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Chunbo Zhang[a]; Longyi Jin[a]; Bingzhu Yin[a]; M. Jamil[b]; Young-Jae Jeon[b]
[a] Key Laboratory of Organism Functional Factors of the Changbai Mountain, Yanbian University, Ministry of Education, Yanji 133002, PR China [b] Department of Chemistry, College of Science, Konkuk University, Seoul 143-701, South Korea

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Synthesis and properties of non-symmetric liquid crystal dimers containing a cholesteryl moiety

CHUNBO ZHANG†, LONGYI JIN†, BINGZHU YIN*†, M. JAMIL‡ and YOUNG-JAE JEON‡

†Key Laboratory of Organism Functional Factors of the Changbai Mountain, Yanbian University, Ministry of Education, Yanji 133002, PR China

‡Department of Chemistry, College of Science, Konkuk University, 1 Hawayang-dong, Kwangjin-gu, Seoul 143-701, South Korea

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A series of non-symmetric liquid crystal dimers having cholesteryl and 4-*trans*-(4-*n*-alkylcyclohexyl)phenoxy groups were synthesized by condensation of cholesteryl ω-bromoalkanoates with appropriate 4-*trans*-(4-*n*-alkylcyclohexyl)phenols. The structures and thermal phase behaviour of the dimers were characterized using IR, ^{1}H NMR and mass spectroscopy, elemental analysis, differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction measurements. Their thermal phase behaviour is significantly different to that of other cholesterol-based liquid crystal dimers. All of these liquid crystal dimers exhibit low phase transition temperatures. The relationships between their properties and chemical structures of these new dimers are discussed.

1. Introduction

Owing to the fact that cholesterol is abundant in nature and a commercially available chiral compound, liquid crystal dimers possessing a cholesteryl ester unit joined to different aromatic mesogens through an alkylene spacer, are currently receiving considerable interest as chiral dimers [1–11]. The main interest behind the designing of new materials containing cholesteryl groups results from its rigid-long shape and chiral structure. A rigid-long shape induces large intermolecular interaction via van der Waals forces stabilizing parallel molecular arrangements and the chiral structure induces chirality in molecular order, i.e. a helical superstructure. However, in one aspect it is not easy to predict the effect of liquid crystalline properties of the dimers due to the cross-sectional area of the cholesterol group, since it is much larger than that of the aromatic mesogens and also the terminal alkyl group of the cholesterol group is branched in dimesogens. They have been seen to self-assemble into various phases, i.e. chiral nematic (N*), chiral smectic C (SmC*), intercalated smectic A (SmA$_{\mathrm{ic}}$), TGB$_{\mathrm{A}}$, TGB$_{\mathrm{C*}}$, blue phase and so on [9–17]. On the other hand, liquid crystals having a cholesteryl unit generally exhibit relatively high phase transition temperatures, narrow phase ranges and high mechanical viscosity. For example, Cha *et al.* [10] reported some non-symmetric liquid crystal dimers consisting of a cholesteryl moiety and an aromatic mesogenic unit interconnected through a pentamethylene spacer, the aromatic units consist of two phenyl rings linked by carboxy, oxycarbonyl, ethylene, ethynylene, azo or Schiff base groups, is quite complex and most of their phase transition temperatures are high and the phase range narrow. Unfortunately, some of these are moisture sensitive and thermally not very stable. To the best of our knowledge the derivatives of 4-(*trans*-4-*n*-alkylcyclohexyl)benzene is found to be more advantageous than benzoic acid phenyl esters, biphenyl derivatives, Schiff's base derivatives, etc, based on viscosity, temperature range of the mesophase and other physical properties [18–20]. Very recently, Tamaoki *et al.* [21] and Wu [22, 23] synthesized a series of novel dimer compounds containing cholesteryl and phenyl benzoate groups or azobenzene dimer in which the two mesogenic units were linked through dicarboxylic ester bonds. This series of compounds exhibited only one liquid crystalline phase (smectic or cholesteric) over a wide temperature range during heating and cooling. In view of these observations we have reported a series of non-symmetric dimers having a cholesteryl moiety and 4-(*trans*-4-*n*-alkylcyclohexyl)-phenoxy mesogen interconnected through a central pentamethylene spacer (the **D*m*5** series), which exhibit simple thermal phase behaviour with low phase transition temperatures and wide phase ranges. The above-mentioned simple mesophases are very suitable for use as a chiral dopant and a component of blended liquid crystals

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*Corresponding author. Email: cbzhang@ybu.edu.cn

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[24]. In order to understand the structure–property relationships, we changed the lengths of the spacer and of the terminal alkyl chain of the dimers and studied the thermal phase behaviour, including odd–even effects at the nematic–isotropic and SmA_{ic}–nematic transitions.

