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Torsional Isomerism and Configurational Assignments in Amides Containing Three Asymmetric Centers. A Method for Distinguishing Meso and DL Secondary Amines[1a,b]

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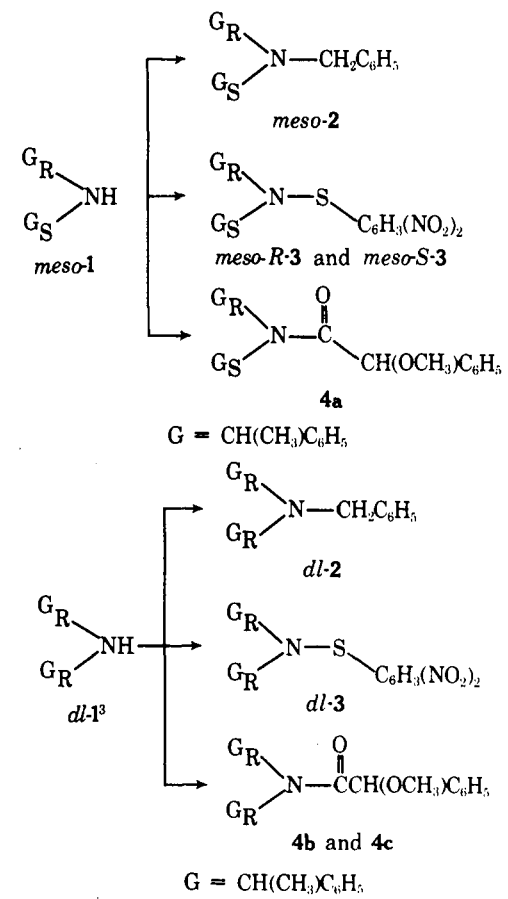
The amides of 1-methoxyphenylacetic acid (*O*-methylmandelic acid) and *dl*- and *meso*-bis(1-phenylethyl)amine were prepared and their NMR spectra obtained under conditions of both slow and rapid torsion about amide bonds. The diastereomeric amides prepared from the meso amine could be interconverted by torsion about the configurationally labile amide bond. The diastereomeric amides prepared from the racemic amine could be separated since they differed in configuration at asymmetric carbon atoms, while the amide bond was not a configurational unit. The free energies of activation for torsion about the amide bond were determined using NMR spectroscopy. The values obtained for the amides prepared from the meso amine (15.6–15.9 kcal/mol) were nearly the same as those obtained for the two amides prepared from the *dl* amine (15.6 and 16.0 kcal/mol), although the stereochemical processes were different, isomerization in the former and topomerization in the latter two compounds. The configurations of the four amides were assigned and it was shown how the stereochemical behavior of the amides could be used to distinguish between meso and *dl* secondary amines.

Torsion about carbonyl to nitrogen bonds is slow enough on the NMR time scale to render this moiety a labile stereochemical unit. Since barriers to rotation generally fall within the range of 5–25 kcal/mol, the stereochemistry of amides is most conveniently studied by observing the coalescence of NMR resonances from diastereotopic groups, although in some cases the barrier is high enough to permit the isolation of a single isomer and the measurement of the rate of isomerization using conventional kinetics.[2] The diastereotopic groups whose NMR resonances coalesce can reside either in the same molecule (for example, in *N,N*-dimethylacetamide) or in different, isomeric molecules (for example, in *N*-methyl-*N*-ethylacetamide). In the former case, we speak of groups which are diastereotopic by internal comparison and the stereochemical process which results in coalescence is a topomerization, while in the latter case, the two groups are diastereotopic by external comparison and the stereochemical process is an isomerization which reversibly interconverts two diastereomeric molecules.

This paper deals with amides which exhibit chemical shift nonequivalence and undergo coalescence which is a reflection of either isomerization or topomerization *depending upon the stereochemistry of the substituents attached to the amide moiety.*

In addition, the ability to distinguish between topomerization and isomerization using NMR spectroscopy can be used to distinguish between diastereomeric meso and *dl* secondary amines 1.[3] NMR methods based upon the magnetic nonequivalence of diastereotopic groups[4] and upon the introduction of pseudo-asymmetry[5] have been developed. The symmetry arguments used in the present approach offer some advantages over those of previous methods.

