Structural Models of Fluorine-Graphite Intercalation Compounds from Density Functional Theory[†]

Holger F. Bettinger,*[‡] Konstantin N. Kudin,[§] and Gustavo E. Scuseria*[§]

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany, and Department of Chemistry, MS-60, and Center for Nanoscale Science and Technology, Rice University, P.O. Box 1892, Houston, Texas 77251-1892

Received: September 23, 2003; In Final Form: January 28, 2004

Density functional theory computations employing periodic boundary conditions and basis sets up to polarized double-ζ quality indicate that the stage 1 C_3F graphite intercalation compound might have a structure with nonplanar arrangement of carbon atoms and a significantly shorter "semi-ionic" C−F bond (1.43−1.49 Å) than estimated earlier (2.1−2.2 Å).

Introduction

While fluorination of graphite at elevated temperatures yields the covalent graphite fluorides $(CF)_x$ and $(C_2F)_x$,[1] fluorination at low temperatures and in the presence of catalysts (e.g., HF, SbF_5, K_2PtF_6) affords fluorine−graphite intercalation compounds (F−GIC).[2] A unique characteristic of F-GIC is the variation of the nature of the C−F bond from ionic to covalent with increasing intercalant concentration.[3,4] With low fluorine concentrations in the graphitic matrix, the C−F bond is ionic with $r(\mathrm{C{-}F}) = 3.0$ Å and the system can be considered to be composed of fluoride anions and graphitic polycations. Thus, F−GICs of low fluorine concentration have higher conductivity than pure graphite. As indicated by NMR experiments, the fluoride anions are highly mobile within the graphite galleries.[5,6] With increasing fluorine concentration, the nature of the C−F bond changes and along with it the physical properties of the F−GIC phases. A further increase of the fluorine concentration in F−GIC will not result in the formation of covalent $(CF)_x$ due to the strong local deformations of the carbon framework associated with islands of higher fluorine concentration in the F−GIC, as discussed and analyzed in detail by Dresselhaus et al.[4]

Bartlett and co-workers[7−9] succeeded in the synthesis of several stage 1 C_xF phases with X-ray photoelectron spectroscopy (XPS) and IR properties between those of ionic and covalent graphite fluorides. Although the X-ray powder data are insufficient to prove the coplanarity of the carbon atoms,[7] it is generally assumed that the planarity of the graphite sheets is maintained even after intercalation of fluorine.[3,7−9] The lengths of the C−F bonds have been estimated from the distances between graphite sheets (c_0 distance) obtained from X-ray data, and the fluorine and carbon van der Waals radii by Mallouk and Bartlett to be 2.1−2.2 Å for C_xF stage 1 phases ($5 > x > 2$).[7] Nakajima[3] arrives at 1.7 Å using the c_0 spacing obtained by Hagiwara et al.[9] for stage 1 C_6F. For comparison, the C−F bonds are 1.41 Å long in the covalent graphite fluorides.[1] The unusually long C−F bonds are called semi-ionic or semicovalent.[3,8] They are assumed to be formed between a sp^2 hybridized carbon atom of the sheet and the fluorine atom.[3,8]

The long C−F distances in the stage 1 C_xF phases ($6 > x > 2$) with semi-covalent C−F bonds are clearly unusual. Bond elongations by 20−50% of their regular lengths are more typical for transition states describing bond-breaking reactions than for minima. The question arises which forces prevent these bonds from shortening in ordered stage 1 C_xF phases, especially as the thermodynamic analysis of Dresselhaus et al. suggests that for $x < 3$ covalent bonds should be favored significantly.[4,10,11] Also, rather short C−F distances typical for covalent bonds were found in computational studies of fluorinated graphite nanoclusters.[12] Nakajima et al. conclude that fluorinated buckminsterfullerene derivatives $C_{60}F_{30}$−$C_{60}F_{50}$ also have semi-covalent C−F bonds,[13−16] although the C−F bond lengths, e.g., in $C_{60}F_{48}$, are well-known from single-crystal X-ray structural analysis to range between 1.29 and 1.43 Å.[17] Here we report a computational investigation of the structural models suggested earlier for the stage 1 graphite intercalation compound of C_3F composition.[8]

