C bond dissociation energies across the first transition metal row.[9] The value of 50 Kcal/mol for the Co-C σ bonds in **3** is absolutely critical. This value is derived from $PhMn(CO)_5$ where the C atom is sp^2 hybridized as it is in **3**. For a M-C σ bond where the C atom is sp^3 hybridized (*e.g.*, $CH_3Mn(CO)_5$) the bond dissociation energy drops typically to 40-45 Kcal/mol.[9] Thus, cyclization of bis(ethylene)CoCp to a cobaltacyclopentane would be expected to be endothermic by 22 to 12 Kcal/mol (the C-C bond energy is 88 Kcal/mol). As noted before, a bis(acetylene)CoCp complex is unknown, whereas, phosphine adducts of the cobaltacyclopentadiene have been isolated. On the other hand, bis(ethylene)CoCp, in fact, does exist.[9] Our finding that **2** is 19 Kcal/mol less stable than **3** has an important implication on the catalytic cycle is Scheme 1. We suspect that a direct conversion of **1** (or a weakly coordinated benzene complex of **1**) to **3** occurs without the intermediacy of **2**.

The fully optimized cobaltacyclopentadiene complex at the HF level suggests that the structure tilts by 25.9 degrees, and takes a form which facilitates coordination of the third acetylene molecule in the catalytic cyclotrimerization of a acetylene. What is surprising is that optimization of **4** at the HF level yields only a van-der-Waals type of complex between the cobaltacyclopentadiene and acetylene. Consequently, at the present time we suspect that the acetylene either directly reacts in a Diels-Alder fashion with **3** to yield **5** or that acetylene insertion into the Co-C bond proceeds from **3** directly to **6** without the intermediacy of **4**. These details, as well as, model computations at more highly correlated levels will be reported in the future.

Acknowledgement. We thank the Robert A. Welch Foundation (grant E-0705) and the Petroleum Research Fund as administered by the American Chemical Society and the President's Research Enhancement Fund as administered by the University of Houston for support of this work. Thanks are due to the Korea Science & Engineering Foundation for financial support. The National Science Foundation is thanked for a generous allocation of computer time to the Pittsburgh Supercomputing Center.

References

1. K. P. C. Vollhardt, *Angew. Chem.*, **96**, 525 (1984).
2. D. R. McAlister, J. E. Bercaw, and R. G. Bergmann, *J. Am. Chem. Soc.*, **99**, 1666 (1977).
3. G. A. Ville, K. P. C. Vollhardt, and M. J. Winter, *Organometallics*, **3**, 1177 (1984).
4. (a) Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 280 (1973); (b) Y. Wakatsuki and H. Yamazaki, *Tetrahedron Lett.*, 3383 (1973); (c) Y. Wakatsuki, T. Kuramitsu, and H. Yamazaki, *ibid.*, 4549 (1974); (d) K. P. C. Vollhardt, *Acc. Chem. Res.*, **10**, 1 (1977); (e) R. L. Hillard and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, **99**, 4058 (1977); (f) R. L. Funk and K. P. C. Vollhardt, *ibid.*, **102**, 5245, 5253 (1980); (g) E. D. Stenberg and K. P. C. Vollhardt, *ibid.*, **102**, 4839 (1980).
5. The *ab initio* calculations were performed on the VAX 8650, FPS 264, and CRAY Y-MP/832 supercomputer by using the program packages GAUSSIAN 86, 90. The standard STO-3G basis set was used for all of C and H in Cp fragment, and 3-21G of H except for Cp fragment and Huzinaga basis set of Co were used.
6. All of the structural parameters were fully optimized at HF level.
7. C. Pedone and A. Sirigu, *Inorg. Chem.*, 7, 2614 (1968).
8. A. R. Luxmoore and M. P. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).
9. J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "*Principles and Applications of Organotransition Metal Chemistry*", University Science Books, Mill Valley, CA (1987).

