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Activation of Carbon Dioxide by Bicyclic Amidines

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Activation of the carbon dioxide molecule was achieved using bicyclic amidines (DBU, PMDBD, and DBN). The solution reaction of CO_2 with amidines yielded the corresponding zwitterionic complexes through the formation of a N−CO_2 bond. ^{13}C NMR data confirmed the carbamic nature of the carbamic zwitterions, DBU−CO_2 and PMDBD−CO_2. However, when these adducts were crystallized, the X-ray analyses of the single crystals were in agreement with bisamidinium bicarbonate salt structures, indicating that structural changes occurred in the crystallization process. The elemental and thermogravimetric analysis data for the carbamic zwitterions, DBU−CO_2 and PMDBD−CO_2, initially obtained by the direct reaction of amidines with CO_2, suggest that these molecules are probably associated with one molecule of water by hydrogen-bond formation (amidinium$^+$−COO^-···H_2O). A correlation was observed between the thermal stability and the transcarboxylating activity for the amidine−CO_2 complexes. Theoretical calculations of hardness were performed at the B3LYP/cc-pVTZ level of theory and showed concordance with the experimental reactivity of DBU and PMDBD toward CO_2.

Introduction

Carbon dioxide is considered to be a weak Lewis acid,[1] and a preliminary activation of the CO_2 molecule[2] is commonly required to insert it into organic molecules. The activation of carbon dioxide has been performed by electrochemical reduction in both aqueous[3] and nonaqueous[4] media. Inorganic and organometallic compounds have also been used for this effect.[5] Hindered amidine and guanidine bases have been used as catalysts in reactions involving the use of carbon dioxide.[2a,c−e,6] The catalytic activity of these bases is, in many cases, associated with their proton-transfer activity.

We have reported, for the first time, the fixation and subsequent transfer of carbon dioxide by 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in the synthesis of *N*-alkylcarbamates.[7] Other authors have also reported nucleophilic catalysis by cyclic amidines and guanidines in diverse carbon dioxide reactions through the formation of an intermediate base−CO_2 adduct.[8]

DBU[9] and 3,3,6,9,9-pentamethyl-2,10-diazabicyclo-[4.4.0]dec-1-ene (PMDBD)[10] in acid−base reactions, with

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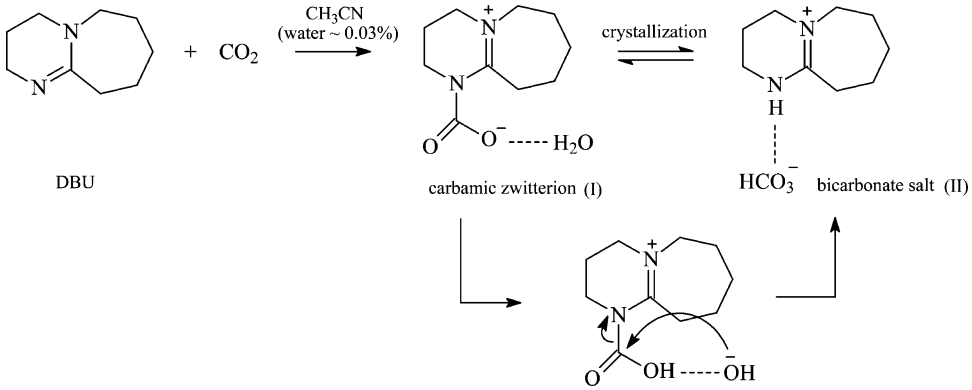
SCHEME 1



the formation of adducts involving the corresponding amidinium cation, are examples of the behavior of amidines as bases, as expected according to their pK_a (conjugate acid pK) values, which are greater than 23.[11]

On the other hand, there are some examples of the use of DBU as a nucleophilic base.[12] DBU has also been used as a nucleophile in its reaction with phosphorochloridates to form DBU−phosphorus intermediates via N−P bond formation.[13] Another study has shown the effect of DBU as a Lewis base in the Baylis−Hillman reaction, leading to abnormal adducts containing the amidine moiety.[14]

The present paper describes a comparative study of the reactivities of a number of cyclic amidines toward the carbon dioxide molecule. Two novel complexes have been obtained from the reaction of DBN and PMDBD amidines with CO_2 in solution. X-ray structures have been determined for the DBU and PMDBD bicarbonates. The transcarboxylating activity, an important reaction for both combinatorial syntheses and simulation of enzymatic systems, is correlated with the thermal stability of the amidine−CO_2 complexes.

