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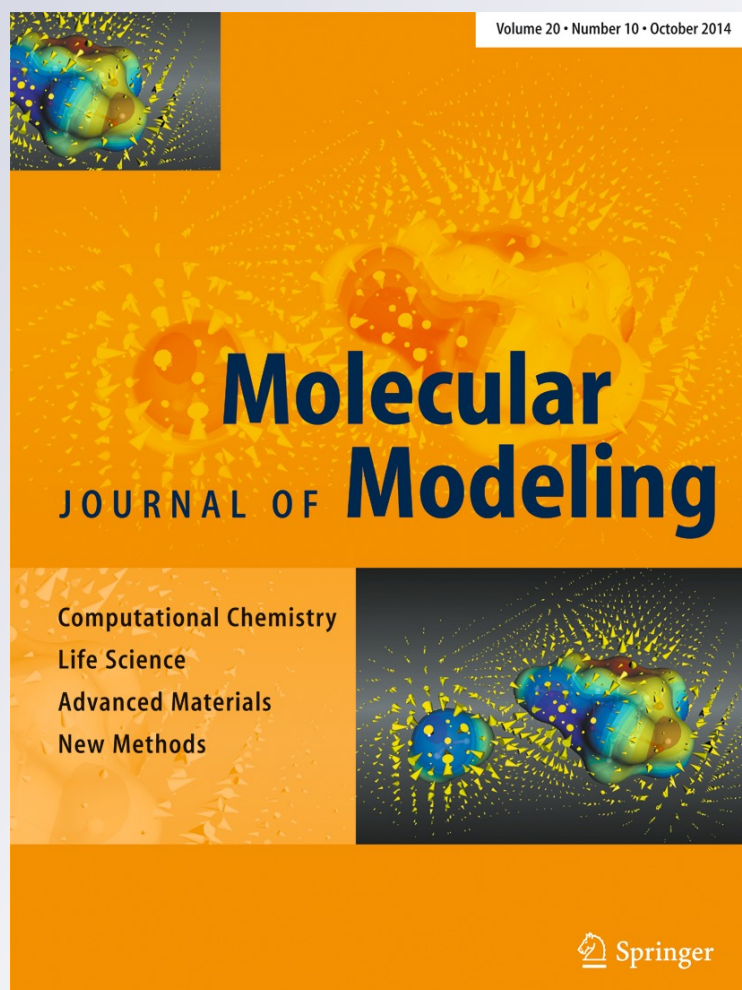
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Optimization of selection of chain amine scrubbers for CO₂ capture

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

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Abstract In order to optimize the selection of a suitable amine molecule for CO₂ 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–CO₂ 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 CO₂. The results presented here provide a means of optimizing the choice of amine molecules for developing new amine scrubbers.

Keywords Diethylenetriamine · Scrubbers · Carbon dioxide · Binding energy

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M. J. Al-Marri · M. M. Khader · M. F. Shibl
Gas Processing Center, College of Engineering, Qatar University, PO
Box 2713, Doha, Qatar

E. P. Giannelis · M. F. Shibl
Department of Materials Science and Engineering (MSE), Cornell
University, Ithaca, NY 14853, USA

M. F. Shibl (✉)
Department of Chemistry, Faculty of Science, Cairo University,
Giza 12613, Egypt
e-mail: mfshibl@cornell.edu

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]. CO₂ is the main combustion product of fossil fuels in power plants, and has been estimated to contribute more than 40 % of worldwide anthropogenic CO₂ emissions. Hence, climate protection has become a major challenge for power producers. Although natural gas is the cleanest fossil fuel, undesirable contaminants such as CO₂ and H₂S lower its fuel production efficiency [1]. Hence, it is necessary to remove CO₂ before and after the combustion process. Removal of CO₂ 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 CO₂ 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 CO₂ capture [7, 8], since they exhibit selective absorption of CO₂ from flue gas [9]. Monoethanolamine aqueous solutions effectively capture CO₂ in a 1:2 ratio (monoethanolamine:CO₂) at low pressure [10]. However, its corrosive effects and degradation in the presence of SO₂, 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ experimentally and theoretically and found that the additives reduced vaporization of ammonia. They suggested that amine and hydroxyl additives could perform well for CO₂ capture.

Schneider et al. [16] showed using DFT-B3LYP calculations that the reaction energies of CO₂ 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 CO₂ in a 1:1 ratio.

