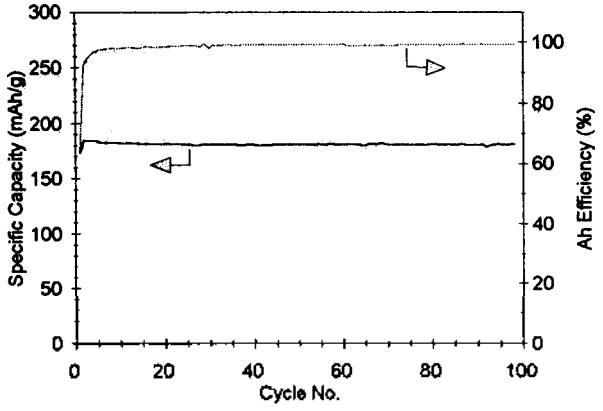


Figure 5. Variation of specific discharge capacity and Ah efficiency of P.Coke12 with charge-discharge cycling. experimental condition: see caption of Figure 3.

carbon from 2nd cycle to 98th cycle. The utilization of P.Coke 12 in this test was 48.4% based on 372 mAh/g of graphite's theoretical specific capacity. Ah efficiency of 63% at 1st cycle was raised to above 98% after 6th cycle. Therefore, the cycling characteristics of P.Coke12 were very stable. Obtained specific capacity of P.Coke12 was corresponding to calculated value from XRD analysis.

Conclusions

Pitch coke was synthesized from coal tar pitch. Synthesized P.Coke12 was found to have turbostratically disordered and buckled layer stack. Average d_{002}, La and Lc were calculated as 3.43 Å, 60 Å and 1600 Å, respectively. In cell test of P.Coke12, Ah efficiency of 63% at 1st cycle was raised to above 98% after 6th cycle. Low Ah efficiency at 1st cycle due to the irreversible intercalation of some lithium ion to carbon. Specific capacity was 180 mAh/g with good cycling behavior. Obtained specific capacity of P.Coke12 was corresponding to predicted value from XRD analysis.

In summary, synthesized P.Coke12 had low specific capacity but good cycling behavior compared, generally, with graphitic carbon.

Acknowledgment. This work has been supported by the Ministry of Trade Industry and Energy and the Ministry of Science and Technology of Korea.

References

1. *Chemistry and Physics of Carbon*; Walker, P. L. Jr., Ed.; Marcel-Dekker, Inc.: New York, U. S. A., 1965~.
2. Dahn, J. R.; Sleigh, A. K.; Shi, H.; Way, B. M.; Weydanz, W. J.; Reimers, J. N.; Zhong, Q.; Sacken, U. von *Lithium Batteries, New Materials, Developments and Perspectives*; Pistoia, G., Ed.; Elsevier; New-York, U. S. A., 1994; p 1.
3. Ergun, S. *Chemistry and Physics of Carbon*; Walker, P. L. Jr., Ed.; Marcel-Dekker, Inc.; New York, U. S. A., 1968; Vol. 3, p 211.
4. Ruland, W.; *ibid*; Walker, E. D. Jr., Ed.; Marcel-Dekker Inc.; New York, U. S. A.; 1968; Vol. 4, p 1.
5. Shi, H.; Reimers, J. M.; Dahn, J. R. *J. Appl. Cryst.* **1993**, *26*, 827.

Cyclic Dimerization of 2-Piperidylglycine

Kyoo-hyun Chung, Dong-reyol Lee, and Hyung-wo Kim

Deptartment of Chemistry, Inha University, Incheon 402-751, Korea

Received April 19, 1996

2-Piperidylglycine (**1**)[1] was prepared for the first time as a model compound for streptolutin (**2**)[2] which might be converted to antitumor agent DKP 593A *via* cyclic dimerizatioin. DKP 593A was isolated from the soil microorganism *Streptomices griseoluteus* and reported to be effective against certain solid tumors and leukemia.[3]

Piperazinedione ring structures are usually prepared by cyclic dimerizations of amino acids. It was reported that glycine and methyl L-alanine were converted to the corresponding piperazinediones by simple heating.[4] In addition to the thermal treatment, activation of the acid functionality is also available. For example, activation *via* *N*-carboxyanhydride[5] or *N*-hydroxysuccinimide ester[6] successfully gave the piperazinediones.

