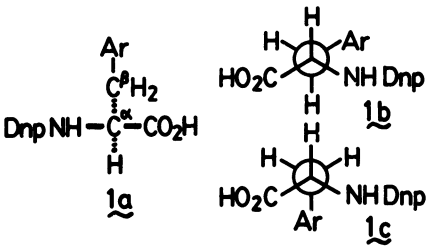
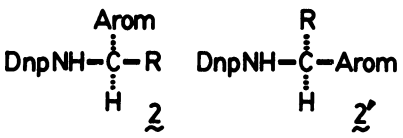
A Method for Determining Absolute Configuration of Cycloalkanamines and Related Compounds by CD Spectra of Their 2,4-Dinitrophenyl Derivatives

Masao KAWAI,* Teruhiko IWASE, Yasuo BUTSUGAN, and Ukon NAGAI†
Department of Synthetic Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466
†*Mitsubishi-Kasei Institute of Life Sciences, Minamiooya 11, Machida, Tokyo 194*
(Received July 16, 1984)

N-(2,4-Dinitrophenyl) derivatives of cycloalkanamines and related compounds having an amino and an aromatic groups in vicinal positions were prepared. Their CD spectra exhibited marked Cotton effect around 400 nm, the sign of which was shown to coincide with the chirality between the two chromophore-bearing bonds. This relation, as a special example of exciton chirality method, is useful for determining absolute configuration of cyclic compounds having a primary amino group.

Chiroptical properties of 2,4-dinitrophenyl (Dnp) derivatives of α-amino acids and related compounds have been investigated extensively.[1-10] Rules have been found which correlate the absolute configuration and the sign of the Cotton effect of the Dnp derivatives of chiral diamines,[1] arylalkylamines,[5] and cyclic secondary amines.[3] Dnp derivatives of L-α-amino acids with aromatic side chain (**1a**) exhibit characteristic CD spectra with negative Cotton effect around 400 nm.[2,5] Further study upon the related compounds led us to the proposal of Dnp-aromatic rule, which predicts negative and positive sign of $[\theta]_{\sim 400}$ value for the arylalkylamines of general formulas **2** and **2'**, respectively.[5] Based on ^{1}H NMR study and theoretical calculation of rotational strength it was concluded that staggered conformer **1b** is responsible for the negative Cotton effect around 400 nm of **1a**.[9] The conformer **1b**, designated as g^-, is characterized by the negative bond chirality between the C^α–NHDnp and C^β–Ar bonds. The present paper deals with CD spectra of carbocyclic analogs of **1a** in which the two chromophoric groups are conformationally fixed to have the same bond chirality as in **1b**. Theoretically, the chirality between electric dipole moments is the essential factor as discussed later. However, bond chirality is more familiar to organic chemists. So, "bond chirality" will be used throughout this paper as the reasonable and convenient approximation.

