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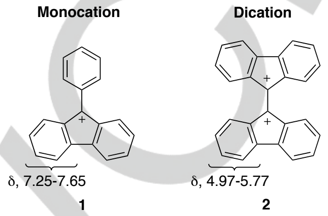
# Use of charge-charge repulsion to enhance π-electron delocalization into anti-aromatic and aromatic systems

Akinari Sumita,[b] Makafui Gasonoo,[a] Kenneth J. Boblak,[a] Tomohiko Ohwada,*[b] and Douglas A Klumpp*[a]

Dedicated to Professor George A. Olah on the occasion of his 90th birthday

**Abstract:** A series of 9-fluorenyl cations has been studied and it is shown that increasing charge on a heterocyclic substituent group enhances the antiaromatic character of the carbocation system. Similarly, a series of dibenzosuberenyl cations has been studied and increasing charge on a substituent group is shown to enhance aromatic character in the carbocation system. These studies include the direct observations of dicationic and tricationic species using stable ion conditions and low temperature NMR. The structures of these ions were further characterized using DFT calculations, confirming that highly-charged organic ions may exhibit unusual distributions of π-electrons and delocalization of electrons in 4n or 4n+2 π-systems.

The use of organic materials for electronic applications continues to be a very active field of research.[1] Organic materials offer distinct advantages over traditional inorganic materials in electronic components. This includes the ease of synthetic modifications, lower costs for syntheses and materials, as well as being amenable for quality control and large-scale processing. Despite the progress made in this area, there continues to be the need for new methods of controlling the electronic and magnetic states of organic materials. Several recent studies of stable organic ions have demonstrated that charge-charge repulsive effects may enhance π-electron delocalization in conjugated π-systems, including both 4n or 4n+2 π-electron systems.[2] For example, Mills and coworkers examined the mono- and dicationic fluorenyl ions (**1**-**2**, Scheme 1).[3] NMR studies showed an increasing degree of anti-aromatic or paramagnetic ring current in the dication **2** compared to the monocation **1**, as the fluorenyl ring $^1$H are significantly shifted upfield with the dication. Calculated nucleus-independent chemical shift (NICS) values are also consistent with the 4n π-system exhibiting greater anti-aromatic character in the dication **2** compared to the monocation **1**.[4]

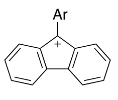


**Scheme 1.** $^1$H NMR data for fluorenyl cations **1** and **2**.

In the design of organic electronics, a critically important phenomenon involves the movement of holes, or cationic charge, through molecules and between molecules.[5] The fluorenyl cation (and the related dibenzosuberenyl cation) provide an ideal opportunity to study structural effects that may influence charge mobility within ionized structures. Our group has previously used protonated *N*-heterocycles in the generation of highly-charged cationic systems.[6] Besides enhancing the chemical reactivities within these superelectrophilic systems, protonated *N*-heterocycles are also capable of inducing charge migration in associated π-systems.[7] Herein, we describe our studies of isoelectronic and isosteric monocations, dications, and trications of the fluorenyl and dibenzosuberenyl cations. These cationic species are studied by low temperature NMR using stable ion conditions with further analysis using computational methods. The results are interpreted according to charge-charge repulsive effects on both the 4n and 4n+2 π-electron systems, leading to enhanced paramagnetic and diamagnetic ring current with charge delocalization.

## Results and Discussion

The phenyl-substituted fluorenyl cation (**3a**) and dibenzosuberenyl cation (**4a**) were previously studied by Olah and colleagues[8,9] and these ions are used for comparison to the more highly charged ions **3b-d** and **4b-c** generated in this study. Two routes were considered to prepare the cations: the aryl ketones (**5a-d**) should cyclize with dehydration to the fluorenyl cation while direct ionization of fluorenols (**6a-d**) or the dibenzosuberenols (**7a-c**) should form the respective cations.