Relating to the present subject, the corresponding piperazinedione was not given from 2-(5-chloro)pyridylglycine upon heating,[7] while the piperazinedione was successfully formed from a β-lactam upon standing at room temperature in the preparation of racemic DKP 593A.[3] This paper aims to find a good method for preparing a piperazine-2,5-dione moiety from 2-piperidylglycine.

Result and Discussion

The ester **5** was prepared from alcohol **4** by oxidation, esterification, and protection in sequence. The ester **5** was treated with KHMDS and 2,4,6-triisopropylbenzenesulfonyl azide (trisyl azide) to give azide **6**. Simple hydrogenation of the azide **6** with or without di-*tert*-butyldicarbonate gave bis Boc ester **8** or mono Boc ester **7** in good yields.[8] During the hydrogenation of the azido ester **6**, or heating the amino ester,[7] none of the desired piperazinedione was detected. Removal of the Boc group from **7** followed by heating under reflux resulted in the intractable mixture.[7]

The acid **9**, prepared from the ester **8** by hydrolysis, was reacted with *N*-hydroxysuccinimide, and the resulting activated ester was treated with TFA and pyridine to give a solid.[6] Unfortunately, the solid was not the desired piperazinedione, but a mixture of polymeric materials by FAB mass spectral analysis.[9]

The coupling of the acid **9** to the amino **7** using HOBt and BOP gave dipeptide **10**. Finally, removal of all Boc groups from **10** followed by the treatment with NMM resulted in the desired piperazinedione **11** (Scheme 1). When the ring nitrogens in **10** were protected by Cbz instead of Boc, the corresponding piperazinedione was not given.

In conclusion, the cyclic dimerization of 2-piperidylglycine was accomplished *via* the peptide formation followed by the cyclization. *N*-Protecting groups on the piperidine rings should be removed prior to the cyclization. Using this methodology, the cyclic dimerization of streptolutin is currently

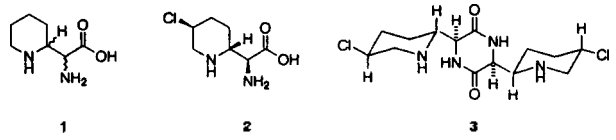
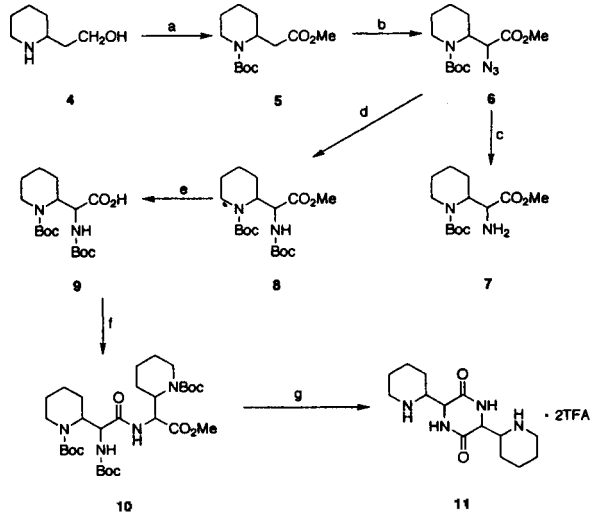


Figure 1.



Scheme 1. Key: a) i) Jones' reagent ii) MeOH/H$^+$ iii) $(Boc)_2O$, Et_3N; b) i) KHMDS, −78 ℃ ii) $TrisN_3$ iii) AcOH; c) 1 atm H_2, Pd/C; d) 1 atm H_2, Pd/C, $(Boc)_2O$; e) KOH, MeOH/H_2O; f) 7, BOP, HOBt, NMM; g) i) TFA/CH_2Cl_2 ii) NMM, Δ.

in progress, and the activation of the acid functionality will be also studied for the better synthesis of DKP 593A.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Brucker AC 250 (250 MHz) spectrophotometer. Infrared spectra were recorded on a Schimadzu IR-435. Mass spectral analyses were performed on VG TRIO 2000. Elemental analyses were determined by Organic Chemistry Research Center, Sogang University, Seoul.

