Carbon···Carbon Weak Interactions

Ibon Alkorta,*,[†] Fernando Blanco,[†] José Elguero,[†] José A. Dobado,[‡] Santiago Melchor Ferrer,[‡] and Isaac Vidal[‡]

Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain, and Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Granada, E-18071 Granada, Spain

Received: April 02, 2009; Revised Manuscript Received: May 30, 2009

A theoretical study of the complexes formed by systems with electron-deficient and electron-excessive carbon atoms was carried out using DFT and ab initio methods up to the CCSD(T)/aug-cc-pVTZ computational level. Stable complexes with interaction energies between −6.0 and −22.8 kJ mol^{-1} were obtained that correspond to weak C···C interactions. The atoms in molecules analysis of the complexes confirmed the presence of these interactions. Natural energy decomposition analysis and electron localization function analysis were performed to gain further insight into the nature of the interaction. Polarization is the most important stabilizing term in these complexes.

Introduction

In general, physical properties smoothly change with continuous variables such as distance and time. This is also true for electron density related properties, as those defined in the bond critical point (bcp).[1−3] This can be illustrated using as an example the nature of the C−C bond. Recently, some of us reported unexpected long C−C bonds (>2.7 Å) in 1,3-metalladiyne complexes.[4] They were characterized using the quantum theory of atoms in molecules and the electron localization function (ELF).

Concerning covalent C−C bonds, very short and very long bond lengths were reviewed by Hoffmann et al. in 2005,[5] and other articles appeared afterward.[6,7] This topic is related to C−C bond dissociation energies.[8−14] Several articles also reported the existence of bond critical points in long C−C bonds: *ortho*-carboranes,[15,16] π−π complexes,[17] interactions of charged aromatic systems with neutral ones,[18] and complexes of HNC with electron-deficient aromatic systems.[19,20]

The existence of two-electron/four-centers (2e/4c) long distance C−C bonds (≥2.9 Å) has been explored experimentally[21] and theoretically.[22,23] These systems are formed by two anionic radicals stabilized by the presence of cationic counterions. The dispersive forces seem to be important in the proper description of the electronic state of these systems.[23] These systems show the presence of bond critical points in the electron density topological analysis between the carbon atoms of both molecules.[24]

In the present article, we focused our attention in the interaction of closed shell systems where the interaction is due to the presence of an electron-excessive carbon atom, in one molecule, and an electron-deficient carbon atom in the other. An additional characteristic important for these molecules is the geometrical accessibility of both carbon atoms to form an interaction. Thus, as carbon-deficient systems, carbon dioxide (CO_2) and cyanogen (NCCN) were chosen. As electron-excessive carbon atoms, those with carbene-type characteristic were selected, including in this group some simple carbenes (:CH_2, :CF_2, and :CCH_2), carbon monoxide and carbon monosulfide (CO and CS), isocyanic acid derivatives (HNC and LiNC), and the two simplest multiple bonded C−C molecules, ethylene and acetylene.

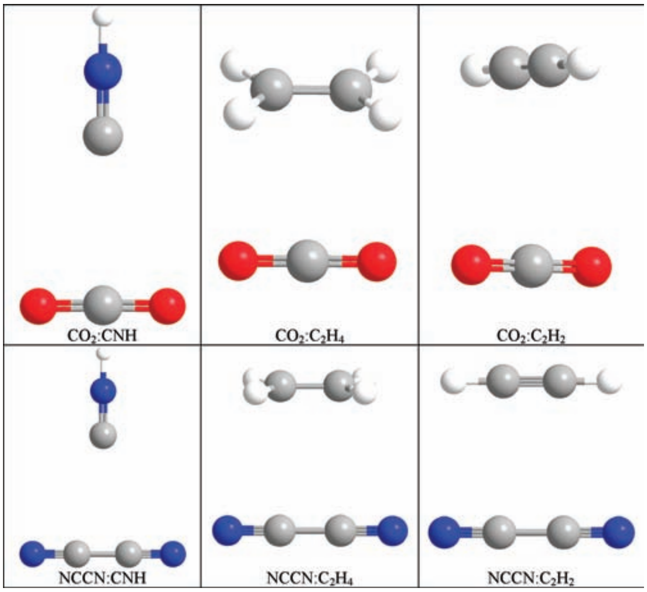

Figure 1. Geometry of some of the complexes optimized at the MP2/aug-cc-pVTZ computational level.

Methods

The geometry of the systems was initially optimized at the M05-2x/6-311++G(d,p)[25,26] computational level. This functional has shown to provide a good description for a large variety of molecular interaction complexes.[27] Frequency calculations at this computational level were performed to confirm that the structures obtained correspond to energetic minima. Further optimization was performed with the MP2/aug-cc-pVTZ,[28,29] and, for selected cases, with the CCSD(T)/aug-cc-pVTZ.[30] All these calculations were carried out within the Gaussian 03 package.[31]

The interaction energy is defined as the difference between the total energy of the complexes minus the sum of the energies

---

* To whom correspondence should be addressed. E-mail: ibon@iqm.csic.es.
[†] Instituto de Química Médica, CSIC.
[‡] Universidad de Granada.