Theoretical calculations have also been carried out to obtain the relative hardness for both DBU and PMDBD molecules and their respective adducts with CO_2. This study provides a better understanding of the selective basic or nucleophilic behavior of the investigated amidines from the point of view of the HSAB principle.

Results and Discussion

Crystal Structure Determination of the $[DBUH]^+HCO_3^-$ Obtained on Crystallization of the Zwitterionic Carbamic DBU−CO_2 Complex. The DBU−CO_2 zwitterion, represented by structure I in Scheme 1, was synthesized following the reported[7] procedure. The ^{13}C NMR data for the DBU−CO_2 adduct showed two signals at 160.7 and 166.4 ppm corresponding to a carbamic and an amidinium carbon, respectively, confirming that it was obtained as a carbamic complex. The elemental and thermogravimetric (TGA) analyses performed on the solid produced in the reaction of DBU with CO_2 (DBU−CO_2 zwitterion) suggest that the complex could be associated with water, probably by a hydrogen-bond interaction with the CO_2 moiety. The carbamic DBU−CO_2 complex was crystallized from a 4:1 (v/v) ethanol/ether solution, and single crystals were collected for X-ray studies. The X-ray revealed that the crystals correspond to a bis$[DBUH]^+HCO_3^-$ structure, suggesting that the structural changes that occur in the crystallization process transformed the starting carbamic zwitterion into a bicarbonate salt. The data for bis$[DBUH]^+HCO_3^-$ were corrected by absorption factors using the PSISCAN method.[15] The structure was solved by the SIR92 method[16] and refined by the full-matrix least-squares[17] and difference Fourier syntheses, using the WingX system.[18] The hydrogen atoms (except those attached to the N and O atoms that are found in the DF map) were located in their ideal positions, with a thermal vibration equal to 1.2 times the U_{eq} of the attached atom, and not refined. All non-hydrogen atoms were refined anisotropically.

The asymmetric unit of $[DBUH]^+HCO_3^-$ with the atom-numbering scheme is depicted in Figure 1a. The molecular structure consists of dimeric species, as shown in Figure 1b.

The dimer exhibits a strong hydrogen bond (N1···O2 = 2.693(2) Å) between the N−H of the protonated DBU molecule and one of the oxygen atoms of the bicarbonate anion. The dimer arises from very strong hydrogen bonds, which are formed between the HCO_3^- ions (O3···O1* = 2.609(2) Å), across the crystallographic inversion center. The hydrogen-bond parameters are given in Table 1.

During the crystallization process of the DBU−CO_2 zwitterionic carbamic complex, an amidinium bicarbonate may be formed by the proton transfer from a water molecule to the zwitterion followed by the nucleophilic attack of the hydroxyl anion on the N−COOH moiety. Therefore, an equilibrium involving a carbamic zwitterion is possible, probably in the forms of (DBU−CO_2)·H_2O (I) and amidinium bicarbonate $[DBUH]^+HCO_3^-$ (II). This explanation is summarized in Scheme 1.

Reaction of PMDBD with Carbon Dioxide. Crystal-Structure Determination of $[PMDBDH]^+HCO_3^-$. Scheme 2 shows the formation of a PMDBD−CO_2 zwit-

