J. Org. Chem. 1988, *53*, 826-829

acetate (10:1): 300 mg (59% yield); ^{1}H NMR (CCl$_4$) 0.3 (m, 15 H, Me$_3$Si and Me$_2$Si), 1.1 (m, 9 H, *t*-Bu), 1.67 (t, 2 H, J = 3 Hz, CH$_2$), 4.37 (t, 2 H, J = 3 Hz, CH$_2$O) ppm.

1-(Trimethylsilyl)-4-(*tert*-butyldimethylsiloxy)-2-pentyne (14). Column chromatography on silica gel, eluant hexane/ethyl acetate (10:1), gave **14**: 300 mg (56% yield); ^{1}H NMR (CCl$_4$) 0.3 (m, 15 H, Me$_3$Si and Me$_2$Si), 1.1 (m, 9 H, *t*-Bu), 1.6 (m, 5 H, CH$_3$ and CH$_2$), 4.7 (t, 1 *H*, J = 3 Hz, CHO) ppm.

1-(Trimethylsilyl)-4-(*tert*-butyldimethylsiloxy)-4-phenyl-2-butyne (15). Column chromatography on silica gel, eluant hexane/ethyl acetate (10:1), gave **15**: 300 mg (45% yield); ^{1}H NMR (CCl$_4$) 0.3 (m, 15 H, Me$_3$Si and Me$_2$Si), 1.1 (m, 9 H, *t*-Bu), 1.7 (d, 2 H, J = 3 Hz, CH$_2$), 5.57 (t, 1 H, J = 3 Hz, CHO), 7.3–7.7 (m, 5 H, arom) ppm.

Preparation of 5-Decyn-4-ol (19). To a solution of 1-hexyne (1 g, 12 mmol) in dry THF (6 mL) at −78 °C was added butyllithium (7.5 mL of a 1.6 M solution in hexane, 12 mmol) slowly. After 30 min at this temperature, butyraldehyde (0.87 g, 12 mmol) in THF (3 mL) was added dropwise. The mixture was then stirred for 3 h at room temperature, diluted with diethyl ether (35 mL), and treated with water (5 mL), followed by a saturated ammonium chloride solution; the ethereal layer was separated and dried on anhydrous sodium sulfate. Evaporation and final distillation gave alcohol **19**: bp 85–89 °C (1 mmHg); ^{1}H NMR (CCl$_4$) 1.00 (m, 6 H, 2 CH$_3$), 1.5 (m, 8 H, 4 CH$_2$), 2.2 (m, 2 H, CH$_2$C), 3.2 (s, 1 H, OH), 4.3 (m, 1 H, CH) ppm.

Hydrostannylation of Propargyl Alcohols 2–19. General Procedure. (*Z*)-1-(Trimethylsilyl)-3-(tributylstannyl)-2-penten-4-ol (22a). The reaction was performed in a sealed tube. Tri-*n*-butylstannyl hydride (0.7 mmol), **3** (1.44 g, 9.2 mmol), and AIBN (3 mg, 0.02 mmol) were heated at 60 °C for 1 h. NMR analysis of the crude product mixture showed quantitative reduction of **3**. Vinylstannane **22a** was isolated by column chromatography on silica gel with hexane/ethyl acetate (11:1): 3 g (92% yield). The spectroscopic data are reported in Table IV as well as products obtained from **2**, **4**, and **19**.

Acknowledgment. NATO collaborative Grant No. 86/0535 is gratefully acknowledged.

