On Aromatic Stability of Oxygen- Imino-, and Sulfur-Bridged [18]Annulenes

J. V. Knop (a), M. Milun (b) (1), and N. Trinajstić (b)

(a) Rechenzentrum der Universität Düsseldorf, 4000 Düsseldorf, F. R. Germany and

(b) The Rugjer Bošković Institute, P. O. B. 1016, 41001 Zagreb, Croatia, Yugoslavia

Oxygen-, imino-, and/or sulfur-bridged [18]annulenes are studied using the A_S-index of aromatic stabilization. Theoretical predictions, which indicate that these compounds should differ among themselves in their aromatic properties, correlate nicely with the available experimental findings. Unknown compounds of this class: [18]annulene imino-dioxide and [18]-annulene oxide-imino-sulfide are predicted to be aromatic and good candidates for preparation. The same prediction is also reached for 1,10-diaza[18]annulene.

A set of conjugated systems with a peripheral 18 π-electrons exhibiting interesting aromatic properties have been recently reported by Badger and co-workers (2-9). In these systems the internal hydrogen atoms of [18]-annulene (see Figure 1) have been replaced by heteroatom bridges (see Figure 2).
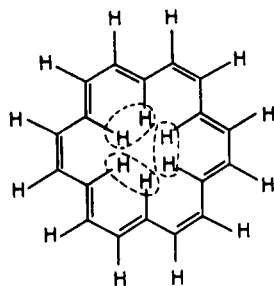

Figure 1. [18]annulene.

From the combinatorial point of view (if we consider only O-, NH-, and/or S-bridges) there are ten such systems possible, but only the following have actually been prepared: [18]annulene trioxide (1) (4,7), [18]annulene dioxide-sulfide (2) (5,8), [18]annulene oxide-disulfide (3) (4,6), [18]annulene trisulfide (4) (2,3), and [18]annulene imino-disulfide (8) (9). In addition, the synthesis of [18]-annulene oxide-imino-sulfide (10) was announced in reference 9.

Experimental evidence (*e.g.*, reactivity, nmr and uv spectra) (2-9), indicates that these compounds differ considerably in their aromatic character from the parent
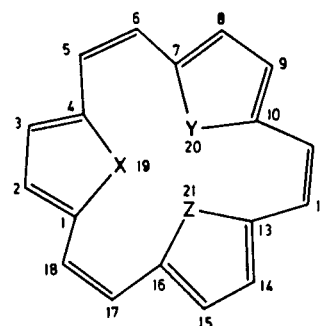

Figure 2. Atomic and skeletal structure of bridged [18]-annulenes.

1	X = Y = Z = O	[18]annulene trioxide
2	X = Y = O, Z = S	[18]annulene dioxide-sulfide
3	X = O, Y = Z = S	[18]annulene oxide-disulfide
4	X = Y = Z = S	[18]annulene trisulfide
5	X = Y = O, Z = NH	[18]annulene imino-dioxide
6	X = O, Y = Z = NH	[18]annulene diimino-oxide
7	X = Y = Z = NH	[18]annulene triimino
8	X = Y = S, Z = NH	[18]annulene imino-disulfide
9	X = S, Y = Z = NH	[18]annulene diimino-sulfide
10	X = O, Y = S, Z = NH	[18]annulene oxide-imino-sulfide.

compound [18]annulene (10-13) and that they also differ among themselves. Thus, for example, the chemical shift criterion ascribes aromatic character to trioxide (1) and dioxide-sulfide (2), and polyene (non-aromatic) character

Table

HMO (a) Energies (in β units) of Bridged Annulenes, Corresponding Reference Structures, and
Values of Aromatic Stabilization per Electron (A_S/N)

Molecule	E_π (Conjugated Molecule)	E_π (Reference Structure)	A_S/N	Status (b) Theoretical Prediction	Experimental Evidence
[18]annulene	23.035	22.680	0.020	A	aromatic (10-13)
[18]annulene trioxide (1)	35.321	34.914	0.017	A	aromatic (4,7)
[18]annulene dioxide-sulfide (2)	33.780	33.502	0.012	A	aromatic (4,7)
[18]annulene oxide-disulfide (3)	32.239	32.090	0.006	NA	polyenic (4,6)
[18]annulene trisulfide (4)	30.701	30.678	0.001	NA	polyenic (2,3)
[18]annulene iminodioxide (5)	34.994	34.751	0.010	A	unknown
[18]annulene diimino-oxide (6)	34.669	34.588	0.003	NA	unknown
[18]annulene triimino (7)	34.346	34.425	-0.003	NA	unknown
[18]annulene imino-disulfide (8)	31.916	31.927	0.000	NA	polyenic (9)
[18]annulene diimino-sulfide (9)	33.131	33.176	-0.002	NA	unknown
[18]annulene oxide-imino-sulfide (10)	34.139	33.339	0.033	A	unknown

