7.25 [m, 5, aryl(Phe)], 7.95 [m, 2, NH(Gly$_3$ and Leu)], 8.2 [d, 1, NH(Phe)], 8.45 [br, 1, NH(Gly$_2$)]. The NMR spectrum was superimposable on that published by Garbay-Jaureguiberry and co-workers.[32]

Acknowledgment. We thank the National Institutes of Health (Grant GM-09706) for support of this work and the National Science Foundation for support toward the purchase of the high-field NMR spectrometers used in this study. Dr. G.-S. Ti is thanked for the synthesis of indene-3-methanol and its *p*-chlorocarbanilate. Cathy Weiss is thanked for improving the synthesis of CLIMOC-OSu, and S. Yahya Sadat-Aalaee, Mathias Senge, Martin Rose, and Tony Truran are thanked for checking the preparation of some of the CLIMOC intermediates.

Registry No. **7**, 95-13-6; **9**, 18427-72-0; **10**, 88099-20-1; **11**, 88099-21-2; **12**, 123150-47-0; **14**, 268-40-6; **15**, 123150-49-2; **16**, 123150-50-5; **17**, 123150-51-6; **18**, 123150-52-7; **24**, 123150-57-2; **25**, 123150-58-3; **26**, 88099-27-8; **27**, 88099-29-0; HONSu·DCHA, 82911-72-6; H-Phe-OH, 63-91-2; CLIMOC-Phe-OH, 88099-22-3; CLIMOC-Phe-Phe-OH, 123150-48-1; H-Gly-OH, 56-40-6; CLIMOC-Gly-OH, 88099-23-4; CLIMOC-Gly-Cl, 88099-24-5; 4-MeOC$_6$H$_4$SO$_2$Cl, 98-68-0; 3-(O$_2$N)-4-(MeO)C$_6$H$_3$SO$_2$Cl, 22117-79-9; BnNHCONHBu, 14117-22-7; BnN=C=NBu, 111681-30-2; H-Leu-OBn·TsOH, 1738-77-8; CLIMOC-Phe-Leu-OBn, 88099-25-6; BIMOC-Phe-OH, 123150-53-8; BIMOC-Gly-OH, 123150-54-9; H-Gly-Gly-OH, 556-50-3; BIMOC-Gly-Gly-OH, 123150-55-0; FMOC-Tyr(Bn)-OH, 71989-40-7; BIMOC-Phe-Leu-OBn, 123150-56-1; (MeO)$_2$Si(CH$_2$)$_3$Cl, 2530-87-2; H-Leu-OBn, 1738-69-8; BzCl, 98-88-4; BnNH$_2$, 100-46-9; BzNHBn, 1485-70-7; 4-(aminomethyl)piperidine, 7144-05-0; Leu-enkephalin, 58822-25-6; polystyrene, 9003-53-6.

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Crystallographic Studies on Retinoidal-Active and -Inactive Aromatic Anilides

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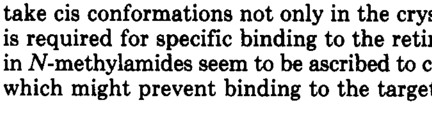
Among various chemical classes of compounds with retinoidal activity, the retinobenzoic acid system having a 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl moiety and a benzoic acid moiety at opposite ends of the molecule has proved to be one of the most promising leads. Many retinoidal-active compounds with various kinds of chemical moieties as the linking group between the above two groups were synthesized, and amide moieties proved to be excellent linkages for potent retinoidal activities. The activities, however, were diminished by methylation at the amide nitrogen. To elucidate the reasons for the loss of the activities, we performed X-ray crystal structure analyses of three free amides and the corresponding three *N*-methylamide compounds. It was proved that all the free amide molecules take an extended trans conformation, whereas all the *N*-methylamide molecules take a folded cis conformation in the crystalline state. In combination with spectroscopic studies (UV and NMR), the above results suggested that these *N*-methylamides adopt remarkable folded conformations compared to the free amide molecules in solution. These facts strongly indicate that all these *N*-methylamides take cis conformations not only in the crystal but also in solution. It is the extended trans conformation that is required for specific binding to the retinoidal receptor macromolecule. Consequently, the loss of activities in *N*-methylamides seem to be ascribed to conformational factors but not to steric hindrance by the methyl group which might prevent binding to the target receptor.