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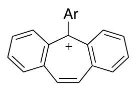

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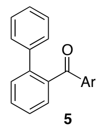

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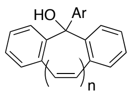

**6**, n=0
**7**, n=1

Ar = a: phenyl c: 2-pyrazinyl
b: 2-pyridyl d: 2-pyrimidyl

In $FSO_3H$-$SbF_5$-$SO_2ClF$ solution, ionization of aryl ketone **5b** and fluorenol **6b** provides clean access to the fluorenyl dication **3b** (Table 1). Thus, ion **3b** exhibits the expected twelve $^{13}$C NMR signals - with a carbocation resonance observed at δ

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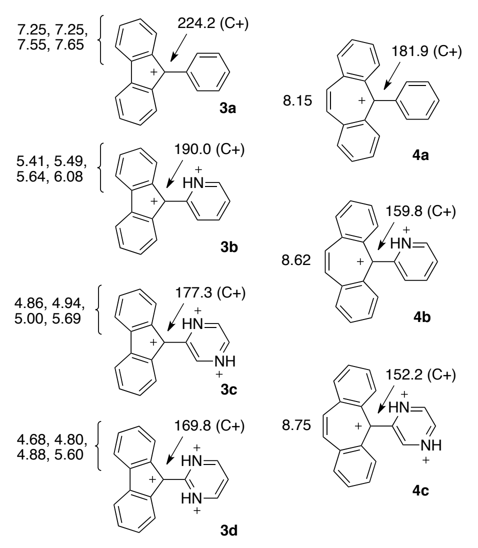
**Table 1.** Selected $^{1}$H and $^{13}$C NMR spectral data for fluorenyl- and dibenzosuberenyl cations (**3a-d** and **4a-c**).[a,b]



[a]Spectral data obtained from $FSO_3H$-$SbF_5$-$SO_2ClF$ solution at -40 °C ($d_6$-acetone external standard). [b]Data for **3a** taken from reference 6.

190 (see Supporting Information for a complete list of peaks). This carbocation signal is shifted considerably from the fluorenyl monocation (**3a**) reported by Olah, et al.,[8] as the carbocation center in **3a** is observed at δ 224 from a $FSO_3H$-$SO_2ClF$ solution. Additionally, the fluorenyl $^{1}$H signals are shifted upfield in the dication **3b** (δ 5.41-6.08) compared to the monocation **3a** (δ 7.25-7.65). Cyclization of substrate **5b** is a convenient means of generating the fluorenyl dication **3b**, so this method of generation was also used for ions **3c** and **3d**. Thus, ionization of the pyrazine-based ketone (**5c**) leads to the expected fluorenyl trication **3c**. Trication **3c** exhibits an even further upfield shift for the carbocation $^{13}$C resonance (δ 177) and upfield shift for the fluorenyl $^{1}$H signals (δ 4.86-5.69) – compared to the mono- and dicationic fluorenyl species (**3a,b**). Likewise, ionization of the 2-pyrimidyl ketone **5d** in superacid provides the fluorenyl trication **3d**. This ion also exhibits strong shielding of the fluorenyl ring protons and shielding of the carbocation $^{13}$C resonance. The $^{1}$H signals of the fluorenyl ring are observed at δ 4.68-5.60, while the carbocation $^{13}$C signal is observed at δ 169.8. In a recent report about the unsubstituted 9-fluorenyl cation, Sander et al. noted the difficulties associated with generating and observing the unstable fluorenyl cation.[10] Our studies show that acid-promoted cyclizations of biaryl ketones (**5**) provide convenient access to these cationic species.

The dibenzosuberenol substrates **7a-c** were also ionized in $FSO_3H$-$SbF_5$-$SO_2ClF$ and studied by low temperature NMR (Table 1). Alcohol **7a** ionizes cleanly to provide the monocationic species **4a**. In the $^{13}$C NMR spectrum, the carbinol $^{13}$C resonance of **6a** (δ 78.8) disappears and it is replaced by a new downfield signal at δ 181.9 – a signal attributed to the dibenzosuberenyl carbocation center. This observation is in accord with the results from Olah and Liang, where **4a** was observed from a $FSO_3H$ solution and the carbocation $^{13}$C resonance is found at δ 183.7.[9] With the pyridyl-substituted dibenzosuberenol **7b**, the dicationic **4b** is formed in superacid. The $^{1}$H NMR of the dication **4b** shows a modest downfield shift of ethenediyl signals compared to the monocation **4a**. The $^{13}$C NMR reveals a sizable upfield shift, as the dication **4b** possesses a carbocation signal at δ 159.8. The isoelectronic trication **4c** was generated by ionization of pyrazinyl-substituted dibenzosuberenol (**7c**). The $^{1}$H NMR spectrum shows further downfield shift of the ethenediyl protons (δ 8.75) and the $^{13}$C NMR shows a carbocation signal with modest upfield shift compared to the dication **4b**.

