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Heteroaromaticity. 11. The Conjugation Energies of Annulenes and Heteroannulenes from Their Molecular Dimensions

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Abstract: A previously described method for the direct calculation of conjugation energies from molecular dimensions has been applied to a range of monocyclic and bridged annulenes and heteroannulenes. As might have been anticipated only those compounds having conjugated peripheries with $(4n+2)\pi$ electrons and adequate overlap between adjacent p-orbitals display substantial conjugation energies. Where comparison is possible the results reported here are in reasonable agreement with those obtained by other methods. © 1997 Elsevier Science Ltd.

INTRODUCTION

The study of aromaticity has been greatly enriched by the synthesis of the monocyclic annulenes by Sondheimer[2,3], and their bridged counterparts by Boekelheide[3,4] and Vogel[3,5]. The principal criteria employed in assessing their aromaticities have been the possession or lack of ring currents as assessed from their ^1H nmr spectra, and the alternation or non-alternation of peripheral bond lengths in those cases where X-ray structural studies have proved possible. The considerable variations in bond length observed even in polybenzenoid compounds makes the latter at best a qualitative criterion. In only a few instances, *vide infra*, has the direct estimation of resonance energies been attempted by thermochemical methods. These resonance energies provide an overall measure of the conjugation energy and accompanying molecular strain energies. In the preceding paper in this series[1] a simple method for calculating conjugation energies from molecular dimensions was presented. In essence this entails calculating the energy, E_B, required to convert each bond of the conjugated system into the single or double bond of the corresponding Kekulé structure using the equation;

$$E_B = F\,(R_s \text{ or } R_d - R)^2\,(a - bR)\ \text{kcal. mole}^{-1} \qquad (5)$$

where R (Å) is the length of the bond.Summation of the E_B values for the Kekulé structure give its conjugation energy E. The lengths of the appropriate single (R_s) and double bonds (R_d) together with the values of the constants F, a and b are listed in Table 1.

Table 1. Constants used for bond energy calculations

Bond	R_s (Å)	R_d (Å)	F	a ($\times 10^4$ Pa)	b($\times 10^4$ Pa)
CC	1.533	1.337	85.94	44.39	26.02
CN	1.474	1.274	62.19	43.18	25.73

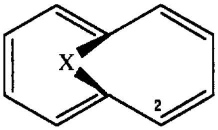
Where more than one Kekulé form is possible a separate energy, E_i, has to be calculated for each of these and the energies for the n forms then summed to give the overall conjugation energy, CE, according to the following expression:

$$CE = n\,E_i\left(1/E_i \div \sum_{i=1}^{i=n} 1/E_i\right) \qquad (2)$$

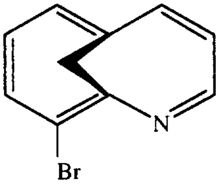
The summation coefficients obtained can also be used to estimate the relative contributions of the individual Kekulé forms. This method has been shown to satisfactorily reproduce independently determined conjugation energies for a wide range of azines and azoles. It is important to emphasise at this juncture that while the energies obtained are normally identical to the thermodynamic resonance energies for six-membered rings and other strain free systems this does not necessarily apply to strained ring systems where appropriate steric energetic corrections may be required. In the present paper conjugation energies have been derived for a wide variety of annulenes and heteroannulenes for which satisfactory X-ray structural data are available.

RESULTS AND DISCUSSION

Monocyclic Annulenes. Application of the above method to the reported dimensions of [14]annulene[6] and [18]annulene[7] yields conjugation energies of 134.8 and 146.6 kcal. $mole^{-1}$ respectively. The heat of formation of crystalline [18]annulene has been reported[8] as -39±4 kcal. $mole^{-1}$ and a heat of sublimation of 28±2 kcal. $mole^{-1}$ was assumed. Using currently recommended[9] bond energies these values lead to a resonance energy of 129±6 kcal. $mole^{-1}$ which, in view of the assumed heat of sublimation, is in satisfactory agreement with the value deduced above. In contrast a much lower resonance energy of 29.6 kcal. $mole^{-1}$ may be calculated for [16]annulene whose structure[10] consists of essentially alternating single and double bonds. The heat of combustion of crystalline [16]annulene[11] leads to a heat of formation of 130.9 kcal. $mole^{-1}$. Once again no direct measurement of the heat of sublimation has been reported but assumption of a value of *ca.* 25 $kcal.mole^{-1}$ leads to an estimated conjugation energy of 20 kcal. $mole^{-1}$.



