

Donator–Acceptor Map and Work Function for Linear Polyene-Conjugated Molecules. A Density Functional Approximation Study

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Carotenoids are one particular type of conjugated chromophores with a great capacity for accepting electrons. The question posed here is how the capacity to accept electrons is related to extension of the conjugation. If there is a connection, any chromophore should represent a good antiradical, a point of interest for those investigating the biological effects of antioxidants. In order to analyze the relationship between the extension of the conjugation and the absorbance and electron–donor properties described in this paper, full geometry optimizations at the BPW91/D5DVZ level of theory are reported for a number of linear conjugated polyene systems. Maximum wavelengths were obtained using the TDDFT methodology. From these results, it is possible to conclude that large conjugated chromophores have a great capacity for accepting electrons but diminished power for donating electrons. Apparently, any chromophore should be a good antiradical, but various mechanisms exist for scavenging free radicals. In the case of linear polyene-conjugated molecules, indigo, blue, and green chromophores represent good antiradicals because they are also good antioxidants (effective electron donors). Yellow and red chromophores represent good antiradicals because they are good antireductants (effective electron acceptors). In the case of the molecules reported in this paper, the ionization energy and the electron affinity come close to the work function of graphite. This may be important for future applications, where the movement of the electrons is crucial.

Introduction

The donator–acceptor map (DAM; see Figure 1) was previously acclaimed¹ as a useful tool for a qualitative comparison among substances, as any molecule can be classified in terms of its electron donating–accepting capability (with respect to F and Na). Given that one of the mechanisms that is discussed in the literature,^{1–29} in the context of radical scavenging, consists of the electron transfer reaction, the DAM may be considered to provide a useful and effective representation, permitting us to study the antiradical capacity of any substance.

It has been claimed that carotenoids (CAR) are responsible for much of the yellow, orange, and red pigmentation manifested in the animal kingdom, and many articles have been written (reviewed in refs 30–33) affirming the idea that CAR consists of pigments and antioxidants. Antioxidants are important as these molecules scavenge free radicals, thus limiting cellular damage. In a previous work,¹ we analyzed the energy–structure relationship for the electron-transfer reaction of CAR. According with the DAM, CAR accept electrons during the charge-transfer process. CAR, along with other animal pigments, constitute conjugated chromophores. There are many kinds of conjugated π -electron systems acting as chromophores, all of which absorb light in the 200–800 nm wavelength range. The importance of chromophore conjugation is now well-known.³⁴ In fact, a set of practical conventions exists for predicting the λ_{\max} of chromophores, namely, the Woodward–Fieser empirical rules. These ascertain that each additional double bond in the conjugated π -electron system shifts the absorption maximum about 30 nm to longer λ_{\max} . Extending conjugation generally results in bathochromic (longer wavelengths) and hyperchromic

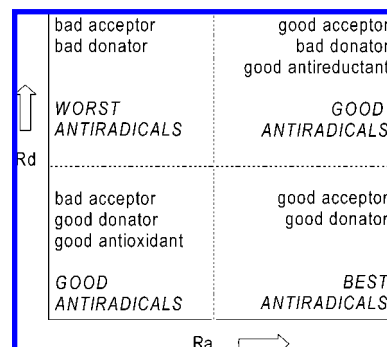


Figure 1. Donator–acceptor map (DAM). Four regions are distinguished as described in detail in the text. Dashed lines separating the regions are only indicative to clarify the image.

(greater absorbance) properties. Increased conjugation brings the HOMO–LUMO orbitals closed together so that the energy required to effect the electron promotion is therefore less, and the wavelength is increased correspondingly.

CAR are conjugate chromophores with a great capacity for accepting electrons. The question here is how the capacity to accept electrons is related to the extension of the conjugation. If there is a connection, any chromophore should represent a good antiradical, something that is of interest for people that work with antioxidants in the animal kingdom.