Registry No. **1**, 13361-64-3; **2**, 90933-84-9; **3**, 108459-75-2; **4**, 111999-85-0; **5**, 108459-81-0; **6**, 111999-86-1; **7**, 111999-87-2; **8**, 108459-79-6; **9**, 108459-76-3; **10**, 111999-88-3; **11**, 18825-29-1; **12**, 111999-89-4; **13**, 111999-90-7; **14**, 111999-91-8; **15**, 111999-92-9; **16**, 111999-93-0; **17**, 764-01-2; **18**, 86486-02-4; **19**, 1817-52-3; **21a**, 111999-94-1; **21b**, 111999-95-2; **22a**, 111999-96-3; **22b**, 111999-97-4; **23a**, 111999-98-5; **23b**, 111999-99-6; **24a**, 112000-00-7; **24b**, 112000-01-8; **25**, 112000-02-9; **26**, 112021-15-5; **27**, 112000-03-0; **28**, 112000-19-8; **29**, 112000-20-1; **30a**, 112000-04-1; **30b**, 112000-05-2; **30c**, 112000-06-3; **30d**, 112000-07-4; **31**, 112000-08-5; **32a**, 112000-09-6; **32b**, 112000-10-9; **33a**, 112000-11-0; **33b**, 112000-12-1; **34a**, 112000-13-2; **34b**, 112000-14-3; **35a**, 79970-55-1; **35b**, 79970-54-0; **36a**, 112000-15-4; **36b**, 112000-16-5; **36c**, 112000-17-6; **36d**, 112000-18-7; **37**, 112000-21-2; Bu$_3$SnH, 688-73-3; H$_2$CO, 50-00-0; CH$_3$CHO, 75-07-0; CH$_3$CH$_2$CH$_2$CHO, 123-72-8; CH$_2$C(O)CH$_3$, 67-64-1; (CH$_2$)$_2$CHCHO, 78-84-2; CH$_3$(CH$_2$)$_5$CHO, 111-71-7; benzaldehyde, 100-52-7; 6,6-dimethyl-3-formylbicyclo[3.1.1]hept-2-ene, 80922-47-0; cyclohexanone, 108-94-1; methyl iodide, 74-88-4; *tert*-butyldimethylsilyl chloride, 18162-48-6; 1-hexyne, 693-02-7.

Correlation of the Circular Dichroic Spectra of 3-Arylphthalides with Absolute Configuration and Conformation

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The circular dichroic and ultraviolet absorption data for a series of configurationally established 3-naphthyl-substituted phthalide enantiomers belonging to three distinct classes are presented. A correlation is made between the observed circular dichroic spectra and absolute configuration, as well as the preferred solution conformations of these phthalide systems.

Introduction

The enantiomers of a series of 3-naphthylphthalides were separated by high-performance liquid chromatography on chiral stationary phases (CSPs) derived from (*S*)-*N*-(3,5-dinitrobenzoyl)leucine on (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine. An a priori chiral recognition model was proposed to relate the absolute configuration of these phthalide enantiomers to their elution orders from the CSPs.[1] In an effort to establish the absolute configurations of these phthalides so as to ascertain the validity of the model, the circular dichroic (CD) spectra of representative enantiomers of the 3-naphthylphthalide series were recorded. Although it had been hoped that configurational assignments could be made through comparison of the CD spectra of the 3-naphthylphthalides with the CD spectra reported by Meyers and coworkers[2] for several asymmetrically synthesized 3-phenylphthalides of known absolution configuration, the clear difference in chromophoric properties between phenyl and α-naphthyl substituents prevented any such correlation of stereochemistry. Ultimately, the absolute configurations of several representative 3-naphthylphthalides were determined by independent chemical and spectroscopic techniques.[3]

Herein we report the CD characteristics obtained for the enantiomers of the various 3-naphthylphthalides investigated. A correlation is made between the CD curves observed for these configurationally established 3-naphthylphthalides and the absolute configuration and *conformation* of the phthalide's naphthyl substituent.

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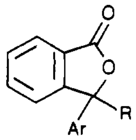
[1] Pirkle, W. H.; Sowin, T. J. *J. Chromatogr.* 1987, 387, 313–321.

[2] Meyers, A. I.; Hanagan, M. A.; Trefonas, L. M.; Baker, R. J. *Tetrahedron* 1983, *39*, 1191–1199.

[3] Pirkle, W. H.; Sowin, T. J. *J. Org. Chem.* 1987, *52*, 3011.

