Enthalpy of Formation of Perhydroquinacene and a Comment on the Strain Energy of Dodecahedrane

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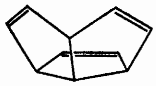
Summary Perhydroquinacene, a building unit of the unknown hydrocarbon dodecahedrane, has a gas-phase enthalpy of formation of $-102{\cdot}39 \pm 3{\cdot}60$ kJ mol^{-1}, suggesting that the strain energy of dodecahedrane should be considerably lower than that predicted by the Allinger empirical force field method.

THE $C_{20}H_{20}$ hydrocarbon dodecahedrane (**1**) contains a symmetrical array of twelve *cis*-fused cyclopentane rings. The nucleus is very rigid, though without a great deal of angle strain, and each peripheral hydrogen atom is perfectly eclipsed with its nearest neighbours. The strain energy of this unique molecule, calculated by molecular mechanics, has been the subject of some conjecture; whereas the empirical force field developed by Schleyer[1] predicts a gas-phase enthalpy of formation, ΔH_f° (g), of $-0{\cdot}92$ kJ mol^{-1} and a strain energy of 179·83 kJ mol^{-1}, that of Allinger[2] gives a ΔH_f° (g) value of $+189{\cdot}45$ kJ mol^{-1} and a strain energy of 369·78 kJ mol^{-1}, a strain energy difference of some 190 kJ mol^{-1}. Unfortunately dodecahedrane is unknown and a direct calorimetric evaluation of its thermodynamic properties is presently not possible. Nevertheless we can now shed some light on the force-field predictions.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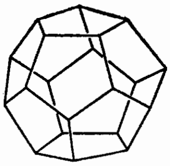
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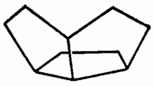
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Woodward's suggestion[3] that triquinacene (**2**) is a possible synthetic precursor of dodecahedrane forms the basis of our analysis, and we view the molecule as a repetitious array of perhydroquinacene ($C_{10}H_{16}$) (**3**) units. Topologically perhydroquinacene closely resembles any corresponding three-ring unit of the dodecahedrane periphery, both in bond angles and in the disposition of the hydrogen atoms on the convex surface. We have measured the enthalpy of formation of perhydroquinacene by combustion calorimetry.

The sample was prepared by the method of Jacobson[4] and purified by chromatography over alumina, sublimation (373 K at 1 atm) and multiple zone-refining (30 molten zone passes); g.l.c., differential scanning calorimetry, and microanalysis revealed no impurities above 0·02%. Combustion was carried out in the Belfast Mark I calorimeter[5] using polythene capsules. Five determinations gave $\Delta E_c^\circ = -6052{\cdot}87 \pm 3{\cdot}18$ kJ mol^{-1}, resulting in a ΔH_f° (c) value of $-158{\cdot}95 \pm 3{\cdot}35$ kJ mol^{-1}. The enthalpy of sublimation was measured by the gas-saturation, temperature scanning technique.[6] Three determinations between 295 and 318 K with nitrogen flow rates of 0·27 to 0·40 ml s^{-1} gave $\Delta H_{sub} = 56{\cdot}56 \pm 1{\cdot}30$ kJ mol^{-1}. The gas-phase enthalpy of formation of perhydroquinacene is therefore $-102{\cdot}39 \pm 3{\cdot}60$ kJ mol^{-1}.

The empirical force-field calculations on perhydroquinacene reflect, to a lesser degree, the differences apparent in the dodecahedrane calculations; Schleyer's force field[1] gives ΔH_f° (g) $= -\ 99{\cdot}33$ kJ mol^{-1} with a strain energy of 66·61 kJ mol^{-1}, whereas Allinger's force field[2] gives ΔH_f° (g) $= -\ 82{\cdot}59$ kJ mol^{-1} with a strain energy of 83·76 kJ mol^{-1}. Clearly our experimental data favour Schleyer's calculated heat of formation of perhydroquinacene, implying that his value for dodecahedrane is more reliable than that obtained with the Allinger force field. This is all the more likely in the light of our recent calorimetric studies on diamondoid hydrocarbons[7] whose heats of formation are generally less reliably calculated by the Allinger force field than by the Schleyer force field. Perhydroquinacene and dodecahedrane possess an unusually large number of H–H interactions and the higher strain energies predicted by the Allinger force field reflect an undue emphasis on the repulsive nature of such interactions.

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