On the other hand, it was reported previously that many properties pertaining to large polynuclear aromatics must approach those of graphite at its largest size limit.^{35–42} Among these properties are included the ionization energy and electron affinity, both of which are expected to approach the work function of graphite. However, in the case of linear polyene-

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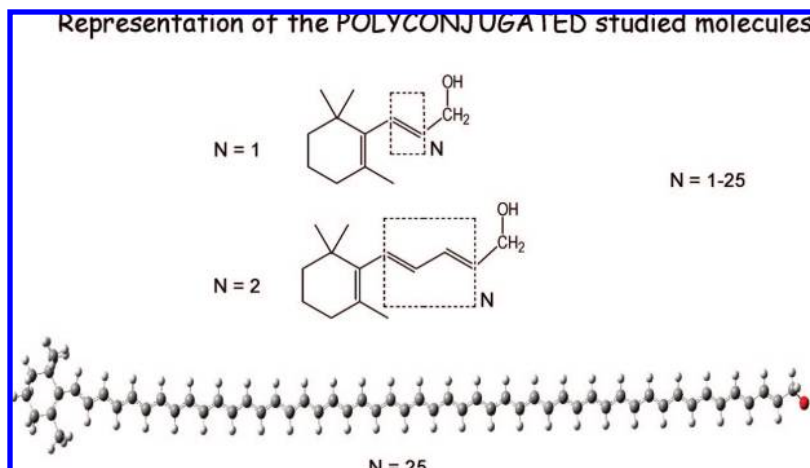


Figure 2. Linear polyene-conjugated studied molecules. Schematic representation of the molecular structure of the molecules being studied. N is the number of conjugated double bonds. Full geometry optimization at the BPW91/D5DVZ level was obtained for all of these molecules.

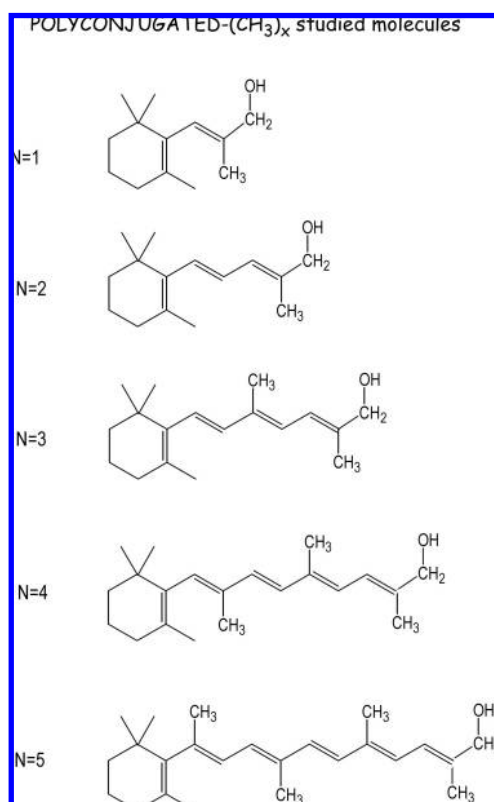


Figure 3. Linear polyene-conjugated molecules with CH_3 . In order to analyze the effect of the methyl groups, the molecules shown in this figure were optimized (at BPW91/D5DVZ level).

conjugated systems, no previous reports exist that are focused on clarifying how various properties observed in graphite differ from those of smaller molecules. It is still not known how the ionization energy and the electron affinity vary as a function of the number of double bonds in a chromophore. The hypothesis here is that the ionization energy and the electron affinity of linear polyene-conjugated systems also approach the work function of graphite.

The aims of this investigation are to rationalize the scavenge activity of linear polyene-conjugated chromophores through the single electron-transfer mechanism and to clarify how various properties of graphite differ from those of smaller molecules. For this purpose, vertical ionization energies (I), vertical electron affinities (A), maximum wavelengths (λ_{max}), and the DAM, for molecules shown in Figures 2 and 3, are reported.