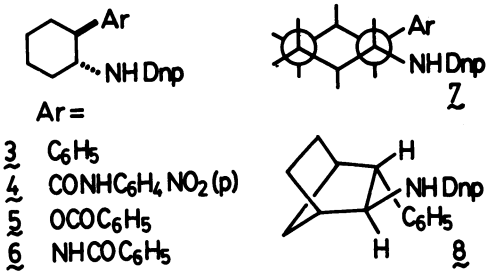




Arom : Achiral group which contains an aromatic chromophore

R : Nonaromatic group

Dnp derivatives of 2-substituted cyclohexanamines **3**—**6** were synthesized. Since the compounds **3**—**6** are considered to take stable chair conformation **7** with two bulky groups (DnpNH and Ar) in equatorial orientation, all of these Dnp derivatives **3**—**6** possess negative bond chirality between C–NHDnp and C–Ar bonds. CD spectra of **3**—**6** recorded in methanol solutions were reproduced in Fig. 1. As expected from theoretical consideration[9] all of these compounds exhibited marked negative Cotton effect around 400 nm. The conformationally fixed Dnp derivatives **3**, **4**, and **5** correspond to the staggered g^- conformers of Dnp derivatives of L-phenylalanine (**1a**, Ar=C_6H_5: $[\theta]_{410}$ −9100),[5] L-aspartic acid β-*p*-nitroanilide (**1a**, Ar=$CONHC_6H_4NO_2(p)$: $[\theta]_{400}$ −9200),[5] and *O*-benzoyl-L-serine (**1a**, Ar=$OCOC_6H_5$: $[\theta]_{408}$ −3400),[5] respectively. The magnitude of Cotton effect around 400 nm of **3**, **4**, and **5** were shown to be 2—3 times as large as the corresponding Dnp amino acids having conformational freedom, which supported the assumption that the staggered conformer g^- of Dnp derivatives of aromatic L-α-amino acids **1a** is responsible for their characteristic negative Cotton effect



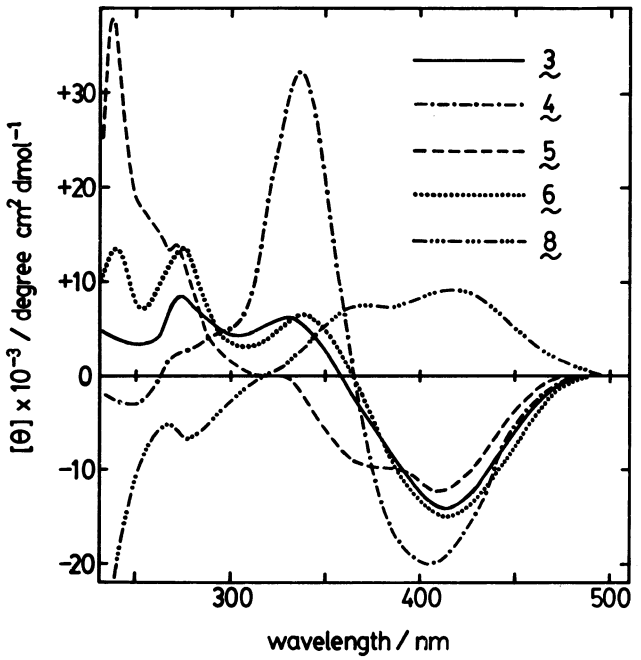


Fig. 1. CD spectra of **3**—**6** and **8** recorded in methanol.

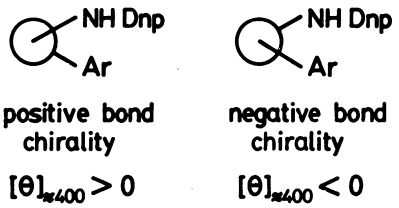
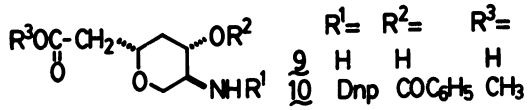


Fig. 2. Relation between bond chirality and sign of Cotton effect.
Ar implies a chromophore which contains an aromatic group.

around 400 nm. In order further to confirm the validity of the relation between bond chirality and the Cotton effect, the norbornane derivative **8** was synthesized. The CD spectrum of the Dnp derivative **8**, as also given in Fig. 1, exhibited positive Cotton effect at 416 nm in accordance with positive bond chirality of the C-NHDnp and C-C_6H_5 bonds. Thus it has been established that sign of the Cotton effect around 400 nm agrees with the bond chirality between C-NHDnp and C-Ar bonds for the conformationally fixed derivatives as described in this paper (Fig. 2).

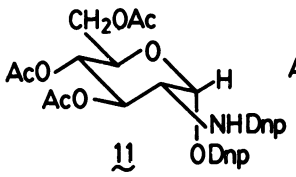
Wakamiya *et al.*[11] already reported successful application of the relation between bond chirality and the sign of Cotton effect to structure elucidation of a natural product. In order to determine absolute configuration of galantinic acid (**9**), a constituent amino acid of a peptide antibiotic galantin



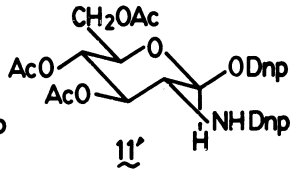
	R¹=	R²=	R³=
9	H	H	H
10	Dnp	COC_6H_5	CH_3

