ORIGINAL PAPER

Optimization of selection of chain amine scrubbers for CO_2 capture

Mohammed J. Al-Marri · Mahmoud M. Khader · Emmanuel P. Giannelis · Mohamed F. Shibl

Abstract In order to optimize the selection of a suitable amine molecule for CO_2 scrubbers, a series of ab initio calculations were performed at the B3LYP/6-31+G(d,p) level of theory. Diethylenetriamine was used as a simple chain amine. Methyl and hydroxyl groups served as examples of electron donors, and electron withdrawing groups like trifluoromethyl and nitro substituents were also evaluated. Interaction distances and binding energies were employed as comparison operators. Moreover, natural bond orbital (NBO) analysis, namely the second order perturbation approach, was applied to determine whether the amine–CO_2 interaction is chemical or physical. Different sizes of substituents affect the capture ability of diethylenetriamine. For instance, trifluoromethyl shields the nitrogen atom to which it attaches from the interaction with CO_2. The results presented here provide a means of optimizing the choice of amine molecules for developing new amine scrubbers.

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Introduction

Carbon dioxide has been implicated in global warming, which in turn promotes ozone layer depletion and leads to melting of the polar ice caps [1]. CO_2 is the main combustion product of fossil fuels in power plants, and has been estimated to contribute more than 40 % of worldwide anthropogenic CO_2 emissions. Hence, climate protection has become a major challenge for power producers. Although natural gas is the cleanest fossil fuel, undesirable contaminants such as CO_2 and H_2S lower its fuel production efficiency [1]. Hence, it is necessary to remove CO_2 before and after the combustion process. Removal of CO_2 gas prior to combustion takes place via the water gas shift reactions technique, which is used only in power plants with integrated coal gasification combined cycle technology that converts coal into synthesis gas [2]. On the other hand, post-combustion CO_2 capture, employing chemical solvents like amine compounds, represents a promising technique because of its simplicity and the ability to implement it in older plants [3–6].

Amine compounds are used widely in industry as a post-combustion CO_2 capture [7, 8], since they exhibit selective absorption of CO_2 from flue gas [9]. Monoethanolamine aqueous solutions effectively capture CO_2 in a 1:2 ratio (monoethanolamine:CO_2) at low pressure [10]. However, its corrosive effects and degradation in the presence of SO_2, as well as high energy consumption upon regeneration, make the process less attractive. Therefore, the challenge for such a process is to find a new amine to minimize these effects. Sterically hindered amines, as 2-amino-2-methyl-1-propanol and piperazine, act in the same way as regular amines but are more resistant against degradation and less energy intensive for regeneration [11, 12]. Hook [13] increased the efficiency of CO_2 capture by introducing non-volatile amino acid salts with sterically hindered amino groups to reduce the volatility of the amine compounds.

Ammonia solutions possess higher CO_2 absorption capacity and require less regeneration energy compared to monoethanolamine [14]. Moreover, aqueous ammonia solutions are more robust against degradation during the absorption/regeneration process. Nevertheless, toxicity problems arise from the high volatility of ammonia solution, which requires cooling of the flue gas to freezing temperature to enhance the absorption of CO_2 and minimize ammonia vapor.

You et al. [15] introduced four kinds of additives into aqueous ammonia solution, namely, 2-amino-2-methyl-1-propanol, 2-amino-2-methyl-1,3-propandiol, 2-amino-2-ethyl-1,3-propandiol and tri(hydroxymethyl) aminomethane. They studied the interaction between ammonia, these additives and CO_2 experimentally and theoretically and found that the additives reduced vaporization of ammonia. They suggested that amine and hydroxyl additives could perform well for CO_2 capture.

Schneider et al. [16] showed using DFT-B3LYP calculations that the reaction energies of CO_2 with amine are a function of both substituents and stoichiometry; in good agreement with the experimental findings [17], they found that a negatively charged amine reacts with CO_2 in a 1:1 ratio.

Park et al. [18] performed a theoretical study using DFT/B3LYP/6-31+G* to examine CO_2 capture efficiency in terms of the reaction of $-NH_2$ and $-COOH$ functional groups of alanine with CO_2. They found that the CO_2 interaction with the amino group of alanine to form carbamate is kinetically more favourable than that with the carboxylic group to form carbonic anhydride. This indicates that the carboxylic group reacts more rapidly with CO_2 in a reversible manner than the amino group does. However, this reaction is reversed thermodynamically.

Grimme [19] showed that B97D functional outperforms the functionals BP86, BLYP [20, 21], PBE [22], TPSS [23] and B3LYP [22, 24] and yields structures and interaction energies for van der Waals complexes comparable to those of, e.g., CCSD(T). A combination of the B97D functional with aug-cc-pVTZ basis set was found to perform pretty well in the case of S22 test set, revised in [25], of weakly bound systems such as hydrogen bonded, dipole–dipole and mixed systems.

Despite the aforementioned studies, to our knowledge, there has been no systematic theoretical investigation of the substituent effects on the interaction of CO_2 with various chain amines. Such studies could provide a useful framework for designing amine scrubbers. In this contribution, diethylenetriamine is considered as a simple model amine of a series of polymeric amines that can be used to capture and release CO_2 (Fig. 1). Diethylenetriamine comprises three active sites for CO_2 absorption, namely N1, N15 and N18 (Fig. 1). Here, the reaction of diethylenetriamine with CO_2 was investigated theoretically using density functional theory (DFT) quantum chemical methods. The methyl-,
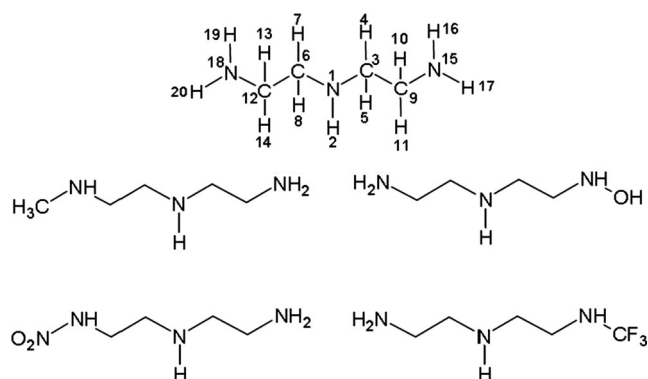
Fig. 1 Numbering system of diethylenetriamine and examples of its methyl-, hydroxy-, trifluoromethyl- and nitro- mono-substituted compounds

trifluoromethyl-, hydroxy- and nitro-substituted diethylenetriamine, formed by substituting one of the hydrogen atoms carried by the nitrogen atoms (examples are shown in Fig. 1), were studied systematically in terms of interaction (binding) energies and distances as well as structural changes.