Solvent Effects on the Optical Rotation of Some Amino Acid Derivatives

Kwang-Youn Ko*, Yeon-Pyo Pak, Seung-ae Choi, and Jin Soo Pak

Department of Chemistry, Ajou University, Suwon 441-749

Received February 8, 1993

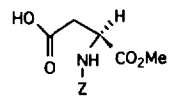
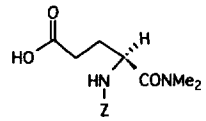
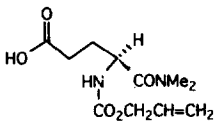
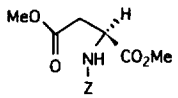
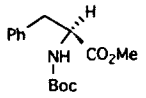
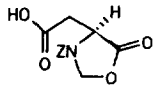
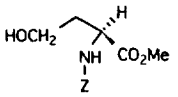
The measurement of the optical rotation of optically active compounds at a single wavelength is widely used for the determination of the absolute configuration and the optical purity.[1-3] However, it is well known that the degree and/or sign of the rotation is sometimes dependent on concentration, solvent and temperature.[3] For example, L-tartaric acid is dextrorotatory in water, but is levorotatory in ethanol-benzene (1 : 1).[4] Another example is (R)-2-benzyloxy-1-octanol that is levorotatory in chloroform, but is dextrorotatory in methanol.[5] In this case C-1 methyl ether derivative is dextrorotatory in both solvents. This reversal in the sign of optical rotation has been ascribed to the conformational change caused by hydrogen bonding.[5] In chloroform, intramolecular hydrogen bonding leads to a OH/OR gauche conformation, whereas in electron pair donor (EPD) solvent[6] such as methanol the intramolecular hydrogen bond is broken by the intermolecular hydrogen bonding with the solvent, resulting in a predominance of different conformer (presumably anti conformer). Similar phenomenon is observed in (S)-5-hydroxy-1,7-diphenyl-3-heptanone, which is dextrorotatory in chloroform and levorotatory in methanol.[7]

We like to report another example of solvent effect on optical rotation observed in the case of some amino acid derivatives[8]

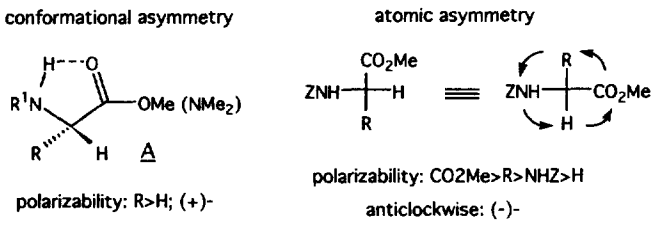
When the optical rotation of *N*-benzyloxycarbonyl-L-aspartic acid α-methyl ester (**1**)[9] was measured in chloroform and methanol, the rotation was dextrorotatory in chloroform but levorotatory in methanol. Similar reverse in sign of the rotation was observed in other amino acids such as methyl ester **4** of **1**, glutamic acid derivatives **2**, **3**[10] and serine derivative **7**,[11] as shown in Table 1. In the case of L-phenylalanine methyl ester **5**[12] the sign reversal was not observed. Instead, the rotation was nearly zero in methanol.

This reversal of sign or the change of magnitude can be explained by the similar reasoning given above in the case

Table 1. Optical Rotation of Amino Acid Derivatives in Chloroform and Methanol[a]

No.	Compounds	Chloroform	Methanol
1		+51.3 (c=2.31)	−58.7 (c=4.00)[b]
2		+12.6 (c=0.50)	−13.7 (c=2.00)[c]
3		+16.0 (c=2.38)	−15.2 (c=2.00)[b]
4		+25.7 (c=2.50)	−15.9 (c=2.50)
5		+57.2 (c=1.09)	+0.2 (c=1.21)[d]
6		+151 (c=1.15)	+113 (c=1.00)[e]
7		+11.7 (c=1.13)	−9.7 (c=1.01)[f]

[a]optical rotation in $[\alpha]_D^{25}$; [b]In Ref. 9 $[\alpha]_D = -17.6$ (c=2, 96% EtOH); [c]optical rotation in methanol taken from Ref. 10; [d]In Ref. 12 $[\alpha]_D = -2.2$ (c=10, MeOH); [e]In Ref. 16 $[\alpha]_D^{25} = +126$ (c=3.53, MeOH); [f]In Ref. 11 $[\alpha]_D^{22} = -12.5$ (c=1, MeOH).



Scheme 1.

of 2-alkoxy alcohol, namely the conformational changes associated with the formation (in chloroform) and breaking (in methanol) of intramolecular hydrogen bond[5,7]; in chloroform the L-amino acids may exist as the H-bonded form **A**, as shown in Scheme 1.