2. Results and discussion

2.1. *Synthesis*

Cholesterol and other reagents were purchased from Aldrich, and were used without further purification. Chloroform was dried by standing over $CaCl_2$ at least 24 h and distilled from $CaCl_2$. All other solvents were used without further purification. Target compound separations were performed using a preparative medium-pressure liquid chromatograph (Yamazen pump 540, Japan).

The targeted non-symmetric dimers (**D*mn***), where D stands for dimer, *m* is the carbon number of the terminal alkyl and *n* is the length of flexible spacer, were synthesized as outlined in scheme 1. Compounds **1*m*** and **2*m*** were prepared by previously reported methods [24].

Compounds **4*n*** were prepared by the esterification of **3** using ω-bromoalpihatic acid chloride or ω-bromoalpihatic acid in $CHCl_3$ [7]. The target compounds (**D*mn***) were synthesized through condensation of corresponding phenol (**2*m***) and bromide (**4*n***) with 43–71% yields in butanone.

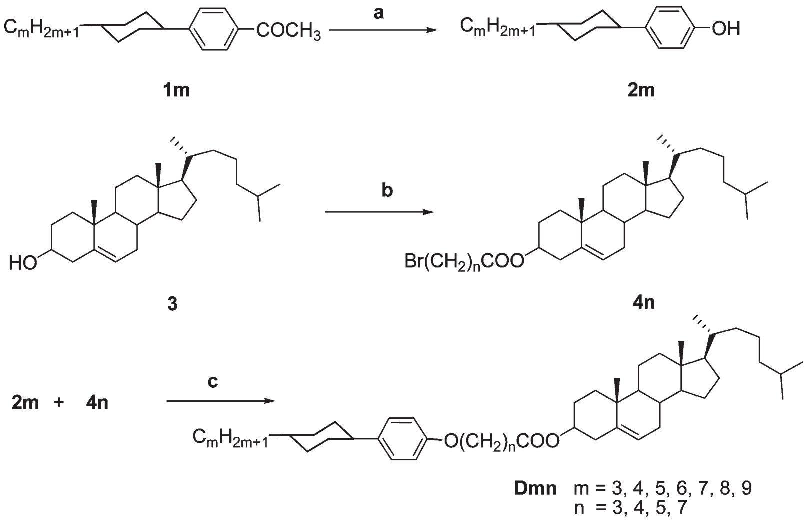
2.2. *Phase transition and mesophases*

The phase transition temperatures were determined using differential scanning calorimetry (DSC, Seiko DSC 200 and PE DSC-7). Table 1 shows the phase sequence, transition temperatures and associated enthalpies of the dimers.

All the dimers exhibited simple thermal phase behaviour; some of them exhibited low phase transition temperatures and wide temperature ranges. For example, dimer **D55** exhibited a cholesteric phase with a wide temperature range from 21°C to 171°C on cooling. The DSC traces for the first heating and cooling cycles obtained at a rate of $5°C\,min^{-1}$ for D55 and D73 are shown in figure 1.

The dimers showed a strong alternation phenomenon on the isotropization temperatures and the corresponding enthalpy changes at the N*–I transition. The N*–I transition temperatures of dimers with an odd spacer (n=3, 5, 7) are much higher than dimers with an even spacer (n=4) (figure 2 a). Similar results appear in the plot of the corresponding enthalpy changes at the N*–I transition (figure 2 b). It was observed that the mesophase morphology strongly depends on the spacer length. Furthermore, it was found that dimers with a longer spacer and shorter terminal alkyl chain tend to exhibit an N* phase, e.g. **D3*n***, **D4*n***, **D37**, **D47**, **D57**, **D67** and **D77** exhibited N* only. Increasing the length of spacer between the two mesogen units tends to reduce the lateral attractions and hence disrupts lamellar packing, and hence favours the nematic phase.