Methods

The equilibrium geometries of diethylenetriamine and its methyl, trifluoromethyl, hydroxy and nitro derivatives, were fully optimized using a gradient minimization technique. Further, geometry optimizations were performed to determine the most stable conformations for the amines and their complexes with CO_2. All minima were characterized by having zero gradient norms and by diagonalizing the matrix of the second derivatives that give positive harmonic vibrational frequencies. Density functional theory (DFT) implemented in the GAUSSIAN09 [26] suit of programs was used for the calculation. Although B97D functional combined with aug-cc-pVTZ basis set performs well for weakly bound hydrogen bonded or dipole–dipole systems, we performed geometry optimization at B3LYP/6-31+G(d,p) [27], B3LYP/6-31++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. The results are presented in Table 1. It turns out that the interaction distance is affected slightly by the choice of the previously mentioned methods at the expense of the electronic energy. The B3LYP/6-31+G(d,p) method yields about 100 kcal mol^{-1}

Table 1 Electronic energies [a.u.] and interaction distances [Å] of the amine:CO_2 complex calculated using different levels of theories

Theory	Energy	Interaction distance
B3LYP/6-31+G(d,p)	−513.11467	2.94
B3LYP/6-31++G(d,p)	−513.11526	2.94
B3LYP/6-311++G(d,p)	−513.24159	2.92
b97D/aug-cc-pvtz	−512.95536	2.89

more stable diethylenetriamine:CO_2 complex than that calculated at B97D/aug-cc-pVTZ level of theory (see Table 1). Therefore, all subsequent calculations were performed using the B3LYP/6-31+G(d,p) level of theory. As long distances are being investigated, the self-interaction errors arising from DFT calculations were considered negligible and were not considered. Moreover, the basis set superposition error (BSSE) was not taken into account for the equilibrium structure of the amine:CO_2 complex, since it was found to be negligible in the DFT calculations of the dimer [28].

The atomistic approach [29] was employed to calculate the enthalpies of formation for the optimized structures at 298 K. The binding energies were calculated by taking the difference between the enthalpy of formation of the amine:CO_2 complex and the enthalpies of formation of the optimized individual components, i.e., amine and CO_2, as follows:

$$E = \Delta H_{f,298}(\text{complex}) - \Delta H_{f,298}(\text{amine}) - \Delta H_{f,298}(CO_2) \tag{1}$$

where E is the binding energy and $\Delta H_{f,298}$ is the enthalpy of formation at 298 K.

The second order perturbation theory, as implemented in natural bond orbital (NBO) analysis, was used to determine whether diethylenetriamine derivatives interact chemically or physically with CO_2 [30]. In this context, the stabilization energies resulting from electron donation between donor and acceptor orbitals were calculated as follows:

$$E(2) = q_i \frac{F(i,j)^2}{\in_i \in_j}$$

where, $E(2)$ is the stabilization energy, q_i is the occupancy of the donor orbital, $F(i,j)^2$ is the off-diagonal NBO Fock matrix elements, $\in_i$ is the orbital energies (diagonal elements) of the donor orbital and $\in_j$ is the orbital energies of the acceptor orbital.

Results and discussion

Optimized diethylenetriamine has a zigzag molecular chain as shown in Fig. 2. The equilibrium geometry of diethylenetriamine comprises hydrogen atoms located out of the plane formed by the heavy atoms. The substituted diethylenetriamines are constructed in such a way as to replace one, two or three hydrogen atoms (for instance, H2, H16 and/ or H17) with hydroxyl, methyl, and trifluoromethyl or nitro group(s).

Examples of the structures of the substituted diethylenetriamine calculated using the B3LYP/6-31+G(d,p)
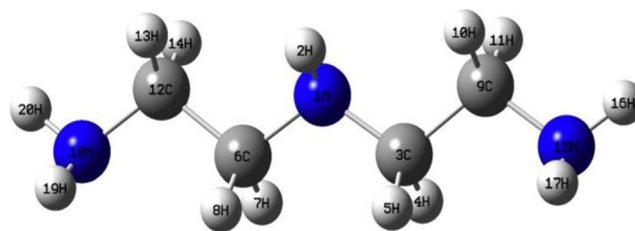


Fig. 2 Calculated diethylenetriamine equilibrium geometry

level of theory are displayed in Figs. 3, 4, 5 and 6, for Cartesian coordinates of all structures (see the Electronic supplementary material). Hydroxy substitution either at N1 (central substitution) or at N15/N18 (terminal substitution) does not affect the planarity of the heavy atoms (Fig. 3).

Introducing a larger group, such as methyl, trifluoromethyl or nitro, influences the geometry to some extent depending on the size of the group. For instance, methyl substitution by substituting H2 at the center of diethylenetriamine involves a change in the planar arrangement of the heavy atoms as torsional rotation of about 20° around the N1–C3 bond takes place (Fig. 4). However, terminal substitution, namely replacing H16 or H17, does not affect the geometry of the main chain much. On the other hand, diethylenetriamine encounters a torsional rotation of about 82° around the N1–C3 bond upon difluoromethyl substitution, indicating that steric effects lead to tilting of the molecule (Fig. 5). The same behavior was observed for nitro substituted amine (Fig. 6). This steric factor may partially hinder the central nitrogen from capturing CO_2, as will be investigated below.