Methyl 2-(*N*-*tert*-butyloxycarbonyl)piperidineacetate (5)[10]. To a solution of methyl 2-piperidineacetate (1.72 g, 10.9 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (2 mL, 14.3 mmol) and di-*tert*-butyldicarbonate (2.95 g, 13.1 mmol). After stirring for 6 hr at room temperature, the resulting mixture was treated with 1 N HCl. The organic layer was separated, washed with water, and brine, and dried (Na_2SO_4). Removal of solvent followed by column chromatography (50 g silicagel, 10 : 90 of ethylacetate/hexane) gave a clear oil (2.61 g, 92.7%).

^{1}H NMR ($CDCl_3$) δ 4.50 (m, 1H, C_2-H), 3.80 (m, 1H, C_6-H_e), 3.44 (s, 3H, OCH_3), 2.60 (m, 1H, C_6-H_a), 2.35 (m, 2H, C_α-H), 1.50-1.10 (m, 6H, ring), 1.22 (s, 9H, *t*-butyl); IR (neat) 2920, 2860, 1735, 1685 cm^{-1}.

Methyl α-azido-2-(*N*-*tert*-butyloxycarbonyl)piperidineacetate (6)[11]. To a solution of ester **5** (3.00 g, 11.7 mmol) in THF (4 mL) was added KHMDS (0.5 M in toluene, 28.0 mL, 14.0 mmol) dropwise at −78 ℃ under nitrogen atmosphere and the mixture was stirred for 45 min. To the above solution of potassium enolate at −78 ℃ was added *via* cannulation a precooled (−78 ℃) solution of trisyl azide (4.33 g, 14.0 mmol) in THF (3 mL). After 3 min, the reaction was quenched with glacial acetic acid (3.10 mL, 53.8 mmol). The cooling bath was removed, and the reaction was stirred at room temparature for 2 hr. The solution was partitioned between CH_2Cl_2 and dilute brine. The aqueous phase was extracted with CH_2Cl_2. The organic phase was combined, washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated *in vacuo*. Chromatography (110 g silicagel, 10 : 90 of ethyl acetate/hexane) gave a pale yellow oil (2.95 g, 84.5%).

^{1}H NMR ($CDCl_3$) δ 4.52 (m, 1H, C_2-H), 4.25-3.90 (m, 2H, C_6-H_e, C_α-H), 3.79, 3.73 (two s, 3H, OCH_3), 2.70 (m, 1H, C_6-H_a), 1.75-1.30 (m, 6H, ring), 1.47, 1.42 (two s, 9H, *t*-butyl); IR (neat) 3090, 2930, 2850, 2100, 1740, 1690 cm^{-1}.

Methyl α-amino-2-(*N*-*tert*-butyloxycarbonyl)piperidineacetate (7)[11]. A mixture of **6** (0.450 g, 1.54 mmol) and 10% Pd/C (0.045 g) in ethyl acetate (30 mL) was hydrogenated at atmospheric pressure and 60 ℃ for 40 min. The catalyst was then filtered off and the mixture was evaporated to give a yellow oil (0.39 g, 95.5%).

^{1}H NMR ($CDCl_3$) δ 4.15-3.90 (m, 2H, C_2-H, C_6-H_e), 3.80-3.60 (m, 1H, C_α-H) 3.68, 3.64 (two s, 3H, OCH_3), 2.80-2.60 (m, 1H, C_6-H_a), 1.70-1.25 (m, 8H, ring, NH_2), 1.44, 1.40 (two s, 9H, *t*-butyl); IR (neat) 3300, 2900, 2800, 1730, 1680 cm^{-1}.

Methyl α-amino-*N*,*N*'-di-*tert*-butyloxycarbonyl-2-piperidineacetate (8)[11]. To a solution of **6** (0.466 g, 1.56 mmol) and di-*tert*-butyldicarbonate (0.421 g, 1.87 mmol) in ethyl acetate (25 mL) was added 10% Pd/C (0.047 g). The mixture was hydrogenated at atmospheric pressure for 3 hr. The catalyst was then filtered off and the resulting mixture was evaporated to give a semisolid (0.493 g, 84.6%).