I,[12] micromolar amount of **9** was converted into *N*-Dnp-*O*-benzoyl derivative **10**. The CD spectrum of **10** exhibited prominent positive Cotton effect at 400 nm, which established the absolute configuration of **9** having positive chirality of the C-N and C-O bonds.[11]

Another example of application of the rule to oxacyclohexanamine derivative is the case of D-glucosamine derivative **11**, which was obtained apparently as a sole product by successive 2,4-dinitrophenylation and acetylation of D-glucosamine. Possible products of the reaction were anomers **11** and **11'**, which possess posi-



11



11'

tive and negative chirality between the C-NHDnp and C-ODnp bonds, respectively, corresponding to **1c** and **1b** in their chromophoric arrangement. Positive Cotton effect ($[\theta]^{sh}_{400}$ +5100) and small coupling constant of the anomeric proton (δ_{DMSO-d_6} 6.48, d, J=3 Hz) in ^{1}H NMR spectrum established the structure **11**.

The agreement between bond chirality and the sign of Cotton effect is rationalized as follows: The Cotton effects in concern can be assumed to be due to exciton coupling of electric transition moments of the two chromophores as expressed by the equation[13]

$$R_a = \frac{\pi}{ch} \cdot \frac{\lambda_a \lambda_b}{\lambda_a^2 - \lambda_b^2} \cdot V \cdot [\boldsymbol{R} \cdot (\mu_a \times \mu_b)]$$

where R_a is rotational strength at wavelength λ_a generated by interaction of the electric transition moment μ_a at λ_a with μ_b at λ_b. V, $\boldsymbol{R}$, c, and h are interaction energy, directional vector from μ_a to μ_b, light velocity, and Planck's constant, respectively. Thus, the sign of term $V \cdot [\boldsymbol{R} \cdot (\mu_a \times \mu_b)]$ determines the sign of Cotton effect to be observed. The electronic spectra of DnpNH chromophore shows a shoulder band around 400 nm (ε 7000) along with strong main band at around 350 nm (ε 17000). SCF-MO[14] calculation showed that direction of the electric transition moment of the longest wavelength band of DnpNH chromophore is roughly parallel to the C-NHDnp bond.[1,15] Interaction of this transition moment with transition moments of the other chromophore is considered to generate the CD band observed around 400 nm. As for the other chromophore there usually exists a strong absorption band, the electric transition moment of which has a direction along the long axis of the chromophore;[16] *i.e.*, the direction of this transition moment is

exactly or approximately parallel to the C–Ar bond. Consequently the sign of the term $\boldsymbol{R}\cdot(\mu_a\times\mu_b)$ in the equation above is expected to coincide with the bond chirality between C–NHDnp and C–Ar bonds, when μ_a and μ_b are the transition moment of the longest wavelength band of DnpNH chromophore and the transition moment along the long axis of the other chromophore, respectively. Since the sign of V-term is positive in most cases usually encountered, the term $V\cdot[\boldsymbol{R}\cdot(\mu_a\times\mu_b)]$ also has the same sign as the bond chirality. Though the transition moments which are not parallel but rather perpendicular to the C–Ar bond are also present and interact with the moment of DnpNH chromophore, their contribution to the spectra are expected to be averaged out due to rotation around the C–Ar bond. Thus the sign of the Cotton effect around 400 nm is expected to agree with the bond chirality of C–NHDnp and C–Ar bonds of these compounds.

Cotton effect around 350 nm is assumed due to exciton coupling of the dipole moment of main band of DnpNH chromophore with dipole moments of the other chromophore. The extremum of CD spectrum at this region is shifted to longer wavelength when the Cotton effect has the same sign as that of 400 nm band as in **5** (shoulder) and **8** and at shorter wavelength when the sign of Cotton effects of 400 and 350 nm bands are different as in **3**, **4**, and **6** by overlapping of the two bands. In the case of **4** having *p*-nitroanilide group as the other chromophore whose absorption maximum is at about 315 nm,[8] another CD band which corresponds to this transition moment can be expected above 300 nm. No significant band is observed, however, around 315 nm in the CD spectrum of **4**, which is presumably due to the result of cancellation of opposite contributions from the two interactions with transition moments of 400 and 350 nm bands of DnpNH chromophore. Compounds **5** and **6** show different sign of Cotton effect around 350 nm in spite of the close similarity of the two compounds. Thus no simple relation seems to exist between the absolute configuration and the sign of Cotton effect around 350 nm, which is understandable from the dissimilarity between the direction of the correspoding transition moment and the C–NHDnp bond.[1]

