JOC Notes

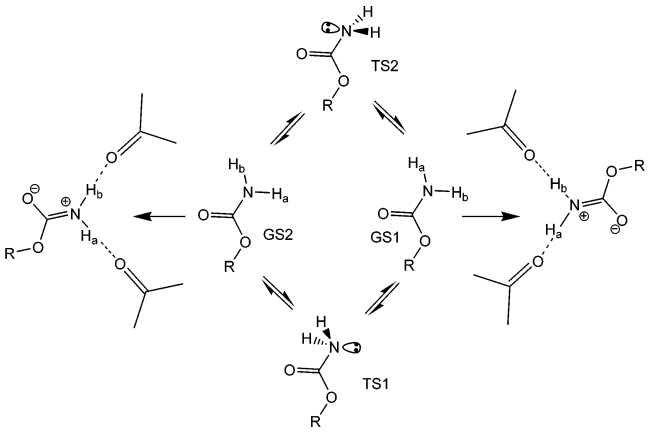
Dynamic ^{1}H NMR Study of the Barrier to Rotation about the C−N Bond in Primary Carbamates and Its Solvent Dependence

Ali Reza Modarresi-Alam,*,† Parisa Najafi, Mohsen Rostamizadeh, Hossein Keykha,† Hamid-Reza Bijanzadeh,‡ and Erich Kleinpeter§

Department of Chemistry, University of Sistan & Baluchestan, Zahedan, Iran, Department of Chemistry, Tarbiat Modarress University, P. O. Box 14115-175, Tehran, Iran, and Department of Chemistry, University of Potsdam, P. O. Box 60 15 53, D-14415 Potsdam, Germany

modaresi@hamoon.usb.ac.ir

Received June 23, 2006



The dynamic ^{1}H NMR study of some primary carbamates in the solvents $CDCl_3$ and CD_3COCD_3 between 183 and 298 K is reported. The free energies of activation, thus obtained (12.4 to 14.3 kcal mol^{-1}), were attributed to the conformational isomerization about the N−C bond. These barriers to rotation show solvent dependence in contrast to the tertiary analogues and are lower in free energy by ca. 2−3 kcal mol^{-1}.

The barrier to rotation about partial C−N double bonds in amides and carbamates (urethanes) has been the subject of substantial investigation.[1−21] The free energies of activation in carbamates (urethanes) are somewhat smaller (2−4 kcal mol^{-1}) than in comparable amides because conjugation between the nitrogen lone pair and the carbonyl group is reduced by the same but competing effects between the oxygen lone pairs and the same carbonyl group. However, one of the oxygen lone pairs can be donated into the carbonyl π system, and thus, it can partially compensate the loss of π conjugation with the nitrogen lone pair when C−N bond rotation takes place.

Carbamates are of particular interest due to their usefulness in various industries[22−24] as agrochemicals[23−26] (herbicides, fungicides and pesticides), in the pharmaceuticals industry[23,24,27] as drug intermediates, and in the polymer industry[23,24] in the synthesis of polyurethane and also in peptide syntheses.[27] In addition, among the various amine-protecting groups, carbamates are commonly used due to their chemical stability toward acids, bases, and hydrogenation.[28] In particular, the pharmacological activity and the importance of syn and anti rotamers of carbamates in their biological acitivities motivated detailed investigations of the energetic properties of these systems as conformational switches in molecular devices.[1,12,15,29]

† University of Sistan & Baluchestan.
‡ Tarbiat Modarress University.
§ University of Potsdam.

