

## X-Ray Crystallographic Observations on a Divinyl–Cyclobutane Cope System in the Solid State

Goverdhan Mehta,\*<sup>a,b</sup> S. Hari Krishna Reddy<sup>a</sup> and Vasantha Pattabhi\*†<sup>c</sup>

<sup>a</sup> School of Chemistry, University of Hyderabad, Hyderabad 500 134, India

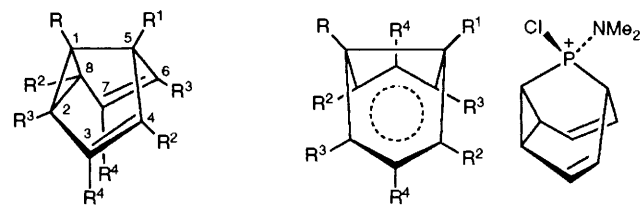
<sup>b</sup> Jawaharlal Nehru Centre for Advanced Scientific Research, Indian Institute of Science Campus, Bangalore 560 012, India

<sup>c</sup> Department of Crystallography and Biophysics, University of Madras, Madras 600 025, India

The X-ray crystal structure of a divinyl–cyclobutane Cope system embedded in a novel heptacyclic framework is determined.

Cope rearrangements in substituted semibullvalenes like **1a–e**, bearing a divinyl–cyclopropane moiety, have been extensively investigated with the object of discovering bishomoaromatic ground states, e.g. **2**.<sup>1</sup> During these studies, X-ray crystal structures of several derivatives e.g. **1a–e** were determined, which revealed many anomalous features like unusually long [C(2)–C(8)] and short [C(4)–C(6)] interatomic distances.<sup>1</sup> These geometrical deviations in the solid state have been interpreted in terms of structures approaching the transition-state of the Cope rearrangement.<sup>1b</sup> Similarly, X-ray analysis of the closely related 9-phosphabarbaralane derivative **3** has also led to the interpretation that its solid state structure approaches the Cope transition state.<sup>2</sup> However, a recent CPMAS <sup>13</sup>C NMR study of **1b** and **1c** has led to the surmise that geometrical deviations in their X-ray structures is a consequence of dynamic disorder associated with rapid divinyl–cyclopropane (Cope) rearrangement.<sup>3</sup> Unlike the divinyl–cyclopropane systems, the Cope process in divinyl–cyclobutane systems, to our knowledge, has not been observed in the solid state. Herein, we report the first solid state structure of a Cope process in a divinyl–cyclobutane moiety embedded within a complex polycyclic framework.

Irradiation of a solution of nonacyclic-dione **4** (1 mmol dm<sup>-3</sup> in EtOAc, N<sub>2</sub>-purged) in sunlight, in a Pyrex vessel for 4 h followed by chromatography (silica gel)



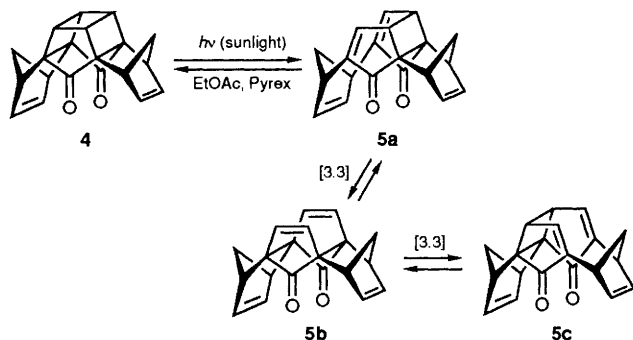
**1a**: R = CN, R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H

**1b**: R = R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>4</sup> = H, R<sup>3</sup> = CN

**1c**: R = R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = CN

**1d**: R = R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = CO<sub>2</sub>Me

**1e**: R = R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = CO<sub>2</sub>Me, R<sup>4</sup> = H



Scheme 1

furnished a crystalline product **5**, m.p. 206–207 °C in 50% yield. The <sup>13</sup>C NMR spectrum (25.0 MHz) of the photoproduct exhibited only five resonances at δ 212.0 (2 C), 135.65 (8 C), 117.5 (4 C), 48.65 (2 C) and 42.7 (4 C), indicating high symmetry and just two sp<sup>3</sup> carbon resonances. The <sup>1</sup>H NMR spectrum (300 MHz) had resonances at δ 6.45 (4 H, t, *J* 1.5 Hz), 5.6 (4 H, s), 3.06 (4 H, br s) and 1.83 (4 H, m) in consonance with a high symmetry structure. The UV spectrum showed an intense absorption at λ<sub>max</sub>/nm (MeOH) 226, characteristic of α-substituted cyclopentenones. These spectral features observed in solution, appeared compatible with the rapidly equilibrating structures **5a–c**. Thus, n–π\* excitation of the carbonyl in the cage dione **4** leads to an uncommon β-cleavage,<sup>5</sup> followed by cyclobutane fragmentation to furnish **5a** which then enters the **5a** ⇌ **5b** ⇌ **5c** Cope manifold (Scheme 1).

