Competition and interplay between the lithium bonding and hydrogen bonding: $R_3C\cdots HY\cdots LiY$ and $R_3C\cdots LiY\cdots HY$ triads as a working model (R=H, CH_3; Y=CN, NC)

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Abstract UMP2 calculations with aug-cc-pVDZ basis set were used to analyze intermolecular interactions in $R_3C\cdots HY\cdots LiY$ and $R_3C\cdots LiY\cdots HY$ triads (R=H, CH_3; Y=CN, NC), which are connected via lithium and hydrogen bonds. To better understand the properties of these systems, the corresponding dyads were also studied. Molecular geometries and binding energies of dyads, and triads were investigated at the UMP2/aug-cc-pVDZ computational level. Particular attention was paid to parameters such as cooperative energies, and many-body interaction energies. All studied complexes, with the simultaneous presence of a lithium bond and a hydrogen bond, showed cooperativity with energy values ranging between −1.71 and −9.03 kJ mol^{-1}. The electronic properties of the complexes were analyzed using parameters derived from atoms in molecules (AIM) methodology. Energy decomposition analysis revealed that the electrostatic interactions are the major source of the attraction in the title complexes.

Introduction

Noncovalent interactions between molecules play a very important role in supramolecular chemistry, molecular biology, and materials science [1]. Although research has focused traditionally on the most common hydrogen bond (HB) interactions,

more recently interest in other types of intermolecular interactions, such as lithium bonds (LB), has grown.

LB is an interesting interaction analogous to HB [2–7]. The common feature of these two interactions is that both hydrogen and lithium atoms possess a single electron in a valence s orbital. The existence of Li-bonding was first suggested as a possibility by Shigorin in 1959 [8], and was predicted theoretically in 1970 by Kollman et al. [9]. Then, in 1975, Ault and Pimentel [10] provided the experimental evidence for Li-bonding, i.e., a large red shift of the Li–Y stretching frequency in X···Li–Y complexes (X=H_3N, Me_3N, H_2O, Me_2O; Y=Cl, Br). To date, LB has been identified in a variety of systems and the concept of Li-bonding has become important in many fields. However, studies on LB interactions are relatively rare [11–13].

One of the new HB possibilities corresponds to that where the electron donor is a radical and participates in the HB via a single electron. It has been shown that the unpaired electron of the methyl radical may attract the hydrogen atom of a proton donor, forming a kind of unconventional HB called a single-electron HB [14]. The single-electron HB has not only been characterized theoretically [15–18] but also investigated experimentally [19]. In view of the similarities between Li bonding and H-bonding, the existence of single-electron LB has been reported theoretically [11].

Careful studies in simple models are of interest in order to extend their conclusion to larger ones. Herein, we designed some simple structures including HB, LB, single-electron HB, and single-electron LB. In this article, we thus constructed $R_3C\cdots HY\cdots LiY$ and $R_3C\cdots LiY\cdots HY$ triads (R=H, CH_3; Y=CN, NC) complexes where four types of bonding coexist. We performed a theoretical study on the eight title triads with the aim of investigating the effect of Li-bonding on a HB and the cooperativity between them. To the best of our knowledge, the study of cooperativity in triads with HB, LB, single-electron HB, and single-electron LB bonding is reported here for the first time.

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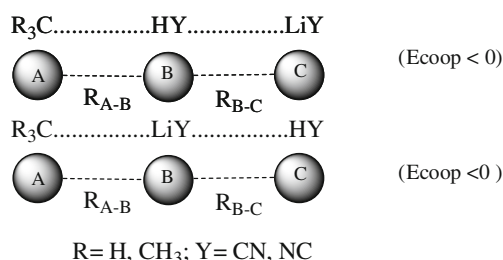
Scheme 1 Disposition of monomers within complexes