Introduction

Retinoic acid has attracted much interest because of its wide-ranging biological activities.[1] A vast number of related compounds have been synthesized and assayed for retinoidal activity so far. From the structure–activity relationship studies on these synthetic compounds, it is suggested that the long polyene chain in natural retinoic acid (1) is not essential for the retinoidal activities, but a carboxylic acid at one end as well as a bulky hydrophobic group at the other end of a long molecule are essential. Furthermore, the permissible structures of the internal group (so-called linkage group) inserted between these two groups are surprisingly wide-ranging, even in compounds with extremely potent activities. This fact seems to show that the linkage group does not play an important role in specific binding to the retinoidal receptor but regulates the positional and conformational relations between the two groups. After many trials of skeletal conversion of retinoic acid, retinobenzoic acids were found, which are defined as a series of benzoic acid derivatives with potent retinoidal activities. Among various kinds of retinobenzoic acid, a structure with a 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl group and a benzoic acid group at opposite ends of the molecule proved to be a promising lead compound[2] showing potent retinoidal activities. Some of these compounds showed much higher activities than retinoic acid in inducing differentiation of human promyelocytic leukemia cells HL-60 and in other bioassays. The generic chemical structure of this series of compounds is illustrated in Figure 1, together with atomic numbering. The linkage



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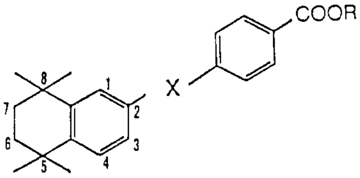
0022-3263/90/1955-0259$02.50/0

Table I. Crystal Data for Six Amides

compd	space group	Z	a, Å	b, Å	c, Å	α, deg	β, deg	γ, deg	D_{calc}, g/cm^3
Am80	$I\bar{4}$	8	19.200 (5)	19.200 (5)	11.569 (3)	90.00	90.00	90.00	1.091
Am580	$P\bar{1}$	4	17.196 (5)	11.461 (3)	10.370 (3)	80.39 (2)	74.28 (2)	84.13 (2)	1.210
Am581	$P2_1/c$	4	14.033 (4)	15.290 (4)	9.893 (3)	90.00	106.78 (2)	90.00	1.195
Am90	$P\bar{1}$	2	13.201 (4)	9.902 (3)	8.183 (3)	90.42 (1)	96.30 (2)	98.56 (2)	1.154
Am590	$P2_1/n$	4	20.313 (5)	11.112 (3)	9.027 (3)	90.00	99.67 (2)	90.00	1.207
Am591	$P2_1/n$	4	15.365 (4)	12.065 (4)	11.936 (3)	90.00	94.99 (1)	90.00	1.142



	X	R	relative activity*
Am80	NH-CO	H	350
Am580	CO-NH	H	720
Am581	CO-NH	CH_3	56
Am90	$N(CH_3)$-CO	H	0
Am590	CO-$N(CH_3)$	H	0
Am591	CO-$N(CH_3)$	CH_3	0

* retinoic acid = 100

Figure 1. Chemical structures of Am80, Am580, Am581, Am90, Am590, and Am591 in generic form.

group X can be replaced with various kinds of chemical groups of appropriate size. In the case of an amide linkage group, two types of benzanilide structures, 4-[(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)carbamoyl]benzoic acid (Am80)[3] and 4-[(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl)carboxamido]benzoic acid (Am580),[4] showed retinoidal activities several times more potent than those of natural retinoic acid in several assay systems. Recently, it was experimentally confirmed by Hashimoto et al.[5] that these amide compounds bind to the same receptor protein as retinoic acid. The corresponding N-methylated amides, Am90 and Am590, however, do not show any such activities. This might be caused by prevention of binding to the receptor, due either to the steric properties of the methyl group on the amide nitrogen or to some conformational factor resulting in an unfavorable molecular shape. UV spectra and ^{1}H NMR spectra of these compounds suggested large differences of the relative positions between the two aromatic moieties in solution. Distinct conformational characteristics were observed spectroscopically for two amide types.[6] To make clear the stable structures of these aromatic amides and to elucidate the reasons for the loss of retinoidal activities, we have analyzed the crystal structures of the *N*-methylamides Am90 and Am590 as well as Am80 and Am580. To avoid possible misunderstandings arising from the crystal packing force, we have also prepared crystals of the methyl esters of Am580 and Am590, Am581 and Am591. Here, we describe the molecular conformations in the crystalline state of three retinoidal-active aromatic amides and the three corresponding inactive *N*-methylamide compounds.

