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STRAIN ENERGIES IN DOUBLE- AND TRIPLE-LAYERED [2.2]PARACYCLOPHANES

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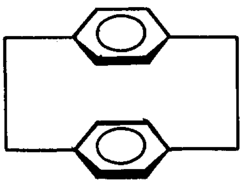
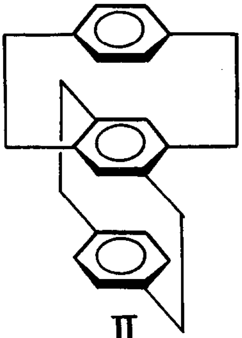
It is well known that double-layered [2.2]paracyclophane (I) exhibits various peculiar properties associated with the anomalous molecular structure[1] in which closely stacked boat-shaped benzene rings and eclipsed, anomalously bent dimethylene bridges are involved. For triple-layered [2.2]paracyclophane (II), the molecular structure has not been determined yet. But X-ray diffraction studies on substituted triple-[2] as well as quadruple-layered[3] [2.2]paracyclophanes (III and IV, respectively) indicate that a molecule of II involves a twist-shaped inner benzene ring in addition to the anomalous features observed for I.



I



II

In order to evaluate the total strain energies in the molecules of I and II, precise determinations of standard enthalpies of combustion and of sublimation have been carried out. Energies of combustion were measured by using a previously described isoperibol rotating bomb calorimeter,[4] calibrated with U.S. National Bureau of Standards S.R.M. 39i benzoic acid. Derived standard enthalpies of combustion ΔH°_c at 298.15 K are -8727.27 ± 3.00 and -14226.10 ± 2.82 kJ mol^{-1} for I and II, respectively.[†] Mean and standard deviation of the mean of carbon dioxide recovery, measured to verify the purity and the completeness of combustion for the both samples, are 99.91 ± 0.02 and 99.94 ± 0.04 % for I and II, respectively. The value of ΔH°_c for I is in close agreement with the one of Rodgers *et al.*[5] among the literature values, namely -8737.0 ± 3.8[6] and -8727.57 ± 0.67[5] kJ mol^{-1}.

Enthalpies of sublimation were determined from the second-law method analysis of the temperature dependence of vapour pressure measured by gas-saturation method using a Du Pont Thermal Evolution Analyzer. Standard enthalpies of sublimation ΔH°_s at 298.15 K and estimated uncertainties are 99.6 ± 1.5 and 123.2 ± 1.5 kJ mol^{-1} for I and II, respectively The value for I is in agreement with the value of Boyd, 96.2 ± 4.2 kJ mol^{-1}, within the sum of individual assigned uncertainties. Resulting standard enthalpies of formation in gaseous state are 244.1 ± 4.0 and 405.0 ± 4.7 kJ mol^{-1} for I and II, respectively. Suspicion on the accuracy of the experimental enthalpy of

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[†] Uncertainties for enthalpies are twice the overall standard deviations of the mean, unless otherwise stated.

formation in gaseous state of I, which has recently been aroused by Kao *et al.*[7] on the basis of a molecular mechanical calculation, does not seem to be correct in view of the agreements observed in the experimental values of ΔH°_c and ΔH°_s.

Total strain energies were evaluated by comparing the experimental standard enthalpies of formation in gaseous state with the values calculated by using group increments derived from the table of Cox *et al.*,[8] which had been proved to be able to account for the standard enthalpies of formation in gaseous state of "unstrained" alkyl benzenes within ±4 kJ mol^{-1}, and by correcting for *PV* term.[9] The total strain energies thus evaluated are 124 and 247 kJ mol^{-1} for I and II, respectively.

It is to be noted that the value for II is twice as much as the one for I. The total strain energy for I has been analyzed principally in terms of contributions from out-of-plane deformations of the benzene rings and of the *para* substituents, bridge methylene eclipsing and nonbonding interactions including transannular repulsive interactions between π-electrons on the neighbouring benzene rings.[10, 11] II is assumed to be essentially similar to III with respect to molecular structure. Bond distances, bond angles and other molecular parameters for III and IV are almost similar to the corresponding ones for I, only significant difference being the twisting of the inner benzene ring. Comparison of the molecular structures of I and II suggests strongly that the contribution from each of the components to the total strain energy in II, excluding that arising from the out-of-plane deformations of the benzene rings, is twice as much as that in I. Accordingly, the sum of these contributions for II would be twice as much as that for I. If the remaining part of the total strain energy could be assigned to the out-of-plane deformation of the benzene rings and the contribution from a boat-shaped benzene ring was assumed to be similar for I and II, the contribution from a twist-shaped benzene ring should be equal to twice the contribution from a boat-shaped benzene ring. In these discussions, minor contributions to the total strain energy are neglected. However, the contribution from a boat-shaped benzene ring has been evaluated to be 21.3[10] and 26.4[12] kJ mol^{-1} on the basis of molecular mechanical and molecular orbital calculations, respectively. If these values are taken into account, it appears to be sure at least that the contribution from a twist-shaped benzene ring is more significant than the one from a boat-shaped analogue.

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