Graph Theory and Molecular Orbitals. XX.*
Local and Long Range Contributions to Bond Order

*I. Gutman,** S. Bosanac, and N. Trinajstić*

**Department of Chemistry, Faculty of Science, University of Kragujevac,*
34000 Kragujevac, P.O.B. 60, Serbia, Yugoslavia, and
»Ruđer Bošković« Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

Local and longe range contributions to bond order are calculat-
ed for several benzenoid and non-benzenoid alternant molecules.
The local effects are found to be linearly correlated with the bond
orders of benzenoid, but not of nonbenzenoid systems. On the basis
of these investigations a measure of the aromatic character of a
bond is introduced.

In a recent paper[1] it was demostrated that the bond order between the
sites r and s of a conjugated molecule may be presented as

$$p_{rs} = \sum_W T(W) \tag{1}$$

where the summation goes over all paths W connecting r and s. For alternant
systems the topological functions $T(W)$ are given by

$$T(W) = (-1)^{\frac{w}{2}-1} \frac{1}{\pi} \int_{-\infty}^{+\infty} \left| \frac{P(G-W, ix)}{P(G, ix)} \right| dx \tag{2}$$

where w is the length of the path W, $P(G, x)$ is the characteristic polynomial
of the graph G and $G-W$ is the graph obtained by deletion of the path W
from G. For non-alternant systems the formulas for $T(W)$ are much more
complicated and are given elsewhere[1].

There is a straighforward interpretation of eq 1, namely $T(W)$ can be
understood as the (additive) contribution of the path W to the bond order p_{rs}.

The case of adjacent r and s is certainly the most interesting one, because
of the well known relations between p_{rs} and bond length, bond strength,
vibrational frequency, reactivity, etc.[2] In the present study we shall consider
exclusively the bond orders between the adjacent centers. Then since there
is always a path of length one between the adjacent centers r and s, i. e., the
bond connecting the atoms r and s, eq 1 is rewritten as

$$p_{rs} = T(rs) + \sum_W{}' T(W) \tag{3}$$

---

* Part XIX: I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem.
Soc.* **99** (1977) 1692.

Σ' denotes summation over all paths between r and s which are longer than
unity. Consequently eq 3 represents the decomposition of the bond order into
a local contribution $T(rs)$ and several long range effects $T(W)$.

These long range interactions are consequences of the presence of cycles
in the π-electron network of the conjugated molecule. Accordingly, in the case
of acyclic polyenes there is a unique path between any two atoms and there
exist no long range contributions. Therefore, for acyclic systems, eq 3 simply
reduces to

$$p_{rs} = T(rs) \tag{4}$$

The analysis based on eqs 1—4 provides better qualitative understanding
of the rather complicated topological relations which determine the bond
order[1]. In order to obtain a quantitative insight into these effects, numerical
work is necessary. In the next section we report results of such numerical
investigations. They enable the formulation of certain general rules and the
characterization of the aromatic character of a conjugated bond. Some discus-
sions on the characterization of local aromatic character of conjugated systems
have been given earlier by several authors, but from a very different viewpoint[3].

NUMERICAL WORK

In Table I are presented the calculated values of quantities p_{rs}, $T(rs)$,
and $T(W)$ for all bonds in four benzenoid and two non-benzenoid hydrocarbons.
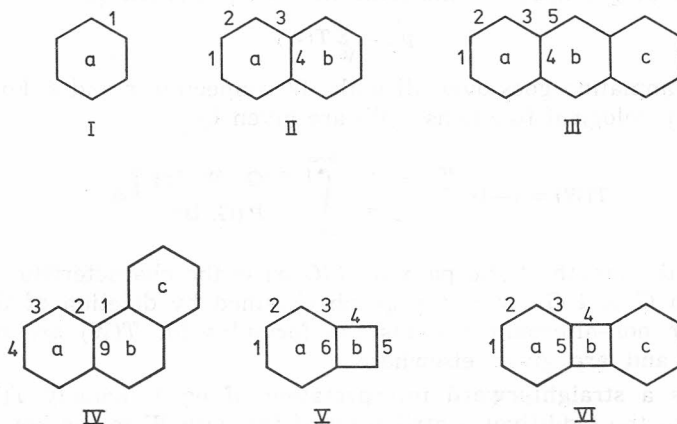The considered molecules are given in Figure 1.

Figure 1.

The following conclusions may be drawn from the available numerical
data. First, the gross part (usually 80—90%) of the bond order comes from
the local interaction effects. The long range effects are, in general, of about
one order of magnitude smaller than the local one. In agreement with eq 2,
paths of length $4m + 1$ have a positive and paths of length $4m + 3$ have
a negative contribution to p_{rs} ($m = 0, 1, 2, \ldots$). Second, although $T(W)$ is a
decreasing function of the path length, all the long range interactions are
roughly of the same order of magnitude. For example, the paths of length 1,
5, 9, and 13 have a contribution of 0.661, 0.045, 0.018, and 0.013, respectively,

TABLE I

The Decomposition of the Bond Order p_{rs} According to eq 3. A Denotes the Path Connecting the Vertices of the Considered Bond Along the Cycle a; A + B is the Path Along Both the Cycles a and b, etc.