Table II. List of Bond Lengths (angstroms) Relating to the Amide Bond for Six Crystals[a]

compd	C*—N	C*=O	N—C_1	C*—C_1'	N—C_m
Am80	1.350 (9)	1.234 (9)	1.429 (8)	1.505 (9)	
Am580	1.356 (3)	1.222 (2)	1.411 (2)	1.489 (2)	
	1.361 (2)	1.222 (3)	1.410 (2)	1.497 (3)	
Am581	1.351 (4)	1.225 (4)	1.420 (4)	1.496 (5)	
Am90	1.355 (5)	1.235 (5)	1.428 (5)	1.512 (4)	1.484 (5)
Am590	1.352 (4)	1.245 (3)	1.435 (4)	1.494 (4)	1.484 (4)
Am591	1.359 (3)	1.230 (3)	1.428 (3)	1.501 (3)	1.473 (3)

[a] Estimated standard deviations are shown in parentheses.

Experimental Section

The X-ray crystal structure analyses were performed on crystals of compounds Am80, Am580, Am581, Am90, Am590, and Am591. A crystal of compound Am580 contains two independent molecules in the asymmetric unit, while crystals of all the other compounds contain one molecule in the asymmetric unit. Crystal data are illustrated in Table I. In spite of the resemblance of the chemical structures of the six compounds, the crystal lattices and packings are different from each other. Intensity data were measured on a Philips PW1100 four-circle diffractometer using Cu Kα radiation monochromated by a graphite plate. Reflections were collected at a scan speed of 4°/min by the θ–2θ scanning method. Corrections for Lorentz–polarization factors were applied in a conventional way, but no correction was made for absorption. Structures were solved by the direct method using the RANTAN81[7] or MULTAN80[8] program and were refined by block-diagonal least-squares calculations, assuming anisotropic temperature factors. In all the crystals, due to conformational disorder in the saturated ring in the 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl moiety, rather abnormally large temperature factors were observed for the carbon atoms C6 and C7 and four methyl carbon atoms at C5 and C8, as well as related hydrogen atoms. When hydrogen atoms could not be located on difference Fourier maps, their positions were computationally generated at the geometrically expected sites and were refined assuming isotropic thermal motions. Final R factors were 0.097, 0.065, 0.063, 0.086, 0.055, and 0.069 for the six crystals, respectively. Atomic scattering factors for carbon, nitrogen, and oxygen atoms were taken from the ref 9 and those for hydrogen atoms were taken from those of Stewart et al.[10] The final atomic coordinates, thermal parameters, bond lengths, and bond angles are available as supplementary material (see the paragraph at the end of the paper).

Results and Discussion

Molecular structures of the three free amide compounds are shown by ORTEP drawings[11] in Figure 2, and those of the *N*-methylamides are shown in Figure 3. A distinct difference in molecular shape is seen between the three free amides and the corresponding *N*-methylamides. All the free amide molecules (Am80, Am580, and Am581)

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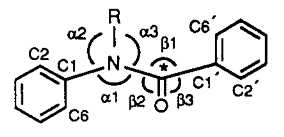
Table III. List of Bond Angles (degrees) Relating to the Amide Bond in Six Amides[a]



R = H or C_m

compd	α_1 (C_1NC^*)	β_1 (NC^*C_1')	β_2 (NC^*O)	β_3 (OC^*C_1')	α_2 (C_1NC_m)	α_3 (C^*NC_m)
Am80	126.7 (6)	115.4 (6)	123.7 (6)	120.8 (6)		
Am580	127.2 (2)	116.6 (2)	122.4 (2)	121.0 (2)		
	128.1 (2)	114.4 (2)	124.2 (2)	121.4 (2)		
Am581	126.9 (3)	115.5 (3)	123.5 (3)	120.9 (3)		
Am90	124.0 (3)	119.3 (3)	121.7 (3)	119.0 (3)	117.3 (3)	118.4 (3)
Am590	125.5 (2)	120.8 (2)	118.7 (2)	120.4 (2)	115.9 (2)	118.1 (2)
Am591	123.7 (2)	118.0 (2)	121.9 (2)	120.0 (2)	117.5 (2)	118.3 (2)

[a] Estimated standard deviations are shown in parentheses.