0022-3263/88/1953-0826$01.50/0

Table I. CD and UV Characteristics of 3-Naphthylphthalides



phthalide enant	Ar	R	config	$[\alpha]_D$	CD λ_{ext}, nm ($\Delta\epsilon$)	UV λ_{max}, nm (ϵ)
1a	1-naphthyl	CH_3	*R*	+	227 (+72.7); 275 (+3.7)	223 (49 520); 280 (6886)
2a	6,7-$(CH_3)_2$-1-naphthyl	CH_3	*R*	+	233 (+71.6); 279 (+4.4)	229 (64 087); 280 (6,983)
2b	6,7-$(CH_3)_2$-1-naphthyl	CH_3	*S*	–	233 (–72.1); 279 (–3.8)	229 (64 087); 280 (6,983)
3a	3.7-$(CH_3)_2$-1-naphthyl	CH_3	*R*	+	233 (+78.1); 279 (+5.0)	227 (75 465); 280 (8,140)
4a	4,7-$(CH_3)_2$-1-naphthyl	CH_3	*R*	+	233 (+84.0); 279 (+4.6)	227 (72 463); 280 (7,940)
5a	6,7-$(CH_3)_2$-1-naphthyl	$CH(CH_3)_2$	*R*	+	233 (+78.9); 279 (+5.8)	227 (69 108); 280 (8,280)
5b	6,7-$(CH_3)_2$-1-naphthyl	$CH(CH_3)_2$	*S*	–	233 (–60.1); 279 (–4.5)	227 (69 108); 280 (8280)
6a	4,7-$(CH_3)_2$-1-naphthyl	$(CH_2)_3CH_3$	*R*	+	233 (+93.4); 279 (+9.2)	229 (69 065); 280 (8,738)
6b	4,7-$(CH_3)_2$-1-naphthyl	$(CH_2)_3CH_3$	*S*	–	233 (–88.8); 279 (–6.3)	229 (69 065); 280 (8,738)
7a	4,7-$(CH_3)_2$-1-naphthyl	$(CH_2)_9CHCH_2$	*R*	+	233 (+77.0); 279 (+4.6)	229 (73 435); 280 (9386)
8a	4,7-$(CH_3)_2$-1-naphthyl	$C{\equiv}(CH_2)_5CH_3$	*R*	+	202 (–67.1); 222 (0.0); 233 (+64.1); 279 (+7.0)	204 (55 929); 227 (85 894); 280 (13 443)
9a	3,7-$(CH_3)_2$-1-naphthyl	phenyl	*R*	+	210 (+20.9); 233 (+51.9); 279 (+5.8)	207 (32 144); 226 (44 199); 280 (5967)
10	1-naphthyl	H	*R*	–	208 (–18.2); 220 (+32.7); 225 (0.0); 231 (–49.4); 277 (+5.3); 296 (–0.8)	221 (53 888); 282 (7289)
11a	4,7-$(CH_3)_2$-1-naphthyl	H	*R*	–	211 (–11.4); 226 (+38.0); 233 (0.0); 239 (+37.1); 279 (–5.8); 206 (–0.9)	229 (63 386); 280 (8182)
11b	4,7-$(CH_3)_2$-1-naphthyl	H	*S*	+	211 (+14.6); 226 (–37.9); 233 (0.0); 239 (+37.1); 279 (–5.8); 306 (+1.4)	229 (63 386); 280 (8182)
12a	2-naphthyl	CH_3	*R*	–	231 (+19.5); 242 (–8.3); 279 (–9.6)	226 (102 400); 278 (7545)
13a	6,7-$(CH_3)_2$-2-naphthyl	$CH(CH_3)_2$	*R*	–	233 (+26.2); 246 (–3.3); 284 (–12.4)	232 (68 287); 278 (6845)
13b	6,7-$(CH_3)_2$-2-naphthyl	$CH(CH_3)_2$	*S*	+	233 (–20.5); 246 (+2.3); 284 (+9.1)	232 (68 287); 278 (6845)

Results and Discussion

Table I presents the CD and UV characteristics for the various 3-naphthylphthalides that were investigated. The (*R*)-3-(1-naphthyl)- and (*R*)-3-(dimethyl-1-naphthyl)-3-alkylphthalide enantiomers exhibit almost identical CD behavior, showing Cotton effects at approximately 230 and 280 nm. The *S* enantiomers provide CD curves which are mirror images of those produced by the *R* enantiomers, as exemplified by the enantiomeric pairs **2a,b**, **5a,b**, and **6a,b**. Phthalide enantiomer **1a** shows a strong positive Cotton effect at 227 nm and a relatively weaker positive Cotton effect at 280 nm, corresponding closely with its strong UV absorption at 223 nm and weaker UV absorption at 280 nm. The 3-(dimethyl-1-naphthyl)-3-alkylphthalides exhibit a bathochromic (red) shift in their CD and UV spectra owing to the electron-releasing properties of the methyl-bearing naphthyl groups. Thus, the *R* enantiomers of these 3-(dimethyl-1-naphthyl)-3-alkylphthalide enantiomers show a strong positive Cotton effect at 233 nm and a weaker positive Cotton effect at 280 nm. Similarly, these phthalides strongly absorb UV light at 229 nm and more weakly at 280 nm. Although, **8a** and **9a** exhibit Cotton effects at wavelengths lower than 215 nm owing to the additional alkyl and phenyl chromophores (respectively) located at the phthalide stereogenic center, their longer wavelength Cotton effects are identical with the other (*R*)-3-(dimethyl-1-naphthyl)-3-alkylphthalide enantiomers.