The interaction distance between the amine and CO_2 is defined as the shortest distance between an atom of the amine molecule and another atom on CO_2. Diethylenetriamine:CO_2 complexes **a** (CO_2 binds N1) and **b** (CO_2 binds N15/N18) are considered as reference compounds for comparison (Fig. 7). These compounds were found to have interaction distances of 2.93 and 2.86 Å, respectively (Table 2). The interaction distances are those between a negatively charged oxygen atom[1] and the positively charged H13, as well as those between a negatively charged oxygen atom and the positively charged H4 (Fig. 7). The interaction distances become comparable for both terminal (N15/N18) and central (N1) nitrogen binding despite the steric hindrance at N1 because of the additional interaction forces between hydrogen and oxygen atoms in addition to that between the carbon atom of CO_2 and N1 (cf. Fig. 7).

Methyl substitution does not significantly affect the interaction distances between CO_2 and the unsubstituted nitrogen atoms (Table 2, Fig. 8). However, the interaction distance of CO_2 with methyl-substituted N1 becomes longer due to the

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[1] Hereafter, mention of oxygen atom(s) refers to the oxygen atom(s) of the CO_2 molecule, while hydrogen and nitrogen atoms will mean the hydrogen and nitrogen atoms of diethylenetriamine.

(a) **(b)**

(c) **(d)**

(e)
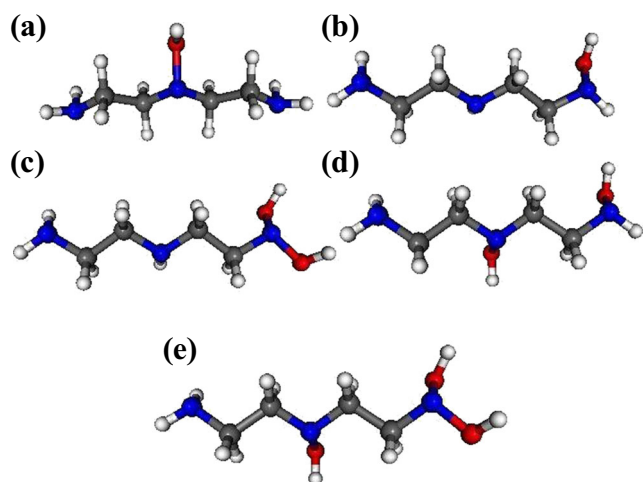
Fig. 3 Optimized geometries of hydroxy derivatives of diethylenetriamine

steric effect of the methyl group, which minimizes the oxygen interactions with hydrogen atoms by driving oxygen atoms away from hydrogen through rotation of CO_2 as in compounds **c**, **k** and **n** (Fig. 8). In case of hydroxy substitution, there are significant decreases in the interaction distances at the substitution center (down to 2.21 Å in some cases; Fig. 9, Table 2). This decrease is due to the additional mode of interaction, namely hydrogen bonding, to the existing dipole–dipole interaction. The interaction distances at unsubstituted active sites (nitrogen atoms) behave similarly to the methyl substituted diethylenetriamine:CO_2 complex.

Since trifluoromethyl is a bulky group, it hinders N1 to bind CO_2 and pushes the latter away from N1 during the optimization procedure to one of the terminal nitrogen atoms (N15/N18). Furthermore, double substitution at the terminal nitrogen atoms prevents CO_2 from binding N15/N18 as shown in Fig. 10. Nevertheless, single substitution at one of the terminal nitrogen atoms (N15/N18) decreases the interaction distance due to the extra force resulting from the

(a) **(b)**

(c) **(d)**

(e)
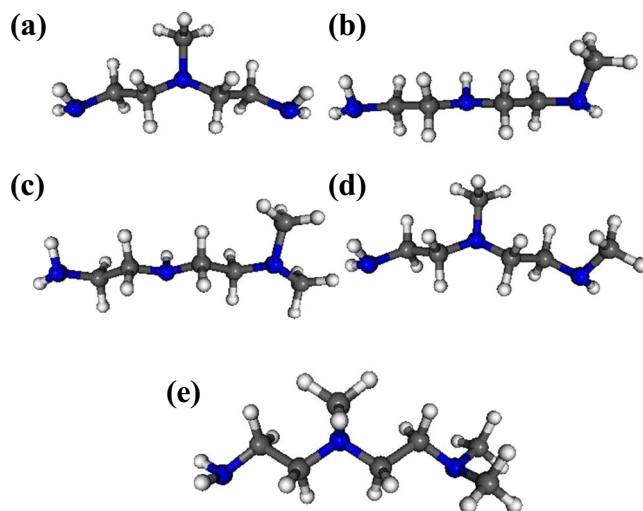
Fig. 4 Optimized geometries of methyl derivatives of diethylenetriamine

(a) **(b)**

(c) **(d)**

(e)
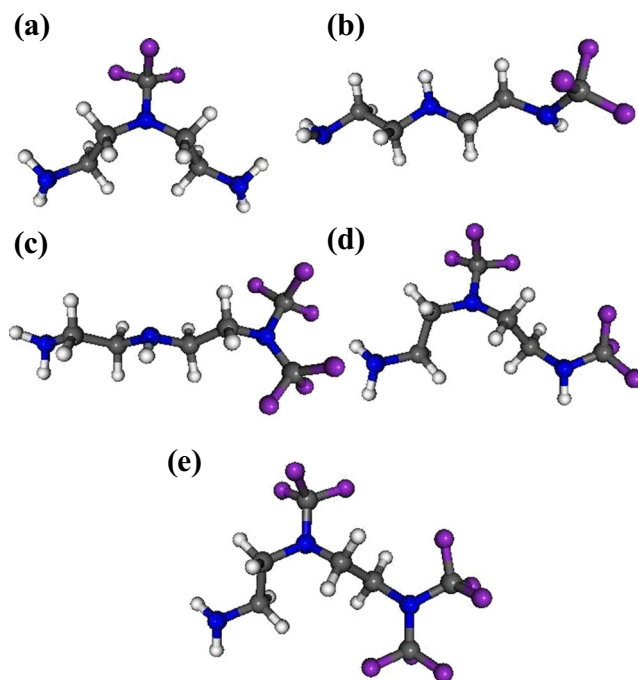
Fig. 5 Optimized geometries of trifluoromethyl derivatives diethylenetriamine

hydrogen bonding (Fig. 10). On the other hand, double substitution at one of the terminal nitrogen atoms produces a larger interaction distance as the dipole–dipole interaction turns out to be between CO_2 and one of the fluorine atoms. Triple substitution drives CO_2 to bind one of the closest ethylenic hydrogens. The nitro group behaves analogously compared to trifluoromethyl except for the interaction of CO_2 with substituted N1, as the nitro group binds CO_2 and prohibits its interaction with N1, H10 and H13 (see Fig. 11).