An X-ray crystal structure of **5** was determined and is shown in Fig. 1.‡ The four molecules in the unit cell are the same and there is no crystallographically-imposed symmetry. The final Δρ value was featureless (0.3 e Å<sup>-3</sup>). Pertinent interatomic distances are presented in Fig. 1 caption. There is a dramatic

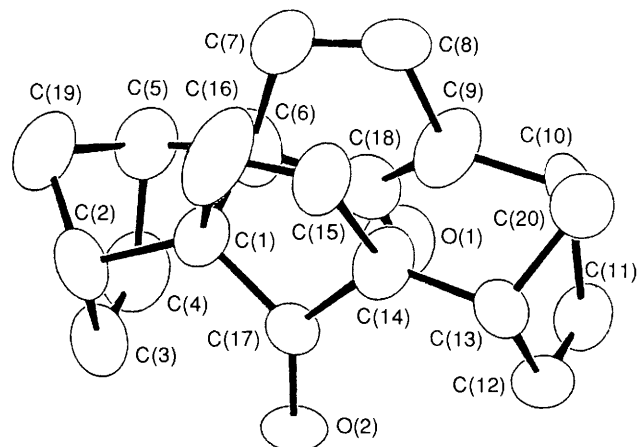
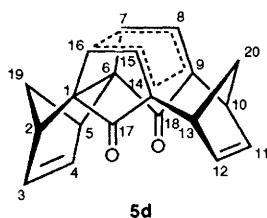


Fig. 1 ORTEP diagram of **5**. Selected interatomic distances (Å): C(1)–C(6) 1.703(18), C(1)–C(16) 1.521(15), C(6)–C(7) 1.517(12), C(7)–C(8) 1.369(18), C(8)–C(9) 1.409(14), C(14)–C(15) 1.404(17), C(15)–C(16) 1.361(18), C(9)–C(14) 2.196(22), C(7)–C(16) 2.207(23).

‡ Crystal data: C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> crystallised from dichloromethane–hexane, space group *P2<sub>1</sub>/c*, *a* = 6.596(4), *b* = 17.070(8), *c* = 12.835(2) Å, β = 105.83(3)°, *V* = 1390.3 Å<sup>3</sup>; *Z* = 4, Cu–Kα radiation, λ = 1.5418 Å. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer in the ω–2θ scan mode. A total of 2423 reflections were measured, of which 2152 were ‘unique’ and 1027 were ‘observed’ with |*F<sub>o</sub>*| ≥ 5.0σ(|*F<sub>o</sub>*|). The intensity was corrected for Lorentz, polarisation and absorption corrections. The structure was solved by SHELXS7 and the full-matrix least-squares refinement on |*F<sub>o</sub>*| with non-H atoms anisotropic and H-atoms isotropic converged to a *R*-factor of 0.096, *R<sub>w</sub>* = 0.103. The (Δρ) final was 0.3 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† For crystallographic enquiries.



change in the symmetry of the molecule from fourfold in solution to apparent  $C_s$  in the solid state. The most significant feature of the structure is the non-bonded C(9)–C(14) and C(7)–C(16) distances of 2.196(22) and 2.207(23) Å, respectively. The C(7)–C(8), C(8)–C(9), C(14)–C(15) and C(15)–C(16) bonds are considerably shorter than the normal C–C bond. However, C(8)–C(9) and C(14)–C(15) bonds are also substantially longer than the  $C_{sp^2}$ – $C_{sp^2}$  bond. In addition, the C(1)–C(6) bond is significantly elongated to 1.70 Å. These structural parameters are reminiscent of the crystal structure data on semibullvalenes<sup>1</sup> and suggest that a Cope process is manifest in the solid state, which can be represented as the intermediate structure **5d**. However, dynamic disorders associated with the rapidly equilibrating valence tautomers (**5a**  $\rightleftharpoons$  **5b**  $\rightleftharpoons$  **5c**) and large amplitude motions of C(7), C(9), C(14) and C(16) as the causative factor for the observed geometry cannot be completely ruled out.<sup>3,6</sup> Nonetheless, a Cope event seems to have been captured in the solid state in a divinylcyclobutane system. §

§ Note added in proof: the abnormal bond lengths observed here could also be a consequence of compositional disorder of the kind discussed recently (K. Yoon, G. Parkin and A. L. Rheingold, *J. Am. Chem. Soc.*, 1992, **114**, 2210).

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