The strong UV absorption and Cotton effects observed at approximately 230 nm for the 3-naphthylphthalides are attributed to a combination of both the phthalide ^1L_a (Platt notation)[4] intramolecular charge-transfer (CT) band and the naphthyl ^1B_b transition. The UV absorptions and CD cotton effects at 280 nm are attributed to a combination of the phthalide ^1L_b and the naphthyl ^1L_a transitions. In principle, one might expect to observe split Cotton effects centered at 230 nm in the CD spectra of these 3-(1-naphthyl)-3-alkylphthalide systems owing to exciton coupling of the phthalide ^1L_a transition (polarized along the benzo–carbonyl bond axis) and the naphthyl ^1B_b transition (polarized along the long axis of the naphthyl ring).[5] However, no split Cotton effects at approximately 230 nm are observed in the CD spectra of the 3-(1-naphthyl)- or 3-(dimethyl-1-naphthyl)-3-alkylphthalide enantiomers. The amplitude of these split-type Cotton effects, in systems whose chromophores are exciton coupled, is *dependent on the dihedral angle between the* electric transition dipole moment vectors of the two coupled chromophores. If the dihedral angle between the two coupled transition dipoles is approximately 70°, a maximum intensity split Cotton effect is observed. On the other hand, if the two coupled transition dipoles are parallel, no split-type Cotton effect is observed.[5] This suggests that for the 3-(1-naphthyl)- and 3-(dimethyl-1-naphthyl)-3-alkylphthalides, the phthalide ^1L_a and the naphthyl ^1B_b transition dipole moment vectors are nearly parallel. Therefore, from the CD curves of the 3-(1-naphthyl)- or 3-(dimethyl-1-naphthyl)-3-alkylphthalide enantiomers, one may conclude that the preferred solution conformation of these systems is as shown in Figure 1. In addition, the preferred solution conformation suggested by CD for these phthalides is also the conformation suggested to be necessary for optimum chiral recognition by the aforemen-

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(4) Platt, J. R. *J. Chem. Phys.* **1949**, *17*, 484.

(5) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy*; University Science Books: Mill Valley, CA, 1983; and references cited therein.

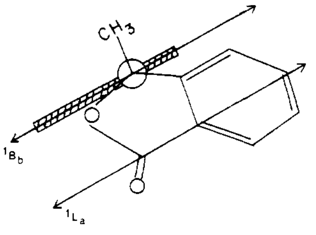

Figure 1. The preferred solution conformation of 3-(1-naphthyl)- and 3-(dimethyl-1-naphthyl)-3-alkylphthalides inferred from CD spectral data. Shown is the parallel alignment of the phthalide ^1L_a and naphthyl ^1B_b transition dipole moment vectors.

tioned CSPs.[1] This perhaps accounts for the high degree of separability observed for these phthalide enantiomers on the CSPs.

In an effort to support the above conclusion and to reproduce the spectral features present in the range 210–260 nm, coupled-oscillator calculations in the DeVoe frame[6,7] were carried out.