^{1}H NMR ($CDCl_3$) δ 5.10 (m, 1H, NH), 4.57 (m, 1H, C_2-H), 4.20-3.85 (m, 2H, C_6-H_e, C_α-H), 3.60, 3.56 (two s, 3H, OCH_3), 2.87 (m, 1H, C_6-H_a), 1.85-1.25 (m, 6H, ring), 1.32 (s, 18H, *t*-butyl); IR (neat) 3300, 2900, 2850, 1760, 1640 cm^{-1}.

α-Amino-*N*,*N*'-di-*tert*-butyloxycarbonyl-2-piperidineacetic acid (9)[11]. A solution of **8** (2.18 g, 5.85 mmol) and KOH (0.724 g, 12.9 mmol) in 1 : 4 of H_2O/MeOH (20 mL) was stirred for 5 hr. The reaction mixture was acidified and extracted with CH_2Cl_2. The organic extracts were washed with brine and dried (Na_2SO_4). Removal of solvent followed by column chromatography (20 g silicagel, 40 : 60 of ethyl acetate/hexane) gave a semisolid (1.78 g, 85%).

^{1}H NMR ($CDCl_3$) δ 5.15 (m, 1H, NH), 4.62 (m, 1H, C_2-H), 4.30-3.90 (m, 2H, C_6-H_e, C_α-H), 2.94 (m, 1H, C_6-H_a), 1.85-1.30 (m, 6H, ring), 1.41, 1.38 (two s, 18H, *t*-butyl).

***N*''-[2-(*N*-*tert*-butyloxycarbonyl)piperidyl]methoxycarbonylmethyl-α-amino-*N*,*N*'-di-*tert*-butyloxycarbonyl-2-piperidylacetamide (10)**[11]. A solution of **7** (0.500 g, 1.84 mmol), **9** (0.600 g, 1.84 mmol), BOP (0.980 g, 2.21 mmol), HOBt (0.300 g, 2.21 mmol) and NMM (0.300 mL, 2.73 mmol) in THF (10 mL) was stirred for 6 hr. The resulting mixture was concentrated *in vacuo* and subjected to chromatography (20 g silicagel, 30 : 70 of ethyl acetate/hexane) to give a semisolid (1.01 g, 89.7%).

^{1}H NMR ($CDCl_3$) δ 4.82 (m, 1H, C_2-H), 4.42-4.03 (m, 3H, C_2'-H, C_α-H, C_α'-H), 3.85 (m, 2H, C_6-H_e, C_6'-H), 3.62, 3.56 (two s, 3H, OCH_3), 2.75 (m, 2H, C_6-H_a, C_6'-H_a), 1.70-1.10 (m,

12H, ring), 1.35, 1.31, 1.30 (three s, 27H, *t*-butyl).

3,6-Bis-(2-piperidyl)piperazine-2,5-dione·2TFA (11)[11]. A solution of **10** (0.260 g, 0.424 mmol) and 1 : 1 mixture of TFA/CH_2Cl_2 (4 mL) was stirred for 2 hr at 0 ℃. The resulting mixture was concentrated *in vacuo*, and NMM (0.154 mL, 1.40 mmol) and 0.1 M AcOH/*i*-PrOH (5.20 mL) were added into the resultant. After heating at refluxing temperature for 2 hr, a solid appeared. The solid was filtered and recrystallized from methanol-ether to give the salt **11** (0.040 g, 36%).

mp 204-206 ℃ (dec.); ^{1}H NMR (DMSO-d_6) δ 4.28 (m, 2H, C_3-H, C_6-H), 3.40-3.22 (m, 4H, C_2'-H, C_2''-H, C_6'-H_e, C_6''-H_e), 2.80 (m, 2H, C_6'-H_a, C_6''-H_a), 1.85-1.33 (m, 12H, C_3'-H, C_4'-H, C_5'-H, C_3''-H, C_4''-H, C_5''-H); MS (FAB) 281 (mono cation); Anal. Calcd for $C_{18}H_{26}F_6N_4O_6$: C, 42.52; H, 5.15; N, 11.02, found: C, 42.08; H, 5.08; N, 10.61.