Marcelis *et al.* [17] also reported that the chiral nematic phase window became wider with increasing spacer length. The mesophase morphology is also dependent upon the length of terminal alkyl chain. Dimers with a long terminal alkyl chain tend to exhibit SmA phases, e.g. all of **D9*n*** and **D8*n*** dimers exhibit SmA in addition to N* phases. It is interesting to note



Scheme 1. Synthetic pathway to the target compounds. Reagents and conditions: (a) i. benzenecarboperoxoic acid, $CHCl_3$, stirring; ii. NaOH, H_2O, ethanol, reflux; (b) ω-bromoacyl chloride, pyridine, $CHCl_3$, stirring; (c) K_2CO_3, butanone, reflux.

Table 1. Transition temperatures (°C) and enthalpies (J g^{-1}, in brackets) of **D*mn*** dimers (I=isotropic liquid; N*=chiral nematic phase; SmA=smetic A phase; Cr=crystal).

Dimer	Cr	Heating Cooling	SmA	Heating Cooling	N*	Heating Cooling	I	ΔT_{N^*-I}
D33		145.5 (46.8)				187.6 (4.8)		42.1
		97.1 (36.1)				186.7 (4.9)		89.6
D43		103.8 (28.4)		146.9 (0.6)		186.7 (4.9)		39.8
		66.9 (20.6)		145.7 (0.6)		184.7 (4.6)		39.0
D53		122.3 (31.5)		164.0 (0.4)		192.8 (5.4)		28.8
		82.5 (23.1)		162.9 (0.5)		192.2 (5.4)		29.3
D63		106.3 (28.7)		163.3 (0.7)		183.2 (4.9)		19.9
		66.7 (22.6)		161.3 (1.0)		181.7 (5.3)		20.4
D73		128.5 (45.5)		172.7 (1.8)		185.2 (5.1)		12.5
		83.9 (32.6)		171.9 (1.6)		184.3 (5.0)		12.4
D83		138.0 (48.4)		177.3 (3.2)		184.0 (6.2)		6.7
		104.0 (36.8)		176.6 (3.1)		183.0 (5.6)		6.4
D93		116.7 (28.2)		162.1 (2.1)		172.5 (8.1)		10.4
		82.9 (25.9)		160.8 (2.1)		171.9 (7.6)		11.1
D34		105.8 (20.5)				114.8 (1.7)		9.0
						112.6 (1.7)		
D44		64.1 (26.2)				98.5 (1.3)		34.4
						98.2 (1.4)		
D54		82.5 (33.9)		107.0 (0.9)		132.3 (1.8)		25.3
				106.6 (0.8)		131.5 (2.2)		
D64		97.3 (45.8)		109.7 (0.5)		129.0 (1.5)		19.3
				109.7 (1.0)		127.8 (1.5)		
D74		85.0 (22.1)		126.1 (0.9)		134.0 (0.9)		7.9
				125.5 (0.9)		133.3 (0.9)		
D84		96.0 (26.2)		121.1 (0.8)		134.1 (0.9)		8.0
				120.8 (0.8)		133.2 (0.9)		
D94		71.1 (14.3)		128.0 (0.9)		133.2 (1.1)		5.2
		17.7 (3.4)		127.7 (0.9)		133.0(1.0)		5.3
D35		103.3 (24.3)				141.1 (1.2)		37.8
						139.8 (2.1)		
D45		101.8 (27.4)				164.0 (4.7)		62.2
		49.0 (16.1)				163.2 (5.0)		114.2
D55		84.9 (25.7)				172.8 (5.7)		87.9
		21.4 (14.2)				171.8 (5.7)		150.4
D65		99.7 (36.9)		138.2 (0.5)		169.4 (4.9)		31.2
		50.9 (32.0)		138.1 (0.5)		168.2 (4.9)		30.1
D75		123.0 (42.9)		138.5 (0.7)		161.2 (5.7)		22.7
		36.0 (5.80)		136.0 (0.8)		161.1 (5.9)		25.1
D85		111.1 (37.0)		152.1 (1.3)		166.8 (5.6)		14.7
		51.8 (16)		152.0 (1.0)		165.6 (5.7)		13.6
D95		97.7 (29.5)		155.5 (2.4)		165.0 (6.8)		9.5
		42.0 (13.4)		154.6 (1.4)		163.7 (6.9)		9.1
D37		116.5 (41.5)				154.7 (5.8)		38.2
		77.5 (28.1)				153.8 (5.9)		76.3
D47		103.7 (35.9)				154.3 (5.7)		50.6
						153.1 (5.8)		
D57		98.1 (39.0)				157.6 (6.0)		59.5
						156.3 (6.4)		
D67		91.4 (41.7)				154.6 (6.1)		63.2
		42.7 (21)				153.5 (6.2)		110.8
D77		85.6 (29.8)				152.0 (6.6)		66.4
		47.8 (19.1)				151.0 (6.7)		103.2
D87		77.8 (45.6)		125.1 (0.4)		151.0 (6.4)		25.9
		66.5 (20.0)		125.2 (0.3)		149.9 (6.4)		24.7
D97		91.2 (47.7)		130.7 (0.9)		149.3 (6.8)		18.6
		55.6 (24.1)		129.9 (0.6)		148.1 (6.8)		18.2

