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Homochiral Helices of Oligonaphthalenes Inducing Opposite-Handed Cholesteric Phases

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Abstract: The helical structure of the chiral nematic phases (cholesterics) obtained by doping nematic solvents with chiral non-racemic compounds is a macroscopic proof of the solute chirality. Oligonaphthalene (tetra-, hexa-, octa-) derivatives linked at the 1,4-positions have been used as chiral dopants: When the chirality axes are configurationally homogeneous (that is, all-*S*), the molecular structures correspond to right-handed helices. Yet, we have found series of derivatives with the surprising property that the handedness of the induced cholesteric phase alternates from positive to negative and to positive again, on passing from tetra- to hexa- and to octanaphthalene. A comparison with oligonapthalene derivatives, which do not exhibit this twisting ability, points to the importance of the substitution pattern. Both the possibility of inducing oppositely-handed cholesteric phases by homochiral helices of different length, and the role played of substituents, are confirmed by calculations performed with the surface chirality model.

Keywords: chirality · helical structures · helical twisting power · liquid crystals · oligonaphthalene

Introduction

Poly- and oligophenylenes and other π-conjugated polymers and oligomers are attractive molecules for their potential application in material science.[1] The rotational barrier around the aryl–aryl bonds may cause the dissymmetry of the molecule and, if the axial configuration can be controlled, generate a helical structure. Helical molecular architectures are very ordered structures, can pack molecular information in a restricted space and consequently have attracted considerable attention.[2]

It has been known for a long time that doping nematic phases with chiral non-racemic compounds transforms them into chiral nematic (cholesteric) phases;[3] however, this discovery was forgotten for almost 50 years and only since the 1960s has it been reconsidered. In this process, the molecular chirality is mapped onto a nematic phase by inducing a helical arrangement of the nematic director. In other words, chirality is transferred from the molecular level to the bulk of the solvent. The study of the cholesteric phases obtained by doping nematics has lead to relevant information about the stereochemistry of the dopant.[4,5] The main goal of this research has been to understand the relation between the cholesteric handedness and a stereochemical descriptor of the molecular chirality; this is not trivial because homochiral molecules with similar structures do not always induce cholesteric phases of the same handedness.[6,7]

A satisfactory understanding of the relation between molecules and phase handedness would require the knowledge of how the chiral information is transferred from the dopant to the solvent. Recently, a theoretical method capable of accounting for the phenomenon of cholesteric induction by using a realistic picture of the chemical constituents in terms of molecular geometry has been proposed.[8] This approach, denoted as the *surface chirality method*, accounts for the short-range solute–solvent interactions modulated by the

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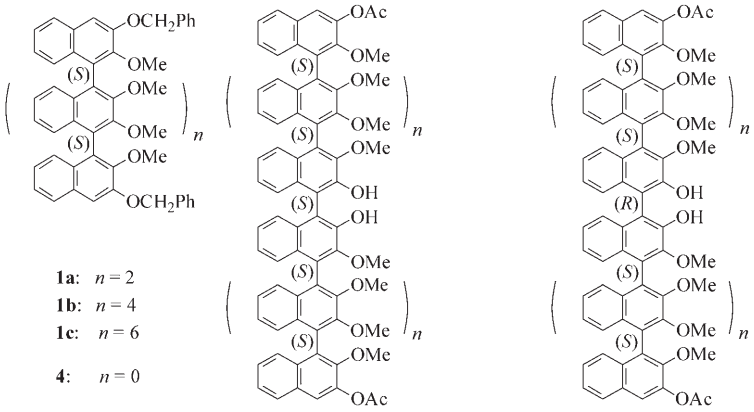
solute molecular shape. The model rests on the assumption that the anisotropy and chirality of such interactions, which determine the twisting ability of the dopant, can be parameterized on the basis of the anisometry and helicity of the molecular surface. The handedness and the pitch of the induced cholesterics are determined by the coupling between the molecular helicity (which is different along different molecular directions) and the orientational behavior of the dopant (which tends to align along the local director with a preferential molecular axis). Changes in the molecular geometry, such as those deriving from substituents or conformational transitions, can have dramatic effect on the twisting ability of a dopant.[4,7] Moreover, in the case of dopants with low twisting power, cholesterics of opposite handedness may be induced in different liquid crystal solvents.[9] However, in the case of solutes with clearly defined helicity and alignment axes, we expect a weak sensitivity to relatively small changes in structure and environment. Indeed, such uniformity of behavior has been observed for helicenes; in penta- and hexa-, carbo- and heterohelicenes, the relationship between the molecular stereochemical descriptor and the cholesteric handedness has been verified and interpreted:[10] (*P*)-helicenes induce (*P*)-cholesterics in all cases investigated.