Park et al. [18] performed a theoretical study using DFT/B3LYP/6-31+G* to examine CO₂ capture efficiency in terms of the reaction of –NH₂ and –COOH functional groups of alanine with CO₂. They found that the CO₂ 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 CO₂ 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 CO₂ 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 CO₂ (Fig. 1). Diethylenetriamine comprises three active sites for CO₂ absorption, namely N1, N15 and N18 (Fig. 1). Here, the reaction of diethylenetriamine with CO₂ was investigated theoretically using density functional theory (DFT) quantum chemical methods. The methyl-,

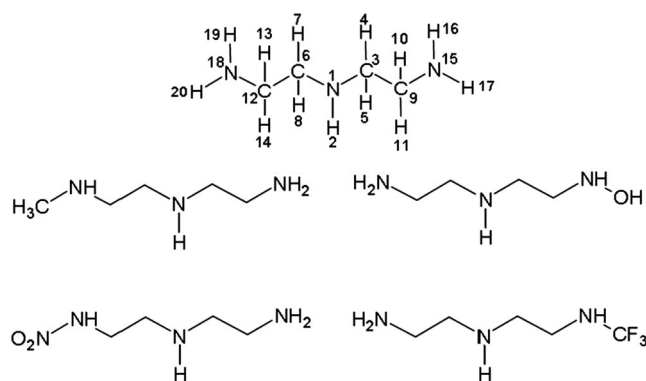


Fig. 1 Numbering system of diethylenetriamine and examples of its methyl-, hydroxy-, trifluoromethyl- and nitro- mono-substituted compounds

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 CO₂. 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:CO₂ 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:CO₂ 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:CO₂ 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:CO₂ complex and the enthalpies of formation of the optimized individual components, i.e., amine and CO₂, as follows:

$$E = \Delta H_{f,298}(\text{complex}) - \Delta H_{f,298}(\text{amine}) - \Delta H_{f,298}(\text{CO}_2) \quad (1)$$

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 CO₂ [30]. In this context, the stabilization energies resulting from electron donation between donor and acceptor orbitals were calculated as follows:

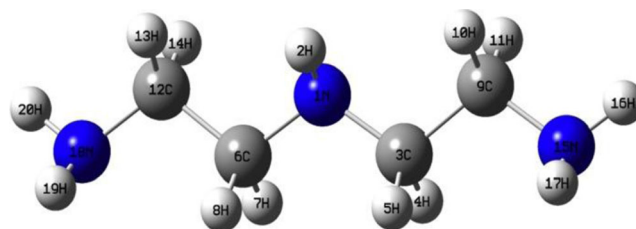
$$E(2) = q_i \frac{F(i,j)^2}{\epsilon_i \epsilon_j}$$

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, ϵ_i is the orbital energies (diagonal elements) of the donor orbital and ϵ_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)



