12812 *J. Phys. Chem. A* **2008,** *112,* 12812–12815

Conjugation in Polyyne Rods: To What Extent Is Charge Delocalization Coupled to Geometrical Changes?[†]

Lior Itzhaki,[‡] Esther Rozental,[‡] Eli Altus,[§] Harold Basch,[‡] and Shmaryahu Hoz*,[‡]

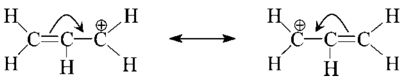
Department of Chemistry, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel, and Faculty of Mechanical Engineering, Technion, Israel Institute of Technology, Haifa, 32000 Israel

Received: January 17, 2008; Revised Manuscript Received: May 19, 2008

Ab initio methods were used to calculate the geometry and the charge distribution (natural bond orbital) in end-protonated polyynes. The geometry obtained is practically identical to that of the corresponding anion and the neutral radical. Thus, the geometry is not much dependent on charge dispersal. Moreover, it is shown that regardless of whether the imposed geometry is that of a cumulenic structure which localizes the charge at one end or that of the neutral molecule which localizes the charge at the other end, the same amount of charge is delocalized to the remote end of the protonated molecule regardless of the imposed structure. The same phenomenon is observed also for polyenes. It is interesting to note that regardless of the charge or its absence, as in the case of the radical, the optimal geometry is obtained as the arithmetic sum of the main resonance structures. Thus, it is concluded that, in these cases, the wave function is only weakly coupled to the geometry of the molecule.

1. Introduction

The use of curved arrows to describe resonance is second nature to the organic chemist. In spite of its artificiality, the concept of resonance is most useful in correlating experimental facts in organic chemistry. Shifting the π electron pair in the allyl cation, for example, from between one pair of carbon atoms to between the other pair, results in the reallocation of the positive charge as well as changes in the carbon−carbon bond lengths.



Since the two resonance structures are of the same energy, they will equally contribute to the final state, and the two C−C bond lengths, as well as the amount of positive charge on the two terminal atoms, will be identical. This demonstrates the accepted paradigm that geometry and charge distribution are usually found to be strongly coupled. In this report we show that charge can be effectively delocalized with only a weak linkage to geometrical changes.

In the course of our studies on the mechanical properties of molecular rods[1,2] we have determined the cross section area of polyynes ranging from C_4 to C_{20}. Since this cross section area may be intimately related to the electronic density, and therefore to the cross section area, we aimed to affect the latter by protonation at a terminus of the rod. However, following this path we discovered an interesting correlation, or the lack of such, between geometry and charge distribution.

2. Results and Discussion

Quantum mechanical calculation on C_{12} using Gaussian03 at the B3LYP/6-31G* theory level[3] shows that bond equalization starts from the protonation site (C12), as would be expected for a cumulenic system, but decays rapidly toward the C1 terminus (Figure 1). Similar results were obtained for C_{20} and C_{40} (see the Supporting Information).

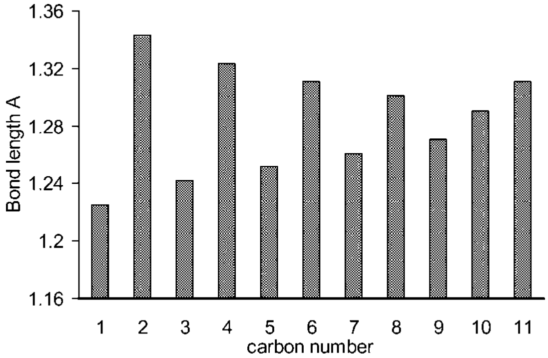


Figure 1. C−C bond lengths in protonated C_{12} polyyne (protonation on C12).

Conjugation in polyynes has been the focus of much debate in recent years. The issues revolved around the question of whether conjugation in butadiyne is stabilizing or not[4] and the suitability of the various computational methods for the accurate evaluation of the polyyne−cumulene isomerization energies.[5,6] In view of these controversies, we have performed computations on polyynes at various theory levels—B3LYP/6-31+G, B3LYP/6-31G*, BPW91/6-31G, and HF/6-31G (see the Supporting Information). The use of MP2/6-31G gave a nonlinear geometry and is not discussed here further. All methods revealed the same phenomenon of a gradual change from a nearly cumulenic (near the protonation site) to a bond alternation geometry (at the other end). Since the polyyne−cumulene isomerization energy is much dependent on the computational method we refer here mainly to the trends which are similar and are method-independent.

