PERKIN 2

Möbius and Hückel spiroaromatic systems†

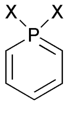
Henry S. Rzepa* and Kieron R. Taylor

Department of Chemistry, Imperial College, London, UK SW7 2AY

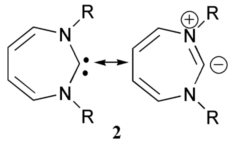
Received (in Cambridge, UK) 20th June 2002, Accepted 16th July 2002
First published as an Advance Article on the web 5th August 2002

We propose a novel class of spiroaromatic ring systems characterised by having a common phosphorus atom in which each ring can independently exhibit either Möbius or Hückel π-electron aromaticity.

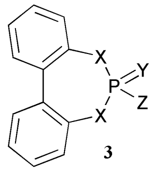
Conventionally constituted aromatic rings can fuse by sharing a mutual bond between two sp^2 hybridised carbon or hetero atoms; (Hückel) ring aromaticity is achieved by parallel overlap of the p-orbitals, forming π molecular orbitals with $4n + 2$ electron occupancy. Although the normal maximum coordination for the aromatic ring atoms is three, Wang and Schleyer[1] have recently shown that four-coordinate phosphinines (**1**), with *e.g.* X = F, Cl, OR, can also exhibit Hückel-like π-aromaticity of the ring.



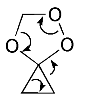
1



2



3



4

An alternative to parallel overlap of the p-orbitals is a 180° phase shift in the p_π–p_π overlap, (ideally) delocalised over the entire ring, to form a so-called Möbius system. This category of aromatic ring, first proposed by Heilbronner in 1964,[2] has been much studied recently.[3–7] For example, the formal 8π 4*n* electron ylide **2**, adopts a C_2 symmetric distortion as a stabilising mode to the otherwise planar 4*n* anti-aromatic Hückel form. Compounds derived by replacing the C^-/carbene atom in **2** with a tri- or tetracoordinate phosphorus atom as in **3** are known for both X = O[8] and X = N,[9] where Y and Z can either be hetero-atoms or be part of *e.g.* a cyclophosphazene ring. The latter example comprises what we term a spiroaromatic ring system in which two aromatic rings are fused by sharing a single atom rather than by a mutual bond. The term spiroaromatic has been previously used[10] to describe two independent aromatic ring systems joined by an sp^3 carbon atom, which is itself not part of any aromatic ring; we propose here a definition which differs in that the *e.g.* P(V) spiro atom can itself participate in the aromatic conjugation.

Several of these systems illustrated by **3** exhibit significant chiral catalytic ability as *e.g.* metal ligands[8h] for enantioselective trapping of arene oxides. The chirality derives from C_2-like symmetry of the 7-ring, but this is normally attributed to the steric effects of the two benzo groups, rather than deriving from aromatising stabilisation. Spiro-conjugation in the sense that we use, but as a transition state property, has also been proposed for so-called coarctate reactions (*e.g.* **4**)[11] for which a 4*n* σ-electron Möbius-like transition state requires the central atom to be tetrahedral (and to be square planar for a $4n + 2$ process). We have recently suggested[12] that this concept of coarctate aromaticity could be extended to minima in the potential energy surface, where the coarctate atom would be a four-coordinate bromine at the intermediate for Br^+ transfer reactions of alkenes. Combining the concepts illustrated by **1**–**4** led us to speculate about the generality of a novel class of aromatic molecule formed by conjugated rings sharing a mutual atom rather than a mutual bond, and whether any aromaticity manifested might be a local phenomenon associated just with each ring, or an intrinsic property of the combined coarctate system.[11] Here we report model calculations investigating these propositions.