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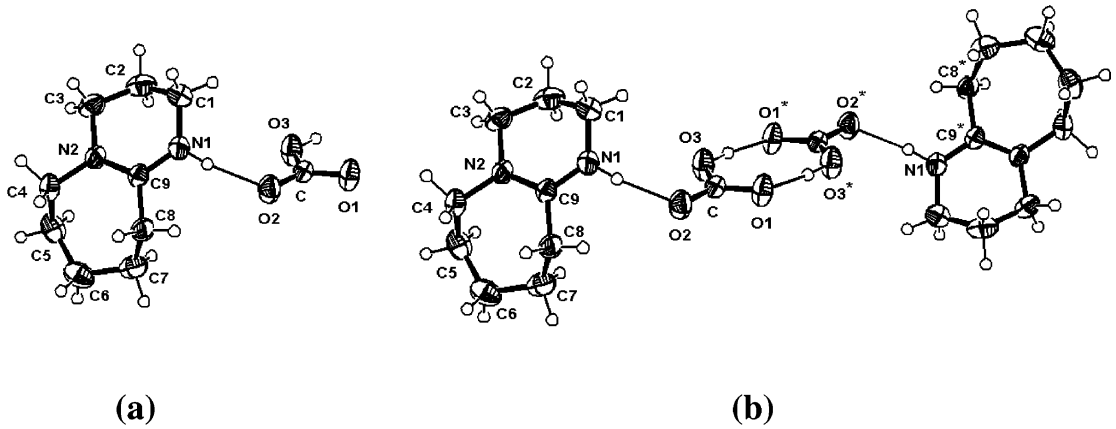
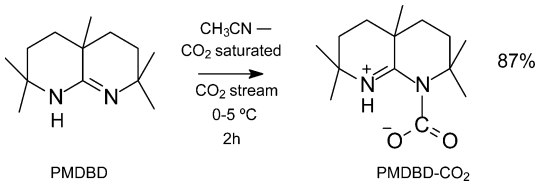


FIGURE 1. (a) ORTEP[19] representation of the asymmetric unit of $[DBUH]^+HCO_3^-$ with the atom-labeling system. (b) Dimer bis$[DBUH]^+HCO_3^-$.

TABLE 1. Hydrogen-Bond Parameters for the Dimer, Bis$[DBUH]^+HCO_3^-$

A−H···B	A−H (Å)	H···B (Å)	A···B (Å)	angle (deg)	symmetry
N1−H17···O2	0.890	1.800	2.693(2)	173	
O3−H19···O1*	0.860	1.760	2.609(2)	167	$-x, -y, 2 - z$

SCHEME 2



terionic complex. The yield of the isolated PMDBD−CO_2 complex was higher than that of the DBU−CO_2 complex (74%) under the same conditions (no water association was considered). On the other hand, the PMDBD−CO_2 adduct is soluble in more weakly polar solvents, such as chloroform and dichloromethane, and seems to be more resistant to hydrolysis than the analogous DBU−CO_2.

The ^{13}C NMR analysis of the PMDBD−CO_2 carbamic complex (without prior crystallization) in deuterated chloroform showed three nonequivalent methyl systems at 24.6, 29.7, and 31.3 ppm. On the other hand, four methylene signals at 31.4, 31.9, 34.7, and 53.3 ppm were detected, revealing the asymmetry of the PMDBD−CO_2 molecule. This suggests that there is some coincidence in shifts for the two other nonequivalent methyl groups. Quaternary carbons were not detected in the ^{13}C NMR spectrum. The assignments were confirmed by DEPT-135° experiments. The ^{13}C NMR spectrum also showed two low-intensity signals at 162.2 and 166.0 ppm (the signal at 162.2 ppm was weaker) assigned to a carbamate (−N−COO) and an amidine (−N=C−N−) carbon, respectively. These signals were attributed using reported NMR data for other amidine derivatives.[8g,20]

As that in the case of the DBU−CO_2 complex, the X-ray structure of the analogous PMDBD−CO_2, after its crystallization from chloroform, is also consistent with the formation of a bicarbonate adduct in the form of

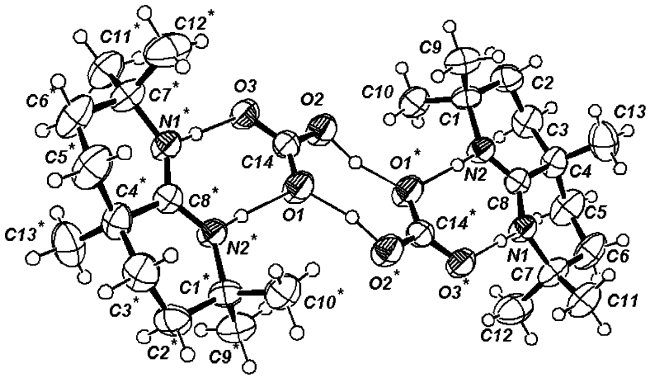


FIGURE 2. ORTEP representation of the X-ray structure for bis$[PMDBDH]^+HCO_3^-$.

bis$[PMDBDH]^+HCO_3^-$. The formation of the bicarbonate is reversible since its dissolution in dry deuterated chloroform regenerated the zwitterionic species, as confirmed by ^{13}C NMR analyses.

