

## Research Note

# Why are the Elemental Nonmetals (F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, S<sub>8</sub>, P<sub>4</sub>) of so Many Hues or of Any Hues and Where is the Chromophore? Insight into *Intera-X-X* Bonds

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## ABSTRACT

A unique approach is used to relate the HOMO-LUMO energy difference to the difference between the ionization potential (IP) and electron affinity (EA) to assist in deducing not only the colors, but also chromophores in elemental nonmetals. Our analysis focuses on compounds with lone pair electrons and  $\sigma$  electrons, namely X<sub>2</sub> (X = F, Cl, Br, I), S<sub>8</sub> and P<sub>4</sub>. For the dihalogens, the [IP – EA] energies are found to be: F<sub>2</sub> (12.58 eV), Cl<sub>2</sub> (8.98 eV), Br<sub>2</sub> (7.90 eV), I<sub>2</sub> (6.78 eV). We suggest that the *interahalogen* X–X bond itself is the chromophore for these dihalogens, in which the light absorbed by the F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> leads to longer wavelengths in the visible by a  $\pi \rightarrow \sigma^*$  transition. Trace impurities are a likely case of cyclic S<sub>8</sub> which contains amounts of selenium leading to a yellow color, where the [IP – EA] energy of S<sub>8</sub> is found to be 7.02 eV. Elemental P<sub>4</sub> with an [IP – EA] energy of 9.09 eV contains a tetrahedral and  $\sigma$  aromatic structure. In future work, refinement of the analysis will be required for compounds with  $\pi$  electrons and  $\sigma$  electrons, such as polycyclic aromatic hydrocarbons (PAHs).

## INTRODUCTION

Many inorganic species are brightly colored. Common examples of this phenomenon generally involve transition metal cations, for example, hydrated cobalt(II) and copper(II) sulfates are bright pink and blue, respectively, while the corresponding alkaline earth hydrated magnesium (II) and calcium (II) sulfates are both colorless. This dichotomy can be understood in terms of the partially filled d orbitals of the metal cation, and their interaction with ligands (e.g. colorless H<sub>2</sub>O) thereby allowing for low energy electronic transitions between ground state and excited state species. The energy of electronic transitions of both closed and open shell compounds often lies in the same range as visible light and therefore these species are identified as “colored”.

The alkaline earth cations, like most organic compounds, have closed shell electron configurations, require greater excitation

energy, and are therefore “colorless”. However, conjugation of multiple bonds either with other multiple bonds and/or suitable substituents in organic compounds decrease the energy gap between ground and excited states, and thereby the resulting color often lies in the visible range (1). Examples include the natural polyene pigments, carotene and lycopene.

The molecular ground state is understood as resulting from the lowest energy “arrangement” of orbitals with their occupying electrons. Electronic excitation accompanying the absorption of light most generally means an electron has been “promoted” to a higher energy orbital. In the current context, it is the electron in the occupied molecular orbital with the highest energy (HOMO) that is removed, ionized, “moved” to the lowest energy unoccupied orbital (LUMO). For closed shell organic compounds, we thus speak of  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  HOMO-LUMO transitions that are defined by which electrons are promoted and to where. Species bound solely by single/ $\sigma$ -bonds with electronically innocuous substituents are usually colorless. As such, aliphatic hydrocarbons and their derivatives, characterized by their C–C and C–H bonds, do not absorb visible light. Indeed, even the “infinitely large” compounds that have only such bonds, for example, diamond and polyethylene, are colorless. Here, we focus our attention on the elemental nonmetals X<sub>2</sub> (X = F, Cl, Br, I), S<sub>8</sub> and P<sub>4</sub>. We ask: *From where do the colors arise? Where are the chromophores?* To address these questions, we use an approach to relate the HOMO-LUMO energy difference to the difference between the ionization potential (IP) and electron affinity (EA).