10.1021/jp903016e CCC: $40.75

TABLE 1: Intermolecular C···C Distances (Å) of the Minima Obtained

complex	M05-2x/6-311++G(d,p)	MP2/aug-cc-pVTZ	CCSD(T)/aug-cc-pVTZ
CO_2:CCH_2	3.041	3.055	3.034
CO_2:CF_2	3.155	3.158	
CO_2:CH_2	3.017	3.049	3.066
CO_2:CNH	3.116	3.088	3.089
CO_2:CNLi	2.982	2.986	2.986
CO_2:CO	3.241	3.181	3.183
CO_2:CS	3.097	3.096	3.091
CO_2:HCCH	3.414	3.367	
CO_2:H_2CCH_2	3.309	3.303	
NCCN:CCH_2	3.271	3.203	
NCCN:CF_2	3.394	3.316	
NCCN:CH_2	3.176	3.217	
NCCN:CNH	3.330	3.224	
NCCN:CNLi	3.208	3.114	
NCCN:CO	3.450	3.343	
NCCN:CS	3.306	3.218	
NCCN:HCCH	3.352	3.258	
NCCN:H_2CCH_2	3.403	3.320	

TABLE 2: Interaction Energy (kJ mol^{-1}) of the Energetic Minima Complexes Obtained

complex	M05-2x/6-311++G(d,p)	MP2/aug-cc-pvtz	CCSD(T)/aug-cc-pVTZ
CO_2:CCH_2	−11.00	−10.66	−10.55
CO_2:CF_2	−6.92	−7.46	
CO_2:CH_2	−14.52	−10.13	−11.20
CO_2:CNH	−8.68	−9.66	−9.45
CO_2:CNLi	−15.18	−15.60	−15.61
CO_2:CO	−4.69	−5.98	−5.74
CO_2:CS	−8.97	−9.58	−8.61
CO_2:HCCH	−4.70	−5.99	
CO_2:H_2CCH_2	−8.01	−9.04	
NCCN:CCH_2	−11.81	−14.58	
NCCN:CF_2	−6.92	−9.54	
NCCN:CH_2	−16.90	−15.44	
NCCN:CNH	−9.87	−13.50	
NCCN:CNLi	−18.09	−22.78	
NCCN:CO	−4.79	−7.52	
NCCN:CS	−9.92	−13.43	
NCCN:HCCH	−9.98	−13.50	
NCCN:H_2CCH_2	−8.36	−12.15	

of the isolated monomers. The basis sets used in this work are of sufficient quality, and thus basis set superposition errors (BSSEs) should be rather small.[32] Moreover, it was shown that uncorrected MP2/aug-cc-pVTZ binding energies lie between corrected and uncorrected MP2/aug-cc-pVQZ energies.[33] BSSE corrections may not always improve binding energies of weakly bonded complexes, since in the counterpoise method,[34] a monomer may utilize the valence and core functions of its partner, which are not available to the monomer in the complex.

The electron density topology and atomic properties were evaluated within the atoms in molecules (AIM) methodology[35] with the AIMPAC[36] and Morphy98[37] programs. The calculation of the atomic properties was carried out by integration within the atomic basins using the default parameters, except in those cases where the integrated Laplacian was larger than 1×10^{-3} where more tight conditions were used. Previous reports showed small errors in the energy and charge for systems where all the values of the integrated Laplacian were smaller than the mentioned value.[38]

ELF, as interpreted by Silvi and Savin[39] was computed with the ToPMoD software package.[40] Isosurfaces represented were taken at the value of 0.75 and represented with the SciAn[41] visualization software.

The orbital interactions were analyzed within the natural bond orbital (NBO)[42] framework and the NBO 5.0G program.[43] This method allows the analysis of the interaction between filled and empty orbitals and associates them to charge-transfer processes. In addition, the natural energy decomposition analysis was carried out to gain insight into the source of the interactions. These calculations were performed using the optimized geometries at the M05-2x/6-311++G(d,p) at the same computational level within the Gamess program.[44]

TABLE 3: Term Contribution (kJ mol^{-1}) to the Interaction of Energy (Ei)

terms	M05-2x/6-311++G(d,p)	MP2/aug-cc-pvtz
NCCN	−1.6	−4.3
:CCH_2	−10.6	−10.5
:CF_2	−6.1	−6.4
:CH_2	−14.9	−10.7
:CNH	−8.5	−9.5
:CNLi	−15.9	−17.1
:CO	−4.0	−4.6
:CS	−8.7	−9.4
:HCCH	−6.6	−7.6
:H_2CCH_2	−7.4	−8.5
R^2	0.994	0.994

Results and Discussion

Geometry. The intermolecular distances obtained for the complexes are gathered in Table 1, and some of them are represented in Figure 1. To the best of our knowledge, no

