Topological Resonance Energies of Conjugated Ions, Radicals, and Ion Radicals[1]

Predrag Ilić[2] and Nenad Trinajstić*

The Rugjer Bošković Institute, 41001 Zagreb, Croatia, Yugoslavia

Received June 21, 1979

Topological resonance energy, TRE, defined as the topological contribution of ring closure with respect to a reference noncyclic structure, is applied to a set of 150 conjugated species. All of them are either closed-shell charged or open-shell neutral and charged species. The calculated TRE values were correlated with 88 experimental observations. It is shown that the TRE method is generally successful in predicting the degree of aromaticity correlated with stability of conjugated ions, radicals, and ion radicals.

Introduction

Study of the chemistry of conjugated ions, radicals, and ion radicals has advanced in the last decade[3-6] owing to improvements in preparative techniques.[7-9] However, the interest in preparation of such π-electronic species goes back into the last century (e.g., the preparation of tropylium bromide[10]) although their true nature was not recognized. The aromaticity (the intuitive but working concept for characterizing unsaturated organic molecules)[11] of ions and radicals, outside of monocyclic systems (annulenes and annular ions and radicals)[12] which follow the Hückel rule,[13] until recently[14] could not be studied within the Hückel theory.[15,16] Because of their definitions, the excellent aromaticity indexes Dewar resonance energy (DRE)[17] and resonance energy per π electron (REPE)[18] can be used to predict the aromatic behavior of only closed-shell conjugated systems.[19] Dewar[20] has calculated the aromatic stabilization energies of several monocyclic ions and radicals by using the MINDO/3 theory. Unfortunately, MINDO/3 is not a simple method to use.[21] Thus, people interested in novel aromatic ions and radicals, and not

familiar with the MO theories of higher level, have lacked a simple working MO method for predicting the aromatic stability of ions and radicals in spite of several currently available methods that work for classical conjugated molecules.[18,22-30]

Recently such a method was developed independently by the Zagreb group[14,31-35] and by Aihara[36-38] by using very different ways of reasoning.[39] In essence, this method is based on the fundamental idea[40,41] of using an acyclic polyene as a reference structure, suggested by Dewar[42] and independently by Breslow and Mohacsi[43] and elaborated by Hess and Schaad[18,44,45] within the Hückel scheme. The latter authors have shown how the Hückel model with proper reference structures is satisfactory for predicting aromatic stability even for heterocycles[46-48] containing

(1) This work is supported in part by (a) the self-managing Authority for Scientific Research of Croatia, (b) National Science Foundation Grant No. F6F006-Y, and (c) the Republic Assembly for Scientific Work of Bosnia and Herzegovina.

(2) Faculty of Natural Sciences and Mathematics, The University in Sarajevo, 71000 Sarajevo, Bosnia and Herzegovina, Yugoslavia.

(3) See, for example, the series of collective volumes and monographs "Reactive Intermediates in Organic Chemistry", G. A. Olah, Ed., Wiley, New York, 1968.

(4) P. J. Garratt and M. V. Sargent, *Adv. Org. Chem.*, 1, 1 (1969).

(5) N. S. Isaacs, "Reactive Intermediates in Organic Chemistry", G. A. Olah, Ed., Wiley, New York, 1974.

(6) D. Lewis and D. Peters, "Facts and Theories of Aromaticity", Macmillan, London, 1975.

(7) G. R. Stevenson, M. Colon, I. Ocasio, J. G. Concepción, and A. McB. Block, *J. Phys. Chem.*, 79, 1685 (1975).

(8) G. A. Olah, J. S. Staral, G. Liang, L. A. Paquette, W. P. Melega, and M. J. Carmody, *J. Am. Chem. Soc.*, 100, 3349 (1978).

(9) T. Bally, E. Haselbach, Z. Lanyiova, and P. Baertschi, *Helv. Chim. Acta*, 61, 2488 (1978).

(10) G. Merling, *Ber. Dtsch. Chem. Ges.*, 24, 3108 (1891).

(11) E.g., "Aromaticity", Special Publication No. 21, The Chemical Society, London, 1967.

(12) P. J. Garratt, "Aromaticity", McGraw-Hill, New York, 1971.

(13) E. Hückel, *Z. Phys.*, 76, 628 (1932).

(14) I. Gutman, M. Milun and N. Trinajstić, *Math. Chem.*, 1, 171 (1975).

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.

(16) E. Heilbronner and H. Bock, "The HMO-Model and Its Application, 1. Basis and Manipulation", Wiley, New York, 1976 (translation from German).

(17) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, 1969.

(18) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, 93, 305 (1971).

(19) B. A. Hess, Jr., private communication (Oct 1978). Hess and Schaad succeeded in defining the reference structure for ions and radicals within the framework of the DRE concept.

(20) M. J. S. Dewar, *Pure Appl. Chem.*, 44, 767 (1975).

(21) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 97, 1285 (1975).

(22) J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.*, 319 (1970).

(23) G. G. Hall, *Int. J. Math. Educ. Sci. Technol.*, 4, 223 (1973).

(24) W. C. Herndon, *J. Am. Chem. Soc.*, 95, 2404 (1973).

(25) C. F. Wilcox, Jr., *Croat. Chem. Acta*, 47, 87 (1975).

(26) P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Theor. Chim. Acta*, 38, 121 (1975).

(27) R. Swinborne-Sheldrake, W. C. Herndon, and I. Gutman, *Theor. Chim. Acta*, 755 (1975).

(28) M. Randić, *Tetrahedron*, 33, 1905 (1977).

(29) M. Randić, *J. Am. Chem. Soc.*, 99, 444 (1977).

(30) J. P. Gastmans, D. F. Gastmans, and M. H. Mendes Ferrez, *Tetrahedron*, 33, 2205 (1977).

(31) I. Gutman and N. Trinajstić, *Acta Chim. Acad. Sci. Hung.*, 91, 203 (1976).

(32) I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta*, 48, 87 (1976).

(33) M. Milun, Ph.D. Thesis, University of Zagreb, 1976.

(34) I. Gutman, M. Milun, and N. Trinajstić, *J. Am. Chem. Soc.*, 99, 1692 (1977).

(35) N. Trinajstić, *Int. J. Quantum Chem.*, S11, 469 (1977).

(36) J.-i. Aihara, *J. Am. Chem. Soc.*, 98, 2750 (1976).

(37) J.-i. Aihara, *J. Org. Chem.*, 41, 2488 (1976).

(38) J.-i. Aihara, *J. Am. Chem. Soc.*, 98, 6840 (1976).

(39) A. Graovac, I. Gutman, and N. Trinajstić, "Topological Approach to the Chemistry of Conjugated Molecules", Lecture Notes in Chemistry, No. 4, Springer-Verlag, Berlin, 1977.

(40) N. C. Baird, *J. Chem. Ed.*, 48, 509 (1971).

(41) I. Gutman, M. Milun, and N. Trinajstić, *Chem. Phys. Lett.*, 23, 284 (1973).

(42) Reference 17, Chapters V and IX.

(43) R. Breslow and E. Mohacsi, *J. Am. Chem. Soc.*, 85, 431 (1963).

(44) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, 93, 2413 (1971).

(45) B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, 36, 3418 (1971).

(46) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, 28, 3657 (1972).

(47) B. A. Hess, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, 95, 3907 (1973).

(48) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, *Tetrahedron*, 31, 295 (1975).

amino nitrogen, ester oxygen, or σ bivalent sulfur. A modification of the Hess–Schaad approach has led to the definition of the acyclic polynomial as the graph theoretical form[50] for an acyclic polyene-like reference structure.[14,51] Introduction of the acyclic polynomial has resulted in a nonparametric variant of DRE, named topological resonance energy,[52] TRE, because this aromaticity index is related only to the connectivity of a given molecular π network. Hence, TRE(acyclic polyene) = 0, whereas DRE(acyclic polyene) $\neq$ 0. TRE has been successfully used to predict the aromatic behavior of closed-shell molecules.[33,34] In all investigated cases for which there were experimental data available, the agreement between the theory and experiment is very good. Furthermore, the TRE index parallels the results obtained by the REPE index[34] in cases where the REPE index could be obtained.

We wish to emphasize that *TRE is not a new aromaticity index but a graph theoretical version of the DRE concept with some advantages.* Analysis by the Zagreb group[14,31-35,53,54] and by Aihara[36-38] has exposed several advantages that TRE has over the DRE (REPE) index (at its present development): (i) TRE does not need any additional numerical parameters (e.g., bond parameters)[17] as far as homoconjugated species are concerned;[55] (ii) TRE can be used rather efficiently for local aromaticity studies and investigations of the validity of the perimeter rule;[56-58] (iii) TRE can be used for studying the aromaticity of electronically excited states of conjugated molecules;[59,60] and (iv) TRE may be applied without further adjustment of the theory to a variety of conjugated ions, radicals, and ion radicals. In the present work we test this last property of the TRE index on a number of ion and radical molecular systems in order to study their aromatic behavior.