## METHODS

The approach taken here analyzes the removal of an electron from the HOMO of the molecule and the addition of the electron to the LUMO of the molecule as a way to examine the photoexcitation process. In order to base the discussion as much as possible on experimental and easily obtained and understood data, Koopmans’ theorem is invoked. This approximation states that the first ionization energy of a molecule equals the negative of the energy of HOMO. An extension of this theorem states that the electron affinity of the molecule approximates the energy of the LUMO. Thus, for each species, the ionization potential, IP and electron affinity, EA are explicitly considered. The IP is the “real” lowest energy cost of electron removal and the EA is the largest energy gain for the addition of an electron. We, thus, relate the HOMO-LUMO energy difference to the [IP – EA] difference.

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## RESULTS AND DISCUSSION

### Elemental dihalogens, X<sub>2</sub>

We start with the elemental halogens, X<sub>2</sub>, where two halogen atoms (F, Cl, Br, I) are bound by a  $\sigma$  bond. Table 1 shows that these elemental halogens, homonuclear diatomic group 17 species, are colored (2). Indeed, the names of two of these elements, chlorine and iodine, are derived from the colors of these elemental species (Fig. 1). The two halogens are bound by a  $\sigma$  bond. Thus, we explore where their colors arise and what the chromophore is in the series. We note that absorption of UV light can readily cleave the intrahalogen bond to dissociate the molecule, to form the separate atoms. Such chemistry is well-known as part of the mechanism of the light-induced halogenation with Cl<sub>2</sub> and Br<sub>2</sub> of the alkanes.

To facilitate further understanding of the colors of the elemental dihalogens species, we show that the ionization of an electron from the HOMO corresponds to removal of an antibonding  $\pi^*$  electron and the ionization potential of the dihalogens is expected by basic chemistry and photochemistry logic to be smaller than that of the corresponding atomic halogen. Accompanying this reasoning, as we proceed down a column in the periodic table, the atomic halogen IPs decrease in the order F > Cl > Br > I (3). The molecular IP order is F<sub>2</sub> (4) > Cl<sub>2</sub> (4,5) > Br<sub>2</sub> (5) > I<sub>2</sub> (6). The addition of an electron to a dihalogen molecule is that of a new antibonding  $\sigma^*$  electron. The electron affinities of the dihalogens are correctly predicted to be smaller than that of the corresponding atomic halogen (7). The atomic halogen EAs are previously reported to be “anomalous” order F < Cl > Br > I (8–10). The diatomic halogen EAs are in the order F<sub>2</sub> (11) > Cl<sub>2</sub> (12) ~ Br<sub>2</sub> (13) ~ I<sub>2</sub> (14). Table 1 gives the values of the IP, EA and [IP – EA] quantities (all energies are given in eV, the “customary” units for discussions of values of ionization potentials and electron affinities, where 1 eV = 23.0609 kcal mol<sup>-1</sup>  $\approx$  96.5 kJ mol<sup>-1</sup>  $\approx$  8066 cm<sup>-1</sup>).

Although the individual IP and EA values may be considered idiosyncratic, the [IP – EA] energy, the excitation energy monotonically decreases. The light absorbed by the dihalogens F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub> proceeds ever toward longer wavelengths in the visible (2). Clearly, the [IP – EA] energy does not correspond with the absorption energy deep into the UV. In terms of orbitals, we go from a  $\sigma^2\pi^{*4} \ ^1\Sigma$  to a  $\sigma^2\pi^{*3}\sigma^{*1} \ ^1$  or  $^3\pi$  electron configuration, and so we may speak of a  $\pi \rightarrow \sigma^*$  transition.

### Elemental sulfur, S<sub>8</sub>

Sulfur has many allotropes of which the best known is the yellow S<sub>8</sub> with its cyclic structure. From Ref. (16), we find the ionization potential of S<sub>8</sub> is smaller than that of any of the dihalogens and the electron affinity is larger than for any of the dihalogens. The difference quantity [IP – EA] of 5.54 eV is