Here we are focusing our attention on oligonaphthalene derivatives linked at the 1,4-positions. When the chirality axes are configurationally homogeneous, the molecular shape resembles that of the bridged terphenylophanes described by Vögtle as "Geländer" helical molecules.[11] Homochiral oligonaphthalenes share with helicenes the feature of a clearly defined helicity and analogous orientational behavior, in this case the helix axis is parallel to the inter-naphthyl bonds and the principal alignment axis is not far from it. For these reasons these might appear as good prototype systems, with an easily understandable twisting ability. We have measured the helical twisting power in liquid crystal solvents for series of enantiopure homochiral oligonaphthalenes and we have found derivatives which exhibit an unexpected sign alternation with length. For the sake of comparison, also a few stereoisomers differing in the configuration of a single stereoaxis have been considered. The experimental findings have been interpreted with the aid of the surface chirality method.

Results and Discussion

In this paper, we consider enantiopure oligonaphthalenes **1a–c**, **2a–c** and **3a–c**. In derivatives **1** and **2**, all chirality axes in each molecule have the same *S* configuration; this allows the formation of homochiral *P* helices from the different oligomers. It is known that steric interactions between adjacent naphthalenes lead to a conformation in which the neighboring naphthalene units adopt an approximately orthogonal geometry.[12–15] Therefore, increasing the number of naphthalene units from 4 (**1a**, **2a**) to 6 (**1b**, **2b**) and finally to 8 (**1c**, **2c**), the right-handed helices (of an approximately constant pitch) describe approximately 3, 5, and 7 quarter-turns, respectively.



1a: $n = 2$
1b: $n = 4$
1c: $n = 6$

4: $n = 0$

2a: $n = 0$
2b: $n = 1$
2c: $n = 2$

3a: $n = 0$
3b: $n = 1$
3c: $n = 2$

Derivatives **3a–c** are the diastereomers of compounds **2a–c** where the central stereoaxis presents an inverted configuration (*R* instead of *S*). This feature creates a sort of stereochemical kink in the middle of the molecules, which prevents the formation of a continuous regular helix. For example, while the configuration of the stereoaxes in **2c** is all-*S*, and the global shape has a helical symmetry, in compound **3c**, which has an axial chirality (from one molecular end to the other) of *S*,*S*,*S*,*R*,*S*,*S*,*S*, the helical symmetry is broken with respect to the central aryl–aryl bond.

Helical twisting power (β): The helical twisting power of a chiral compound expresses its ability to torque a nematic phase.[16] This quantity is numerically expressed by Equation (1) where p is the pitch, c the dopant molar fraction and r its enantiomeric excess.

$$\beta = (p \times c \times r)^{-1} \quad (1)$$

The sign of β is taken as positive if the induced cholesteric is right-handed.

Our and other research groups have already analyzed the twisting power of several 1,1′-binaphthalene derivatives with the aim of obtaining information on the structural features controlling the handedness of the induced cholesterics.[17–19] The conclusion was that nematic phases may act as probes of the binaphthyl helicity (i.e., of the dihedral angle between the two naphthalene rings)[4] and when the two rings are almost orthogonal, a negligible value of β is expected.[8]

The twisting powers of the oligonaphthalenes under investigation measured in the nematic solvent E7 are reported in Table 1. It appears that the absolute values of β are higher than those reported in the literature for quasi-orthogonal binaphthyls;[17–19] furthermore, binaphthyl **4**, that presents the same substituents of **1a–d**, shows the smallest β value ($+11\ \mu m^{-1}$).

Table 1. Helical twisting powers of compounds **1a–d**, **2a–c** and **3a–c** measured in the nematic solvent E7 at the same reduced temperature ($T = T_c - 10\,°C$).[a] The standard error is about 10%.

