

Resonance Energies of Unsaturated Cyclophanes with $4N$ and $(4N+2)$ Perimeters

ULF NORINDER * and OLOF WENNERSTRÖM

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

The resonance energies of a series of paracyclophanes with unsaturated perimeters have been calculated by the methods of Hess and Schaad (RE) and Trinajstić *et al.* (TRE). The two methods give similar results. The resonance energies (TRE) of some dianions of the paracyclophanes were also evaluated. An alternating effect of the resonance energies as a function of the size of the perimeter, whether it is of the $4n$ or $(4n+2)$ type, was observed for a series of paracyclophanes with one benzene ring. The effect is almost quenched in cyclophanes with three or four benzene rings. However, it is somewhat restored in the dianions of paracyclophanes with four benzene rings. It can be concluded that calculated resonance energies are dominated by the effect of the local aromatic rings and that the effect of the size of the perimeter is somewhat masked. The chemistry of these large cyclophanes appears to be better understood in terms of frontier orbital considerations.

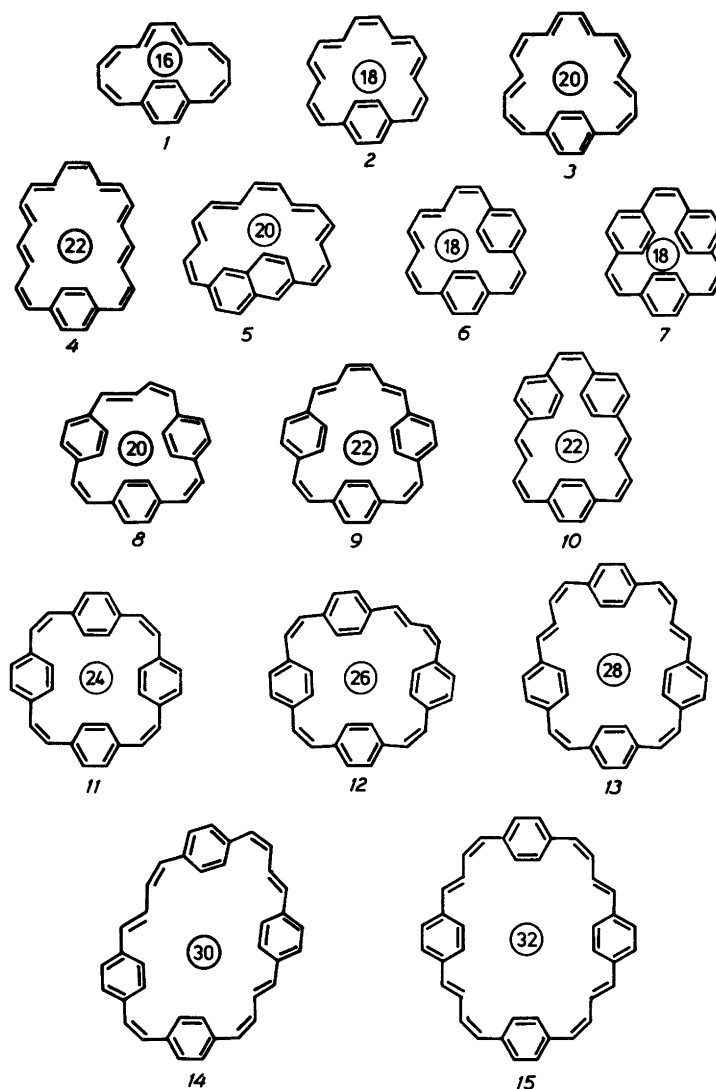
Since the first concept of extra stability of conjugated compounds appeared in the literature,¹ a steady flow of papers has appeared on the subject. Many of them deal with the failure of the original Hückel delocalisation energies (DE) in predicting this extra stability, often called aromaticity. This fact was proved by the synthesis of compounds such as fulvene,² heptafulvene³ and fulvalene,³ which all have large DE values,⁴ although none of them are to be considered aromatic. This lack of agreement

