ORGANIC LETTERS

2008
Vol. 10, No. 24
5605−5608

Antiaromaticity in Distal Bisfluorenyl Dications Separated by Multiple Discrete Spacer Units

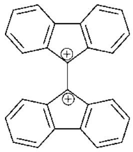
Bart J. Dahl and Nancy S. Mills*

Trinity University, San Antonio, Texas 78212

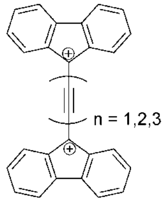
nmlls@trinity.edu

Received October 16, 2008

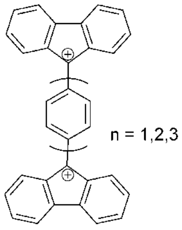
ABSTRACT



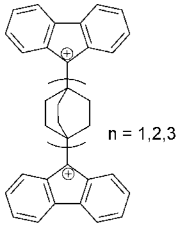
1



2a,b,c



3a,b,c



4a,b,c

The effect of spacers on the antiaromaticity of bisfluorenyl dications was examined. For systems such as 4a−c in which extensive delocalization of the positive charge through the π-system is not possible, a relationship based primarily on localized hyperconjugation as well as the distance between the fluorenyl systems and their antiaromaticity was demonstrated. Dications 2a−c and 3a−c also show the relationship, but it is further modulated by delocalization through the π-system. Calculated assessment of antiaromaticity was supported by experimental shifts for 2a,b and 3a−c.

Bisfluorenyl 1,2-carbodications, such as **1**, and numerous substituted analogues prepared via oxidation of neutral olefins with SbF_5 have been previously shown to be highly antiaromatic.[1−4] The kinetic stability of these dicationic species have allowed for laboratory generation and experimental confirmation of their antiaromaticity via NMR spectroscopy. In order to expand the scope of these studies and to afford routes to potentially less-stabilized dications, we have recently explored the antiaromaticity of spacer-separated dications **2a** and **3a** generated via superacid ionization of diols and diethers.[5] We have found that while the antiaromaticity of **2a**/**3a** was attenuated compared to **1**, they were both much more antiaromatic than analagous monocationic species. These results indicated that there was significant electronic communication between the charges through the spacer unit, forcing delocalization into the fluorenyl system. Additionally, dication **2a** was substantially more antiaromatic than **3a**, which could be the result of the closer distance between the fluorenyl systems in **2a** or the result of a different type of delocalization in the two systems. In order to further probe the effect of spacer units on the antiaromaticity of fluorenyl dications, we have expanded our studies to include multiple π-conjugating spacer separated dications **2b**,**c** and **3b**,**c** as well as dications separated by non π-conjugating bicyclo[2.2.2]octane spacers **4a−c**. This report describes the synthesis and characterization of **2b** and **3b**,**c** and is the first example of antiaromatic dications formed experimentally in which the cations are separated by multiple spacer units in succession. In addition, although we were not able to successfully prepare dications **2c** and **4a−c** experimentally, we report their antiaromaticity through calculation of NICS values for these species.

The synthesis of the precursors to **1**, **2a**, and **3a** have been reported previously.[5] Biphenyl alcohol **5b** was prepared from 4,4′-dibromobiphenyl and *t*-BuLi, followed by double ad-