	β [μm^{-1}]
1a	+ 78
1b	+36
1c	+9
2a	+14
2b	−54
2c	+49
3a	−23
3b	+14
3c	−77

[a] T_c: clearing temperature.

As already noted, compounds **1a–c** possess, as a common feature, a homochiral *P*-helicity and the cholesteric phases induced in nematic solvents is indeed homogeneously right-handed (*P*). However, the relation "molecular *P*-helicity" → "cholesteric *P*-handedness" is not of general application. In fact, also compounds **2a–c** are homochiral and have the same *P*-helicity as **1a–c**, but despite this and surprisingly, their twisting powers alternate from positive to negative and to positive again on passing from **2a** to **2b** to **2c**. This finding clearly indicates that the molecular helical descriptor alone is not useful in the prediction of the cholesteric handedness (and, vice versa, the cholesteric handedness cannot allow a direct assignment of the helical configuration).

Changing the configuration of the central stereoaxis (see **3a–c**), the handedness of the induced cholesteric reverts with respect the corresponding diastereomers **2a–c** and, increasing the length of the oligomers, an alternating effect similar to that described for compounds **2** is observed (the twisting powers go from negative to positive and to negative values passing from **3a** to **3b** to **3c**, respectively.

This positive/negative alternation of β resembles the odd–even effect observed in homologous series of chiral nematogenic compounds containing a single stereocentre.[20]

The β values were also determined at variable temperature to check for any evidence of pitch inversion as a function of temperature.[21] In all cases the pitches increase with temperature without any inversion in the range experimentally accessible (from 10 °C to T_c). The helix handednesses have been also verified in the different nematic host ZLI 2359. In fact, for flexible molecules, a strong solvent dependence (including change of handedness) may be observed.[9] Again, in all cases the induced cholesterics have the same handedness in both solvents. This indicates that the positive/negative alternation of β with increasing the number of naphthyl units is not accidentally due to the temperature at which β is determined or to the molecular structure of the solvent.

To test the possibility of inducing oppositely-handed cholesteric phases by homochiral helices of different length we have performed some model calculations with the surface chirality method.[8] Within this approach, the twisting power of a given dopant in a nematic solvent can be calculated as Equation (2):

$$\beta = (N_A\ \xi/2\ \pi\ K_{22}\ \nu_m)\ Q \qquad (2)$$

where N_A is the Avogadro number, K_{22} and ν_m are the twist elastic constant and the molar volume of the liquid crystal solution, respectively, the parameter ξ *is* the orienting strength of the medium (and is related to the degree of order of the liquid crystalline dolvent). Q, denoted as chirality parameter, depends on the coupling of the chirality and orientational behavior of the dopant. In fact, the chirality parameter Q can be expressed in terms of the ordering tensor $\boldsymbol{S}$ and the helicity tensor $\boldsymbol{Q}$:

$$Q = -\sqrt{(2/3)}\ (Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \qquad (3)$$

The ordering tensor—its Cartesian component S_{ii} specifies the degree of alignment to the local director of the *i*th-molecular axis—is in turn obtained from a molecular tensor $\boldsymbol{T}$ which is calculated on the basis of the molecular surface of the dopant. The components T_{ii} and Q_{ii} quantify, respectively, the anisometry and the helicity of the molecular surface, as viewed along the *i* axis. In the case of flexible molecules, the chirality parameter Q is obtained as the average of the values calculated for each possible conformation, weighted over the Boltzmann distribution.[19]

The oligonaphthyls of the present work have several internal degrees of freedom, comprising the aryl–aryl bonds and all the torsional angles of the lateral substituents; this would make the conformational analysis really cumbersome. However, the detailed information associated with the huge number of accessible conformations, although necessary to get reliable twisting power predictions, goes beyond our present purpose of grasping the reasons behind the observed alternation of handedness: this will be simply accomplished by focusing on a single conformer. Adoption of a "representative" conformer, selected with the criterion of simplicity, should be intended as a metaphor, aimed at singling out a few relevant features, useful for the comprehension of the counter-intuitive phenomenon under investigation.