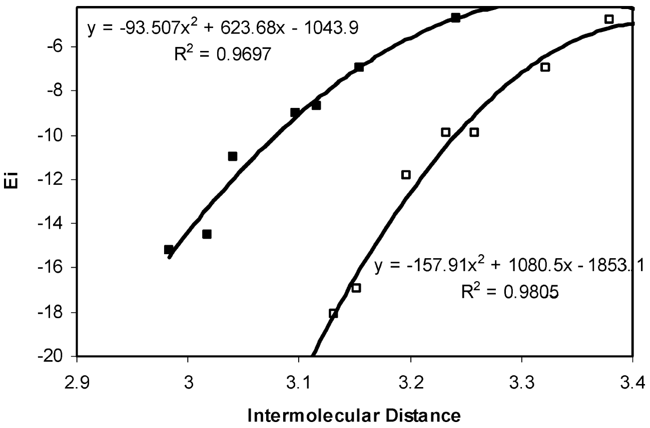

Figure 2. C•••C distance vs Ei obtained at the M05-2x/6-311++G(d,p) computational level. Black and white squares correspond to the CO_2 and NCCN complexes, respectively.

experimental geometrical information for any of these complexes is available in the literature, but the related CO_2:NCH complex shows a C_{2v} symmetry with the nitrogen pointing toward the carbon atom of the CO_2 and an intermolecular distance of 3.0 Å.[45] A search in the literature indicates that only one of the complexes studied here, CO_2:CO, was previously studied.[46] The geometrical and energetic results reported for that complex are analogous to those described here.

All the complexes obtained in the present work show C_{2v} symmetry and correspond to energetic minima. Since the purpose of the article is to study C•••C interactions, other possible dispositions of the complexes were not explored. The intermolecular distances obtained range from 2.99 to 3.16 Å in the CO_2 series and from 3.04 to 3.32 Å in the cyanogen one. In general, the observed intermolecular distances are longer in the cyanogen complexes than in the carbon dioxide ones with the exception of the complexes with :CH_2. The three computational methods considered here provide similar intermolecular distances for a given complex.

The interaction energy and symmetry of the complexes are reported in Table 2. The results obtained for the carbon dioxide complexes are very similar in the three computational methods, while for the cyanogen ones, the M05-2x/6-311++G(d,p), in general, slightly underestimate the ones obtained with the MP2/aug-cc-pVTZ one. On the basis of these results, it can be concluded that the DFT method used here provides reasonable results and thus it can be used for larger systems.

The comparison of the results obtained for the two series indicates that stronger complexes are obtained with cyanogen for a given electron donor. In addition, on the basis of the