to oxide-disulfide (3), trisulfide (4), and imino-disulfide (8), respectively. This difference in the aromatic character may be attributed partially to the greater aromaticity of thiophene (pyrrole) than the furan ring system (14) (thus, for example, one may think of [18]annulene trisulfide as three thiophene units joined by ethylene groups) and partially to the greater steric requirements of the sulfur atoms and/or imino groups when compared with oxygen atoms.

Earlier theoretical studies have been concerned only with the individual systems of this series in the course of their synthesis being published ([18]annulene trisulfide, [18]annulene trioxide) (15,16). No theoretical study comparing 1-10 has been reported besides the single attempt (17) to compare 1-4 by considering the correlation of the change in the bond order of the C_5-C_6, C_{11}-C_{12}, and C_{17}-C_{18} bonds with the localization of ethylene group charge density, i.e. with the smaller charge density delocalization of the π system as a whole. Therefore, it appears that bridged annulenes are a suitable set of molecules to study using the index of aromatic stabilization (A_S) of Milun, et al. (18), which is close in its concept (19) to the REPE (resonance energy per electron) index of Hess and

Schaad (20). Besides the intrinsic theoretical interest in this series, there is considerable interest in the chemistry of these molecules according to several review articles of a recent date (13, 21-23).

The index of aromatic stabilization per electron (A_S/N) is evaluated using the simple relation (18-20):

$$A_S/N = (1/N)\left\{E_\pi \text{ (conjugated structure) - } E_\pi \text{ (reference structure)}\right\},$$

where N is the total number of π electrons in the system (18 here). The E_π (reference structure) in the present work is approximated by

$$E_\pi \text{ (reference structure) = n } E_\pi \text{ (five-membered heterocycle)} + n_1 E_. + n_2 E_.$$

where $E_.$ and $E_.$ are parameters usually interpreted (24) as "polyene" single (E_{C-C}, E_{C-N}, ...) and double ($E_{C=C}$, $E_{C=N}$, ...) bond energies, respectively, and n, n_1, and n_2 are the numbers of five-membered heterocycles, single and double bonds, respectively. The E_π (conjugated structure) and E_π (five-membered heterocycle) are calculated using Hückel theory (though generally speaking any other more sophisticated π-approximation MO theory could be employed) and the heteroatomic parametrization scheme of Hess and Schaad (25-27). The values of E_{C-C} (0.52 β) and
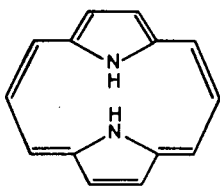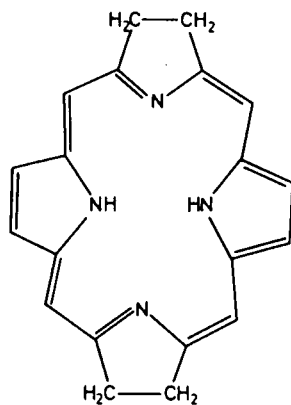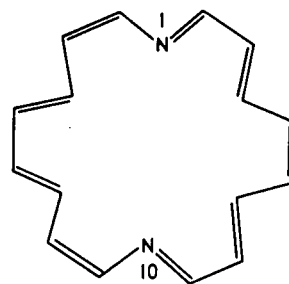
Figure 3. 1,4:8,11-bisimino[14]annulene.

12

Figure 4. 18 π-electron porphin.

E$_{C=C}$ (2.00 β) are adopted from our earlier work (18,28). The results of our calculations are listed in the Table. (A$_s$/N) index indicates 1, 2, 5, and 10 to be aromatic according to criterion (A$_s$/N) > 0.010 β and the others nonaromatic. Quite correctly [18]annulene is predicted to be aromatic. Experimental evidence (2-13) is in accordance with calculations. For example, the uv spectrum of [18]annulene trioxide is remarkably similar to that of tridehydro[18]annulene and similar to that of [18]annulene itself. As the other extreme [18]annulene trisulfide reacts with bromine by addition. It is interesting to note that [18]annulene imino-dioxide (5) is predicted to be borderline aromatic. but this compound is still unknown. Therefore, if there are any difficulties involved in the preparative work on this compound, they must be related to unfavourable stereochemistry of NH group within [18]-annulene ring. On the other hand, this compound is certainly a better candidate for synthesis than [18]annulene imino-disulfide (8) which preparation has been reported years ago (9).

