

Correlation of Hückel Calculations and Reduction Potentials for Some Conjugated Cyclophanes

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For a series of cyclophanes with extended conjugated π -systems, the energies of the lowest unoccupied molecular orbitals from simple Hückel calculations have been correlated with the reduction potentials for the reversible formation of dianions of the cyclophanes. Depending on the number of π -electrons around the perimeter of the cyclophanes an alternating behaviour on reduction is observed, the effect being reproduced by the calculations. The validity of the Hückel rule for large conjugated dianions is briefly discussed.

The understanding of the conditions for delocalisation of π -electrons in unsaturated hydrocarbons has had a large impact on the development of organic chemistry. Much effort from synthetic chemists as well as theoreticians has contributed to our present knowledge. The original Hückel rule,¹ which differentiates between $(4n+2)$ and $4n$ π -systems (n is an integer), has been modified, and it is now generally accepted that the alternating effect predicted by Hückel's rule is greatly diminished in large conjugated monocyclic π -systems (e.g. annulenes) if the ring size exceeds 22–26 carbon atoms.² Recent modifications of the reference structures used in the calculations of the resonance energies support the experimental observations.^{3a-d} Haddon^{3d} has shown explicitly that for large, planar N -annulenes (N equals the number of carbon atoms in the conjugated ring) the resonance energy is proportional to $1/N$, whereas the magnitude of induced diamagnetic ring currents is proportional to N . However, effects such as the degree of planarity, conformational mobility, bond alternation and steric effects must also be

considered and this complicates the comparison between calculation and experiment. According to theory,^{3b,d} $[4n]^{2+ \cdot 2-}$ annulene ions should exhibit essentially the same resonance and ring current effects as the corresponding neutral $(4n+2)$ species. This issue is further complicated, however, by problems such as the choice of suitable reference structures, and the effects of solvation in polar media. There is also a dearth of experimental data, although a direct comparison of the relative stabilities of the dianions of cyclo-octatetraene and [16]annulene has been carried out recently.⁴

During the last few years, we have been able to prepare a number of cyclophanes with unsaturated bridges *via* multiple Wittig reactions.⁵ Several of these cyclophanes contain a perimeter of conjugated double bonds, and we have also shown that some of them undergo a remarkable, completely reversible, two-electron reduction to dianions in polar solvents such as DMF.^{6a} One rather surprising requirement for the reversible two-electron process is that the cyclophane must contain a perimeter of $4n$ conjugated π -electrons which, on reduction, could give a $4n+2$ π -system.^{6b} In order to better understand this reduction process we have now compared results from Hückel calculations with the electrochemical data.

RESULTS AND DISCUSSION

For a series of cyclophanes having extensive π -systems, we have carried out simple Hückel calculations assuming planar structures with constant β -values (Table 1). The size of the π -systems

Table 1. Reduction potentials (*vs.* SCE in V) for the reversible two-electron reduction, and energies of the lowest unoccupied molecular orbitals from Hückel calculations (in β) for a series of unsaturated cyclophanes 1–11.

Compound	1	2	3	4	5	6	7	8	9	10	11
Reduction potentials	-1.70	—	-1.60	—	-1.53	—	-1.71	—	-1.74 ⁹	-1.83	-1.77
LUMO energies	0.254	0.323	0.210	0.281	0.183	0.361	0.274	0.349	0.288	0.316	0.288

precludes the use of *ab initio* calculations. On the other hand, the high molecular symmetry and the absence of heteroatoms should give comparable and relevant results even for simple calculations. We have correlated the energies of the lowest unoccupied molecular orbital (LUMO, in β -units) with the reduction potential (from cyclic voltammetry) for a series of cyclophanes 1, 3, 5, 7, 9, 10 and 11 in Fig. 1 (see also Table 1). Within the experimental range, the correlation is good and the results can easily be fitted to a straight line with a slope corresponding to a β -value of 50.1 kcal mol⁻¹. Previous correlations of irreversible one-electron reduction potentials for a large number of molecules with delocalised π -systems have given similar results but with a somewhat different slope of the straight line, corresponding to β -values of 54.6 kcal mol⁻¹ and 55.6 kcal mol⁻¹ for aqueous dioxane and 2-methoxyethanol, respectively.⁷ In this paper, the potentials refer to reversible processes and no

