

Multiple *Z/E*-Photoisomerizations of Deuterium-Labelled [2₆]Paracyclophanes

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While the effect of macrocyclic conjugation in neutral molecules has been thoroughly studied, much less is known about the effect of perimeter conjugation in charged derivatives (cations and anions). It has become clear that in the ground state, the cyclic nature of the π -system is more important in the charged derivatives than in the neutral molecules.¹ What about the effect of macrocyclic conjugation on the excited state reactions? To gather some experimental information on this matter we have studied multiple *Z/E*-photoisomerizations in paracyclophanes with six unsaturated bridges, i.e. [2₆]paracyclophanes.

We have previously provided evidence for multiple *Z/E*-isomerizations in two such [2₆]paracyclophanes, but no unequivocal mechanistic proofs were given.² More recently, however, we found a clear-cut case of a *six-fold Z/E*-photoisomerization of all-*Z* to all-*E* [2₆]orthoparacyclophane; the isomerization, which proceeds via the triplet state, is strongly exothermic (40 kcal mol⁻¹ from molecular mechanics calculations) and interconverts the two isomers without recourse to any ground state intermediates.³ We have now returned to our initial example to examine whether or not multiple *Z/E*-photoisomerizations are possible between isomers of similar ground-state energy.

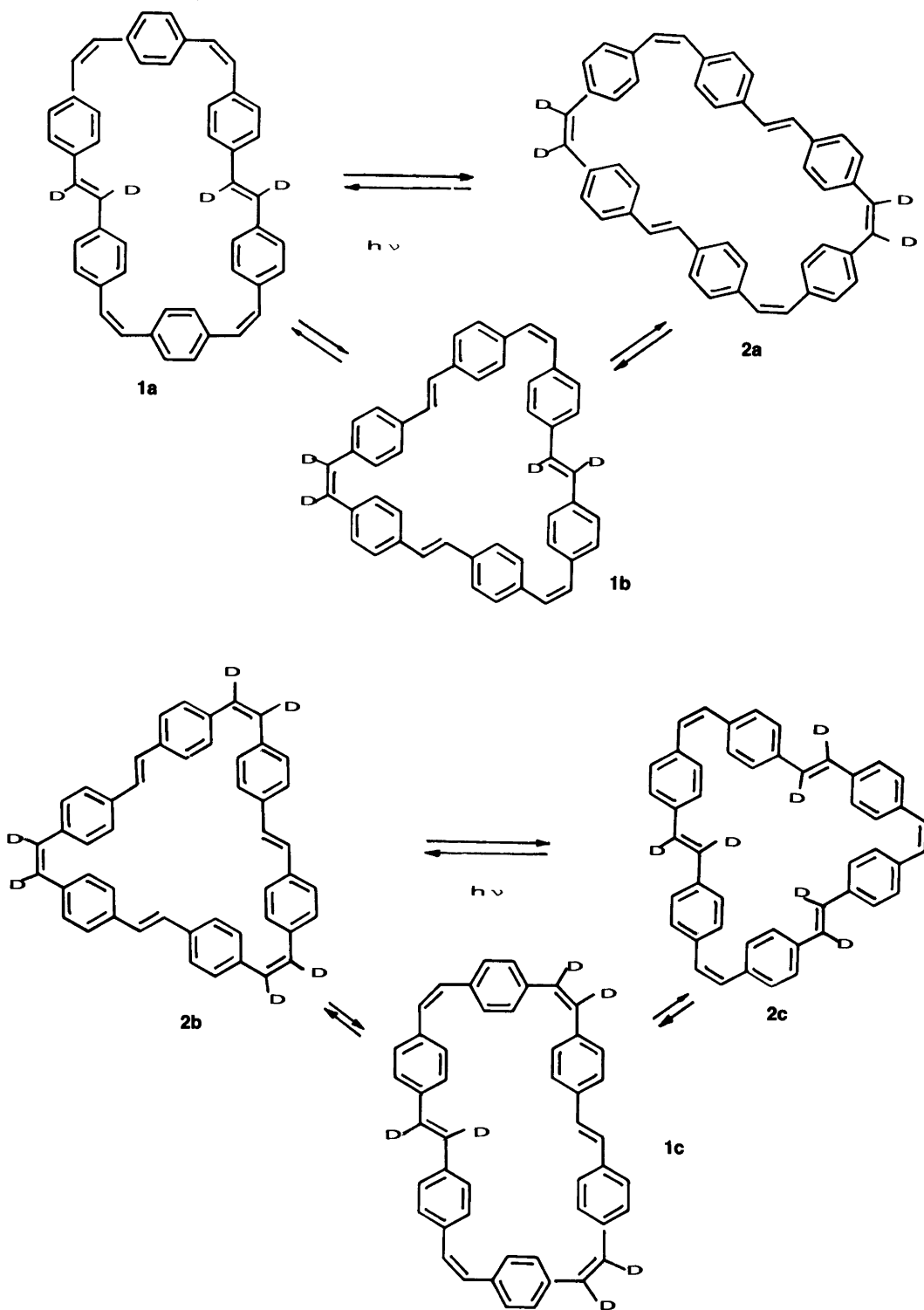
Two new deuterium-labelled [2₆]paracyclophanes of known stereochemistry, **1a** and **2b**, were synthesised. The cyclophane **1a** was prepared by a four-fold Wittig reaction between