In particular, these calculations were performed in order to account for the strong nonsplit Cotton effect observed for the derivatives **1**–**9**. In the DeVoe model, each allowed electronic transition is represented in terms of experimental data such as the polarization directions of absorption bands and by the ultraviolet spectra of suitable model compounds. Therefore, in the present case, the ^1B_b transition has been described by means of a single dipole, located in the center of the naphthalene system, and directed along the long axis of this chromophore. To it has been attributed a dipolar strength of 90 D^2 centered at 220 nm, to provide a satisfactory description of the intensity[8] of the ^1B_b transition. As previously discussed, the phthalide chromophore shows an allowed transition at 230 nm polarized along the benzo–carbonyl bond axis. Thus, a single polarizability centered at 230 nm and directed as indicated has been employed to describe this transition. Furthermore, other transitions in the phthalide chromophore have to be taken into account. In the spectrum of the benzoate chromophore (a good model of the phthalide moiety) an absorption band is observed at 195 nm ($\epsilon \simeq$ 40 000). In order to have better insight into the nature of the latter absorption band, a CNDO/S-CI calculation, using the standard parametrization, was carried out on methyl benzoate. In addition to the known absorption at 230 nm, a couple of quasi-degenerate excitations, lying in the aromatic plane and polarized along and perpendicular to the benzo–carbonyl bond axis, can be found at about 190 nm. Therefore, these dipoles centered at the above wavelength and polarized as suggested by the MO calculations have been also taken into account in the CD computations. Thus, by employing the conformational situation depicted in Figure 1, a CD curve in the range 210–260 nm can be calculated as reported in Figure 2 ($\Delta\epsilon_{\text{calcd}}$ trace). The good agreement between the calculated and the experimental CD spectra is in keeping with the aforementioned interpretation and its chromatographic implications. Interestingly, these calculations also point out the origin of the Cotton effect observed between 210 and 260 nm for compound **1**–**9**. This effect arises from the coupling of transitions occurring at different energies, namely, the ^1B_b band of the naphthalene chromophore and one of the two components of the 190-nm absorption of the phthalide moiety.

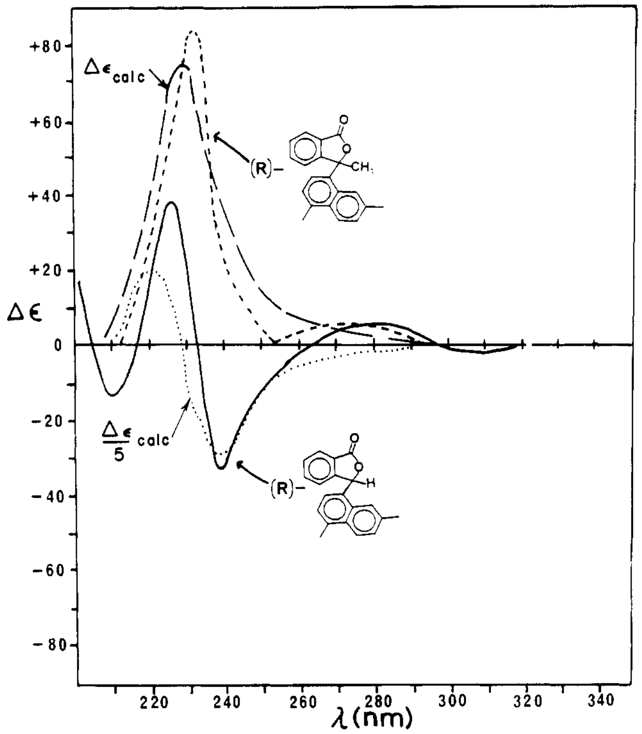

Figure 2. The CD spectra of 4a and 11a. Shown is the positive non-split Cotton effect at 233 nm for **4a** compared to the exciton coupled split-type Cotton effect centered at 223 nm for **11a**. The $\Delta\epsilon_{\text{calcd}}$ and $\Delta\epsilon_{\text{calcd}}/5$ curves are the computed CD spectra corresponding to the conformations reported in the Figures 1 and 3, respectively.