Outline of the Theory

In this section we give a brief outline of the topological theory of aromaticity.[61] TRE in β units is defined in a standard way[62] (eq 1), where E_π(reference structure) in the

$$\text{TRE} = E_\pi(\text{conjugated molecule}) - E_\pi(\text{reference structure}) \quad (1)$$

TRE model contains exclusively acyclic contributions to E_π(conjugated molecule). Thus, *TRE represents only cyclic conjugation in a given structure.* Use is made of the Coulson integral formula[63] for E_π(conjugated structure) and the Sachs theorem[64] adapted for chemical application[65]

in deriving[34] the explicit form of TRE. The final expression for TRE is given as eq 2, where g_j is the occupancy

$$\text{TRE} = \sum_{j=1}^{N} (g_j x_j - g^{ac}{}_j x^{ac}{}_j) \quad (2)$$

number of the jth MO, x_j are the roots of the characteristic (Hückel) polynomial, $P(G;x)$, of a conjugated molecule, and $x^{ac}{}_j$ represents the roots of the acyclic polynomial and $g^{ac}{}_j$ the occupancy number of the jth energy level of the corresponding acyclic structure. In many cases $g_j = g^{ac}{}_j$; then eq 2 reduces to

$$\text{TRE} = \sum_{j=1}^{N} g_j (x_j - x^{ac}{}_j) \quad (2')$$

The acyclic polynomial, $P^{ac}(G;x)$, is a polynomial obtained by selective counting of linear noncyclic elements in Sachs' method,[64] applied to the graph of a molecular skeleton. The acyclic polynomial is defined as

$$P^{ac}(G;x) = \sum_{j=0}^{N} a^{ac}{}_j(G) x^{N-j} \quad (3)$$

and it can be constructed by using the conveniently adopted Sachs theorem,[14]

$$a^{ac}{}_j(G) = \sum_{s \in S^{ac}{}_j} (-1)^{c(s)} \quad (4)$$

where s stands for the Sachs graph,[65] $S^{ac}{}_j$ contains only complete graphs of degree one,[50] K_2, and $c(s)$ denotes the total number of K_2 components. There are several studies in the literature[66-68] independently reporting proofs (or partial proofs) that all roots of an acyclic polynomial are real. Consequently, we state the following theorem:

Theorem: the TRE values of all conjugated systems are real

Construction of an acyclic polynomial by using the Sachs theorem becomes impractical because of the enormous increase in the number of Sachs graphs with the increase in size of the studied system. This becomes a problem for evaluation of TRE even by using the appropriate computer program.[58] Therefore, instead of counting the Sachs graphs, we use for the computer generation of $P^{ac}(G;x)$ the recurrence relation

$$P^{ac}(G;x) = P^{ac}(G-e; x) - P^{ac}(G-(e); x) \quad (5)$$

the derivation of which is based on the results obtained by Greenwood,[69] Heilbronner,[70] Hosoya,[71] and Lovász and Pelikán.[72] The symbols have the following meaning: G stands for a graph of a given conjugated system, $G - e$ denotes the subgraph obtained by deletion of an edge, e, from G, while $G - (e)$ denotes the subgraph obtained by deletion of both vertices incident to e from G.
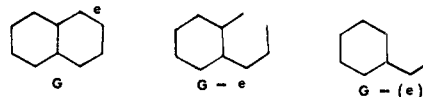
Application of formula 5 is straightforward and it can be easily programmed for the computer construction of $P^{ac}(G;x)$. Our computer program is written in a way that

(49) F. Harary, "Graph Theory", Addison-Wesley, Reading, MA, 1971 (second printing).

(50) I. Gutman and N. Trinajstić, *Top. Curr. Chem.*, **42**, 49 (1973).

(51) The "acyclic polynomial" in Aihara's terminology[36] is a "reference polynomial". In mathematical literature, this polynomial is called a "matching polynomial".

(52) The TRE index in Aihara's work is called "A-II resonance energy".

(53) P. Ilić, Ph.D. Thesis, University of Zagreb, 1979.

(54) I. Gutman and H. Hosoya, *Theoret. Chim. Acta*, **48**, 279 (1978).

(55) In our work on heteroconjugated molecules, we use the Hückel parameters recommended by Hess and Schaad.[46-48]

(56) I. Gutman and S. Bosanac, *Tetrahedron*, **33**, 1809 (1977).

(57) J.-i. Aihara, *J. Am. Chem. Soc.*, **99**, 2048 (1977).

(58) B. A. Hess, Jr., L. J. Schaad, and I. Agranat, *J. Am. Chem. Soc.*, **100**, 5268 (1978).

(59) J.-i. Aihara, *Bull. Chem. Soc. Jpn.*, **51**, 1788 (1978).

(60) P. Ilić, B. Sinković, and N. Trinajstić, *Isr. J. Chem.*, in press.

(61) In the topological theory of aromaticity the resonance energy is a topological quantity.

(62) N. Trinajstić, in "Modern Theoretical Chemistry", Vol. 7, G. A. Segal, Ed., Plenum Press, New York, 1977.

(63) C. A. Coulson, *Proc. Cambridge Philos. Soc.*, **36**, 201 (1940).

(64) H. Sachs, *Publ. Math. (Debrecen)*, **11**, 119 (1964).

(65) A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theor. Chim. Acta*, **26**, 67 (1972).

(66) O. J. Heilmann and E. H. Lieb, *Comm. Math. Phys.*, **25**, 190 (1972).

(67) C. D. Godsil and I. Gutman, in "Proceedings of the International Colloquium on Algebraic Methods in Graph Theory", Szeged, Hungary, in press.
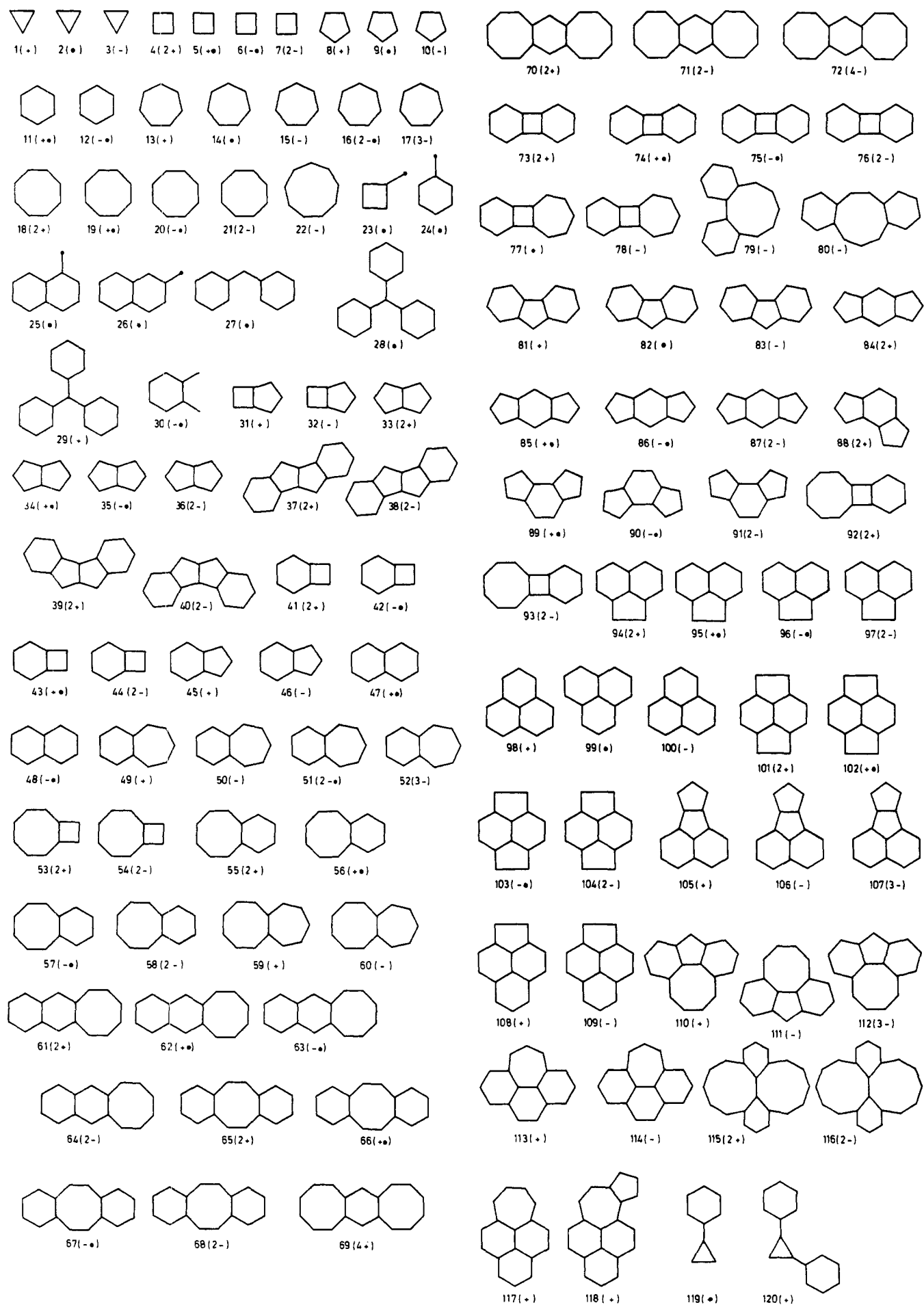
(68) L. J. Schaad, B. A. Hess, Jr., J. B. Nation, N. Trinajstić, and I. Gutman, *Croat. Chem. Acta*, **52**, 233 (1979).

(69) H. H. Greenwood, Ph.D. Thesis, University of London, 1951.

(70) E. Heilbronner, *Helv. Chim. Acta*, **36**, 170 (1954).

(71) H. Hosoya, *Bull. Chem. Soc. Jpn.*, **44**, 2332 (1971).