Apparently, the replacement of hydrogen atoms by bulkier group(s) changes the geometry of diethylenetriamine. This

(a) **(b)**

(c) **(d)**

(e)
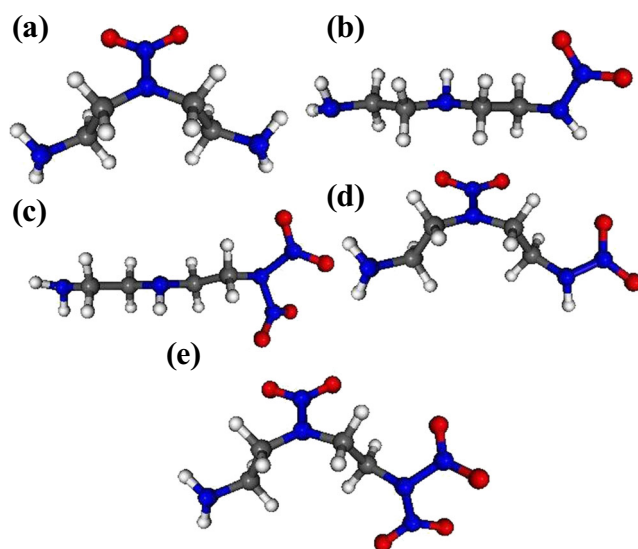
Fig. 6 Optimized geometries of nitro derivatives of diethylenetriamine
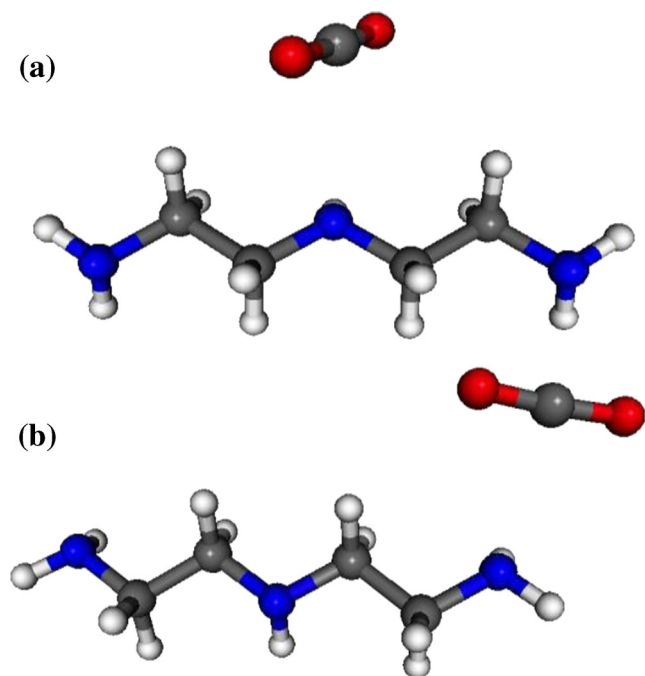
Fig. 7 Optimized geometries of diethylenetriamine:CO_2 complexes with CO_2 attached to **a** N1 and **b** N15/N18

change in geometry is reflected in the binding properties. The binding energies for all diethylenetriamine:CO_2 complexes are summarized in Table 2. The negative signs of the binding energies of the CO_2 interaction with unsubstituted diethylenetriamine at N1 and N15/N18 indicate that CO_2 is very likely binding diethylenetriamine and giving rise to stable complexes. The binding energy of **b** is twice that of **a**,

suggesting a preference of CO_2 to bind primary more than secondary amines (Table 2).

All binding energies are negative upon adding an electron-donating substituent such as a methyl or hydroxyl group. CO_2 interaction with N1 produces smaller binding energies of about 0.5 kcal mol^{-1} on methyl substitution at the latter (compounds **c**, **k** and **n**), while there is no effect when the substitution takes place at N15/N18 (compounds **e** and **h**). The substitution, which is away from the interaction center, does not affect the binding energies. Methyl terminal substitution leads to smaller binding energies, with the interaction occurring at the substitution site due to the steric hindrance arising from the methyl group. On the other hand, interaction at terminal nitrogen atom opposite to the substituted one increases the binding energies by about 1.0 kcal mol^{-1}.

In contrast to methyl substitution, introducing a hydroxyl group enhances the binding of CO_2 with diethylenetriamine at the substitution site (compounds **c**, **f**, **k** and **n**) because of the extra hydrogen bond formed between the oxygen and hydrogen of the hydroxyl group (see Fig. 9). However, double substitution at the terminal nitrogen generates competition between hydrogen bonding and the steric effect of the second hydroxyl group, resulting in a comparable binding energy to the reference value as in compounds **i** and **o**. Hydroxy substitution at N1/N15/N18 does not affect the binding of CO_2 with unsubstituted nitrogen (compounds **d**, **e**, **h**, **j** and **p**).