Computational details

Structures of monomers and complexes were optimized and characterized by frequency computations at the MP2/aug-cc-pVDZ computational level. The stabilization energy was calculated as the difference of the total energy of the complexes and the sum of the isolated monomers in their minima configuration. The full counterpoise (CP) method [20] was used to correct the stabilization energy from the inherent basis set superposition error (BSSE). Atoms in molecules (AIM) methodology [21] was used to analyze the electron density of the systems considered at the MP2/aug-cc-pVDZ computational level. The topological analysis was carried out with the AIMAll program [22]. To gain a deeper insight into the nature of the interactions in terms of meaningful physical components, interaction energies were decomposed using the following partitioning of interaction energy components [23]:

$$E_{int} = E_{elst} + E_{exch-rep} + E_{pol} + E_{disp} \qquad (1)$$

Where E_{elst} is the electrostatic term describing the classical Coulomb interaction of the occupied orbitals of one monomer with those of another monomer, $E_{exch-rep}$ is the repulsive exchange component resulting from the Pauli exclusion principle. E_{pol} and E_{disp} correspond to polarization and dispersion terms, respectively. The polarization term contains all classical induction, exchange-induction, etc., from the second order up to infinity.

All geometry optimizations, interaction energies and energy components were calculated using the GAMESS package [24].

Results and discussion

Geometries

The systems studied form stable triads with C_{3v} symmetry (Scheme 1). In Scheme 1, A, B, and C stand for molecular moieties interacting in title complexes. For instance, A and C denote those molecules located at the end of the chain, and B denotes the molecule located in the middle.

The intermolecular distances found for these systems are in the range of 1.86–2.44 Å for H···C(N) HBs and 2.04–2.43 for Li···C(N) LBs (Table 1). For the systems connected with lithium and hydrogen bonds, the Li···C(N) and H···C(N) distances in the triads are smaller than the corresponding values in the dyads, with differences in the range between 0.005 and 0.024 Å and 0.01 to 0.16 Å, respectively. The values given are the differences in distances between trimers and dimers (Table 1). This trend can be interpreted as a cooperative effect of LB and hydrogen bonds.

Energies

The stabilization energy in the dyads can be regarded as the energy difference between the complex and the monomers: Ei(AB)=E_{AB}−(E_A+E_B) and the corresponding value in the triads [Ei(ABC)] is calculated in a similar way. Ei(AB,T) and Ei(BC,T) are the interaction energies of AB and BC dyads while they are in the geometry of triads. Table 2 presents the stabilization energy of the eight studied triads and respective dyads. All results were corrected for BSSE using the counterpoise method. As shown in Table 2, the stabilization energy of the title complexes ranges from −65.12 to −108.78 kJ mol^{-1}. Results in the first column of Table 2 indicate that triads of HNC are more stable than HCN triads. It may be also concluded that triads with LB, and single-electron HB interactions are more stable than triads with HB, and single-electron LB connectivity.

An energetic cooperativity parameter was calculated using Eq. 2 [25, 26]:

$$E_{Coop} = Ei(ABC) - Ei(AB) - Ei(BC) - Ei(AC) \qquad (2)$$

Table 1 Intermolecular distances R (in Å) in the investigated triads (T), and dyads. ΔR indicates the changes relative to the respective dyads

Triads(A···B···C)	R(AB, T)	R(AB)	ΔR$_{AB}$	R(BC,T)	R(BC)	ΔR$_{BC}$
H$_3$C···HCN···LiCN	2.441	2.602	−0.161	2.049	2.057	−0.008
H$_3$C···HNC···LiNC	2.150	2.278	−0.128	2.175	2.188	−0.013
H$_3$C···LiCN···HCN	2.438	2.443	−0.005	2.012	2.024	−0.012
H$_3$C···LiNC···HNC	2.427	2.444	−0.017	1.866	1.877	−0.011
(CH$_3$)$_3$C···HCN···LiCN	2.138	2.289	−0.151	2.039	2.057	−0.018
(CH$_3$)$_3$C···HNC···LiNC	1.883	1.993	−0.110	2.164	2.188	−0.024
(CH$_3$)$_3$C···LiCN···HCN	2.320	2.329	−0.009	2.005	2.024	−0.019
(CH$_3$)$_3$C···LiNC···HNC	2.310	2.321	−0.011	1.859	1.877	−0.018

Table 2 Interaction energies Ei (kJ mol^{-1}) of hydrogen bonding and lithium bonding in the studied dyads and triads (T) at MP2/aug-cc-pVDZ level

