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Determination of the Reaction Enthalpy and Kinetic Parameters for the Isomerization of Bridged Dewar Benzenes to 8,9-Disubstituted [6]Paracyclophanes by Differential Scanning Calorimetry

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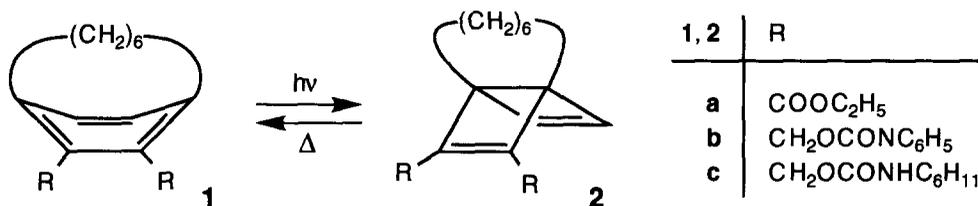
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Abstract: In solution the reaction enthalpy for the thermal isomerization of the Dewar isomers **2a** and **2b** to their corresponding 8,9-disubstituted [6]paracyclophanes **1a** and **1b** was determined as -128 ± 13 kJ·mol⁻¹ and -146 ± 15 kJ·mol⁻¹, while the activation energies were found to be 101 ± 10 kJ·mol⁻¹ and 117 ± 12 kJ·mol⁻¹ respectively. An improved calorimetric technique was employed using samples in sealed NMR tubes.

Due to the torsional strain of the hexamethylene chain, the benzene ring of [6]paracyclophanes is sufficiently deformed to allow photochemical transformations of the thermodynamically more stable paracyclophanes **1** to their Dewar isomers **2** to take place.¹ We have already investigated these photochemical reactions in previous publications^{2,3} using the disubstituted compounds diethyl [6]paracyclophane-8,9-dicarboxylate (**1a**) and 8,9-bis-(N-cyclohexylcarbamoyloxymethyl)[6]paracyclophane (**1c**). Due to the decomposition of either **1c** or **2c** at elevated temperatures, an attempt to determine the heat of the reaction **2c**→**1c** had failed,³ while a value of $\Delta_r H = -19.8 \pm 3.8$ kJ·mol⁻¹ had been given for the reaction **2a**→**1a**.²

Since this value is surprisingly low compared to a value of $\Delta_r H = -249$ kJ·mol⁻¹ for the isomerization of the hexamethyl Dewar benzene to the less strained hexamethyl benzene,^{4,5} and because this result contradicts recent quantum mechanical computations,^{6,7} we decided on the redetermination of this value by an improved calorimetric technique (see *Experimental*). To complete the thermal reaction at the lowest possible temperature, an extremely low scan rate (0.2–0.3 K·min⁻¹) was selected. Furthermore, the sample tubes fitted into NMR tubes, so that an NMR analysis of the sample was possible before and after every calorimetric run or UV irradiation without opening the sample.

The heat of reaction was obtained from the peak area. Because of the small heat capacity change during the reaction, the heat of reaction can be identified with the enthalpy of reaction $\Delta_r H$. The rate of reaction as a function of temperature was determined by the BORCHARDT-DANIELS method^{8,9} assuming a reaction order of one. Application of the ARRHENIUS law of the temperature dependence of the rate of reaction then furnished the activation



energy E_a and the frequency factor A . We investigated the systems **2a**→**1a** and **2b**→**1b**, which markedly differ in the amount of conjugation between the substituent and the benzene ring. As determined by ¹H NMR analysis, less than 3% of by-products were formed provided that the final temperature was below 135 °C. The significant parameters of the isomerization reaction are compiled in Table 1. Independent NMR analyses at selected temperatures provided rate constants identical with those of the calorimetric experiment within 10%. Evidently, minute side reactions detected in the NMR spectra do not falsify the Δ_rH values within the margins of error. We therefore conclude that the published² Δ_rH value for the system **2a**→**1a** is incorrect. Neither a change of the solvent nor different substituents in the 8,9-position of the [6]paracyclophane system significantly influence the difference in energy of the valence isomers. Theoretical ab initio calculations with large AO basis sets (triple-zeta plus polarization) published by Frank, Grimme and Peyerimhoff⁷ find values for the isomerization enthalpy between 35 kcal·mol⁻¹ (147 kJ·mol⁻¹, SCF level) and 45 kcal·mol⁻¹ (189 kJ·mol⁻¹, SCF/MP2 level) in the case of **2a**→**1a**. By comparing the results for benzene and Dewar benzene, these authors conclude that the SCF/MP2 values might be too high by several kcal·mol⁻¹ units. Assuming that neither substituents in the 8,9-positions nor the solvent have a drastic effect on the reaction enthalpy – an assumption that is supported by the theoretical study⁷ as well as experimental evidence (*see Table 1*) – the agreement between computed and experimental values is quite good.