smaller than for any of the dihalogens. So, why is S<sub>8</sub> “merely” yellow, that is, why does it visually appear more like fluorine than it does like iodine? The authors of Ref. (16) suggest that the experimentally observed [S<sub>8</sub>]<sup>-</sup> has a chain-like structure and acknowledged the possibility of a cyclic species with lower energy. A recent theoretical study (17) presented such a cyclic structure with a corresponding electron affinity significantly lower. We derive a value of [IP – EA] of 7.02 eV. This value is closer to that of iodine than to that of any other dihalogen. Thus, we still ask: *Why is sulfur yellow?* Sulfur is less colorful than would have been expected, indeed it is white at 77 K, where trace amounts of selenium (~150 ppm) in natural elemental sulfur has been reported to produce a yellow color (18). The yellow color of cyclic S<sub>8</sub> has also been suggested to be due to trace contamination (19). The vividness of sulfur’s yellow color may not be all due to trace contamination, which would leave an explanation of the origin of this yellow color contentious. The Franck–Condon factors are also likely key. The global minimum of S<sub>8</sub> is a crown structure (D<sub>4d</sub>) (17), where a difference relative to the S<sub>8</sub><sup>-</sup> and S<sub>8</sub><sup>+</sup> structures would cause Franck–Condon factors connecting the neutral to either ion to be quite low so that S<sub>8</sub> has a pale color. Varied colors of sulfur allotropes have been reported for S<sub>7</sub> and S<sub>10</sub> (yellow), S<sub>12</sub>, S<sub>20</sub>, S<sub>∞</sub> (gray/yellow) and S<sub>6</sub> (brown/yellow).

### Elemental phosphorus, P<sub>4</sub>

What about phosphorus? Let us only consider the long-known, well-defined species, the allotrope P<sub>4</sub>. This molecular species is generally called white phosphorus, although it is also referred to as yellow phosphorus due to its pale yellow color (20). Because of its tetrahedral geometry, the white allotrope of elemental phosphorus, P<sub>4</sub>, has an extremely perplexing and contentious electronic structure (21). Using theoretical magnetic criteria (NICS), P<sub>4</sub> has been described as “strongly [ $\sigma$ ] aromatic” (22–24). The ionization potentials of P<sub>4</sub> (25) and I<sub>2</sub> (6) are fortuitously very close. The electron affinity of P<sub>4</sub> remains unmeasured but that the solution phase electrochemical reduction of P<sub>4</sub> is irreversible suggestive of considerable distortion accompanying the addition of an electron (23). A small, or even negative, electron affinity of P<sub>4</sub> is consistent with these results—we recall the experimentally measured negative electron affinity of the aromatic, carbocycle benzene and its alkyl derivatives (26). In lieu of a directly determined value for the EA of P<sub>4</sub>, the derived value of 0.19 eV (27) gives us the ionization energy of [P<sub>4</sub>]<sup>-</sup> (1.35 eV) and the structural reorganization energy to the equilibrium structure of P<sub>4</sub> (1.16 eV). The [IP – EA] value for phosphorus is found to be between that of diatomic fluorine and chlorine. We are, thus, not particularly surprised that elemental phosphorus as found in its P<sub>4</sub> allotrope is a white or pale yellow. One question remains: If P<sub>4</sub> is to be understood as aromatic, but ca. 20 kJ mol<sup>-1</sup> (0.2 eV) above the more stable red and black allotropes (28),

**Table 1.** Ionization potentials, electron affinities and the difference quantities for the dihalogens.

X <sub>2</sub>	Hue	IP in eV	EA in eV	[IP – EA] in eV (kcal mol <sup>-1</sup> )	Ref.
F <sub>2</sub>	Very pale yellow	15.697 ± 0.003	3.120 ± 0.070	12.58 [292]	(4,11)
Cl <sub>2</sub>	Green	11.480 ± 0.005	2.50 ± 0.20	8.98 [207]	(4-5,12)
Br <sub>2</sub>	Red-orange	10.518 ± 0.003	2.68 ± 0.1	7.90 [182]	(5,15)
I <sub>2</sub>	Purple	9.3074 ± 0.0002	2.524 ± 0.005	6.78 [156]	(6,14)

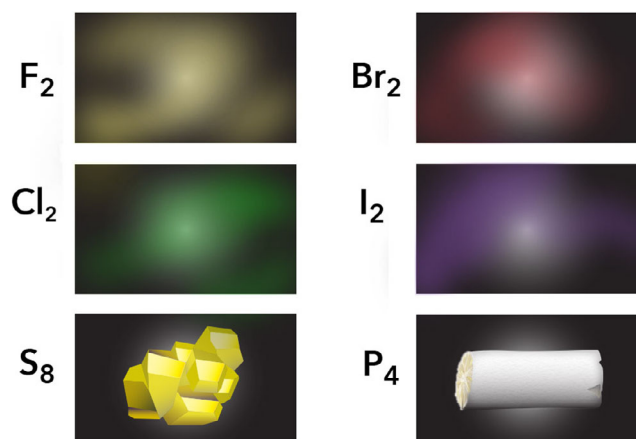


Figure 1. Colors of the elemental nonmetals  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $S_8$  and  $P_4$ .