Computational Details and Construction of the DAM

Density functional approximation^{43–45} as implemented in Gaussian 03⁴⁶ was used for all of the calculations. Becke's 1988 functional, which includes the Slater exchange along with corrections involving the gradient of the density,⁴⁷ and Perdew and Wang's 1991 gradient-corrected correlation functional⁴⁸ were employed in the calculations for complete optimizations, without symmetry constraints. D5DV basis sets were also employed.^{49–51} Harmonic frequency analyses permitted us to verify optimized minima. In order to compute I and A , further single-point calculations were necessary. I was calculated as the difference between the energy of the cation and that of the neutral molecule, assuming that both of these have the ground-state nuclear configuration of the neutral molecule. A was also calculated as vertical and represents the energy difference between the neutral and the anion, calculated with the ground-state nuclear configuration of the neutral molecule.

Another useful way of measuring electrodonating and electroaccepting power has recently been described by Gázquez et al.⁵² They established a simple charge-transfer model and analyzed the global response of a molecule immersed in an idealized environment that may either withdraw or donate charge. An alternative quadratic interpolation for the energy as a function of the number of electrons was proposed in order to evaluate the response of a molecule to charge acceptance or withdrawal in terms of its electron affinity and ionization potential. Referring to this approximation, these authors conclude that the propensity to donate charge, or electrodonating power, may be defined as

$$\omega^- = \frac{(3I + A)^2}{16(I - A)} \quad (1)$$

whereas the propensity to accept charge, or electroaccepting power, may be defined as

$$\omega^+ = \frac{(I + 3A)^2}{16(I - A)} \quad (2)$$

In the case of electrodonating power, lower values imply a greater capacity for donating charge. In the case of electroaccepting power, higher values imply a greater capacity for accepting charge. It is important to note that I and A refer to

donating or accepting a single, whole electron, whereas ω^- and ω^+ refer to fractional charges. In this way, the electrodonating and electroaccepting powers are based on a simple charge-transfer model, expressed in terms of chemical potential and hardness. Chemical potential measures the charge flow direction, together with the capacity to donate or accept charge, assigning more emphasis to ionization potential than to electron affinity in the context of the charge-donation process. Contrarily, electroaccepting power assigns more significance to electron affinity than to ionization potential. Hardness assesses resistance to the electron flow. The absorption spectra of neutral molecules have been computed with time-dependent density functional theory (TDDFT) using the same functional and basis sets.

In order to make a comparison with other well-known antioxidant and antireductant substances, experimental values of I and A for F and Na atoms were used to obtain the corresponding ω^+ and ω^- values. F represents a good electron acceptor, whereas Na represents a good electron donor. For any substance L, we define the electron acceptance index as

$$\text{Ra} = \frac{\omega_{\text{L}}^+}{\omega_{\text{F}}^+} \quad (3)$$

If $\text{Ra} = 1$, then $\omega_{\text{L}}^+ \cong \omega_{\text{F}}^+$, and L represents as effective of an electron acceptor as F. If $\text{Ra} > 1$, then $\omega_{\text{L}}^+ > \omega_{\text{F}}^+$, and L represents a more effective electron acceptor than F. If $\text{Ra} < 1$, then $\omega_{\text{L}}^+ < \omega_{\text{F}}^+$, and L represents a less effective electron acceptor than F. In the same way, the electron donation index is defined as

$$\text{Rd} = \frac{\omega_{\text{L}}^-}{\omega_{\text{Na}}^-} \quad (4)$$

If $\text{Rd} = 1$, then $\omega_{\text{L}}^- \cong \omega_{\text{Na}}^-$, and L is as effective of an electron donor as Na. If $\text{Rd} > 1$, then $\omega_{\text{L}}^- > \omega_{\text{Na}}^-$, and L is a less effective electron donor than Na. If $\text{Rd} < 1$, then $\omega_{\text{L}}^- < \omega_{\text{Na}}^-$, and L is a more effective electron donor than Na. If Ra and Rd are both known, then any substance L can be characterized in terms of its electron donor–acceptor capacity. These values allow us to place any substance L on the DAM, shown in Figure 1.