[†] Part of the "Sason S. Shaik Festschrift".

* Corresponding author. E-mail: shoz@mail.biu.ac.il.

[‡] Bar-Ilan University.

[§] Israel Institute of Technology.

10.1021/jp800467g CCC: $40.75

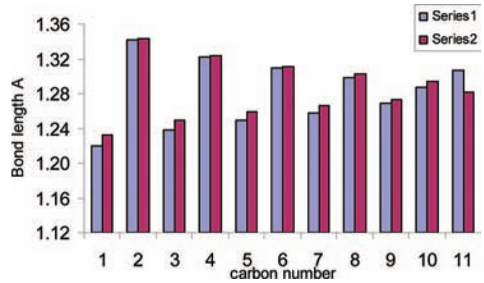


Figure 2. C−C bond lengths in protonated C_{12} polyyne: series 1, arithmetically constructed structure based on structures **1a**−**1f**; series 2, fully optimized geometry.

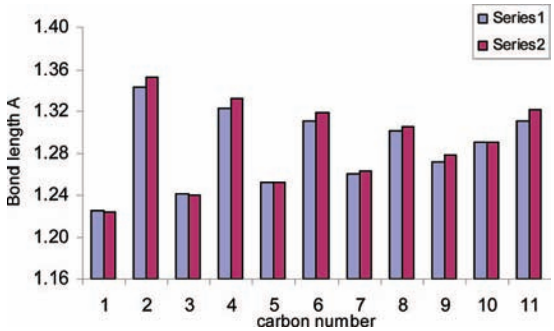
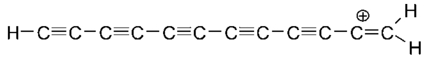


Figure 3. C−C bond lengths in series 1, fully optimized geometry of the radical, and series 2, fully optimized geometry of protonated C_{12} polyyne.

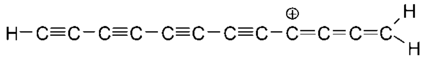
The geometric pattern of the polyyne cations are in fact the summation of the geometrical resonance structures **1a** and **1f** shown below for C12.

1a



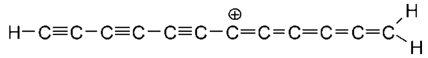
$\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\oplus}{C}{=}CH_2}$

1b



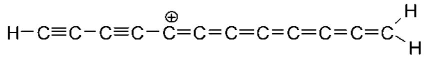
$\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\oplus}{C}{=}C{=}C{=}CH_2}$

1c



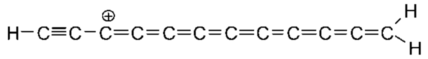
$\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\oplus}{C}{=}C{=}C{=}C{=}C{=}CH_2}$

1d



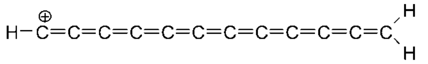
$\mathrm{H{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\oplus}{C}{=}C{=}C{=}C{=}C{=}C{=}C{=}CH_2}$

1e



$\mathrm{H{-}C{\equiv}C{-}\overset{\oplus}{C}{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}CH_2}$

1f



$\mathrm{H{-}\overset{\oplus}{C}{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}C{=}CH_2}$

Figure 2 shows the geometry of the polyyne cation constructed "arithmetically" using the single- and triple-bond lengths of the neutral polyyne with the double-bond length taken as the average of these bonds (1.281 Å). Each resonance structure was assigned the same weight. The average bond length deviation between the quantum mechanically calculated geometry and the one based on the arithmetic average of the resonance structures **1a**−**1f** is 0.008 ± 0.007 Å (Supporting Information).

The geometry of the corresponding radical (generated by adding $H^{\bullet}$ rather than H^{+}) was computed at the B3LYP/6-31G level. Figure 3 shows that the neutral radical follows the same pattern as the cation. The average deviation between the geometry of the radical and that of the cation is 0.0048 ± 0.004 Å (Supporting Information).