led to new concepts in estimating resonance energies. Dewar and co-workers calculated a new type of resonance energies (DRE) using a semi-empirical SCF MO-method.⁵ The DRE-values predict aromaticity or lack of it rather successfully. It soon became apparent that it was not the changeover to more sophisticated calculations, but rather the change of reference system, that made these new resonance energies more reliable. Hess and Schaad have proposed an elegant method within the Hückel framework, which predicts the amount of extra stability present in a conjugated structure.⁶ They classified the bonds of acyclic polyenes into eight different types, which they correlated against twenty-two such structures.⁷ These values were then used to calculate π resonance energies (RE) using the equation

$$RE = E_{\text{HMO}} - E_{\text{LOC}}$$

where E_{HMO} is the total HMO π energy and E_{LOC} the π energy of the corresponding "localised" structure.⁸ To obtain a comparable quantity, compensating the variation in size of molecules investigated, Hess and Schaad proposed the resonance energy per π electron (REPE) as such. Trinajstić *et al.* have proposed a similar idea, the HMO index of aromatic stabilisation (A_s), using correlated values of only one type of polyene double and single bonds.⁹ A comparison between the REPE and the HMO index per π electron (A_s/e) gives in most cases similar results.¹⁰ A most promising topological interpretation of resonance energies has lately appeared through the works of Aihara¹¹ and Trinajstić *et al.*¹² Using

* To whom correspondence should be addressed.



Scheme 1.

graph theory,¹³ they have extended the previous ideas of predicting aromatic stability. Utilizing topological resonance energies (TRE), one can treat any conjugated system, neutral or ion, cyclic or acyclic in a nonempirical way. TRE-values are calculated using the equation

$$TRE = \sum_{j=1}^N g_j (x_j - x_j^{ac})$$

where g_j is the occupancy number of the j th MO, x_j the Hückel eigenvalues, and x_j^{ac} the roots of the reference polynomial. TRE gives exactly $TRE=0$ for all acyclic structures. To compensate for size, Trinajstić *et al.* have proposed a quantity similar to REPE, namely the topological resonance energy per π electron [$TRE(PE)$].

Recently we have found that a series of cyclophanes with unsaturated bridges on reduction gives a new type of dianion with aromatic

Table 1. Resonance energies (in β) of conjugated cyclophanes.

Compound	TRE	TRE(PE)	RE	REPE	Predicted status ²¹
1	0.0117	0.0007	0.1980	0.0110	NA
2	0.2482	0.0124	0.4416	0.0221	A
3	0.0418	0.0019	0.2451	0.0111	NA
4	0.2322	0.0097	0.4418	0.0184	NA/A
5	0.2041	0.0085	0.4197	0.0175	NA
6	0.4328	0.0197	0.7130	0.0324	A
7	0.6378	0.0266	1.0195	0.0425	A
8	0.5510	0.0212	0.9349	0.0360	A
9	0.6143	0.0219	1.0410	0.0359	A
10	0.6105	0.0218	0.9979	0.0356	A
11	0.7864	0.0246	1.2877	0.0402	A
12	0.8100	0.0238	1.3138	0.0386	A
13	0.7694	0.0214	1.2773	0.0355	A
14	0.7876	0.0207	1.2982	0.0342	A
15	0.7422	0.0186	1.2675	0.0317	A

character, *e.g.* having a perimeter of $(4n+2)$ π -electrons, sustaining large diamagnetic ring currents in strong magnetic fields.¹⁴ We now report an evaluation of the relative amounts of extra stabilisation in these large dianions, their parent cyclophanes and some smaller members based upon RE and TRE calculations.

RESULTS AND DISCUSSION

The resonance energies RE and TRE for paracyclophanes with one, two, three and four benzene rings connected by unsaturated bridges to give compounds with conjugated perimeters ranging from 16 to 32 π -electrons have been calculated within the Hückel framework (Table 1). Thus, we assumed that the minimum energy conformations of the paracyclophanes are near

Table 2. Resonance energies (in β) of dianions of some selected cyclophanes.