Molecule	bond	p_{rs}	$T(rs)$	$T(A)$	$T(B)$	$T(A+B)$	$T(A+C)$	$T(A+B+C)$
I	1	0.667	0.556	0.111	—	—	—	—
II	1	0.603	0.515	0.056	—	0.033	—	—
	2	0.725	0.636	0.056	—	0.033	—	—
	3	0.555	0.466	0.056	—	0.033	—	—
	4	0.518	0.406	0.056	0.056	—	—	—
III	1	0.586	0.510	0.045	—	0.018	—	0.013
	2	0.737	0.661	0.045	—	0.018	—	0.013
	3	0.535	0.459	0.045	—	0.018	—	0.013
	4	0.485	0.391	0.045	0.031	—	0.018	—
	5	0.606	0.526	—	0.031	0.018	0.018	0.013
IV	1	0.461	0.398	—	0.026	0.013	0.013	0.010
	2	0.590	0.496	0.071	—	0.013	—	0.010
	3	0.702	0.608	0.071	—	0.013	—	0.010
	4	0.623	0.529	0.071	—	0.013	—	0.010
	5	0.707	0.613	0.071	—	0.013	—	0.010
	6	0.575	0.481	0.071	—	0.013	—	0.010
	7	0.506	0.444	—	0.026	0.013	0.013	0.010
	8	0.775	0.712	—	0.026	0.013	0.013	0.010
	9	0.542	0.432	0.071	0.026	—	0.013	—
V	1	0.732	0.707	0.218	—	—0.194	—	—
	2	0.563	0.538	0.218	—	—0.194	—	—
	3	0.728	0.704	0.218	—	—0.194	—	—
	4	0.215	0.704	—	—0.295	—0.194	—	—
	5	0.897	1.386	—	—0.295	—0.194	—	—
	6	0.550	0.627	—	—0.295	—	—	—
VI	1	0.691	0.611	0.141	—	—0.036	—	—0.026
	2	0.621	0.451	0.141	—	—0.036	—	—0.026
	3	0.683	0.603	0.141	—	—0.026	—	—0.026
	4	0.263	0.446	—	—0.085	—0.036	—0.036	—0.026
	5	0.565	0.544	0.141	—0.085	—	—0.036	—

to the bond order of bond 2 in anthracene (III). Third, several long range effects are mutually equal. This is a natural consequence of eq 2 since G—W, and therefore also $T(W)$, depend on the vertices which belong to the path W, but not on their order in W.

In Figure 2 a plot of p_{rs} vs. $T(rs)$ is given.

There is a good linear correlation between the quantities p_{rs} and $T(rs)$ for benzenoid molecules, but no correlation is obtained for non-benzenoids. Moreover, the slope of the least-squares line is a very close to 45⁰. Therefore, the following empirical relation holds for benzenoid systems

$$p_{rs} \approx T(rs) + A \qquad (5)$$

A is approximately a constant (A $\approx$ 0.08 $\pm$ 0.02).
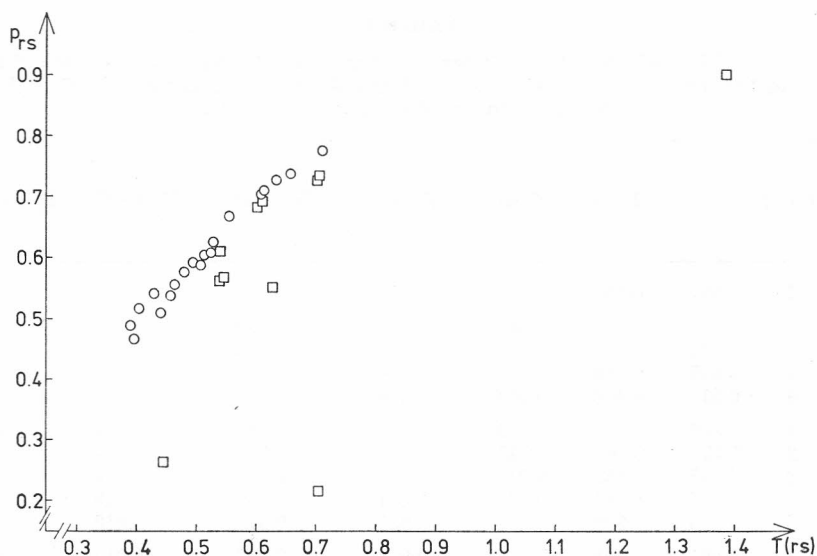
Figure 2.