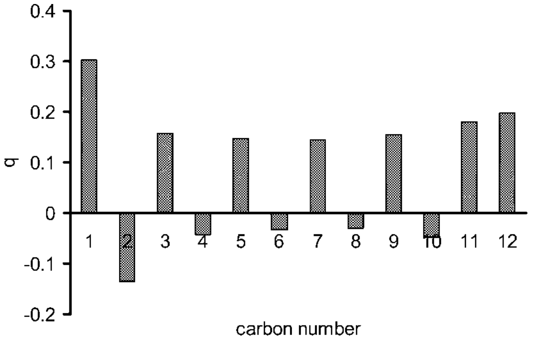


Figure 4. Atomic charge in protonated C12 polyyne (**3**). Protonation at C12.

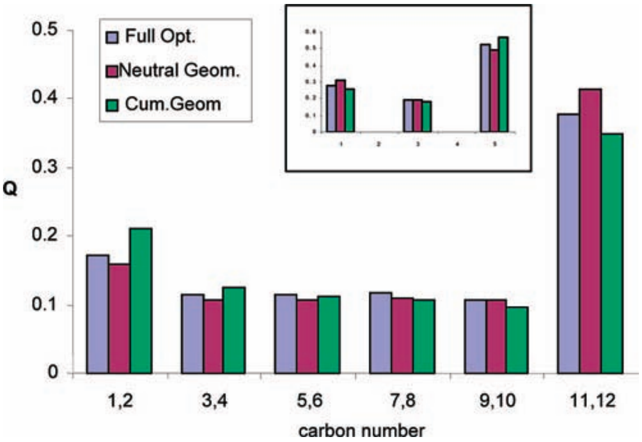


Figure 5. Atomic charges as a function of the geometry for C12 Polyyne. In the inset are data for C6.

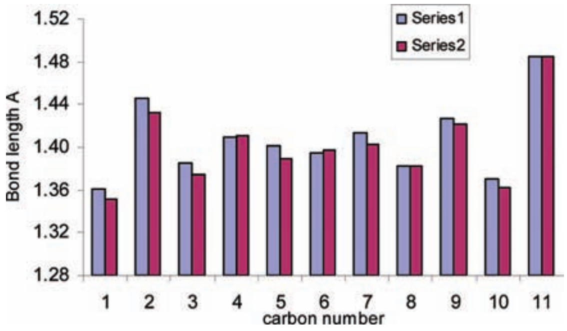


Figure 6. C−C bond lengths in protonated C_{12} polyene: series 1, arithmetically constructed structure based on structures **2a**−**2f**; series 2, fully optimized geometry.

Intrigued by the practically negligible effect of the charge on the geometry, we examined the charge along the singly protonated molecule to see if indeed it follows the six resonance structures with an equal weight. Figure 4 shows the natural bond orbital (NBO) charge computed at the B3LYP/6-31G* level (Supporting Information).

In order to avoid the complications resulting from the charge alternation phenomenon, we will examine the charges on pairs of neighboring carbon atoms (Figure 5). It is clear from the figure that indeed, apart from the terminal carbon atoms which are affected by the hydrogen atoms, the charge is indeed evenly distributed along the chain, in line with the fact that the geometry corresponds very much to a structure constructed from all the resonance structures with equal weights. However, Figure 5 shows two additional sets of data for the charge distribution.

TABLE 1: Sum of NBO Charges on the Left Half of the Molecule (HC1−C6) and the Right Half of the Molecule C7−C12H$_2$)

		NBO charges on	
entry	computational method	left half	right half
1	B3LYP/6-31G*	0.40	0.60
2	B3LYP/6-31G*, optimized with all C−C bonds having equal length (1.2796 Å)	0.45	0.55
3	B3LYP/6-31G* C1−C10 bond lengths are identical to the neutral, C11−C12H$_2$ reoptimized	0.37	0.63
4	CCSDT/6-31G*//B3LYP/6-31G*	0.29	0.71
5	CCSDT/6-31G*//B3LYP/6-31G* optimized with all C−C bonds having equal length (1.2796 Å)	0.39	0.61
6	CCSDT/6-31G*//B3LYP/6-31G* C1−C10 bond lengths are identical to the neutral, C11−C12H$_2$ reoptimized	0.23	0.77