The increasing positive charge leads to significant changes in the NMR spectra of both the fluorenyl cations and dibenzosuberenyl cations. These changes may be understood as a consequence of charge-induced enhancement of paramagnetic and diamagnetic ring current in the respective cationic systems. Our results are consistent with the findings of Mills and coworkers and their earlier work with fluorenyl cations.[3] That is, an increasing charge on the substituent group leads to a greater degree of charge delocalization in the fluorenyl cation, and consequently, increasing anti-aromatic character in the 12π-electron system. In the case of the dibenzosuberenyl cations, increasing charge on the substituent group leads to a similar delocalization of π-electrons, but as a 4n+2 π-system, there is an increasing aromatic character and diamagnetic ring current observed in the NMR spectra.

This chemistry was further studied by theoretical calculations.[11] (Anti-)aromaticity of π-systems is a multiphasic issue. However, thermochemical evaluations were inappropriate in our system, because thermodynamic (de)stabilization of the system included both effects arising from (anti)aromatization and increase/decrease of charge-charge repulsion. Therefore, we focused on the evaluation of (anti-)aromaticity in terms of magnetic and geometrical aspects. The nucleus-independent chemical shifts (NICS) method has been used previously to evaluate magnetic properties of the aromaticity and anti-aromaticity of π-systems, including fluorenyl mono- and dications.[12] NICS calculations were done on the present systems at the CPCM-B3PW91/6-311++G(2d,p) (solvent = $CF_3SO_3H$) level with the test atom calculated 1 Å above the center of the 5, 6, and 7 carbon rings of the optimized fluorenyl and dibenzosuberenyl cation structures. To reduce the influence of σ-aromaticity, we used NICS(1)zz values, along with $NICS(1)_{iso}$ values.[13] In the case of the fluorenyl cations (**3a-d**), the $NICS(1)_{zz}$ values become increasingly positive as the charge on the heterocycle increases – a result consistent with increasing anti-aromatic character (Figure 1).

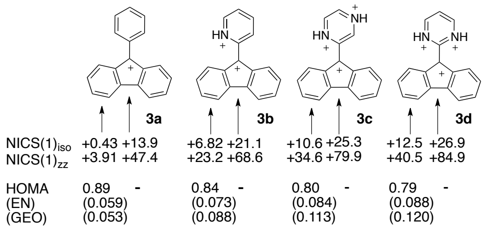


**Figure 1.** Calculated NICS values (6 and 5-carbon rings) and HOMA (6-carbon rings) values for cations (**3a-d**).

Besides generating anti-aromatic character, delocalization of the $\pi$-electrons in ions **3a-d** should lead to decreasing aromaticity in the benzenoid rings. Aromatic character may be evaluated using the calculated harmonic oscillator model of aromaticity (HOMA) index – a computational model based on the variance of ring-perimeter bond lengths (see Supporting Information).[14,15] HOMA index can be divided into two terms; a bond weakening/strengthening term (EN) and a measured bond alternation term (GEO). When the HOMA index values are calculated for the series of ions **3a-d**, a consistent increase in the GEO values is seen in the benzenoid ring as the charge increases at the heterocycle – verifying large-scale delocalization of the $\pi$-electrons of the fluorenyl cation.

The dibenzosuberenyl cations were also examined by NICS calculations and the results are in agreement with the trends observed from low temperature NMR studies (Figure 2).

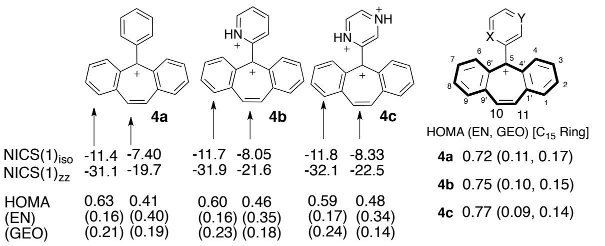


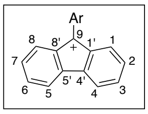
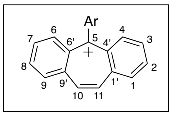
**Figure 2.** Calculated NICS values and HOMA values for cations (**4a-c**).