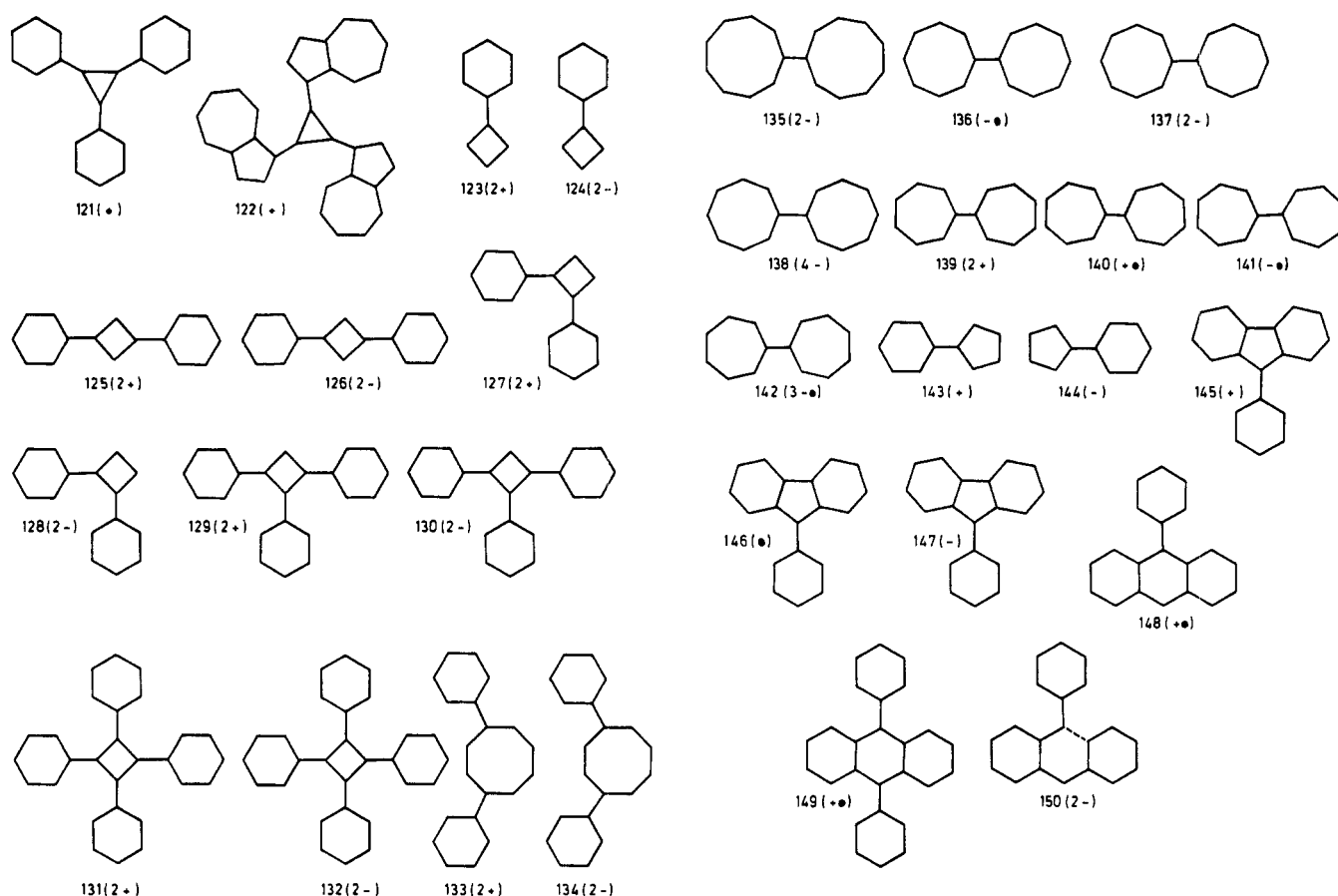(72) L. Lovász and J. Pelikán, *Period. Math. Hung.*, **3**, 175 (1973).

1(+)　2(•)　3(-)　4(2+)　5(+•)　6(-•)　7(2-)　8(+)　9(•)　10(-)

11(+•)　12(-•)　13(+)　14(•)　15(-)　16(2-•)　17(3-)

18(2+)　19(+•)　20(-•)　21(2-)　22(-)　23(•)　24(•)

25(•)　26(•)　27(•)　28(•)

29(+)　30(-•)　31(+)　32(-)　33(2+)

34(+•)　35(-•)　36(2-)　37(2+)　38(2-)

39(2+)　40(2-)　41(2+)　42(-•)

43(+•)　44(2-)　45(+)　46(-)　47(+•)

48(-•)　49(+)　50(-)　51(2-•)　52(3-)

53(2+)　54(2-)　55(2+)　56(+•)

57(-•)　58(2-)　59(+)　60(-)

61(2+)　62(+•)　63(-•)

64(2-)　65(2+)　66(+•)

67(-•)　68(2-)　69(4+)

70(2+)　71(2-)　72(4-)

73(2+)　74(+•)　75(-•)　76(2-)

77(•)　78(-)　79(-)　80(-)

81(+)　82(•)　83(-)　84(2+)

85(+•)　86(-•)　87(2-)　88(2+)

89(+•)　90(-•)　91(2-)　92(2+)

93(2-)　94(2+)　95(+•)　96(-•)　97(2-)

98(+)　99(•)　100(-)　101(2+)　102(+•)

103(-•)　104(2-)　105(+)　106(-)　107(3-)

108(+)　109(-)　110(+)　111(-)　112(3-)

113(+)　114(-)　115(2+)　116(2-)

117(+)　118(+)　119(•)　120(+)

Figure 1. Graphs of studied ions, radicals, and ion radicals.

constructs $P(G;x)$ and $P^{ac}(G;x)$, calculates x_j and x^{ac}_j, and then produces the TRE index of a given structure.

In order to compare structures of various sizes, TRE is normalized in two ways. The first one is to take into account the total number of π electrons in a system, N, thus obtaining the index TRE per electron, TRE(PE) (eq 6). This kind of normalization is, for example, extensively

$$\text{TRE(PE)} = \text{TRE}/N \qquad (6)$$

used by Hess and Schaad.[18,44-46,58-60] TRE(PE) in some ways averages the effects of species topology and of its π-electron content; it reflects whether a species is neutral or in a cationic or anionic state. The second way of normalization stems from the fact that TRE represents only cyclic contributions to E_π(conjugated structure). Thus, TRE is normalized with respect to ringlike components producing the index TRE per ring bond, TRE(PRB) (eq 7), where B_r stands for the number of bonds within a given

$$\text{TRE(PRB)} = \text{TRE}/B_r \qquad (7)$$

ring(s). In other words, by the procedure of TRE(PRB) normalization, one ignores completely all side chains as well as the actual number of π electrons. A similar way of normalizing resonance energy has been considered by several authors.[73-75]

Results and Discussion

A family of 150 conjugated species was tested by using the TRE method (see Figure 1 and Table I). These

conjugated species may be divided with respect to the skeleton properties into

    (A) monocyclic species
        (1) simple monocycles
        (2) monocycles with exocyclic bonds
    (B) polycyclic species
        (1) cyclic structures connected by an essential single bond
        (2) condensed structures
            (a) catacondensed structures
            (b) pericondensed structures

The most relevant datum is that all of these species are conjugated radicals, conjugated ions, or ion radicals. The above systems are selected in order to cover, as much as possible, cases of open-shell neutral or charged and closed-shell charged conjugated species that may be of interest theoretically or experimentally. The TRE of all these structures were calculated by a computer-aided decomposition[77] of a molecular graph into its Hückel and matching spectrum.[51] The TRE values were normalized in two ways, (i) with respect to the total number of π electrons, TRE(PE), and (ii) with respect to the number of ring bonds, TRE(PRB). That these two ways do not give essentially different indexes is apparent from Figure 2.

Thus, our discussion will be based on the TRE and TRE(PE) values by following approximately the division of the population of the conjugated structures given above. Since the TRE index is an intrinsic quantity, because it expresses merely a cyclization of a chain into a ring, it will be used for discussing the aromatic properties of the structures with an equal number of atoms. However, TRE

(73) R. Zahradník, J. Michl, and J. Pancíř, *Tetrahedron*, **22**, 1353 (1966).
(74) D. H. Lo and M. A. Whitehead, *Can. J. Chem.*, **46**, 2027 (1968).
(75) J.-i. Aihara, *Bull. Chem. Soc. Jpn.*, **50**, 3057 (1977).

(76) Reference 16, p 182.
(77) B. Džonova-Jerman-Blažič, B. Mohar, and N. Trinajstić, *Informatica*, **77**, 6-223 (1977).
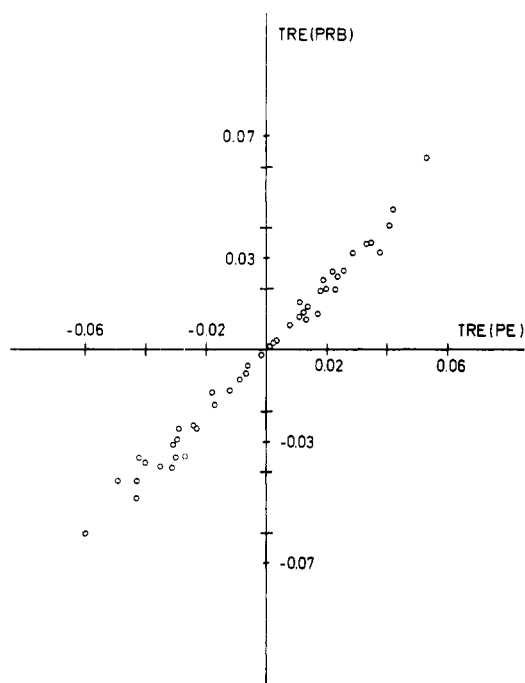
Figure 2. TRE(PRB) values are plotted vs. the corresponding TRE(PE) values of approximately one-third of randomly chosen species from Table I.

can have extrinsic contributions too; that is, for some systems TRE is size-dependent and it requires normalization in order to avoid the size effect. Having this in mind, we will use both TRE and TRE(PE) in the most appropriate situations.