Computational Details

The density functional theory computations employed the Perdew−Burke−Ernzerhof (PBE)[18,19] general gradient approximation, the all-electron Gaussian 3-21G and 6-31G* basis sets,[20,21] and periodic boundary conditions (PBC).[22−24] The PBC were chosen to simulate either individual C_3F sheets or three-dimensional structures. As the structural parameters obtained from 2D or 3D simulations are very similar, we will focus here on the 3D-PBE/6-31G* data. Harmonic vibrational frequencies were computed by finite differences of analytic gradients, but the current implementation does not allow determining the infrared intensities. All computations employed a development version of the Gaussian[25] program.

Results and Discussion

A. Structural Data. Based on the available experimental data, Mallouk et al.[7,8] suggested a structural model for their stage 1 C_3F compound with the following characteristics: (i) the carbon sheets are eclipsed; (ii) fluorine atoms are not at the midpoint between two sheets but approach carbon atoms of the upper or lower sheet; (iii) the carbon sheets remain planar and the C−F

[†] Part of the special issue "Fritz Schaefer Festschrift".

* Corresponding authors. E-mail: Holger.Bettinger@rub.de; guscus@rice.edu.

[‡] Ruhr-Universität Bochum.

[§] Rice University.

10.1021/jp0310854 CCC: $27.50

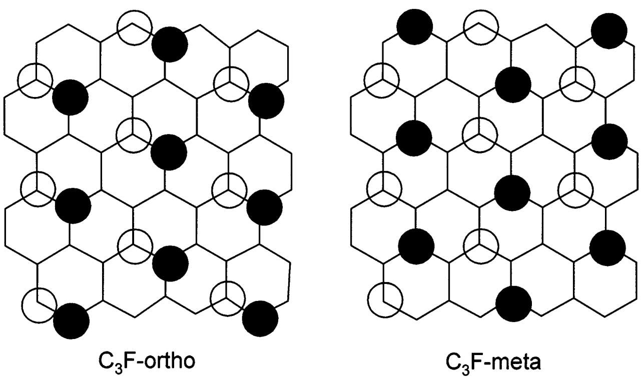

Figure 1. Two possible arrangements of fluorine atoms (open and filled circles symbolize F atoms below and above the graphene plane, respectively) can be characterized by their relative orientation on opposing sides of the sheet, "ortho" or "meta". Note that the "para" orientation is identical to "ortho" for C_3F.

bond involves $C(sp^2)-F$ interactions with C−F distances of 2.1−2.2 Å; and (iv) fluorine atoms are distributed between two sheets so as to allow interlocking of the layers and thus close packing of the sheets in agreement with the measured c_0 distance. To explain the increased electric conductivity compared to covalent $(CF)_x$,[7,8] it was further assumed that the fluorine atoms on opposing sides of a graphite sheet are bonded to neighboring carbon atoms ("ortho arrangement", Figure 1) as then nonfluorinated conjugated π-bonds result.[8] Another arrangement, C_3F-meta, where the fluorine atoms on opposing sides of the graphitic sheet are in meta position, is, however, also possible.

While by virtue of the meta arrangement an interlocking of intercalant layers is ensured for a A/A[26] stacking sequence (C_6F_2 computational unit cell), we need to double the unit cell for C_3F-ortho to allow interlocking of the intercalant layers ($C_{12}F_4$ computational unit cell, see Figure 2). Changes in the stacking sequences should not affect the intraplanar structure, an assumption which has also been invoked in a previous computational study of $(CF)_n$.[27]