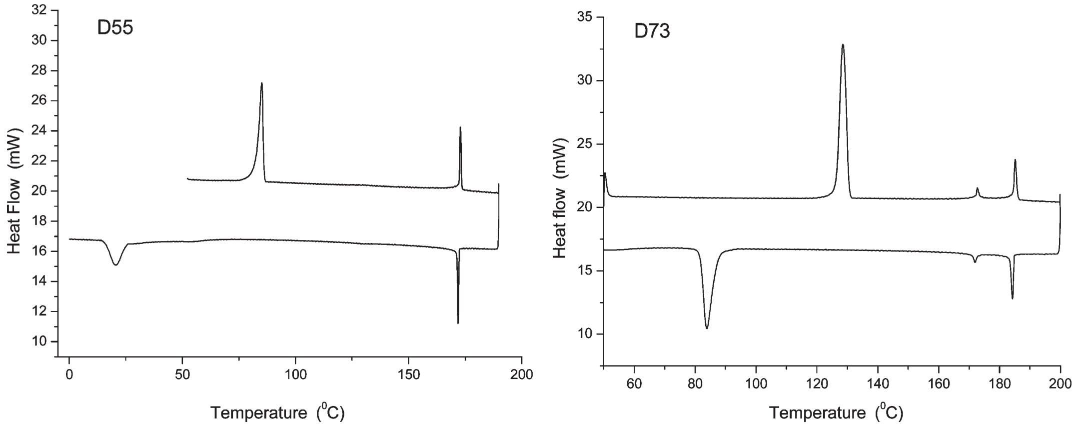


Figure 1. DSC thermograms of **D55** and **D73**.

that in this series the appearance of SmA phase started when just the number of carbons of the terminal alkyl equals the number of methylenes of the spacer (i.e. $m=n+1$), as shown in figure 3.

The presence of SmA and N* mesophases of the dimers was confirmed via observations using a polarizing optical microscope (Olympus BHSPBH-2) equipped with a hot stage. As an example, the typical textures of the SmA and N* mesophases of **D74** were shown in figure 4.

2.3. *X-ray diffraction study*

As shown in table 1, the dimers with a longer terminal alkyl chain and shorter spacer tend to exhibit SmA phases. The SmA phase was further confirmed using X-ray diffraction (XRD, Rigaku Rint 2100 system with a Linkam HFS-91 hot stage at Ni-filtered Cu Kα