In conclusion the relation between the absolute configuration of cycloalkanamines and the sign of Cotton effect around 400 nm of the Dnp derivatives was ascertained experimentally as given in Fig. 2 and was rationallized theoretically using exciton coupling mechanism. Thus it has been shown that absolute configuration can be determined chiroptically for a cyclic compound having a primary amino group, if suitable derivatization can afford a Dnp derivative in which C–NHDnp and C–Ar bonds possess unambiguous bond chirality.

The relation is valid when the chirality of interacting transition moments can be approximated by the bond chirality. In general, combination of conformational analysis and rotational strength calculation will afford useful information for predicting or explaining the CD spectra. The relation described here falls under the generalization "exciton chirality method" developed by Harada and Nakanishi.[17] Attempt to determine the absolute configuration of amino compounds with exciton chirality method using salicylideneamino chromophore was reported by Smith *et al.*[18,19]

Experimental

Melting points were uncorrected. UV and CD spectra were recorded in methanol solution at room temperature on a HITACHI 124 spectrometer and on a JASCO J-40 spectropolarimeter, respectively. Optical rotations were measured with a JASCO J-20 spectropolarimeter or a JASCO DIP-4 digital polarimeter. ^{13}C NMR spectra were determined with a Varian XL-200 spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal standard. ^{1}H NMR ($CDCl_3$, acetone-d_6, or DMSO-d_6 solution) and IR (KBr disk) spectra of all the derivatives, recorded on a HITACHI R-24 or R-24A spectrometer and on a JASCO IRA-1 or A-102 spectrophotometer, respectively, were consistent with the assigned structures.

(1R,2S)-N-(2,4-Dinitrophenyl)-2-phenylcyclohexanamine (3). (±)-*trans*-2-Phenylcyclohexanamine hydrochloride, mp 252—254 °C (lit,[20] mp 249—251 °C), was prepared from 2-phenylcyclohexanone oxime, mp 174—175 °C (lit,[20] mp 168—169 °C) as described by Masamune *et al.*[20] No significant amount of the *cis*-isomer was detected in the ^{13}C NMR of the dihydrochloride measured in D_2O solution (δ=24.8, 25.6, 31.4, 34.1, 49.0, 55.8, 128.5, 128.7, and 142.0). Optical resolution of (±)-*trans*-2-phenylcyclohexanamine using equimolar amount of (+)-tartaric acid was undertaken. Recrystallization from 3:1 (v/v) methanol–ether as described by Verbit and Price[21] afforded tartrate of (+)-amine as colorless needles, mp 150—151 °C, $[\alpha]_D$ +38° (c 0.85, methanol), while recrystallization from 1:5 (v/v) methanol–H_2O resulted in the crystallization of tartrate of (−)-amine as colorless prisms, mp 139—140 °C, $[\alpha]_D$ −16° (*c* 1.0, methanol). Usual workup of the tartrates gave (+)-(1*S*,2*R*)-2-phenylcyclohexanamine, mp 41.5—42 °C, $[\alpha]_D$ +51° (*c* 0.33, methanol) [lit,[21] mp 36—38 °C, $[\alpha]_D$ +45° (*c* 0.074, methanol)] and (−)-(1*R*,2*S*)-2-phenylcyclohexanamine, mp 43.5—44 °C, $[\alpha]_D$ −49° (*c* 0.28, methanol) [lit,[21] mp 37.5—39 °C, $[\alpha]_D$ −48° (*c* 0.2, methanol)]. A mixture of the levorotatory amine (70 mg, 0.43 mmol), 1-fluoro-2,4-dinitrobenzene (FDNB: 94 mg, 0.5 mmol), $NaHCO_3$ (53 mg, 0.63 mmol), acetone (5 mL), and H_2O (2 mL) was stirred at room temperature for 2 h. Usual workup followed by SiO_2 column chromatography (benzene–petroleum ether) gave **3** (125 mg, 85%), yellow needles from benzene–petroleum ether, mp 126.5—127 °C. UV 410 (sh, ε 6200), 353 (18500), and 257 nm (8800); CD $[\theta]_{415}$ −13600, $[\theta]_{358}$ 0, $[\theta]_{340}$ +6000, $[\theta]_{305}$ +4200, $[\theta]_{274}$ +8000, and $[\theta]_{250}$ +3400. Found: C, 63.50; H, 5.54; N, 12.30%. Calcd for $C_{12}H_{19}N_3O_4$: C, 63.33; H, 5.61; N, 12.31%.