EXPERIMENTAL

The differential scanning calorimeter used was a CALVET-type heat-flux instrument with a cylindrical measuring system (C80, Setaram, Caluire, France) accepting much larger samples than the disk-type heat-flux instrument used before (TA 500, Hereaus, Hanau, Germany).² The experiments were performed in thin-walled pyrex tubes (4 mm outer diameter, 35–55 mm length) fitting precisely into copper cylinders of 16.9 mm outer diameter and 80 mm length, which are the dimensions of the measuring cylinders of the calorimeter. The calorimetric calibration was performed using electrical energy released in standard Joule cells. For temperature calibration and determination of the thermal lag and time constant of the measuring system, high-purity indium and gallium were used.

The compounds **1a** and **2b** were synthesized according to ref.^{3,10} A solution of about 10 mg in 200 μl of deuterated solvent in a pyrex tube was degassed by repeated freeze-pump cycles, sealed and characterized by ¹H NMR. The sample containing **1a** was irradiated next on an optical bench at 0 °C behind a 324 nm filter until a substantial amount of **2a** had been formed (*see Table 1*). The amount of Dewar isomer formed was determined by ¹H NMR (Bruker WM 250). NMR parameters were identical with those reported previously.^{3,10} Next, the thermal rearrangement was conducted in the calorimeter and the products were quantified by ¹H NMR. The heat of

Table 1. Calorimetric Data and ARRHENIUS Parameters for the Rearomatization 2→1.

Run	Compound	Solvent ^a	Total Sample Weight in mg	Fraction of Dewar Isomer in %	Temperature Range in °C
1	2a	p-Xylene	14.1	61	15 – 125
2	2a	DMCH ^b	7.40	80	1 – 110
3	2a	DMCH ^b	6.96	74	0 – 120
4	2a	p-Xylene	14.1	60	0 – 120
5	2a	DMSO	16.9	44	0 – 120
6	2b	DMSO	10.6	100	20 – 135
7	2b	DMSO	11.7	100	20 – 140

Run	Heating Rate in K·min ⁻¹	$\Delta_r H$ in kJ·mol ⁻¹	E_a in kJ·mol ⁻¹	lg(A/s ⁻¹)
1	0.2	-123	101	11.7
2	0.2	-127	104	11.9
3	0.3	-129	99	11.2
4	0.2	-134	102	11.9
5	0.2	-125	97	11.6
6	0.2	-137	119	12.9
7	0.2	-154	115	12.4

Notes: ^a Deuterated solvents were used in all experiments. – ^b Dimethylcyclohexane.

reaction was determined from the calorimetric curve by integration between the initial and final temperature of the reaction. An experimental curve measured immediately after the thermal rearrangement with the same samples under identical conditions was used as baseline. Depending on the shift between the initial and final baseline, a straight line or a curve proportional to the degree of conversion¹¹ was additionally subtracted. Because the reaction rate was small compared to the time constant of the calorimeter, no deconvolution procedure was necessary.

The uncertainty of the enthalpy determination is estimated to be about 10%. This estimate comprises the uncertainty of the calibration (*ca.* 1%), the uncertainty of the peak area determination (*ca.* 5% because of the small signal to noise ratio and the resulting problems of baseline construction) and the uncertainty of the determination of the initial concentration by ¹H NMR spectroscopy (*ca.* 5%). Whereas the rate of reaction can be determined by this method with high accuracy (*ca.* 5% uncertainty), the derived parameters E_a and lg(A) are far more uncertain because of their strong statistical correlation.

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