For the bis$[PMDBDH]^+HCO_3^-$ complex, the X-ray data collection was conducted at a low temperature (200 K) since a disordered chloroform molecule was observed in previous analyses. However, even at low temperatures, the disorder persists. Figure 2 shows an ORTEP representation of the molecule with the atoms identified. For clarity, the disordered chloroform molecule has been omitted.

The structure of the complex involved the presence of hydrogen bonds between the nitrogen and oxygen atoms of the carbonate. These connections are represented in Figure 2. The distances of N1···O3 and N2···O1 are 2.754(3) and 2.744(3) Å, respectively, indicating the presence of hydrogen bonds of medium strength. The dimer is formed by the H bonding of two hydrogen bonds between the O2 and O1 atoms of the HCO_3^- ions (O2···O1* = 2.609(3) Å). Table 2 lists the corresponding hydrogen-bond parameters.

Reactivity of 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) toward Carbon Dioxide. The reactivity of DBN toward CO_2 was also studied for comparison. DBN amidine is structurally related to DBU; therefore, a similar behavior was expected in its reaction with CO_2 and in the transcarboxylation of amines. Scheme 2 shows the reaction of DBN with CO_2.

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TABLE 2. Hydrogen-Bond Parameters for the Dimer, Bis[PMDBDH]$^+HCO_3^-$

A−H···B	A−H (Å)	H···B (Å)	A···B (Å)	angle (deg)	symmetry
O2−H1O2···O1	1.150(4)	1.490(4)	2.609(3)	162(3)	$^1/_2 - x$, $^3/_2 - y$, $-z$
N1−H1N···O3	0.980	1.770	2.754(3)	178	
N2−H2N···O1	0.950	1.790	2.744(3)	176	

SCHEME 3

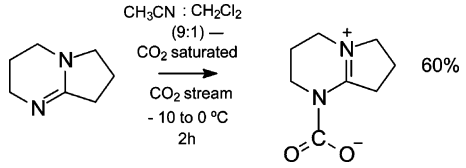

TABLE 3. Comparative TGA Results of the DBU−CO_2, PMDBD−CO_2, and DBN−CO_2 Complexes

compound	sample weight (mg)	first weight loss T (°C); mg, %	second weight loss T (°C); mg, %
DBU−CO_2	5.4180	58−107; 1.5549, 28.70	107−170; 3.8631, 68.29
PMDBD−CO_2	5.1629	80−104; 1.2040, 23.32	104−150; 3.9650, 76.81
DBN−CO_2	5.4660	30−75; 1.5113, 27.65	75−94; 0.7034, 12.87

As shown in Scheme 3, the formation of the DBN−CO_2 complex required special conditions. Thus, a solvent mixture containing 10% (v/v) of a nonpolar solvent was used to ensure a high concentration of carbon dioxide in the reaction medium, and the temperature was decreased to −10 °C to induce the precipitation of the complex as it formed. This complex was carefully filtered off from the solvent and washed with cold ether. It was found to be more hygroscopic than the DBU−CO_2 homologue and, therefore, had to be stored under dry and freezing conditions.

Thermal Stability and Transcarboxylating Activity of the Amidine−CO_2 Carbamic Complexes. The complexes were studied by TGA to determine their thermal stability (Table 3). The first weight loss was considered to correspond to CO_2 release. The results from the transcarboxylation of the cyclohexylamine with the amidine−CO_2 zwitterionic complexes were used to correlate thermal stability with transcarboxylating activity.

