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Stereochemical effect of covalent chemistry on the electronic structure and properties of the carbon allotropes and graphene surfaces

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ABSTRACT

We consider the covalent chemistry of the carbon allotropes with an emphasis on the newest member—graphene. We focus on the effect of such chemistry on the geometric and electronic structure of the functionalized materials and the way in which the conjugation is modified by such processes. We conclude that there are two limiting cases: (a) Conventional addition chemistry leading to the formation of σ-bonds to the graphitic surface in which there is full rehybridization of the derivatized carbon atoms from sp^2 to sp^3; thus these carbon atoms are effectively removed from conjugation and from the electronic band structure (referred to as destructive rehybridization). (b) Covalent chemisorption with formation of an organometallic hexahapto-metal bond that largely preserves the graphitic band structure (constructive rehybridization) and accompanies the formation of bis-hexahapto-metal bonds such as those in (η^6-SWNT)Cr(η^6-SWNT) which serve to interconnect adjacent graphitic surfaces and significantly reduces the internanotube junction resistance in SWNT networks. The formation of η^2 di-hapto bonds represent an intermediate case of covalent chemistry and is known to be important in carbon nanotubes and particularly the fullerenes but this situation has been treated in detail in previous publications.

1. Introduction

In 2004 graphene joined the fullerenes and carbon nanotubes as the third new form of conjugated carbon materials to take its place in the spotlight of scientific research [1,2]. All of these materials are composed of the same basic building block—tri-coordinate, formally sp^2 hybridized carbon atoms which are predominantly contained within six-membered rings thereby leading to polybenzenoid structures. These carbon allotropes are normally divided into two categories: molecules and materials, with the fullerenes being the only members of the first category. Nevertheless, in either case these substances can be viewed as continuous arrays of conjugated carbons as the fullerenes have no boundaries and (except for the terminal carbon atoms), carbon nanotubes and graphene are periodic structures which can in principal be extended without limit. Thus the question of functionalization of these continuous polybenzenoid structures has been of interest from the first isolation of the fullerenes as any chemistry, apart from redox processes, must involve an addition reaction which will normally saturate the carbon atoms that become functionalized and lead to sp^3 hybridized carbon atoms. Furthermore the question of covalent functionalization of graphene surfaces is an important question that must be addressed if the carbon allotropes are to play a role in assembling functional electronic structures based on polybenzenoid carbon surfaces [3].

In the case of graphene the sp^3 carbon atoms have been shown to act as scattering sites and their presence leads to a reduction in the conductivity and mobility of the samples that have been examined [4]. Nevertheless it is of interest to understand the effect of the introduction of sp^3 carbon centers on the electronic structure of the surrounding carbon atoms and the manner in which it modifies the geometrical strain and conjugation. Effects such as these have been studied for many years in organic chemistry and their ability to influence the stability and reactivity

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of molecules is well known [5]. For example, it has long been recognized that the geometries of the annulenes limit the reach of the Huckel (4n + 2)π-electron rule and it is the interplay of the geometrical requirements of the remainder of the molecule with the electronic structure of the π-system that ultimately determines the chemical stability of these compounds [6]. Within organic chemistry the necessity of balancing these two contributions is often considered under the title of steric inhibition of resonance.

In the present paper we compare the properties and the effect of geometry on conjugation in the carbon allotropes both before and after addition chemistry with model compounds drawn from the literature of organic chemistry in order to benchmark these materials against well-known molecules which can be structurally and physically characterized.

We begin by briefly reviewing the structures and stereochemical features of the fullerenes and single-walled carbon nanotubes (SWNTs) in the context of their functionalization (addition) chemistry in order to provide a benchmark for the analysis of graphene prototype structures which we draw from the literature on the 15,16-dihydropyrenes and theoretical calculations. The dihydropyrenes have been studied for a number of years by Boekelheide and Mitchell and their properties are well known [7–10]—there is an obvious relationship between pyrene and the 15,16-dihydropyrenes and between graphene and its addition products as discussed in more detail below.