Results and Discussion

Vertical Ionization Energy and Electron Affinity. Figures 2 and 3 present schematically the chemical structure of the compounds being analyzed in this investigation. In order to observe the effect of conjugation and the impact of the methyl groups on the electron-transfers properties of these molecules, different numbers of conjugated carbon atoms, as well as distinct numbers of CH_3 groups, were used. Table 1 presents the I and A for all of the molecules being studied. The lowest I value corresponds to $N = 25$ and the highest to $N = 1$ for molecules both with and without CH_3 (N representing the number of conjugated double bonds). The low I values represent the most easily oxidized substances and indicate the most efficient antiradicals, expressed in terms of their electron-donating capability. Generally, I values from Table 1 indicate that large molecules generally represent better antioxidant molecules than small ones. An inverse correlation exists between I and the number of conjugated carbon atoms; effectively, as the number of conjugated carbon atoms increase, the I values decrease, meaning that molecules become better antioxidants. In Table 1, it is possible to see that A is both large and positive, in the

TABLE 1: Vertical Ionization Energies (I), Vertical Electron Affinities (A), Electron Donation and Acceptance Powers (ω^- and ω^+), and Indexes (Rd and Ra), Obtained with Equations 1–4^a

N	I (eV)	A (eV)	ω^- (don)	ω^+ (acep)	Rd	Ra	λ_{max} (nm)	$(I + A)/2$
1	7.17	-1.73	2.75	0.03	0.79	0.01	255	2.72
2	6.71	-0.82	3.09	0.15	0.89	0.04	310	2.94
3	6.36	-0.19	3.41	0.32	0.98	0.09	359	3.09
4	6.22	0.49	4.00	0.65	1.16	0.19	421	3.36
5	5.85	0.64	3.97	0.72	1.15	0.21	457	3.25
6	5.67	0.91	4.22	0.93	1.22	0.27	503	3.29
7	5.53	1.13	4.47	1.13	1.29	0.33	549	3.33
8	5.41	1.32	4.70	1.34	1.36	0.39	597	3.36
9	5.31	1.47	4.93	1.54	1.42	0.45	647	3.39
10	5.22	1.61	5.16	1.74	1.49	0.51	699	3.41
11	5.14	1.72	5.38	1.94	1.55	0.57	751	3.43
12	5.07	1.83	5.59	2.14	1.62	0.63	804	3.45
13	5.01	1.92	5.80	2.34	1.68	0.69	857	3.46
14	4.95	2.00	6.01	2.53	1.74	0.74	910	3.48
15	4.90	2.07	6.21	2.72	1.79	0.80	963	3.49
16	4.86	2.16	6.48	2.97	1.87	0.87	1015	3.51
20	4.71	2.34	7.17	3.64	2.07	1.07	1221	3.52
25	4.61	2.57	8.26	4.67	2.39	1.37	1483	3.59

Molecules with CH_3

N	I (eV)	A (eV)	ω^- (don)	ω^+ (acep)	Rd	Ra	λ_{max} (nm)	$(I + A)/2$
1	7.15	-1.98	2.60	0.01	0.75	0.0	248	2.59
2	6.57	-0.85	2.99	0.13	0.86	0.04	310	2.86
3	6.17	-0.27	3.23	0.28	0.93	0.08	364	2.95
4	6.12	0.24	3.68	0.50	1.06	0.15	411	3.18
5	5.80	0.29	3.55	0.51	1.03	0.15	417	3.05

^a Complete optimizations without symmetry constrains were done at the BPW91/D95V level. The λ_{max} (in nm) obtained with TDDFT is also reported. I and A values were obtained according to $\text{CAR} \rightarrow \text{CAR}^+ + 1\text{e}$; [$I = E(\text{CAR}^+) - E(\text{CAR})$]; $\text{CAR}^- \rightarrow \text{CAR} + 1\text{e}$; [$A = E(\text{CAR}) - E(\text{CAR}^-)$].

case of molecules with $N \geq 4$. One important conclusion that we can derive from these results is that these molecules are able to accept an electron. A is positive, which means that the anion is more stable than the neutral molecule, that is, they are more capable of accepting electrons, and thus, they represent the most efficient antiradicals (expressed as their electron-accepting capability). Molecules with $N < 4$ have negative A values. This implies that these molecules will not accept an electron, that is, it is necessary to give away some energy in order to form the anion. These molecules are the most inefficient antiradicals (expressed in terms of their electron-accepting capability). As in order to trap free radicals, substances must either donate or accept electrons; molecules with more than four conjugated carbon atoms represent better antiradicals as they have lower I values than small molecules (meaning that they are better antioxidants), and also, they are able to act as antireductants, without losing energy.