(1) Dugave, C.; Demange, L. *Chem. Rev.* **2003**, *103*, 2475−2532.
(2) Kaur, S.; Eberhardt, E. S.; Doucette, A.; Chase, A.; Dalby, C. *J. Org. Chem.* **2002**, *67*, 3937−3940.
(3) Garratt, P. J.; Thom, S. N.; Wrigglesworth, R. *Tetrahedron* **1994**, *50*, 12211−12218.
(4) Kleinpeter, E. *J. Mol. Struct.* **1996**, *380*, 139−156.
(5) Stewart, W. E. and Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517−551.
(6) Wibreg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831−840.
(7) Wiberg, K. B.; Rablen, P. R.; Rush, D. J.; Keith, T. A. *J. Am. Chem. Soc*. **1995**, *117*, 4261−4270.
(8) Lustig, E.; Benson, W. R.; Duy, N. *J. Org. Chem.* **1967**, *32*, 851−852.
(9) Tanny, S. R.; Pickering, M.; Springer, C. S., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6227−6232.
(10) Pirkle, W. H.; Simmons, K. A.; Boeder, C. W. *J. Org. Chem.* **1979**, *44*, 4891−4896.
(11) Kornberg, N.; Kost, D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1661−1664.
(12) Woolley, G. A.; Jaikaran, A. S. I.; Zhang, Z.; Peng, S. *J. Am. Chem.* Soc. **1995**, *117*, 4448−4454.
(13) Avenoza, A.; Busto, J. H.; Corzana, F.; Jimenez-Oses, G.; Peregrina, J. M. *Tetrahedron* **2003**, *59*, 5713−5718.
(14) Yamagami, C.; Takao, N.; Takeuchi, Y. *Aust. J. Chem.* **1986**, *39*, 457−463.
(15) Cox, C.; Lectka, T. *J. Org. Chem.* **1998**, *63*, 2426−2427.
(16) Rablen, P. R. *J. Org. Chem.* **2000**, *65*, 7930−7937.
(17) Basso, E. A.; Pontes, R. M. *THEOCHEM* **2002**, *594*, 199−206.
(18) Marcovici-Mizrahi, D.; Gottlieb, H. E.; Marks, V.; Nudelman, A. *J. Org. Chem.* **1996**, *61*, 8402−8406.
(19) Smith, B. D.; Goodenough-Lashua, D. M.; D'Souza, C. J. E.; Norton, K. J.; Schmidt, L. M.; Tung, J. C. *Tetrahedron lett.* **2004**, *45*, 2747−2749.
(20) Moraczewski, A. L.; Banaszynski, L. A.; From, A. M.; White, C. E.; Smith, B. D. *J. Org. Chem.* **1998**, *63*, 7258−7262.
(21) Deetz, M. J.; Forbes, C. C.; Jonas, M.; Malerich, J. P.; Smith, B. D.; Wiest, O. *J. Org. Chem.* **2002**, *67*, 3949−3952.
(22) Mindl, J.; Hrabík, O.; Stěrba, V.; Kaválek, J. *Collect. Czech. Chem. Commun.* **2000**, *65*, 1262−1272.
(23) Dibenedetto, A.; Aresta, M.; Fragale, C.; Narracci, M. *Green Chem.* **2002**, *4*, 439−443.
(24) Gupta, S. P.; Shivarkar, A. B.; Chaudhari, R. V. *J. Chem. Soc., Chem. Commun.* **2001**, 2620−2621.
(25) Motolcsy, G.; Nadasy, M.; Andriska, V. *Pesticide Chemistry*; Academiai Kiado: Budapest, 1988; p 90.
(26) Thompson, A. *Pesticide Outlook* **2002**, *13*, 84−86.
(27) Lawrence, M.; Klein, D. L.; Nemotho, P. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 157−162.
(28) Greene, W. T.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991; pp 327 and 403.
(29) Takayama, H.; Shirakawa, S.; Kitajima, M.; Aimi, N.; Yamaguchi, K.; Hanasaki, Y.; Ide, T.; Katsuura, K.; Fujiwara, M.; Ijichi, K.; Konno, K.; Sigeta, S.; Yokota, T.; Baba, M. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1993−1996.

10.1021/jo061301f CCC: $37.00
Published on Web 02/20/2007

TABLE 1. Dynamic ^{1}H NMR Data for the Primary Carbamates 1a−d in $CDCl_3$ and CD_3COCD_3