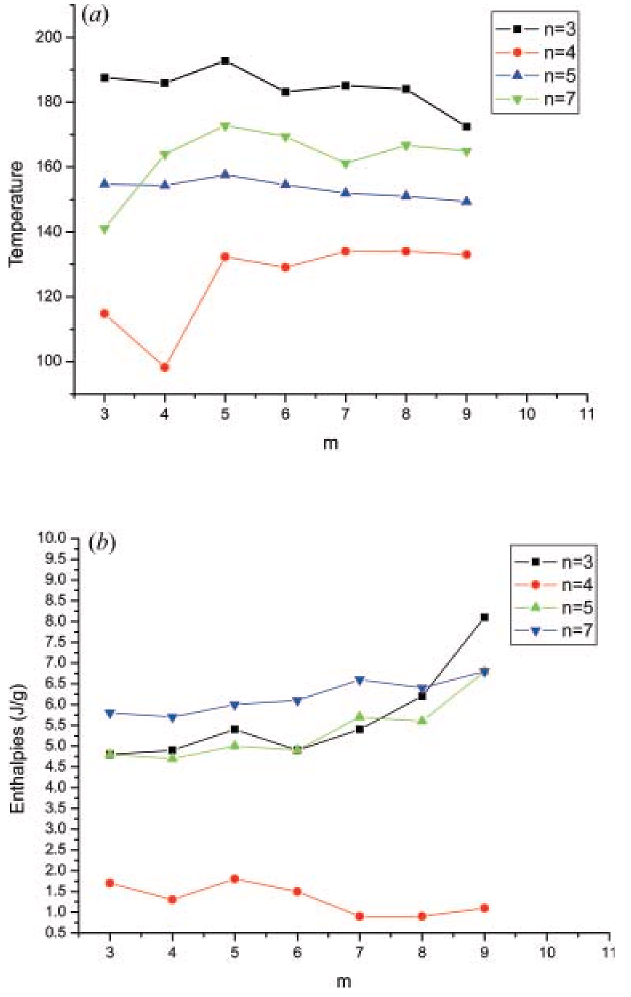


Figure 2. The dependence of (a) T_I and (b) ΔH on the number of carbons of the terminal alkyl (*m*) in **D*mn*** dimers.

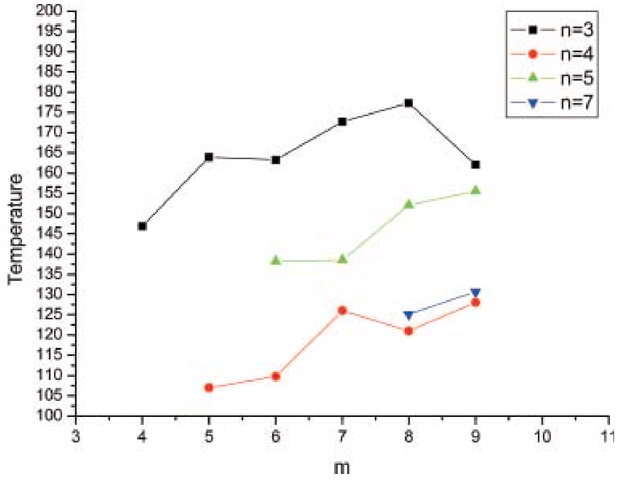


Figure 3. The dependence of transition temperature of SmA phase on the number of carbons of the terminal alkyl (*m*) in **D*mn*** dimers.

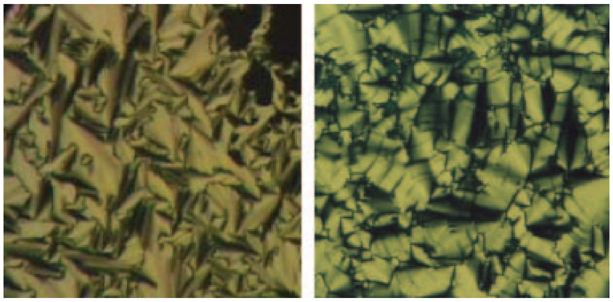

(*a*) (*b*)

Figure 4. (a) Focal-conic texture of SmA phase observed on cooling from isotropic phase at 115°C for the **D73**. (b) Cholesteric focal-conic fan texture of N* phase observed on cooling from isotropic phase at 180°C for the **D73**.

radiation and at various temperatures). XRD reveals that the smectic layer spacing of the dimers with an odd number of methylenes in the spacer is much larger than that of the dimers with an even number of methylenes in the spacer, in which the value of m+n are same. For example, **D65** and **D74** both have a molecular length of 39.7 Å, but the smectic layer spacing of **D65** is 39.8 Å, whereas that of **D74** is 33.0 Å, as shown in table 2. The pronounced change in smectic layer spacing of the dimers is most often attributed to the all-trans conformation of molecules.