Triads(A⋯B⋯C)	Ei(ABC)	Ei(AB)	Ei(BC)	Ei(AB,T)	Ei(BC,T)	E$_{Coop}$
H$_3$C⋯HCN⋯LiCN	−84.70	−3.98	−73.54	−2.66	−73.28	−3.02
H$_3$C⋯HNC⋯LiNC	−90.18	−8.47	−75.03	−6.89	−74.50	−5.11
H$_3$C⋯LiCN⋯HCN	−65.12	−25.06	−38.10	−25.06	−38.10	−1.71
H$_3$C⋯LiNC⋯HNC	−85.98	−25.18	−57.96	−24.94	−57.96	−2.32
(CH$_3$)$_3$C⋯HCN⋯LiCN	−94.19	−12.07	−73.54	−20.22	−80.89	−6.22
(CH$_3$)$_3$C⋯HNC⋯LiNC	−108.78	−21.83	−75.03	−32.74	−79.78	−9.03
(CH$_3$)$_3$C⋯LiCN⋯HCN	−84.35	−43.44	−38.10	−53.59	−44.66	−2.29
(CH$_3$)$_3$C⋯LiNC⋯HNC	−105.51	−43.54	−57.96	−53.34	−66.39	−3.22

where Ei(ABC) is the stabilization energy of the trimer, Ei(AB) and Ei(BC) are the stabilization energy of the isolated dimers within their corresponding minima configuration, and Ei(AC) is the interaction energy of the molecules A and C in the geometry they have in the trimer. In all cases studied, a favorable cooperativity is observed for the calculated triads with values that range between −1.71 and −9.03 kJ mol^{-1}. The maximum and minimum energetic cooperativity values correspond to the most and least stable complexes studied in the present work (Table 2).

We also analyzed the electrostatic potentials at the 0.001 electrons/Bohr^3 isodensity surfaces of the HCN, HNC, LiCN, LiNC, CH$_3$ and C(CH$_3$)$_3$ monomers by means of the WFA surface analysis suite [27–29]. Table 3 gives the magnitudes of the most positive ($V_{S,max}$) and most negative electrostatic potentials ($V_{S,min}$) on the surface of these molecules. From Table 3, it is evident that the $V_{S,max}$ values associated with the lithium atom of the LiY are larger than those of hydrogen atom of HY. This means that the lithium atom in the LiY is a better electron acceptor than the HY molecule. Furthermore, the negative electrostatic potential associated with nitrogen atom of LiCN molecule is slightly larger than that of HCN molecule. For the C(CH$_3$)$_3$, the $V_{S,min}$ associated with the central carbon atom are more negative than those in the radical methyl. These values correlate with the calculated interaction energies of R$_3$C⋯HY and R$_3$C⋯LiY (Table 2), which supports the conclusion that electrostatic interaction plays an important role in the stability of these complexes.

Many-body interaction analysis

The two- and three-body contributions to total binding energy were obtained by many-body analysis [30, 31]. The two-body terms (ΔE_{A-B}, ΔE_{B-C}, and ΔE_{A-C}) can be calculated as the interaction energy of each molecular pair in the geometry of triad minus the energy sum of the monomers, all of them frozen in the geometry of the triad. The three-body term ΔE_{A-B-C} was calculated as the interaction energy of the triad minus the interaction energy of each pair of monomers, all of them frozen in the geometry of the triad using Eq. 3 [32]:

$$\Delta E_{A-B-C} = Ei(ABC)' - \Delta E_{A-B} - \Delta E_{A-C} - \Delta E_{B-C} \qquad (3)$$

Ei(ABC)′ was obtained by subtracting the total energy of optimized triads from the energy sum of the monomers frozen in the geometry of the triads.