2. Experimental and computational

Normally π-electron systems are considered to be planar and this is the case for undistorted graphene in the absence of scrolling (which can lower the total energy by van der Waals forces). In order to treat nonplanar π-electron systems it is convenient to use the π-orbital axis vector (POAV) analysis to divide the structural distortions into one-center and two-center terms as shown in Fig. 1 [5]. The one-center term makes use of the POAV1 pyramidalization angle and the vector defined by this procedure which is constructed to make equal angles to the three σ-bonds at the conjugated carbon atoms. While the vector defining the POAV1 rehybridized π-orbital direction depends on the geometrical construction defined above and shown in Fig. 1a, the corresponding POAV2 vector is based on the rehybridized π-orbital which is constructed to be orthogonal to the three σ-bonds. The POAV2 hybridizations and the resulting direction of the rehybridized π-orbital are obtained analytically by solving a set of homogeneous linear equations [11]. In the case of C_{3v} symmetry (equal angles between the 3 σ-bonds), the two constructions are identical; thus the POAV1 approach assigns an equal average σ-bond hybridization to the 3 σ-bonds, whereas the POAV2 approach solves for the individual hybridizations of each σ-bond hybridization in addition to the π-orbital [5].

The geometries of the compounds were obtained from X-ray crystal structures or from theoretical calculations and used directly in the analysis. For the ring current analysis of the experimental proton NMR chemical shifts, the C—H bond lengths of the X-ray structures were normalized to 1.1 Å [14,15].

3. Results and discussion

3.1. Analysis of covalent σ-bonding requirements (full rehybridization from sp^2 to sp^3)

3.1.1. Fullerenes

The effect of the spheroidal structure of C_{60} on its electronic structure is now well known—because the fullerenes are curved in two-dimension the geometry of the π-system imposes a very strong pyramidalization of the carbon atoms [16,17], but maintains a high degree of alignment of the π-orbitals (perfect in C_{60}) [18]. Thus the fullerenes readily undergo 1,2 addition reactions because this relieves the strain of pyramidalization without disrupting the favorable π-orbital alignment [17,19–22]. Nevertheless it is important to note that the larger high symmetry fullerenes become faceted and because the pyramidalization is concentrated at the vertices of the (12) five-membered rings the minimum pyramidalization angle in such fullerenes remains quite large ($\theta_P > \sim 9^\circ$) [23].

3.1.2. Carbon nanotubes

The carbon nanotubes are only curved in 1-dimension and thus in general the degree of pyramidalization required for the formation of structures of equivalent diameter is much less than in the case of the fullerenes (by about a factor of $^1/_2$ at small diameters); for example, the diameters (d) of C_{60} and the (5,5) SWNT are both about $d = 7$ Å, but the difference in the required pyramidalization angles is apparent in Fig. 2 and Fig. 3 [25].

It is apparent from Fig. 3 that the nonplanarity in carbon nanotubes not only leads to pyramidalization but also produces significant π-orbital misalignment which is distributed unequally among the π-bonds depending on their orientation with respect to the nanotube axis. Thus it is apparent that bonds which do not lie parallel or perpendicular to the nanotube axis will experience some degree of π-orbital misalignment and particularly for the smaller carbon nanotubes this may be quite severe. In fact for diameters smaller than C_{60}, it is likely that π-orbital misalignment is more