3. Conclusions

Liquid crystal dimers consisting of a cholesteryl moiety and 4-(*trans*-4-*n*-alkylcyclohexyl)phenoxy mesogens interconnected through different lengths of spacers have been synthesized. Our main findings are as follows: (i) compared with previously studied dimers, the mesophases observed in this paper are simple; (ii) dimers with a shorter terminal alkyl chain and longer spacer tend to exhibit only an N* mesophase; (iii) in this series SmA phase appears only when $m>n+1$; (iv) some selected dimers in the present investigation exhibit a wide temperature range for the N* phase. These dimers are promising candidates for applications in liquid crystalline displays and electro-optical devices.

Table 2. The layer length, *d*, and molecular length of some selected dimers.

Dmn	Layer spacing in SmA phase/nm	Estimated molecular length/nm
D74	3.20	3.97
D84	3.26	4.17
D94	3.36	4.33
D65	3.85	3.97
D75	4.17	4.17
D85	4.23	4.33
D95	4.46	4.50

4. Experimental

4.1. *Characterization*

The structure of the targeted products and intermediates were confirmed by elemental analyses (Perkin Elmer PE-2400 elemental analyzer), infrared spectroscopy (Perkin Elmer FTIR 1730 spectrophotometer), ^{1}H NMR spectroscopy (Bruker AV-300 spectrometer, recorded using Me_4Si as an internal standard) and mass spectroscopy (Agilent 1100-HP LC/MSD instrument).

4.2. *Cholesteryl 4-(4-*trans*-(4-propylcyclohexyl)phenoxy) butanoate (D33)*

A 50 ml flask equipped with a water condenser was charged with 2-butanone (30 ml), cholesteryl ω-bromobutanoate (214 mg, 0.4 mmol), 4-(*trans*-4-*n*-propylcyclohexyl) phenol (87.2 mg, 0.4 mmol), anhydrous potassium carbonate (55 mg, 0.4 mmol), and then flushed with argon several times. The reaction mixture was heated under reflux for 24 h while stirring. The solvent was evaporated and the residue was treated with 20 ml of dichloromethane. The solid material was filtered and washed with another 20 ml of dichloromethane. The filtrate was concentrated and the residue was purified by preparative medium-pressure liquid chromatography on a silica gel column using $CHCl_3$ as eluent and recrystallized from acetone–chloroform (10:1) to give cholesteryl 4-(4-*trans*-(4-propylcyclohexyl)phenoxy)butanoate (**D33**). White needle crystals, yield 70%, m.p. 145.5°C. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.13 (d, J=8.6 Hz, 2H), 6.83 (d, J=8.6 Hz, 2H), 5.38 (m, 1H), 4.62–4.65 (m, 1H), 3.99 (t, J=6 Hz, 2H), 2.50 (t, J=7.2 Hz, 2H), 2.41 (t, J=10.5 Hz, 1H), 2.10–1.03 (m, 49H), 0.93 (d, J=6.4 Hz, 3H), 0.88(d, J=6.4, 6H), 0.70 (s, 3H). FTIR (KBr, cm^{-1}): 2926, 1737, 1249, 1172. MS: m/z 673[M+1]$^+$. Elemental analysis: calculated for $C_{46}H_{72}O_3$, C 82.09, H 10.78; found, C 81.99, H 10.78%.

The other compounds in the **D*mn*** series were prepared using the same general procedures. The compounds (yields) prepared were **D43** (65%), **D53** (60%), **D63** (69%), **D73** (61%), **D83** (60%), **D93** (55%), **D34** (56%), **D44** (54%), **D54**(54%), **D64** (53%), **D74** (50%), **D84** (51%), **D94** (52%), **D35** (63%), **D45** (55%), **D55** (58%), **D65** (55%), **D75** (53%), **D85** (57%), **D95** (57%), **D37** (58%), **D47** (55%), **D57** (63%), **D67** (46%), **D77** (43%), **D87** (66%) and **D97** (64%). All other dimers had appropriate ^{1}H NMR, IR and MS spectral data and their elemental analyses were in acceptable agreement with the calculated values.

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