Thus, the NICS(1)$_{zz}$ values decrease through the series **4a** -> **4b** -> **4c**, an observation consistent with increasing aromatic character. Above the benzenoid rings, the NICS(1)$_{zz}$ value (six-carbon ring) does not change from **4a** to **4c**. On the other hand, analysis of the NICS(1)$_{zz}$ properties above the seven-carbon ring reveals a consistent decrease from -19.7 in the monocation (**4a**), to -21.6 in the dication (**4b**), to -22.5 in the trication (**4c**). The HOMA values were also calculated for the dibenzosuberenyl cations **4a-c**. Several notable observations may be made regarding ions **4a-c**. First, the HOMA values for the six-carbon ring decreases in the series **4a** -> **4b** -> **4c**. This is consistent with greater delocalization of the carbocation charge as a result of the charge-charge repulsive effects. In the same series, there is a modest increase in HOMA values in the seven-carbon ring and in the fifteen-carbon perimeter. This trend may also be understood to be a consequence of increasing charge delocalization – less character of a triarylmethyl cation and more character of a 4n+2 $\pi$-system. Interestingly, the changes in NICS(1)$_{zz}$ and HOMA values are comparatively small in the dibenzosuberenyl cations **4a-c**, when compared to the changes in NICS(1)$_{zz}$ and HOMA values for the fluorenyl cations **3a-d**.

In order to further evaluate charge-charge repulsive effects in these ions, natural population analysis (NPA) of atomic charges was calculated (CPCM-MP2/6-31G+(d) level; solvent = $CF_3SO_3H$). The results show a clear trend within the series of fluorenyl ions **3a** -> **3d**: as the amount of positive charge increases on the heterocyclic substituent, the NPA charge at the carbocation center (C9) becomes more negative, while the other fluorenyl ring carbons (i.e., C3 and C4) and hydrogen atoms become increasingly positive (Table 2). The complete list of NPA charges is found the Supporting Information. These data are consistent with the previous results (NICS(1)$_{zz}$ and HOMA studies) revealing greater delocalization of the cationic charge throughout the fluorenyl ring with the more highly charged ions. The increasing NPA charges on the fluorenyl ring hydrogen atoms also suggest electronic effects involving both $\pi$- and $\sigma$-electrons. While charge-charge repulsion clearly leads to delocalized $\pi$-electrons, there is also an inductive electron effect involving the C-H $\sigma$-bonds. However, because the anti-aromaticity is strong, $^1$H signals of dication (**3b**) or trication (**3c**, **3d**) appeared upfielded (Table 1). It is also notable that the summation of carbon and hydrogen NPA charge increases at the fluorenyl ring - proceeding from 0.756 for **3a** to 1.118 for **3d**. This sizable increase in positive charge may be interpreted as evidence for two effects: donation of some electron density from the phenyl group to the fluorenyl ring system in **3a** and removed of some electron density from the fluorenyl ring and towards the highly charged heterocyclic substituents in **3b-d**.

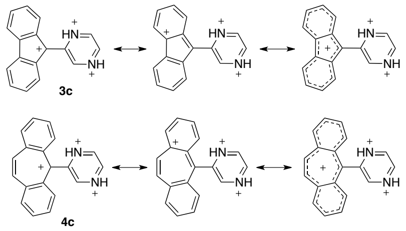
The NPA charges were also calculated for the dibenzosuberenyl cations (Table 2) and the results are consistent with the previous data – increasing charge on the substituent heterocyclic rings enhance delocalization of the carbocation charge center. Thus, the calculated NPA charge on C5 decreases from 0.299 to 0.163 to 0.101 through the series **4a** to **4c**. Likewise, the NPA charges increase on the atoms of the central seven carbon ring (i.e., C-4') and the fused benzenoid rings (i.e., C1 and C3). These data reveal an increasing delocalization of positive charge throughout the dibenzosuberenyl cation as the charge increases on the heterocyclic substituent. The results are in accord with the experimental NMR data and the calculated NICS and HOMA values.