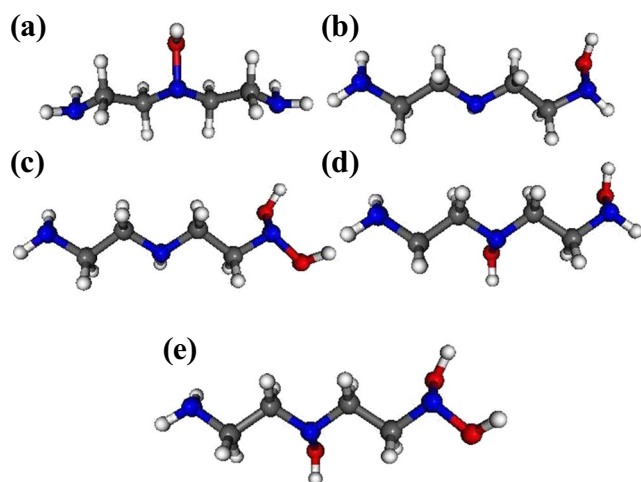


Fig. 3 Optimized geometries of hydroxy derivatives of diethylenetriamine

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

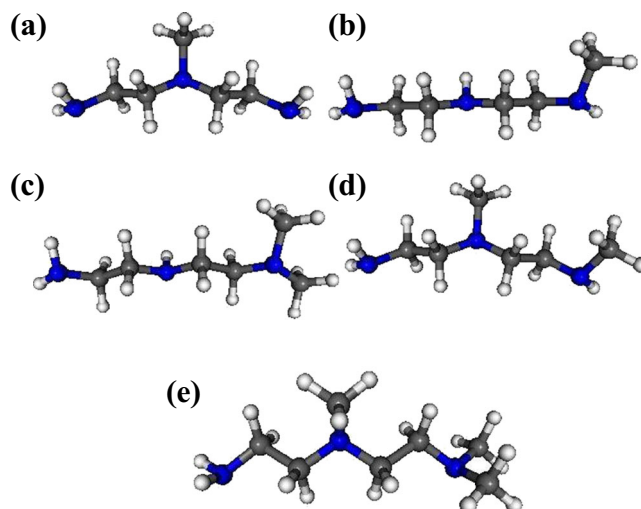


Fig. 4 Optimized geometries of methyl derivatives of diethylenetriamine

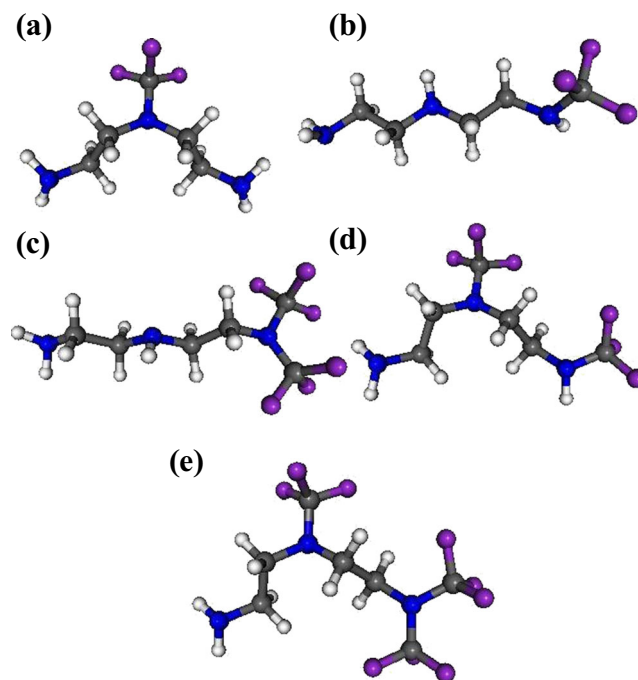


Fig. 5 Optimized geometries of trifluoromethyl derivatives of diethylenetriamine

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

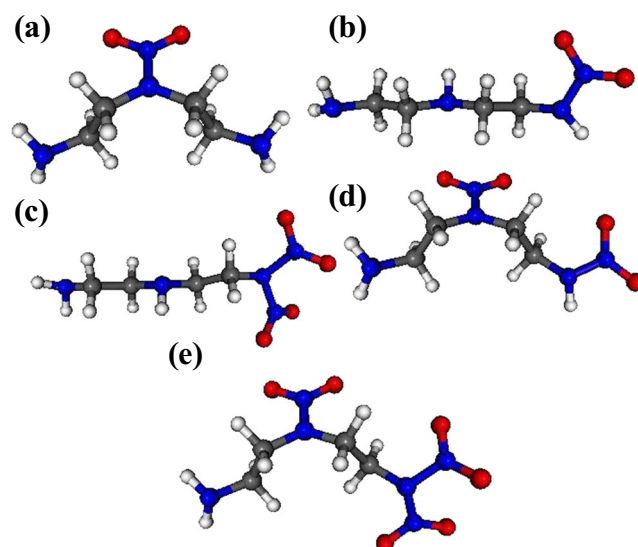


Fig. 6 Optimized geometries of nitro derivatives of diethylenetriamine

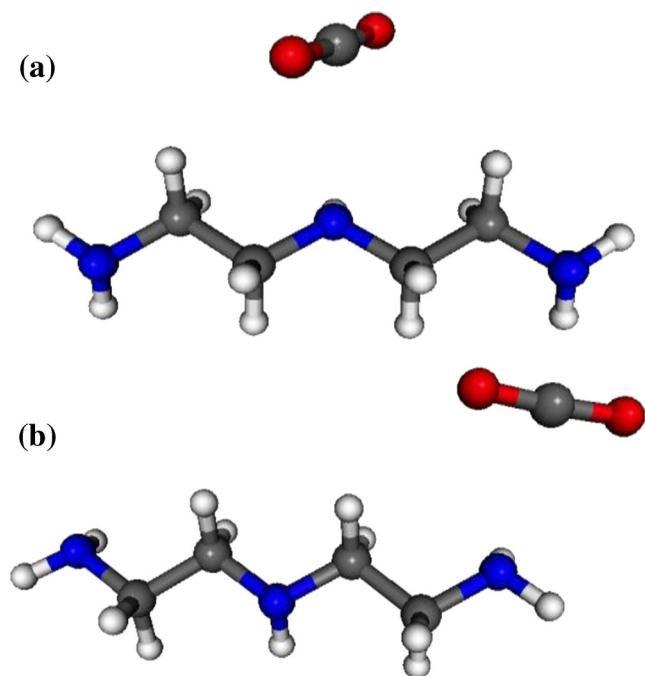


Fig. 7 Optimized geometries of diethylenetriamine:CO₂ complexes with CO₂ attached to **a** N1 and **b** N15/N18