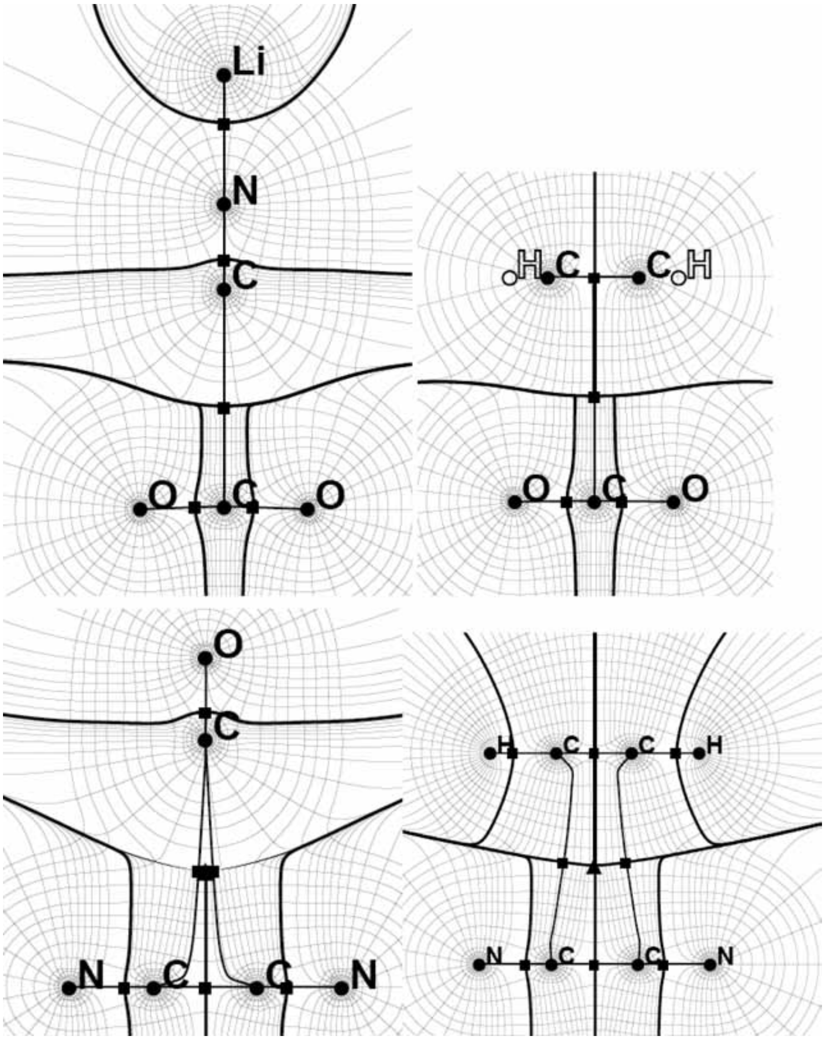

Figure 3. Electron density map of the CO_2:CNLi, CO_2:C_2H_4, NCCN:CO, and NCCH:HCCH complexes obtained at the M05-2x/6-311++G(d,p) computational level. The circles, squares, and triangles represent the position of the atoms, bond, and ring critical points, respectively. The bond paths are shown.

TABLE 4: Properties at the bcp (au) and Integrated Values of the Energy (kJ mol^{-1}) and Charge (e) within the AIM Methodology

complex	ρ_{bcp}	$\nabla^2\rho$	ΔE (CO_2 or NCCN)	charge transfer
CO_2:CCH_2	0.0091	0.0332	−143.6	−0.020
CO_2:CF_2	0.0074	0.0273	123.0	−0.015
CO_2:CH_2	0.0109	0.0357	−68.0	−0.029
CO_2:CNH	0.0075	0.0279	−93.4	−0.016
CO_2:CNLi	0.0103	0.0353	−147.7	−0.029
CO_2:CO	0.0055	0.0216	4.7	−0.009
CO_2:CS	0.0078	0.0291	514.4	−0.017
CO_2:HCCH	0.0067	0.0246	−170.6	−0.017
CO_2:H_2CCH_2	0.0064	0.0209	−255.6	−0.018
NCCN:CCH_2	0.0070	0.0243	−72.2	−0.012
NCCN:CF_2	0.0057	0.0191	259.8	−0.008
NCCN:CH_2	0.0095	0.0314	−26.2	−0.020
NCCN:CNH	0.0060	0.0207	−10.0	−0.009
NCCN:CNLi	0.0079	0.0272	−62.2	−0.020
NCCN:CO	0.0045	0.0157	99.7	−0.004
NCCN:CS	0.0063	0.0218	682.5	−0.009
NCCN:HCCH	0.0054	0.0165	−98.3	−0.009
NCCN:H_2CCH_2	0.0053	0.0148	−181.0	−0.011

interaction energy, the complexes can be ordered for the two series in a similar way according to the interacting molecule. Thus, these results indicate that the electronic population around the interacting carbon atom is determinant for the value of the electron density. Thus, the strongest complexes correspond to the carbenes being their ability to interact with electron-deficient atoms modulated by the atoms bonded to it.

The fact that the interaction order is preserved, independently from which electron-deficient molecule (CO_2 or NCCN) it is connected to, suggests that the magnitude of the attraction is a proportional combination of the characteristics of the isolated binding units.

The interaction energies of Table 2 are related by linear regressions of significant to highly significant quality:

All complexes: Ei (M05-2x) = (0.86 ± 0.04) Ei (MP2), $n = 18$, $R^2 = 0.964$

CO_2 complexes: Ei (M05-2x) = (1.00 ± 0.06) Ei (MP2), $n = 9$, $R^2 = 0.971$

NCCN complexes: Ei (M05-2x) = (0.80 ± 0.04) Ei (MP2), $n = 9$, $R^2 = 0.977$

CO_2 complexes: Ei [CCSD(T)] = (1.00 ± 0.02) Ei (MP2), $n = 6$, $R^2 = 0.997$

M05-2x: Ei (NCCN) = (1.15 ± 0.06) Ei (CO_2), $n = 9$, $R^2 = 0.979$

MP2: Ei (NCCN) = (1.44 ± 0.06) Ei (CO_2), $n = 9$, $R^2 = 0.984$

Then, we tried an analysis of the contribution of the different molecules to the Ei energies and found the coefficients of Table 3.

Both methods yield similar results with the exception of the :CH_2 complexes. The stabilization order is CNLi > CH_2 > CCH_2 > CS > CNH > H_2CCH_2 > HCCH > CF_2 > CO.

A clear relationship is found between the interatomic distance and the Ei when the complexes with HCCH and H_2CCH_2 are not considered (Figure 2). Thus, the shorter the intermolecular distance, the strongest the complex.