Since trifluoromethyl substitution at N1 changes the structure of diethylenetriamine, the binding energies are changed to some extent depending on the position of the reaction center. For instance, trifluoromethyl acts as a shield preventing CO_2 from approaching N1 and enhancing its interaction with N15/

Table 2 Interaction energies (E; kcal mol^{-1}) and interaction distances (d; Å) of the amine:CO_2 complexes

| References	E	d					
A	−0.65	2.93					
B	−1.30	2.86					
Compound	$E(CH_3)$	$d(CH_3)$	$E(OH)$	$d(OH)$	$E(NO_2)$	$d(NO_2)$	$E(CF_3)$	$d(CF_3)$
C	−0.12	3.04	−1.43	2.21	−1.07	3.12	−1.32	2.79
D	−1.36	2.87	−1.41	2.05	−1.30	2.67	−1.32	2.79
E	−0.65	2.63	−0.70	2.61	−0.78	2.51	−0.69	2.57
F	−0.99	2.93	−1.93	2.21	−1.92	2.16	−1.17	2.31
G	−2.18	2.89	−0.49	2.87	−0.53	2.85	−0.81	2.90
H	−0.64	2.75	−0.65	2.77	−0.43	2.51	−0.41	2.52
I	−0.76	2.81	−1.21	2.27	−0.09	3.04	0.51	3.27
J	−1.30	2.90	−1.33	2.89	−1.26	2.78	−1.24	2.81
K	−0.13	3.06	−1.29	2.22	−0.66	3.11	−1.96	2.63
L	−0.96	2.81	−1.82	2.22	−1.99	2.15	−0.82	2.25
M	−2.27	2.85	−1.04	2.83	−3.63	2.66	−2.02	2.77
N	−0.11	3.09	−1.28	2.21	−0.93	2.97	0.33	2.81
O	−0.77	2.76	−1.25	2.28	−1.46	2.71	0.16	2.81
P	−1.34	2.81	−1.44	2.83	−1.30	2.59	−1.11	2.76

Fig. 8 Optimized geometries of diethylenetriamine and its methyl derivatives

(n)

(o)
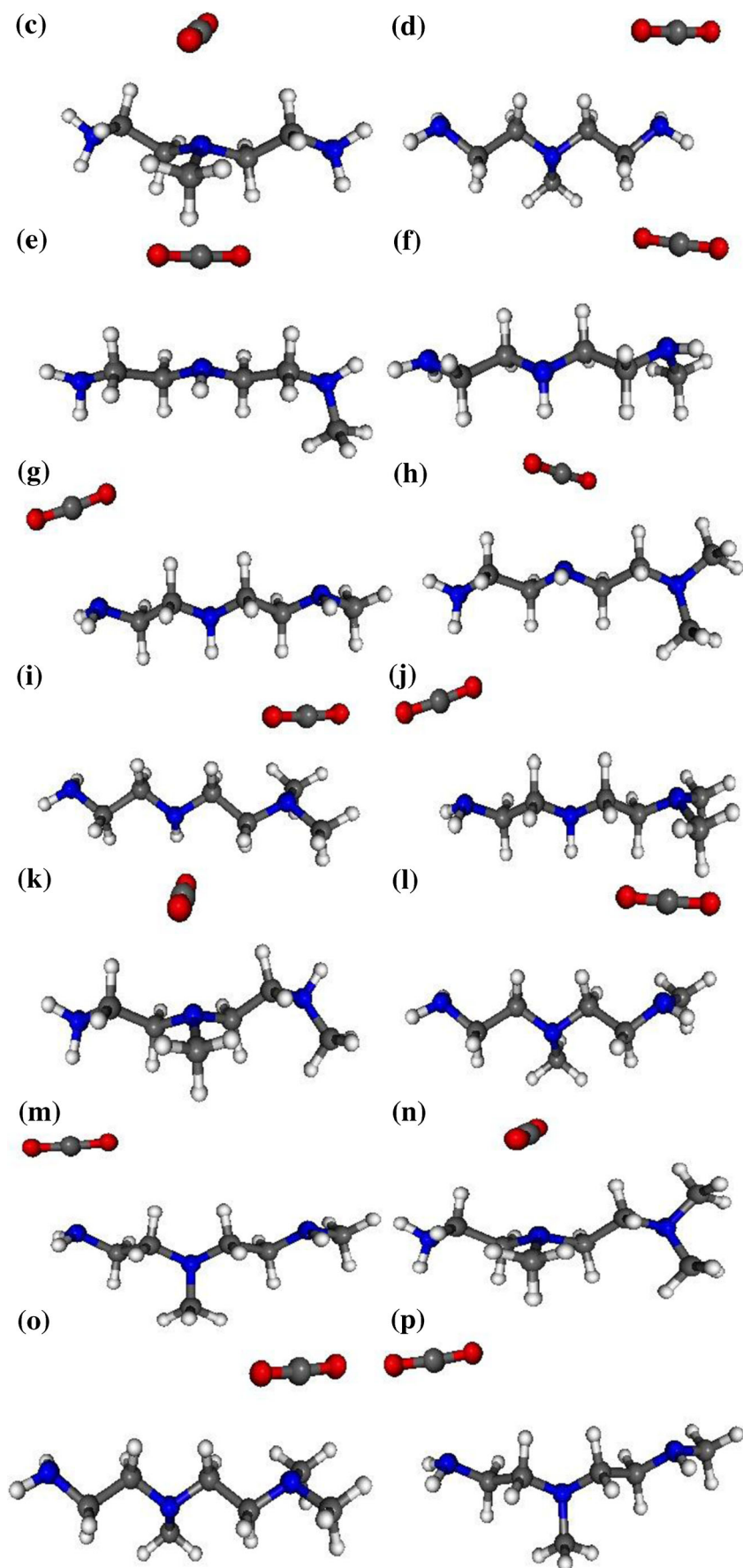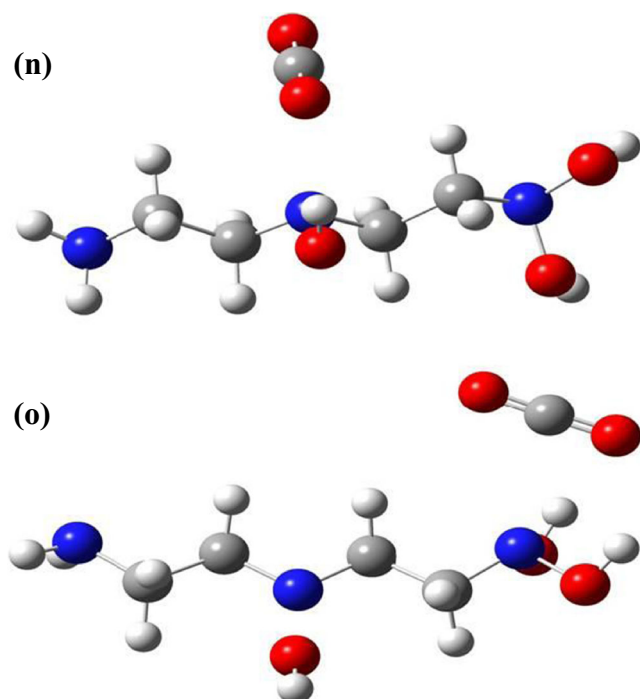
Fig. 9 Optimized geometries of hydroxy substituted diethylenetriamine:CO_2 complexes involving hydrogen bonds