entry	compd	solvent	chemical shifts δ (ppm) [a]	lowest temp reached (K)	$\Delta\nu$ (Hz)	T_c, °C (K)	k_c (s^{-1})	$\Delta G^{\ddagger}$ [b] (kcal mol^{-1})	$\Delta\Delta G^{\ddagger}$ [c] (kcal mol^{-1})
1	**1a**	CD_3COCD_3[d]	6.749, 6.585	183	82.0	13 (286)	182.04	13.8	1.4
2	**1a**	$CDCl_3$	5.726, 4.868	233	429.0	3 (276)	952.38	12.4	0
3	**1b**	CD_3COCD_3	6.484, 6.299	233	92.5	18 (291)	205.35	13.9	0.9
4	**1b**	$CDCl_3$	6.003, 5.592	233	205.5	8 (281)	456.21	13.0	0
5	**1c**	CD_3COCD_3	6.953, 6.628	233	162.5	29 (302)	360.75	14.2	1.7
6	**1c**	$CDCl_3$	5.619, 5.221	233	199.0	−3 (270)	441.78	12.5	0
7	**1d**	CD_3COCD_3	7.309, 6.958	203	175.5	33 (306)	389.61	14.3	1.2
8	**1d**	$CDCl_3$	7.036, 5.296	213	870.0	27 (300)	1931.10	13.1	0

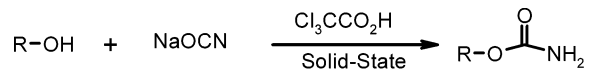
[a] Chemical shift of the protons of NH_2 group. [b] Margin of error ± 0.2 kcal mol^{-1}. [c] $\Delta\Delta G^{\ddagger}$ = diffence in the free energy of activation in solvents CD_3COCD_3 and $CDCl_3$. [d] Same result obtained in completely dry acetone-d_6; thus, trace water in the normal NMR solvent is of no influence on $\Delta G^{\ddagger}$.

NMR measurements, both in the gas phase and in solution, have shown that the rotational barrier in amides is strongly affected by the medium.[2,7,15−17,30−34] Nevertheless, a different behavior was observed for tertiary carbamates if studied by dynamic NMR spectroscopy in solution: Actually, it has been found that the rotational barrier proved to be apparently insensitive to the solvent polarity.[15−17] Recently, we reported dynamic ^{1}H NMR spectroscopy studies of various carbamates and other nitrogen-containing organic compounds.[4,33−37]

To the best of our knowledge, quantitative experimental studies concerning conformational variations, occurring in primary carbamates, have not yet been undertaken. Thus, it is the major aim of this paper to determine the barriers to rotation of some primary carbamates by dynamic NMR spectroscopy and to answer the question of if, in contrast to tertiary carbamates, their barriers to rotation will be solvent dependent.

The carbamates **1a−d** were prepared from alcohols and phenols **2**, sodium cyanate **3**, and trichloroacetic acid in the solid state[38] (cf. Scheme 1).

SCHEME 1. Synthesis of the Carbamates 1a−d



2a-d **3** **1a-d**

a, R = Menthyl; **b**, R = 2-isopropoxyethyl; **c**, R = 4-CH_3-C_6H_4; **d**, R = 2-*t*-Bu-4-CH_3-C_6H_3

Results of the dynamic ^{1}H NMR study of the carbamates **1a−d** are shown in Table 1. Gradual cooling of the samples broadens the ^{1}H NMR signals of the hydrogens of the NH_2 group, which coalesce and then, at lower temperatures, split into two signal of perfectly equal intensity. For example, the variable-temperature ^{1}H NMR spectra of **1a** in $CDCl_3$ are given in Figure 1; exchange broadening of the NH_2 protons in **1a−d** were employed for determining the C,N barriers to rotation.

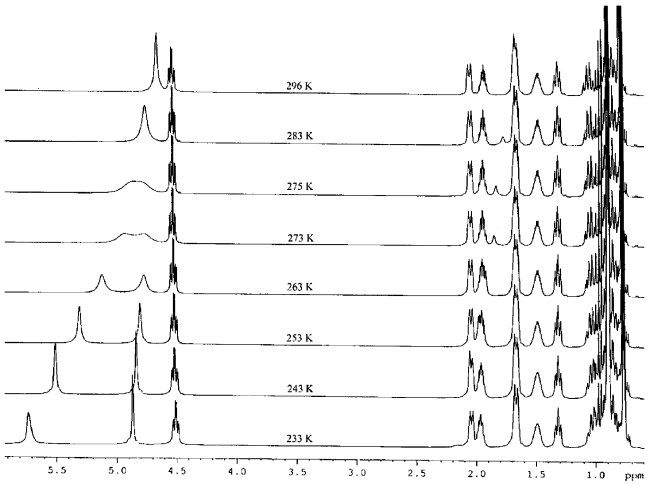


FIGURE 1. Variable-temperature ^{1}H NMR study of the primary carbamate **1a** in $CDCl_3$.