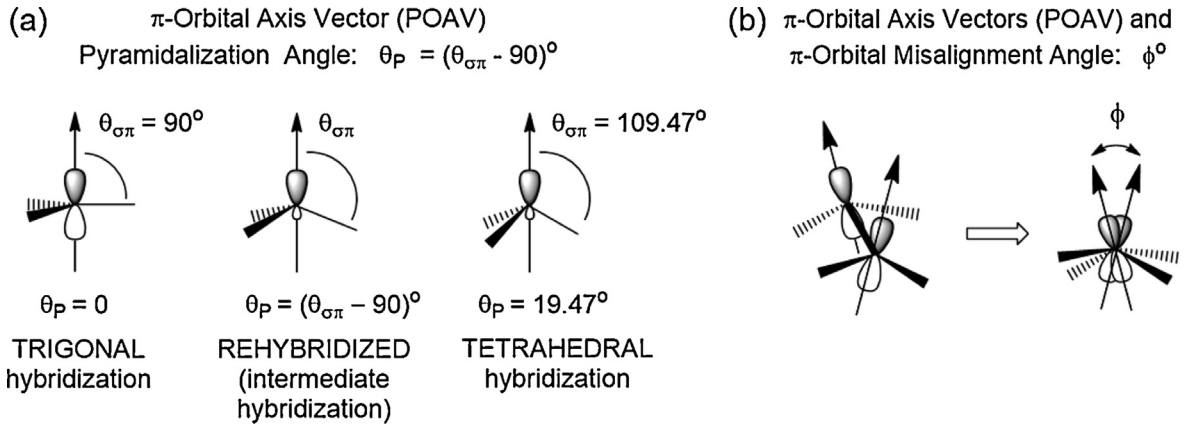

Fig. 1. Geometrical construction of the π-orbital axis vector (POAV), the POAV pyramidalization angle (θ_P) and π-orbital misalignment angle (φ) [6,11–13].

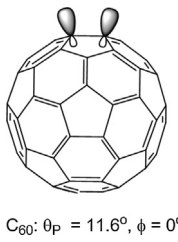

Fig. 2. A schematic illustration of the rehybridized π-orbital in $C_{60,}$ the calculated POAV pyramidalization angles (θ_P) and π-orbital misalignment angle (φ), which holds for all atoms and bonds in C_{60} [18]. For a common bond length of a = 1.42 Å, the diameter (d) of C_{60} is d = 7.04 Å [24].

critical in destabilizing and increasing the chemical reactivity in carbon nanotubes than the enforced pyramidalization which is considerably less than is required in C_{60} and this point is further supported by comparisons to the literature on small molecules [5,26].

3.1.3. Graphene

In the case of C_{60} there is a high degree of pyramidalization and perfect π-orbital alignment whereas in the carbon nanotubes there is both pyramidalization and π-orbital misalignment. On the other hand, pristine graphene is perfect in both respects and there is a complete absence of pyramidalization and π-orbital misalignment in the parent structure. In fact functionalization chemistry serves to introduce a contribution from both of these factors into the remaining conjugated carbon atoms in order to accommodate the newly rehybridized carbon atoms.

In this section we assess these effects by reference to the 15, 16-dihydropyrenes which serve as excellent model compounds for the 1,2-addition products of graphene. These and related structures have been implicated in many theoretical studies which have considered the effect of graphene functionalization via the formation of sp^3 carbon atoms in the basal plane of graphene. The conversion of sp^2 hybridized carbon atoms to sp^3 hybridization leads to a reduction in the conductivity and mobility of the carriers in functionalized graphene and theoretical treatments show that such sites in the basal plane of graphene act as resonant scatterers [27,28].

We have characterized the presence of such sites in the conjugated carbon allotropes as destructive rehybridization in that the carbon atom which is involved is removed from conjugation (saturated) and from the electronic band structure in the vicinity of the Dirac point [29]. Thus such functionalization schemes are unsatisfactory in electronically interconnecting and conjugating the graphene surfaces of carbon nanotubes and graphene. For this reason we have investigated other covalent chemistries and it is now apparent that the use of transition metal atoms to form bis-hexahapto bonds which bridge adjacent graphene surfaces (atomtronics) [30] is a viable solution to the problem and it is very successful in maintaining the conductivity of networks of single-walled carbon nanotubes (SWNTs) where the density of network connections becomes critical (below the percolation threshold) [31], presumably due to the formation of (η^6-SWNT)M(η^6-SWNT) bonds (Fig. 4).

In the sections below we treat both of these modes of chemical functionalization with particular reference to graphene—past papers have already discussed some of these issues in the case of the fullerenes and carbon nanotubes [17,25,32].

3.2. Analysis of covalent σ-bond requirements in graphene (full rehybridization from sp^2 to sp^3)

There have been a number of experimental and theoretical studies involving the addition of radicals to the basal plane of graphene and the resulting structural forms of the functionalized graphenes are expected to be quite similar, irrespective of the nature of the addends although the bulk of the substituents undoubtedly affects the degree of coverage [29,33–45]. The structures of these products are available from theoretical calculations [35,36] but in order to examine the resulting structures we chose to focus on the 15,16-dihydropyrenes [7–10] which provide well-characterized small molecule analogs of the 1,2-addition products that correspond to single-sided and two-sided functionalization chemistry of graphene.