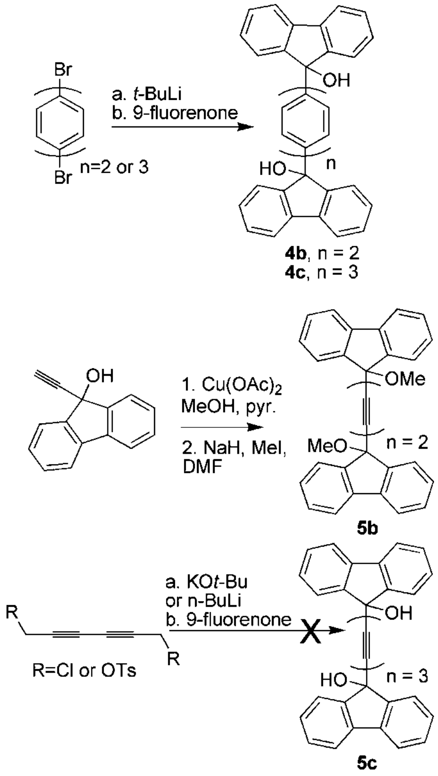
---

(1) Malandra, J. L.; Mills, N. S.; Kadlecek, D. E.; Lowery, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 11622–11624.
(2) Mills, N. S. *J. Am. Chem. Soc.* **1999**, *121*, 11690–11696.
(3) Mills, N. S.; Benish, M. A. *J. Org. Chem.* **2006**, *71*, 2207–2213.
(4) Mills, N. S.; Llagostera, K. B. *J. Org. Chem.* **2007**, *72*, 9163–9169.
(5) Dahl, B. J.; Mills, N. S. *J. Am. Chem. Soc.* **2008**, *130*, 10179–10186.

10.1021/ol802389n CCC: $40.75

dition of 9-fluorenone (Scheme 1). Terphenyl alcohol **5c** was prepared similarly from 4,4′-dibromoterphenyl. Diyne **6b** was prepared by an Eglinton homocoupling[6] of 9-ethynylfluorenol followed by methylation of the alcohols. Triyne **6c** could not be prepared from KO-*t*-Bu and 1,6-dichlorohexadiyne[7] or *n*-BuLi and the ditosyl derivative of 2,4-hexadiyne-1,6-diol[8] and subsequent addition to 9-fluorenone due to decomposition of the dianion intermediate. In both attempts, 9-fluorenone was recovered quantitatively.

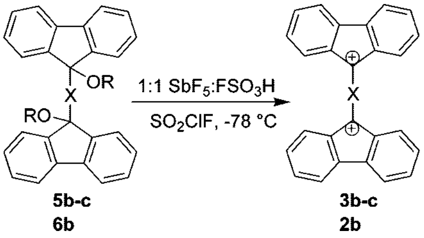
Scheme 1. Synthesis of the Dication Precursors



The dibromo precursor to **4a**, 1,4-dibromobicyclo-[2.2.2]octane,[9] was synthesized from the analagous dicarboxylic acid[10] via a double Cristol−Firth-modified Hunsdiecker reaction.[11] However, 9-fluorenone was recovered in near-quantitative yields (along with small amounts of 9-fluorenol) after attempts at dilithiation of this dibromo species and subsequent addition using methods identical to the synthesis of **3a**−**c**. It is known that the intermediate (4-bromobicyclo[2.2.2]octan-1-yl)lithium is unstable and will readily eliminate;[12] thus, the dilithiation could not occur. The precursors to **4b** and **4c** were to be prepared similarly and would also be predicted to be elusive via elimination of the monolithiated species, so no further attempts were made at synthesizing these species.

The neutral precursors **5b**,**c** and **6b** were then converted to their respective bisfluorenyl dications **3b**,**c** and **2b** via ionization with Magic acid in SO_2ClF at −78 °C (Scheme 2). The samples were quickly analyzed by ^1H and ^{13}C NMR.

Scheme 2. Generation of Spacer-Separated Dications



The experimental and calculated shifts for **2b** and **3b**,**c** are given in Table 1. The agreement between experimental and calculated shifts (shown in Figure 1 for **1**, **2a**,**b**, and **3a**−**c**) is good, correlation coefficient of 0.974, and supports the use of this basis set for the calculation of NICS values. The paratropic chemical shifts of the protons of the fluorenyl systems clearly demonstrate their antiaromaticity. The average values of the experimental ^1H shifts for the fluorenyl system in **3a**−**c** are 5.865 ppm,[5] 6.184 ppm, and 6.542 ppm, respectively. The average values of the experimental ^1H shifts for the fluorenyl system in **2a**,**b** are 5.520 ppm[5] and 5.551 ppm, respectively. This data indicates experimentally that the antiaromaticity of similar bisfluorenyl dicationic systems decreases as the distance between the individual fluorenyl cations increases.