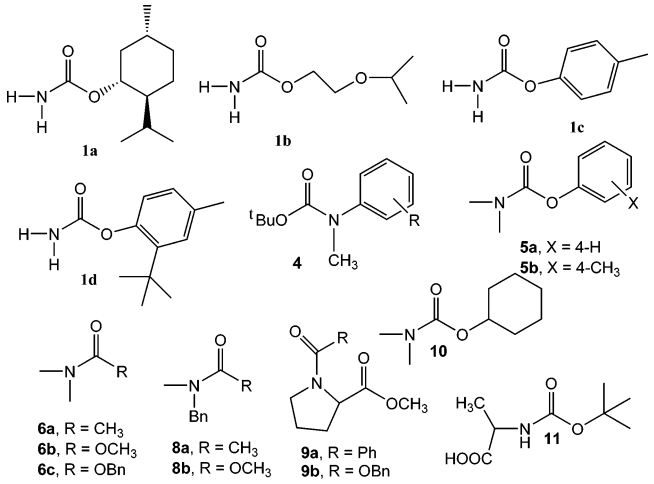
The rate constants, *k*, for the present dynamic process in the carbamates **1a−d** were calculated at the coalescence temperature (T_c) employing the Gutowsky−Holm equation ($k_c = \pi\Delta\nu/2^{-1/2}$).[3,14,34,37,39,40] Assuming the transmission coefficient, κ, to be unity, the free energies of activation ($\Delta G^{\ddagger}$) were calculated according to the Eyring equation ($\Delta G^{\ddagger} = RT_c[\ln T_c - \ln k_c + 23.76]$).[3,14,34,37,39,40]

Barriers to rotation, thus obtained for the carbamates **1a−d**, are given in Table 1 and proved to be very similar if compared in the same solvent. However, the free energies of activation were found to be solvent dependent; i.e., in CD_3COCD_3 they are about 1−1.7 kcal mol^{-1} greater than in $CDCl_3$ as the solvent. In addition, a number of conclusions can be drawn from the dynamic NMR data in Table 1, and they will be compared with results reported for similar compounds in the literature (cf. Scheme 2).

The carbamates **1a−d** studied reveal barriers to rotation which are 2−3 kcal mol^{-1} lower than in *N*-alkyl-substituted carbamates;[8−11,14−19] in other words, the electron-donating alkyl substituents increase the contribution of the canonical form **B** in Scheme 3 and hence the barrier to rotation. Electron-withdrawing groups, on the other hand, e.g., in aryl-substituted *tert*-butyl *N*-methyl-*N*-arylcarbamates **4**, decrease $\Delta G^{\ddagger}$ (from

(30) Wibreg, K. B.; Rush, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 2038−2046.
(31) Drakenberg, T.; Dahlquist, K. J.; Forsen, J. *J. Phys. Chem.* **1972**, *76*, 2178−2183.
(32) LeMaster, C.B.; True, N.S. *J. Phys. Chem.* **1989**, *93*, 1307−1311.
(33) Dabbagh, H. A.; Modarresi-Alam, A. R. *J. Chem. Res., Synop.* **2000**, 44−45.
(34) Dabbagh, H. A.; Modarresi-Alam, A. R. *J. Chem. Res., Synop.* **2000**, 190−192.
(35) Dabbagh, H. A.; Modarresi-Alam, A. R.; Tadjarodi, A.; Taeb, A. *Tetrahedron* **2002**, *58*, 2621−2625.
(36) Modarresi-Alam, A. R.; Khamooshi, F. *Synth. Comun.* **2004**, *34*, 129−135.
(37) Modarresi-Alam, A. R.; Keykha, H.; Khamooshi, F.; Dabbagh, H. A. *Tetrahedron* **2004**, *60*, 1525−1530.
(38) Modarresi-Alam, A. R.; Rostamizadeh, M.; Najafi, P. *Turk. J. Chem.* **2006**, *30*, 269−276.
(39) Günther, H. *NMR Spectroscopy*, 2nd ed.; Wiley: New York, 1995; Chapter 9.
(40) Oki, M. *Application of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: New York, 1985.