For the triangular species (1–3) the calculated resonance energies correlate with experimental evidence as could have been anticipated; e.g., the species become less and less stable as the available MOs become filled with electrons.

Cyclobutadienylic structures (4–7) are not very stable either in the form of a dianion, which shows some stability as manifested by its being able to exchange protons with deuterons,[78] or in the form of a dication, which can exist as a tetraphenyl derivative.[79] The fact that both of these ions possess a 2 mod 4[80] number of π electrons would imply a more stable species; however, a brief inspection reveals that (i) two electrons of the dianion enter the nonbonding molecular orbital(s), and (ii) the dication is formed by excising as much as half the number of π electrons from a molecule. As for the anion and cation (both radicals) of cyclobutadiene, their having the 1 mod 4 and 3 mod 4 numbers of π electrons, respectively, does not seem a very promising prospect for stability.

The experimental data[81–83] on the cation, radical, and anion of cyclopentadienyl (8–10) agree well with the order of their TRE and TRE(PE) values. Benzenyl radical cation and radical anion (11, 12) show π-electron delocalization, at least for the unpaired electron, as was experimentally observed.[84] Their stabilities are grossly diminished, however, by a disturbance of the π-electron

sextet, which is illustrated by the fact that the radical anion was isolated in an adamantane–$Me_3N\cdot BH_3$ matrix at 121 K.[85]

The five cycloheptatrienyl species (13–17) illustrate the value of the topological approach to the concept of resonance energy (RE) and to aromatic stability. Stability in this series falls off in the order cation > trianion > radical > dianion radical > anion. The corresponding TRE values are +0.225, +0.181, −0.220, −0.242, and −0.665. Thus, while the cation was isolated as solid crystals,[86] the anion was found to be stable in solution only, and at temperatures not higher than 260 K.[87] The other members of the series have properties which interpolate nicely between these two boundary examples.[88]

A similar correlation of TRE values with experimental stability is found in the cyclooctatetraene (COT) series (18–21). The "unusual stability"[89] of the COT dianion is firmly backed up by its TRE value (0.186). Negative TRE values of the COT cation radical and the COT anion radical indicate their instability, which is a recognized experimental property.[89]

Both the calculated TRE values and the physicochemical properties related to thermodynamic stability of the cyclononatetraenyl (CNT) anion (22) and higher annulenic ions follow the mod 4 rule applied to the number of π electrons.[90] It should be recollected that the meaning of the RE concept fades away with the increase in numbers of atoms in the annulene series[91] as a consequence of the general mathematical properties of the model used in the LCAO approach.[92] A similar trend occurs with the TRE concept as a consequence of the progressive lesser ring-term algebraic contributions in constructing the Hückel and the reference polynomials. Quite a different approach, based on the free-electron molecular orbital (FEMO) model, was used by Hobey[93] to obtain numeric results related to the aromatic character of the annulenic species. Comparative analysis of the TRE and the FEMO results obtained for 11 ionic and three neutral annulenes reveals that the two approaches give similar predictions of aromaticity. However, by the FEMO theory, cyclononatetraenyl cation and cyclodecapentaenyl dication (both have $4n$ π electrons) are classified as aromatic species, which disagrees with the results from the TRE approach.

The series of simple rings with exocyclic bonds (23, 24) fits the linear relation between the calculated TRE values and the experimental stabilities. This correlation may appear not quite convincing in consequence of the meager experimental data on the stabilities of these compounds. It is to be noted that an inconsistency between the TRE value and the experimentally observed stability occurs in the case of 1,2-benzenquinododimethide (o-xylylene) anion radical (30),[94] which might have been observed under

(78) J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 365 (1972).

(79) H. H. Freedman and A. M. Frantz, *J. Am. Chem. Soc.*, **84**, 4165 (1962).

(80) I. Gutman and N. Trinajstić, *J. Chem. Phys.*, **64**, 4921 (1976).

(81) K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.*, **445**, 266 (1925).

(82) B. A. Trash, *Nature (London)*, **178**, 155 (1956).

(83) J. Thiele, *Ber. Dtsch. Chem. Ges.*, **33**, 660 (1900).

(84) T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1960).

(85) M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, **98**, 2053 (1976).

(86) W. von Doering and L. R. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954).

(87) H. J. Dauben and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963).

(88) (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960); (b) P. J. Garratt and M. V. Sargent, *Adv. Org. Chem.*, **6**, 29 (1969); (c) J. J. Bahl, R. B. Bates, W. A. Beavers, and C. R. Launer, *J. Am. Chem. Soc.*, **99**, 6126 (1977).

(89) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960).

(90) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963).

(91) I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta*, **49**, 441 (1977).

(92) H. C. Longuet-Higgins and L. Salem, *Proc. R. Soc. (London), Ser. A*, **257**, 445 (1960); **251**, 172 (1959).

(93) W. Hobey, *J. Org. Chem.*, **37**, 1137 (1972).

(94) (a) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976); (b) R. N. Warrener, R. A. Russel, and T. S. Lee, *Tetrahedron Lett.*, **49** (1977); (c) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horak, *J. Am. Chem. Soc.*, **99**, 3876 (1977).

rather drastic conditions;[95] its TRE value (0.095), however, indicates some slight aromaticity. There seems to be no reasonable explanation for that discrepancy in terms of TRE approach at present.

The largest set of analyzed species is that of condensed ring systems. There are unfortunately no experimental data for about one-third of them; however, the other two-thirds show a good agreement between the experimental data and the calculated TRE values. Thus, cyclobutadienocyclopentadienyl anion (32), with TRE(PE) = -0.043, exists only in an extremely basic medium[96] achieved by *tert*-butoxide ion–*tert*-butyl alcohol in a dipolar aprotic solvent. On the other hand, pentalenyl dianion (36), which is an example of two $4n + 2$ π-electron rings fused together into an overall $4n + 2$ π-electron ring (bicyclooctatetraene dianion), has TRE(PE) well over 0.010. It has been isolated as a white salt.[97] Benzocycloheptatrienyl cation (49) with TRE(PE) = 0.032 and cycloheptatrieno[*def*]phenanthrenyl cation (113) were isolated as stable salts;[98,99] the same applies to the indacenyl dianion 87, with TRE(PE) = 0.034.[97] The asymmetric indacenyl dianion 91, with TRE(PE) over 0.040, is even more stable.[97] The species with lower TRE(PE) values, for example, in a range from 0.010 to 0.003, are of appreciably lower stability; most of them exist only in solution at room temperature, e.g., naphthalenyl radical ions (47, 48)[100,101] and symmetric (COT)₂Bzl tetraanion (72).[102] In this class fall the species obtained by polarographic reduction or reduction with alkali metals in aprotic solvents, for example, benzo-COT anion radical (57)[103] and its dianion (58),[103] COT-cycloheptatrienyl anion (60),[104] COT[*b*]naphthalenyl anion radical (63)[103] and its dianion (64),[103] and dibenzocyclobutadienyl anion radical (75).[105]

Many condensed ring systems have negative TRE(PE) values. Those with TRE(PE) values in the range -0.010 to -0.040 are stable in solution at temperatures of 193 to 218 K, like benzocyclobutadienyl anion radical (42)[106] and 8,9-benzobicyclo[5.2.0]nonatetraenyl anion (78).[107] Some of these species, like benzocyclobutadienyl dication (41), are stable at "higher" temperatures, e.g., 240 K, in the form of a methyl derivative.[108] It is apparent that the conjugated species with TRE(PE) values over 0.010 are to be classified as aromatic and stable; the species with TRE(PE) values in the range +0.010 to -0.010 are to be classified as nonaromatic and of borderline stability; and those species with TRE(PE) values less than -0.010 are known as antiaromatic and are usually quite unstable.

The actual situation is not always that perfect, however. For example, the TRE(PE) value of 8,9-benzobicyclo[5.2.0]nonatetraenyl cation (77) is 0.008 and clearly indicates that the species should be nonaromatic and of low stability. The experimental fact is that the species was isolated as nice solid crystals.[110] On the contrary, the TRE(PE) indexes of the two dibenzo-CNT anions (79, 80) classify them as stable, aromatic species.[111] Experimental observations are that they are stable in solution at temperatures slightly below 273 K,[111,112] that is to say under conditions required for nonaromatic–slightly antiaromatic species. Similar observations can be made in the case of the pyracyclenyl ions (101-104) and 8*H*-cyclopent[*a*]acenaphthylenyl anion (106), as well as in the case of substituted cyclopropenyl cations and substituted cyclobutadienyl ions. Let us make a closer inspection of the first of these examples. It is to be understood that TRE, TRE(PE), and TRE(PRB) values were calculated with respect to a complete molecular skeleton; that is, all vertices and edges (atoms and bonds) were taken as equal participants in conjugated structures. Inspection of 8,9-benzobicyclo[5.2.0]nonatetraenyl cation (77) reveals the presence of tropylium cation. The relevant data seem to be the TRE(PE) value of benzene (0.046), the TRE(PE) value of tropylium cation (0.038), and the observed experimental stability of a species containing a benzene ring fused to the tropylium cation[110] via two bonds, rather than benzene fused to the bicyclononatetraenyl cation. This example seems to justify the concept of local aromaticity.[113] The cation behaves as a slightly perturbed tropylium cation, and the middle cyclobutadienylic ring is an "empty" ring[114] from the aspect of conjugation.