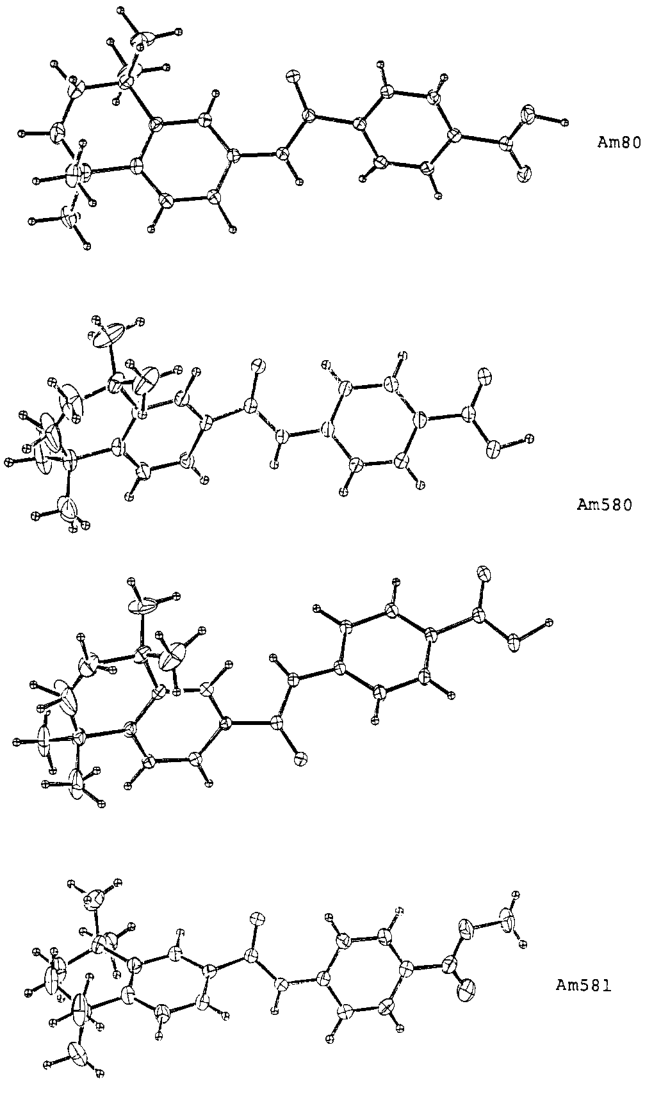


Figure 2. Molecular structures of the free amides, Am80, Am580 and Am581, drawn by the ORTEP program.

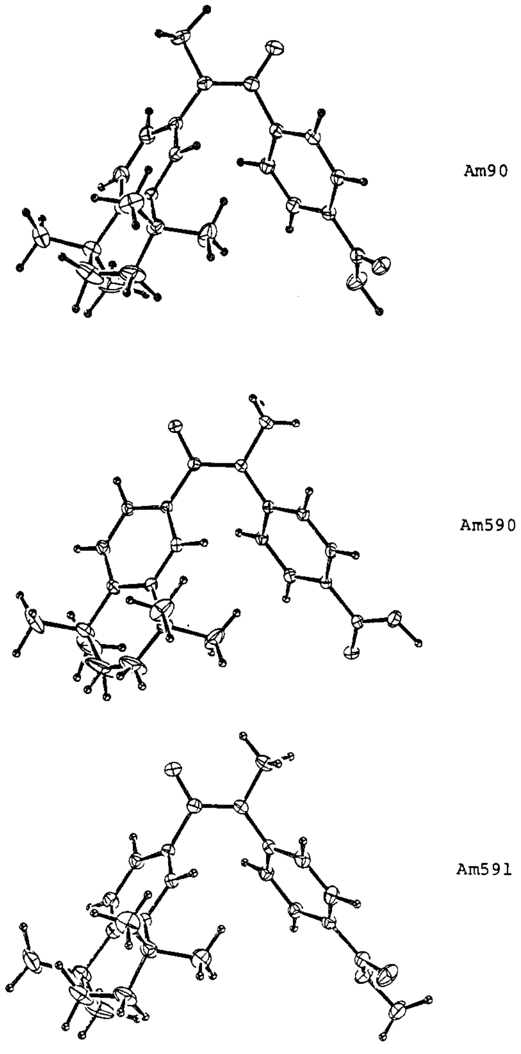


Figure 3. Molecular structures of the N-methylamides Am90, Am590, and Am591, drawn by the ORTEP program.

adopt an extended conformation, whereas all the N-methylamide molecules (Am90, Am590, and Am591) adopt a folded conformation. The characteristic differences are ascribed mainly to the differences in torsional angles at the amide bond.