According to the Brewster's rule, the sign and magnitude can be predicted by considering two factors, namely atomic asymmetry and conformational asymmetry, as shown in Scheme 1.[13,14] In the case of L-amino acids, the cyclic form **A** is predicted to contribute to positive rotation, since the alkyl group has higher polarizability than hydrogen atom (conformational asymmetry). On the other hand, if was assume that the polarizability order is CO_2Me (or $CONMe_2$)>alkyl >NHZ (or NHBoc)>H, then such amino acid would show negative rotation (atomic asymmetry). As far as the L-amino acids reported in Table 1 is concerned, the sign of rotation in chloroform is positive, which suggests the perdominance of the cyclic form **A**, as expected. In methanol solvent it seems that the atomic asymmetry is more important, resulting in the negative rotation.[15] In this context, it is noted that the oxazolidine **6**[16] that is analogous conformationally to the structure **A** shows a larger dextrorotation in both solvents than **1** and the sign is the same as that of **1** in chloroform.

In conclusion, some amino acid derivative can show a solvent-dependent reversal in sign of rotation, presumably due to the conformational change. Further study by means of ORD and CD measurement will be necessary to obtain more definite information on the preferred conformer in various solvents.

Acknowledgement. The present study was supported by the grant from the KOSEF (92-25-00-08) and the Basic Science Research Institute Program, Ministry of Education. The authors thank the Yungjin Pharm. Co., Ltd. for measuring the optical rotation.

References and Notes

1. G. G. Lyle and R. E. Lyle, in *Asymmetric Synthesis;* J. D. Morrison, Ed.; Academic: New York, Vol. 1, Chapter 2 (1983).
2. V. Schurig, *Kontakte (Darmstadt),* 54 (1985).
3. J. March, *Advanced Organic Chemistry,* 2nd Ed., McGraw-Hill: New York, pp. 87-88 (1977).
4. R. L. Shriner, R. Adams, and C. S. Marvel, in *Advanced Organic Chemistry,* Gilman, H. Ed.; John Wiley & Sons: New York, 2nd Ed., Vol 1, p. 298 (1943).
5. K.-Y. Ko and E. L. Eliel, *J. Org. Chem.,* **51**, 5353 (1986).
6. Reichardt, C. Solvents and Solvent Effects in Organic Chemistry; VCH, Weinheim, Germany, 1988.
7. S. Ohta, *Bull. Chem. Soc. Jpn.,* **59**, 1181 (1986).
8. It is known that the sign of rotation of a free amino acid is dependent on the solvent. For example, L-serine has $[\alpha]_D$ equal to −6.83 and +14.45 in water and 1 M HCl, respectively. See Barrett, G. C. in *Chemistry and Biochemistry of the Amino Acids,* Barrett, G. C. Ed.; Chapman and Hall: London, p. 4 (1985).
9. G. H. L. Nefkens, and R. J. F. Nivard, *Rec. Trav. Chim.,* **84**, 1315 (1965); *Chem. Abstr.,* **64**, 3675e (1966).
10. K.-I. Lee, J. H. Kim, K.-Y. Ko, and W.-J. Kim, *Synthesis,* 935 (1991).
11. E. Schroeder, *Liebigs Ann. Chem.,* **670**, 127 (1963).
12. J. Boger, L. S. Payne, D. S. Perlow, N. S. Lohr, M. Poe, E. H. Blaine, E. H. Ulm, T. W. Schorn, B. I. LaMont, T.-Y. Lin, M. Kawai, D. H. Rich, and D. F. Veber, *J. Med. Chem.,* **28**, 1779 (1985).
13. E. L. Eliel, *Stereochemistry of Carbon Compounds;* McGraw-Hill: New York, pp. 401-406 (1962).
14. D. Nasipuri, *Stereochemistry of Organic Compounds*; John Wiley & Sons: New Delhi, pp. 501-504 (1991).
15. The specific rotation of *N*-(*tert*-butoxycarbonyl)-L-alanine methyl ester was found to be −0.3 (c=1.07) in chloroform and −39.5 (c=1.02) in methanol. It seems that the polarization order given above is not obeyed in this case.
16. J. M. Scholtz and P. A. Bartlett, *Synthesis,* 542 (1989).