Computational procedure

Molecular structures were optimised using Gaussian98[13] at the closed shell B3LYP/6-31G(d) level. Calculations of NICS values[14] were conducted either at the ring centroid only for rings with C_2 distortions, or at the ring centroid and 1 Å above the ring centroid [NICS(0) and NICS(1) respectively] for the essentially planar rings. Coordinates are available as electronic supplementary information (ESI). †

Results and discussion

The systems **5**–**10** were designed to explore both formal 4*n* π-electron occupancy in the ring A component of the spirocyclic system (systems **5**, **6**, **9**, **10**) and $4n + 2$ occupancy (systems **7**, **8**). Likewise ring B can have either $4n + 2$ (**5**–**8**) or 4*n* (**9**, **10**) π occupancy as either a phosphacarbocycle (**6**, **8**, **10**) or a cyclophosphazene (**5**, **7** or **9**) ring. Of these models, systems **5** and **7** have close analogy to known molecules.[8] Thus analogues of **5** differing only in dibenzo substitution of ring A and in tri- rather than mono-substitution at each phosphorus are known, and likewise for **7**. *Ab initio* B3LYP/6-31G(d) energies and geometries are listed in Table 1. †

To avoid concealing the electronic conformational preference of the ring, we calculated the sterically unhindered parent ring systems in most cases. The ring substituents R = H and also R = F were studied, the latter having being shown to enhance Möbius aromatic character in particular.[4–6] With **5** and **6**, X = O, only a C_2 symmetric conformation could be located but for R = F, X = NF, two conformations could be located, that with C_2 symmetry being of lower energy than that with C_s symmetry. This result contrasts with the conformational surface found[6] for the related heteropine ring systems **11**, for which C_s symmetric conformations are invariably lower in energy than the C_2 Möbius forms. This reinforces the interpretation that the C_2 symmetry in **5** and **6** arises from Möbius electronic contributions rather than originating entirely from steric factors.

The NICS values for **5** and **6** show essentially non-aromatic characteristics for ring A with R = H, X = NH, O, true also

---

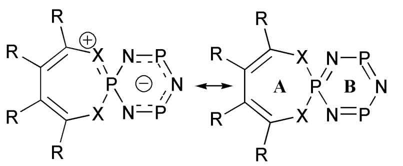
† Electronic supplementary information (ESI) available: coordinates for computed and experimental geometries. See http://www.rsc.org/suppdata/p2/b2/b205988f/

DOI: 10.1039/b205988f

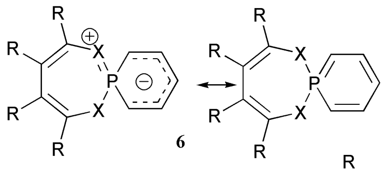
Table 1 B3LYP/6-31G(d) Calculated energies (hartree) and NICS[a] values (ppm) for **5**–**10**

Substituents	Energy	NICS[a]	Substituents	Energy	NICS[a]
5, X = O, R = H	−1493.59245	1.0 (−2.2)/−0.4	**5**, X = NH, R = H	−1453.84743	1.9 (−1.8)/−0.3
5, X = O, R = benzo	−1800.91060	1.5 (−1.7)/1.2			
5, X = O, R = F	−1890.49767[b]	0.9 (−2.3)/−5.0	**5**, X = NF, R = F	−2049.05166 (2.8)[c]	1.5 (−2.0)/−9.6
6, X = O, R = F	−1237.02783[b]	−7.9 (−7.7)/−5.9	**6**, X = NF, R = F	−1395.58808 (7.0)[c]	−7.7 (−7.6)/−11.6
6, X = S, R = F	−1882.94836	−5.3 (−5.6)/−9.5			
6, X = O, R = F, As[d]	−3129.40995	−7.6 (−8.0)/−7.8	**6**, X = NF, R = F, As[d]	−3287.97290	−7.3 (−7.8)/−12.2
7, X = O, R = F	−1614.62798	0.3 (−2.8)/−7.8	**7**, X = NF, R = F	−1773.19255 (5.2)[e]	2.4/−9.2
8, X = O, R = F	−961.16074	−8.8 (−8.6)/−7.1	**8**, X = NF, R = F	−1119.72821 (4.0)[e]	−7.7 (−7.5)/−9.2
9, X = O, R = F	−1494.32476	−0.9 (0.2)/−4.5	**9**, X = NF, R = F	−1652.88226	0.4 (0.6)/−8.6
10, X = O, R = F, R′ = H	−1159.51846	2.6/−4.8	**10**, X = NF, R = F, R′ = H	−1318.07670	5.2/−8.3
10, X = O, R = F, R′ = F	−1457.18499	−17.2/−4.6	**10**, X = NF, R = F, R′ = F	1615.74390 (1.3)[f]	−16.2/−8.3