Thus, for the purpose of comparison, the transcarboxylation of cyclohexylamine,[7] as a model amine, was performed at −5 °C with both DBU−CO_2 and DBN−CO_2, and the corresponding ethyl carbamates were obtained by a subsequent reaction of the carbamate intermediates with ethyl iodide for 6 h at 10 °C. Under these conditions, the yields of the isolated carbamates were 57 and 68% from the transcarboxylation with DBU−CO_2 and DBN−CO_2, respectively. No reaction was detected when the PMDBD−CO_2 complex was used in the range from −5 to 80 °C.

The experimental values of the first weight loss for the DBU−CO_2 and PMDBD−CO_2 carbamic complexes are more in agreement with the loss of CO_2 and a water molecule (calculated values were 28.9 and 22.9%, respectively) than with the loss of only carbon dioxide (calculated values were 22.4 and 17.4%, respectively), suggesting that these zwitterions were probably associated with one molecule of water by a hydrogen-bond interaction. In the case of the DBN−CO_2 adduct, the first weight loss value was more in accordance with the release of a CO_2 molecule only.

A comparison among the starting temperatures (in parentheses) for the first weight loss associated with the amidine−CO_2 breakup allowed the determination of the following order of thermal stability for the investigated complexes: PMDBD−CO_2 (80 °C) > DBU−CO_2 (58 °C) > DBN−CO_2 (30 °C).

On the other hand, from the transcarboxylation experiments using *N*-cyclohexylamine (yields of carbamates in parentheses), it was possible to define an order of reactivity, which correlates inversely to thermal stability as follows: DBN−CO_2 (68%) > DBU−CO_2 (57%) ≫ PMDBD−CO_2 (negligible).

The theoretical calculations discussed below predict the occurrence of hydrogen-bond interactions between the CO_2 oxygen and both a quaternary N^+−H bond in PMDBD−CO_2 (stronger) and a C−H bond in DBU−CO_2 (weaker), H_{20} and H_{25}, respectively (Figure 3). This could be a reasonable explanation for both the higher thermal stability and the lower transcarboxylating activity of the PMDBD−CO_2 complex.

Hardness Calculations. In a N-electron system, with energy E and external potential $v(\vec{r}$, the hardness (η) is defined using the density functional theory (DFT),[21] as shown in eq 1.

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\rho/r)} \tag{1}$$

A finite difference approximation of eq 1 gives

$$\eta = \frac{I - A}{2} \tag{2}$$

where I and A are the ionization potential and the electron affinity, respectively.

Koopman's theorem[22] can be applied to approximate eq 2

$$\eta = \frac{E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}}{2} \tag{3}$$

where E_{LUMO} and E_{HOMO} are the energies associated with the lowest unoccupied and highest occupied molecular orbitals, respectively.

Figure 3 shows the DBU−CO_2 and PMDBD−CO_2 labeling scheme. Table 4 shows the eigenvalues of frontier orbitals, HOMO and LUMO, the gap between them (in atomic units), and the hardness values (in electronvolts) calculated at the B3LYP/cc-pVTZ level of theory.

First, it is interesting to compare the stability of carbon dioxide (CO_2) and ethanol with DBU and PMDBD. According to our hardness values, the Lewis bases DBU and PMDBD are on the borderline of the soft−hard scale (they have hardness values of 3.06 and 3.23 eV, respectively, and PMDBD is a harder base), and both can react