1 $X = CH_2$
2 $X = CF_2$
3 $X = CF_2$



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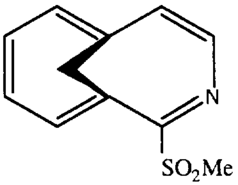

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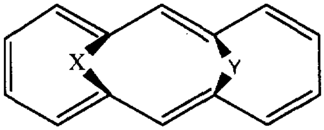
1,6-Bridged [10]Annulenes. The dimensions recorded for 1,6-methano[10]annulene **1**[12] and its 11,11-difluoro analogue **2**[13] yield conjugation energies of 79.2 and 84.9 kcal. mole $^{-1}$ respectively. The 2-carboxylic acid derivative of **1**[14] yields a value of 75.95 kcal. $mole^{-1}$. While the conjugated periphery deviates from planarity with a maximum torsion angle of 35° the resulting decrease in π-overlap would be expected to result in bond lengthening with a concomitant decrease in conjugation energy. It should also be noted that conjugation energy varies with the cosine of the angle of twist[15]. Although the enthalpy of formation of **1** has been reported[16] as

75.2 kcal. mole^{-1}, which leads to a net stabilisation energy of 25 kcal. mole^{-1}, this figure also incorporates contributions from steric energies. Empirical force field calculations[17] have deduced a value of 30.7 kcal.mole^{-1} for the latter. A Dewar resonance energy of 17.2 kcal.mole^{-1} has been deduced[18] for **1** compared to values of 26.1 for benzene and 40.7 for naphthalene though it is not clear whether allowances have been made for steric strain effects. However, application of the relationship established[19] between diamagnetic susceptibility exaltation and resonance energies to the diamagnetic susceptibility exaltations observed for **1** and 1,6-oxido[10]annulene[20] **3** indicates these molecules to possess a conjugation energy of about 85.6 kcal.mole^{-1} in good accord with our calculations.

Replacement of one of the ring carbon atoms by a nitrogen one to give the quinoline/isoquinoline analogues of 1,6-methano[10]annulene, namely **4**[21] and **5**[22], has little effect on the overall geometry and these compounds display conjugation energies of 83.4 and 73.1 kcal. mole^{-1} respectively, similar to the parent carbocycle.

Bridged [14]Annulenes. In the case of the doubly bridged [14]annulenes, which can be regarded as having an anthracene perimeter, two possible stereoisomers are possible namely what may be termed the *syn* series **6-17** and the *anti* series **18,19** differing only in the relative orientations of the two bridges. Despite the repulsion between the bridging groups in the *syn* series, which leads to a steric energy of 43.35 kcal. mole^{-1} *versus* 28.1 kcal. mole^{-1} for the *anti* isomer according to force field calculations,[17] overall this is more than compensated

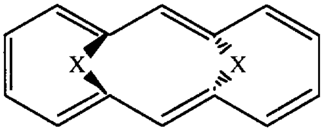
Table 2. Conjugation energies for *syn*-1,6: 8,13-Bridged[14]annulenes, **6** - **17**.



Annulene	X	Y	CE kcal. mole^{-1}	Ref.*
6	CH_2	CH_2	117.5	23
7	CO	CO	109.8	24
8	-CH.CH_2.CH-		106.5	25
9	-CH.CH_2.CH_2.CH-		108.0	26
10	CH_2	NH	125.5	27
11	NH	NH	113.1	28
12	NH	NMe	113.6	28
13	NMe	NMe	109.8	28
14	-N.CH_2.N-		111.7	29
15	-N.CH_2.CH_2.N-		108.1	29
16	-N.CH_2.CH_2.CH_2.N-		109.5	29
17	O	O	113.2	30

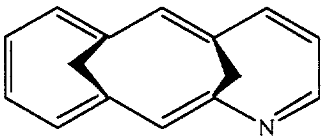
* Reference to source of molecular dimensions.

for by the larger conjugation energies resulting from the smaller misalignment angles between the directions of adjacent 2p carbon orbitals in the *syn* series. Thus, compounds in the *syn* series **6-17** show misalignment angles in the range 12 to 25° with conjugation energies in the range 106-125 kcal. mole^{-1},*cf.* Table 2, only a little lower than the value adduced above for [14]annulene. Presumably the variations reflect modifications in the conjugated periphery but so far attempts to correlate these with any simple geometric criterion have been unsuccessful. In each case the two Kekulé forms contribute roughly equally to the overall assessment. Replacement of one of the peripheral carbon atoms in the *syn* series by nitrogen, as in **20**,[31] results in a conjugation energy of 105.5 kcal. mole^{-1}. In contrast, in the *anti* series exemplified by **18**[32] and **19**[33] torsion angles as high as 75° are observed leading to marked bond alternation and conjugation energies of only 31.7 and 41.4 kcal. mole^{-1} respectively, with one of the two Kekulé forms contributing to an extent of about 92%.