The topological analysis of the electron density of the complexes shows a variety of patterns (Figure 3). In the case of the CO_2 complexes, a unique bond path links the two interacting carbon atoms, except in the complexes with acetylene and ethylene where the bond path reaches the center of the multiple bond and then bifurcates to each carbon atom as in the symmetric HB complexes with π-systems.[47,48] In the case of the complexes with cyanogen, the molecules presenting a unique electron-rich carbon atom show a V-shaped molecular graph connecting this atom with the two electron-deficient ones of the cyanogen. In those of cyanogen with acetylene and ethylene, two intermolecular bond paths are found connecting each electron-deficient carbon atom with the nearest electron-rich one. The latter type of molecular graph resembles those found in the 2-electron/4-atom C−C bonds.[24]

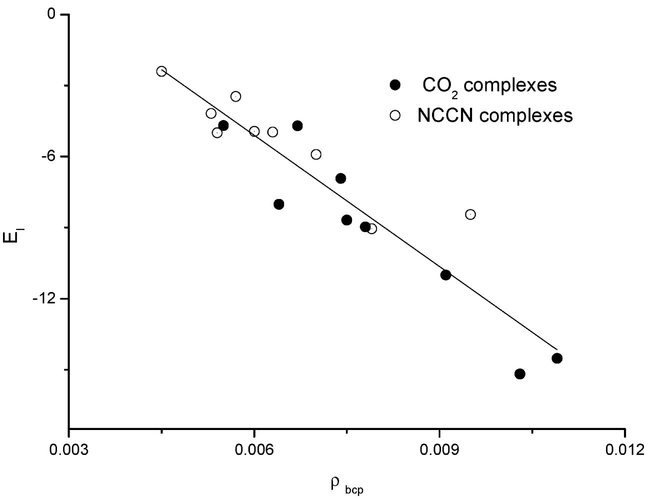

Figure 4. Ei per interaction (kJ mol^{-1}) vs ρ_{bcp} (au). The adjusted linear correlation presents a square correlation coefficient of 0.87.

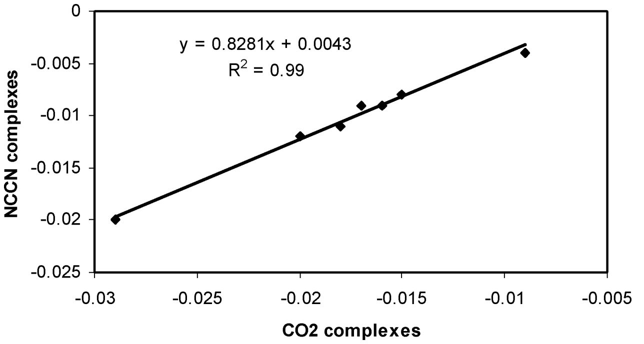

Figure 5. Charge transfer (e) in the NCCN vs CO_2 complexes.

The characteristics of the intermolecular bcp's are reported in Table 4. The small value of the electron density and positive value of the Laplacian are indicative of closed shell interactions as those found in weak HB and vdW complexes.[49] In general, the stronger the interaction, the larger the ρ_{bcp}. Interestingly, the representation of the interaction energy per interaction (two intermolecular bcp's in the NCCN complexes) vs the electron density presents all the points grouped along a straight line (Figure 4). This linearity indicating a relationship in these complexes between the interaction energy and the electron density has been described for hydrogen-bonded complexes.[50]

The integrated charge within the atomic basins shows a charge transfer from the molecules containing the electron-rich carbon atoms to those with the electron-deficient ones. The values of the charge transfer are linearly correlated in the two series, being larger in the CO_2 complexes than in the NCCN ones (Figure 5).

The integrated energy for each molecule within the complex shows a stabilization of the electron acceptor except for the complexes with CO, CS, and CF_2 where the opposite happens. These complexes are, in general, the ones with the smallest charge transfer observed in the two series.