Methyl substituents are effective electron-donor groups, and the ionization energy would be expected to decrease with the number of CH_3 groups. As can be appreciated from Table 1, this is the case for these molecules. I values of the conjugated molecules with CH_3 groups are smaller than the corresponding values without methyl groups.

Electrodonating (ω^-) and Electroaccepting Power (ω^+). The propensity to accept or donate charge can be analyzed using ω^- and ω^+ , as expressed in eqs 1 and 2. Results are presented in Table 1. In the case of electrodonating power (ω^-), low values

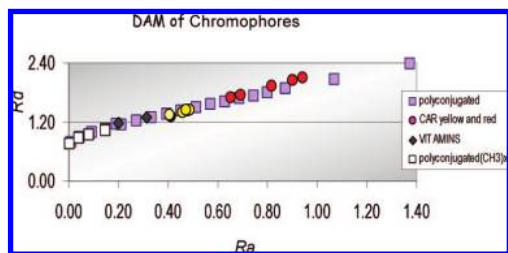


Figure 4. DAM for linear conjugated polyenes. Polyenes with and without CH₃ located on the DAM. Results for vitamins and yellow and red carotenoids (CAR) from previous reports¹ are included for comparison.

imply a strong capacity to donate electrons. In the case of electroaccepting power (ω^+), high values imply a strong capacity to accept electrons. For all of the molecules described in this paper, high values for I imply low values for ω^- . There is evidently a contradiction between these two results, as a low value for ω^- indicates that the molecule represents an effective electron donor, whereas a high value for I indicates that the molecule is a poor electron donor. These results suggest that it is very important to analyze the charge flow direction, together with the capacity to donate or accept charge. In order to have a complete description of the charge-transfer process, it is crucial to consider I and A together, as Gázquez et al. proposed for the electrodonating or electroaccepting power indexes. In the approximation put forward by Gázquez et al., they consider that molecules can donate or accept fractional amounts of charge, something that must be of importance. It was previously reported¹ in the case of vitamins that ω^- is apparently a better indicator of antioxidant power than I , as it is well-known that vitamin E represents an effective antioxidant substance. When the electron-transfer properties of vitamin E were analyzed, it was found that this molecule presents a very high I value and a very low ω^- value. In this case, ω^- conforms to the experimental information, and for this reason, we consider that ω^- is a better indicator of the electrodonating power. For the analysis of A and ω^+ , in Table 1, it is possible to appreciate that ω^+ correlates well with A . Large molecules represent better “antireductants” (effective electron acceptors) than small ones. The reactivity order, considering A and ω^+ values, is as follows

large molecules > small molecules

Thus, it is possible to reach the same conclusion using both parameters. As can be seen in Table 1, the presence of methyl substituents is not very important in terms of electrodonating and electroaccepting powers.

Donator–Acceptor Map (DAM). Figure 4 presents the DAM for the substances in the study, and CAR and vitamins previously described¹ are included for comparison. It is evident that as the number of conjugated carbon atoms increases, the antireductant capacity also increases, but the antioxidant capacity decreases. Large molecules fall within the good antireductant zone, whereas small molecules belong to the good antioxidant sector. The behavior both with and without methyl groups is the same. Small molecules, which have many methyl groups, fall within the good antioxidant sector, as do the corresponding molecules which have no methyl groups. It is worth noting that the relationship between the tendency to donate and receive electrons, in the case of all of the molecules shown in Figure 4, is remarkably linear. For CAR, it is little bit different from that of the polynuclear molecules described here. The slope of the fitted straight lines is slightly larger for CAR than that for linear polyene-conjugated molecules, but in both cases, it is

