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Correlation of Substituent Effects and Energy Levels of the Two Lowest Excited States of the Azulenic Chromophore

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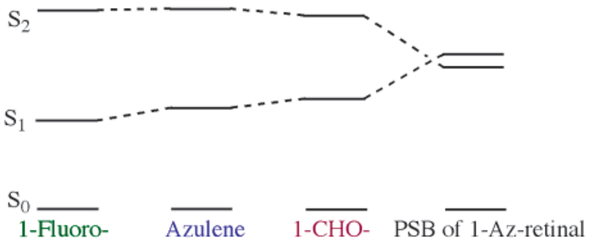
ABSTRACT



Experimental and calculated data show that the relative energy levels of the two lowest excited states of azulene are sensitive to the nature and position of substituents on the nonalternant hydrocarbon. Extending such investigations led to a rational explanation for some of the baffling data on azulenic bacteriorhodopsin analogues in the literature.

Azulene is well known for its unusual excited state properties. Its characteristic blue color is due to the exceptionally low-lying S_1 state, a consequence of a reduced amount of repulsive energy between the two electrons in the nearly orthogonal HOMO and LUMO orbitals.[1] Its unique property of exclusive emission from S_2[2] is due to the unusually large S_1−S_2 energy gap and the presence of a chemical channel for rapid relaxation of the S_1 state.[3] We now would like to demonstrate that the energy separation of the S_1 and S_2 states can be controlled by a proper choice of the nature and position of the substituents on the azulenic chromophore. The results provide a colorful array of azulenic derivatives and additionally a logical explanation for some of the “baffling” data in the literature on analogues of bacteriorhodopsin (bR).

The Hückel HOMO and LUMO orbitals of azulene are shown in Figure 1, clearly reflecting a small overlap of electrons occupying the two orbitals. The different density of the two electrons occupying the two orbitals accounts for the alkyl substituent effects on their absorption properties.[1a] Thus, the red-shift of the S_1 level of 1-methylazulene from azulene was attributed to selective destabilization of the HOMO and not the LUMO. Conversely, the S_2 level is unaffected by 1-alkyl substitution.

The π-donating effect of a fluoro substituent in perturbing electronic excitations of aromatic systems is well documented.[4] When applied to the azulenic system, the F resonance donating effect could provide a handle for amplifying the above-noted perturbation brought about by alkyl substituents. Recently, we reported the preparation of several fluoroazulenes.[5] In Table 1 are listed the absorption maxima of 1-fluoro- and 1,3-difluoroazulene (**1** and **2**) along

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[1] (a) Heilbronner, E. *Tetrahedron* **1963**, *19*, supplement, 289−313. (b) Michl, J.; Thulstrup, E. W. *Tetrahedron* **1976**, *32*, 205−209.

[2] (a) Beer, M.; Longuet-Higgins, H. C. *J. Chem. Phys.* **1955**, *23*, 1390−1391. (b) Viswath, G.; Kasha, M. *J. Chem. Phys.* **1956**, *24*, 574−577. (c) Sidman, J. W.; McClure, D. S. *J. Chem. Phys.* **1956**, *24*, 757−763.

[3] Bearpark, B. R.; Vreven, T. *J. Am. Chem. Soc.* **1996**, *118*, 169−175.