The prototypical example of these compounds is *trans*-15, 16-dimethyl-dihydropyrene [7] which was first isolated in 1967, while *cis*-derivatives were isolated and structurally characterized more recently [46,47]. We have previously made use of the geometries of 2,7-diacetoxy-*trans*-15,16-dimethyl-dihydropyrene to assess the geometric, electronic and magnetic properties of this series of compounds [6,11,12].

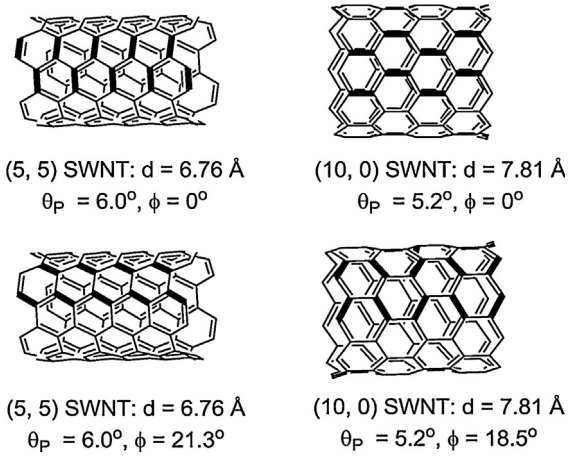

Fig. 3. Calculated diameters (d), POAV pyramidalization angles (θ_P) and π-orbital misalignment angles (φ) for the bolded atoms and bonds in selected SWNTs [25].

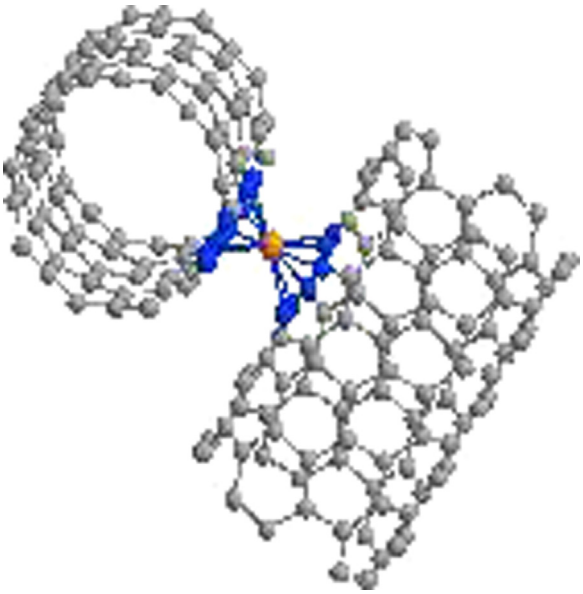

Fig. 4. Chem-3D depiction of (η^6-SWNT)M(η^6-SWNT) bonds, where M is a transition metal such as chromium [29,30].

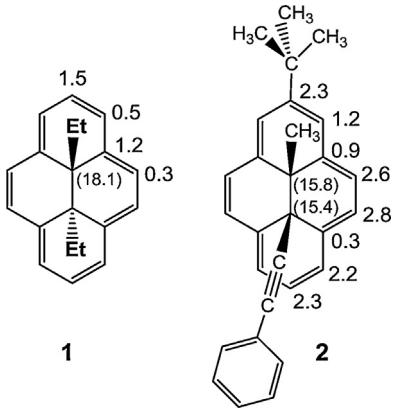

Fig. 5. Calculated POAV pyramidalization angles (θ_P, deg) as obtained from experimental X-ray structures (see Fig. 1) [11,12,46,47]. The parenthesized values correspond to the (saturated) carbon atoms that are rehybridized in the transformation from sp^2 to sp^3 based on pyrene as a model compound for 1,2-addition and thus the atoms used in defining the POAV are those which comprise the original pyrene conjugated carbon atoms.