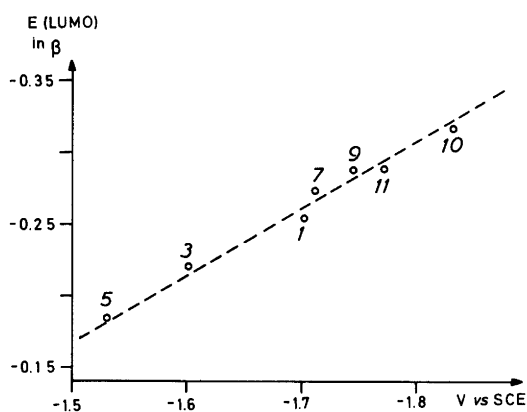
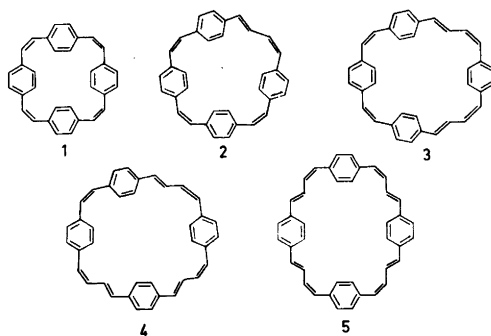
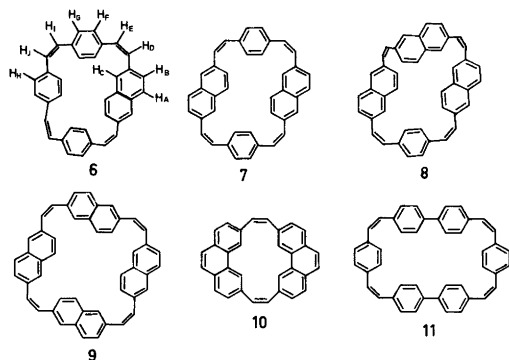


Fig. 1. Correlation of the energies of the LUMO orbitals (from Hückel calculations) with the potentials for the reversible two-electron reduction of a series of cyclophanes.



assumptions of diffusion rates *etc.* have to be made. It may seem surprising that data for a series of non-planar compounds give such a good correlation with quantities which have been calculated assuming a planar arrangement of the extended π -system. However, this indicates that the dianions are more planar and rigid than the neutral cyclophanes, and this has recently been confirmed for the dianion of cyclophane 1 which shows an unusually large diamagnetic ring current as well as a rigid structure (no rotation of the benzene rings).⁸

The alternating behaviour of the cyclophanes 1–5 on electrochemical reduction has already been demonstrated.⁶ Under identical conditions, cyclophanes 1, 3 and 5 undergo a reversible two-electron reduction, whereas cyclophanes 2 and 4 do not. To further test this observation, we have also prepared the cyclophane 6 which contains one naphthalene ring connected to the rest of the cyclophane at the 2- and 6-positions, thus serving as a six-electron bridge. As expected, cyclophane 6 is not reduced at -1.71 V/SCE in DMF to the dianion, but instead undergoes an irreversible reduction. For the series of cyclophanes 1, 5, 6, 7, 8 and 9 there thus appears to be the same type of alternating behaviour on reduction. This has, however, not yet been verified for 8. The size of the π -



systems in cyclophanes 1–5 and 1, 5–9 ranges formally from 24 to 32 π -electrons around the perimeter, which well exceeds the accepted limit for the Hückel rule.² A clear alternating effect which is chemically significant is thus observed for a series of large dianions of cyclophanes containing four aromatic subunits. It should be pointed out that although NMR chemical shifts are very sensitive to the effects of diamagnetic and paramagnetic ring currents, no alternating effects have been observed in the neutral molecules.

The Hückel calculations reproduce the alternating behaviour in the two series of

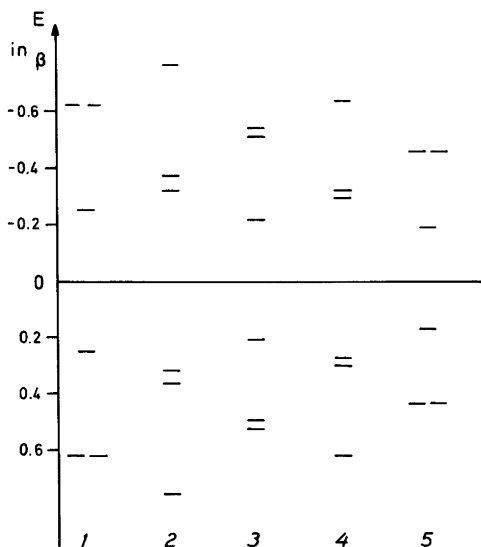


Fig. 2. Energies of the higher occupied and lower unoccupied molecular orbitals from Hückel calculations (in β) for a series of $[2_n][4_4-n]$ paracyclophanes 1–5.