Some other existing or hypothetical species could be analyzed in similar terms. The COT-cycloheptatriene (59)[104] cation has TRE = -0.123, which is in effect an averaged value of contributions of COT cation radical fused to cycloheptatriene radical and of COT fused to tropylium cation. The species behaves as quite a stable compound, and it is far better described simply as COT-tropylium cation. Furthermore, bicyclo[6.2.0]decapentaenyl dication and dianion (53, 54) have TRE(PE) values -0.037 and -0.024, respectively, and are thus predicted to be of low stability. There seems to be no experimental evidence concerning either of them. However, if bicyclo[6.2.0]decapentaene is looked upon as a COT system with a biconnected olefinic bond, the dication and dianion would probably have TRE values only slightly lower than 0.186 (COT dication) and thus would be readily accessible to synthesis. This is the case with azuleno[4,5,6-*cd*]phenalenyl cation (118) which is quite stable[115] although its TRE(PE) value is only 0.012. The fact is that this species possesses an "empty" five-membered ring and its actual TRE(PE) should be more like that of the parent, cyclohepta[*cd*]phenalenyl cation (117), TRE(PE) = 0.032. There are other effects that should be considered. For example, both variants, i.e., 1,2:3,4- and 1,2:5,6-dibenzocyclononatetraenyl (CNT) anions (79, 80), are of similar stability,[111,112] which happens to be lower than that of the parent anion, CNT (22).[90] Both dibenzo derivatives as well as benzo-CNT anion[116] preserve the delocalization of π electrons of the CNT anion. The slightly higher TRE(PE) values of the 1,2:3,4- and 1,2:5,6-dibenzo-CNT anions (0.024 and 0.023) compared to the parent anion, TRE(PE) = 0.018, could lead to the assumption of greater stability.

(95) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977).
(96) R. Breslow and W. Washburen, *J. Am. Chem. Soc.*, **92**, 427 (1970).
(97) T. J. Katz and M. Rosenberg, *J. Am. Chem. Soc.*, **84**, 865 (1962).
(98) G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **43**, 1221 (1960).
(99) I. Murata, K. Yamamoto, Y. Kayane, and H. Ori, *Tetrahedron Lett.*, 131 (1975).
(100) G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **98**, 4086 (1976).
(101) S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).
(102) L. A. Paquette, G. D. Ewing, S. Traynor, and J. M. Gardlik, *J. Am. Chem. Soc.*, **99**, 6115 (1977).
(103) G. R. Stevenson, M. Colon, I. Ocasio, J. G. Concepción, and A. McB. Block, *J. Phys. Chem.*, **79**, 1685 (1975).
(104) R. Breslow, W. Horspool, H. Sagiyama, and W. Vitale, *J. Am. Chem. Soc.*, **88**, 3677 (1966).
(105) N. L. Bauld and D. Banks, *J. Am. Chem. Soc.*, **87**, 128 (1965).
(106) N. L. Bauld and F. Farr, *J. Am. Chem. Soc.*, **91**, 2788 (1969).
(107) S. V. Staley, F. Heinrich, and A. W. Orvedal, *J. Am. Chem. Soc.*, **98**, 2681 (1976).
(108) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **98**, 3033 (1976).
(109) Reference 35, p 474.

(110) L. Lombardo and D. Wege, *Tetrahedron Lett.*, 4859 (1972).
(111) P. J. Garratt and K. A. Knapp, *J. Chem. Soc., Chem. Commun.*, 1215 (1970).
(112) M. Rabinovitz and I. Willner, *Tetrahedron Lett.*, 4447 (1974).
(113) M. Randić, *Tetrahedron*, **31**, 1477 (1975).
(114) E. Clar, "The Aromatic Sextet", Wiley, London, 1972, p 42.
(115) K. Nakasuji, E. Todo, and I. Murata, *Angew. Chem.*, **89**, 821 (1977).

Table I. TRE, TRE(PE), and TRE(PRB) Values of Analyzed Ions, Radicals, and Ion Radicals
Whose Graphs Are Given in Figure 1

species[a]	TRE	TRE(PE)	TRE(PRB)	status	ref to prep work
1	0.536	0.268	0.179	stable	b
2	−0.464	−0.155	−0.155		
3	−1.464	−0.366	−0.488	transient species	c
4	0.304	0.152	0.076	stable as tetraphenyl derivative	d
5	−0.461	−0.154	−0.115		
6	−0.461	−0.092	−0.115		
7	0.304	0.051	0.076	highly reactive species, but it could be deuterated	e
8	−0.919	−0.230	−0.182	transient intermediate at 213 K	f
9	−0.301	−0.060	−0.060	transient intermediate	g
10	0.317	0.053	0.063	stable	h
11	−0.300	−00.42	−0.035		
12	−0.210	−0.030	−0.035	stable in an adamantane-Me$_3$N·BH$_3$ matrix at 121 K	i
13	0.225	0.038	0.032	stable	j
14	−0.220	−0.031	−0.031	short-lived species	k
15	−0.665	−0.083	−0.095	transient intermediate at 253 K	l
16	−0.242	−0.027	−0.035	isolated in solution	m
17	0.181	0.018	0.026	black precipitate in TMEDA at room temperature	n
18	0.186	0.031	0.023	stable as 1,3,5,7-tetramethyl derivative in SO$_2$ClF	o
19	−0.205	−0.029	−0.026		
20	−0.205	−0.023	−0.026	short-lived species in solution	p
21	0.186	0.019	0.023	stable in solution	p
22	0.175	0.018	0.019	in THF under inert atmosphere, good yield	q
23	−0.404	−0.081	−0.101		
24	0.155	0.022	0.026	stable	r
25	0.287	0.026	0.026	stable	s
26	0.266	0.024	0.024	stable	t
27	0.383	0.029	0.032	stable in an inert atmosphere	u
28	0.627	0.033	0.035	stable in toluene	v
29	0.632	0.035	0.035	stable	w
30	0.095	0.011	0.016	detected in Ar matrix at 8 K	x
31	−0.341	−0.049	−0.043		
32	−0.341	−0.043	−0.043		
33	−0.478	−0.030	−0.033	attempted preparations unsuccessful	y,z
34	−0.346	−0.049	−0.038	electrochemically prepared at 196 K	z
35	0.124	0.014	0.014	1,3,5-tri-*tert*-butylpentalenyl radical ions	
36	0.464	0.046	0.052	stable	aa
37	−0.341	−0.024	−0.018	dibenzo derivative stable in SbF$_5$/SO$_2$ClF at 198 K	bb
38	0.516	0.029	0.027	dibenzo derivative stable in THF-d_8 solution	bb
39	−0.032	−0.002	−0.002		
40	−0.032	−0.002	−0.002		
41	−0.045	−0.007	−0.005	as 1,2-dimethyl derivative in SbF$_5$SO$_2$ClF up to 243 K	cc
42	−0.219	−0.024	−0.024	generated by alkali metal in THF or DME at 196 K	dd
43	−0.219	−0.031	−0.024		
44	−0.045	−0.006	−0.005		
45	−0.226	−0.028	−0.023		
46	0.364	0.036	0.036		
47	0.124	0.014	0.011	stable in SbF$_5$/SO$_2$ClF system	ee
48	0.124	0.011	0.011	stable in THF	ff
49	0.316	0.032	0.026	stable	gg
50	0.090	0.008	0.008		
51	−0.117	−0.009	−0.010		
52	−0.097	−0.007	−0.008		
53	−0.294	−0.037	−0.027		
54	−0.294	−0.024	−0.027		
55	0.193	0.019	0.015		
56	0.044	0.004	0.003		
57	0.044	0.003	0.003	observed in H$_2$O-free THF	hh
58	0.193	0.014	0.015	in HMPA, in equilibrium with the radical anion	hh
59	−0.123	−0.010	−0.009	stable salt, mp ~372 K	ii
60	−0.123	−0.008	−0.009	in liquid medium of extreme basicity	ii
61	0.189	0.013	0.010		
62	0.150	0.010	0.008		
63	0.150	0.009	0.008	in HMPA, in equilibrium with the dianion and neutral form	hh
64	0.189	0.101	0.101	in HMPA, comproportionates to the radical anion	hh
65	0.228	0.016	0.013		
66	0.238	0.016	0.013		
67	0.238	0.014	0.013	stable in THF	jj
68	0.228	0.013	0.013	stable in THF	
69	0.238	0.017	0.012		
70	−0.039	−0.002	−0.002		
71	−0.039	−0.002	−0.002	stable in solution	kk
72	0.238	0.011	0.012	stable in solution	kk
73	−0.085	−0.008	−0.006	observed in SbF$_5$/SO$_2$ClF system at low temperatures	ll
74	0.019	0.002	0.001		
75	0.019	0.001	0.001	observed in THF	mm