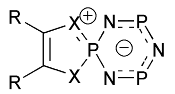
[a] NICS(0) value at ring B centroid [NICS(1) value 1 Å above ring B centroid]/NICS(0) value at ring A centroid. [b] Geometry optimisation converges to C_2 symmetric conformation. [c] Relative energy (kcal mol^{-1}) of C_s symmetric conformation. [d] As replacing P. [e] Relative energy (kcal mol^{-1}) of *anti*-conformation, with no symmetry. [f] Relative energy (kcal mol^{-1}) of chiral diastereoisomer.



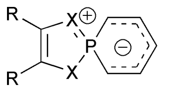
5, X=O, NR



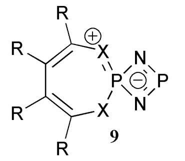
6



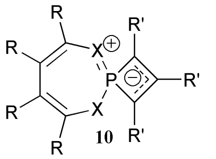
7



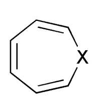
8



9



10



11, X=O, NR, S, PR

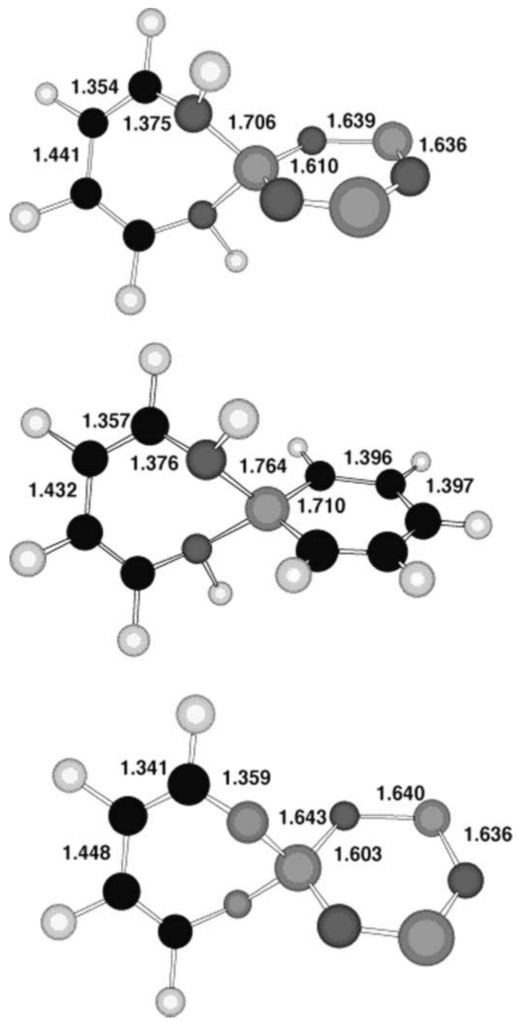


Fig. 1 Calculated B3LYP/6-31G(d) bond lengths (Å) for (a) **5**, X = NF; (b) **6**, X = NF; (c) **5**, X = O.