SCHEME 2



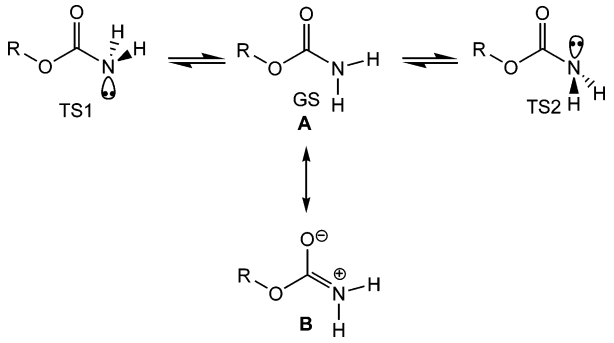
13.2 kcal mol^{-1} in the 4-MeO to 10.7 kcal mol^{-1} in the 4-CN derivative).[19]

In contrast to the influence of N-substituents in **4**, carbamates **1a**−**d** show little substituent dependence. Indeed, it is found that in **1a**−**d** the rotational barrier about the N−C bond proves to be apparently insensitive to both electronic and steric effects of the various substituents at oxygen (cf. Table 1). In the carbamates **1c** and **1d**, however, carrying aromatic substituents on oxygen, obviously one of the oxygen lone pairs is less capable of being donated into the carbonyl group than in the case of aliphatic substituents; in other words, the *O*-aryl substituent withdraws π−electron density, and thus, more π-electron density is available for delocalization with the carbamate carbonyl. Consequently, **1c** and **1d** have little higher barrier to rotation than the aliphatic analogues. Similar results have been reported for *N*,*N*-dimethylaryl carbamates **5** (cf. Scheme 2) by Yamagami et al.[14]

Larger differences in the barrier to rotation were obtained in the two different solvents (cf. Table 1); $\Delta\Delta G^{\ddagger}$ values are well above the experimental error and almost the same as obtained for amides. For instance, the rotational barriers in *N*,*N*-dimethylacetamide (DMA) **6a** and in *N*,*N*-dimethylformamide (DMF) **7** were found to increase by 2.4 and 1.4 kcal mol^{-1}, respectively, on going from the gas phase to acetonitrile solution (the same results were obtained for the amides **6a**, **8a**, and **9a** in Scheme 2).[7,15−17] This result implies that solvation or hydrogen bonding, or both, proved to be more important in carbamates **1**: If the polarity of the solvent increased on going from less polar $CDCl_3$ ($\epsilon = 4.9$) to the more polar CD_3COCD_3 ($\epsilon = 20.7$) the barriers to rotation also increased by 1−1.7 kcal mol^{-1}. Thus, the question arises why the dynamic behavior of primary carbamates **1a**−**d** shows almost the same solvent dependence as amides in contrast to the tertiary *N*-substituted analogues which proved independent.

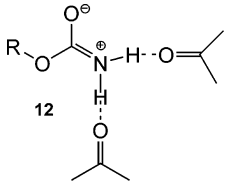
Theoretical and experimental studies have been published to explain both the amide and the carbamate isomerization processes in the gas phase and in solution.[2,7,14−17,30,41] There are two possible transition states for the rotational process, TS1 and TS2, where the lone pair of the pyramidalized nitrogen can be anti or syn to the carbonyl oxygen (cf. Scheme 3). Theoretical calculations at the 6-31G* level of theory of DMA (**6a**) have shown that TS1 is more stable than TS2 by 4.1 kcal mol^{-1} and that both transition states have a lower dipole moment than the ground state.[15,41] Thus, it was concluded for amides that the

SCHEME 3. Restricted Rotation in Primary Carbamates[a]



[a] Ground-state GS (**A**), N-lone pair delocalization (**B**), and transition states (TS1 and TS2).

