Tetrahedron Letters No.47, pp. 4147-4150, 1969. Pergamon Press. Printed in Great Britain.

STUDIES ON THE THERMOCHEMISTRY OF syn- and anti-[2.2](1,4)NAPHTHALENOPHANE AND DIBENZOEQUININE. STRAIN ENERGIES.

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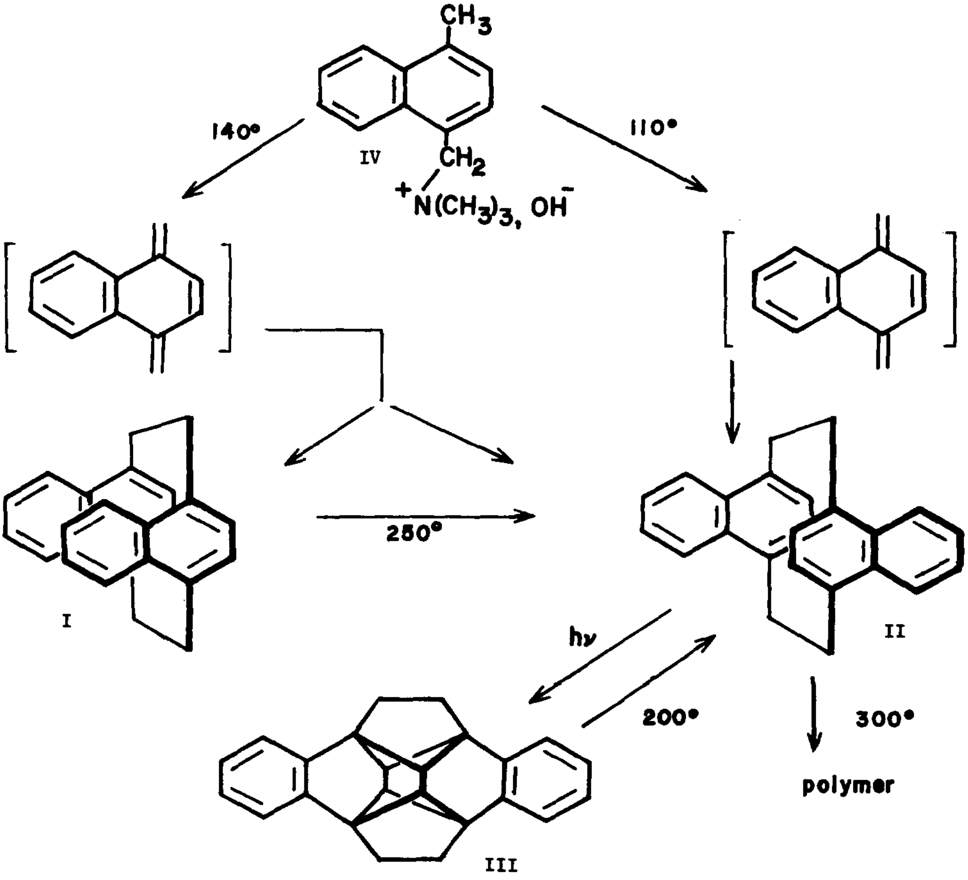
(Received in UK 2 September 1969; accepted for publication 11 September 1969)

We have recently reported[1] the preparation of syn-[2.2](1,4)naphthalenophane (I) and its conversion, on heating, to the anti-isomer (II). As shown below, only the cyclophane (II) is isolated from the pyrolysis of IV in toluene at 110°[2], while in xylene at 140°, significant amounts of the syn-form (I) are found along with II. On irradiation, II is transformed to dibenzoequinine (III) which may be reconverted to II when heated in the solid phase at 200°[3].



The existence of these clean thermal interconversions suggested the possibility of using differential scanning calorimetry to determine kinetic and thermodynamic properties of I, II and III. Their sparing solubility has frustrated efforts to determine reliable kinetic parameters, but we are able to report enthalpies for reactions of the pure crystalline compounds.

Reaction heats were measured with a Perkin-Elmer DSC-1B calorimeter using samples sealed in aluminum volatile-sample capsules. Baselines were extrapolated through regions of reaction by rescanning the reacted sample at the completion of each run. The instrument was standardized on the heat of fusion of NBS-calorimeter standard benzoic acid in sealed capsules. Our results are summarized in the table.

While the precise shape of the traces depends on particle size as well as scanning rate, total exothermicities, as measured by integration of the peaks (figure 1), are independent of these variables. The consistency of the total exothermicity for the second transition in runs of I and III with that for the transition of pure II leaves no doubt that I and III are first converted to crystalline II.

Table

	Wt. (mg.)	Overall Exothermicity (kcal/mole)			Relative Enthalpy (kcal/mole)
		III → II	I → II	II → polymer	
II	1.7[a]			11.5	[0]
	4.375			14.4	
	3.830			12.3	
	3.290			12.3	
I	4.0[a,b]		5.9	11.6	6
	1.1[a,b]		7.2	12.3	
	3.540		6.7	12.1	
	4.140		6.1	11.4	
III	3.125[a]	12.5		11.3	13
	3.190[a]	13.0		--	
	4.105	13.2		12.5	
	4.800	12.4		12.9	