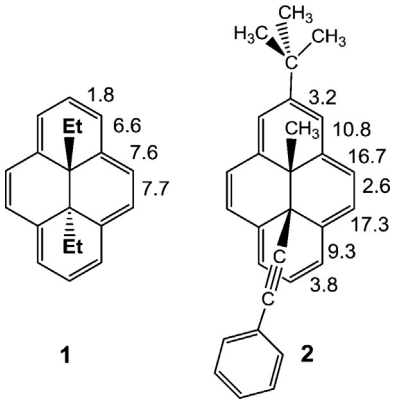

Fig. 7. Calculated POAV2 π-orbital misalignment angles (φ, deg) as obtained from experimental X-ray structures (see Fig. 1) [11,12,46,47].

In Fig. 5 we report the POAV pyramidalization angles for representative *trans*- and *cis*-15,16-dihydropyrenes (**1**,**2**) [46,47] and it is clear that the degree of pyramidalization imposed by the 1,2-addition process is modest and quite comparable in the two structural forms and with other bridged annulenes [6,11,12].

The geometrical structures of the two compounds are shown in Fig. 6 as Chem-3D renderings in which the internal functionalities at the 15,16-carbon atoms have been replaced by hydrogen atoms to allow clear visualization.

In Fig. 7 we report the POAV2 π-orbital misalignment angles for *trans*- and *cis*-15,16-dihydropyrenes and it is clear that the degree of misalignment is greater in case of the *cis*-geometry although still quite low in comparison with other bridged annulenes which in many cases have values of $\varphi > 20^\circ$ and still show delocalization and aromatic character [6,11,12]. Because the overlap integral in twisted π-electron systems scales as the cosine function of the dihedral angle between adjacent pairs of pπ orbitals (π-orbital misalignment angle, see Fig. 1) [11,12], the effective resonance integrals ($\beta^{R,B}$) in the conjugated periphery are largely maintained due to rehybridization, and in *trans*-15,16-diethyl-15,16-dihydropyrenes (**1**), β^R and $\beta^B \geq 0.99\,\beta$ [11,12].

A particularly direct way to experimentally address the degree of electron delocalization in such distorted π-systems is by analysis of the magnetically induced ring currents which may be directly related to the NMR chemical shifts by the Biot–Savart law providing the molecular geometry is known [14,15]. By parameterization of the London theory of ring currents it is therefore possible to devise experimental measures of the degree to which the theoretically calculated ring current is maintained in a given cyclic π-electron system in which the overlap is less than perfect. Perfect π-orbital overlap is only ensured if the π-electron system is contained within a plane, as is the case in benzene and graphene [5]. The parameterization of the London theory is usually accomplished by reference to experimental diamagnetic susceptibilities (Scheme A) or by use of experimental NMR chemical shifts (Scheme B) [14,15]. Scheme B is based on the experimental NMR chemical shifts reported for *trans*-15,16-dimethyl-dihydropyrene, and thus this compound has a Fraction of the Maximum Calculated Ring Current (FMCRC) of FMCRC ≡ 1. In the original work [14,15] we utilized the geometry of 2,7-diacetoxy-*trans*-15,16-dimethyl-dihydropyrene as this was the only structurally characterized *trans*-15,16-dimethyl-dihydropyrene available at the time. In the present work we used the structure of *trans*-15,16-diethyl-dihydropyrene (**1**) in order to provide a check and obtained values of FMCRC = 0.96 (**1**), whereas the *cis*-isomer gave FMCRC = 0.91 (**2**). Thus, we conclude that for the 1,2-addition products the trans-isomers (addition on opposite graphene faces), gives slightly better π-orbital overlap than the cis-isomer (addition on the same graphene face).

3.3. Analysis of covalent η^6-hexahapto organometallic bonding requirements

3.3.1. Fullerenes and carbon nanotubes

Because the marked pyramidalization of the fullerenes splays the π-orbitals, the organometallic chemistry is confined to η^2-complexation reactions [48], and thus there are no structurally characterized examples of stable pentahapto- or hexahapto-complexes in which the remaining C_{60} carbon atoms are all tricoordinate [32,49,50]. Nevertheless it has been argued that some of the lanthanide compounds of C_{60} possess significant covalent character, perhaps because the d-orbitals of these large metals are able to effectively overlap with the rehybridized C_{60} π-orbitals [51–53]. The overlap of transition metal d-orbitals with the carbon nanotube π-orbitals has been extensively discussed previously and clearly constitutes an intermediate case between the fullerenes and graphene [32,54,55].