Table I (*Continued*)

species[a]	TRE	TRE(PE)	TRE(PRB)	status	ref to prep work
76	−0.085	−0.006	−0.006	observed in THF	*mm, nn*
77	0.090	0.008	0.006	stable	*oo*
78	−0.258	−0.018	−0.017	observed in liquid ammonia at 218 K	*pp*
79	0.440	0.024	0.023	stable and aromatic when planar	*qq*
80	0.421	0.023	0.022	stable in THF at 256 K	*rr*
81	0.102	0.008	0.007	observed in mass spectrum of 1,2-diphenylcyclohexene	*ss*
82	0.283	0.022	0.019		
83	0.464	0.033	0.031	sensitive to oxygen, otherwise stable	*tt*
84	−0.762	−0.076	−0.054		
85	−0.353	−0.032	−0.025		
86	0.265	0.020	0.019		
87	0.475	0.034	0.034	generally stable, but sensitive to air	*uu*
88	−0.514	−0.051	−0.037		
89	−0.410	−0.037	−0.029		
90	0.134	0.010	0.010		
91	0.573	0.041	0.041	stable	*uu*
92	0.030	0.002	0.002		
93	0.030	0.002	0.002		
94	−0.412	−0.041	−0.029		
95	−0.029	−0.003	−0.002		
96	0.324	0.025	0.023	stable in THF at 273 K	*vv*
97	0.294	0.021	0.021	stable in THF at 273 K	*vv*
98	0.410	0.034	0.027	stable	*ww*
99	0.410	0.032	0.027	stable	*ww*
100	0.410	0.030	0.027	stable	*ww*
101	−0.289	−0.024	−0.017		
102	−0.091	−0.007	−0.005		
103	0.323	0.022	0.019		
104	0.539	0.034	0.032	stable in THF at 195 K	*xx*
105	−0.247	−0.018	−0.014		
106	0.520	0.033	0.029	stable in THF under vacuum	*yy*
107	0.329	0.018	0.018		
108	0.072	0.005	0.004		
109	0.554	0.035	0.031	stable in THF at 203 K under vacuum	*zz*
110	−0.179	−0.011	−0.009		
111	0.267	0.015	0.013	dissolved in THF	*aaa*
112	0.393	0.020	0.020		
113	0.498	0.031	0.025	stable	*bbb*
114	0.302	0.017	0.015		
115	−0.020	−0.001	−0.001		
116	0.432	0.018	0.017	stable in THF at 273 K	*ccc*
117	0.519	0.032	0.026	stable	*ddd*
118	0.220	0.012	0.009	stable	*eee*
119	0.661	0.083	0.073		
120	0.821	0.059	0.055	stable	*fff*
121	0.999	0.050	0.048	stable	*ggg*
122	0.671	0.021	0.019	quite stable as tri-3-guaiazulenyl derivative	*hhh*
123	0.005	0.001	0.001		
124	0.005	0.000	0.001		
125	0.278	0.020	0.017	stable as 2,4-dihydroxy derivative	*iii*
126	0.278	0.015	0.017		
127	0.193	0.014	0.012	stable in SO_2ClF at temperatures below 210 K	*jjj*
128	0.193	0.011	0.012		
129	0.456	0.023	0.021		
130	0.456	0.019	0.021		
131	0.714	0.027	0.026	stable in SO_2 at 213 K	*kkk*
132	0.714	0.024	0.026		
133	0.491	0.027	0.025		
134	0.491	0.022	0.025		
135	0.320	0.016	0.018		
136	−0.487	−0.029	−0.030	observed in THF–HMPA binary solvent system	*lll*
137	−0.212	−0.012	−0.013	unstable	*lll*
138	0.336	0.017	0.021	stable in anhydrous HMPA	*mmm*
139	0.412	0.034	0.029	solid crystals, stable in dry Ar	*nnn*
140	0.097	0.007	0.007	observed in THF at 196 K	*ooo*
141	−0.531	−0.035	−0.038	observed in THF at 196 K	*ooo*
142	−0.549	−0.032	−0.039	observed in THF at 206 K	*ppp*
143	−0.402	−0.040	−0.037		
144	0.506	0.042	0.046	observed in DME at room temperature	*qqq*
145	0.410	0.023	0.020		
146	0.551	0.029	0.026		
147	0.692	0.035	0.033		
148	0.569	0.030	0.026	stable in solution at room temperature	*rrr*
149	0.814	0.033	0.029	stable in solution at room temperature	*rrr*
150	0.508	0.023	0.023	Möbius system, might have been observed	*sss*

Table I *(Continued)*

[a] Numbers correspond to structures in Figure 1. [b] R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, 92, 984 (1970). [c] R. Breslow and M. Battiste, *Chem. Ind. (London)*, 1143 (1958). [d] H. H. Freedman and A. M. Frantz, *J. Am. Chem. Soc.*, 84, 4165 (1962). [e] J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 365 (1972). [f] K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.*, 445, 266 (1925). [g] B. A. Trash, *Nature (London)*, 178, 155 (1956). [h] J. Thiele, *Ber. Dtsch. Chem. Ges.*, 33, 660 (1900). [i] M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, 98, 2053 (1976). [j] W. von Doering and L. R. Knox, *ibid.*, 76, 3203 (1954). [k] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, 82, 5593 (1960). [l] H. J. Dauben and M. R. Rifi, *ibid.*, 85, 3041 (1963). [m] P. J. Garratt and M. V. Sargent, *Adv. Org. Chem.*, 6, 29 (1969). [n] J. J. Bahl, R. B. Bates, W. A. Beavers, and C. R. Launer, *J. Am. Chem. Soc.*, 99, 6126 (1977). [o] G. A. Olah, J. S. Staral, and L. Paquette, *ibid.*, 98, 1267 (1976). [p] T. J. Katz, *ibid.*, 82, 3784, 3785 (1960); W. Gaussing and G. Willer, *Angew. Chem.*, 90, 380 (1978). [q] E. A. LaLancette and R. E. Benzon, *J. Am. Chem. Soc.*, 85, 2853 (1963); T. J. Katz and P. J. Garratt, *ibid.*, 85, 2852 (1963). [r] J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959). [s] A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, 82, 1052 (1960). [t] N. Buu-Hoi, *Justus Liebigs Ann. Chem.*, 556, 18 (1944). [u] J. Holmes and R. Pettit, *J. Org. Chem.*, 28, 1695 (1963). [v] T.-L. Chu and S. Weissman, *J. Am. Chem. Soc.*, 73, 4462 (1951). [w] T.-L. Chu and S. I. Weissman, *J. Chem. Phys.*, 22, 21 (1954). [x] K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, 99, 4840 (1977). [y] B. Trost and P. L. Kinson, *ibid.*, 97, 2438 (1975). [z] R. W. Johnson, *ibid.*, 99, 1461 (1977). [aa] T. J. Katz and M. Rosenberg, *ibid.*, 84, 865 (1962). [bb] I. Willner and M. Rabinovitz, *ibid.*, 100, 337 (1978). [cc] G. A. Olah and G. Liang, *ibid.*, 98, 3033 (1976). [dd] N. L. Bauld and F. Farr, *ibid.*, 91, 2788 (1969). [ee] G. A. Olah and D. A. Forsyth, *ibid.*, 98, 4086 (1976). [ff] S. I. Weissman, *ibid.*, 78, 116 (1956). [gg] G. Naville, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, 43, 1221 (1960). [hh] G. R. Stevenson, M. Colon, I. Ocasio, J. G. Concepcion, and A. McB. Block, *J. Phys. Chem.*, 79, 1685 (1975). [ii] R. Breslow, W. Horspool, H. Sagiyama, and W. Vitale, *J. Am. Chem. Soc.*, 88, 3677 (1966). [jj] T. J. Katz, M. Yoshida, and L. C. Siew, *ibid.*, 87, 4516 (1965). [kk] L. A. Paquette, G. D. Ewing, S. Traynor, and J. M. Gardlik, *ibid.*, 99, 6115 (1977). [ll] G. A. Olah and G. Liang, *ibid.*, 99, 6045 (1977). [mm] N. L. Bauld and D. Banks, *ibid.*, 87, 128 (1965). [nn] R. Waack, M. A. Doran, and P. West, *ibid.*, 87, 5508 (1965). [oo] L. Lombardo and D. Wege, *Tetrahedron Lett.*, 4859 (1972). [pp] S. W. Staley, F. Heinrich, and A. W. Orvedal, *J. Am. Chem. Soc.*, 98, 2681 (1976). [qq] P. J. Garratt and K. A. Knapp, *J. Chem. Soc., Chem. Commun.*, 1215 (1970). [rr] M. Rabinovitz and I. Willner, *Tetrahedron Lett.*, 4447 (1974). [ss] F. Jachimowicz, G. Levin, and M. Szwarc, *J. Am. Chem. Soc.*, 99, 5977 (1977). [tt] H. Staudinger, A. Gaule, and J. Siegwart, *Helv. Chim. Acta*, 4, 212 (1921). [uu] T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, 84, 865 (1962). [vv] R. G. Lawler and C. V. Ristagno, *ibid.*, 91, 1534 (1969). [ww] D. H. Reid, *Q. Rev.*, 19, 274 (1965). [xx] B. M. Trost, D. Buhner, and G. M. Bright, *Tetrahedron Lett.*, 2787 (1973). [yy] K. Yamamoto, M. Morioka, and I. Murata, *ibid.*, 3009 (1975). [zz] I. Murata, K. Yamamoto, M. Morioka, M. Tamura, and T. Hirotsu, *ibid.*, 2287 (1975). [aaa] I. Willner and M. Rabinovitz, *ibid.*, 1223 (1976). [bbb] I. Murata, K. Yamamoto, Y. Kayane, and H. Ori, *ibid.*, 131 (1975). [ccc] M. Rabinovitz and I. Willner, *J. Am. Chem. Soc.*, 99, 4507 (1977). [ddd] I. Murata, K. Yamamoto, and Y. Kayane, *Angew. Chem.*, 86, 862 (1974). [eee] K. Nakasuji, E. Todo, and I. Murata, *ibid.*, 89, 821 (1977). [fff] R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, 83, 2375 (1961). [ggg] R. Breslow and H. W. Chang, *ibid.*, 83, 2367 (1961); R. Breslow, *ibid.*, 79, 5318 (1957); R. Breslow and C. Yuan, *ibid.*, 80, 5991 (1958). [hhh] I. Agranat and E.-A. Shalom, *J. Org. Chem.*, 41, 2379 (1976). [iii] D. G. Farnum and B. Webster, *J. Am. Chem. Soc.*, 85, 3504 (1963). [jjj] G. A. Olah and J. S. Staral, *ibid.*, 98, 6290 (1976). [kkk] H. H. Freedman and A. E. Young, *ibid.*, 86, 734 (1964). [lll] G. R. Stevenson and I. Ocasio, *ibid.*, 98, 890 (1976). [mmm] L. A. Paquette, G. D. Ewing, and S. G. Traynor, *ibid.*, 98, 273 (1976). [nnn] I. S. Akhrem, E. I. Fedin, B. A. Kvasov, M. E. Vol'pin, *Tetrahedron Lett.*, 5265 (1967). [ooo] M. D. Sevilla, S. H. Flajser, G. Vincow, and H. J. Dauben, Jr., *J. Am. Chem. Soc.*, 91, 4139 (1969). [ppp] N. L. Bauld and C.-S. Chang, *Tetrahedron Lett.*, 153 (1973). [qqq] E. S. Bowman, G. B. Hughes, and J. B. Grutzner, *J. Am. Chem. Soc.*, 98, 8273 (1976). [rrr] N. Kakeya, M. Nojima, and N. Tokura, *J. Chem. Soc., Perkin Trans. 1*, 87 (1976). [sss] N. L. Bauld, J. Cessac, C.-S. Chang, F. R. Farr, and R. Halloway, *J. Am. Chem. Soc.*, 98, 4561 (1976).