For the series **2a–c** and **3a–c** the following choices have been taken: the naphthyl–naphthyl angle is assumed equal to 90°, with OH and OAc groups in the plane of the adjacent aromatic ring, and methoxy groups perpendicular to this plane. In particular, the OCH_3 groups attached to the middle naphthyl groups are rotated opposite to each other, just as opposite to each other as the OCH_3 groups linked to the same aromatic ring; on the contrary, adjacent methoxy substituents on different rings are oriented in the same direction. The structure obtained in this way for molecule **2c** is shown in a ball-and-stick representation in Figure 1. The geometries of **2b** and **2a** are obtained by removing from this structure one and two naphthyl groups at each end, respectively. The structures of **3a–c** differ from those of **2a–c** in a change of the sign of the dihedral angle between the central naphthyl groups. The Q values thus calculated are reported in Figure 1, together with model representations displaying the molecular surface of the conformers of **2a–c** and **3a–c**. Colored patches correspond to contributions to the chirality parameter Q from different groups in the molecule.[22]

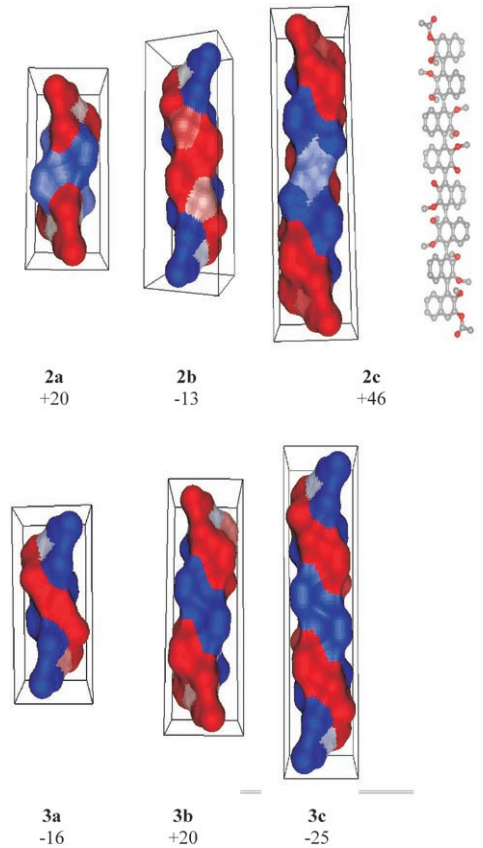


Figure 1. Molecular surface and chirality parameter Q ($Å^{-3}$) for the selected conformers of **2a–c** and **3a–c**. The smoothed molecular surface was obtained by using a rolling sphere radius of 3 Å, and colors are used to show the contribution of different groups to the whole Q value. The color code is such that red and blue correspond to right- and left-handed contributions to Q, respectively. The box shows the orientation of the principal axes of the Saupe matrix **S** (describing the molecular alignment to the local director).

We can see that, despite the common *P* helicity, the **2a–c** structures are characterized by chirality parameters which alternate in sign with length; namely, the same sign alternation exhibited by the experimental β values is obtained. It appears from Figure 1 that the molecular surfaces of **2a** and **2b** or **2b** and **2c** look quasi-enantiomorphic and the various groups in a molecule can give contributions of different magnitude and sign to the twisting power. The contribution of a given group depends on its average orientation in the liquid-crystal environment, therefore it is not a constant, but can change from molecule to molecule. Moreover, it can be modified by a conformational change. This clearly appears from Figure 1, where one can see that, for example, the terminal groups give contributions of opposite sign in **2b** and **2a** (or **2c**). These considerations point to the importance of local effects and the lack of significance of a global parameter as the stereochemical descriptor, for the phenomenon of cholesteric induction. Analogous considerations could be made for **3b** in comparison with **3a** and **3c**. This loose mirror image relationship also exists between the pairs **2a–3a**, **2b–3b** and **2c–3c**. Noteworthy these simple relations between molecular shapes according to the number of naphthyl groups in an oligomer, and the corresponding changes of cholesteric handedness, derive from the roughly perpendicular geometry of the naphthyl–naphthyl bond; a different sign dependence on oligomer length could be obtained for other values of this angle.