One case is when the geometry is enforced to be that of resonance structure **1a**, and the other is **1f**—the cumulenic structure (see the Supporting Information). The first one corresponds to charge localization on C11, and the second corresponds to charge localization on C1. *Yet, in spite of these geometry enforcements, as can be seen from this figure, the differences in the charge distribution are essentially minimal, indicating a very small coupling between charge delocalization and geometric structure*. The inset in Figure 5 shows the same pattern for C6. It should be pointed out that we have limited our study to relatively short rods because, for the much longer ones, such an analysis is not useful as the charge on an atom is very small. Having ca. 0.4 positive charge units residing on two carbons at the protonation site results in an average of 0.03 charge units for each of the other carbon pairs. This is clearly beyond any reliability criterion for charge calculations.

In order to check whether these results are computational method-dependent we have performed calculations also at the CCSD(T)/6-31G*//B3LYP/6-31G* level. For the sake of simplicity we have examined the charges on the two halves of the molecule: HC1−C6 and C7−C12H$_2$. The results are given in Table 1 (and in the Supporting Information). The data show that the difference between the two extremes structures, **1a** localizing the positive charge on the right-hand side of the molecule and **1f** delocalizing the charge all the way to the other side, is very small. It amounts to 8% (0.45−0.37) of the unit charge at the B3LYP/6-31G* level and 16% (0.37−0.23) at the CCSDT/6-31G* level, whereas formally the **1a** geometry should localize 100% of the charge on the right-hand side and **1f** 100% on the other.

Since there are different methods to calculate atomic charges, we have examined also the CHELPG charges (Supporting Information). At the B3LYP/6-31G* level we observe the following: at the fully optimized geometry, 0.37 units of the positive charge is transferred to the left-hand side of the molecule; at the **1f** and the **1a** geometries 0.42 and 0.33 units of the positive charge were transferred, respectively. Thus, the observed phenomenon of weak linkage between geometry and charge delocalization seems to be independent of the computational methods used to determine the geometry and the electronic structure as well as the translation of the latter into atomic charges.

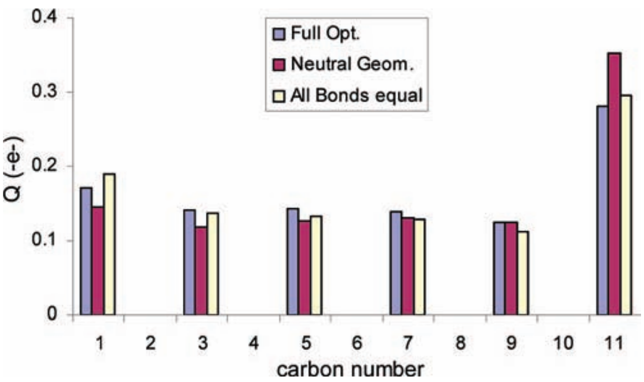
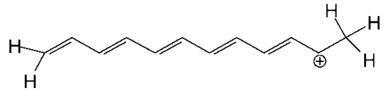


Figure 7. NBO charge distribution as a function of the geometry in C12 polyene cation.

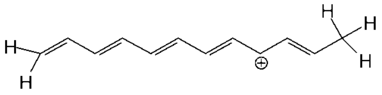
The observed phenomenon is not unique to a positive charge. A negative charge obtained by addition of hydride to C12 resulted also in the manifestation of a similar geometry (B3LYP/6-31+G*) and little coupling between the geometry and the electronic changes (see the Supporting Information).[7]

Finally, in order to examine the generality of the phenomenon we have investigated also the polyenic system focusing on the cation $C_{12}H_{15}^+$. Here again, as shown in Figure 6, the geometry of the cation calculated at the B3LYP/6-31G* level corresponds nicely to the arithmetic average of the six main resonance structures **2a**−**2f** (Supporting Information).