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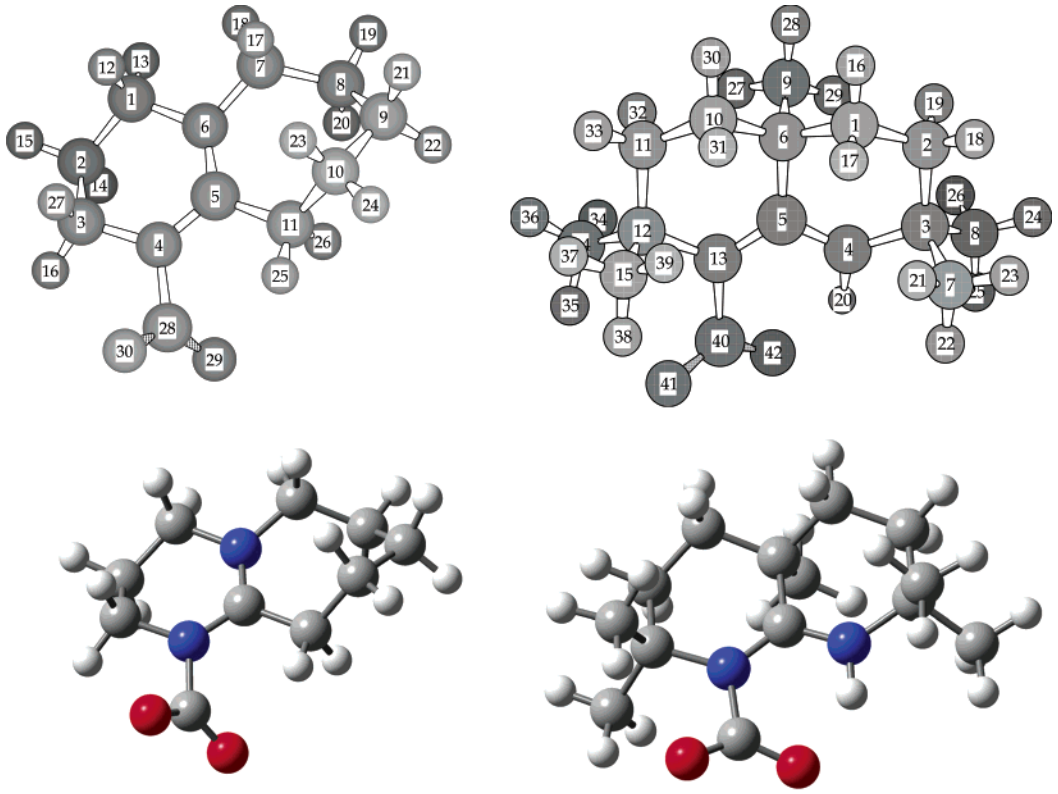

FIGURE 3. DFT/B3LYP optimized geometries for DBU−CO_2 (left) and PMDBD−CO_2 (right) with atom labeling.

TABLE 4. B3LYP/cc-pvtz Frontier Orbital Eigenvalues and Hardness Values

molecule	E_{HOMO} (au)	E_{LUMO} (au)	gap (au)	hardness (eV)
DBU	−0.21337	0.01145	−0.22482	3.06
DBU−CO_2	−0.25407	−0.03135	−0.22272	3.03
CO_2	−0.34430	−0.13945	−0.20485	2.79
PMDBD	−0.22076	0.01667	−0.23743	3.23
PMDBD−CO_2	−0.25913	−0.03418	−0.22495	3.06
ethanol	−0.27422	0.03919	−0.31341	4.26

with the Lewis acid CO_2. Ethanol (calculated as a model molecule for the purpose of comparison), which is a harder acid than CO_2, should only react with PMDBD due to the high hardness of the PMDBD compared to that of DBU. This behavior can also be inferred from the charge values summarized in Table 5.

Table 5 shows the NBO atomic charges for all of the species. The NBO scheme was adopted for one good reason; that is, NBO is an approach that comes quite close to intuitive chemical concepts.

In an initial step, orbitals were associated almost entirely with a single atom (i.e., core orbitals and lone pairs are localized just as the so-called natural atomic orbitals (NAOs)). Next, the orbitals involving bonding (or antibonding) between pairs of atoms were localized using only the basis set AOs of those atoms. Finally, the remaining Rydberg-like orbitals were identified, and all orbitals were made orthogonal to one another. The result is that all NAOs and Rydberg orbitals are described using the basis set AOs of a single atom, and all NBOs are described using the basis set AOs of two atoms. Thus, the NBO analysis provided an orbital picture that is as close as possible to a classical Lewis structure for a given molecule.

In addition to orbital analysis, it is possible to obtain further information about the C−N bond character by comparing the NBO charges of the relevant atoms (Table 5). N_{13} in PMDBD−CO_2 is slightly more negative than N_4 in DBU−CO_2 (−0.53125 and −0.50408, respectively). The charges on C_{40} (PMDBD−CO_2) and C_{28} (DBU−CO_2) have the same tendency, suggesting that the N−CO_2 bond in PMDBD−CO_2 is comparatively harder (more polarized) than the corresponding one in DBU−CO_2.