Compound	TRE	TRE(PE)	Predicted status ²¹
11	0.5912	0.0174	A
12	0.4544	0.0126	A
13	0.6218	0.0164	A
14	0.4822	0.0121	A
15	0.6186	0.0147	A

planar, which may be doubtful in some cases. The structures of the cyclophanes are depicted in Scheme 1, and the topological resonance energies (*TRE*) for some selected dianions are shown in Table 2.

Although the theoretical foundations for the topological resonance energy method have been questioned recently,¹⁵ it has generally been observed that TRE values and RE values are proportional.^{12c} Other methods suggested by Haddon¹⁶ and Aihara¹¹ give, for annulenes, essentially the same results. We have found the correlation between TRE and RE values to exist for the series of cyclophanes discussed in this paper as well (Fig. 1, *TRE* and *RE* values for some annulenes have been included for comparison).

Only a few [18]annulene derivatives with para-substituted benzene rings as a part of the π -system have been reported. A bridged [18]annulene prepared by photocyclisation of [2.2](3,6)phenanthrenoparacyclophanediene shows a large diamagnetic ring current in a strong magnetic field.¹⁷ For the neutral paracyclophanes with three or four benzene rings the situation is different. They do not show any significant ring current effects regardless if they formally have $4n$ or $(4n+2)$ perimeters. Most of these cyclophanes do not attain a planar conformation to allow for an efficient overlap between the rings and the unsaturated bridges. Their spectroscopic prop-

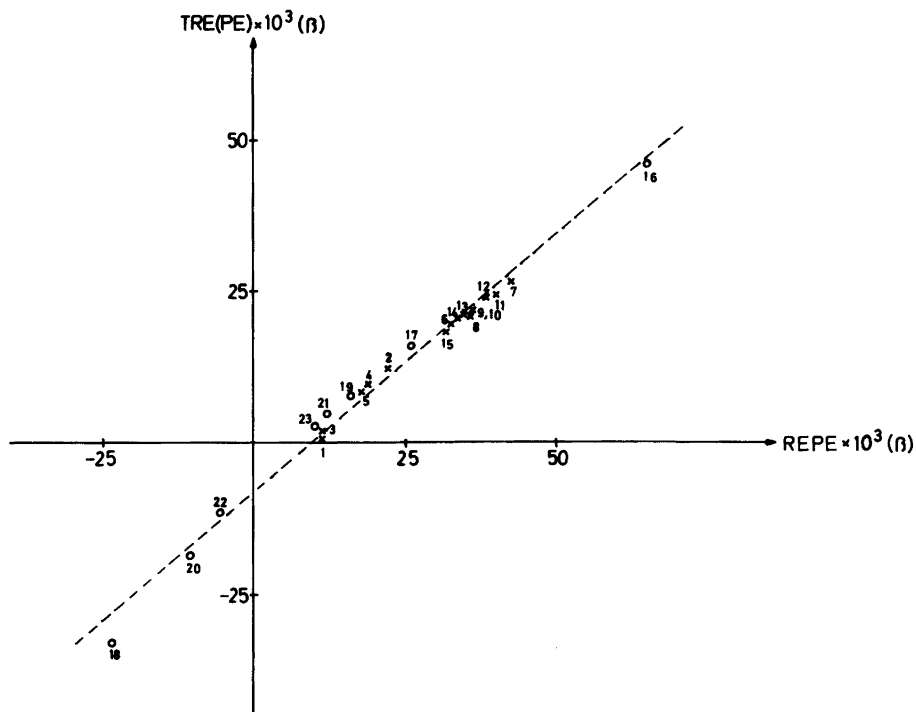


Fig. 1. A plot of $TRE(PE)$ vs. $REPE$ of cyclophanes with unsaturated bridges. (Annulenes included for comparison: 16=benzene, 17=[10]annulene, 18=[12]annulene, 19=[14]annulene, 20=[16]annulene, 21=[18]annulene, 22=[20]annulene, 23=[22]annulene.)

erties are very much those expected for normal aromatic compounds.¹⁸ Whether the preferred conformations are due solely to steric effects or result from the lack of resonance stabilisation of the more planar conformations, cannot be determined without more extensive quantum mechanical calculations. The simple resonance arguments presented here are, however, consistent with the experimental findings.