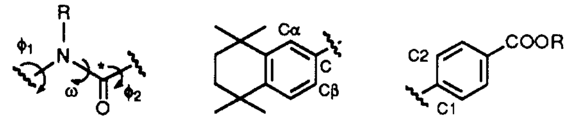
As for the bond lengths, no significant differences were observed between those in the free amides and the corresponding ones in the N-methylamides. Bond lengths relevant to the amide bond in the six molecules are listed in Table II. As for the bond angles, differences between the two amide types are rather clear compared to the bond lengths. As can be seen from the bond angles relating to the amide bond listed in Table III, the angles α_1 and β_1 in free amides seem to be significantly larger than those in the N-methylamides, and the angle β_2 has the opposite tendency. These results can be ascribed to steric crowdedness due to the cis amide conformation.

Table IV. Deviations (angstroms) of Neighboring Atoms to the Amide Bond from the Amide Plane, Together with the Estimated Standard Deviations in Parentheses[a]

compd	C_1	C_1'	C_m
Am80	−0.099 (5)	−0.013 (5)	
Am580	0.131 (2)	0.026 (2)	
	0.051 (2)	0.015 (2)	
Am581	−0.063 (2)	−0.014 (2)	
Am90	0.175 (3)	−0.021 (2)	−0.042 (3)
Am590	0.164 (2)	−0.035 (2)	−0.003 (3)
Am591	−0.383 (2)	0.086 (2)	0.225 (2)

[a] The plane was calculated from the amide nitrogen, carbonyl carbon, and oxygen atoms.

Table V. List of Torsion Angles (degrees) Relating to the Amide Bond for Six Crystals



ω: C_1— N — C*— C
φ1: C_2— C_1— N— C*
φ2: N — C* — C — C_α

compd	ω	ϕ_1	ϕ_2
Am80	174.4[a]	27.1[b]	26.0[c]
Am580	172.1	20.1	36.3[d]
	−176.7	22.7	49.8
Am581	176.2	25.1	41.4[d]
Am90	9.4[a]	57.5[b]	46.0[c]
Am590	−6.5	52.4	41.0
Am591	22.5	51.2	46.8

[a] ω = C—N-C*-C_1. [b] ϕ_1 = Cα-C-N-C*. [c] ϕ_2 = N-C*-C_1-C_2. [d] ϕ_2 = N-C*-C-C_β.

The partial double-bond character in the amide bond seems to be preserved in both amide types, as evidenced by the short bond lengths of amide bonds. The bond lengths of the amide bonds in *N*-methylamides are 1.355, 1.352, and 1.359 Å, while the values are 1.350, 1.356 (and 1.361), and 1.351 Å in the free amides. The double-bond character can be further supported by the planar atomic hybridization at the nitrogen atom as well as the coplanarity of the -CO-NR- group. As for the hybridization character of the amide nitrogen in the *N*-methylamides, the sums of the three bond angles around the nitrogen atom are almost 360° (359.7, 359.5, and 359.5° for Am90, Am590, and Am591, respectively). These facts suggest almost perfect sp_2 character for the amide nitrogen atom, although quantitative comparisons of the geometries with those of the free amides could not be made due to the poor reliability of the atomic coordinates of hydrogens obtained from the X-ray analyses. The amide groups in the *N*-methylamides are a little nonplanar compared to the free amides. Deviations of the neighboring atoms from the least-squares planes, calculated from amide nitrogen and carbonyl carbon and oxygen, are illustrated in Table IV. These results are reflected in the torsion angles around the amide bond. The values of the three torsion angles for C—N(R)—C(=O)—C, C—C—N(R)—C(=O), and N(R)—C(=O)—C—C, which are denoted as ω, ϕ_1, and ϕ_2, are summarized in Table V. All the free amides take the trans conformation with amide torsion angles of 174.4, 172.1 (and −176.7), and 176.2°, whereas all the *N*-methylamides take the cis conformation with amide torsion angles of 9.4, −6.5, and 22.5°. Thus, the deviations of the angles from 180° in the free amides are within 10°, whereas in the *N*-methylamides, the deviations from 0° are rather large. The extremely large deviation, 22.5°, observed for Am591 would be ascribed to the crystal packing force, because the molecular conformation should not be affected by the esterification of Am590 at the end of the molecule.

