

THE CONFORMATION OF CYCLODECA-1,6-DIENE

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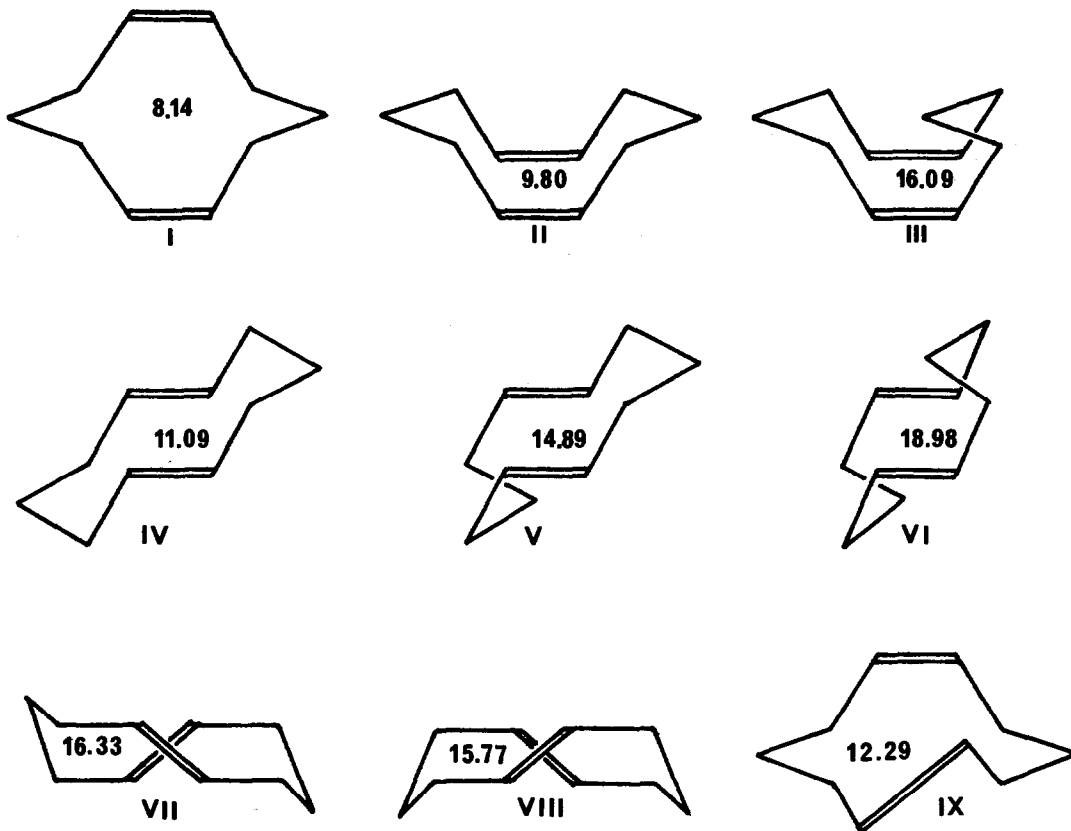
There has been continuing and sustained interest in the calculation of alkane and alkene structures by molecular mechanics procedures over the past decade¹, and although considerable attention has been devoted to cyclic hydrocarbons the cyclononadienes and cyclodecadienes have received an unduly small proportion of this effort^{2,3,4}. In particular, although there has been some speculation in the literature^{4,5,6}, the minimum energy conformation of trans, trans-cyclodeca-1,6-diene has yet to be established.

The steric energies of nine cyclodeca-1,5-diene conformers were computed during the course of a programme of calculations designed to extend the scope of Schleyer's alkane force-field¹. The extended force-field⁷ is based upon a larger body of experimental data than previous parameterisations and the excellent agreement between calculation and experiment (e.g. mean $\Delta\Delta H_f$ over 35 diverse alkenes is 0.25 k.cal.mole⁻¹) enables some confidence to be placed in the results for the cyclodeca-1,6-dienes. (I - IX, steric energies in k.cal.mole⁻¹).

The results for the cis, cis-isomers are in good agreement with the electron diffraction experiments⁸ and are qualitatively similar to other calculations^{2,3}. The latter results probably underestimate the difference between the boat and chair forms at 0.16 and 0.30 k.cal.mole⁻¹, as the only directly comparable experimental evidence⁸ suggests that the boat form is barely present in the gas phase at 35°C.

The minimum energy conformation of trans, trans-cyclodeca-1,6-diene is calculated as IV, identical to the conformer observed in the crystalline state⁶, and 4.7 k.cal.mole⁻¹ lower in steric energy than the structure proposed by Grob and Schiess⁹, (VIII). This is not altogether too surprising as VIII suffers from appreciable Pitzer strain around the four bonds immediately adjacent to the double bonds, whereas IV is essentially strain free. The difference in steric energy between the preferred cis, cis- and trans, trans-isomers is calculated to be 2.95 k.cal.mole⁻¹, in excellent agreement with the observation that only the former is detectable when the two isomers are equilibrated¹⁰. On the basis of these calculations trans, trans-cyclodeca-1,6-diene should consist solely of conformer IV in the gas phase, a proposal which could be verified by electron diffraction experiments thereby providing an experimental measure of the molecular geometry as a not inconsiderable bonus!

Details of the alkene force-field will be given in reference 7 and the energy minimisations were accomplished by means of our Newton-Raphson procedure¹¹.



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