Table 1. Experimental and Calculated[a] ^1H Chemical Shifts for **2b**, **3b**, and **3c**

^1H	**2b**(exp)	**2b**(calc)	**3b**(exp)	**3b**(calc)	**3c**(exp)	**3c**(calc)
1,8	5.712	7.034	6.377	7.532	6.665	7.456
2,7	5.357	6.728	5.971	7.003	6.338	7.192
3,6	5.891	7.291	6.377	7.497	6.749	7.627
4,5	5.244	6.688	5.971	7.097	6.414	7.317
ring 1 *o*′			7.141	8.251	7.192	8.252
ring 1 *o*″			7.220	8.432	7.333	8.378
ring 2 *o*′					7.368	8.382

[a] Shifts were calculated with the GIAO method and basis set B3LYP/6-311 g(d,p) on geometries optimized at basis set B3LYP/6-31 g(d).

The NICS$(1)_{zz}$[13,14] values for the fluorenyl system of **1**, **2a**−**c**, **3a**−**c**, and **4a**−**c** along with the distance between the

---

(6) Eglinton, G.; Galbraith, A. R. *Chem. Ind.* **1956**, *73*, 7–8.

(7) Hlavaty, J.; Kavan, L.; Sticha, M. *Perkin 1* **2002**, 705–706.

(8) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943–9.

(9) Dewar, M. J. S.; Goldberg, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 1582–6.

(10) Chang, H. X.; Kiesman, W. F.; Petter, R. C. *Synth. Commun.* **2007**, *37*, 1267–1272.

(11) Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961**, *26*, 280.

(12) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, n/a.

(13) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.

(14) Fallah-Bagher-Shaidaei, H.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 863–866.

positive charges calculated at the geometrical centers of the fluorenyl systems, are listed in Table 2. The relationship between the summation of NICS(1)$_{zz}$ and distance for **2a**−**c** and **3a**−**c** is shown in Figure 2a. If the primary mode of interaction between the two cationic fluorenyl systems was only the distance between them, then a linear relationship for the distance between the fluorenyl cations versus the antiaromaticity of the bisfluorenyl dications, NICS(1)$_{zz}$, would be expected.

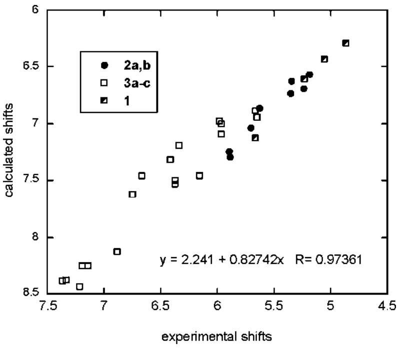


Figure 1. Relationship between experimental and calculated shifts for **1**, **2a**−**c**, and **3a**,**b**. Shifts were calculated with the GIAO method with basis set B3LYP/6-311 g(d,p) on geometries optimized with B3LYP/6-31 g(d).

However, it is clear from Figure 2a that there is a distinct difference between the distance versus NICS(1)$_{zz}$ plots of those systems containing alkynyl spacers **2a**−**c** and those containing aryl spacers **3a**−**c**. The slopes of the individual lines for **2a**−**c** and **3a**−**c** are very similar, and the primary difference between the two lines arises from their intercept values. This indicates that only when comparing dications containing similar spacer units can distance between cations be an accurate predictor of antiaromaticity. Thus, both the mode/effectiveness of delocalization and the distance between charges influences the antiaromaticity of the bisfluorenyl dications.

Table 2. NICS(1)$_{zz}$ for Each Ring of the Fluorenyl System^{a}, ΣNICS(1)$_{zz}$, the Magnetic Susceptibility Exalation, and the Distance between the Geometrical Centers of Each Fluorenyl System

	5-ring	6-ring	ΣNICS(1)$_{zz}$	distance (Å)
1	72.21	30.12	266.30	4.88
2a	70.32	28.23	253.55	7.49
2b	65.28	23.34	223.91	10.02
2c	61.84	20.27	204.75	12.58
3a	61.80	17.16	192.22	9.20
3b	54.35	9.95	148.53	13.53
3c	49.24	5.79	121.65	17.86
4a	62.12	14.97	184.13	9.24
4b	57.44	10.97	158.77	13.49
4c	55.23	9.00	146.47	17.85

[a] NICS(1)$_{zz}$ were calculated with the GIAO method using B3LYP/6-311g(d,p) on geometries optimized with B3LYP/6-31g(d).