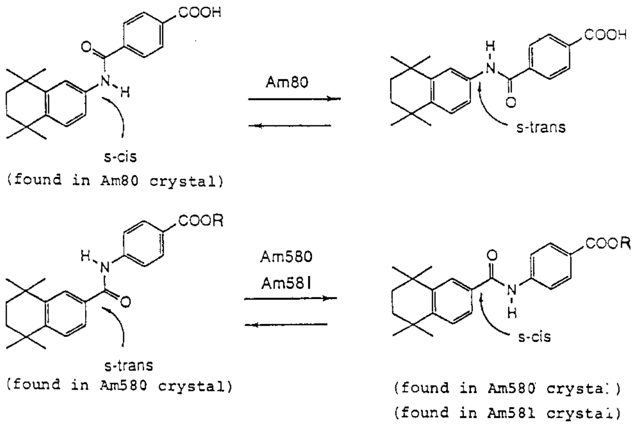


Figure 4. Definition of the two conformational states s-cis and s-trans for Am80 and Am580.

Resonances between the amide group and neighboring benzene rings do not seem to contribute much to the total stability, because the torsional angles, ϕ_1 and ϕ_2, deviate significantly from 0°, as can be seen from Table V. The ϕ_1 angle values can clearly be classified into two groups, depending on the amide types. Those for the free amides vary from 20 to 27°, whereas those for *N*-methylamides vary from 51 to 57°. This is due to the steric hindrance between the carbonyl oxygen atom and the *N*-methyl group. On the other hand, no distinct characteristics were found in the distribution of the ϕ_2 angle values, which ranged from 26 to 50°. The conformations of the *N*-methylamides differ from those of the free amides not only in the amide cis or trans conformation but also in the interplanar angles between the amide and aromatic groups. The *N*-methylamide molecules are sterically more restricted by the bulkiness of the methyl moiety than the free amide molecules as a matter of course. Minor conformational differences among *N*-methylamides may probably be ascribed to the crystal packing forces rather than to the intrinsic conformational stability.

Due to the folded cis conformation, the two aromatic groups face each other in N-methylated benzanilides. This situation might cause large shielding due to the ring current anisotropy of the two benzene rings, compared to the corresponding free amides. These observations are in good agreement with NMR and UV results.[12] The molecular conformations in solution are supposed to be similar to those in the crystal, especially in relation to the amide bond. As to the reasons for the distinct preference of the cis amide conformation in N-methylated benzanilides, both stereochemical and electrostatic factors should be taken into account.

Arising from the asymmetric structure of the 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenyl group, the trans amide conformation in these benzanilide molecules can be further classified into two different conformational states, that is, the stereochemistry about the single bond between the naphthalenyl moiety and the amide group. Two states of s-cis and s-trans conformations are possible for both Am80 and Am580 as shown in Figure 4. From the viewpoint of molecular shape, the s-cis form of Am80 resembles the s-trans form of Am580. In the Am580 crystal, both the s-cis and the s-trans forms are observed as two independent molecules in the asymmetric unit, whereas the structures of both Am80 and Am581 molecules in the crystal were s-cis. Therefore, it is suggested that there is no major intrinsic stability difference between the two conformational states in the trans free amides: the observed forms in the crystal are probably determined by the crystal packing. Overall, from our viewpoints, the potent retinoidal activities of these free amides seem to be a consequence of the trans extended conformation with the s-cis or the s-trans form.