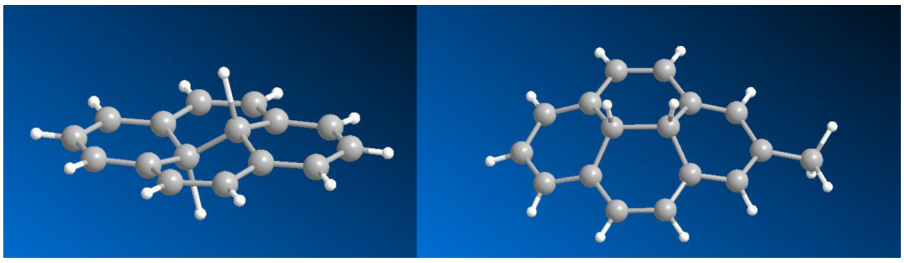

Fig. 6. Chem-3D representations of the compounds shown in Figs. 5 and 7, in which the internal functionality at the 15,16-positions has been replaced with hydrogen atoms for display purposes.

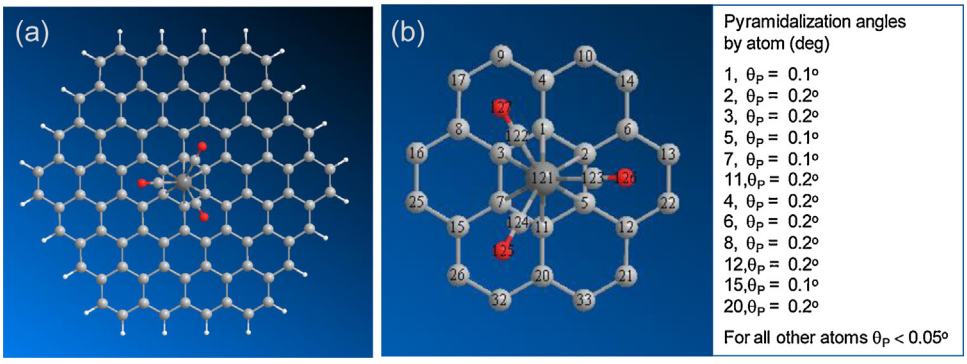

Fig. 8. Chem-3D structures of a $Cr(CO)_3$ unit complexed with a $C_{96}H_{24}$ graphene fragment obtained from the coordinates given by Gloriozov and coworkers (structure 4-Cr $(CO)_3$ in their notation) [58], (a) Chem-3D structure of the complete $C_{96}H_{24}$-$Cr(CO)_3$ graphene fragment, (b) Sub-Unit, with numbering and calculated POAV pyramidalization angles (θ_P, deg).

3.3.2. Graphene

There are a number of calculations on the geometrical and electronic structure of hexa-hapto complexes of graphene model structures [56–58], and in Fig. 8 we show the Chem-3D structure of a $Cr(CO)_3$ unit complexed with a $C_{96}H_{24}$ graphene fragment obtained from the coordinates given by Gloriozov and coworkers (structure 4-$Cr(CO)_3$ in their notation) [58].

As noted by a number of authors [29,31,56–58], the hexa-hapto bond to chromium exerts a very small perturbation of the geometric structure of the graphene sheet and this is reflected in transport studies of such structures [4]. Thus, the overlap of orbitals in the plane of the graphene sheet is not disturbed and the modification of the electronic structure is accomplished simply by changes in the wave function itself, a process which we have termed constructive rehybridization [30]. As shown in Fig. 8, the pyramidalization brought about by hexa-hapto complexation is extremely small ($\theta_P \leq 0.2°$) in the calculated structure of (η^6-$C_{96}H_{24}$)$Cr(CO)_3$ which is even less than in bis(benzene) chromium [(η^6-$C_6H_6)_2Cr$] for which $\theta_P = 1.7°$ [29], presumably because of the rigidity of the polybenzenoid π-system.