Table 2. Summary of ionization potentials, electron affinities and difference quantities for elemental sulfur and phosphorus.

$X_n$	Hue	IP in eV	EA in eV	[IP – EA] in eV (kcal mol <sup>-1</sup> )	Ref.
$S_8$	Light yellow	$9.04 \pm 0.03$	2.02	7.02 [162]	(17)
$P_4$	White or pale yellow	$9.28 \pm 0.10$	0.19	9.09 [209.6]	(16,25)

why then is  $P_4$  so much more reactive, for example, it is the sole form of elemental phosphorus that is pyrophoric, that is, that it self-ignites on exposure to air? We note red and black phosphorus are both polymeric solids and so any comparison involving them and the discrete molecular  $P_4$  has inherent complications.

Elemental phosphorus  $P_4$  has a tetrahedral structure. Because of its tetrahedral geometry, there are many occupied and low lying unoccupied orbitals of degenerate energy. These degenerate levels are of the same energy, and indeed removing a single electron in the study of ionization potentials, and adding a single electron in the study of electron affinity results in degenerate orbitals with unequal occupancies. This is precisely the condition for Jahn–Teller distortions in both the radical cation and radical anion of  $P_4$ . That is, both  $P_4^+$  and  $P_4^-$  are not expected to be tetrahedral nor to have the same geometry. We are unaware of a way of predicting how the tetrahedral geometry becomes distorted. But what is the geometry of the radical ions and even, what is the orbital energies for the radical ions. If the distortion is large and hence unpredictable enough, then the Franck–Condon factor will be large, the absorption will be minimized (the color weak), and the orbital description more complicated than we would have expected. By diverse criteria,  $P_4$  has also been calculated to be aromatic, even if it is still strained and less stable, compared to the polymeric and solid red and black phosphorus.  $P_4$  is pyrophoric, even if it is aromatic (Table 2).

## SUMMARY AND APPENDIX

We have used HOMO-LUMO energy difference as being related to the (IP – EA) difference. We, therefore, suggest that the “*interhalogen*” X–X bond itself is the chromophore for the dihalogens. For the dihalogens, our analysis also relates to the prefix *inter* introduced by El-Sayed and Bhaumik in a photochemical

context (29) and used by us to denote interactions that simulate intermolecular interactions but are, in fact, intramolecular. The first general example is that of catalytic sites of protein-based enzymes in which well-positioned functional groups of amino acids and/or affixed coenzymes are poised for action, but are almost not on adjacent aminoacids as defined by the primary structure of the protein. The second example is that of “London Dispersion in Molecular Chemistry Reconsidering Steric Effects” (30). This generally entails nonbonded attractions in medium-sized molecules (large compared to our elements but small compared to the aforementioned enzymatic system). There most generally is a resulting surprisingly thermodynamic and kinetic stable species that otherwise would be unstable and/or labile, or at least less stable and more labile. Perhaps the simplest example is for the stable hydrocarbon, propane, in which 1,3-dialkyl contacts (here dimethyl) is stabilized relative to methane and ethane. Still concerned with seemingly simple hydrocarbons, we note the energetic tendency for adequately long-chain alkanes to fold rather than have an all-trans conformation. We use the prefix “*inter*” for all of these combined intramolecular, seemingly intermolecular interactions. We, therefore, reiterate our suggestion that the *interhalogen* X–X bond itself is to be recognized as the chromophore for the dihalogens.