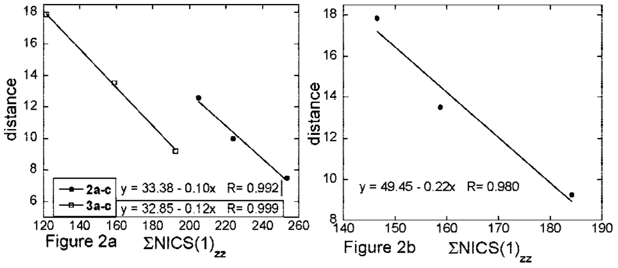


Figure 2. Relationship between ΣNICS(1)$_{zz}$ and the distance from the geometrical center of the fluorenyl ring system for **2a**−**c**, **3a**−**c**, and **4a**−**c**: (a) **2a**−**c** and **3a**−**c**; (b) **4a**−**c** only.

To further examine the effect that different spacer units have on the antiaromaticity of bisfluorenyl dications, **3a** and **2b** can be compared directly. These two dications have similar distances between the cations (9.20 and 10.02 Å), but the ΣNICS(1)$_{zz}$ values (192.22 and 223.91) are very different. The bisfluorenyl dication with the two alkynyl spacers **2b** is more antiaromatic than the species with one phenyl spacer **3a**. **2c** is more antiaromatic (204.75) than **3a** despite having an even larger distance (12.58 Å) between the fluorenyl cations. This effect is likely the result of more effective delocalization in phenyl systems and the relative ability of sp^2 vs sp hybridized carbons to support a positive charge.[15]

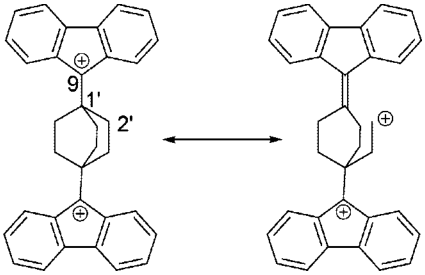
The spacer units in **2a**−**c** and **3a**−**c** are predicted to stabilize the bisfluorenyl dications primarily by delocalization of the positive charge of the π-system of the spacers. Increasing the number of spacer units should allow for more effective π bond delocalization of the charge on the fluorenyl system into the spacer units. This is illustrated by an average overall downfield chemical shift of the spacer protons in **3a** (6.885 ppm), **3b** (7.181 ppm), and **3c** (7.300 ppm). It is therefore interesting that the bicyclo[2.2.2]octyl spacers **4a**−**c**, which have no π electrons in the spacer units, are also able to attenuate antiaromaticity, as shown by a decrease in the ΣNICS(1)$_{zz}$, relative to **1**. Table 2 shows that there is a decrease in the ΣNICS(1)$_{zz}$ with an increase in the number of bicyclic spacers. Compound **4a** has almost the same distance between fluorenyl systems as **3a** yet it is less antiaromatic and presumably more stable. The modes of stabilization are clearly different by a comparison of the distance vs NICS(1)$_{zz}$ plots for all three systems. For dications **4a**−**c** (Figure 2b), the plot is linear but the slope of the line, −0.22, is greater than the slopes for both **2a**−**c** and **3a**−**c** (Figure 2a). While the bicyclic spacers cannot π conjugate, the units should be able to stabilize the dications through a type of hyperconjugation which allows a partial postive

---

(15) Delocalization into the triple bond would give an allenyl cation. The related vinyl cations have been shown to be less stable than alkyl ations: Seva Alem, K.; Lodder, G.; Zuilhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681–10690.

charge at the carbons of the spacer next to the bridgehead carbons. As Scheme 3 shows, hyperconjugation would result in a decrease in the calculated bond length between carbon-9 of the fluorenyl system and the bridgehead carbon of the bicyclo-octyl substituent and an increase in the length of the adjacent bond. Table 3 shows that hyperconjugation increases as the number of bicyclo[2.2.2]octyl spacers increases.