SCHEME 4



increase in $\Delta G^{\ddagger}$ with higher solvent polarity must be attributed to different solvation of GS and TS1/TS2 and that more polar solvents preferentially stabilize the more polar ground state relative to the less polar rotational transition states.[15−17] Lectka et al.[15] and Rablen et al.[7,16] also calculated the dipole moments of GS and TS1/TS2; in DMF **7** and DMA **6a**, for example, transition states have dipole moments lower than the ground states, while in cyclohexyl *N*,*N*-dimethylcarbamate **10** (CDMC) and MDMC **6b** TS2 has the larger dipole moment compared with TS1s and GSs.[17,21] Indeed, theoretical calculations showed that there are differences in the dipole moment of GS and TS1/TS2 and that they are similar for amides and carbamates; thus, a similar response could be expected for both systems. The lower total molecular dipole moment of carbamates relative to amides was pointed out as the main factor for the insensitivity of their rotational barrier to solvent polarity. The results confirmed that MDMC **6b** is insensitive to the bulk solvent polarity, probably as a result of the relatively small molecular dipole moment. In the following, we will propose another mechanism to explain the solvent effect on the rotational barrier in primary carbamates like **1**.

The total dipole moment does not seem to be the main factor for the solvent dependence of the rotational barrier in carbamates **1a**−**d**; the dipole moments of three primary carbamates, namely methyl carbamate, ethyl carbamate, and 2-methyl-2-pentyl carbamate, are 2.40, 2.59, and 2.64 D, respectively,[42,43] almost equal with the dipole moments of the tertiary carbamates MDMC **6b** (2.51,[15] 2.55[16] and 2.57 D,[44] respectively) and CDMC **10** (2.4 D[17]). In fact, this is not consistent with a rotational process that involves a relatively dipolar ground state (due to resonance contributor **B**) and less polar transition states TS1 or TS2 as in amides.

The observed solvent effects on $\Delta G^{\ddagger}$ in carbamates **1** can be discussed also in terms of hydrogen bonding: If the NH_2 group in primary carbamates is subject to hydrogen bonding, resonance form **B** will be strengthened; thus, the double bond character in the C−N bond can be increased (cf. Schemes 3 and 4). In the acetone solutions, the NH_2 protons of carbamates may be

strongly bonded to the carbonyl oxygen in the acetone molecule, while in chloroform solution they are left relatively free. In other words, the main difference can be due to the hydrogen bond accepting ability of acetone relative to chloroform. The carbonyl oxygen of acetone donates stronger hydrogen bond to more acidic hydrogens of NH_2 in the ground state (form **B**) rather than less acidic hydrogens of NH_2 in TS1 or/and TS2 as shown in Scheme 4. Therefore, the rotational barrier about the C−N bond in carbamates **1a**−**d** is expected to increase in acetone.

Hydrogen-bonding effects on the carbonyl oxygen of acetone and other carbonyl oxygen atoms even with a C−H group (C−H−O═C) are well-established.[45−50] A similar effect appears to be operative in hydrogen bonding of secondary and primary amides such as formamide, acetamide, and *N*-methyacetamide in solvents dioxane, formaldehyde, acetone, and methyl propyl ketone (MPK), respectively.[31,51−57]

A second question is raised here: Do the primary carbamates **1a**−**d** show aggregation as self-association (dimer and/or polymer)? Since primary amides are excellent proton donors, as well as proton acceptors, they are strongly associated in solutions via intermolecular hydrogen bonds; this influences the barrier to C,N rotation ($\Delta G^{\ddagger}$) which is slightly increased.[47,51,53−55] For studying self-association, the use of a nonpolar solvent is desirable. Dioxane was employed since this is a relatively weak proton acceptor compared with the carbonyl group of amides. Dilution in dioxane is expected to easily break self-associated species and shift the ^{14}N signal upfield.[54]

In carbamates **1a**−**d**, in both solvents, the two NH_2 proton signals are shifted further downfield when the temperature is lowered (cf. Figure 1 and Supporting Information); the effect proved to be greater for the more downfield N−H proton, resulting in a gradual increase in $\Delta\nu$ in $CDCl_3$ but not so in acetone. The downfield shift of the proton signal is usually employed as a probe of hydrogen bonding. Thus, in $CDCl_3$ (the nonpolar solvent), it seems likely that there is an equilibrium of carbamate−carbamate and carbamate−chloroform via hydrogen bonding and dipolar−dipolar interactions. However, if these interactions were strong, a marked increase in the rotation barriers must have been observed in $CDCl_3$ but not in acetone.