for the dibenzo system substituted analogue of **5**, X = O, R = benzo. We have noted previously[4] that such ring systems can exhibit a continuum between 8π planar anti-aromaticity and 8π non-planar Möbius aromaticity. The latter is enhanced by fluorine substituents, and accordingly with **6**, X = NF, R = F, ring A now exhibits an aromatic negative NICS(0) value [compared to benzene for which NICS(0) ~−10 ppm]. Where ring B is a phosphabenzene, it too shows modest aromatic character, as reported previously by Wang and Schleyer.[1] The cyclophosphazene system however appears only very mildly aromatic (Table 1) using the NICS(1) criterion [and slightly anti-aromatic using the NICS(0) probe], a property not previously reported, and rather surprising given the essential planarity of this ring and the equivalence of all the ring bonds (Fig. 1). This may in part be related to the ability of the three nitrogen ring atoms in this ring to bear negative charge, favouring contributions such as the dipolar resonance form shown for **5**. Computed bond lengths support this interpretation, the X–P values for **5** being 1.706/1.643 Å (X = NF/O) compared with those in **6** of 1.764/1.698 Å (X = NF/O) (Fig. 1).

Finally in this category of ring, we note that the (experimentally unknown) ring system **6**, X = S, R = F, shows both rings to be significantly aromatic and the aromaticity is even more prominent with the arsenic analogue[15] of **6**, R = F, X = O.

Systems **7** and **8** are the formal 4*n* + 2 homologues of ring A. With X = O, ring A is essentially planar with only a small distortion to C_s symmetry, in agreement with observed structures.[16] NICS values show it to be aromatic. As before, the cyclophosphazene ring B is non-aromatic, whereas the phosphabenzene ring B is clearly aromatic. With X = NF, pyramidalisation of the nitrogen occurs in either *cis* or *trans* fashion. In each case, the *cis* form was of lower energy, and showed C_s symmetry, whereas the *trans* form had no symmetry, possibly due to a Jahn–Teller-like distortion of the anti-aromatic Möbius form of a 4*n* + 2 ring.

The pair of systems **9** and **10** reveal a Möbius conformation and NICS(0) values corresponding to aromaticity for ring A, and in the case of **6**, R = F, X = O, NF, also a C_2 Möbius non-planar aromatisation for the phosphacyclobutadiene ring B, especially when it too is fluorinated (R′ = F). As before, the O–P length for **9** (1.638 Å) is shorter than that for **10**, R′ = H (1.661 Å) or **10**, R′ = F (1.640 Å), indicating contributions from ionic forms.

Comparing the pair **5/9**, X = O, R = F, reveals the NICS(0) value for ring A to vary little (-4.5 to -5.0 ppm), whilst the essentially planar ring B changes from a formally $4n + 2$ π aromatic to a $4n$ π planar anti-aromatic system, reflected in a change of the NICS(1) value from -2.3 to 0.2 ppm. The NICS(0) value for ring B, which at the ring centroid also includes more paratropic contributions from the σ framework[13] reveals a small opposing trend. Similar trends occur for **5/9**, X = NF, R = F. The pair **6/10**, X = O, R = F, shows similar constancy for ring A (-5.9 to -4.6), whilst ring B varies from -7.9 to -17.2 ppm (changing from a formally $4n + 2$ π aromatic to a $4n$ π Möbius aromatic). An alternative way in which to count the π electrons is as a single ring system linked *via* a coarctate phosphorus atom involving some degree of dπ orbital participation, analogous to the transition state coarctic model proposed by Herges and co-workers.[11] For this model, **5/6** are 14 ($4n + 2$) electron systems whereas **9/10** are 12 ($4n$) π electron systems. The NICS values imply that the aromaticity is in fact localised to each ring, and does not follow coarctate rules, with the obvious caveat that measuring NICS values at individual ring centroids may not be an appropriate measure of overall coarctate aromaticity.

Conclusions

We conclude that spiro-conjugated rings can exhibit both conventional Hückel π aromaticity and for systems such as **5**, of which there are known analogues, more unusual Möbius contributions to the aromaticity in one ring. With phosphorus as the coarctate atom, each ring appears to sustain aromaticity associated with its own $4n$ or $4n + 2$ π-electron count. Spiro-aromatic systems where the aromaticity of each ring is more strongly coupled *via* the spiro atom remain an intriguing possibility, as do systems where the spiro atom could reveal square planar rather than tetrahedral geometry.