(1R,2R)-2-(2,4-Dinitroanilino)cyclohexanecarboxylic Acid p-

Nitroanilide (4). (±)-*N*-Benzoyl-*trans*-2-aminocyclohexanecarboxylic acid was prepared from anthranilic acid as described by Hünig and Kahanek,[22] and was subjected to optical resolution according to Nohira *et al.*[23] to afford (−)-(1*R*,2*R*)-*N*-benzoyl-2-aminocyclohexanecarboxylic acid quinine salt, mp 134—136 °C, $[\alpha]_D$ −112° (*c* 2.3, ethanol) [lit,[23] mp 143—145 °C, $[\alpha]_D$ −111.6° (*c* 2.5, ethanol)]. Treatment of the quinine salt with 3M HCl (1M=1 mol dm^{-3}) gave (1*R*,2*R*)-*N*-benzoyl-2-aminocyclohexanecarboxylic acid, $[\alpha]_D$ −45° (*c* 0.66, ethanol) [lit,[23] $[\alpha]_D$ −44.5° (*c* 0.67, ethanol)]. The *N*-benzoyl derivative (96 mg, 0.39 mmol) was dissolved in a mixture of conc HCl (6 mL) and acetic acid (3 mL) and was refluxed for 24 h. Evaporation of the mixture afforded crude debenzoylated product, which was 2,4-dinitrophenylated with FDNB according to Sanger[24] to give (1*R*,2*R*)-2-(2,4-dinitroanilino)cyclohexanecarboxylic acid (101 mg, 83%). To the Dnp derivative (77 mg, 0.25 mmol) was added oxalyl dichloride (1.5 mL) and stirred overnight. Excess oxalyl dichloride was evaporated *in vacuo* and *p*-nitroaniline (250 mg, 1.8 mmol) in acetonitrile (2 mL) was added to the residue, which was stirred overnight. After the evaporation of the solvent the residue was washed with hot H_2O and recrystallized from acetone–ethyl acetate to give **4** (24 mg, 20%) as yellow needles, mp 259—261 °C. UV 400 (sh, ε 5800), 330 (24000), 266 (11000), and 219 nm (21800); CD $[\theta]_{406}$ −19800, $[\theta]_{368}$ 0, $[\theta]_{336}$ +32200, $[\theta]^{sh}_{275}$ +2400, $[\theta]_{263}$ 0, and $[\theta]_{250}$ −2500. Found: C, 52.67; H, 4.41; N, 16.00%. Calcd for $C_{19}H_{19}N_5O_7 \cdot 1/4H_2O$: C, 52.60; H, 4.53; N, 16.14%.