Bond order vs. $T(rs)$ term. 0 = benzenoid molecules, $\square$ = non-benzenoid molecules. A least--squares fit line for benzenoids reads $p_{rs} = 0.9899\ T(rs) + 0.9401$ with a correlation coefficient 0.971.

LOCAL AROMATIC CHARACTER

In this section the quantity $p_{rs} - T(rs)$ will be considered, for which it can be shown to reflect certain characteristic properties of the bond rs. The introduction of such a topological index is motivied by the following arguments. First, eq 4, namely $p_{sr} - T(rs) = 0$ is to be compared with the experimental evidence that acyclic polyenes are typical non-aromatic compounds[4]. Second, eq 5 is now to be interpreted as an expression of the fact that all the carbon--carbon bonds in a benzenoid compound possess closely similar aromatic character[5,6].

The above consideration suggests one to understand $p_{rs} - T(rs)$ as a measure of the aromatic character of a bond. In particular, bonds with $p_{rs} - T(rs) \approx$ $\approx 0.08 \pm 0.02$ may be described as fully aromatic, those with smaller positive values of this index as partially aromatic, those with $p_{rs} \approx T(rs)$ as antiaromatic. The numerical data collected in Table I show that this classification scheme is in agreement with the chemical behaviour of the conjugated molecules. For example, according to our result bonds denoted by 4 in biphenylene (see Figure 1) should be antiaromatic ($p_{rs} - T(rs) = -0.183$) while others could be classified as aromatic bonds ($p_{rs} > Trs$). Some experimental results[7] seem to suggest that the bonds connecting two benzene units in biphenylene are very different from the others and are actually weak spots in the biphenylene structure.

ADDENDUM

One of the referees rised an interesting question whether the procedure outlined in this note would be able to distinguish the contribution of (formally similar) central linkages (denoted by a) in perylene (VII) and peropyrene (VIII).

(VII)   (VIII)

In perylene the central linkages connecting two naphthalenic units appear always as single bonds in all Kekulé structures whereas the corresponding bonds in peropyrene participate in the conjugation, thus contributing to aromatic stability of the system. This fact is fully reflected in the calculated »ring-current« intensities in the central ring of both molecules,[8] these being six times larger in peropyrene (1.446) than in perylene (0.239).

Our calculations produced the following results,

	Perylene	Peropyrene
$T(a)$	0.39442	0.45217
$\sum'_W T(W)$	0.01924	0.06409
$p(a)$	0.41366	0.51626

Therefore, it appears that the contribution over all paths W, $\sum'_W T(W)$, to the bond order $p(a)$ is three times larger in peropyrene than in perylene. This result is in fair agreement with the calculations of Mallion.[8] It also indicates the very different aromaticity of central linkages in perylene and peropyrene, the central bonds in peropyrene being aromatic while in perylene non-aromatic.

REFERENCES

1. I. Gutman, *Z. Naturforsch.* **32a** (1977) 765.
2. See for example: L. Salem, *The Molecular Orbital Theory of Conjugated Systems,* Benjamin, New York 1966.
3. O. E. Polansky and G. Derflinger, *Int. J. Quantum Chem.* **1** (1967) 379; M. Randić, *Tetrahedron* **30** (1974) 2067.
4. See for example: N. C. Baird, *J. Chem. Educ.* **48** (1971) 509.
5. E. Clar, *Polycyclic Hydrocarbons,* Academic Press. London 1964.
6. M. Randić, *J. Amer. Chem. Soc.* **99** (1977) 444; Tetrahedron **33** (1977) 1905.
7. P. J. Garratt, *Aromaticity,* McGraw-Hill, London 1971, p. 144.
8. R. B. Mallion, *J. Medicinal Chem.* **14** (1971) 824; see also C. W. Haigh, R. B. Mallion, and E. A. G. Armour, *Mol. Phys.* **18** (1970) 751.

SAŽETAK

Teorija grafova i molekularne orbitale. XX. Lokalni i daljinski doprinosi redu veze

I. Gutman, S. Bosanac i N. Trinajstić

Izračunani su lokalni i daljinski doprinosi redu veze za nekoliko benzenoidnih i ne-benzenoidnih alternantnih molekula. Nađeno je da se lokalni doprinosi linearno koreliraju s redom veze samo kod benzenoidnih molekula. Na temelju ovih istraživanja predložena je mjera aromatičnosti veze kod konjugiranih molekula. Pokazalo se da su neke veze kod konjugiranih sustava aromatične, druge ne-aromatične, a da ih ima i koje su antiaromatične.

ODJEL ZA KEMIJU SVEUČILIŠTA
U KRAGUJEVCU, 34000 KRAGUJEVAC, SRBIJA
I INSTITUT »RUĐER BOŠKOVIĆ«,
4100 ZAGREB, HRVATSKA