18 X = CH$_2$

19 X = CF$_2$



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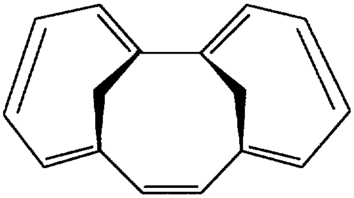

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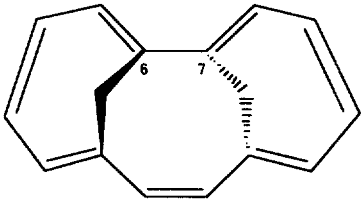

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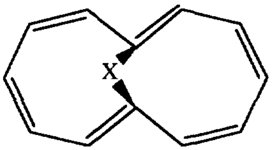
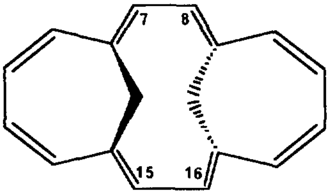
The molecular dimensions reported for the *syn* bridged analogue of phenanthrene **21**[34] show torsion angles up to 45° which is reflected by the calculated conjugation energy of 91.5 kcal. mole^{-1}. In the *anti* bridged analogue **22**[35] most torsion angles are in the range 22-35° but that between C6 and C7 reaches 84° so that substantial bond fixation occurs with a reduced conjugation energy of 51.7 kcal.mole^{-1} . The depicted Kekulé forms for **21** and **22** contribute to the extent of 72 and 89% respectively to the overall assessment. Again force field calculations[36] indicate that the *anti* isomer has a lower strain energy of 40 kcal. mole^{-1} compared to the *syn* isomer with 46.5 kcal. mole^{-1}.

Bridged [12] and [16]annulenes. As anticipated much smaller conjugation energies are observed for 4nπ electron systems. Thus the bridged [12]annulene **23**[37] and the doubly bridged [16]annulene **25**[38] both show systematic alternation of double and single bond lengths around the annulene periphery leading to values of 21.9 and 24.3 kcal.mole^{-1} respectively. A steric energy of 30.1 kcal.mole^{-1} has been calculated[17] for 1,7-methano[12]annulene **24**. In the case of **25** the observed *anti* conformer has been calculated[38] to be 19 kcal. mole^{-1} more stable than the *syn* conformer. Although it is grossly planar the torsional angles about the C7-C8



23 X = CF_2

24 X = CH_2



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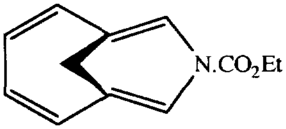

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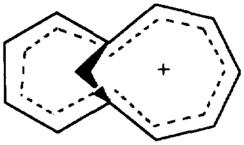
and C15-C16 bonds in **25** are 46° making these esentially single bonds in character. A conjugation energy of 25.2 kcal. mole^{-1} may be calculated for the 12π analogue of pyrrole **26**.[39]



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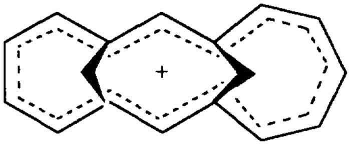

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Annulene Cations. Such calculations may also be extended to the annulene cations, **27**[40] and **28**,[41] and provide conjugation energies of 88.7 and 134.2 kcal. mole^{-1} respectively. These values are higher than those for the corresponding 10π and 14π annulenes **1** and **6** in keeping with the higher resonance energy predicted for the tropylium cation over benzene.[42]

REFERENCES

1. Part 10.Bird, C.W. *Tetrahedron*, **1996**, 53, 13111-13118..
2. Sondheimer, F. *Acc. Chem. Res.*, **1972**, *5*, 81-91.
3. Lloyd, D. *Non-benzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam, 1984 ; Balaban, A.T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers*, CRC Press, Boca Raton, 1987.
4. Boekelheide, V. in *Topics in Nonbenzenoid Aromatic Chemistry,* Ed. Nozoe, T.; Hirokawa, Tokyo, 1973, 1, 47-79.
5. Vogel, E. *Lecture Notes in Heterocyclic Chemistry*, **1985**, *8*, 103.
6. Chiang, C.C.; Paul, I.C. *J. Am. Chem. Soc.*, **1972**, *94*, 4741-4743.
7. Bregman, J.; Hirshfeld, F.L.; Rabinovitch, D.; Schmidt, G.M.J. *Acta Cryst.*, **1965**, *19*, 227-234.
8. Beezer, A.E.; Mortimer, C.T.; Springall, H.D.; Sondheimer, F.; Wolovsky, R. *J. Chem. Soc.*, **1965**, 216-20
9. Bird, C.W. *Tetrahedron*, **1992**, *48*, 335-340.
10. Johnson, S.M.; Paul, I.C.; King, G.S.D. *J. Chem. Soc.(B)*, **1970**, 643-649.
11. Stevenson, G.R.; Forch, B.E. *J. Am. Chem. Soc.*, **1980**, *102*, 5985-5988.
12. Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Cryst.*, **1980**, *B36*, 3146-3148.
13. Pilati, T.; Simonetta, M. *Acta Cryst.*, **1976**, *B32*, 1912-1913.
14. Dobler, M.; Dunitz, J.D. *Helv. Chim. Acta*, 1965, 48, 1429-1440.