Unlike a report by Michl and Thulstrup (31) on why azulene is blue and anthracene white, we do not use MO theory. Instead, we discuss  $P_4$  and  $S_8$  and the dihalogens, where the overlap with larger molecules is not yet established. We describe lone pair-containing elemental nonmetals, but not other compounds with  $\pi$  electrons and  $\sigma$  electrons. An analysis of anthracene and azulene (31) using our analysis with IP(azulene)  $\sim$  IP(anthracene) and EA(azulene)  $\sim$  EA(anthracene) would suggest the “same” color for these two hydrocarbons. Thus, further refinement of our formula will be required in future work. Furthermore, TD-DFT would be required to predict the energy of the  $S_0 \rightarrow S_1$ ,  $S_0 \rightarrow S_2$ ,  $S_0 \rightarrow T_1$  transitions. Such calculations will enable predictions of whether transitions are dominated by HOMO  $\rightarrow$  LUMO or HOMO-1  $\rightarrow$  LUMO, such as assignments of  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ,  $\pi \rightarrow \sigma^*$ , etc.

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## REFERENCES

- Luo, Y.-R. (2000) Why is the human visual system sensitive only to light of wavelengths from approximately 760 to 380 nm? An answer from thermochemistry and chemical kinetics. *Biophys. Chem.* **83**, 179–184.
- Steunenberg, R. K. and R. C. Vogel (1956) Absorption spectrum of fluorine. *J. Am. Chem. Soc.* **78**, 901–902.
- Moore, C. E. (1970) Ionization potentials and ionization limits derived from the analyses of optical spectra. *Nat. Stand. Ref. Data. Ser., Nat. Bur. Stand. (U.S.), NSRDS-NBS 34*.
- Van Lonkhuyzen, H. and C. A. De Lange (1984) High-resolution UV photoelectron spectroscopy of dihalogens. *Chem. Phys.* **89**, 313–322.
- Yencha, A. J., A. Hopkirk, A. Hiraya, R. J. Donovan, J. G. Goode, R. R. J. Maier, G. C. King and A. Kvaran (1995) Threshold photoelectron spectroscopy of  $Cl_2$  and Br 2 up to 35 eV. *J. Phys. Chem.* **99**, 7231–7241.
- Cockett, M. C. R., R. J. Donovan and K. P. Lawley (1996) Zero kinetic energy pulsed ionization (ZEKE-PFI) spectroscopy of electronically and vibrationally excited states of  $I_2^+$ : The  $A^2\Pi_{3/2,u}$  state