**Table 2.** CPCM-MP2/6-31G+(d) ($CF_3SO_3H$) calculated NPA charges of selected fluorenyl ring and dibenzosuberenyl ring carbon atoms and ring hydrogen atoms (hydrogen charges in parentheses).[a]

| | | | | | |
|---|---|---|---|---|---|
| | | **3a** | **3b** | **3c** | **3d** |
|  | C3<br>(C3-H) | -0.112<br>(0.264) | -0.062<br>(0.269) | -0.040<br>(0.273) | -0.028<br>(0.275) |
| | C4' | 0.027 | 0.058 | 0.035 | 0.053 |
| | C9 | 0.438 | 0.362 | 0.289 | 0.209 |
| Summation of total NPA charge (C,H) on fluorenyl ring system | | 0.756 | 0.973 | 1.074 | 1.118 |
| | | **4a** | **4b** | **4c** | |
|  | C1<br>(C1-H) | -0.247<br>(0.262) | -0.225<br>(0.267) | -0.224<br>(0.271) | |
| | C4' | 0.029 | 0.031 | 0.040 | |
| | C3<br>(C3-H) | -0.239<br>(0.265) | -0.210<br>(0.271) | -0.184<br>(0.275) | |
| | C5 | 0.299 | 0.163 | 0.101 | |
| Summation of total NPA charge (C,H) on dibenzosuberenyl ring system | | 0.968 | 1.034 | 1.093 | |

[a] Complete list of charges provided in Supporting Information

The above data present a consistent picture: the highly-charged heterocyclic substituents enhance charge delocalization in the fluorenyl cations (**3**) and dibenzosuberenyl cations (**4**). Thus, charge-charge repulsive effects tend to favor the delocalized resonance forms of trications **3c** and **4c**. This is seen in the greater anti-aromaticity and aromaticity of the respective π-systems.



## Conclusions

In this study, we have shown that cationic 4n+2 or 4n π-electron systems may show enhanced aromaticity or anti-aromaticity through charge-charge repulsive effects. Evidence for the charge-induced π-electron delocalization includes observing by NMR greater paramagnetic ring current in the fluorenyl cation system (4n π-system) and diamagnetic ring current in the dibenzosuberenyl cation system (4n+2 π-system). These results were further supported by theoretical calculations, as NICS calculations confirmed increased anti-aromatic character as charge increased adjacent to the fluorenyl cation. Likewise, charge was correlated to increased aromatic character in the dibenzosuberenyl cation series. Both the NICS and HOMA calculations revealed an increasing aromatic character as the charge increased adjacent to the dibenzosuberenyl cation. These results have several implications. They confirm that highly-charged organic ions possess extensive delocalization of π-electrons. Moreover, the results suggest that charge-charge repulsive interactions may be a useful tool in the design and manipulation of the electronic and magnetic states of organic materials. Charged *N*-heterocycles are conveniently incorporated into organic structures and the results show that they may be effectively used to control the distribution of electrons in organic structures.

## Experimental Section

The biaryl ketones **3b-d** were prepared by the reactions of 2-lithiobiphenyl with the corresponding hetrocyclic nitriles, using a method described previously.[16] The dibenzosuberenols **4a-c** were prepared from the reactions of aryllithium reagents with 9-dibenzosuberenone following a literature procedure.[17]

Low temperature NMR studies: The magic acid solution is first prepared by dissolving ca. 0.5 g $SbF_5$ in 1 mL of $FSO_3H$ in a test tube (sealed with a cork). After thorough mixing (Vortex mixer), the tube is placed in a dry ice-acetone bath maintained at -40 °C. To this solution is added 0.5 mL of pure $SO_2ClF$ and the acidic media is kept cold. The desired substrate (50-70 mg) is then added to the superacid solution and this solution is thoroughly mixed (while keeping the tube cold). When most of the substrate has dissolved, 0.5 mL of the solution is transferred into a cold NMR tube (-40 °C) and the NMR tube is quickly sealed with a coaxial insert containing $d_6$-acetone as the external standard. NMR analysis is then done using a previously cooled NMR instrument/probe.

## Acknowledgements

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**Keywords:** aromatic • anti-aromatic • dication • trication • superacid

[1] *Organic Electronics*, Eds.: F. Cicoira, C. Santato, Wiley-VHC: Weinheim, Germany, 2013.