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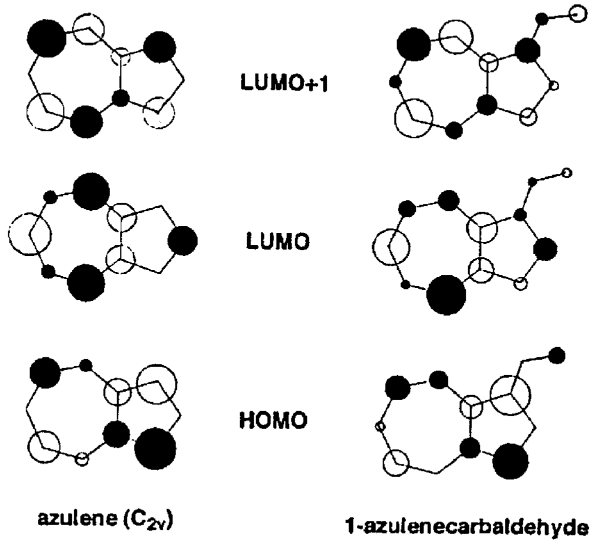
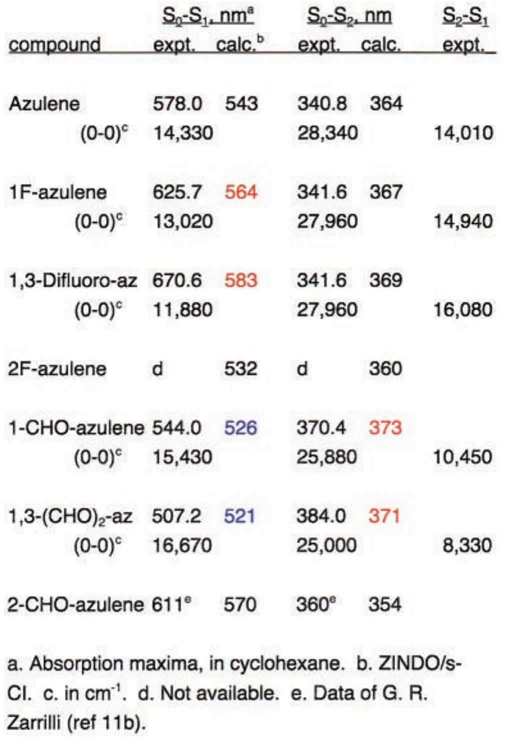


Figure 1. AM1 Hückel MO's (coefficients of HOMO and the two lowest LUMO's) of azulene, C_{2v} (left), and 1-azulenecarbaldehyde, **3** (right).

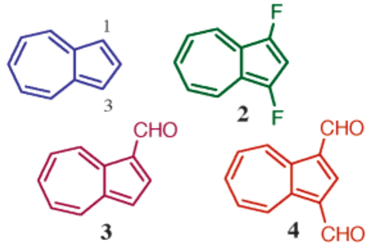
Table 1. Observed (λ_{max}) and Calculated State Energies of Azulene and Substituted Azulenes



compound	S_0-S_1, nm[a] expt.	calc.[b]	S_0-S_2, nm expt.	calc.	S_2-S_1 expt.
Azulene	578.0	543	340.8	364	
(0-0)[c]	14,330		28,340		14,010
1F-azulene	625.7	564	341.6	367	
(0-0)[c]	13,020		27,960		14,940
1,3-Difluoro-az	670.6	583	341.6	369	
(0-0)[c]	11,880		27,960		16,080
2F-azulene	d	532	d	360	
1-CHO-azulene	544.0	526	370.4	373	
(0-0)[c]	15,430		25,880		10,450
1,3-(CHO)$_2$-az	507.2	521	384.0	371	
(0-0)[c]	16,670		25,000		8,330
2-CHO-azulene	611[e]	570	360[e]	354	

a. Absorption maxima, in cyclohexane. b. ZINDO/s-CI. c. in cm^{-1}. d. Not available. e. Data of G. R. Zarrilli (ref 11b).

with those of azulene. The fluorinated compounds show a lowering of the S_1 states while retaining the original level of the S_2 state. Thus, a red-shift of the S_1 band is accompanied by an increase of the S_1-S_2 gap. For example, in the case of 1,3-difluoroazulene, the 0−0 energy gap of the upper S_1-S_2 transition (16 080 cm^{-1}) is, in fact, significantly larger than the gap for the lower S_0-S_1 transition (11 880 cm^{-1}), a rarity for any organic compound.[6] Selective red-shift of the S_1 band allowed transmission of some yellow light, turning the characteristic blue color of azulene to green for **2**.