E-stilbene-4,4'-dicarbaldehyde, deuterium-labelled on the double bond, and the bis-ylid from the bis(triphenylphosphonium) salt of 1,4-bis(bromomethyl)benzene. The deuterium-labelled reactant was prepared from 4-bromobenzyltriphenylphosphonium periodate, generating the ylid in C₂H₅OD with C₂H₅OLi.⁴ The periodate serves as an oxidizing reagent to produce aldehyde which then reacts with the ylid. The deuterium-hydrogen exchange is faster than the oxidation, and this results in very efficient deuterium labelling. The resultant dideuterio-4,4'-dibromo-*E*-stilbene was then converted to the desired dideuterio-*E*-stilbene-4,4'-dicarbaldehyde by lithiation (BuLi), reaction with DMF and subsequent hydrolysis.

The cyclophane **2b** was prepared by the following synthetic route: *E*-stilbene-4,4'-dicarbaldehyde was converted to its bis-thioacetal using TiCl₄ and 1,3-propanedithiol,⁵ and the product was then treated with BuLi at low temperature followed by D₂O.⁶ Deprotection of the deuterium-labelled thioacetal (HgCl₂, HgO) then yielded the dideuterio dialdehyde.⁶ The dialdehyde was then partially reduced with NaBD₄ to the monoalcohol, which in turn reacted with HBr to give the trideuterio-4-bromomethyl-*E*-stilbene-4'-carbaldehyde; the monoaldehyde was obtained in 42% yield when separated from the bis(CD₂Br) derivative (14%) and the bis(CDO) derivative (18%) by chromatography on silica gel. The monobromo compound was treated with triphenylphosphine to yield the monophosphonium salt. This monophosphonium salt-monoal-

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SHORT COMMUNICATION



dehyde reacted with base in a three-fold Wittig reaction yielding the desired cyclophene **2b**.⁷ The isotopic purity of the compounds was >95% for **1a** and about 90% for **2b**.

The photoisomerization of **1a** was carried out using a 3 mM solution in benzene-*d*₆ by irradiation of an NMR sample in a Rayonet reactor with light of maximum intensity near 300 nm. The reaction was carefully monitored by ¹H NMR spectroscopy (Bruker WH 270), the signals from the protons on the *E*-double bonds being used to calculate the relative proportions of the three isomers **1a**, **1b** and **2a**. The formation of **1b** and **2a** from **1a** must involve *Z/E*-isomerization at a minimum of four and three double bonds, respectively. The accuracy of the NMR analysis is not sufficient for a complete treatment of the kinetics. However, the initial rates of formation of **1b** and **2a** were found to be almost identical and then changed towards a ratio of ≈1:6. No induction period was observed. This experimental observation requires that **1b** is formed from **1a** without **2a** as a necessary intermediate. Thus, both routes in the reaction scheme are possible.

The irradiation of **2b** was carried out and monitored as above (3 mM in C₆D₆). In one experiment, biacetyl was added as a sensitizer and the irradiation was carried out using a filter solution (wavelength >400 nm) to avoid direct excitation of the cyclophenes. Again, no induction period for the isomerization of **2b** to **2c** was observed. Initially, the relative ratio of formation of **2c** and **1c** was ≈1:1. The formation of **2c** from **2b** requires *Z/E*-isomerization at all six double bonds, and **1c** can be ruled out as a necessary intermediate on the basis of the observed rates of isomerization. In the two cases reported here, no ground state intermediates were observed by NMR spectroscopy (limit of detection <5%). The results presented here, together with unpublished results on *Z/E*-photoisomerization of a series of configurational isomers of [2₆]paracyclo-

phenes, clearly point towards direct isomerizations of **1a** to **1b** and **2b** to **2c** by triplet state reactions.

The isomerizations interconvert isomers of equal energy and there can be no large barriers on the triplet energy surfaces, although the barriers to isomerization in the ground states are considerable. So far, our observations of multiple *Z/E*-isomerisations (up to six-fold) are limited to molecules with formal π-perimeters (*ortho*- and *para*-substituted benzene rings linked by vinylene bridges). Further work will reveal whether or not this is a necessary condition. We also hope to be able to explore further the energetics of the triplet energy surface by preparing new configurational isomers of the [2₆]paracyclophenes, allowing us to reach the triplet energy surface at new points by sensitized excitation.

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