

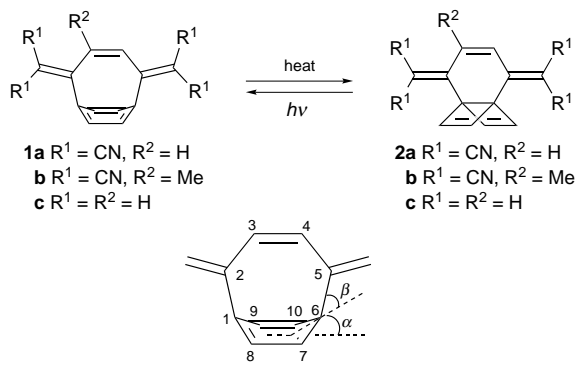
# The first observation of thermal transformation of strained paracyclophane into the Dewar isomer

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The kinetic stabilization of the [4]paracyclophane structure in the 2,5-bis(dicyanomethylene)-2-ene derivative permits the first observation of thermal isomerization of a strained paracyclophane to the Dewar valence tautomer; the activation free energy for the process is  $18.3 \pm 0.3 \text{ kcal mol}^{-1}$  at  $-20^\circ\text{C}$ .

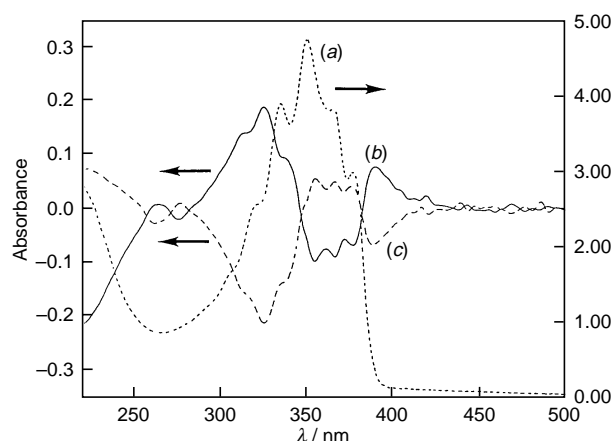
Isomerization of benzene to the Dewar valence tautomer is a highly endothermic process and the benzene ring is expected to be extremely bent in its late transition state.<sup>1,2</sup> A similar distortion of the benzene ring is effected in paracyclophane bridged by a short side chain,<sup>†</sup> and recent theoretical calculations suggest that the Dewar form becomes almost isoenergetic to or slightly higher in energy than the benzene form when the bridging chain is shortened to tetramethylene  $[-(\text{CH}_2)_4-]$ .<sup>3</sup> Thus, it is suggested that thermal isomerization of the latter to the former is, at least, energetically feasible in [4]paracyclophane. [4]Paracyclophane and its derivatives have successfully been generated,<sup>4,5</sup> but their extreme thermal instability has impeded the observation of their possible cyclization to the Dewar forms.<sup>4</sup> We recently succeeded in stabilizing the skeleton of [4]paracyclophane in the 2,4-bis(dicyanomethylene)-2-ene derivative **1a** to permit the measurement of its <sup>1</sup>H NMR spectrum for the first time.<sup>6</sup> We report here that **1a** and **1b** undergo thermal isomerization to the Dewar forms **2a,b**, respectively, and that their lifetimes in dilute solution are essentially limited by the above reactivity in the absence of air.



Compound **2a** in diethyl ether–isopentane glass at 77 K exhibits a characteristic absorption band with fine structure in the wavelength region of  $\lambda = 300\text{--}390 \text{ nm}$  [Fig. 1(a)]. Irradiation of the glassy mixture with a 365 nm light source leads to the generation of **1a** exhibiting broad absorption in the 280–420 nm range at the expense of **2a**, as clearly displayed in the difference spectrum [Fig. 1(b)].<sup>6</sup> When the resulting mixture was thawed, briefly warmed up to room temperature, and refrozen at 77 K in the dark, the difference spectrum obtained from the absorptions before and after the heating was a near mirror image to the first one, as shown in Fig. 1(c), indicating the nearly quantitative thermal reversion of **1a** to **2a**. The half-