The strain energy (E_S) is defined as the energy sum of the monomers frozen in the geometry of the triads minus the energy sum of the optimized monomers. Thus, the total binding energy of the triad is obtained using Eq. 4 [32]

$$Ei(ABC) = \Delta E_{A-B} + \Delta E_{A-C} + \Delta E_{B-C} + \Delta E_{A-B-C} + E_S. \qquad (4)$$

Table 3 The most positive ($V_{S,max}$, kcal mol^{-1}) and most negative ($V_{S,min}$, kcal mol^{-1}) electrostatic potentials in the monomers

Molecule	$V_{S,max}$	$V_{S,min}$
HCN	59	−33
HNC	71	−29
LiCN	218	−61
LiNC	212	−55
CH$_3$	15	−9
C(CH$_3$)$_3$	9	−12

Table 4 Decomposition of stabilization energy (kJ mol^{-1}) of the studied triads using the geometry within the triads

Triads (A⋯B⋯C)	ΔE_{A-B}	ΔE_{B-C}	ΔE_{A-C}	ΔE_{A-B-C}	E_S
H$_3$C⋯HCN⋯LiCN	−5.51	−74.07	−1.34	−3.91	0.13
H$_3$C⋯HNC⋯LiNC	−10.50	−75.88	−1.58	−6.04	3.81
H$_3$C⋯LiCN⋯HCN	−27.83	−38.59	−0.26	−1.63	3.19
H$_3$C⋯LiNC⋯HNC	−28.09	−62.22	−0.53	−2.10	6.96
(CH$_3$)$_3$C⋯HCN⋯LiCN	−11.77	−74.17	−2.05	−8.40	2.20
(CH$_3$)$_3$C⋯HNC⋯LiNC	−23.46	−76.09	−2.42	−11.53	4.72
(CH$_3$)$_3$C⋯LiCN⋯HCN	−44.28	−38.76	−0.44	−2.77	1.90
(CH$_3$)$_3$C⋯LiNC⋯HNC	−44.83	−62.41	−0.75	−3.53	6.02

Table 5 Changes in atoms in molecules (AIM) parameters (in au) of the triads relative to the respective dyads

Triads(A⋯B⋯C)	$\Delta\rho_{AB}$	$\Delta\nabla^2_{AB}$	$\Delta\rho_{BC}$	$\Delta\nabla^2_{BC}$
$H_3C\cdots HCN\cdots LiCN$	0.0028	0.0059	0.0007	0.0045
$H_3C\cdots HNC\cdots LiNC$	0.0043	0.0094	0.0009	0.0047
$H_3C\cdots LiCN\cdots HCN$	0.0002	0.0009	0.0007	0.0023
$H_3C\cdots LiNC\cdots HNC$	0.0003	0.0012	0.0011	0.0004
$(CH_3)_3C\cdots HCN\cdots LiCN$	0.0058	0.0109	0.0015	0.0103
$(CH_3)_3C\cdots HNC\cdots LiNC$	0.0083	0.0033	0.0016	0.0091
$(CH_3)_3C\cdots LiCN\cdots HCN$	0.0005	0.0021	0.0010	0.0035
$(CH_3)_3C\cdots LiNC\cdots HNC$	0.0005	0.0023	0.0018	0.0006
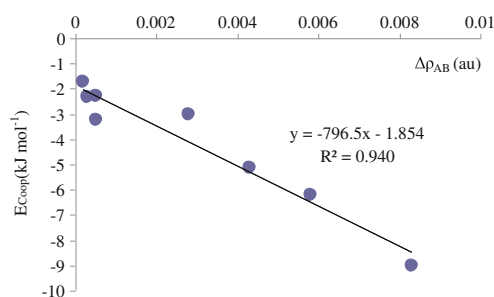
The results are presented in Table 4, in which all energies are corrected for BSSE. As seen in Table 4, two-body interaction energy provides the largest contribution of the total interaction energy.

For all triads, the two-body and three-body interaction energies ΔE_{A-B}, ΔE_{B-C}, and ΔE_{A-B-C} are attractive, reinforcing to the total interaction energy. For all triads ΔE_{A-C} is the smallest two-body interaction term that is consistent with the largest distance between them. The results in Table 4 reveal that the contribution of different interactions in stability of title triads is as follow; LB>HB>single-electron LB>single-electron HB.

The strain energy can be taken as a measure of the degree of strain that drives the distortion of the ternary system. As seen in Table 4, the strain energy is positive, and thus makes a destabilizing contribution to the total stabilization energy of the triads. The strain energy is larger for complexes of $C(CH_3)_3$ than complexes with CH_3, which is in line with order of stabilities in these triads.