Conclusion

The three *N*-methylanilide molecules examined adopt cis amide conformations in the crystalline state, whereas the corresponding free amides take the trans amide conformation. The structures in solution are considered to be similar to those in the crystal on the basis of various spectroscopic studies. From the structure–activity relationships of various synthetic retinoidal active compounds,[12] we conclude that the trans extended conformation is required for specific binding to the target receptor. This fact strongly supports our postulation. The loss of activity upon N-methylation of retinoidal active benzanilides should not be ascribed to the steric hindrance of the methyl group or to the potential loss of a hydrogen bond from amide nitrogen to the receptor but to the large conformational change unfavorable for binding. The reasons for stabilization of the cis amide conformation in *N*-methylanilide are under investigation by computational methods, using molecular mechanics and molecular orbital calculations. The generality of this cis stabilization by N-methylation from benzanilide to other anilide compounds will be discussed elsewhere.

Registry No. Am80, 94497-51-5; Am580, 102121-60-8; Am581, 102121-59-5; Am90, 110383-33-0; Am590, 116193-58-9; Am591, 116233-28-4.

Supplementary Material Available: Find atomic coordinates, thermal parameters, bond lengths, and bond angles (28 pages). Ordering information is given on any current masthead page.

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[12] Kagechika, H.; Himi, T.; Namikawa, K.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1989**, *32*, 1098.

Synthesis and Unusual Selenium Extrusion Reaction of a Cyclic Triselenide

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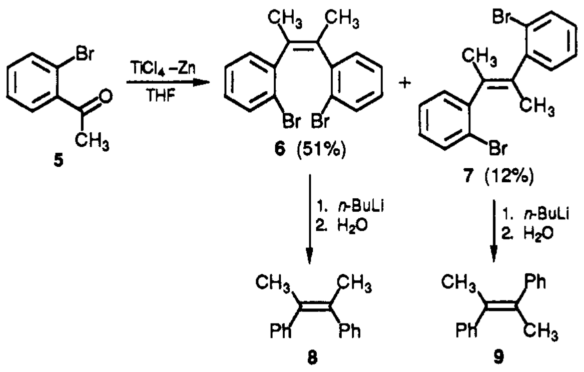
Reaction of (*Z*)-2,3-bis(2-lithiophenyl)-2-butene (**10**) with selenium gave 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**) rather than either 11,12-dimethyldibenzo[*c*,*g*]-1,2-diselenocine (**2**) or 13,14-dimethyldibenzo-[*e*,*i*]-1,2,3,4-tetraselenecine (**4**). Thermolysis and photolysis of **3** gave 5a,10a-dihydro-5a,10a-dimethyldibenzo-[*b*,*f*]seleno[3,2-*b*]selenophene (**12**) via extrusion of a selenium atom and a novel intramolecular addition of arylselenyls to a double bond. Ab initio molecular orbital calculations and X-ray structural analyses are made to elucidate the reaction mechanism of **10** → **3** → **12**.

Introduction

The chemistry of cyclic polysulfides[1] has attracted attention, because of chemical, theoretical, and biological interest. They exhibit unique chemical properties such as skeletal rearrangements, unusual structures, and the transfer of sulfur atoms to acceptors. Compared to syntheses and reactions of sulfur compounds, few examples of those of cyclic di-, tri-, and polyselenides have been reported.[2] We have examined the preparation and a reaction of a cyclic triselenide. We now report a reaction of (*Z*)-2,3-bis(2-lithiophenyl)-2-butene (**10**) with selenium, giving 12,13-dimethyldibenzo[*d*,*h*]-1,2,3-triselenonine (**3**) and the result of thermal and photochemical reactions of **3**.

Scheme I



The aim of this work is to examine how the Se–Se bond is incorporated into a cyclic polyselenide and the polyselenide linkage is converted to C–Se bonds thermally or photochemically. On the basis of the present result, the

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[1] For some recent papers for cyclic polysulfides, see: (a) Nicolaou, K. C.; Hwang, C.-K.; DeFrees, S.; Stylianides, N. A. *J. Am. Chem. Soc.* **1988**, *110*, 4868. (b) Steliou, K.; Salama, P.; Brodeur, D.; Gareau, Y. *J. Am. Chem. Soc.* **1987**, *109*, 926. (c) Chenard, B. L.; Dixon, D. A.; Harlow, R. L.; Roe, D. C.; Fukunaga, T. *J. Org. Chem.* **1987**, *52*, 2411 and references cited therein.

[2] For reviews, see: (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1986; Vol. 1, Chapter 13. (b) Claus, P. K. *Organic Compounds of Sulphur, Selenium, and Tellurium* **1981**, *6*, 233.

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