However, conversion of the planar, fully delocalized structure of the parent anion to the nonplanar, partially delocalized structure[111] of the dibenzo derivatives affects the overall stability, which is in accord with the experimental observation.

As for radical anions of conjugated species, it is known that they disproportionate to dianions; on the other hand, dianions comproportionate[116a] to radical anions. An equilibrium established for those processes appears to be strongly affected by solvent and counterion effects.[117,118] In most cases disproportionation is favored by the difference in TRE values between dianion and radical anion. Thus, for example, COT dianion has a TRE value greater by 0.391[97] than its radical ion (21, 20), the TRE value of benzo-COT dianion is greater by 0.149 than the TRE value of the corresponding radical anion[103] (58, 57), and the TRE value of naphtho[b]COT dianion is greater by 0.029 than the TRE value of its radical anion (64, 63).[103] In the case of *sym*-dibenzo-COT dianion and radical anion (67, 68), disproportionation is not favored by the difference in TRE values. In certain cases, however, (75, 76)[105,119,120] disproportionation takes place although the process is contrary

to the relative TRE values. "Extensive disproportionation"[120] in this case is explained in terms of aromatic stabilization of the cyclobutadienyl dianion. Such a localization of a negative charge in the middle ring is disputable in terms of simple HMO theory and certainly is not predicted by the TRE method.

With regard to complex pericondensed systems a question exists whether some species behave more like (i) a structure of condensed rings or (ii) an annulene of the order of the perimeter and which is perturbed by internal bridge(s). For example, the acenaphthylenyl skeleton (94-97) could be analyzed as a structure obtained by fusing a cyclopentadienylic ring to that of naphthalene, or as a perturbed [11]annulene system. The TRE and TRE(PE) values of radical anion and dianion, 0.324, 0.025, and 0.294, 0.021, respectively, indicate that the compounds should be stable, which is experimentally observed.[121] The TRE value (-0.412) of the dication 94 seems to indicate the resistance of the naphthalene system to be ionized—as is visible in the TRE values of naphthalenyl ions—while the TRE (-0.029) for the cation radical 95 indicates a significant participation of the penta ring. The TRE values of the corresponding [11]annulene ions,[91] TRE(monoanion) = -0.426, TRE(dianion) = -0.147, TRE(cation) = 0.143, and TRE(dication) = -0.124, are in agreement with the available experimental observations.[121a] Moreover, the

(116) (a) A. G. Anastassiou and R. C. Griffith, *J. Am. Chem. Soc.*, 96, 611 (1974); (b) F. R. Stevenson and I. Ocasio, *ibid.*, 98, 890 (1976).
(117) A. G. Evans and B. J. Tabner, *J. Chem. Soc.*, 4613 (1963).
(118) E. R. Zabolotny and J. F. Garst, *J. Am. Chem. Soc.*, 86, 1645 (1964).
(119) M. A. Doran and R. Waack, *J. Organomet. Chem.*, 3, 93 (1965).
(120) R. Waack, M. A. Doran, and P. West, *J. Am. Chem. Soc.*, 87, 5508 (1965).

(121) (a) R. G. Lawler and C. V. Ristagno, *J. Am. Chem. Soc.*, 91, 1534 (1969). (b) E. Vogel, R. Feldman, and A. Duewell, *Tetrahedron Lett.*, 1941 (1970); W. Grimme, H. Hoffmann, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 4, 295 (1976).

charge-induced[122] chemical shifts of the dianion[121] do not reflect the evenly distributed negative charge densities, as would probably be the case of the [11]annulene ring.

The pyracyclenyl dianion (104) could be analyzed in similar terms. Its TRE(PE) = 0.034 indicates a species of high aromatic stability; however, the experimental observations do not back up such a prediction.[123] The pyracyclenyl structure could be analyzed either as (i) a fusion of two penta rings to naphthalene or (ii) a perturbed [12]annulene. Were it considered as four fused rings, the addition of two electrons, or the loss of two protons, would result in (a) stabilization in two penta rings and (b) destabilization in the naphthalene ring. These two effects, when averaged, are given as the TRE value. Were the pyracyclenyl structure analyzed in terms of [12]annulene chemistry, the addition of two electrons, or the loss of two protons, in a $4n$ π-electron system would simply result in a $4n + 2$ π-electron system; that is, ionization would be energetically favored from the aspect of simple Hückel molecular orbital theory. The data[123] corroborate the idea that pyracyclenyl is a perturbed [12]annulene dianion. The TRE for [12]annulene dianion is 0.009; that is, it classifies pyracyclenyl dianion as a nonaromatic species of moderate stability, which is consonant with the experimental observations.[123] 8H-Cyclopent[a]acenaphthalenyl anion (106) is another interesting complex system.[124] Were it analyzed as a structure built up of four rings equally participating in the overall conjugation, it is either a case of a cyclopentadienyl ring, TRE(PE) = −0.060, fused to the acenaphthalenyl radical anion (96), TRE(PE) = −0.025, or the case of pentalenyl anion (10), TRE(PE) = 0.014, fused to naphthalene, TRE(PE) = 0.039. It could be considered as some averaged contribution of all possible combinations. The fact is that in all cases the TRE(PE) corresponds to a rather stable, aromatic species. This would be particularly noticeable had the structure been considered as a naphthalene ring connected to a cyclopentadienyl ring via an "empty" penta ring, as is the usual way of representing it. The NMR data for the similar fluoranthene dianion seem to corroborate such an idea.[121] In that case, it is very likely that the negative charge would be partially localized to the penta ring, thus resulting in a highly aromatic species. Either this is not the real situation or more experimental data related to 8H-cyclopenta[a]acenaphthylenyl anion are needed. Similar dissonance between the calculated TRE and TRE(PE) values and the experimental stability occurs in the case of cyclopent[cd]phenalenyl anion (109). TRE contribution of one π electron to that species could result in (i) a stability similar to that of pyrene, TRE(PE) = 0.051,[33] or (ii) the stability of phenalenyl anion, TRE(PE) = 0.029, slightly perturbed by an olefinic double bond. The treatment of the cyclopent[cd]phenalenyl system[73] as a perturbed (by a central bond) [13]annulene[125] gives TRE(PE) around 0.008, which certainly does not classify the species as a very aromatic one; however, the addition of one electron to that system results in a slight destabilization by −0.001 with respect to the TRE(PE) values. It could be tentatively concluded that the system behaves more like a perturbed annulenic ring as far as the experimental stability is concerned.[126]

Phenyl substitution on the cyclopropenyl cation pro-

duces a progressive increase in the TRE values. The data on the stability of these compounds are not sufficiently precise to be correlated with these TRE values, but the trend does correlate with an increase in pK_{R^+}.[127,128]

cation	TRE	pK_{R^+}
cyclopropenyl	0.536	−7.4
phenylcyclopropenyl	0.661	
diphenylcyclopropenyl	0.821	0.3
triphenylcyclopropenyl	0.999	3.1

The TRE value trend is even better illustrated by pK_{R^+} values of corresponding propyl derivatives.[128] Such a correlation is not linear but the order is identical. This nonlinearity is probably due to medium effects which are elusive, even for more sophisticated theories than the TRE approach.[129,130] Relatively high TRE values in the phenylcyclopropenyl series are the consequence of a significant contribution of ringlike terms to the graph spectrum and seems not to be quite paralleled by the experimental stability.[131-134] The same could be applied to the cyclobutadienyl series.[135-138] This seems to be a problem of proper weighting of the contribution of particular rings to the topology of the complete system. From this point of view it is interesting to note the series of homogeometric bicyclic species (135–142). In this case the TRE values are derived from the TRE values of the corresponding monocyclic species connected by essentially single bonds.[139] Thus, heptafulvenyl radical cation (140) represents a weighted sum of unstable heptafulvene radical and stable tropylium cation; the resulting compound has TRE = 0.097, which is experimentally supported by its low stability.[140] The dication of this compound (139) is built up of two tropylium ions and both the TRE of heptafulvenyl dication (0.412) and the experimental evidence classify it as a stable, aromatic species.[141] The same reasoning could be straightforwardly applied to the bicyclooctatetraenyl series.[116a,142]

Conclusion

The topological contribution of a cyclic graph relative to a linear graph is quantified in the form of topological resonance energy, TRE. Topological resonance energy is

(122) G. Frankel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, 82, 5846 (1960).

(123) B. M. Trost, D. Buhner, and G. M. Bright, *Tetrahedron Lett.*, 2787 (1973).