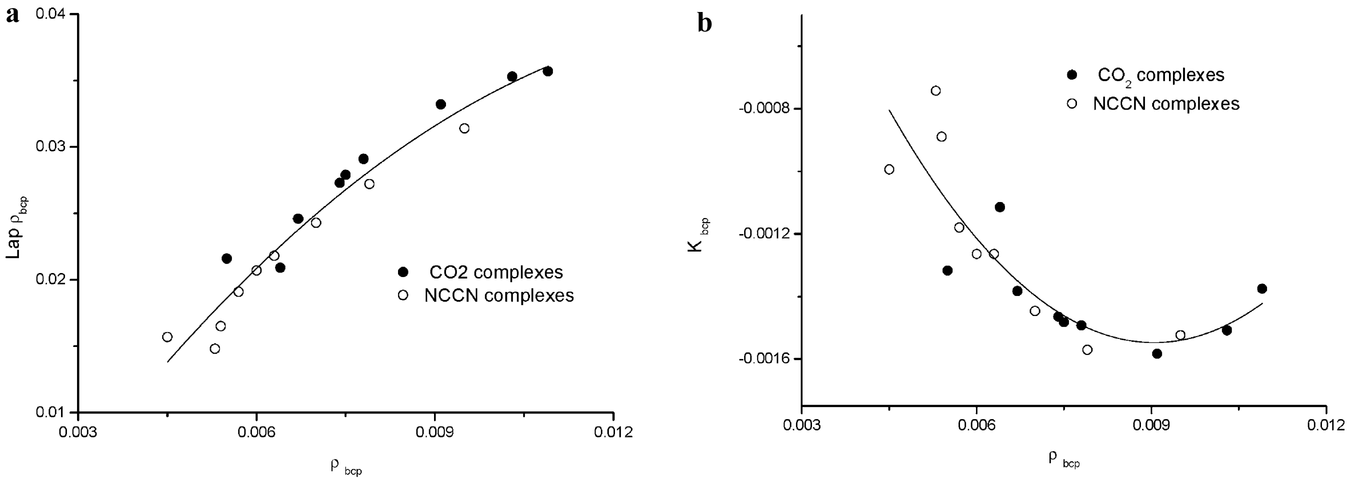

Figure 6. Electron density at the bcp vs (a) Laplacian and (b) kinetic energy density, *K* (au).

The interactions obtained are weak, but the associated bond path presents a relative broad range, which suggests the existence of a continuous variation of the bond properties, and therefore an ordered classification according to the measured AIM parameters was attempted. Thus, the electronic parameters computed at the intermolecular C···C bcp's was represented using the schemes proposed by Wozniak et al.[51] and Nakanishi et al.[52]

In Figure 6a, the Laplacian is plotted against the electron density at the bcp according to the proposal of Wozniak and co-workers, and Figure 6b shows the kinetic energy density, *K*, against $\rho(r)$ according to the scheme proposed by Nakanishi and co-workers. The result is a narrow, highly ordered sequence, where the bonds formed with NC−CN generally appear nearer the origin, indicating the weakest character and presenting the lowest values of both $\nabla^2\rho(r)$ and $\rho(r)$.

However, there are several compounds from both families that overlap their values, such as compound NC−CN:CCH_2, whose values lie between those of compounds formed with CO_2. The data of Figure 6a,b fit into second-order polynomial, resulting in r^2 values of 0.946 and 0.974, respectively.

The coincidence between the Wozniak and Nakanishi plots is not a surprise, because for such small electronic densities, both $\nabla^2\rho$ and K behave almost linearly with the electron density, and therefore the correlation for all points is coherently good. Although this is an expected behavior, it is worth noting that the proportionality constant is the same for all compounds, indicating the presence of a common trend for these weakly bound complexes. As the bonding becomes stronger, the group of points starts to deviate from the linear regime toward more negative values of the Laplacian and positive K, for Wozniak and Nakanishi schemes, respectively.

With regard to the ELF analysis of the C···C interaction, it reveals that the charge density is depleted near the interaction zone, as noticed in the retraction of the ELF isosurfaces. In addition, a slight influence can be seen in the basin populations with respect to the isolated monomers. Overall, charge tends to abandon the interaction area, because of the mentioned depletion. In Figure 7, this behavior is exemplified for the H_2CCH_2:NC−CN complex. Here, an electron displacement in the C=C double bond toward the basin farthest from the other interacting unit is observed. The previous equilibrium in the population between the two C−C basins is broken due to the interaction, and population of the higher basin is reinforced. Complementarily, in the NCCN, charge flows from the central C−C basin and the external N basins toward the C basins, which are those that participate in the long bond formation.

TABLE 5: Main Component of the NBO Orbital Interaction Obtained with the NBO and Components of the NEDA Analysis (kJ mol^{-1})

		NEDA					
	Lp C → σ^* C−X	charge transfer	electrostatic	polarization	exchange	deformation (CO_2/NCCN)	deformation (e-donor)
CO_2:CCH_2	9.7	−15.2	−18.5	−34.7	−19.8	21.8	55.7
CO_2:CF_2	6.2	−11.7	−11.0	−8.4	−10.1	7.2	27.7
CO_2:CH_2	13.6	−16.8	−26.7	−26.8	−21.0	16.0	62.1
CO_2:CNH	6.9	−8.8	−13.2	−17.9	−12.9	12.8	31.6
CO_2:CNLi	15.1	−16.4	−26.8	−32.6	−20.6	27.3	53.4
CO_2:CO	3.4	−5.7	−5.8	−9.0	−8.0	5.7	18.5
CO_2:CS	6.9	−14.8	−13.2	−30.3	−17.0	21.1	46.2
CO_2:HCCH	3.5	−4.5	−5.5	−11.9	−11.3	12.6	16.4
CO_2:H_2CCH_2	4.1	−12.0	−11.9	−17.9	−17.2	27.0	24.6
NCCN:CCH_2	8.4	−14.6	−16.7	−37.0	−21.0	17.4	60.6
NCCN:CF_2	5.4	−11.9	−9.1	−9.9	−10.9	5.9	29.5
NCCN:CH_2	14.6	−15.2	−24.6	−32.6	−23.1	10.7	70.8
NCCN:CNH	6.0	−9.0	−12.8	−19.7	−14.0	11.3	34.6
NCCN:CNLi	11.7	−15.7	−25.4	−35.6	−21.9	23.6	57.4
NCCN:CO	3.2	−6.1	−5.2	−10.1	−8.9	5.1	20.8
NCCN:CS	6.2	−14.9	−12.5	−34.3	−19.2	18.0	54.0
NCCN:HCCH	4.4	−11.1	−12.4	−23.0	−19.2	25.0	31.2
NCCN:H_2CCH_2	4.5	−11.0	−10.6	−18.7	−17.9	22.6	27.8