Also for secondary carbamates, no dimerization or self-association in acetone and chloroform was reported, the latter being a nonpolar solvent,[10,19−21,43,44,58] but the formation of complexes of carboxylic acid moieties via hydrogen bonding such as **11** in Scheme 2 was demonstrated.[19−21] However, Garcia and co-workers reported the formation of a cyclic dimers of hydroxamic acids in acetone solution.[45] Both hydroxamic acids and their derivatives are stronger acids (pK_a 8−10) than the corresponding amides and carbamates. Therefore, the tendency for the formation of dimers of hydroxamic acids by hydrogen bonding is strong but acetone cannot replace the carbonyl group of one of the hydroxamic acid molecules.

For more quantitative discussions on specific interactions of individual solvents with primary carbamates, more theoretical and experimental information should be obtained. The current data are sufficient to emphasize, however, that the barrier to internal rotation about the N−C bond in the primary carbamates **1a**−**d** are higher in acetone than in chloroform and they proved to serve as significantly useful probe for the investigation of solvent effects and the presence of hydrogen bonds.

Acknowledgment. The Sistan & Baluchestan University Graduate Council supported this research. We thank one of the reviewers for pointing to the possible effect of trace water on the rotational barriers.

Supporting Information Available: Variable-temperature ^1H NMR spectra of **1a**−**d** in different solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061301F

(41) Gao, J. *J. Am. Chem. Soc.* **1993**, *115*, 2930−2935.
(42) Lee, C. M.; Kumler, W. D. *J. Am. Chem. Soc.* **1961**, *83*, 4596−4600.
(43) Oki, M.; Nakanish, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3148−3151.
(44) Bandekar, J.; Okuzumi, Y. *THEOCHEM* **1993**, *281*, 113−122.
(45) (a) Mora-Diez, N.; Senent, M. L.; Garcia, B. *Chem. Phys.* **2006**, *324*, 350−358. (b) Garcia, B.; Ibeas, S.; Leal, J. M.; Secco, F.; Venturini, M.; Secent, M. L.; Nino, A.; Munoz, C. *Inorg. Chem.* **2005**, *44*, 2908−2919. (c) Garcia, B.; Ibeas, S.; Leal, J. M. *Inorg. Chem.* **2003**, *42*, 5434−5441. (d) Secent, M. L.; Nino, A.; Munoz, C.; Ibeas, S.; Garcia, B.; Leal, J. M.; Secco, F.; Venturini, M. *J. Org. Chem.* **2003**, *68*, 6535−6542.
(46) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441−449.
(47) Frey, J. A.; Leutwyler, S. *J. Phys. Chem. A* **2005**, *109*, 6990−6990 and references cited therein.
(48) Zhang, R.; Li, H.; Lei, Y.; Han, S. *J. Phys. Chem. B* **2005**, *109*, 7482−7487.
(49) Abraham, M. H.; Duce, P. P.; Prior, D. V.; Barratt, D. G.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1355−1375.
(50) Lipczynska-Kochany, E.; Iwamura, H. *J. Org. Chem.* **1982**, *47*, 5277−5282.
(51) Umemoto, K., Ouchi, K. *Org. Magn. Reson.* **1981**, *15*, 13−17.
(52) Del Bene, J. E. *J. Chem. Phys.* **1975**, *62*, 1961−1970.
(53) Drakenberg, T. *Tetrahedron Lett.* **1972**, 1743−1746.
(54) Saito, H.; Tanaka, Y.; Nukada, K. *J. Am. Chem. Soc.* **1971**, *93*, 1077−1081.
(55) Kamei, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2269−2273.
(56) Whittaker, A. G.; Siegel, S. *J. Chem. Phys.* **1965**, *42*, 3320−3324.
(57) Suezawa, H.; Tsughiya, K.; Tahara, E.; Hirota, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4057−4065.
(58) Pomares, M., Grabuleda, X.; Jaime, C.; Virgili, A.; Alvarez-Larena, A.; Piniella, J. F. *Magn. Reson. Chem.* **1999**, *37*, 885−890.