N18, as reflected in the binding energy value of **c/d** (see Table 2). Moreover, double substitution at a terminal nitrogen leads to an unstable complex as can be inferred from the positive sign of the binding energies of compounds **i**, **n** and **o**. Further, substitution at the terminal does not much affect the binding energies of CO_2 interaction at N1 (compounds **e** and **h**). The hydrogen bond arising at single terminal substitution

(f) **(i)**

(k) **(l)**

(n) **(o)**
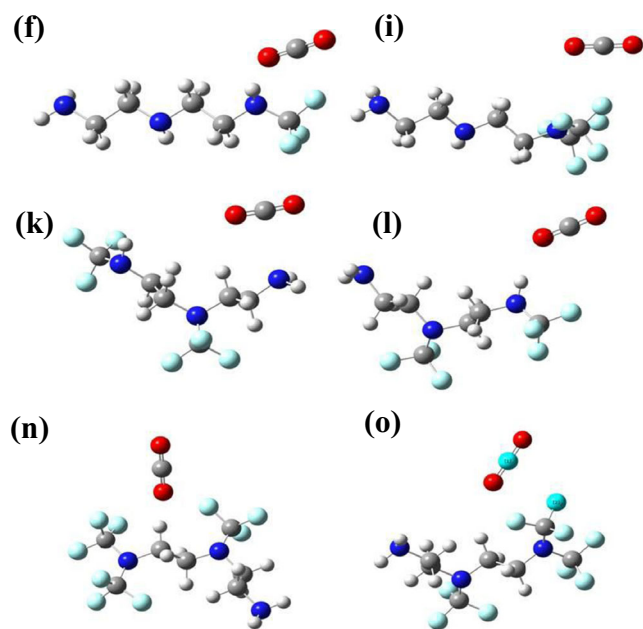
Fig. 10 Optimized geometries of some trifluoromethyl-substituted diethylenetriamine:CO_2 complexes

(c) **(d)**

(h) **(k)**

(l) **(o)**

(p)
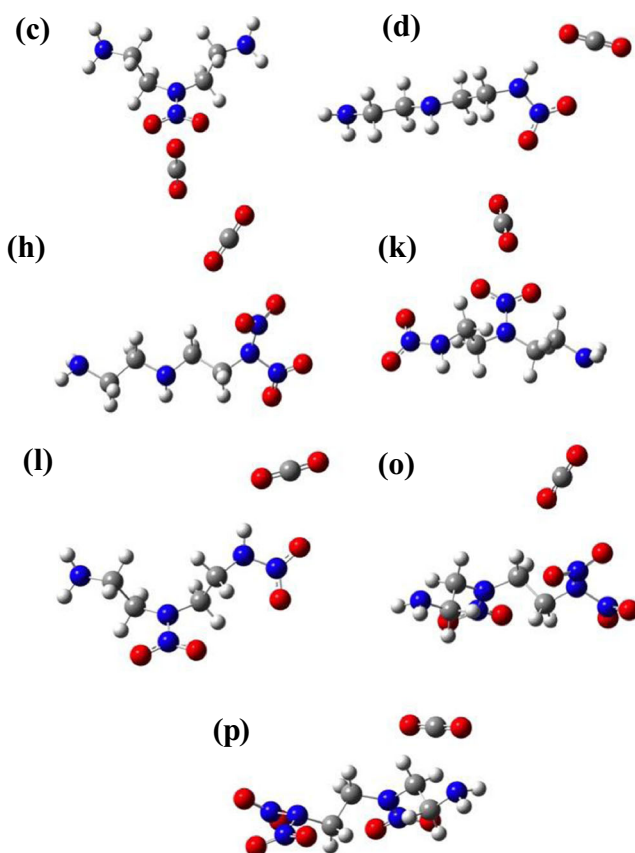
Fig. 11 Optimized geometries of some nitro-substituted diethylenetriamine:CO_2 complexes

was expected to increase the binding energy; however, the latter decreased slightly because the centers of interaction changed from N15 and H4 to F22 and H16.

Despite the analogous structural characteristics of nitro and trifluoromethyl complexes (except for interactions at the substituted N1), all binding energies have negative signs, revealing the stability of compounds **i**, **n** and **o** of nitro complexes as compared to those of trifluoromethyl complexes. This result is attributed to CO_2 interaction with the nitro group attached to N1. Interestingly, compound **m** has large binding energy compared with that of the unsubstituted complex due to the increasing atomic charge on H4 of the complex (0.2 **e** compared to 0.1 **e**), which increases the dipole–dipole interaction. Although the presence of the nitro group retards CO_2 interaction with N1, it interacts with CO_2, resulting in increasing the binding energy.

In order to investigate the nature of interaction between diethylenetriamine and its derivatives and CO_2, NBO analysis was employed. The stabilization energies reflect the delocalization of electrons between donor and acceptor orbitals, which in turn highlight the type of interaction between diethylenetriamine and CO_2. The stabilization, $E(2)$, as well as the delocalization energies (SUM of the stabilization energies corresponding to donor–acceptor interaction) of the

unsubstituted diethylenetriamine interaction with CO_2 are collected in Tables 3 and 4. Stabilization energies of the donor–acceptor interaction between all substituted diethylenetriamines and CO_2 on an NBO basis are presented in the electronic supplementary materials (Tables S1–S56). All delocalization energies are collected in Table 5. Tables 3 and 4 reveal that the delocalization energy of compound **b** is larger than that of compound **a**, indicating that chemical interaction between unsubstituted diethylenetriamine and CO_2 to form compound **b** prevails. This chemical interaction is favored by compound **b** since its interaction energy is twice that of **a**.