The following structural data were obtained for C_3F-ortho and C_3F-meta: (i) carbon sheets are eclipsed; (ii) all sp^2 hybridized carbon atoms are found to be coplanar in C_3F-meta, but they form a dihedral angle of ±9.3° in C_3F-ortho; (iii) in C_3F-meta, the carbon atoms carrying the fluorine atoms are displaced out of the plane spanned by the sp^2 hybridized carbon atoms by ±0.38 Å; (iv) the C−C bond lengths are not equal but range between 1.39 and 1.53 Å (C_3F-ortho) and 1.42−1.49 Å (C_3F-meta), where the shorter C−C bonds are between the (formally) sp^2 hybridized atoms; (v) the C−F bonds lengths are 1.43 Å (C_3F-ortho) and 1.49 Å (C_3F-meta); and (vi) the interlayer distances, available from the length of the translational vectors in z-direction, are 4.80 Å (C_3F-ortho) and 4.84 Å (C_3F-meta).

Hence, both structural models differ from the one derived from experimental X-ray data: the coplanarity of *all* carbon atoms, and consequently the unusually long C−F bonds, cannot be confirmed. However, the interpretation of experimental data assumed coplanarity of the carbon atoms, as otherwise the C−C "bond distances projected into the *ab* plane are required to be coincidentally the same as the in-plane pristine graphite distances."[7] This was considered to be unlikely.[7]

In the structure computed for C_3F-meta, the projected C−C distances have lengths (1.435 Å at 3D-PBE/6-31G*; 1.420 at 2D-PBE/3-21G) very similar to the in-plane C−C bonds (1.420 Å at 2D- and 3D-PBE/6-31G*). The F atoms are ±1.9 Å above the *ab* plane, in reasonable agreement with the 2.1−2.2 Å derived by Mallouk and Bartlett based on van der Waals radii and interlayer spacings.[7] The closest distances between fluorine atoms bound to adjacent sheets is 2.71 Å, which is about twice the van der Waals radius of fluorine.[28] The interlayer spacing of 4.84 Å computed here is somewhat shorter than the 5.45 Å given for $C_{3.20}F$ by Mallouk and Bartlett.[7] The interlayer spacing should strongly depend on the ability of the computational method to correctly describe the interactions between sheets, but density functional theory might not be particularly well suited for this purpose. As 2D and 3D computations give similar qualitative descriptions of an individual C_3F sheet, we assume that an improved treatment of the interaction between sheets should not change the structure of an individual sheet qualitatively. The band gaps in C_3F-meta and C_3F-ortho are negligible. Hence, there is the possibility of charge carrier mobility and increased electric conductivity in C_3F-meta, despite the lack of extended chains of conjugated π bonds. Finally, the intraplanar structure of C_3F-ortho is so strongly distorted that projection

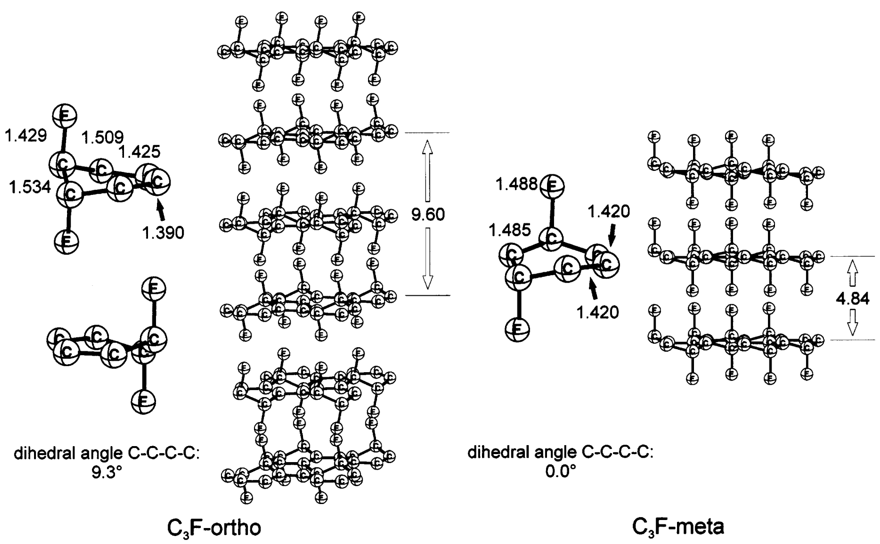

Figure 2. Structures of C_3F graphite fluorine intercalation compounds C_3F-ortho and C_3F-meta as computed at the 3D-PBE/6-31G* level of theory. For clarity, the unit cells are depicted in larger scale than the parts of the extended structures. Bond lengths are given in Å, the dihedral angles given involve the carbon atoms with no fluorine atoms attached.