change in geometry is reflected in the binding properties. The binding energies for all diethylenetriamine:CO₂ complexes are summarized in Table 2. The negative signs of the binding energies of the CO₂ interaction with unsubstituted diethylenetriamine at N1 and N15/N18 indicate that CO₂ 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 CO₂ 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. CO₂ 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.

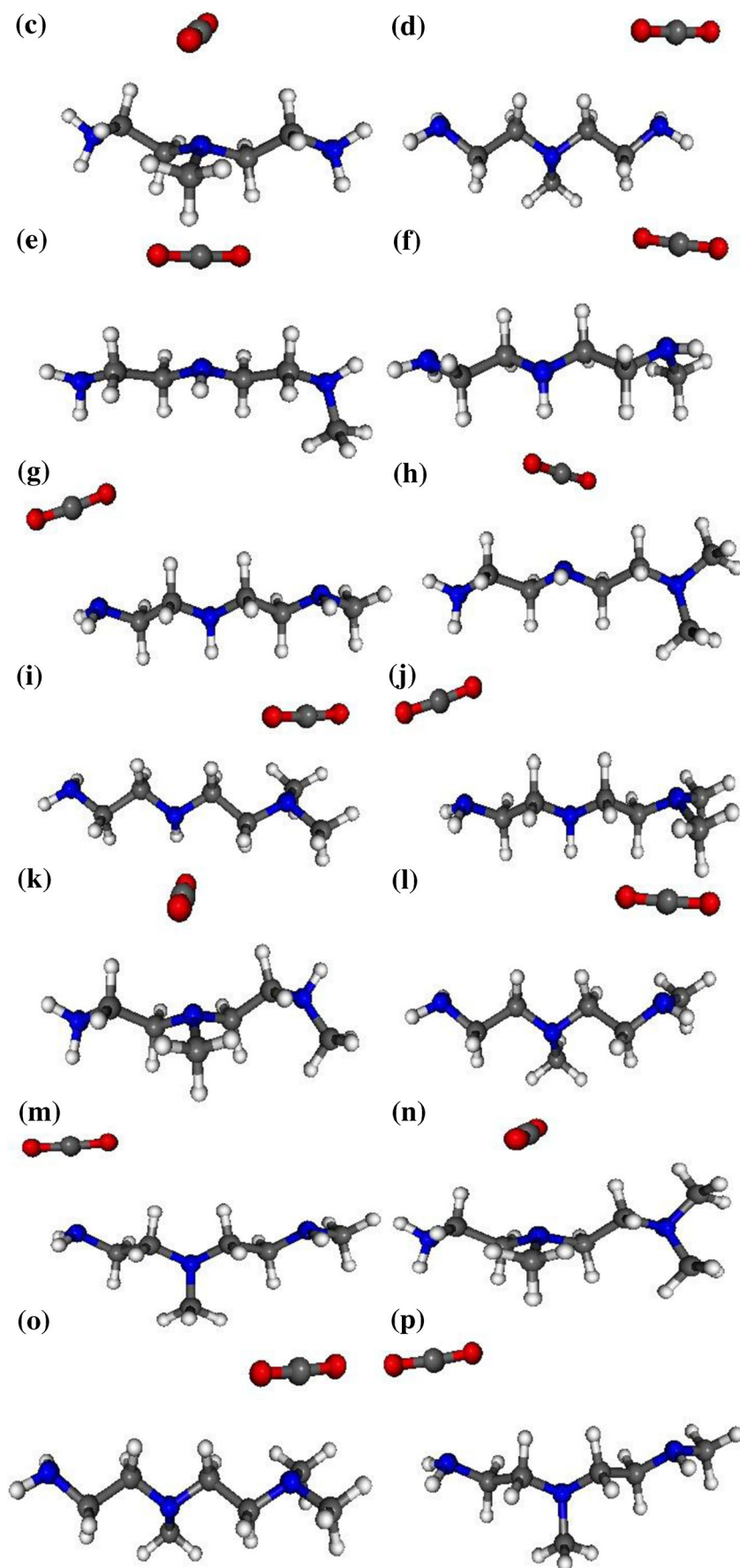
In contrast to methyl substitution, introducing a hydroxyl group enhances the binding of CO₂ with diethylenetriamine at the substitution site (compounds **c**, **f**, **k** and **n**) because of the extra hydrogen bond formed between the oxygen and hydrogen of the hydroxyl group (see Fig. 9). However, 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 CO₂ 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 CO₂ 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:CO₂ complexes

