Supplementary Material (ESI) for *PCCP*

Supplementary Information

Table S1. Aromatic amines investigated in this study

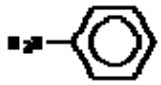
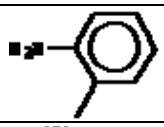
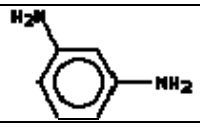
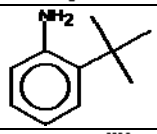
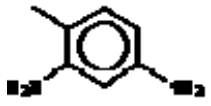
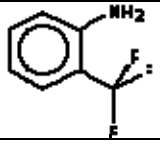
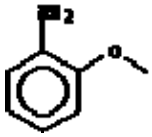
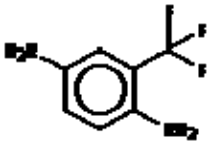
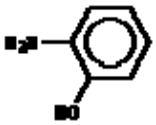
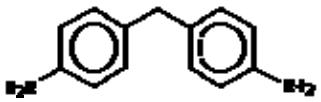
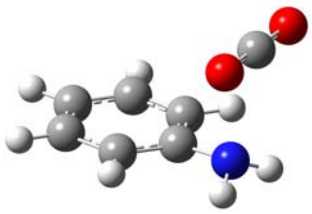
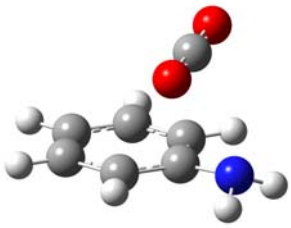
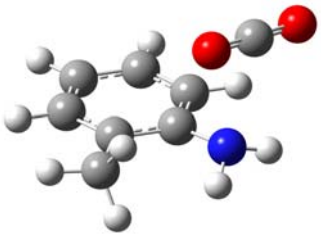
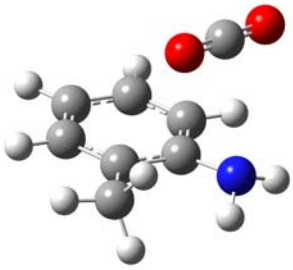
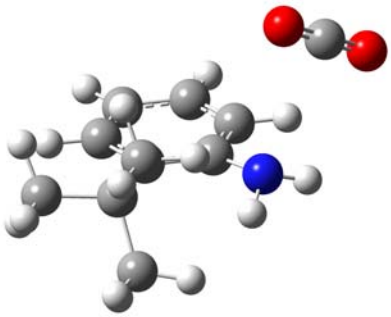
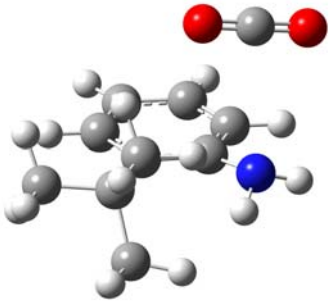
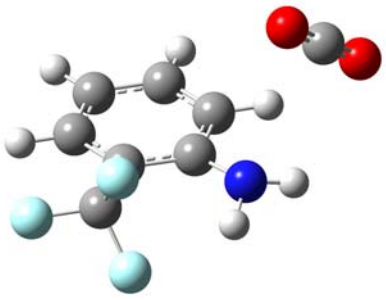
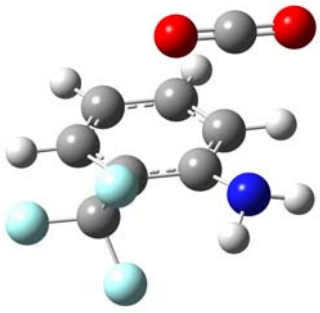
Monoamines		Diamines	
	Aniline (Ani) : Aldrich ≥99.5%		1,4-Benzenediamine (pNH2) : Fluka technical, ≥97.0% (GC/NT)
	2-methyl aniline (oCH3) : Aldrich ≥99%		1,3-Benzenediamine (mNH2) : Aldrich flakes, ≥99%
	2-tertbutyl aniline (otBu) : Aldrich 99%		1,3-Benzenediamine, 4-methyl (oCH3mNH2) : Aldrich 98%
	2-trifluoromethyl aniline (oCF3) : Aldrich 99%		1,2-Benzenediamine, 3-methyl (oCH3oNH2) : Aldrich 97%
	2-methoxy aniline (oOMe) : OEKANAL®, analytical standard (Riedel-de Haën)		1,4-Benzenediamine ,2-(trifluoromethyl) (oCF3pNH2) : Aldrich 97%
	2-hydroxy aniline (oOH) : Fluka puriss., ≥99.0% (NT)		Benzenamine, 4,4'-methylenebis (diPhpNH2) : Fluka purum, ≥97.0% (GC)
	3-hydroxy aniline (mOH) : Fluka purum, ≥98.0% (T)		

Table S2. Concentration and demixing pressures for the aromatic amines investigated in this study (the melting point of each chemical is reported for information).