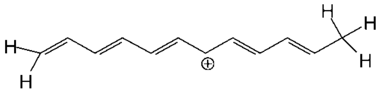
2a



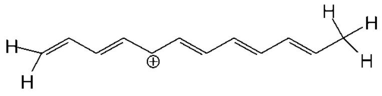
2b



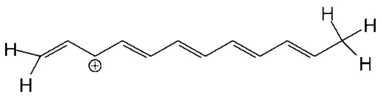
2c



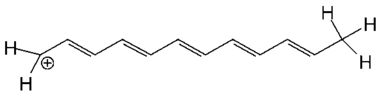
2d



2e



2f



The atomic charges on pairs of neighboring carbon atoms of the fully optimized geometry and of structures **2a** and **2f** are given in Figure 7. The similarity in the charge distribution of the three structures displays the same phenomenon observed in the polyynes above.

In summary, we have shown that charge distribution and geometry are only weakly linked. This was demonstrated for the positively and negatively charged and neutral (radical) polyyne system as well as for cationic polyene. A word of caution is here in order. Atomic charges are not physical observables. Yet, this intuitive concept is very helpful in our portraying of chemical behavior. It is therefore understandable that the discrepancy we described above is only within the framework of the intuitive model chemists are currently using.

The observations made here are likely to be another facet of the weak coupling between geometry and electronic properties. In his pioneering work on aromaticity, Shaik et al.[8] demonstrated that resonance energy is also only weakly coupled to the geometrical changes. A lack of synchronicity between charge development and geometry changes was suggested also for ionic transition states by Bernasconi.[9] These outcomes suggest that caution should be exercised when relating to the back of an envelope pushing of arrows as well as in our teaching of basic organic chemistry.

Acknowledgment. This work was supported by the Israeli Science Foundation.

Supporting Information Available: Complete ref 3 and detailed geometries and charge distributions for all the computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Itzhaki, L.; Altus, E.; Basch, H.; Hoz, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7432–7435.

(2) Pour, N.; Itzhaki, L.; Hoz, B.; Altus, E.; Basch, H.; Hoz, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5981–5983.

(3) Frisch, M. J.; et al. *Gaussian 03*, revision B.04. See the Supporting Information.

(4) (a) Jarowski, P. D.; Wodrich, M. D.; Wannere, C. S.; Schleyer, P. v. R.; Houk, K. N. *J. Am. Chem. Soc.* **2004**, *126*, 15036–15037. (b) Cappel, D.; Tüllmann, S.; Krapp, A.; Frenking, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 2–5. (c) Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A.; McLafferty, F. J.; Liebman, J. F. *Org. Lett.* **2003**, *5*, 2373–2375. (d) Rogers, D. W.; Matsunaga, N.; McLafferty, F. J.; Zavitsas, A. A.; Liebman, J. F. *J. Org. Chem.* **2004**, *69*, 7143–7147. (e) Wilson, E. K. *Chem. Eng. News* **2004**, *82* (Dec 20).

(5) Woodcock, H. L.; Schaefer, H. F., III; Schreiner, P. R. *J. Phys. Chem. A* **2002**, *106*, 11923–11931.

(6) (a) Parasuk, V.; Almof, J.; Feyereisen, M. W. *J. Am. Chem. Soc.* **1991**, *113*, 1049–1050. (b) Seburg, R. A.; McMahon, R. J.; Stanton, J. F.; Gauss, J. *J. Am. Chem. Soc.* **1997**, *119*, 10838–10845. (c) Wiberg, K. B.; Hammer, J. D.; Zilm, K. W.; Cheeseman, J. R. *J. Org. Chem.* **1999**, *64*, 6394–6400.

(7) Somewhat relevant to this is the work by Tolbert and Ogle (Tolbert, L. M.; Ogle, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9515−9527; Tolbert, L. M.; Ogle, M. E. J. Am. Chem. Soc. 1989, *111*, 5958−5959) who studied the delocalization of a negative charge along a polyenic chain. The probe used in their work was the delocalization of the negative charge onto terminal aromatic rings. It was concluded that after a delocalization over a certain chain length of the polyene, the charge density did not provide enough drive to delocalize the charge onto the aromatic ring.

(8) Shaik, S.; Shurki, A.; Danovich, D.; Hiberty, P. C. *Chem. Rev.* **2001**, *101*, 1501–1540.

(9) Bernasconi, C. F. *Acc. Chem. Res.* **1992**, *25*, 9–16.

JP800467G