(1R,2R)-2-(2,4-Dinitroanilino)cyclohexyl Benzoate (5). (1*R*,2*R*)-2-Aminocyclohexanol (+)-tartrate[25] (44 mg, 0.17 mmol), supplied by Prof. T. Suami, was 2,4-dinitrophenylated with FDNB (62 mg, 0.33 mmol) and $NaHCO_3$ (76 mg, 0.90 mmol) in ethanol (1.7 mL) and H_2O (0.7 mL). The crude product was subjected to SiO_2 column chromatography (benzene–ethyl acetate) to afford (1*R*,2*R*)-2-(2,4-dinitroanilino)cyclohexanol (44 mg, 92%). To the ice-cooled solution of the Dnp derivative (44 mg, 0.16 mmol) in pyridine (0.4 mL) was added benzoyl chloride (0.06 mL, 0.5 mmol) and was stirred overnight at room temperature. After addition of 1 M H_2SO_4 (6 mL) the mixture was extracted with ethyl acetate. The extract was purified by SiO_2 column chromatography (benzene–hexane) and recrystallized from benzene–hexane to give **5** (43 mg, 71%) as yellow powder, mp 143—145 °C. UV 400 (sh, ε 6600), 349 (17700), 265 (9300), and 230 nm (22000); CD $[\theta]_{408}$ −12300, $[\theta]^{sh}_{370}$ −9600, $[\theta]_{320}$ 0, $[\theta]_{271}$ +13800, and $[\theta]_{238}$ +38100. Found: C, 59.39; H, 4.80; N, 10.73%. Calcd for $C_{19}H_{19}N_3O_6$: C, 59.21; H, 4.97; N, 10.90%.

(1R,2R)-N¹-Benzoyl-N²-(2,4-dinitrophenyl)-1,2-cyclohexanediamine (6). 1,2-Cyclohexanediamine (Tokyo Kasei Chemicals; 22.8 g, 0.2 mol) and adipic acid (29.2 g, 0.2 mol) were treated in 2-propanol as described in literature[26] to give *trans*-1,2-cyclohexanediamine adipate (50.0 g, 96%), which was converted into free diamine (13.0 g, 56%) with NaOH. The racemic diamine (8.0 g, 70 mmol) was resolved *via* (+)-tartrate according to Asperger *et al.*[27] to give (1*R*,2*R*)-1,2-cyclohexanediamine dihydrochloride (1.83 g, 27%): $[\alpha]_D$ −15.8° (*c* 2.53, H_2O) [lit,[27] $[\alpha]_D$ −15.8° (*c* 20, H_2O)]. A mixture of the hydrochloride (0.37 g, 2.0 mmol), FDNB (0.37 g, 2.0 mmol), and $NaHCO_3$ (0.60 g, 7.0 mmol) in ethanol (20 mL) and H_2O (10 mL) was stirred for 2 h at room temperature. After evaporation of ethanol benzoyl chloride (0.47 mL, 4 mmol) and 1 M NaOH (7.0 mL) were added and the mixture was stirred overnight. H_2O was added and the precipitate was collected by filtration and washed with H_2O. The precipitate was dissolved in ethanol and insoluble di-Dnp derivative was filtered off. The filtrate, which contained dibenzoyl derivative and *N*-benzoyl-*N'*-Dnp derivative, was concentrated *in vacuo* to induce crystallization of the latter compound. Recrystallization from ethanol gave **6** (63 mg, 8%) as yellow needles, mp 254—258 °C. UV 410 (sh, ε 7000), 352 (16000), 260 (sh, 10500), and 220 nm (17600); CD $[\theta]_{414}$ −15000, $[\theta]_{364}$ 0, $[\theta]_{338}$ +6400, $[\theta]_{310}$ +2900, $[\theta]_{274}$ +13500, $[\theta]_{253}$ +7000, and $[\theta]_{240}$ +13400. Found: C, 58.54; H, 5.25; N, 14.53%. Calcd for $C_{19}H_{20}N_4O_5 \cdot 1/4H_2O$: C, 58.68; H, 5.31; N, 14.41%.