Amine	Concentration (mmol/L)	Demixing pressure (MPa)	Melting point (°C)
Monoamines			
Ani	5.1	8.0	−6
oCH3	4.3	8.0	−28
otBu	3.0	8.0	−60
oCF3	3.7	8.0	−31
oOMe	4.1	8.8	5
oOH	7.3	30.0	173
mOH	7.6	30.0	122
Diamines			
pNH2	4.7	30.0	141
mNH2	7.8	30.0	65
oCH3mNH2	7.1	30.0	98
oCH3oNH2	6.7	11.0	62
oCF3pNH2	3.5	9.4	56
diPhpNH2	3.1	30.0	90

Figure S1: Optimized structure of the amine-CO_2 complexes at the B3LYP and MP2 level using the aug-cc-pVDZ basis set.

Amines	B3LYP	MP2
(A) Ani		
(B) oCH3		
(C) otBu		
(D) oCF3		

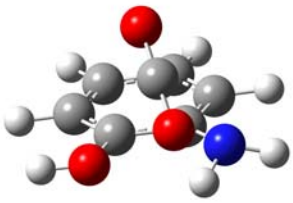
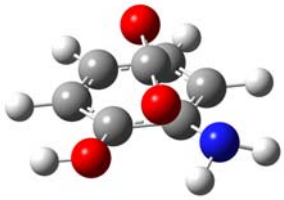
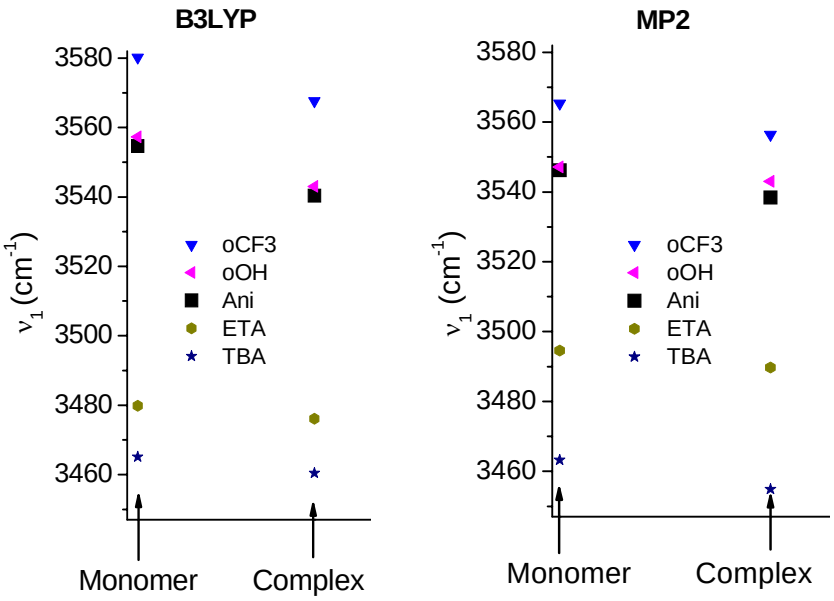
(E) oOH		

Figure S2. Comparison of the calculated frequencies (unscaled) of the ν_1 band of monoamines and their complex with CO_2 at the B3LYP/Aug-cc-pVDZ and MP2/Aug-cc-pVDZ computational level.



In order to validate the frequency calculations performed in the DFT approximation, we have also performed a vibrational analysis of few monoamines (Ani, oOH, oCF3, ETA, TBA) and their complexes with CO_2 using ab-initio method at the MP2 level. The unscaled calculated frequencies at the B3LYP and MP2 level associated with the symmetric stretching mode (ν_1) of the NH_2 group of the amines and their complexes with CO_2 are compared on figure S2. We observe that the predicted frequencies using the two different methods agree nicely. Indeed, although the absolute values of (ν_1) are not strictly the same, we observe that the frequency values follow the same order: ν_1(oCF3) > ν_1(oOH) > ν_1(Ani) > ν_1(ETA) > ν_1(TBA). Moreover, the shift to lower frequencies upon the complex formation is reproduced by both types of calculations. Therefore, although the DFT method do not estimate accurately dispersion forces, the vibrational behavior of the NH_2 group in theses amines and their complexes with CO_2 is well reproduced by the B3LYP method. This result is somehow coherent with the fact that the NH_2 group is primarily influence by the EDA interactions occurring between CO_2 and the amines, which have been shown to be well accounted by the B3LYP method.