Thus we conclude that the hexa-hapto organometallic bond offers the only possibility for bridging the π-systems of the carbon allotropes in a manner which preserves the delocalization and conductivity within the subunits and also offers a seamless electronic interconnection between the conjugated fragments.

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References

[1] C. Berger, Z. Song, T. Li, X. Li, A.Y. Ogbazghi, R. Feng, Z. Dai, A.N. Marchenkov, E. H. Conrad, P.N. First, W.A. de Heer, J. Phys. Chem. B 108 (2004) 19912–19916.
[2] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666–669.
[3] R.C. Haddon, A.A. Lamola, Proc. Nat. Acad. Sci. USA 82 (1985) 1874.
[4] S. Sarkar, H. Zhang, J.-W. Huang, F. Wang, E. Bekyarova, C.N. Lau, R.C. Haddon, Adv. Mater. 25 (2013) 1131–1136.
[5] R.C. Haddon, Acc. Chem. Res. 21 (1988) 243–249.
[6] R.C. Haddon, L.T. Scott, Pure Appl. Chem. 58 (1986) 137–142.
[7] V. Boekelheide, J.B. Phillips, J. Am. Chem. Soc. 89 (1967) 1695–1704.
[8] R.H. Mitchell, V. Boekelheide, J. Am. Chem. Soc. 92 (1970) 3510–3512.
[9] R.H. Mitchell, V. Boekelheide, J. Am. Chem. Soc. 96 (1974) 1547–1557.
[10] R.H. Mitchell, V.S. Iyer, N. Khalifa, R. Mahadevan, S. Venugopalan, S.A. Weerawarna, P. Zhou, J. Am. Chem. Soc. 117 (1995) 1514–1532.
[11] R.C. Haddon, J. Am. Chem. Soc. 108 (1986) 2837–2842.
[12] R.C. Haddon, J. Am. Chem. Soc. 109 (1987) 1676–1685.
[13] R.C. Haddon, J. Phys. Chem. A 105 (2001) 4164–4165.
[14] R.C. Haddon, Tetrahedron 28 (1972) 3613–3633.
[15] R.C. Haddon, Tetrahedron 28 (1972) 3635–3655.
[16] R.C. Haddon, L.E. Brus, K. Raghavachari, Chem. Phys. Lett. 125 (1986) 459–464.
[17] R.C. Haddon, Science 261 (1993) 1545–1550.
[18] R.C. Haddon, L.E. Brus, K. Raghavachari, Chem. Phys. Lett. 131 (1986) 165.
[19] F. Wudl, Acc. Chem. Res. 25 (1992) 157–161.
[20] A. Hirsch, Top. Curr. Chem. 199 (1999) 1–65.
[21] M. Prato, Top. Curr. Chem. 199 (1999) 173–187.
[22] A. Hirsch, M. Brettreich, Fullerenes: Chemistry and Reactions, Wiley-VCH Verlag GmbH & Co., Weinheim, 2005.
[23] R.C. Haddon, G.E. Scuseria, R.E. Smalley, Chem. Phys. Lett. 272 (1997) 38–42.
[24] R.C. Haddon, J. Am. Chem. Soc. 119 (1997) 1797–1798.
[25] S. Niyogi, M.A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M.E. Itkis, R.C. Haddon, Acc. Chem. Res. 35 (2002) 1105–1113.
[26] R.C. Haddon, J. Am. Chem. Soc. 112 (1990) 3385–3389.
[27] H. Zhang, E. Bekyarova, J.-W. Huang, Z. Zhao, W. Bao, F. Wang, R.C. Haddon, C.N. Lau, Nano Lett. 11 (2011) 4047–4051.
[28] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, Rev. Mod. Phys. 81 (2009) 109–162.