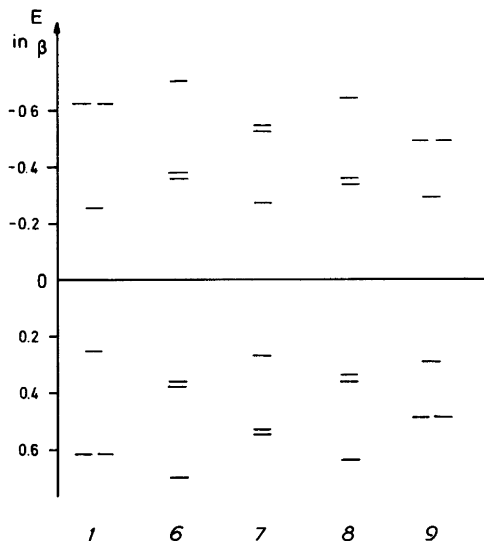


Fig. 3. Energies of the higher occupied and lower unoccupied molecular orbitals from Hückel calculations (in β) for a series of $[2_4](2,6)$ naphthalenoparacyclophanetetraenes 1, 6–9.

cyclophanes. The energies of the frontier orbitals for the two series are depicted in Fig. 2 and Fig. 3. The energy gap between the HOMO and LUMO varies with the size of the π -system. In cyclophanes with formally $(4n+2)$ π -electrons around the perimeter, the energy gap is large, while in cyclophanes with formally $4n$ π -electrons the gap is smaller. In the former series both the HOMOs and the LUMOs are near-degenerate, while in the latter the HOMOs and LUMOs can be identified with the two nonbonding orbitals of the $[4n]$ annulenes² which, in the cyclophanes, have been split by the presence of the aromatic rings. The splitting is least in cyclophane 5 which contains the least number of aromatic rings per double bond in the conjugated system.

Even if a clear alternation of behaviour on reduction is observed for large cyclophanes with π -systems containing 24 to 32 electrons around the perimeter, this is not conclusive proof that resonance stabilisation occurs in the doubly charged $(4n+2)$ π -systems. However, the occurrence of reversible two-electron processes shows that the dianions are slow to react in solution and that they are formed more easily than the corresponding radical anions, despite the extra interelectron

repulsion present in the dianions. Geometrical factors cannot be decisive as apparent, for example, from a comparison of the cyclophanes 1–5, nor can simple Hückel calculations give any clear answer. Further work on the question of resonance stabilisation in large conjugated dianions of cyclophanes is now in progress.

EXPERIMENTAL

UV spectra were obtained on a Beckman DK-2A, IR spectra on a Beckman IR9 and mass spectra on an AEI MS 902 instrument. ^1H NMR spectra were obtained on a Bruker WH 270 instrument, using CDCl_3 as solvent and TMS as internal standard. Melting points were determined on a Reichert hot-stage apparatus.

[2](2,6)Naphthaleno[2]para[2]para[2]para-cyclophanetetraene, 6. The bis(triphenyl)phosphonium salt from 1,4-bis(bromomethyl)benzene (3.94 g, 5 mmol) and benzene-1,4-dicarbaldehyde (1.34 g, 10 mmol) were mixed in dry DMF and the stirred mixture cooled, under nitrogen, to -40°C . A solution of lithium ethoxide in absolute ethanol was then added dropwise until no further colour change occurred on addition of base. The bis(triphenyl)phosphonium salt from 2,6-bis(bromomethyl)naphthalene (4.19 g, 5 mmol) was then added and addition of base continued. On completion of the reaction, the mixture was worked up in the usual way and the desired product isolated by column chromatography (silica gel, tetrachloromethane). Recrystallisation from dichloromethane/methanol yielded yellow needles m.p. $172-173^\circ\text{C}$. (93 mg, 4%). UV (cyclohexane): λ_{max} 240 nm, $\log \epsilon$ 4.83; 282 nm, 4.54; 320 nm, 4.67. IR(KBr): 3000(m), 1600(m), 1500(m), 1420(m), 910(s), 880(s), 810(s), and 720(m) cm^{-1} .

NMR 270 MHz: δ 7.72 (2H, broad s, H_C), 7.48 (2H, d, H_A , J_{AB} 8.5 Hz), 7.17 (2H, dd, H_B , J_{BC} 1 Hz), 7.27 (4H, s, H_I), 7.24 and 7.04 (8H, AA'BB' pattern, H_F , H_G), 6.86 (2H, d, H_I or H_J , J_{IJ} 12 Hz), 6.70 (2H, d, H_I or H_J), 6.46 (4H, AB pattern, H_D , H_E , J_{DE} 12 Hz).

MS (70 eV): (m/e) 458 (M^+ , 100%), 457(6), 229(M^{2+} , 7). Abs mass: 458.2035, calc. for $\text{C}_{36}\text{H}_{26}$ 458.2035.

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- The reduction potential previously reported for compound 9 (-2.17 V, see Ref. 5) had not been corrected to the SCE scale.

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