The enantiomers of 3-(1-naphthyl)phthalide (**10a**,**b**) and 3-(4,7-dimethyl-1-naphthyl)phthalide (**11a**,**b**) exhibit split-type Cotton effects centered at approximately 230 nm, owing to exciton coupling of the phthalide ^1L_a and naphthyl ^1B_b transitions. The preferred solution conformation of these phthalides is presumably different than that of the 3-(1-naphthyl)-3-alkylphthalides as a consequence of the much smaller steric requirement of the hydrogen (relative to an alkyl group) born on the stereogenic center of the phthalide. Figure 2 shows the observed CD spectra of (*R*)-3-(4,7-dimethyl-1-naphthyl)-3-methylphthalide (**4a**) and (*R*)-3-(4,7-dimethyl-1-naphthyl)phthalide (**11a**). Comparison of the CD spectra of **4a** and **11a** clearly illustrates the split-type Cotton effect of **11a**, centered at 233 nm, in relation to the non-split Cotton effect exhibited by **4a** at the same wavelength. The split-type Cotton effect of **11a** is centered at the same wavelength as the non-split positive Cotton effect of **4a** owing to the identical nature of the chromophores of the two phthalides in question. Enantiomer **11a** exhibits a split-type Cotton effect of so-called "negative chirality" according to Harada and Nakanishi.[5] This is indicated by the negative Cotton effect at 239 nm coupled to the positive Cotton effect at 226 nm. A negative sense of chirality indicates a left-handed screw spatial relationship between the phthalide ^1L_a and the naphthyl ^1B_b transition dipole moment vectors. Therefore, by knowing both that a left-handed screw spatial relationship must exist between the transition dipole moment vectors of **11a** and the absolute configuration of **11a**, the preferred solution conformation of these types of phthalide systems may be approximated as shown in Figure 3. Furthermore, the preferred solution conformation as approximated by CD is in accord with the proposed chiral recognition mecha-

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[6] DeVoe, H. *J. Chem. Phys.* **1965**, *43*, 3199.

[7] For application of the DeVoe model to the solution of structural problems, see, for instance: Rosini, C.; Giacomelli, G.; Salvadori, P. *J. Org. Chem.* **1984**, *49*, 3394. Rosini, C.; Bertucci, C.; Salvadori, P.; Zandomeneghi, M. *J. Am. Chem. Soc.* **1985**, *107*, 17.

[8] Jaffe, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; Wiley: New York, 1962.

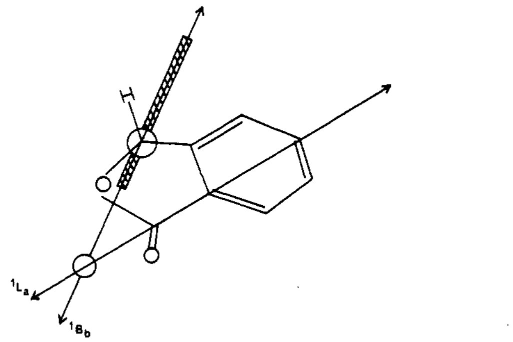

Figure 3. The preferred solution conformation of 3-(1-naphthyl)phthalides inferred from CD spectral data. Shown is the "left-handed" screw spatial relationship between the phthalide ^1L_a and naphthyl ^1B_b transition dipole moment vectors for the (*R*)-phthalide illustrated.

nisms and the observed poor separability of the enantiomers of these phthalides on the CSPs. In comparison to the previously mentioned 3-(1-naphthyl)-3-alkylphthalides, the naphthyl ring of the 3-(1-naphthyl)phthalides is not so favorably disposed conformationally for chiral recognition by the CSPs. Hence, the degree of enantiomeric separation is reduced.

This structural hypothesis has also been verified by means of coupled oscillator calculations. In fact, when DeVoe calculations, employing the same spectroscopic parameters described before to represent the interacting chromophores, are repeated for the conformation reported in Figure 3, a strong negative couplet is obtained (Figure 2, $\Delta\epsilon_{calcd}/5$). These calculations provide a couplet of the same sign as observed experimentally for **11a** (Figure 2). The difference in intensity between experimental and observed CD curves of **11a** in Figure 3 is owing to the presence of other conformers in solution which have different contributions to the CD. Therefore, the conformaton depicted in Figure 3 is the predominant but not the only conformer present.

The *R* enantiomers of the 3-(2-naphthyl)-3-alkylphthalides, **12a** and **13a**, exhibit a positive non-split Cotton effect at approximately 230 nm, similar to, but of somewhat lesser intensity, than the 230-nm positive Cotton effects exhibited by the *R* enantiomers of the 3-(1-naphthyl)-3-alkylphthalides. However, **12a** and **13a** show negative Cotton effects at 280 nm and negative signs of rotation at 589 nm while the *R* enantiomers of the 3-(1-naphthyl)-3-alkylphthalides show positive Cotton effects at 280 nm and positive signs of rotation at 589 nm. In addition, **12a** and **13a** exhibit small negative Cotton effects at 242 nm which are not observed in the CD spectra of the 3-(1-naphthyl)-3-alkylphthalide enantiomers. The difference in the observed CD spectra of the 3-(1-naphthyl)-3-alkylphthalides and the 3-(2-naphthyl)-3-alkylphthalides is attributed to the different spatial relationships between the transition dipoles of the chromophores responsible for the Cotton effects observed in the two phthalide systems in question. Owing to conformational dissimilarities, opposite sense Cotton effects have been observed in the CD spectra of structurally similar systems having the same absolute configuration.[9,10] This difference in the spatial relationship of the transition dipole moments of the 1-naphthyl- and 2-naphthyl-substituted phthalide systems arises from the difference in the positions at which the naphthyl rings are substituted and the resulting difference in the conformational preference and rigidity of the two naphthyl systems.