References	<i>E</i>	<i>d</i>						
A	-0.65	2.93						
B	-1.30	2.86						
Compound	<i>E</i> (CH ₃)	<i>d</i> (CH ₃)	<i>E</i> (OH)	<i>d</i> (OH)	<i>E</i> (NO ₂)	<i>d</i> (NO ₂)	<i>E</i> (CF ₃)	<i>d</i> (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



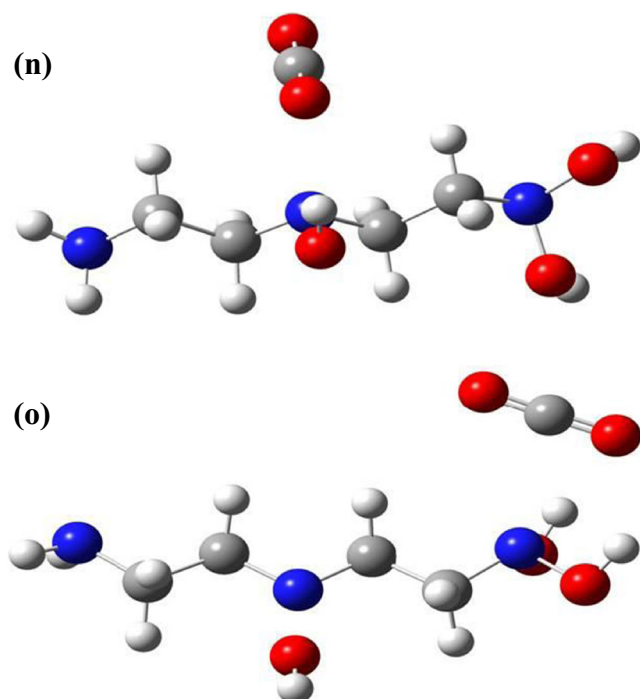


Fig. 9 Optimized geometries of hydroxy substituted diethylenetriamine:CO₂ complexes involving hydrogen bonds

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 CO₂ interaction at N1 (compounds **e** and **h**). The hydrogen bond arising at single terminal substitution

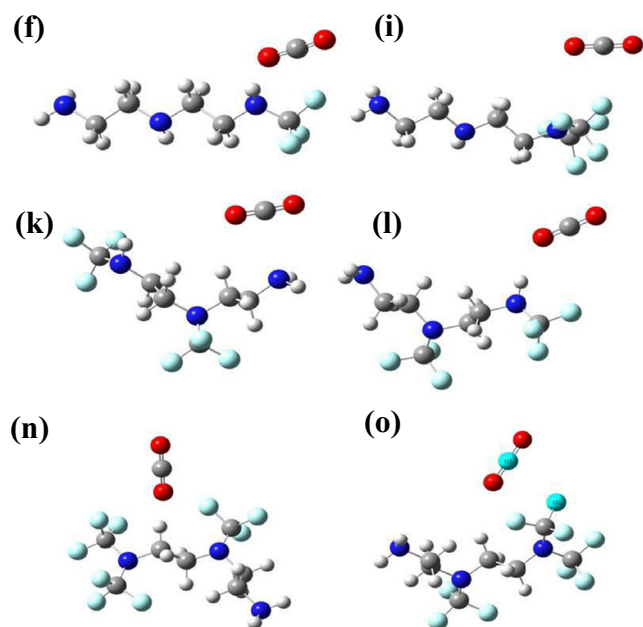


Fig. 10 Optimized geometries of some trifluoromethyl-substituted diethylenetriamine:CO₂ complexes