The [6]–[22]annulenes with one parasubstituted benzene ring, compounds 1–4, show a distinct alternation of their RE and TRE values, although less pronounced than in the annulene series (Fig. 1).

The change of the aromatic unit from benzene to naphthalene within the same size of the perimeter, cyclophanes 3 and 5, increases the calculated resonance energies (Table 1). In the naphthalenophane the influence of the aromatic unit dominates the total resonance energy. The same trend is observed on increasing the number of benzene rings within the [18]annulene peri-

meter, cyclophanes 2, 6 and 7. Both methods give a regular increase in the calculated resonance energies, which for the [2.2.2]paracyclophanetriene, 7, is very large and dominated by the three benzene rings.

The resonance energies of the cyclophanes with three benzene rings and perimeters of 18, 20 and 22 π -electrons, compounds 7–10, are similar but slightly smaller for the [20]annulene derivative, cyclophane 8. On further increase of the number of benzene rings and size of the perimeter, the calculated resonance energies show even less alternation between Hückel and Möbius systems, as expected. The RE and TRE values for the series of cyclophanes 11–15 differ by only a few per cent within each method of calculation. The total resonance energies are dominated by the influence of the benzene rings. The results demonstrate that it is irrelevant to consider these paracyclophanes as annulene derivatives even if they were planar. This conclusion is consistent with the chemical and spectro-

scopic properties (especially NMR data) of the cyclophanes, as pointed out above. It seems safe to conclude, not only from this investigation but also from previous studies of benzannulenes with more than one aromatic unit,¹⁹ that the local aromatic units dominate the character of the total π -electron structure. On the other hand, the cyclophanes with only one benzene ring are more interesting and might well be considered as annulene derivatives.

What is true for the neutral cyclophanes may, however, not hold for the charged species. Recently, we have shown that certain cyclophanes readily form dianions with complete delocalisation of the charge over the total π -system and that these dianions are of the $(4n+2)$ type and show large diamagnetic ring current effects.¹⁴ The resonance energies (*TRE*) of the dianions from cyclophanes 11–15 show a more pronounced alternating behaviour than the neutral cyclophanes, although all of them should be characterised as aromatic (Table 2). Even in these dianions, which must be nearly planar to sustain large ring currents in strong magnetic fields, the total resonance energy is dominated by the contributions from the local aromatic rings. It may be questioned whether resonance arguments are of use for the understanding of these types of dianions. There are certainly severe problems with the definition of resonance energy and the choice of reference structure for compounds of this type. Such problems, already large for neutral cyclophanes, are even more important for the dianions. At present, there is also a lack of experimental data with which to verify the various recent theories of large π -systems.^{11,12b-c,20} These theories generally predict similar behaviour for the neutral and charged species with the same number of π -electrons, which does not seem to be consistent with the, admittedly limited, experimental findings.

There have been numerous attempts to correlate ring currents and resonance energy¹⁶ or more generally aromaticity. Such correlations are necessarily more complicated for cyclophanes with an annulene character due to the presence of the local aromatic subunit. For example, the dianion of cyclophane 11 shows a large diatropic shift of the signals from the inner and outer protons, whereas the tetra-anion shows somewhat smaller paratropic shifts.^{14b} Both species are aromatic, much more so than the neutral

annulenes with the same π -electron perimeters due to the benzene rings.

In cyclophanes with an annulene character, regardless of charge, the effect of the aromatic unit must clearly be eliminated when discussing the effect of the size of the total perimeter, regardless if it is of the Hückel or the Möbius type. One approach to this problem is to limit the discussion to frontier orbitals rather than to consider the total resonance energies. The simplest approach is to correlate energies of the Hückel HOMO and LUMO orbitals with experimental observables, e.g. the reduction potentials for the reversible formation of dianions, which results in an unexpectedly good correlation.^{14a}

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