Upon methyl substitution, there is no significant change in delocalization energies except for compounds **e**, **i** and **o**, at ca. 47.6, 3.77 and 3.87 kcal mol^{-1}, respectively. This proposes a chemical interaction; however, the small values of the inter-action energies suggest an electrostatic interaction between methyl substituted diethylenetriamine and CO_2 to form compounds **e**, **i** and **o**. The remaining methyl substituted diethylenetriamine compounds do not change much as compared to the reference values of compounds **a** and **b**. Compounds **c**, **f**, **k** and **n** of the hydroxy diethylenetriamine:CO_2 complex have larger delocalization energies than the corresponding reference values of compounds **a** and **b**, revealing a chemical interaction between hydroxy diethylenetriamine and CO_2 as the associated interaction energies are large. The large interaction energies of compounds **c**, **f**, **i**, **k**, **l**, **n** and **o** result from the extra force arising from hydrogen bond formation (electrostatic interaction). This implies that the chemical

interactions of compounds **c**, **f**, **i**, **k**, **l**, **n** and **o** are dictated by electrostatic interactions. Similarly, in the case of the nitro diethylenetriamine:CO_2 complex, the large values of the de-localization and interaction energies of compounds **f** and **l** show chemical interactions associated with electrostatic inter-actions. On the other hand, the interaction between trifluoromethyl diethylenetriamine and CO_2 is mainly physi-cal as the delocalization energies are associated with small values of interaction energies (see Tables 2 and 5).

Details of quantum mechanical descriptors as described in Refs. [30, 31] are useful but the large number of compounds

Table 3 Stabilization energies (kcal mol^{-1}) of donor-acceptor interaction between diethylenetriamine **a** and CO_2 on a natural bond orbital (NBO) basis

Donor NBO	Acceptor NBO	E(2)
LP (1) N1	RY*(4) C21	0.33
LP (1) N1	RY*(1) O22	0.12
LP (1) N1	RY*(3) O22	0.06
LP (1) N1	RY*(6) O22	0.06
LP (1) N1	RY*(1) O23	0.20
LP (1) N1	RY*(6) O23	0.10
LP (1) N1	BD*(2) C21-O22	0.20
LP (1) N1	BD*(3) C21-O22	1.11
LP (1) N1	BD*(1) C21-O23	0.05
BD (3) C21-O22	RY*(1) N1	0.12
BD (3) C21-O22	BD*(1) C9-H11	0.18
BD (1) C21-O23	RY*(2) N1	0.06
LP (1) O22	BD*(1) C9-H11	0.08
LP (1) O23	BD*(1) C12-H14	0.07
LP (3) O23	BD*(1) C12-H14	0.09
BD*(3) C21-O22	RY*(1) N1	0.07
		SUM=2.90

Table 4 Stabilization energies (kcal mol^{-1}) of donor–acceptor interaction between diethylenetriamine **b** and CO_2 on a NBO basis

Donor NBO	Acceptor NBO	E(2)
LP (1) N15	RY*(4) C21	0.19
LP (1) N15	RY*(13) C21	0.05
LP (1) N15	RY*(1) O22	0.23
LP (1) N15	RY*(3) O22	0.08
LP (1) N15	RY*(1) O23	0.19
LP (1) N15	BD*(1) C21-O22	0.06
LP (1) N15	BD*(3) C21-O22	1.78
LP (1) N15	BD*(1) C21-O23	0.06
BD (3) C21-O22	RY*(1) H4	0.05
BD (3) C21-O22	RY*(1) N15	0.08
BD (3) C21-O22	BD*(1) C3-H4	0.18
LP (1) O22	BD*(1) C3-H4	0.21
BD*(3) C21-O22	RY*(1) N15	0.08
		SUM=3.24

Table 5 Delocalization energies (kcal mol^{-1}) of all donor-acceptor interaction between substituted diethylenetriamine and CO_2 on a NBO basis

Compound	CH_3	OH	NO_2	CF_3
c	2.81	6.78	2.40	3.58
d	3.44	3.46	3.76	3.59
e	47.6	3.94	4.12	3.90
f	3.03	6.46	8.60	4.03
g	3.19	3.17	3.10	3.02
h	3.13	3.05	4.04	4.28
i	3.77	4.43	0.38	0.15
j	3.21	3.16	3.13	3.15
k	2.75	6.56	4.39	3.69
l	3.29	4.42	8.71	4.52
m	3.35	3.49	3.42	3.12
n	2.44	6.37	4.56	0.53
o	3.87	4.46	1.85	0.46
p	3.41	3.51	3.63	3.05

requires that they are compiled in another contribution [Khader MM, Shibl MF (2014) Substituent effects on the geometry of chain amine scrubbers for the CO_2 capture. Unpublished work]. In brief, chemical hardness gives a strong statement about the stability of a compound, electrophilicity reflects reactivity, and dipole moments highlight the electrostatic interaction between polar compounds (diethylenetriamine and its derivatives) and the non-polar CO_2.

Conclusions

In summary, ab initio calculations of the CO_2 interaction with different active sites (nitrogen atoms) of unsubstituted diethylenetriamine and their substituted counterparts revealed the following: primary amines are more active towards CO_2 capture than secondary amines, suggesting that primary amines are more efficient as CO_2 scrubbers. However, secondary amines are energetically effective (less energy is needed for the regeneration process) at the expense of capture efficiency; bulky groups substitutions (e.g., trifluoromethyl and nitro groups) retard the interaction of CO_2 with amine at the substitution center. Therefore, bulky substituents are not preferred for amine scrubbers; introducing substituents with atoms that can hydrogen bond to CO_2 enhances the interaction of the latter with amine. According to NBO analysis, the terminal nitrogen atoms of unsubstituted diethylenetriamine interact chemically with CO_2, whereas substituted diethylenetriamine compounds interact mainly through electrostatic interactions and even chemical interaction behavior is dictated by electrostatic interactions.