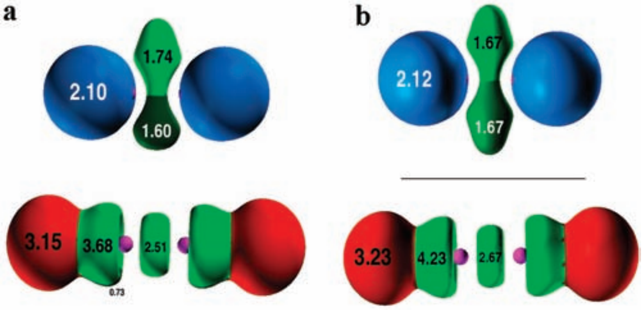

Figure 7. ELF isosurface representation for (a) compound NCCN: H_2CCH_2 and (b) the isolated monomers.

For compounds formed with NCCN, this displacement was evaluated to be in a narrow range of 0.18−0.21 e. For those formed with CO_2, a similar displacement of about 0.12−0.16 e is appreciated. As a result of this charge concentration, in some circumstances the basin receiving this charge excess is split in two, mainly caused by the symmetry breakdown of the previous torus-like attractor. However, it was noticed that neither this splitting nor the population proportion is related to the strength of the interaction. This stresses again the subtle characteristics of these C−C interactions, which, however, may induce noticeable changes in the overall electronic pairing.

The NBO analysis shows a stabilizing interaction of the lone pair or π-electrons with a CO or a CN antibonding orbital of the CO_2 and NCCN molecules. This interaction is very similar to the value of the interaction energy (Table 4), especially in the CO_2 complexes. Of the four stabilization terms (charge transfer, electrostatic, polarization, and exchange), the natural energy decomposition analysis (Table 5) shows that almost always the most important is the polarization term (only two exceptions: CO_2:CF_2 and NCCN:CF_2) followed by the exchange (11 cases) or the electrostatic term (six cases); only in two cases, the charge transfer is the most important contribution (CO_2:CF_2 and NCCN:CF_2). The electronic deformation energy, which corresponds to the difference between the energies of the perturbed and relaxed monomer densities, is larger for the electron donor molecule than for the acceptor one except in one complex with ethylene (CO_2:H_2CCH_2).

Summary

A theoretical study of the complexes formed by the interaction of electron-rich and electron-poor carbon atoms was carried out using DFT and ab initio methods, up to the CCSD(T)/aug-cc-pVTZ computational level. Two molecules with electron-poor carbon atoms were chosen (carbon dioxide and cyanogen) as well as nine molecules with electron-rich carbon atoms, including three carbenes (CH_2, CF_2, and CCH_2), two isocyanide derivatives (CNH and CNLi), carbon monoxide and carbon monosulfide (CO and CS), as well as multiple bonded CC systems (acetylene and ethylene).

Stable complexes with interaction energies that range between −6.0 and −22.8 kJ mol^{-1} at the MP2/aug-cc-pVTZ computational level were obtained. The analysis of the electron density of the complexes shows the presence of intermolecular bonds connecting the carbon atoms of both molecules.

The NBO analysis indicates that the electron-rich carbon atoms transfer electrons to the antibonding orbital of the molecules with electron-poor carbon atoms. The NEDA partition shows that the polarization term is the most important source of stabilization followed by the electrostatic one.

Acknowledgment. This work was carried out with financial support from the Ministerio de Educación y Ciencia (Project No. CTQ2007-61901/BQU) and Comunidad Autónoma de Madrid (Project MADRISOLAR, ref S-0505/PPQ/0225). Thanks are given to the CTI (CSIC) for allocation of computer time.

References and Notes

(1) Knop, O.; Boyd, R. J.; Choi, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 7299.

(2) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. *J. Chem. Phys.* **2002**, *117*, 5529.

(3) Alkorta, I.; Barrios, L.; Rozas, I.; Elguero, J. *J. Mol. Struct.: THEOCHEM* **2000**, *496*, 131.

(4) Vidal, I.; Melchor, S.; Dobado, J. A. *J. Phys. Chem. A* **2008**, *112*, 3414.

(5) Huntley, D. R.; Markopoulos, G.; Donovan, P. M.; Scott, L. T.; Hoffmann, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7549.

(6) Mo, Y. *Org. Lett.* **2006**, *8*, 535.

(7) Kawai, H.; Takeda, T.; Fujiwara, K.; Wakeshima, M.; Hinatsu, Y.; Suzuki, T. *Chem.—Eur. J.* **2008**, *14*, 5780.

(8) Vreven, T.; Morokuma, K. *J. Phys. Chem. A* **2002**, *106*, 6167.