Conclusion

Circular dichroism can be used as a reliable means of determining the relative configurations of phthalides belonging to the same class (i.e., 3-(1-naphthyl)-3-alkyl vs 3-(1-naphthyl) vs 3-(2-naphthyl)-3-alkyl in which the spatial relationship of the chromophores responsible for the CD Cotton effects are nearly the same. However, caution must be exercised in relating by CD the absolute configurations of phthalide enantiomers belonging to different classes. Conformational differences between classes of phthalides can cause significant differences in the CD spectra of phthalides enantiomers of the same configuration, thus leading to a misassignment of absolute configuration. Alternatively the preferred solution conformations of the 3-(1-naphthyl)-3-alkyl- and 3-(1-naphthyl)phthalides may be deduced from their CD spectra and a knowledge of their absolute configurations.

Experimental Section

All of the 3-(naphthyl)phthalides presented herein have been previously described.[3] Enantiomerically enriched phthalide samples for CD analysis were obtained directly by semipreparative (5–15 mg) HPLC using an Altex 100A pump, an Altex 210 injector equipped with a 225-μL sample loop, an Altex Model 152 dual-wavelength (254 and 280 nm) detector, and columns containing covalently bonded (*S*)-*N*-(3,5-dinitrobenzoyl)leucine or covalently bonded (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine (250 mm × 10 mm i.d.) chiral stationary phases. Phthalide enantiomers for CD analysis were of greater than 98% ee except for **10a** (45.6% ee) and **13b** (48.4% ee). The CD values of these compounds have been corrected to 100% ee. The enantiomeric purities of the phthalide enantiomers were determined by analytical HPLC using a Beckman 100A pump, an Altex 210 injector, a Beckman 165 variable wavelength detector, an Altex C-RIA integrating recorder, and a column containing covalently bonded (*S*)-*N*-(3,5-dinitrobenzoyl)leucine (250 mm × 4.6 mm i.d.) chiral stationary phase. A Rudolph Autopol III digital polarimeter containing a 20-cm flow cell was used in series with the ultraviolet detector to simultaneously monitor the sign of $[\alpha]_D$ as the enantiomers eluted. Circular dichroic (CD) spectra were obtained on a Jasco J-40 recording spectropolarimeter using a 1-mm path-length cell and spectrophotometric grade methanol as solvent. Sample concentrations for CD analysis were typically $(1-4) \times 10^{-4}$ M. Ultraviolet–visible absorption spectra were obtained on a Perkin-Elmer Model 552 spectrophotometer using a 1-cm path-length cell and spectrophotometric grade methanol as solvent. Sample concentrations of UV–vis analysis were typically $(1-4) \times 10^{-5}$ M.

Acknowledgment. This work was supported by grants from the National Science Foundation and from Eli Lilly and Company.

Registry No. **1a**, 107796-87-2; **2a**, 107733-10-8; **2b**, 107733-11-9; **3a**, 97866-66-5; **4a**, 107733-19-7; **5a**, 107733-12-0; **5b**, 107733-13-1; **6a**, 112347-98-5; **6b**, 112347-99-6; **7a**, 107732-78-5; **8a**, 107732-77-4; **9a**, 107733-15-3; **10a**, 107796-86-1; **11a**, 107733-18-6; **11b**, 107733-17-5; **12a**, 107732-84-3; **13a**, 107732-86-5; **13b**, 107732-85-4.

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(10) Brossi, A.; Blount, J. F.; O'Brien, J.; Teitel, S. *J. Am. Chem. Soc.* **1971**, *93*, 6248.