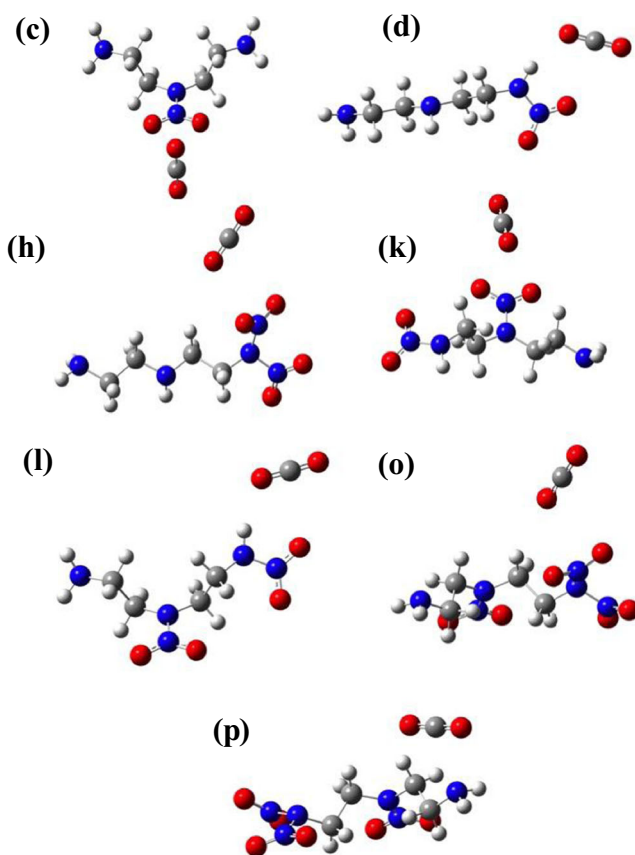


Fig. 11 Optimized geometries of some nitro-substituted diethylenetriamine:CO₂ complexes

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 CO₂ 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 CO₂ interaction with N1, it interacts with CO₂, resulting in increasing the binding energy.

In order to investigate the nature of interaction between diethylenetriamine and its derivatives and CO₂, 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 CO₂. 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 CO₂ are collected in Tables 3 and 4. Stabilization energies of the donor–acceptor interaction between all substituted diethylenetriamines and CO₂ 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 CO₂ 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 interaction energies suggest an electrostatic interaction between methyl substituted diethylenetriamine and CO₂ 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:CO₂ complex have larger delocalization energies than the corresponding reference values of compounds **a** and **b**, revealing a chemical interaction between hydroxy diethylenetriamine and CO₂ 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

Table 3 Stabilization energies (kcal mol^{−1}) of donor–acceptor interaction between diethylenetriamine **a** and CO₂ 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 CO₂ 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

interactions of compounds **c**, **f**, **i**, **k**, **l**, **n** and **o** are dictated by electrostatic interactions. Similarly, in the case of the nitro diethylenetriamine:CO₂ complex, the large values of the delocalization and interaction energies of compounds **f** and **l** show chemical interactions associated with electrostatic interactions. On the other hand, the interaction between trifluoromethyl diethylenetriamine and CO₂ is mainly physical 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 5 Delocalization energies (kcal mol^{−1}) of all donor–acceptor interaction between substituted diethylenetriamine and CO₂ 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 CO₂ 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 CO₂.

Conclusions

In summary, *ab initio* calculations of the CO₂ interaction with different active sites (nitrogen atoms) of unsubstituted diethylenetriamine and their substituted counterparts revealed the following: primary amines are more active towards CO₂ capture than secondary amines, suggesting that primary amines are more efficient as CO₂ 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 CO₂ with amine at the substitution center. Therefore, bulky substituents are not preferred for amine scrubbers; introducing substituents with atoms that can hydrogen bond to CO₂ enhances the interaction of the latter with amine. According to NBO analysis, the terminal nitrogen atoms of unsubstituted diethylenetriamine interact chemically with CO₂, whereas substituted diethylenetriamine compounds interact mainly through electrostatic interactions and even chemical interaction behavior is dictated by electrostatic interactions.

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