The method of Hill and Chan[4] involves conversion of the secondary amines 1 into tertiary amines 2, which bear a prochiral atom, such as that in a benzyl group, attached to nitrogen. The two benzyl methylene protons in *dl*-2 are diastereotopic and appear as an AB quartet while those in *meso*-2 are enantiotopic. The observation of chemical shift nonequivalence allows an unambiguous assignment of the *dl* configuration to the parent amine. However, the obser-



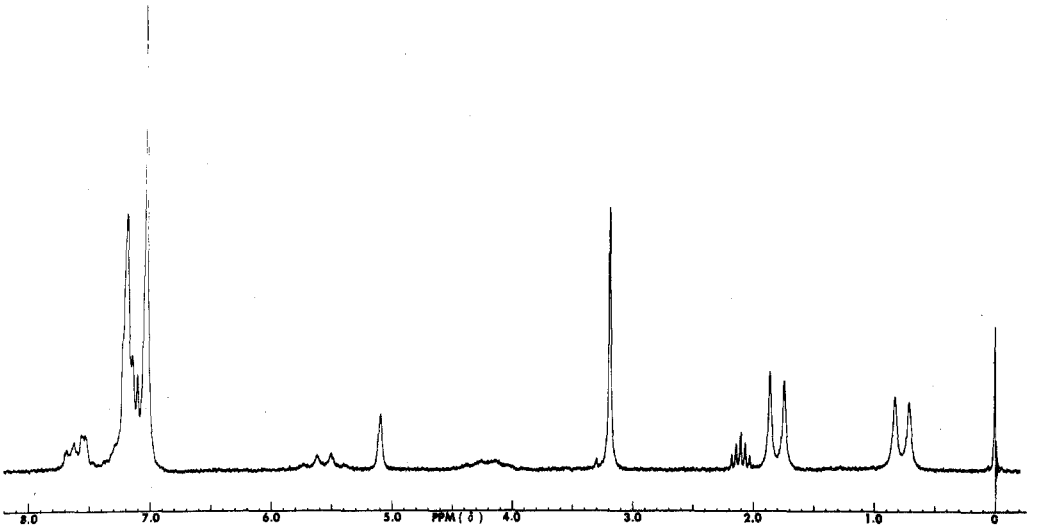


Figure 1. NMR spectrum of (*RS,RS*)-*N,N*-bis(1-phenylethyl)-(*SR*)-1-methoxyphenylacetamide (**4b**) at −18° in toluene-d_8.

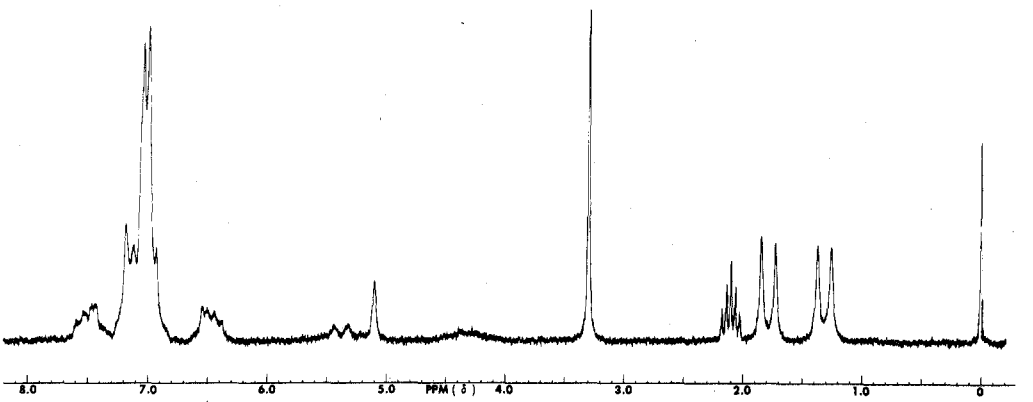


Figure 2. NMR spectrum of (*RS,RS*)-*N,N*-bis(1-phenylethyl)-(*RS*)-1-methoxyphenylacetamide (**4c**) at −18° in toluene-d_8.