References

1 Z.-X. Wang and P. von R. Schleyer, *Helv. Chim. Acta*, 2001, **84**, 1578–1600.

2 E. Heilbronner, *Tetrahedron Lett.*, 1964, **29**, 1923.

3 M. Mauksch, V. Gogonea, H. Jiao and P. von R. Schleyer, *Angew. Chem., Int. Ed.*, 1998, **37**, 2395.

4 C. Kastrup, S. Oldfield and H. S. Rzepa, *Chem Commun.*, 2002, 642–643.

5 (*a*) S. Martin-Santamaria and H. S. Rzepa, *Chem. Commun.*, 2000, 1089; (*b*) S. Martin-Santamaria and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2372–2377.

6 W. L. Karney, C. J. Kastrup, S. P. Oldfield and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 2002, 388–392.

7 (*a*) R. P. Johnson and K. J. Daoust, *J. Am. Chem. Soc.*, 1996, **118**, 7381–7385; (*b*) R. W. A. Havenith, J. H. Van Lenthe and L. W. Jenneskens, *Int. J. Quantum Chem*, 2001, **85**, 52–60.

8 (*a*) I. Dez, J. Levalois-Mitjaville, H. Grützmacher, V. Gramlich and R. de Jaeger, *Eur. J. Inorg. Chem.*, 1999, 1673; (*b*) S. D. Pastor, S. P. Shum, R. K. Rodebaugh, A. D. Debellis and F. H. Clarke, *Helv. Chim. Acta*, 1993, **76**, 900; (*c*) K. Tani, T. Yamagata and K. Nagata, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 1274; (*d*) J. Hans, R. O. Day, L. Howe and R. R. Holmes, *Inorg. Chem.*, 1992, **31**, 1279; (*e*) O.-S. Jung, Y. T. Kim, Y.-A. Lee, Y. J. Kim and H. K. Chae, *Inorg. Chem.*, 1999, **38**, 5457; (*f*) H. R. Allcock, M. T. Stein and J. A. Stanko, *J. Am. Chem. Soc.*, 1971, **93**, 3173; (*g*) C. B. Dieleman, P. C. Kamer, J. N. H. Reek and P. W. N. M. Van Leeuwen, *Helv. Chim. Acta*, 2001, **84**, 3269–3280; (*h*) F. Bertozzi, P. Crotti, F. Del Moro, B. L. Feringa, F. Macchia and M. Pineschi, *Chem. Commun.*, 2001, 2606–2607; (*i*) D. Kumar and A. D. Gupta, *Macromolecules*, 1995, **28**, 6323–6329.

9 E. E. Nifantiev, A. I. Zavalishina, E. I. Orzhekovskaya, N. N. Nurkulov, L. K. Vasyanina, A. R. Bekker, V. K. Belskii and A. I. Stash, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1997, **123**, 89.

10 N. Horada, H. Ono, T. Nishiwaki and H. Uda, *J. Chem. Soc., Chem. Commun.*, 1991, 12753.

11 (*a*) R. Herges, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 255; (*b*) C. Berger, C. Bresler, U. Dilger, D. Geunenich, R. Herges, H. Rottele and G. Schroder, *Angew. Chem., Int. Ed.*, 1998, **37**, 1850.

12 F. Hernandez Blanco, D. C. Braddock, S. Martin-Santamaria and H. S. Rzepa, *Internet J. Chem.*, 2001, **4**, article 10.

13 Gaussian98 (Revision A.11), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

14 (*a*) P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.*, 1996, **118**, 6317; (*b*) H. Jiao and P. von R. Schleyer, *J. Phys. Org. Chem.*, 1998, **11**, 655.

15 L. K. Krannich, U. Thewalt, W. J. Cook, S. R. Jain and H. H. Sisler, *Inorg. Chem.*, 1973, **12**, 2304.

16 (*a*) H. R. Allcock, M. L. Levin and R. R. Whittle, *Inorg. Chem.*, 1986, **25**, 41; (*b*) U. Diefenbach, H. R. Allcock and K. B. Visscher, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 1215.