[29] E. Bekyarova, S. Sarkar, F. Wang, M.E. Itkis, I. Kalinina, X. Tian, R.C. Haddon, Acc. Chem. Res. 46 (2013) 65–76.
[30] S. Sarkar, M.L. Moser, X. Tian, X.J. Zhang, Y.F. Al-Hadeethi, R.C. Haddon, Chem. Mater. 26 (2014) 184–195.
[31] X. Tian, M.L. Moser, A. Pekker, S. Sarkar, J. Ramirez, E. Bekyarova, M.E. Itkis, R.C. Haddon, Nano Lett. 14 (2014) 3930–3937.
[32] I. Kalinina, E. Bekyarova, S. Sarkar, F. Wang, M.E. Itkis, X. Tian, S. Niyogi, N. Jha, R.C. Haddon, Macromol. Chem. Phys. 213 (2012) 1001–1019.
[33] E. Bekyarova, M.E. Itkis, P. Ramesh, R.C. Haddon, Phys. Stat. Sol. RRL 3 (2009) 184–186.
[34] S. Niyogi, E. Bekyarova, J. Hong, S. Khizroev, C. Berger, W.A. de Heer, R.C. Haddon, J. Phys. Chem. Lett. 2 (2011) 2487–2498.
[35] D. Jiang, B.G. Sumpter, S. Dai, J. Phys. Chem. B 110 (2006) 23628–23632.
[36] D.W. Boukhvalov, M.I. Katsnelson, Phys. Rev. B 78 (2008) 085413.
[37] S. Ryu, M.Y. Han, J. Maultzsch, T.F. Heinz, P. Kim, M. Steigerwald, L.E. Brus, Nano Lett. 8 (2008) 4597–4602.
[38] K.F. Kelly, W.E. Billups, Acc. Chem. Res. 46 (2013) 4–13.
[39] P. Huang, L. Jing, X. Gao, Acc. Chem. Res. 46 (2013) 43–52.
[40] A. Hirsch, J.M. Englert, F. Hauke, Acc. Chem. Res. 46 (2013) 87–96.
[41] A. Penicaud, C. Drummond, Acc. Chem. Res. 46 (2013) 129–137.
[42] M. Quintana, E. Vazquez, M. Prato, Acc. Chem. Res. 46 (2013) 138–148.
[43] G.L.C. Paulus, Q.H. Wang, M.S. Strano, Acc. Chem. Res. 46 (2013) 160–170.
[44] J. Park, M. Yan, Acc. Chem. Res. 46 (2013) 181–189.
[45] F.M. Koehler, W.J. Stark, Acc. Chem. Res. 46 (2013) 2297–2306.
[46] K. Ayub, Doctoral Thesis, Chemistry Department, University of Victoria, Victoria, 2008.
[47] K. Ayub, R.H. Mitchell, J. Org. Chem. 79 (2014) 664–678.
[48] P.J. Fagan, J.C. Calabrese, B. Malone, Acc. Chem. Res. 25 (1992) 134–142.
[49] J.R. Rogers, D.S. Marynick, Chem. Phys. Lett. 205 (1993) 197–199.
[50] R.C. Haddon, J. Comput. Chem. 19 (1998) 139–143.
[51] P.H. Citrin, E. Ozdas, S. Schuppler, A.R. Kortan, K.B. Lyons, Phys. Rev. B 56 (1997) 5213–5227.
[52] X.H. Chen, G. Roth, Phys. Rev. B 52 (1995) 15534–15536.
[53] A.S. Ginwalla, A.L. Balch, S.M. Kauzlarich, S.H. Irons, P. Klavins, R.N. Shelton, Chem. Mater. 9 (1997) 278–284.
[54] E.Y. Li, N. Marzari, ACS Nano 5 (2011) 9726–9736.
[55] S. Sarkar, S. Niyogi, E. Bekyarova, R.C. Haddon, Chem. Sci. 2 (2011) 1326–1333.
[56] S.M. Avdoshenko, I.N. Ioffe, G. Cuniberti, L. Dunsch, A.A. Popov, ACS Nano 5 (2011) 9939–9949.
[57] J. Dai, Y. Zhao, X. Wu, X.C. Zeng, J. Yang, J. Phys. Chem. C 117 (2013) 22156–22161.
[58] I.P. Gloriozov, R. Marchal, J.-Y. Saillard, Y.F. Oprunenko, Eur. J. Inorg. Chem. 2015 (2015) 250–257.