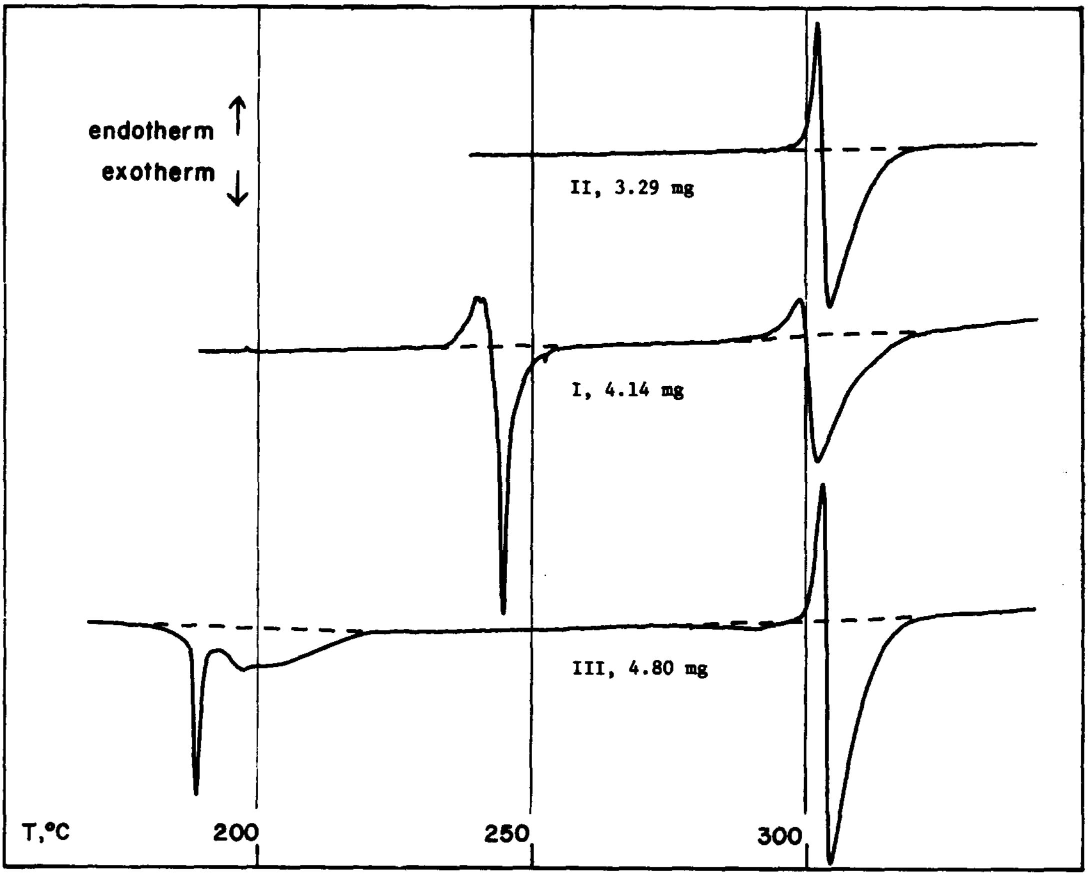
[a] Scanned at 10°/min., all others at 5°/min.

[b] Mixture of I and II; results calculated on the basis of 80% I as measured by nmr.

Although single crystals of III become opaque during conversion to II, they retain their shape. Together with the absence of an endotherm for the transition, this fact presumably reflects a similarity in crystal packing between II and III. I melts during transformation and recrystallizes as II. A subtle difference between II formed in this way and that formed from III or crystallized from benzene is reflected in the peak shapes for transformation of II in each of these cases. This difference was reproducible, while the small (<1 kcal/mole) exotherm preceeding the transformation of II was evident in only half the runs of II and III.

Crystallinity of starting materials and products complicates interpretation of our results by necessitating separation of heats of fusion from the observed enthalpy changes. These contributions tend to cancel between starting material and product for I ⟶ II and III ⟶ II, so that the overall enthalpies should correspond to heats of reaction to within 2-3 kcal/mole.

Figure 1. Typical DSC Traces at 5°/minute



For the conversion of II to polymer there can be no such cancellation and the observed exothermicity must be increased by the heat of fusion of II to give the heat of reaction. A lower limit for this heat of reaction is established by the exothermic peak from 303 to 325° C. For scans of II and III this value ranged from 15.2 to 16.7 kcal/ mole. With 10 kcal/mole as a reasonable upper limit for the heat of fusion of II,[4] we calculate an upper limit of 23 kcal/mole for the heat of reaction.

If the clear yellow glassy polymer obtained from II is not less stable than polynaphthoquinodimethide, the heat of reaction II ⟶ polymer provides an upper limit for the strain of II. This upper limit (16-23 kcal/mole) is significantly lower than previous estimates of the strain energy in [2.2]paracyclophane.[5] Experiments in progress suggest that benzo-fusion may reduce strain by stabilizing the distorted aromatic rings of [2.2]paracyclophane more than planar rings. It is also possible that the strain of [2.2]paracyclophane has previously been overestimated. Calculations which agree on strain energy of ∿32 kcal/mole for [2.2]paracyclophane differ widely on the fraction of this strain assigned to ring deformation (48%[6]; 79%[7]). These estimates could be high because of extrapolation of vibrational potentials to substantial deformations.

Acknowledgements: This work was supported by Grants GM-13854 and GM-15166 from the National Institutes of Health, U.S. Public Health Service.

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(4) The heats of fusion of anthracene (mp 217°) and of phenanthrene (mp 99°) are 6.89 and 4.46 kcal/mole respectively. M. Kotake, Constants of Organic Compounds, Asakura, Tokyo, 1963, pp. 555 ff.

(5) Estimates of this strain have ranged from 31[6] to 155[8] kcal/mole.

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