It is also possible to incorporate structural features that lead to a closing of the S_1-S_2 gap. In Table 1 are also listed the UV−vis absorption maxima of 1-azulenecarbaldehyde, **3**, and 1,3-azulenedicarbaldehyde, **4**.[7] Obviously, there is an increase of the S_1 levels (blue shift) and a decrease of the S_2 levels (red-shift). We believe this is due to dual effects from the electron-withdrawing and conjugative properties of the aldehyde group(s). For reasons outlined above, electron-withdrawing substituents at the 1,3-positions are expected to cause a decrease of the HOMO and LUMO+1 levels. Also, conjugation is expected to have a significant perturbation only on HOMO and LUMO+1, due to the large coefficients at C-1 and C-3. However, in addition to an increase in the energy of HOMO and a decrease in the energy of LUMO+1, the resultant more delocalized orbitals will be less "azulene-like" in character. The latter would mean a reduced orthogonality between the HOMO and LUMO compared to the parent azulene, leading to an increase in the repulsive energy between the two electrons occupying the two orbitals (see atoms 1, 2, 3, and 6 in Figure 1). Thus, inductive and part of the conjugative (with added e−e correlation) effects work in concert leading to the surprising observation of a blue-shift of the long wavelength band upon an apparent increase in conjugation.[8] Furthermore, the simultaneous blue-shift of the S_1 band and red-shift of the S_2 band results in progressive loss of the blue light and transmission of the red light. Therefore, **3** is purple and **4** is red.

The above conclusions on relative energy levels of the two lowest excited states are based on qualitative reasoning using the Hückel MO's. We have now carried out higher level calculations including configuration interactions (ZINDO/s-CI) on compounds **1**−**4**.[9] Their calculated absorption maxima are listed in Table 1. The red-shift and the blue-shift trends for respectively the fluoro and formyl azulenes

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(4) See, for example: Michl, J. *Tetrahedron* **1984**, *40*, 3845−3934.

(5) Muthyala, R. S.; Liu, R. S. H. *J. Fluorine Chem.* **1998**, *89*, 173−175.

(6) In the same vein, the red-shift of the 2-, 4-, 6-, and/or 8-cyanoazulenes has been attributed to selective lowering of the LUMO: Schmitt, S.; Baumgarten, M.; Simon, J.; Hafner, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1078−1081.

(7) Compound **4** was prepared according to a literature procedure: Hafner, K.; Bernhard, C. *Angew. Chem.* **1957**, *69*, 533.

(8) For absorption spectra of azulenes with other electron-withdrawing substituents, see: Dhingra, R. C.; Poole, J. A. *Chem. Phys. Lett.* **1968**, *2*, 108−109.

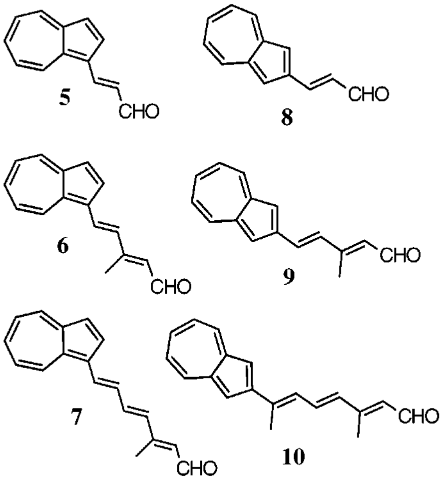
are clearly in good agreement with the experimental data.