The population analysis clearly shows that the nucleophile center is strongly concentrated on PMDBD's N_{13} and DBU's N_6 and N_4. From the two electrons that populate the HOMO (this population analysis is based on the 6-311+g* basis set), 1.90418 are on N_{13} (lone pair), with 27.92% of s and 72.03% of p character (in PMDBD), and 1.72022 on N_6, with 3.21% of s and 96.78% of p character (in DBU). Interestingly, the HOMO-1 of DBU has 1.91240 on N_4, the site where the reaction with CO_2 occurs, with 30.46% of s and 69.48% of p character, clearly showing a mixture (hybridization) of the sp^2 form (N_{13} in PMDBD also shows this behavior). This hybridization favors the formation of the N−CO_2 bond since the HOMO-1 orbital of DBU can overlap easily with the p_z orbital of CO_2 (the LUMO orbital of CO_2 is 100% p_z), due to a more favorable geometry, in contrast to the p_y lone pair of N_6 (the main contribution of the HOMO orbital in DBU). As a consequence, a HOMO-1 (DBU) to LUMO (CO_2) overlapping occurs when the reaction takes place.

The Wiberg bond indexes (WBI) relative to CO_2 and some atoms of DBU and PMDBD provide additional information about the extra PMDBD−CO_2 stability. A

TABLE 5. Natural Charges on Relevant Atoms

		molecules				molecules	
atom	no.	DBU	DBU−CO_2	atom	no.	PMDBD	PMDBD−CO_2
C	3	−0.20042	−0.17134	N	4	−0.67439	−0.58717
N	4	−0.62629	−0.50408	C	5	0.49901	0.59998
C	5	0.48135	0.58997	C	6	−0.13496	−0.11863
N	6	−0.53488	−0.44371	C	12	0.08860	0.14602
C	11	−0.42680	−0.43819	N	13	−0.60067	−0.53125
H	25	0.20839	0.24001	H	20	0.39369	0.43416
H	26	0.22463	0.24316	C	40		0.93327
H	27	0.21197	0.20993	O	41		−0.72774
C	28		0.91933	O	42		−0.77949
O	29		−0.75563				
O	30		−0.76164				

hydrogen bond occurs between O_{42} and H_{20} (Wiberg bond index value of 0.0575, greater than the value of 0.0012 between O_{29} and H_{25} in DBU−CO_2), forming a ring consisting of O_{42}, C_{40}, N_{13}, C_5, N_4, and H_{20}. This hydrogen bond influences the rotation along the C−N axis between the planes CO_2 vis-à-vis PMDBD. The rotation in DBU−CO_2 is 50° (the dihedral angle C_5−N_4−C_{28}−O_{29}), which is much steeper than the angle of 29° in PMDBD. If one takes into account that H_{20} is deflected by 9° when the reaction occurs, the O_{42}−H_{20} distance (this distance in the optimized geometry is 1.710 Å) becomes shorter. For instance, the interaction between CO_2 and nitrogen (N_4−C_{28}) is also weaker in DBU−CO_2, whose WBI value is 0.7697, compared to 0.7883 in PMDBD−CO_2.

Another important consequence of bonding CO_2 with PMDBD and DBU is the delocalization of the double bonds between nitrogen and a neighboring carbon, namely, N_4−C_5−N_6 (DBU) and N_{13}−C_5−N_4 (PMDBD). The N_4=C_5 double bond (WBI value of 1.6828) is now a resonance bond, for example, part of N_4−C_5−N_6 (Wiberg bond index values of 1.3692 and 1.3362 between N_4−C_5 and C_5−N_6 in DBU−CO_2, respectively). The N_4−C_5 and C_5−N_6 bond lengths have also changed from their initial values in DBU to the corresponding ones in DBU−CO_2. Thus, the N_4−C_5 bond length changed from 1.290 to 1.330 Å, and the C_5−N_6 bond length changed from 1.380 to 1.340 Å. The same phenomenon occurs among the N_{13}−C_5−N_4 atoms. The N_{13}=C_5 double bond in PMDBD, which has a Wiberg bond index value of 1.7374, becomes a resonance bond with a WBI of 1.3408 (the bond length changed from 1.280 to 1.340 Å), and the C_5−N_4 bond, once a single bond with a Wiberg bond index value of 1.1278, now has a double bond character with a WBI value of 1.4049, with the C_5−N_4 bond length shifting from 1.390 Å in PMDBD to 1.320 Å in PMDBD−CO_2.

