(2,4,6,8) signal of **1** present as an internal standard, and their temperature sensitivities were found to be +0.250 and -0.248 ppm/deg, respectively. Thus **2** (and by analogy **1**) is not homoaromatic in solution.<sup>17,18</sup>

The semibullvalene **1** is thermochromic in both the solution and solid states. Such thermochromism is correlated with a very flat double-minimum ground state potential energy surface in which the activation barrier to the Cope rearrangement is exceptionally low.<sup>13b</sup>

In the solution and solid states the novel semibullvalene **1** is not homoaromatic. This is contrary to the predictions based on quantum mechanical calculations, although the latter, of course, refer only to the gas phase. Perhaps the most surprising feature of **1**, when compared with other previously studied semibullvalenes,<sup>15,16,19</sup> is the near degeneracy over a wide temperature range of the valence tautomers in the solid state. Whether this reflects a fundamental property of the molecule itself or merely the crystal environment is not clear.

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**Supporting Information Available:** Spectroscopic and analytical data for compounds **1** and **2** and a table of internuclear distances for **1** at 123 and 293 K (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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