vation of a singlet does not ensure that the amine has the meso configuration unless the possibility of accidental equivalence can be excluded.[6]

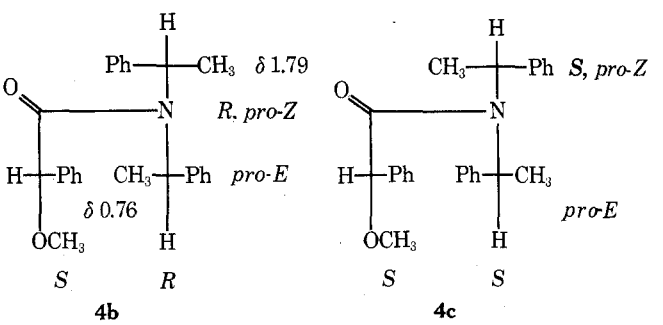
The method involving pseudo-asymmetry[5] is complementary in that it can provide an unambiguous assignment for the meso isomer. Reaction of the achiral amine *meso*-**1** with 2,4-dinitrobenzenesulfenyl chloride produced two diastereomeric product sulfenamides, *meso-R*-**3** and *meso-S*-**3**, which differed in configuration at the pseudo-asymmetric axis of the S–N bond. Since stereomutation via torsion about the S–N bond was slow on the NMR time scale, the equilibrium mixture of torsional diastereomers gave rise to two unequally intense *C*-methyl doublets, one for each of the two diastereomers. Although the sulfenamide produced from *dl*-**1** consists of a single diastereomer, it also gave rise to two doublets, but of equal intensity, since the two methyl groups within a molecule are diastereotopic.

Results and Discussion

The introduction of a third chiral center provides an additional means of distinguishing amines **1**. A convenient means of adding an additional unit of chirality is reaction with a chiral acid chloride, here 1-methoxyphenylacetyl chloride, to produce amides **4**. The introduction of the amide linkage introduces a further element of stereochemical complexity which is of utility in making the configurational assignment.

If we disregard, for the moment, the complexity introduced by slow rotation about the amide bond, reaction of *dl*-**1** with racemic 1-methoxyphenylacetyl chloride yields two diastereomeric amides,[7] (*RS,RS,SR*)-**4** (**4b**) and (*RS,RS,RS*)-**4** (**4c**), which give rise to observably different NMR spectra. Since the reaction occurs with asymmetric induction, one of the diastereomeric amides, **4b**, is produced in excess over the other. The assignment of the *RS,RS,SR* configuration to the major isomer **4b** was made by carrying out the reaction with optically active amine and acid chloride. Reaction of (*S,S*)-**1** with (*R*)-1-methoxyphenylacetyl chloride gave rise to a single diastereomer (*S,S,R*)-**4** whose NMR spectrum was identical with that of **4b**.

The low-temperature NMR spectra of both **4b** and **4c** (Figures 1 and 2) exhibit pairs of doublets for the phenethyl groups indicating that torsion about amide bonds is slow on the NMR time scale. The doublets in **4b** are centered at δ 1.79 and 0.76 while those in **4c** appear at δ 1.78 and 1.31. The differences in chemical shifts between **4b** and **4c** can arise only from diastereomeric interactions between the phenethyl groups and the asymmetric 1-methoxybenzyl moiety. It seems most reasonable to assume that the methyl group in **4b** which exhibits the greatest chemical shift relative to the corresponding methyl group in **4c** derives