- and a new electronic state, the a  $^4\Sigma^+$ u state. *J. Chem. Phys.* **105**, 3347–3360.
7. Lowe, J. P. (1977) Qualitative molecular orbital theory of molecular electron affinities. *J. Am. Chem. Soc.* **99**, 5557–5570.
  8. Berry, S. R. and C. W. Reimann (1963) Absorption spectrum of gaseous  $F^-$  and electron affinities of the halogen atoms. *J. Chem. Phys.* **38**, 1540–1543.
  9. Politzer, P. (1969) Anomalous properties of fluorine. *J. Am. Chem. Soc.* **91**, 6235–6237.
  10. Balighian, E. D. and J. F. Liebman (2002) How anomalous are the anomalous properties of fluorine? Ionization energy and electron affinity revisited. *J. Fluor. Chem.* **116**, 35–39.
  11. Artua, A., K. E. Nizzi, B. T. Hill, L. S. Sunderlin and P. G. Wenthold (2000) Bond dissociation energy in trifluoride ion. *J. Am. Chem. Soc.* **122**, 10667–10670.
  12. Bowen, K. H., G. W. Liesegang, R. A. Sanders and D. W. Herschbach (1983) Electron attachment to molecular clusters by collisional charge transfer. *J. Phys. Chem.* **87**, 557–565.
  13. Schulze, T., H. J. Meyer and U. Ross (1984) Measurement of charge-transfer collisions of calcium, strontium and barium with molecular bromine near threshold. *Chem. Phys. Lett.* **112**, 563–566.
  14. Zanni, M. T., T. R. Taylor, B. J. Greenblatt, B. Soep and D. M. Neumark (1997) Characterization of the  $I_2^-$  anion ground state using conventional and femtosecond photoelectron spectroscopy. *J. Chem. Phys.* **107**, 7613–7619.
  15. Hughes, B. M., C. Lifschitz and T. O. Tiernan (1973) Electron affinities from endothermic negative-ion charge-transfer reactions. III. NO, NO<sub>2</sub>, CS<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, and C<sub>2</sub>H. *J. Chem. Phys.* **59**, 3162–3181.
  16. Hunsicker, S., R. O. Jones and G. Ganteför (1995) Rings and chains in sulfur cluster anions  $S_n^-$  to  $S_9^-$ : Theory (simulated annealing) and experiment (photoelectron detachment). *J. Chem. Phys.* **102**, 5917–5936.
  17. Jin, Y., G. Maroulis, X. Kuang, L. Ding, C. Lu, J. Wang, J. Lv, C. Zhang and M. Ju (2015) Geometries, stabilities and fragmental channels of neutral and charged sulfur clusters:  $S_n^Q$  ( $n = 3-20$ ,  $Q = 0, \pm 1$ ). *Phys. Chem. Chem. Phys.* **17**, 13590–13597.
  18. Steudel, R., E. M. Strauss, M. Papavassiliou, P. Braetter and W. Gatschke (1987) Sulfur compounds. Part 98. Selenium content of naturally occurring elemental sulfur, of industrially produced sulfur, and of the mineral selenosulfur. *Phosphorus Sulfur Relat. Elem.* **29**, 17–21.
  19. Steudel, R., G. Holdt and T. A. Young (1986) On the colors of Jupiter's satellite Io: Irradiation of solid sulfur at 77 K. *J. Geophys. Res.* **91**, 4971–4977.
  20. Schroder, D. (2002) News about oxygen. *Angew. Chem. Int. Ed.* **41**, 573–574.
  21. Brundle, C. R., N. A. Kuebler, M. B. Robin and H. Basch (1972) Ionization potentials of the tetraphosphorus molecule. *Inorg. Chem.* **11**, 20–25.
  22. Moran, D., M. Manoharan, T. Heine and P. V. R. Schleyer (2003)  $\sigma$ -Antiaromaticity in cyclobutane, cubane, and other molecules with saturated four-membered rings. *Org. Lett.* **51**, 23–26.
  23. Cossairt, B. M. and C. C. Cummins (2009) Properties and reactivity patterns of AsP<sub>3</sub>: An experimental and computational study of group 15 elemental molecules. *J. Am. Chem. Soc.* **131**, 15501–15511.
  24. Cossairt, B. M., C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel and G. Wu (2010) On the molecular and electronic structures of AsP<sub>3</sub> and P<sub>4</sub>. *J. Am. Chem. Soc.* **132**, 8459–8465.
  25. Zimmerman, J. A., S. B. H. Bach, C. H. Watson and J. R. Eyler (1991) Ion/molecule reactions of arsenic and phosphorus cluster ions: Ionization potentials and novel reaction pathways. *J. Phys. Chem.* **95**, 98–104.
  26. Jordan, K. D., J. A. Michejda and P. D. Burrow (1976) The relative stability of alkyl-substituted benzene anions in the gas phase. *J. Am. Chem. Soc.* **98**, 1295–1296.
  27. Jones, R. O., G. Ganteför, S. Hunsicker and P. Pieperhoff (1995) Structure and spectroscopy of phosphorus cluster anions: Theory (simulated annealing) and experiment (photoelectron detachment). *J. Chem. Phys.* **93**, 9549–9562.
  28. Schlesinger, M. E. (2002) The thermodynamic properties of phosphorus and solid binary phosphides. *Chem. Rev.* **102**, 4267–4301.
  29. El-Sayed, M. A. and M. L. Bhaumik (1963) Inter-intra-(inter) molecular energy transfer to rare-earth ions in chelates. *Chem. Phys.* **39**, 2391–2393.
  30. Wagner, J. P. and P. R. Schreiner (2015) London dispersion in molecular chemistry—reconsidering steric effects. *Angew. Chem. Intl. Ed. Engl.* **54**, 12274–12296.
  31. Michl, J. and E. W. Thulstrup (1976) Why is azulene blue and anthracene white? A simple MO picture. *Tetrahedron* **32**, 205–209.