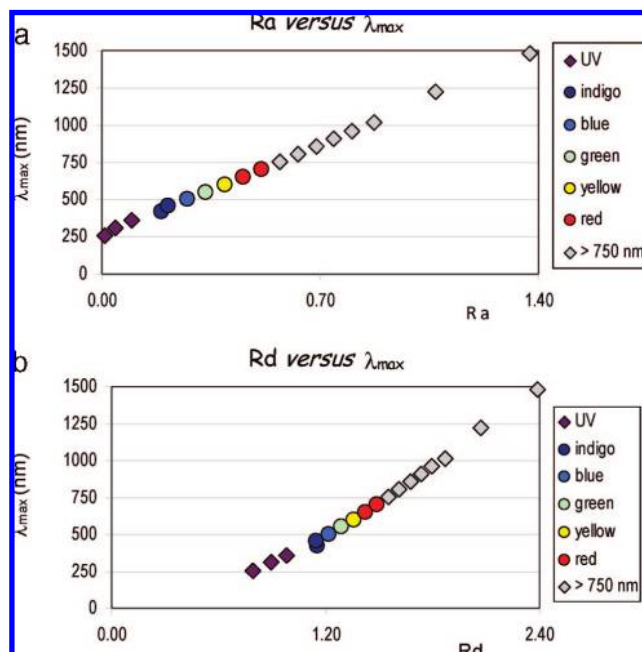


Figure 5. (a) R_a versus λ_{\max} (in nm) for linear polyenes. (b) R_b versus λ_{\max} (in nm) for linear polyenes. Absorbance was obtained using TDDFT methodology.

extremely linear. The observed linearity of R_a versus R_d (or ω^- vs ω^+) may be important for future analysis of these properties.

The values of the λ_{\max} , obtained using the TDDFT, are presented in Table 1. As may be observed, this conforms to the Woodward–Fieser empirical rules, as each additional double bond in the conjugated π -electron system shifts the absorption maximum about 30 nm to longer λ_{\max} . It is possible to correlate R_a and R_d with λ_{\max} (obtained using the TDDFT). Figure 5 presents R_a versus λ_{\max} and R_d versus λ_{\max} . A large R_a indicates an effective electron acceptor. As is evident in Figure 5a, red and yellow chromophores are better antireductants (more effective electron acceptors) than indigo, blue, or green ones. Small molecules present a λ_{\max} in the UV region and are poor electron acceptors, whereas large molecules are effective electron acceptors, even though they are not chromophores ($\lambda_{\max} > 750\text{nm}$). The reactivity order in terms of R_a is as follows:

colorless > red > yellow > green > blue > indigo > UV

In Figure 5b, R_d is related to λ_{\max} . A small R_d indicates an effective electron donor. Evidently, yellow and red chromophores are less effective electron donors (worse antioxidants) than indigo, blue, or green ones. The reactivity order, considering R_d , is as follows:

UV > indigo > blue > green > yellow > red > colorless

With these results, it is possible to conclude that large conjugated chromophores have a great capacity for accepting electrons but a diminished power for donating electrons. Apparently, any chromophore should constitute a good antiradical, but different mechanisms exist for scavenging free radicals. Concerning linear polyene-conjugated molecules, indigo, blue, and green chromophores are good antiradicals because they are also good antioxidants (effective electron donors). Yellow and red chromophores are good antiradicals because they are also good antireductants (effective electron acceptors). The capacity to accept electrons is directly related to the extension of the conjugation.