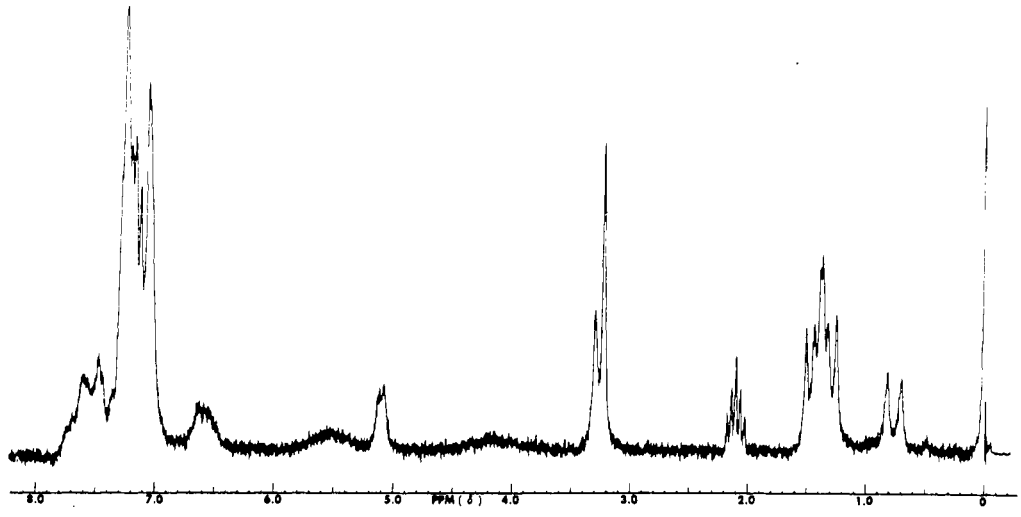
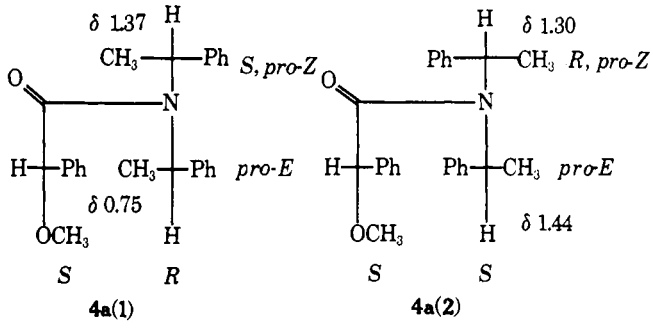


Figure 3. NMR spectrum of amides **4a** prepared from *meso*-bis(1-phenylethyl)amine and *dl*-1-methoxyphenylacetic acid at −18° in toluene-d_8.

from the *pro-E* phenethyl methyl group. Thus, we may tentatively assign the doublets in **4b** at δ 0.76 and 1.79 to the *pro-E* and *pro-Z* methyl groups, respectively.[9]

One possibility for this dramatic upfield shift is that the methyl group in **4b** lies within the shielding cone of the phenyl ring in the acyl group. Since interchanging the position of the methyl groups and phenyl groups in the phenethyl moieties converts **4b** into its diastereomer **4c**, we may ask whether one of the phenethyl phenyl groups suffers a similar upfield shift in **4c**. Inspection of the spectrum of **4c** reveals that two aromatic protons suffer a similar upfield shift and appear as an unstructured multiplet at δ 6.5. This upfield shift is in accord with a model which involves upfield shifts for protons in the phenethyl moiety which lie in the shielding cone of the 1-methoxybenzyl phenyl ring. This observation of upfield shifts for the methyl protons in **4b** and aromatic protons in **4c** provides the basis for the assignment of configurations in the meso amides **4a.**

Reaction of *meso*-1 with 1-methoxyphenylacetyl chloride yields amide **4a**, which represents a single diastereomer on the isolation time scale. However, the amide bond is a labile configurational unit and, on the NMR time scale, two torsional diastereomers are present, **4a(1)** and **4a(2)**. The



presence of two diastereomers in equilibrium is evident from the NMR spectrum (Figure 3) which features two singlets for the *O*-methyl groups and four doublets for *C*-methyl groups (K_{eq} = 1.4 at −18°).