[2] a) T. Suzuki, T. Ohwada, K. Shudo *J. Am. Chem. Soc.* **1997**, *119*, 6774-6785. b) T. Ohwada, K. Shudo *J. Am. Chem. Soc.* **1988**, *110*, 1862-1870. c) C. Blackburn, C. F. Childs *J. Chem. Soc., Chem. Commun.* **1984**, 812-813. d) G. A. Olah, J. L. Grant, R. J. Spear, J. M. Bollinger, A. Serianz, G. Sipos, *J. Am. Chem. Soc.* **1976**, *98*, 2501–2507. e) P. J. Stang, G. Mass, D. L. Smith, J. A. McCloskey, *J. Am. Chem. Soc.* **1981**, *103,* 4837-4845.

[3] a) N. S. Mils, S. P. McClintock *Chem. Commun.* **2012**, *48*, 8099-8101. b) N. S. Mils, C. Tirla, M. A. Benish, A. J. Rakowitz, L. M. Bebell, C. M. M. Hurd, A. L. M. Bria *J. Org. Chem.* **2005**, *70*, 10709-10716. c) S. P. McClintock, N. S. Mils *J. Org. Chem.* **2011**, *76*, 10254-10257.

[4] N. S. Mils *J. Am. Chem. Soc.* **1999**, *121*, 11690-11696.

[5] H. Chung, Y. Ding *J. Mat. Chem. C: Mat. Opt. Elec. Dev.* **2016**, *4*, 3915-3933.

[6] a) K. N. Boblak, D. A. Klumpp *J. Org. Chem.* **2014,** *79*, 5852-5857. b) R. R. Naredla, E. K. Raja, D. A. Klumpp, *Tetrahedron Lett.* **2013**, *54*, 3245-3247.

[7] a) R. R. Naredla, C. Zheng, S. O. Nilsson Lill, D. A. Klumpp *J. Am. Chem. Soc.* **2011**, *133*, 13169-13175. b) M. Gasonoo, R. R. Naredla, S. O. Nilsson Lill, D. A. Klumpp *J. Org. Chem.* manuscript in press, DOI 10.1021/acs.joc.6b02220.

[8] G. A. Olah, G. K. S. Prakash, G. Liang, P. W. Westerman, K. Kunde, J. Chandrasekhar, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1980**, *102*, 4485-4492.

[9] G. A. Olah, G. Liang *J. Org. Chem.* **1975**, *40*, 2108-2116.

[10] P. Costa, I. Trosien, M. Fernandez,-Oliva, E. Sanchez-Garcia, W. Sander *Angew. Chem., Int. Ed.* **2015**, *54*, 2656-2660.

[11] M. J. Frisch, et al., Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

[12] a) R. Gershoni-Poranne, A. Stanger *Chem. Soc. Rev.* **2015**, *44*, 6597-6615. b) R. Das, A. Chakraborty, S. Pan, P. K. Chattaral *Curr. Org. Chem.* **2013**, *17*, 2831-2844.

[13] a) P. v. R. Schleyer, H. Jiao, N. J. R. v. E. Hommes, V. G. Malkin, O. Malkina, *J. Am. Chem. Soc.* **1997***, 119*, 12669. B) P. v. R. Schleyer, Z. W. Manoharan, X. B. Kiran, H. Jiao, R. Puchta, N. J. R. v. E. Hommes, *Org. Lett.* **2001**, *3*, 2465.

[14] T. M. Krygowski, M. K. Cyranski *Chem. Rev.* **2001**, *101*, 1385-1419.

[15] NICS(1)$_{zz}$ parameters are not largely be affected by change of the charge of the fluorenyl cation, or the number of hetero atoms in the hetero-ring (See SI).

[16] K. N. Boblak, M. Gasonoo, Y. Zhang, D. A. Klumpp *J. Org. Chem.* **2015**, 80, 11948-11952.

[17] F. J. Villani, C. A. Ellis, R. F. Tavares, C. Bigos *J. Med. Chem.*, **1964**, 7, 457–460.

10.1002/chem.201606036

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Layout 1:

# COMMUNICATION

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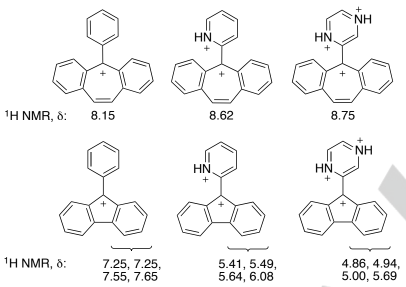

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