(2S,3R)-2-(2,4-Dinitroanilino)-3-phenylnorbornane (8). Cyclopentadiene (60 g, 0.9 mol) and *trans*-β-nitrostyrene (60 g, 0.4 mol) in benzene (150 mL) were refluxed for 15 h to afford a mixture of stereoisomers of *trans*-5-nitro-6-phenyl-2-norbornenes (78.7 g, 91%), bp 126 °C/3 Torr (lit,[28] bp 110—115 °C/0.3 Torr; 1 Torr=133.322 Pa). This adduct (21.5 g, 0.1 mol) was treated with Sn (24 g, 0.2 mol) and acetic acid (90 mL) as described by Weinstock *et al.*[29] and the reaction mixture was purified by SiO_2 chromatography (ethyl acetate–acetone) to give *trans*-5-amino-6-phenyl-2-norbornenes (7.0 g, 38%), which was hydrogenated over 5% Pd–carbon in ethanol (120 mL) and 2M HCl (30 mL) at atmospheric pressure affording a mixture of 2-*endo*-amino-3-*exo*-phenyl- and 2-*exo*-amino-3-*endo*-phenylnorbornanes [TLC, SiO_2, benzene, R_f 0.7 (major) and 0.5 (minor), respectively]. The former (3.14 g, 15%) was separated from the latter by SiO_2 column chromatography (acetone–hexane) and resolved with (+)-tataric acid (2.35 g, 16 mmol) in ethanol according to Smith *et al.*[28] to give (2*S*,3*R*)-2-amino-3-phenylnorbornane (+)-tartrate (865 mg, 32%), mp 189—191 °C, $[\alpha]_D$ +42.7° (*c* 1.0, H_2O) [lit,[28] $[\alpha]_D$ +42° (*c* 1.0, H_2O)]. A mixture of the tartrate (169 mg, 0.5 mmol), FDNB (200 mg, 1.07 mmol), $NaHCO_3$ (200 mg, 2.38 mmol), ethanol (10 mL), and H_2O (5 mL) was stirred overnight at room temperature. Usual workup and preparative SiO_2 TLC (benzene) gave **8** (85 mg, 24%), yellow prisms from benzene–hexane, mp 168.5—169.5 °C. UV 410 (sh, ε 6000), 351 (16400), and 262 nm (8700); CD $[\theta]_{416}$ +9200, $[\theta]_{370}$ +7600, $[\theta]_{320}$ 0, $[\theta]_{280}$ −7100, and $[\theta]_{233}$ −44300. Found: C, 64.80; H, 5.47; N, 11.42%. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.58; H, 5.42; N, 11.89%.

2,4-Dinitrophenyl 3,4,6-Tri-O-acetyl-2-deoxy-2-(2,4-dinitroanilino)-β-D-glucoside (11a). This compound was supplied by Dr. H. Kohno, who obtained **11a** during synthetic study of neamine[30] by 2,4-dinitrophenylation of 2-deoxy-2-amino-D-glucose followed by acetylation with acetic anhydride-pyridine. ^1H NMR (DMSO-d_6) δ=1.82 (3H, s, CH_3CO_2), 2.00 (3H, s, CH_3CO_2), 2.04 (3H, s, CH_3CO_2), 4.1—4.3 (3H, m, CH_2–O and CH–N), 5.1—5.6 (3H, m, 3×CH–O), 6.48 (1H, d, *J*=3 Hz, O–CH–O), 7.76 (2H, d, *J*=9 Hz, 2×*o'*–H of Dnp), 8.42 (1H, dd, *J*=9 and 3 Hz, *m'*–H of Dnp), 8.63 (1H, dd, *J*=9 and 3 Hz, *m'*–H of Dnp), 8.87 (1H, d, *J*=3 Hz, *m*–H of Dnp), and 8.90 (1H, d, *J*=3 Hz, *m*–H of Dnp); UV 400 (sh, ε 4400), 335 (18600) and 250 nm (19200); CD $[\theta]^{sh}_{400}$ +5100, $[\theta]_{334}$ +18000, $[\theta]_{315}$ 0, $[\theta]_{309}$ −6000, $[\theta]_{299}$ 0, $[\theta]_{278}$ +16000, $[\theta]_{258}$ 0, and $[\theta]_{248}$ −16000.

The authors are grateful to Professor Tetsuo Suami of Keio University and Dr. Hideki Kohno of Mitsubishi Chemical Industries Ltd. for their kind gifts of

optically active 2-aminocyclohexanol and D-glucosamine derivative, respectively. Thanks are also to Mrs. Motoko Arai for her technical assistances.