Acknowledgment. This work was supported in part by the Organic Chemistry Research Center-the Korean Science and Engineering Foundation, and by Inha University Research Found, 1995.

References

1. Golding, B. T.; Smith, A. J. *J. C. S. Chem. Commun.* **1980**, 702.
2. Herdeis, C.; Nagel, U. J. *Heterocycles* **1983**, 2163.
3. Fukuyama, T.; Frank, T. K.; Jewell, C. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 2122.
4. Schollkorpf, U.; Hartwig, W.; Groth, U. *Angew. Chem., Int. Ed.* **1979**, *18*, 863.
5. Schollkorpf, U.; Hartwig, W.; Pospischil, K.-H.; Kenhne, H. *Synthesis* **1981**, 966.
6. Bergeron, R. J.; Otto Phenstiel IV; Yao, G. W.; Milstein, S.; William, R. W. *J. Am. Chem. Soc.* **1994**, *116*, 8479.
7. Edgar, M. T.; Pettit, G. R.; Krupa, T. S. *J. Org. Chem.* **1979**, *44*, 396.
8. Saito, S.; Nakajima, H.; Inaba, M.; Moriwake, T. *Tetrahedron Lett.* **1989**, *30*, 837.
9. The unknown material has peaks at m/z 317, 339, 513, 633, 785, and 943 on FAB mass spectrum.
10. Morley, C.; Knight, D. W.; Share, A. C. *Tetrahedron: Asymmetry*, **1990**, *1*, 147.
11. Compound **6**, **7**, **8**, **9** and **10** are the mixture of diastereomers.

Thermal Bleaching Reactions of Spirooxazine in Ethanol and PMMA

In-Ja Lee* and Young-Duk Huh†

**Department of Chemistry, Dongguk University, Kyongbuk 780-714, Korea*
†Department of Chemistry, Dankook University, Seoul 140-714, Korea

Received May 20, 1996

It is well known that reactions of photochromic compounds dopped in amorphous solids follow non-single exponential kinetics even if their elementary steps are unimolecular processes which lead to first order reaction in solutions. Examples of deviations from first order kinetics behavior in polymer matrices are thermal bleaching reaction of photochromic compounds of azobenzenes,[1~4] indolinospirans,[5~7] and stilbenes.[4,8]

In an attempt to provide explanation of the departures from the first order kinetics of the thermal reactions in glassy matrices, distribution of local free volume,[2~4,8] distribution of activation energy,[5,6] and stretched exponential model (Kohlraush-Williams-Watts (KWW))[9,10] were suggested. Actually, the first two models are similar in their expression and in considering the distribution of a physical parameter to dispersive kinetic model for hole burning.[11,12] Both the thermal fading reaction of photochromic compounds and nonphotochemical hole burning (NPHB) (for above ~15 K) occur *via* thermally activated processes and are affected by the inhomogeneity of the surroundings of guest molecules leading to nonlinear reaction. However, the former process goes with the structral change of guest molecules in the ground electronic states while the latter process in the excited states without the structral change of guest molecules. Therefore, there is some difficulties in using the local free volume model to explain the burning process. Therefore, we expect that in the analysis of the non-single exponential kinetics occuring in polymers, using the dispersive kinetic model is more general way than using the local free volume model.

In this work we investigated the matrix effect on the thermal bleaching reaction of spironaphthooxazine using the dispersive kinetics model which is utilized to explain the persistent spectral hole burning.

Experimental

1,3-dihydro-1,3,3-trimethyl-spiro[2H-indol-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (spironaphthooxazine, NSO) was purchased from Tokyo Kasei Kogyo Co. and used without further purification. Polymethylmethacrylate (PMMA) and spectrograde ethanol were purchased from Aldrich. Thin films of NSO/PMMA was prepared by dissolving polymer plus NSO in toluene and chloroform, respectively, and allowing the solvent to evaporate from a specially designed evaporation tray. After drying in air, the films were dried in a vacuum oven for several days at temperatures above the glass transition temperatures of polymer involved. The weight percent of NSO in the film was approximately 3%.