References

1. Bates ED, Mayton RD, Ntai I, Davis JH (2002) CO_2 capture by a task-specific ionic liquid. J Am Chem Soc 124:926–927
2. Scholes A, Smith KH, Kentish SE, Stevens GW (2010) CO_2 capture from pre-combustion processes-strategies for membrane gas separation. Int J Greenh Gas Con 4:739–755
3. Drage T, Smith K, Pevida C, Arenillas A, Snape C (2009) Development of adsorbent technologies for post-combustion CO_2 capture. Energy Procedia 1:881–884
4. Reynolds AJ, Verheyen TV, Adeloju SB, Meuleman E, Feron P (2012) Towards commercial scale post-combustion capture of CO_2 with monoethanolamine solvent: key considerations for solvent management and environmental impacts. Environ Sci Technol 46:3643–3654
5. Sayari A, Heydari-Gorji A, Yang Y (2012) CO_2-induced degradation of amine-containing adsorbents: reaction products and pathways. J Am Chem Soc 134:13834–13842
6. Lu W, Sculley JP, Yuan D, Krishna R, Wei Z, Zhou H-C (2012) Polyamine-tethered porous polymer networks for carbon dioxide capture from flue gas. Angew Chem Int Ed 51:7480–7484
7. Amos R, Handy N, Knowles P, Rice J, Stone A (1985) Ab-initio prediction of properties of carbon dioxide, ammonia, and carbon dioxide…ammonia. J Phys Chem 89:2186–2192
8. Jackson P, Robinson K, Puxty G, Attalla M (2009) In situ fourier transform-infrared (FT-IR) analysis of carbon dioxide absorption and desorption in amine solutions. Energy Procedia 1:985–994
9. Astaria G, Savage DW, Bisio A (1983) Gas treating with chemical solvents. Wiley, New York
10. Bonenfant D, Mimeault M, Hausler R (2003) Determination of the structural features of distinct amines important for the absorption of CO_2 and regeneration in aqueous solution. Ind Eng Chem Res 42: 3179–3184
11. Sartori G, Savage DW (1983) Viscosity, density and surface tension of binary mixtures of water and n-methyldiethanolamine and water and diethanolamine and tertiary mixtures of these amines with water over the temperature range 20–100 °C. Ind Eng Chem Fundam 22:239–249
12. Aroonwilas A, Veawab A (2004) Characterization and comparison of the CO_2 absorption performance into single and blended alkanolamines in a packed column. Ind Eng Chem Res 43:2228–2237
13. Hook RJ (1997) An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. Ind Eng Chem Res 36:1779–1790
14. Ciferno JP, DiPietro P, Tarka T (2005) Final report. National Energy Technology Laboratory, US Department of Energy, Pittsburgh
15. You JK, Park H, Yang SH, Hong WH, Shin W, Kang JK, Yi KB, Kim J-N (2008) Influence of additives including amine and hydroxyl groups on aqueous ammonia absorbent for CO_2 capture. J Phys Chem B 112:4323–4328
16. Mindrup E, Schneider W (2010) Computational comparison of the reactions of substituted amines with CO_2. ChemSusChem 3:931–938
17. Gurkan BE, de la Fuente JC, Mindrup EM, Ficke LE, Goodrich BF, Price EA, Schneider WF, Brennecke JF (2010) Equimolar CO_2 absorption by anion-functionalized ionic liquids. J Am Chem Soc 132:2116–2117
18. Kim N, Yoon S, Park G (2013) Evaluating the CO_2-capturing efficacy of amine and carboxylic acid motifs: *ab initio* studies on thermodynamic versus kinetic properties. Tetrahedron 69:6693–6697
19. Grimme S (2006) Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J Comput Chem 27: 1787–1799
20. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38:3098–3100
21. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 37:785–789
22. Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865–3868
23. Tao J, Perdew JP, Staroverov VN, Scuseria GE (2003) Climbing the density functional ladder: non-empirical meta–generalized gradient approximation designed for molecules and solids. Phys Rev Lett 91: 146401
24. Becke A (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648–5652
25. Takatani T, Hohenstein EG, Malagoli M, Marshall MS, Sherrill CD (2010) Basis set consistent revision of the S22 test set of non-covalent interaction energies. J Chem Phys 132:144104
26. Frisch M, Trucks G, Schlegel H, Scuseria G, Robb M, Cheeseman J, Scalmani G, Barone V, Mennucci B, Petersson G, Nakatsuji H, Caricato M, Li X, Hratchian H, Izmaylov A, Bloino J, Zheng G, Sonnenberg J, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery J, Peralta J, Ogliaro F, Bearpark M, Heyd J, Brothers E, Kudin K, Staroverov V, Kobayashi R, Normand J, Raghavachari

K, Rendell A, Burant J, Iyengar S, Tomasi J, Cossi M, Rega N, Millam N, Klene M, Knox J, Cross J, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R, Yazyev O, Austin A, Cammi R, Pomelli C, Ochterski J, Martin R, Morokuma K, Zakrzewski V, Voth G, Salvador P, Dannenberg J, Dapprich S, Daniels A, Farkas O, Foresman J, Ortiz J, Cioslowski J, Fox D (2009) Gaussian 09

27. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. J Chem Phys 72:650–654

28. Farbos B, Tassaing T (2009) Substituent effect on the interaction of aromatic primary amines and diamines with supercritical CO2 from infrared spectroscopy and quantum calculations. Phys Chem Chem Phys 11:5052–5061

29. DeYonker NJ, Grimes T, Yockel S, Dinescu A, Mintz B, Cundari TR, Wilson AK (2006) The correlation-consistent composite approach: application to the G3/99 test set. J Chem Phys 125:104111

30. Armakovic S, Armakovic SJ, Setrajcic JP, Jacimovski SK, Holodkov V (2014) Sumanene and its adsorption properties towards CO, CO_2 and NH_3 molecules. J Mol Model 20:2170

31. Armakovic S, Armakovic SJ, Setrajcic JP (2013) Hydrogen storage properties of sumanene. Int J Hydrogen Energy 38:12190