TABLE 1: Comparison of CF Bond Lengths and Vibrational Frequencies for C_xF Graphite Intercalation Compounds[a]

		r(C−F)/Å		ν(C−F)/cm^{-1}	
compound	dim.	theory	exp.	theory	exp.
$(CF)_n$	2D	1.380		1204	
	3D	1.380, 1.37[b]	1.41[c]	1165	1215−1219[d]
C_3F-ortho	3D	1.428		935	∼1100, br.[e]
C_3F-meta	3D	1.48		671	

[a] Theoretical data obtained at the PBC−PBE/6-31G* level of theory, unless noted otherwise. [b] Plane wave local density approximation, see ref 27. [c] References 32, 33. [d] References 29−31. [e] Reference 8.

of the carbon atoms into the plane does not result in approximately equal CC distances.

B. Vibrational Frequency Data. We computed the harmonic vibrational frequencies of the two structural models as the IR spectrum of the C_3F GIC is known from experiments. The IR spectral data of $(CF)_n$ can serve as a guide for the quality of our approach: the experimental spectrum shows an intense band at around 1215−1219 cm^{-1}, which has been assigned to the ν_{as}(CF) vibration.[1,29−31] We obtain a value for the C−F stretching vibration (ν(CF)) of 1204 cm^{-1} for a two-dimensional $(CF)_n$ sheet and of 1165 cm^{-1} for three-dimensional $(CF)_n$. Mallouk et al. observed a strong and very broad IR absorption centered around 1100 cm^{-1} for their F-GIC and assigned this to C−F stretching vibrations.[8] We find ν(CF) at 935 cm^{-1} for C_3F-ortho, while it is computed at 671 cm^{-1} in C_3F-meta. Hence, the C_3F-ortho model is in better agreement with the experimental IR data.

Conclusions

Based on the computed geometric and electronic structure, C_3F-meta is a suitable model for the stage 1 C_3F phase synthesized by Mallouk et al.[7,8] Its structure is characterized by a buckled carbon sheet and, as a consequence thereof, by short C−F bond lengths (1.49 Å). The structural features of C_3F-ortho do not agree as well with the model derived from experiment. However, its even shorter C−F bonds (1.42 Å) result in a higher ν_{as}(CF) frequency (935 cm^{-1}) than that computed for C_3F-meta (671 cm^{-1}). If the strong, intensive band observed experimentally at 1100 cm^{-1} is indeed due to a CF stretching vibration, then the C−F bonds must be drastically shorter than assumed previously (2.1−2.2 Å). Indeed, Panich concluded after reviewing NMR investigations that the CF bonding in F−GIC and graphite fluorides do not show significant difference and that available data can be explained without involving semi-ionic CF bonds.[34]

Acknowledgment. H.F.B. is grateful to the Fonds der Chemischen Industrie for a Liebig Fellowship and to Professor Sander for encouragement. This work was supported by the National Science Foundation and the Welch Foundation.

References and Notes

(1) Watanabe, N.; Nakajima, T.; Touhara, H. *Graphite Fluorides*; Elsevier: Amsterdam, 1988.

(2) *Fluorine-Carbon and Fluoride-Carbon Materials*; Nakajima, T., Ed.; Marcel Dekker: New York, 1995.

(3) Nakajima, T. Synthesis, Structure, and Physicochemical Properties of Fluorine-Graphite Intercalation Compounds. In *Fluorine-Carbon and Fluoride-Carbon Materials*; Nakajima, T., Ed.; Marcel Dekker: New York, 1995; p 1.