References

1) M. Kawai, U. Nagai, and T. Kobayashi, *Tetrahedron Lett.*, **1974**, 1881.
2) M. Kawai, U. Nagai, and M. Katsumi, *Tetrahedron Lett.*, **1975**, 2845.
3) U. Nagai and Y. Kani, *Tetrahedron Lett.*, **1977**, 2333.
4) M. Kawai and U. Nagai, *Tetrahedron Lett.*, **1977**, 3889.
5) M. Kawai, U. Nagai, M. Katsumi, and A. Tanaka, *Tetrahedron*, **34**, 3435 (1978).
6) U. Nagai, M. Kawai, T. Yamada, S. Kuwata, and H. Watanabe, *Tetrahedron Lett.*, **22**, 653 (1981).
7) U. Nagai, N. Taki, and M. Kawai, *Chem. Pharm. Bull.*, **29**, 1750 (1981).
8) K. Sato, M. Kawai, and U. Nagai, *Biopolymers*, **20**, 1921 (1981).
9) M. Kawai, U. Nagai, and A. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 1213 (1982).
10) M. Kawai and U. Nagai, *Bull. Chem. Soc. Jpn.*, **55**, 1327 (1982).
11) T. Wakamiya, T. Ando, T. Teshima, and T. Shiba, *Bull. Chem. Soc. Jpn.*, **57**, 142 (1984).
12) J. Shoji, R. Sakazaki, Y. Wakisaka, K. Koizumi, M. Mayama, and S. Matsuura, *J. Antibiot.*, **28**, 122 (1975).
13) J. A. Schellman, *Acc. Chem. Res.*, **1**, 144 (1968).
14) Z. Yoshida and T. Kobayashi, *J. Chem. Phys.*, **54**, 4538 (1971).
15) DnpNH group is assumed to take planar conformation having a hydrogen bond between NH and *o*-NO_2 groups.
16) The electric transition moments of the longer wavelength π-π^* bands of *p*-nitroanilide, benzoate, and benzamide chromophores were shown to be aligned approximately along the long axis of the benzene ring by SCF-MO[14] calculation. Consequently, considering *s-trans* geometry of amide and ester moiety, the direction of those transition moments are roughly parallel to the chromophore attached bond C-Ar.
17) N. Harada and K. Nakanishi, *Acc. Chem. Res.*, **5**, 257 (1972).
18) H. E. Smith, J. R. Neergaard, E. P. Burrows, and F. Chen, *J. Am. Chem. Soc.*, **96**, 2908 (1974).
19) H. E. Smith, *Chem. Rev.*, **83**, 359 (1983).
20) T. Masamune, M. Ohno, M. Koshi, S. Ohuchi, and T. Iwadare, *J. Org. Chem.*, **29**, 1419 (1964).
21) L. Verbit and H. C. Price, *J. Am. Chem. Soc.*, **94**, 5143 (1972).
22) S. Hünig and H. Kahanek, *Chem. Ber.*, **86**, 518 (1953).
23) H. Nohira, K. Ehara, and A. Miyashita, *Bull. Chem. Soc. Jpn.*, **43**, 2230 (1970).
24) F. Sanger, *Biochem. J.*, **39**, 507 (1945).
25) S. Umezawa, T. Tsuchiya, and K. Tatsuta, *Bull. Chem. Soc. Jpn.*, **39**, 1235 (1966).
26) K. Yamamoto and S. Fujitake (Mitsui Toatsu Chemicals Co., Ltd.), Japan Kokai 70,29,655; *Chem. Abstr.*, **74**, 12700u (1971).
27) R. G. Asperger and C. F. Liv, *Inorg. Chem.*, **4**, 1492 (1965).
28) H. E. Smith and T. C. Willis, *Tetrahedron*, **26**, 107 (1970).
29) J. Weinstock, N. Schwartz, and M. F. Kormendy, *J. Org. Chem.*, **26**, 5427 (1961).
30) H. Kohno, H. Fukami, and M. Nakajima, *Agr. Biol. Chem.*, **39**, 1091 (1975).