(124) K. Yamamoto, M. Morioka, and I. Murata, *Tetrahedron Lett.*, 3009 (1975).

(125) P. Ilić and N. Trinajstić, *Pure Appl. Chem.*, in press.

(126) I. Murata, K. Yamamoto, M. Morioka, M. Tamura, and T. Hirotsu, *Tetrahedron Lett.*, 2287 (1975).

(127) R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, 83, 2375 (1961).

(128) (a) R. Breslow and J. T. Groves, *J. Am. Chem. Soc.*, 92, 984 (1970); (b) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, 83, 2375 (1962).

(129) J. Hylton McCreery, R. E. Christoffersen, and G. G. Hall, *J. Am. Chem. Soc.*, 98, 7191 (1976).

(130) J. Hylton McCreery, R. E. Christoffersen, and G. G. Hall, *J. Am. Chem. Soc.*, 98, 7198 (1976).

(131) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 83, 2367 (1961).

(132) R. Weis, C. Schllerf and K. Schloter, *J. Am. Chem. Soc.*, 98, 4668 (1976).

(133) Z. Yoshida, S. Miki, and S. Yoneda, *Tetrahedron Lett.*, 4731 (1973).

(134) I. Agranat and E.-A. Shalom, *J. Org. Chem.*, 41, 2379 (1976).

(135) D. G. Farnum and B. Webster, *J. Am. Chem. Soc.*, 85, 3502 (1963).

(136) G. A. Olah and J. S. Staral, *J. Am. Chem. Soc.*, 98, 6290 (1976).

(137) H. H. Freedman and A. E. Young, *J. Am. Chem. Soc.*, 86, 734 (1964).

(138) G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.*, 92, 1431 (1970).

(139) P. Ilić and N. Trinajstić, work in preparation.

(140) M. D. Sevilla, S. H. Flajser, G. Vincow, and J. J. Dauben, *J. Am. Chem. Soc.*, 91, 4139 (1969).

(141) I. S. Akhrem, E. I. Fedin, B. A. Kvasov, and M. E. Vol'pin, *Tetrahedron Lett.*, 5265 (1967).

(142) L. A. Paquette, G. D. Ewing, and S. G. Traynor, *J. Am. Chem. Soc.*, 98, 273 (1976).

divided by the number of π electrons that fill the levels resulting from the difference of the HMO energy levels and the levels resulting from the matching (acyclic) polynomial of a molecular graph. Thus, the index TRE(PE) is obtained by measuring the aromaticity that results from the $4n + 2$ rule with respect to the number of π electrons. The TRE method is straightforwardly applied to closed-shell charged and to open-shell neutral and charged conjugated compounds. In almost all cases the TRE method classifies species according to their chemical characteristics. Used with no refinements, the TRE method is generally applicable to any conjugated ion, radical, or ion radical. In some cases the agreement between the predictions based upon the calculated TRE values and the actual experimental properties is not properly quantified; an in-depth analysis reveals as main causes of the disagreement an incomplete conjugation, a time-dependent nonplanarity, and medium effects. Simple refinements are easily applicable to the TRE method and result in a simple, complete method generally applicable to conjugated species be they neutral closed shell, neutral open shell, or charged, both closed and open shell.

Acknowledgment. We thank Professors B. A. Hess, Jr. (Nashville), I. Murata (Osaka), and M. Rabinovitz (Jerusalem) for helpful discussions, and Professor M. Randić (Ames) for correspondence about the aromatic stability of conjugated ions, radicals, and ion radicals.

Registry No. 1, 26810-74-2; 2, 60512-06-3; 3, 20829-57-6; 4, 12240-33-4; 5, 34531-09-4; 6, 34561-57-4; 7, 59963-50-7; 8, 29661-18-5; 9, 62744-94-9; 10, 12127-83-2; 11, 34504-50-2; 12, 34562-85-1; 13, 26811-28-9; 14, 3551-27-7; 15, 34464-18-1; 16, 34568-48-4; 17, 64113-53-7; 18, 37306-59-5; 19, 34484-44-1; 20, 34510-85-5; 21, 34510-09-3; 22, 45730-23-2; 23, 62668-20-6; 24, 2154-56-5; 25, 7419-60-5; 26, 7419-61-6; 27, 4471-17-4; 28, 2216-49-1; 29, 13948-08-8; 30, 60644-50-0; 31, 72844-22-5; 32, 36510-10-8; 33, 72866-10-5; 34, 62697-82-9; 35, 62673-28-3; 36, 12107-28-7; 37, 72866-13-8; 38, 72844-18-9; 39, 72881-39-1; 40, 72866-14-9; 41, 64062-09-5; 42, 34527-68-9; 43, 72881-24-4; 44, 64062-12-0; 45, 12203-21-3; 46, 12128-54-0; 47, 34512-27-1; 48, 34509-91-6; 49, 29432-93-7; 50, 12203-30-4; 51, 72791-66-3; 52, 72844-19-0; 53, 72866-11-6; 54, 72844-14-5; 55, 72852-80-3; 56, 72881-23-3; 57, 51053-95-3; 58, 54447-98-2; 59, 72844-15-6; 60, 72844-05-4; 61, 72852-81-4; 62, 72881-22-2; 63, 56843-00-6; 64, 62684-05-3; 65, 63397-57-9; 66, 42299-42-3; 67, 34471-83-5; 68, 64492-53-1; 69, 72852-79-0; 70, 72866-21-8; 71, 72843-94-8; 72, 72843-95-9; 73, 62157-22-6; 74, 34533-10-3; 75, 34478-97-2; 76, 72843-96-0; 77, 59926-11-3; 78, 72844-02-1; 79, 72844-03-2; 80, 72844-04-3; 81, 72866-22-9; 82, 2299-68-5; 83, 12257-35-1; 84, 72852-82-5; 85, 72844-01-0; 86, 72881-21-1; 87, 72844-16-7; 88, 72866-16-1; 89, 72881-19-7; 90, 72881-20-0; 91, 72844-17-8; 92, 72866-17-2; 93, 72866-19-4; 94, 62684-07-5; 95, 35612-78-3; 96, 34493-60-2; 97, 62684-08-6; 98, 12147-01-2; 99, 3924-44-5; 100, 42464-32-4; 101, 12564-47-5; 102, 72881-18-6; 103, 34539-26-9; 104, 12564-35-1; 105, 72844-11-2; 106, 57891-91-5; 107, 72866-15-0; 108, 69742-87-6; 109, 62684-01-9; 110, 72844-12-3; 111, 60016-22-0; 112, 72844-13-4; 113, 55563-45-6; 114, 69717-97-1; 115, 72866-20-7; 116, 63882-11-1; 117, 59659-00-6; 118, 64045-03-0; 119, 26811-00-7; 120, 12319-46-9; 121, 12190-17-9; 122, 72881-40-4; 123, 49598-08-5; 124, 72843-98-2; 125, 72866-18-3; 126, 72843-99-3; 127, 61189-58-0; 128, 72866-09-2; 129, 72866-07-0; 130, 72866-08-1; 131, 28084-93-7; 132, 72844-23-6; 133, 72866-06-9; 134, 72844-24-7; 135, 72844-00-9; 136, 72881-17-5; 137, 72844-25-8; 138, 64317-43-7; 139, 12312-62-8; 140, 34468-12-7; 141, 34468-13-8; 142, 72866-23-0; 143, 72844-20-3; 144, 26811-02-9; 145, 72844-21-4; 146, 72905-11-4; 147, 31468-22-1; 148, 40807-34-9; 149, 34480-04-1; 150, 72866-12-7.

Chemical Effects of Steric Strains. 24. 13C NMR Study of the Interaction of 9-Borabicyclo[3.3.1]nonane with Amines of Increasing Steric Requirements

Herbert C. Brown* and Kung K. Wang[1]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

The 13C NMR spectra of the interaction of 9-borabicyclo[3.3.1]nonane (9-BBN) with two series of amines, involving regularly increasing steric requirements, were used to study the role of steric strains as a factor in the stability of addition compounds formed and their exchange with the amine. A set of pyridine bases, including pyridine and 2-methyl-, 2-ethyl-, 2-isopropyl-, and 2-*tert*-butylpyridines, and a set of aliphatic amines, including *n*-propylamine, isopropylamine, diethylamine, diisopropylamine, and triethylamine, with increasing steric requirements were selected for examination. Quinuclidine was also selected, as a base of relatively low steric requirements, for comparison with triethylamine, a base with very large steric requirements. The results reveal four types of behavior: formation of stable complexes with no observable exchange with excess amine; formation of stable complexes with rapid exchange of amine; formation of partially dissociated complexes with rapid exchange; and no detectable interaction of 9-BBN and amines of large steric requirements. In general, there is a regular progression along these four types of behavior with increasing steric requirements in both series of amines. Thus, triethylamine fails to show any interaction with 9-BBN, whereas quinuclidine forms a stable adduct which does not exchange with excess amine. 13C NMR provides a valuable tool for exploring the role of such steric effects in the formation and stability of molecular addition compounds.

It was previously observed that the complex of pyridine (Py) with 9-borabicyclo[3.3.1]nonane (9-BBN), Py·9-BBN, exhibits an unusual 13C NMR spectrum.[2] The two halves of the cyclooctyl ring of 9-BBN are different. Also, rapid exchange with excess free pyridine does not occur. Therefore, it was of interest to examine how these spectral characteristics would change with increasing steric requirements of the base.[3,4] Two series of bases with in-

(1) Graduate research assistant on Grant CHE 76-20846 of the National Science Foundation.

(2) Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* 1980, 45, 846.

(3) For a summary of the data and conclusions see: Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; Chapters 5–8.