In analyzing the spectra of the azulene chromophore containing electron-withdrawing substituents, we recall the red-shifted protonated Schiff bases (PSB) of the 1-azulenic retinal analogues in studies of near-IR absorbing bR analogues.[10] In contrast, Nakanishi and co-workers reported earlier that 2-azulenic retinal analogues failed to yield any red-shifted bR analogues.[11] (Available experimental data on PSB's are listed in Table 2.) The red-shifted bands of the PSB of 1-azulenic retinal analogues were not usually accompanied by a low-extinction, long-wavelength band, characteristic of the azulene chromophore.[10] We note that the blue-shift of the S_1 band of **3** and **4** is accompanied by a red-shift of the corresponding S_2 band (Table 1). Since a PSB of an azulenic retinal is in reality an azulene appended with a strong electron-withdrawing, conjugative substituent, we postulated possible closing of the S_1-S_2 gap in PSB's (or even crossing of the two states). We have, therefore, carried out ZINDO/s-CI calculations of UV excitation energies of the methyl Schiff bases (SB) and PSB's of azulenic enal (**5**), dienal (**6**), and trienal (**7**). Data in Table 2 show that from the SB to the PSB of **5** there is a significant closing of the two lowest transition bands and for the dienal **6** and the trienal **7**, the more allowed HOMO to LUMO+1 transition (marked in brown color) is significantly red-shifted, becoming lower in energy than that of the forbidden HOMO to LUMO transition (i.e., a crossing of the two states). This accounts for the strongly absorbing, much red-shifted absorption bands of the PSB and bR pigments of **6** and **7** and other 1-azulenic retinal analogues. For the 2-substituted series, the small coefficient at C-2 for both HOMO and LUMO+1 (Figure 1) suggests that the allowed S_0-S_2 transition is insensitive to extending conjugation. Experimental data for analogues **9** and **10** (Table 2) are indeed in agreement with this expectation. However, calculated results, while suggesting a similar trend, are not fully compatible with experimental data (Table 2), e.g., the calculated red-shifted, forbidden HOMO−LUMO band was not detected experimentally. Further calculations with the inclusion of the counteranion and medium effects will be attempted, hopefully to resolve the problems with the 2-substituted PSB's as well as mimicking the cyanine-like pigments observed for the azulene bR analogues.[10]

Table 2. Calculated[a] and Experimental[b] λ_{max} of Schiff Bases (SB) and Protonated Schiff Bases (PSB) of Azulenic Retinal Analogues **5**−**10**

	SB			PSB		
	expt.	calc.		expt.	calc.	
compound	nm	S_n-S_0	f[c]	nm	S_n-S_0	f[c]
5		590	0.063		468	0.146
	418[d]	394	0.609	494[d]	450	1.164
6		596	0.023	515	518	1.742
	414	405	1.022		497	0.041
7		607	0.082	541	587	2.246
	430	414	1.200		520	0.006
8	e	551	0.029	e	667	0.049
		370	0.167		428	1.325
9		546	0.025		663	0.042
	401[d]	379	0.488	443[d]	488	1.799
10	e	546	0.024		645	0.055
		391	1.009	450[f]	544	2.175

a. ZINDO/s-CI, methyl SB. b. Butyl SB. c. Oscillator strength. d. Guaiazulenic analogs (ref 10). e. Not available. f. Data of Zarrilli (ref. 11b).



In conclusion, qualitative reasoning using Hückel MO's has been successfully applied to account for observed absorption spectra of several substituted azulenes. Extension of the same reasoning provides a simple explanation for the contrasting azulenic bR data in the literature. The conclusions have been confirmed by higher level ZINDO/s-CI calculations.

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(9) For recent calculations on other azulenic compounds, see: Wang, P.; Zhu, P.; Ye, C.; Asato, A. E.; Liu, R. S. H. *J. Phys. Chem.* **1999**, *103*, 7076−7082.

(10) (a) Asato, A. E.; Li, X.-Y.; Mead, D.; Patterson, G. L. M.; Liu, R. S. H. *J. Am. Chem. Soc.* **1990**, *112*, 7398−7399. (b) Liu, R. S. H.; Krogh, E.; Li, X.-Y.; Mead, D.; Colmenares, L. U.; Thiel, J. R.; Ellis, J.; Wong, D.; Asato, A. E. *Photochem. Photobiol.* **1993**, *58*, 701−705.

(11) (a) Nakanishi, K.; Derguini, F.; Rao, V. J.; Zarrilli, G.; Okabe, M.; Lien, T.; Johnson, R. *Pure Appl. Chem.* **1989**, *61*, 361−364. (b) Zarrilli, G. R. Ph.D. Thesis, Columbia University, 1984.

(12) For the enal, only data of the guaiazulene analogues of **5** are available in the literature.