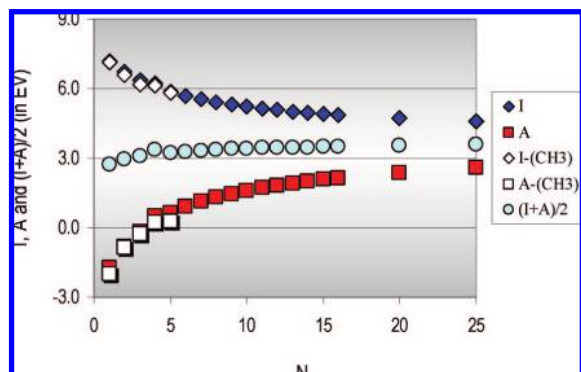


Figure 6. I , A and the electronegativity (in eV) of linear conjugated polyenes. N represents the number of conjugated double bonds.

It is important to note that effective electron acceptors are also efficient oxidants. We proposed in a previous work¹ that CAR might play an antiradical role, accepting electrons from free radicals, that is, oxidizing free radicals. However, CAR may be able to remove electrons from other molecules and thus may also be toxic and therefore not always beneficial for organisms. This should be the case concerning any effective electron acceptor. Following this logic, the effective electron acceptors described in this paper may perhaps be toxic oxidants, rather than important antiradicals. Evidently, further research is necessary in order to analyze these ideas.

Electronegativity and Work Function. It is well-known that properties like ionization energy and the electron affinity of large polynuclear aromatics must approach those of graphite at its largest size limit. The work function may be regarded as a macroscopic property of the material that provides a classical limit for the ionization energy and electron affinity of the large aromatics. The purpose of this investigation is to study whether this classical limit is also valid for linear polyene-conjugated systems.

In order to define whether the ionization energy and electron affinity of linear polyene-conjugated systems approach the work function of graphite, I , A , and the electronegativities $[(I + A)/2]$ are presented in Table 1 and Figure 6. It is evident that an increment of the conjugation brings I and A closer together, which conforms to the statement that HOMO–LUMO orbitals become closer as the conjugation rises. It is evident that, as the number of conjugated carbon atoms increases, the electronegativity becomes constant. For graphite, two experimental values (3.93 and 4.8 eV) for the mean electron work function were previously reported.^{40,42} Two approximations were also employed in order to theoretically deduce the electron work function. In the first, it is equal to the HOMO energy (defined for semiconducting carbon tubes⁴⁰); as the HOMO energy is equal to the ionization energy (within the ionizations theorems of Perdew et al.; see ref 53), the ionization energy for large systems can be considered to be equivalent to the electron work function. As it was pointed out before in this paper, in the second approximation, this represents the classical limit for ionization energy and electron affinity,³⁶ which, in the case of large systems, is represented as $I = A =$ electron work function.

In order to obtain estimations of the electron work function, the I and A values in Figure 6 can be conveniently fitted to a function expressed as $y = a + b(c)^N$, with a , b , and c being constants; as c turns out to be less than 1, a is the value for y at infinite N . When $y = I$, $a = I = 4.63$ eV at infinite N . This value is the electron work function, as defined in the first approximation, and it is in agreement with one of the experi-

mental results (4.8 eV). To consider the second approximation, I and A in Figure 6 were simultaneously fitted using common a and c parameters and independent b values. At infinite N , I and A converge to 3.78 eV for the electron work function; this value coincides with the other experimental result (3.93 eV). Hence, the application of both approximations to the linear polyene-conjugated molecules studied here appears to produce electron work function values for graphite, which tally reasonably with those from the experiment. From these results, it is possible to conclude that I and A of these linear polyene-conjugated systems approach the electron work function of graphite. This may be important for future applications, where the electron transfer is crucial.

Conclusions

The DAM for the molecules studied in this paper indicates that large molecules fall within the good antireductant zone, whereas small molecules belong to the good antioxidant sector. Apparently, any chromophore should be a good antiradical, but a variety of mechanisms exist for scavenging free radicals. Concerning linear polyenes chromophores, indigo, blue, and green are good antiradicals because they are also good antioxidants (effective electron donors). Yellow and red chromophores are good antiradicals because they are also good antireductants (effective electron acceptors), but they may also be dangerous oxidants. More experiments are necessary in order to analyze this behavior.

I and A approach the work function of graphite. This fact should be important for future applications, where the movement of the electrons is crucial.

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