(9) Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158.

(10) Zavitsas, A. A. *J. Phys. Chem. A* **2003**, *107*, 897.

(11) Cao, C.; Yuan, H. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 600.

(12) Frenette, M.; Aliaga, C.; Font-Sanchis, E.; Scaiano, J. C. *Org. Lett.* **2004**, *6*, 2579.

(13) Alkorta, I.; Elguero, J. *Chem. Phys. Lett.* **2006**, *425*, 221.

(14) Alkorta, I.; Elguero, J. *Chem. Phys. Lett.* **2006**, *429*, 58.

(15) Lyssenko, K. A.; Antipin, M. Y.; Lebedev, V. N. *Inorg. Chem.* **1998**, *37*, 5834.

(16) Oliva, J. M.; Allan, N. L.; Schleyer, P. v. R.; Viñas, C.; Teixidor, F. *J. Am. Chem. Soc.* **2005**, *127*, 13538.

(17) González Moa, M. J.; Mandado, M.; Mosquera, R. A. *J. Phys. Chem. A* **2007**, *111*, 1998.

(18) Quiñonero, D.; Frontera, A.; Deyà, P. M.; Alkorta, I.; Elguero, J. *Chem. Phys. Lett.* **2008**, *460*, 406.

(19) Alkorta, I.; Rozas, I.; Elguero, J. *J. Org. Chem.* **1997**, *62*, 4687.

(20) Alkorta, I.; Rozas, I.; Elguero, J. *J. Am. Chem. Soc.* **2002**, *124*, 8593.

(21) Novoa, J. J.; Lafuente, P.; Sesto, R. E. D.; Miller, J. S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2540.

(22) Sesto, R. E. D.; Miller, J. S.; Lafuente, P.; Novoa, J. J. *Chem.—Eur. J.* **2002**, *8*, 4894.

(23) García-Yoldi, I.; Mota, F.; Novoa, J. J. *J. Comput. Chem.* **2007**, *28*, 326.

(24) Miller, J. S.; Novoa, J. J. *Acc. Chem. Res.* **2007**, *40*, 189.

(25) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(26) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(27) (a) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. C* **2008**, *112*, 6860. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(28) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(29) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(30) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03; Gaussian, Inc.: Wallingford, CT, 2004.

(32) Dunning, T. H. *J. Phys. Chem. A* **2000**, *104*, 9062.

(33) Bene, J. E. D.; Shavitt, I. In *Molecular Interactions: From Van der Waals to Strongly Bound Complexes*; Scheiner, S., Ed.; Wiley: Sussex, 1997; p 157.

(34) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(35) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(36) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317.

(37) Popelier, P. L. A. with a contribution from Bone, R. G. A. MORPHY98, a topological analysis program, 0.2 ed.; University of Manchester Institute of Science and Technology: Manchester, England, 1999.

(38) Alkorta, I.; Picazo, O. *Arkivoc* **2005**, *ix*, 305.

(39) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.

(40) (a) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. ToPMoD; Université Pierre et Marie Curie: Paris, 1999. (b) Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *Comput. Chem.* **1999**, *23*, 597. (c) Matito, E.; Silvi, B.; Duran, M.; Solá, M. *J. Chem. Phys.* **2006**, *125*, 024301.

(41) Pepcke, E.; Lyons, J. SciAn 1.2; Florida State University: Tallahassee, FL, 1996.

(42) Weinhold, F.; Landis, C. R. *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge Press: Cambridge, 2005.

(43) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. NBO 5.G; University of Wisconsin: Madison, WI, 2004.

(44) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. Gamess, version 11; Iowa State University: Ames, IA, 2008.

(45) Leopold, K. R.; Fraser, G. T.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 1039.

(46) Venayagamoorthy, M.; Ford, T. A. *J. Mol. Struct.: THEOCHEM* **2005**, *717*, 111.

(47) Rozas, I.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **1997**, *101*, 9457.

(48) Prieto, P.; de la Hoz, A.; Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Phys. Lett.* **2001**, *350*, 325.

(49) Bone, R. G. A.; Bader, R. F. W. *J. Phys. Chem.* **1996**, *100*, 10892.

(50) Mata, I.; Alkorta, I.; Espinosa, E.; Molins, E.; Elguero, J. Topological Properties of the Electron Distribution in Hydrogen Bonded Systems. In *The Quantum Theory of Atoms in Molecules*; Matta, C. F., Boyd, R. J., Eds.; Wiley-VCH: Weinheim, Germany, 2007.

(51) Dominiak, P. M.; Makal, A.; Mallinson, P. R.; Trzinska, K.; Eilmes, J.; Grech, E.; Chruszcz, M.; Minor, W.; Wozniak, K. *Chem.—Eur. J.* **2006**, *12*, 1941.

(52) Nakanishi, W.; Nakamoto, T.; Hayashi, S.; Sasamori, T.; Tokito, N. *Chem.—Eur. J.* **2007**, *13*, 225.

JP903016E