15. Dewar, M.J.S. *J. Am. Chem. Soc.*, **1952**, *74*, 3341-3345.

16. Bremser, W.; Hagen, R.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta*, **1969**, *52*, 418-431.

17. Favini, G.; Simonetta, M.; Sottocornola, M.; Todeschini, R. *J. Chem. Phys.*, **1981**, *74*, 3953-3960.

18. Roth, W.R.; Böhm, M.; Lennartz, H.-W.; Vogel, E. *Angew. Chem., Int. Edn. Engl.* **1983**, *22*, 1007-1008; *Angew. Chem. Suppl.*, **1983**, 1379-1387.

19. Bird, C.W. *Tetrahedron*, **1996**, *52*, 9945-9952.

20. Dauben Jr., Hyp.J.; Wilson, J.D.; Laity, J.L. in *Nonbenzenoid Aromatics*, Ed. Snyder, J.P.; Academic Press New York, **1971**, *2*, 167-206.

21. Destro, R.; Simonetta, M.; Vogel, E. *J.Am. Chem. Soc.*, **1981**, *103*, 2863-2865.

22. Tückmantel, W.; Andree, G.; Seidel, A.; Schmickler, H.; Lex, J.; Kraka, E.; Haug, M.; Cremer, D.; Vogel, E *Angew. Chem., Int. Edn. Engl.*, **1985**, *24*, 592-594.

23. Destro, R.; Pilati, T.; Simonetta, M. *Acta Cryst.*, **1977**, *B33*, 940-942.

24. Destro, R.; Simonetta, M. *Acta Cryst.*, **1977**, *B33*, 3219.

25. Mugnoli, A.; Simonetta, M. *Acta Cryst.*, **1974**, *B30*, 2896-2898.

26. Gramaccioli, C.M.; Mimun, A.S.; Mugnoli, A.; Simonetta, M. *Acta Cryst.*, **1972**, *B28*, 2365-2370.

27. Destro, R.; Gavezzotti, A.; Simonetta, M. *Acta Cryst.*, **1982**, *B38*, 1352-1354.

28. Destro, R.; Pilati, T.; Simonetta, M.; Vogel, E. *J. Am. Chem. Soc.*, **1985**, *107*, 3185-3191.

29. Destro, R.; Pilati, T.; Simonetta, M.; Vogel, E. *J. Am. Chem. Soc.*, **1985**, *107*, 3192-3196

30. Ganis, P.; Dunitz, J.D. *Helv. Chim. Acta*, **1967**, *50*, 2369-2378.

31. Lex, J.; Vogel, E.; Simonetta, M. *Acta Cryst.*, **1983**, *C39*, 770-771.

32. Gramaccioli, C.M.; Mugnoli, A.; Pilati, T.; Raimondi, M.; Simonetta, M.*J. Am. Chem. Soc.*, **1973**, *95*, 3149-3154.

33. Destro, R.; Simonetta, M. *Tetrahedron*, **1982**, *38*, 1443-1446.

34. Vogel, E.; Püttmann, W.; Duchatsch, W.; Schieb, T.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Edn. Engl.* **1986**, *25*,720-723.

35. Vogel, E.; Schieb, T.; Schulz, W.H.; Schmidt, K.; Schmickler, H.; Lex, J. *Angew. Chem., Int. Edn. Engl.*, **1986**, *25*,723-725.

36. Favini, G.; Simonetta, M.; Todeschini, R. *J. Chem. Phys.*, **1983**, *78*, 1895-1897.

37. Destro, E.; Ortoleva, E.; Simonetta, M.; Todeschini, R. *J. Chem. Soc., Perkin Trans. II*, **1983**, 1227-1231.

38. Vogel, E.; Kürschner, U.; Schmickler, H.; Lex, J.; Wennerström, O.; Tanner, D.; Norinder, U.; Krüger, C. *Tetrahedron Lett.*, **1985**, *26*, 3087-3090.

39. Lange, W.; Haas, W.; Schmickler, H.; Vogel, E. *Heterocycles*, **1989**, *28*, 633-638.

40. Destro, R.; Simonetta, M. *Acta Cryst.*, **1979**, *B35*, 1846-1852.

41. Bianchi, R.; Destro, R.; Simonetta, M. *Acta Cryst.*, **1979**, *B35*, 1002-1005.

42. Cotton, F.A. "*Chemical Applications of Group Theory*", Interscience, New York, 1963, p.136.

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