It is interesting to see how the chirality parameter Q changes when the chemical structure differences between the series **2** and **1** are introduced in the "representative" conformer. To model derivatives **1**, a wider twist angle (120°) was assumed between the central naphthalene rings, taking into account the steric hindrance between the two facing OCH_3 groups (replacing the two hydroxy groups). In the terminal OCH_2Ph groups, the OCH_2 bond was taken in the same plane of the adjacent naphthyl and perpendicular to the phenyl plane, as predicted by semiempirical PM3 calculations. By averaging over the four structures differing only in the orientation of terminal phenyls (on either side of the nearby naphthyl), positive values of similar magnitude, $Q \sim +30\ Å^{-3}$, were obtained for all derivatives **1b–c**. Thus, calculations confirm that changes in the substitution pattern, can modify the dependence of β sign on length of homochiral oligonaphthalenes.

Circular dichroism (CD): Circular dichroism is widely employed for studying the conformation and configuration of chiral molecules because it is highly sensitive to small variations of the molecular structure.[23] In the case of binaphthyl compounds, CD spectroscopy exploits the analysis of the exciton couplet originating from the ^1B electronic transition of the naphthalene chromophore at about 230 nm. When the axial absolute configuration is *S*, a positive couplet is observed with a positive branch at low energy and a negative one at high energy (provided that the dihedral angle between the two naphthyl rings is smaller than a critical value estimated around 100–110°, as usually observed).[24] (all-*S*)-

Oligonaphthalenes present, as expected, a positive couplet[14,25] corresponding to the ^{1}B transition: this couplet is non-conservative, with the low-energy branch more intense than the low-energy one. The inversion of the central stereoaxis does not affect, to an appreciable extent, the CD spectra and derivatives **3a–c** present spectra very similar to those of the corresponding compounds **2a–c** (see, for example, CD spectra of compounds **1b**, **2b** and **3b** reported in Figure 2). Therefore, in the case of these oligonaphthalenes, CD spectroscopy is not able to detect any relevant difference in compounds differing only in the number of monomeric units, while cholesteric induction is sensitive to this structural variation, as shown above.[26]

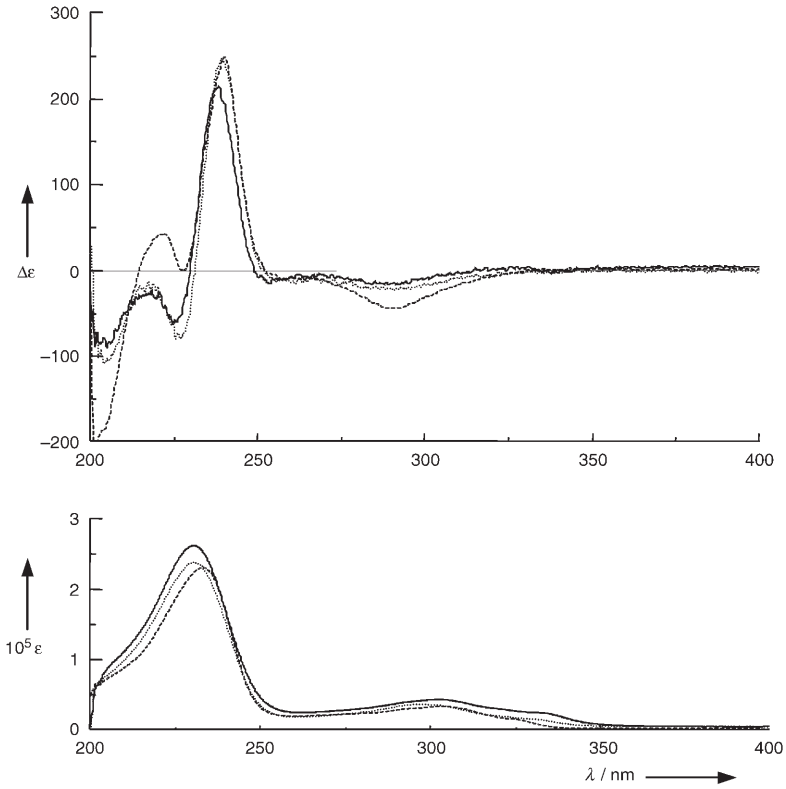


Figure 2. CD (upper frame) and absorption (lower frame) spectra of compounds **1b** (dashed line), **2b** (dotted line) and **3b** (full line) recorded in THF at room temperature.