Electron density analysis

Table 5 presents the variation in electron density and Laplacian of the electron density at two bond critical points (BCP) located between molecules A, B, and C. The results in Table 5 indicate that the ρ_{BCP} and $\nabla^2\rho_{BCP}$ values at the A⋯B critical points in the triad are slightly greater than that in the corresponding dyad. This result confirms that the A⋯B interaction in the triad is reinforced with respect to the binary system. The same behavior is also evident for the ρ_{BCP} and $\nabla^2\rho_{BCP}$ values at the B⋯C critical points in the triad. This reveals that the B⋯C interaction is also strengthened in the triad system. The estimated amount of electron density change upon trimer formation ranges from 0.0002 to 0.0083 au for the A⋯B and 0.0007 to 0.0018 au for the B⋯C interactions. However, comparison between $(CH_3)_3C\cdots H(Li)$ and $CH_3\cdots H(Li)$ interactions indicates a larger electronic density redistribution in the former. These results are in good agreement with the tendencies of shortening of intermolecular distances of these systems, as discussed above. In fact, a linear correlation between E_{coop} and $\Delta\rho$ at the A⋯B critical points is found in Fig. 1 ($R^2=0.940$).

Fig. 1 Correlation between cooperative energies and $\Delta\rho$ values at the A⋯B bond critical points of the triads

$y = -796.5x - 1.854$
$R^2 = 0.940$

Table 6 Calculated binding energy components (in kJ mol^{-1}) for the title complexes

Triads (A⋯B⋯C)	E_{elst}	$E_{exch-rep}$	E_{pol}	E_{disp}	$\%E_{elst}$	$\%E_{pol}$
$H_3C\cdots HCN\cdots LiCN$	−89.04	44.12	−32.3	−1.06	73	28
$H_3C\cdots HNC\cdots LiNC$	−95.34	60.52	−41.00	−17.84	62	27
$H_3C\cdots LiCN\cdots HCN$	−83.39	52.33	−36.95	−0.33	69	31
$H_3C\cdots LiNC\cdots HNC$	−108.89	95.59	−59.77	−19.68	58	32
$(CH_3)_3C\cdots HCN\cdots LiCN$	−105.55	66.25	−50.03	−7.14	65	31
$(CH_3)_3C\cdots HNC\cdots LiNC$	−113.61	98.85	−65.91	−32.72	54	31
$(CH_3)_3C\cdots LiCN\cdots HCN$	−93.13	62.57	−50.07	−5.60	63	34
$(CH_3)_3C\cdots LiNC\cdots HNC$	−118.92	106.84	−73.19	−25.99	55	34

Energy decomposition analysis

Insights into the origin and nature of the interactions in title triads can be found from a partitioning of the interaction energy into different contributions. It has been demonstrated that LB and HB are dominated by an electrostatic interaction [33, 34]. Thus, the interaction energies in the complexes were partitioned into electrostatic (E_{elst}), exchange-repulsion ($E_{exch-rep}$), polarization (E_{pol}) and dispersion (E_{disp}) terms. The results of energy decomposition for the title complexes given in Table 6 reveal that the attractive electrostatic and polarization components make the major contribution to the interaction energies. Based on the energy decomposition results, it was also found that electrostatic effects account for more than 50 % of the overall attraction in all the studied triads. By comparison, the polarization component of these interactions represents about 30 % of the total attractive forces. This reveals that the electrostatic interactions are essentially responsible for the stability of the title triads.

Conclusions

Ab intio calculations at UMP2/aug-cc-pVDZ level were used to explore the cooperativity in $R_3C\cdots HY\cdots LiY$ and $R_3C\cdots LiY\cdots HY$ triads (R=H, CH_3; Y=CN, NC) triads. The equilibrium structures, energetics, and cooperative effect on the properties of the complexes were analyzed.

All studied triads showed energetic cooperativity. In fact, a linear correlation between E_{coop} and $\Delta\rho$ at the A···B critical points was established in present study. According to energy decomposition analysis (EDA), electrostatic interactions are the major source of the attraction in the title complexes. These findings will aid a better understanding of the cooperative role of hydrogen and lithium bonding in molecular recognition, crystal engineering and biological systems.

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