A tentative assignment of the configuration **4a(2)** to the major isomer can be made on the basis of the analysis of chemical shifts of phenethyl methyl and aromatic protons made for the *dl* amides **4b** and **4c.** The low-temperature spectrum of **4a** features four doublets arising from phenethyl methyl groups since all four phenethyl moieties are diastereotopic and anisochronous. One methyl doublet, which integration revealed as deriving from the minor isomer, suffers a considerable upfield shift and appears at nearly the same chemical shift as the *pro-E* methyl group in **4b.** By analogy we assign this doublet to the *pro-E* methyl group in **4a(1)**, since this isomer also has phenethyl and 1-methoxybenzyl groups with opposite configurational designations in a geometry where interaction can occur. A complementary upfield shift of aromatic protons was observed. Integration indicates that the broad unstructured multiplet at ca. δ 6.6 derives from a pair of aromatic protons in the major isomer. Since the cis phenethyl and methoxybenzyl moieties in **4a(2)** have the same configurational relationship as those in **4c,** which also exhibits a pair of shielded aromatic protons, this provides further support for our assignment of the configuration of **4a(2)** to the major isomer.[10]

Table I
Dynamic Nuclear Magnetic Resonance Data

Compd[a]	$\Delta\nu$, Hz[b]	T_c, °C[c]	$\Delta G^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kJ/mol
4a[f]	3.4	12	15.7,[d] 15.9[e]	65.5,[d] 66.3[e]
4a[g]	31	36	15.6,[d] 15.8[e]	65.3,[d] 66.1[e]
4a[h]	4.1	14	15.7,[d] 15.8[e]	65.4,[d] 66.2[e]
4b	23	32	15.6	65.2
4c	52	51	16.0	66.8

[a] All data refer to solutions (ca. 15% w/v) in toluene-d_8. [b] Chemical shift differences at the coalescence points were obtained by extrapolation of shifts measured at temperatures below the coalescence point. [c] The temperature is considered accurate to ±2°. This results in uncertainties in the free energies of activation of ±0.1 kcal/mol (±0.5 kJ/mol). [d] Free energy of activation for conversion of minor isomer to major isomer. [e] Free energy of activation for conversion of major isomer to minor isomer. [f] Signals from methoxy methyl groups. [g] Signals from *C*-methyl groups which exhibit the larger chemical shift difference [*pro-E* in 4a(1) and *pro-Z* in 4a(2)]. [h] Signals from *C*-methyl groups which exhibit the smaller chemical shift difference [*pro-Z* in 4a(1) and *pro-E* in 4a(2)].

Torsion about amide bonds in **4a, 4b,** and **4c** becomes rapid on the NMR time scale at elevated temperatures and the spectra of all three compounds exhibited coalescence of *C*-methyl doublets (and *O*-methyl singlets for **4a**) when the temperature was increased. The coalescence temperatures, chemical shift differences, and free energies of activation derived from calibration curves based upon complete line shape analysis[11] are given in Table I. While the free energies of activation are comparable for all three amides, the stereochemical description of the process which results in coalescence in **4b** or **4c** is quite different from the process

Table II
Characterization of Amides

Compd	Mp, °C	Anal., % C	H	N
Calcd for $C_{25}H_{27}NO_2$		80.4	7.3	3.8
rac-4a	83–84°	80.33	7.05	3.64
rac-4b	105–116°	80.15	7.18	3.58
(*S,S,R*)-4b	117.5–118°			
rac-4c	95–96°	80.31	7.25	3.62

which results in coalescence in **4a**. When rotation about the amide bond is rapid the diastereotopic *pro-E* and *pro-Z* phenethyl groups in **4b** become homotopic (equivalent) on the NMR time scale (as do those in **4c**) and a single doublet is observed as an averaged chemical shift. The exchange in these compounds is between groups residing in the same molecule, groups which are diastereotopic by internal comparison.[12] By contrast, torsion about the amide bond in **4a**(1) does not interchange the *pro-E* and *pro-Z* groups. These remain diastereotopic and anisochronous even when rotation about amide bonds is rapid on the NMR time scale. Rather, rapid rotation about amide bonds exchanges the *pro-E* group in **4a**(1) with the *pro-Z* group in **4a**(2). As a result, the high-temperature limit spectrum of **4a** features two equally intense methyl doublets. This amide is unusual in that the two constitutionally equivalent moieties at nitrogen cannot be rendered isochronous by torsion about the amide bond. Since the reversible isomerization involves the interchange of groups which are diastereotopic by external comparison,[12] we might describe this stereochemical process as an *intermolecular topomerization*. By the same token, the exchange which results from the degenerate isomerization of **4b** (or **4c**) might be termed an *intramolecular topomerization* in order to distinguish it from the present situation.