Conclusions

Two novel zwitterionic carbamic complexes were obtained by the reaction of amidines PMDBD and DBN with CO_2.

The crystallization of the previously reported DBU−CO_2 complex and the new PMDBD−CO_2 analogue yields the respective bisamidinium bicarbonates assembled in a hydrogen-bond network.

The elemental analysis and TGA data suggest that DBU−CO_2 and PMDBD−CO_2 carbamic complexes could be associated with water by hydrogen-bond interaction involving the CO_2 moiety. Therefore, in the crystallization of the DBU−CO_2 and PMDBD−CO_2 zwitterions, a hydrolysis occurs leading to the formation of the respective bis[DBUH]$^+HCO_3^-$ and bis[PMDBDH]$^+HCO_3^-$ salts.

There are inverse correlations between the thermal stability and the transcarboxylating activity for the investigated amidine−CO_2 complexes.

From the theoretical calculations, the reaction of DBU with CO_2 occurs under orbitalic control involving the HOMO-1 orbital of DBU, which can give higher overlapping with the LUMO of the CO_2 molecule. In addition, the application of the HSAB principle is useful for understanding the higher reactivity of PMDBD (compared with that of DBU) in proton-transfer reactions with alcohols and the high reactivity of the two amidines toward the carbon dioxide molecule.

On the other hand, conformational data show the existence of strong hydrogen-bond interactions stabilizing the PMDBD−CO_2 complex. This, among other factors, can rationalize the selective reaction of PMDBD with carbon dioxide in the presence of a stronger nucleophile, such as *N*-cyclohexylamine.

Finally, the amidines investigated are able to activate and transfer (DBU and DBN) the carbon dioxide molecule to amines. The amidine−CO_2 complexes show an enzyme-like behavior. Hence, we suggest the use of the investigated cyclic amidines and their analogues as model compounds for biological studies involving carbon dioxide.

Experimental Section

N-Cyclohexylamine, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 3,3,6,9,9-pentamethyl-2,10-diazabicyclo[4.4.0]dec-1-ene (PMDBD) were purchased from commercial sources and used without further purification. The other reagents and solvents were also commercial and had the required purity.

The data collections for X-ray analyses were performed in a Cad4 Enraf Nonius diffractometer for bis[DBUH]$^+HCO_3^-$ at room temperature and in a Kappa CCD at 200 K for bis[PMDBDH]$^+HCO_3^-$. The structures were solved using the WinGX system,[18] and the structural analyses were performed by PLATON.

For the estimation of the hardness of all of the molecules (DBU, DBU−CO_2, PMDBD, PMDBD−CO_2, ethanol, and CO_2), the following procedure was adopted. Geometries were first optimized without any constraints (except for CO_2, where the bond angle was constrained to 130.0°). All calculations were performed using the DFT/B3LYP[23] method and 6-311+g* basis set within the Berny algorithm.[24]

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From the optimized geometries, frequency calculations were performed to determine whether a structure is a true minimum-energy structure with no imaginary frequency. Because it was observed that the HOMO−LUMO gap in soft acids and bases demanded better basis sets to be correctly described,[25] single-point calculations were performed using the B3LYP/cc-pVTZ[26] level of theory in order to estimate the hardness. Solvent effects were incorporated in all calculations through the PCM method[27] since it was observed that the hard−soft effect changed drastically in the presence of a solvent. All computations were performed using the Gaussian package of programs.[28]

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Supporting Information Available: General analytical and compound characterization details. Crystallographic data were deposited in the Cambridge Crystallographic Data Centre with numbers CCDC 237594 and 237595. Crystal data and details, as well as bond distances and angles, for DBU and PMDBD amidinium bicarbonates are reported. The geometrical parameters and the complete list of natural charges for DBU, PMDBD, and their respective complexes with carbon dioxide are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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