(4) Dresselhaus, M. S.; Endo, M.; Issi, J.-P. Physical Properties of Fluorine- and Fluoride-Graphite Intercalation Compounds. In *Fluorine-Carbon and Fluoride-Carbon Materials*; Nakajima, T., Ed.; Marcel Dekker: New York, 1995; p 95.

(5) Panich, A. M.; Nakajima, T.; Goren, S. D. *Chem. Phys. Lett.* **1997**, *271*, 381.

(6) Panich, A. M.; Nakajima, T.; Vieth, H.-M.; Privalov, A. F.; Goren, S. D. *J. Phys.: Condens. Matter* **1998**, *10*, 7633.

(7) Mallouk, T.; Bartlett, N. *J. Chem. Soc., Chem. Commun.* **1983**, 103.

(8) Mallouk, T.; Hawkins, B. L.; Conrad, M. P.; Zilm, K.; Maciel, G. E.; Bartlett, N. *Philos. Trans. R. Soc. London A* **1985**, *314*, 179.

(9) Hagiwara, R.; Lerner, M.; Bartlett, N. *J. Chem. Soc., Chem. Commun.* **1989**, 573.

(10) di Vittorio, S. L.; Dresselhaus, M. S.; Dresselhaus, G. *J. Mater. Res.* **1993**, *8*, 1578.

(11) Oshida, K.; Endo, M.; Nakajima, T.; di Vittorio, S. L.; Dresselhaus, M. S.; Dresselhaus, G. *J. Mater. Res.* **1993**, *8*, 512.

(12) Saito, R.; Yagi, M.; Kimura, T.; Dresselhaus, G.; Dresselhaus, M. S. *J. Phys. Chem. Solids* **1999**, *60*, 715.

(13) Nakajima, T.; Matsuo, Y.; Kasamatsu, S.; Nakanishi, K. *Carbon* **1994**, *32*, 1177.

(14) Matsuo, Y.; Nakajima, T. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1943.

(15) Scuseria, G. E.; Odom, G. K. *Chem. Phys. Lett.* **1992**, *195*, 531.

(16) Scuseria, G. E. *Chem. Phys. Lett.* **1991**, *176*, 423.

(17) (a) Neretin, I. S.; Lyssenko, K. A.; Antipin, M. Y.; Slovokhotov, Y. L. *Russ. Chem. Bull.* **2002**, *51*, 754. (b) Hitchcock, P. B.; Taylor, R. *Chem. Commun.* **2002**, 2078.

(18) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(19) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396(E).

(20) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(21) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(22) Kudin, K. N.; Scuseria, G. E. *Phys. Rev. B* **2000**, *61*, 16440.

(23) Kudin, K. N.; Scuseria, G. E. *Phys. Rev. B* **2000**, *61*, 5141.

(24) Kudin, K. N.; Scuseria, G. E.; Schlegel, H. B. *J. Chem. Phys.* **2001**, *114*, 2919.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian Development Version 2003*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **1981**, *30*, 139.

(27) Charlier, J.-C.; Gonze, X.; Michenaud, J.-P. *Phys. Rev. B* **1993**, *47*, 16162.

(28) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(29) Rüdorff, W.; Brodersen, K. *Z. Naturforsch.* **1957**, *12b*, 595.

(30) Kita, Y.; Watanabe, N.; Fujii, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3832.

(31) Lagow, R. J.; Badachhape, R. B.; Wood, J. L.; Margrave, J. L. *J. Chem. Soc., Dalton Trans.* **1974**, *12*, 1268.

(32) Touhara, H.; Kadono, K.; Fujii, Y.; Watanabe, N. *Z. Anorg. Allg. Chem.* **1987**, *544*, 7.

(33) Mahajan, V. K.; Badachhape, R. B.; Margrave, J. L. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1103.

(34) Panich, A. M. *Synth. Metals* **1999**, *100*, 169.