Scheme 3. Hyperconjugation in **4a**



Hyperconjugation is more effective as the dihedral angle of the C1′–C2 bond with the fluorenyl system approaches 90°. Adamantyl dications[16,17] also demonstrated an increase in carbodication stabilty with increasing charge separation.[18] In those systems, deshielding of the carbons corresponding to 2′ in **4a** was used as support for hyperconjugation. Table 3 also shows the change in chemical shift for **4a**–**c** for carbons 9 and 2′. For the species with the greatest hyperconjugation, carbon 2′ would be the most deshielded and the trends seen support the suggestion that there is increasing hyperconjugation with an increase in the number of biocyclo[2.2.2]octyl spacers. While one might also expect an upfield shift for carbon 9 as a function of the increased electron density from hyperconjugation, this effect is less important than the increase in stability and decrease in antiaromaticity seen with increasing hyperconjugation. We and others have shown that as the antiaromaticity of a fluorenyl system decreases, the ^{13}C NMR shift of carbon 9 moves downfield.[19] Addition of multiple bicyclic spacer units increases the through-space distance between the partial positive charges on the spacer units and thus facilitates hyperconjugation.

Table 3. Selected Bond Lengths (Å) and Dihedral Angles (deg) with Fluorenyl System Shown in Parentheses[1] and ^{13}C NMR Shifts for **4a**–**c**

	9–1′	1′–2′	1′–2′	1′–2′	C9	C2′
4a	1.5082	1.5721 (−63.9)	1.5652 (55.2)	1.5486 (−5.0)	232.6	33.9
4b	1.4983	1.5786 (−64.2)	1.5705 (54.7)	1.5473 (−5.1)	239.9	37.2
4c	1.4937	1.5822 (−64.2)	1.5721 (54.5)	1.5471 (−5.34)	243.0	38.9

[1] Geometries optimized at B3LYP/6-31g(d).

In conclusion, we have shown that both the distance between positively charged fluorenyl systems and the mode of charge delocalization affects the antiaromaticity of the spacer containing bisfluorenyl dications. Both alkynyl spacer systems **2a**–**c** and aryl spacer system **3a**–**c** can effectively delocalize the charge on the fluorenyl cations through π-conjugation. However, **3a**–**c** is much more effective at stabilizing that charge. Bisfluorenyl dications with bicyclo-[2.2.2]octyl spacers **4a**–**c** effectively stabilize the charge on the fluorenyl cation through hyperconjugation and attenuate the overall antiaromaticity relative to **1**. Additionally, this report describes the first example of antiaromatic dications (**2b** and **3b**,**c**) formed experimentally in which the cations are separated by multiple spacer units in succession.

Acknowledgment. We thank the Welch Foundation (Grant No. W-794) and the National Science Foundation (Grant Nos. CHE-0242227, CHE-0553589, CHE-0552292, and CHE-0138640) for their support of this research.

Supporting Information Available: Experimental details on the preparation of precursors to **2b**, **3b**, and **3c**, calculated geometries, dihedral angles, and energies for **2b**,**c**, **3b**,**c**, and **4a**–**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL802389N

---

(16) Heagy, M. D.; Wang, Q.; Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1995**, *60*, 7351–7354.

(17) Miller, G. P.; Jeon, I.; Wilson, G.; Athans, A. J. *Org. Lett.* **1999**, *1*, 1771–1773.

(18) Klumpp, D. A. *Chem. Eur. J.* **2008**, *14*, 2004–2015.

(19) Mills, N. S.; Malandra, J. L.; Burns, E. E.; Green, A.; Unruh, K. E.; Kadlecek, D. E.; Lowery, J. A. *J. Org. Chem.* **1997**, *62*, 9318–9322.