The most interesting prediction of our model is that [18]annulene oxide-imino-sulfide (10) should be aromatic compound. Unfortunately, the synthesis of 10. announced in reference 9, has not been published yet. Of course, the

13

Figure 5. 1,10-diaza[18]annulene.

simplicity of the model may lead to an erroneous prediction in this case because it neglects the unfavourable effects due to the size of S and NH.

Though our results agree well with the known facts about the molecules of this series, we have tested our model on some related molecules and have obtained agreement with experiment again. For example, a recent synthesis of [14]annulene diimino (11) (see Figure 3), by Flitsch and Peters (29) has shown that this compound is aromatic. (A$_s$/N) for this molecule is 0.016 β. Because of this, we hope that our predictions may produce a stimulus for further preparative efforts leading to compounds 5 and 10.

Note that 18 π-electron porphin (30) (tetrahydroporphin (12), see Figure 4) is also related to heterobridged-annulenes, and may be regarded as a derivative of the hypothetical 1,10-diaza[18]annulene (13) (see Figure 5).

(A$_s$/N) values are 0.053 β and 0.063 β for tetrahydroporphin and 1,10-diaza[18]annulene, respectively. Therefore, the latter compound seems to be also a good candidate for preparation.

REFERENCES AND NOTES

(1) Permanent address: The Pharmaceutical and Chemical Works PLIVA, 41000 Zagreb, Croatia, Yugoslavia.

(2) G. M. Badger, J. A. Elix, and G. E. Lewis, *Proc. Chem. Soc. London*, 82 (1964).

(3) G. M. Badger, J. A. Elix, and G. E. Lewis, *Aust. J. Chem.*, 18, 70 (1965).

(4) G. M. Badger, J. A. Elix, G. E. Lewis, U. P. Singh, and T. M. Spotswood, *Chem. Commun.*, 269 (1965).

(5) G. M. Badger, J. A. Elix, G. E. Lewis, U. P. Singh, and T. M. Spotswood, *ibid.*, 492 (1965).

(6) G. M. Badger, J. A. Elix, and G. E. Lewis, *Aust. J. Chem.*, 257 (1966).

(7) G. M. Badger, J. A. Elix. and G. E. Lewis, *ibid.*, 19, 1221 (1966).

(8) G. M. Badger, J. A. Elix, and U. P. Singh, *ibid.*, 19, 1461 (1966).

(9) G. M. Badger, G. E. Lewis, and U. P. Singh, *ibid.*, 20, 163 (1967).

(10) F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962).

(11) L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *ibid.*, **84**, 4307 (1962).

(12) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohman, G. Di Mayo, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc. Spec. Publ.*, **21**, 75 (1967).

(13) R. C. Haddon, V. R. Haddon and L. M. Jackman, *Top. Curr. Chem.*, **16**, 103 (1971).

(14) N. Trinajstić, *Rec. Chem. Prog.*, **32**, 85 (1971).

(15) C. A. Coulson and M. D. Poole, *Proc. Chem. Soc. London*, 220 (1964).

(16) N. Trinajstić, *Croat. Chem. Acta*, **37**, 307 (1965).

(17) N. Trinajstić, *Monatsh. Chem.*, **98**, 2077 (1967).

(18) M. Milun, Ž. Sobotka, and N. Trinajstić, *J. Org. Chem.*, **37**, 139 (1972).

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

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

(21) P. J. Garratt and M. Y. Sargent, in "Advances in Organic Chemistry," E. C. Taylor and H. Wynberg, Eds., Interscience, New York, 1968, Vol. 6, p. 1.

(22) M. J. Cook, A. R. Katritzky, and P. Linda, in "Advances in Heterocyclic Chemistry," A. R. Katritzky and A. J. Boulton, Eds., Academic Press, London, 1974, Vol. 17, p. 256.

(23) M. V. Sargent and T. M. Cresp, *Top. Curr. Chem.*, **57**, 111 (1975).

(24) See, for example, M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, 1969, p. 176.

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

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

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

(28) M. Milun, *M. Sci. Thesis*, University of Zagreb, 1973.

(29) W. Flitsch and M. Peters, *Tetrahedron Letters*, 1293 (1975).

(30) R. B. Woodward and V. Škarić, *J. Am. Chem. Soc.*, **83**, 4676 (1961); R. B. Woodward, *Ind. Chim. Belge*, 1293 (1962).