life of **1a** at  $-20^\circ\text{C}$  is  $15 \pm 5 \text{ min}$  and, accordingly, the activation free energy for the isomerization of **1a** to **2a** is  $\Delta G^\ddagger = 18.3 \pm 0.3 \text{ kcal mol}^{-1}$  at the same temperature.<sup>‡</sup> The agreement of this energy barrier with a recent theoretical value ( $22 \text{ kcal mol}^{-1}$ ) for the isomerization of parent [4]paracyclophane **3** to 1,4-tetramethylene Dewar benzene **4**<sup>3b</sup> is extremely good, especially when a slightly higher exothermicity for the process from **1a** to **2a** as compared to that from **3** to **4** is taken into account. Similar photochemical generation of **1b** from **2b** and its clean thermal reversion at ambient temperature was also observed by UV–VIS spectrometry.

For such thermal unimolecular transformation to be observed the process must be exothermic. To gain information on the structures and energetics of **1** and **2**, computational analysis was undertaken. Geometrical optimization was carried out for truncated systems **1c** and **2c** using the GAUSSIAN 94 program package<sup>7</sup> since *ab initio* computations for **1a** and **2a** to reasonable accuracy exceeded the capacity of available computers. The optimized structures of **1c** and **2c** at the MP2/6-31G\* and B3LYP/6-31G\* levels are all C<sub>2v</sub> symmetric and the former lies higher in energy than the latter by  $14.3 \text{ kcal mol}^{-1}$  at the MP2/6-31G\* level and by  $14.4 \text{ kcal mol}^{-1}$  at the B3LYP/6-31G\* level, proving the exothermicity of the process from **1** to **2**.<sup>§</sup> The deformation angles  $\alpha$  and  $\beta$ , which give a measure of the degree to which the benzene ring is bent, and the interatomic distance between the bridgehead carbons, C(1) and C(6), in **1c** are  $27.4$  and  $44.5^\circ$ , and  $2.700 \text{ \AA}$  at the MP2/6-31G\* level and  $28.6$  and  $43.0^\circ$ , and  $2.686 \text{ \AA}$  at the B3LYP/6-31G\* level.<sup>¶</sup> The diminution of this interatomic distance by further distortion of the benzene ring as compared to that in **1a** will certainly result in a lowered energy barrier to isomerization to the Dewar form, and hence in a diminished lifetime of the



**Fig. 1** UV–VIS absorption spectra in diethyl ether–isopentane (1 : 1) at 77 K: (a) for **2a**; (b) difference spectrum obtained from the spectra before and after the irradiation of **2a** with 365 nm light; (c) difference spectrum obtained from those before and after the subsequent brief heating of the photolysed mixture to room temperature

benzene form. || Thus, **1** represents almost a limiting case of experimentally accessible strained paracyclophanes.

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### Footnotes

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† The isomerization path has been predicted by calculations to have  $C_{2v}$  symmetry (ref. 2).

‡ The photochemical isomerization of **2a** to **1a** is reversible and the latter constitutes only ca. 6% of the mixture in a photostationary state. The observation of the cycloreversion by another method, e.g.  $^1\text{H}$  NMR spectroscopy, was, therefore, experimentally difficult.

§ The total electronic energies of **1c** and **2c** are  $-461.563666$  and  $-461.586464$  a.u. at the MP2/6-31G\* level and  $-463.095426$  and  $-463.118401$  a.u. at the B3LYP/6-31G\* level, respectively.

¶ Other geometrical parameters for **1c** calculated at the MP2/6-31G\* level (those at the B3LYP/6-31G\* level in parenthesis; bond length in Å and bond angle in degrees): C(1)–C(2) = 1.496 (1.507), C(2)–C(3) = 1.497 (1.505), C(3)–C(4) = 1.385 (1.377), C(1)–C(8) = 1.413 (1.410), C(7)–C(8) = 1.391 (1.392), C(1)–C(2)–C(3) = 113.31 (113.00), C(2)–C(3)–C(4) = 138.58 (138.64), C(8)–C(1)–C(9) = 117.10 (116.98), C(1)–C(8)–C(7) = 117.60 (117.32).

|| The interatomic distance between the reaction centres in the transition state for the benzene–Dewar benzene isomerization has been calculated to be in a range of 2.0–2.2 Å (refs. 2, 3).

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