Although the stereochemical process which results in coalescence in **4a** is different from that which takes place in **4b** and **4c**, the structural change is similar and the barriers are not very different. The barriers obtained for **4** are within the range which might be expected considering the barriers reported for similar amides.[2]

Experimental Section

Spectra were recorded on a Varian A-60A spectrometer equipped with a V-6040 variable-temperature accessory. Temperatures were determined using methanol and ethylene glycol spectra as described in the Varian manual. Melting points were measured on a Thomas-Hoover oil bath apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-dm cell.

1-Methoxyphenylacetyl Chloride (*O*-Methylmandelyl Chloride). 1-Methoxyphenylacetic acid and thionyl chloride (1.5 equiv) were heated under reflux in benzene for 1 hr. The solvent and excess thionyl chloride were removed under reduced pressure. The NMR spectrum of the residual oil exhibited only the resonances ascribed to the acid chloride (in $CDCl_3$, δ units): OCH_3, s, 3.49; CH, s, 5.00; C_6H_5, m, 7.45.

(*RS,SR,RS*)-*N,N*-Bis(1-phenylethyl)-1-methoxyphenylacetamide (4a). A solution of 0.40 g (2.2 mmol) of freshly prepared *dl*-1-methoxyphenylacetyl chloride in 20 ml of benzene was added dropwise over a period of 1 hr, at room temperature, to a stirred solution of 0.96 g (4.3 mmol) of *meso*-bis(1-phenylethyl)amine[5] in 30 ml of benzene. The reaction mixture was allowed to stand at room temperature for 20 hr and the solvent was evaporated in vacuo. The residue, composed of solid and oil, was triturated with hexane and the insoluble amine hydrochloride was removed by filtration. The mother liquor was washed successively with dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water, and then dried over magnesium sulfate. Evaporation of the solvent followed by recrystallization from hexane–pentane (1:1) afforded white crystals, mp 83–84°.

(*RS,RS,SR*)- and (*RS,RS,RS*)-*N,N*-Bis(1-phenylethyl)-1-methoxyphenylacetamide (4b and 4c). Racemic bis(1-phenylethyl)amine was treated with racemic 1-methoxyphenylacetyl chloride in the same manner as described above for the meso amine. Upon evaporation of the hexane mother liquor, the product was revealed to be a ca. 5:1 mixture of two diastereomeric amides, **4b** and **4c**. Treatment of the mixture with benzene–hexane resulted in crystallization of **4b** which was recrystallized from hexane, mp 105–106°. The benzene–hexane mother liquor was evaporated, dissolved in hexane–pentane, and left to stand for 1 week. Two kinds of crystals formed, colorless, transparent cubes and white granules. The former were separated mechanically and recrystallized from hexane–pentane (2:1) affording pure **4c**, mp 95–96°.

(*S,S,R*)-*N,N*-Bis(1-phenylethyl)-1-methoxyphenylacetamide (4b). Optically active (−)-*S,S*-bis(1-phenylethyl)amine was prepared by catalytic hydrogenation of (−)-*S*-1-phenylethylidene-1-phenylethylamine as previously reported[13] at 0° in ethyl acetate solvent, resulting in 87% asymmetric induction. The final separation of *S,S* amine from meso amine was accomplished by recrystallization of the benzoate salt of the *S,S* amine from 2-propanol,[14] mp 112–113°. The free amine was obtained by treatment with sodium bicarbonate, extraction with ether, and removal of solvent in vacuo: $[\alpha]^{25}D$ −187.9° (*c* 6.87, benzene) [lit.[13b] $[\alpha]^{25}D$ −197.3° (*c* 3.65, benzene)]. The optically active amine was treated with the acid chloride of (−)-(*R*)-1-methoxyphenylacetic acid[15] as described above. Recrystallization from hexane afforded white crystals in 52% yield, mp 117.5–118°, $[\alpha]^{26.4}D$ −73.4° (*c* 6.10, benzene). The NMR spectrum was identical with that of racemic **4b**.