Conclusion

Chirality is a peculiar molecular feature and its manifestations elude any trivial interpretation. Indeed, chirality is not an experimental property and different, often completely uncorrelated responses are obtained depending on the experiment used to probe it. The homochiral oligonaphthalenes considered in this work are a striking example. Their structure has a clear helicity and their CD spectra, sensitive to the arrangement of the aromatic rings, simply reflect the helical right-handed distribution of the latter. On the contrary, a more complex behavior is displayed by the helical twisting power, which can even alternate in sign with oligomer length within a given series. Model calculations have been performed to shed some light on the mechanism underlying such unexpected behavior; they show the importance of substituents in the aromatic rings in mediating the twisting ability of oligonaphthalenes. As a consequence, the twisting power cannot simply be correlated with a global stereochemical descriptor of the molecule. The same is true also for a homochiral series of propeller-like heptalenes for which the handedness of the induced cholesteric depends critically on the substituents attached to the chiral core.[6]

The results presented in this work, contrary to any simple intuition, are a confirmation of the subtle effects underlying transfer of chirality from molecular to mesoscopic level. This is not a peculiarity of cholesteric induction: recently, Monte Carlo simulations have shown that molecules of a given chirality can self-assemble into helical or twisted aggregates of opposite handedness;[27] also the packing of macroscopic right-handed helical screws depends critically on the ratio between helical pitch and diameter.[4a,28] Namely, there is increasing awareness of the scarce meaning of simple descriptors in phenomena governed by chirality of intermolecular interactions, which rather require a physically grounded modeling.

Experimental Section

The preparation of compounds **2a–c** and **3a–c** has been described elsewhere[14] as well as the preparation of **1a**, **1c** and **4**.[25] Derivative **1b** was prepared according to the same procedure of **1a** and **1c**.[25]

(all-*S*)-1b: m.p.168–169 °C; $[\alpha]_D^{22} = -184$ ($c = 0.474$ in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.75$ (s, 6H), 3.82 (s, 6H), 3.84 (s, 6H), 3.88 (s, 6H), 3.90 (s, 6H), 5.39 (s, 4H), 7.10–7.50 (m, 30H), 7.60–7.65 (m, 4H), 7.80–7.90 (m, 2H); IR (KBr): $\tilde{\nu}$ = 3060, 2936 1596, 1452, 1113, 1018 cm^{-1}; HRMS: m/z: calcd for $C_{84}H_{70}O_{12}$: 1270.4868; found: 1270.4882 [M^+]; elemental analysis calcd (%) for $C_{84}H_{70}O_{12}\cdot H_2O$: C 78.24; H 5.63; found: C 78.14, H 5.51.

Cholesteric pitch and handedness were obtained at variable temperature using the lens version of the Grandjean–Cano method.[29] The commercially available (Merck) nematic solvents E7 and ZLI 2359 are composed by eutectic mixtures of cyanobiphenyl (and terphenyl) compounds and cyanobicyclohexyl compounds, respectively. CD spectra were recorded with a JASCO J-710 Spectropolarimeter.

Calculations: The chirality parameter Q was calculated with a homemade code, based on the following procedure.[8] 1) Given the nuclear positions, the molecular surface was generated. This was defined as the surface

drawn by the center of a bead rolling on the assembly of interlocking van der Waals spheres centered on the nuclei[30] and was approximated by a set of triangles, obtained with the algorithm developed by Sanner et al.[31] A united atom representation was used for the calculation of the surface, with the following radii: $r_{CH} = r_{CH_3} = 2$ Å and $r_O = 1.5$ Å, along with a rolling sphere radius $r_O = 3$ Å. 2) The ***T*** and ***Q*** tensors were calculated by exploring the molecular surface by unit normal vectors and summing the contributions from all the triangles. 3) The elements of the Saupe ordering matrix ***S*** and the chirality parameter Q were calculated. The data reported in Figure 2 were obtained by giving the orienting strength the value $\xi = 0.025$ Å^{-2}. Given the molecular geometry, calculations could be performed on a desktop computer in a few seconds. Group contributions to the chirality parameter were evaluated with a homemade code and visualized with the software Geomview.[32]

Acknowledgements

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