Registry No.—*meso*-**1**, 21003-57-6; *rac*-**1**, 21003-56-5; (−)-(*S,S*)-**1**, 56210-72-1; **4a**, 56210-73-2; *rac*-**4b**, 56271-09-1; (−)-**4b**, 56271-10-4; *rac*-**4c**, 56271-11-5; *dl*-1-methoxyphenylacetylchloride, 56271-12-6; *dl*-1-methoxyphenylacetic acid, 7021-09-2; (−)-(*R*)-1-methoxyphenylacetic acid, 3966-32-3.

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(6) The symmetry argument based upon resolvability has the same property, in that resolution provides unambiguous assignment of the *dl* isomer, while an inability to achieve optical activation can arise from extraneous experimental factors.

(7) Except for the preparation of optically active **4b** described below, all experiments were performed using racemic materials. The first two configurational designations refer to the configurations of the phenylethyl substituents at nitrogen; the third refers to the configuration at the asymmetric carbon atom in the *O*-methylmandelyl moiety. The symbol (*RS,RS,SR*)-**4** denotes the racemic mixture of (*R,R,S*)-**4** and (*S,S,R*)-**4**.[8] Both enantiomers, of course, give rise to identical NMR spectra under the conditions employed.

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(9) The assignment of the two methyl doublets in **4c** is less certain. An assignment could be made by assuming that the *pro-Z* methyl group lies downfield relative to *pro-E* methyl group in **4c**, also possibly as a result of deshielding by the anisotropic carbonyl group. However, in *N,N*-dimethylamides, the *N*-methyl group cis to oxygen (*pro-Z*) appears at higher field than that of the *pro-E* methyl.[2] Furthermore, analysis of the spectra of the meso amides **4a**, vide infra, demonstrates unequivocally that in one isomer the *pro-Z* methyl group lies upfield with respect to the *pro-E* methyl group (this isomer seems to be related to **4c**). However, in the other isomer (which has some similarities with **4b**) the *pro-Z* methyl group lies downfield. Using this analogy to the meso isomers a reversed assignment could be made. Independent of which assignment is correct, we can be sure that one of the methyl groups in **4b** suffers a dramatic upfield shift relative to its counterpart in **4c**.

(10) The assignment of the remaining *C*-methyl doublets follows naturally from the assignment of the doublet at δ 0.75 to the *pro-E* methyl in **4a**(1). Integration indicated that the doublet at δ 1.37 also derived from the minor isomer; thus it can be assigned to the *pro-Z* methyl group in **4a**(1). The assignment of the two methyl groups in **4a**(2) follows from the coalescence at higher temperatures, vide infra. Analysis of spectra below and above the coalescence point indicated that the signal at δ 0.75 in **4a**(1) coalesces with that at δ 1.30 in **4a**(2) and the signal at δ 1.37 coalesces with that at δ 1.44. Since rapid rotation about the amide

bond exchanges the *pro-E* methyl in **4a(1)** with the *pro-Z* methyl in **4a(2)**, the later must give rise to the doublet at δ 1.30.
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Synthesis of Mono- and Bis(trimethylsilyl)anthracenes

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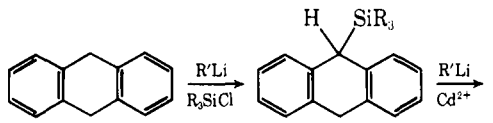
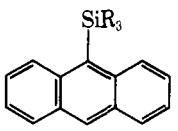
Synthesis of the previously unknown 1-, 2-, and 9-trimethylsilylanthracenes and of the 9,10- and 1,3-bis(trimethylsilyl)anthracenes has been accomplished. Aromatization of 9-trimethylsilyl-9,10-dihydroanthracene via the dianonic intermediate generated with the *n*-butyllithium–TMEDA reagent and cadmium chloride afforded 9-trimethylsilylanthracene in overall yield exceeding 90%. Reaction of trimethylsilyl chloride with the anthracene–lithium–TMEDA complex gave *cis*- and *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene and *trans*-1,2-bis(trimethylsilyl)-1,2 dihydroanthracene. Aromatization of the trans-9,10 isomer afforded 9,10-bis(trimethylsilyl)anthracene, while similar reaction of the trans-1,2 isomer led to 1- and 2-trimethylsilylanthracene and 1,3-bis(trimethylsilyl)anthracene. Details of the mechanisms of these reactions and the 270-MHz NMR spectra are discussed.

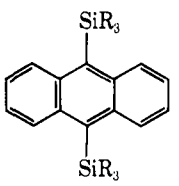
Synthesis of the isomeric trialkylsilylanthracenes has not previously been achieved. Reaction of 9-bromoanthracene with Mg and Me_3SiCl reportedly afforded only the parent hydrocarbon.[1] In our experience, cross metalation of 9-bromoanthracene with *n*-butyllithium, followed by Me_3SiCl, failed to furnish 9-trimethylsilylanthracene (**2**), although analogous reaction of 9-bromophenanthrene gave 9-trimethylsilylphananthrene in good yield (95%).[2]

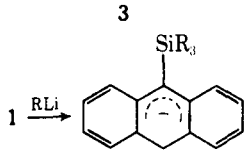
Synthesis of **2** has now been accomplished through reaction of Me_3SiCl with 9-lithio-9,10-dihydroanthracene[3] at −78° followed by aromatization with *n*-butyllithium–TMEDA and cadmium(II) chloride.[4] The overall yield exceeded 90%. The intermediacy of the dianion of 9-trimethylsilylanthracene was evidenced by the success of the second step and by the characteristic purple color of the solution before the addition of the cadmium salt. The ability of the trimethylsilyl group to stabilize the adjacent negative charge contrasts with the contrary effect of the *tert*-butyl group in this regard; similar reaction of 9-*tert*-butyl-9,10-dihydroanthracene was found earlier to afford a dimeric product arising from the 10-monoanion.[4] Attempted aromatization of 9-trimethylsilyl-9,10-dihydroanthracene (**1**) with trityl trifluoracetate in trifluoroacetic acid,[5] a reagent found to be effective in dehydrogenation of many hydroaromatic compounds, furnished anthracene as the sole product. Undoubtedly, this is a consequence of the facility of acidic cleavage (protodesilylation) of aryl silanes.[2]





Attempted synthesis of 9,10-bis(trimethylsilyl)anthracene (**3**) through repetition of the sequence of trimethylsilylation and aromatization on **1** was not successful owing to preferential formation of the monoanion at the 9 position. Reaction of **1** with *n*-butyllithium (10% excess) in tetrahydrofuran at 0° afforded a deep red solution of the monoanion which failed to undergo trimethylsilylation with Me_3SiCl. Similar reaction employing a large excess (200%) of the lithium reagent also failed, as might have been anticipated from the known resistance to formation of the anthracene dianion via deprotonation in ethereal solvents.[4]





However, reaction of Me_3SiCl with the anthracene dianion in the form of its lithium *N,N,N',N'*-tetramethylethylenediamine complex generated by the method described[4] gave a mixture of *cis*- and *trans*-9,10-bis(trimethylsilyl)-9,10-dihydroanthracene (*cis*- and *trans*-**4**) and 1,2-bis(trimethylsilyl)-1,2-dihydroanthracene (**5**) in a molar ratio of 10:5:4 by NMR analysis. Similar reaction with the addition of Me_3SiCl carried out at 0° afforded a cleaner product with *cis*- and *trans*-**4** and **5** in the molar ratio 10:1:5. Chromatography on basic alumina and recrystallization furnished the pure compounds as crystalline solids melting at