

Effects of Carborane-Containing Liquid Crystals on the Stability of Smectic Phases

Andrew G. Douglass, Krzysztof Czuprynski,[‡] Michelle Mierzwa, and Piotr Kaszynski*

Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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The mesogenic properties of three structurally similar compounds containing 1,10-dicarbodecaborane, 1,12-dicarbodecaborane (carboranes), or bicyclo[2.2.2]octane are investigated in pure states and binary mixtures. The carborane-containing compounds (**BC10** and **BC12**) exhibit nematic and monotropic smectic C transitions at lower temperatures than the analogous bicyclo[2.2.2]octane compound (**BO1**). The thermal stabilities of the smectic phases for **BO1** are generally reduced by addition of the carborane analogues except for the smectic C phase, the stability of which is enhanced for equimolar concentrations. The effects exerted by the carborane mesogens on mesophase stability are consistent with their relative molecular sizes.

Introduction

p-Carboranes **1** and **2** (Figure 1) are chemically and thermally robust inorganic ring systems that can serve as effective structural elements of calamitic liquid crystals.^{1–6} The relatively high acidity of the C–H group ($pK_a = 27.1$ and 26.8 for **1** and **2**, respectively⁷) and the high nucleophilicity of the conjugate bases make them easy to incorporate into a variety of chemical structures^{8,9} to produce the necessary rodlike molecular shapes. The carboranes combine unique symmetries (either 4- or 5-fold rotation axes), molecular dimensions (Figure 1), and electronic properties. For example, they are three-dimensional σ -aromatic compounds¹⁰ with marginal UV absorption^{11,12} and highly polarizable electrons.¹³ These molecular properties will, in turn, influence bulk properties of materials such as mesophase stability, birefringence, and photochemical stability. For instance, we have recently demonstrated

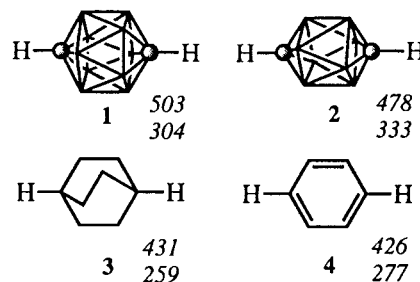


Figure 1. Rings **1–4** with calculated (HF/6-31G*) molecular dimensions in picometers: diameter of cylinder of rotation carved by hydrogen atoms (top value) and HC...CH interbridgehead distance (bottom value). In **1** and **2** each vertex corresponds to a BH fragment and the sphere represents a carbon atom.

that the nematic and isotropic refractive indices of a mesogen can be increased without increasing the UV absorption or birefringence by using carborane **1** as a structural element.⁵

Our other studies indicate that derivatives of carborane **1** prefer the formation of nematic phases and are effective suppressants of smectic phases in binary mixtures.^{1,4–6} This, in turn, might make them good candidates for nematic devices.¹⁴ In fact, smectic phases in pure carborane-containing mesogens are rare and only monotropic S_A and S_C phases have been found thus far.^{1,4}

The observation of the smectic C phase in **BC12**¹ prompted us to undertake systematic studies comparing and contrasting the relative effects of three ring systems, 1,12-dicarbodecaborane (**1**), 1,10-dicarbodecaborane (**2**), and bicyclo[2.2.2]octane (**3**), on the mesogenic properties. Here we report synthesis, optical microscopy, differential scanning calorimetry, and the

[‡] The 1997 COBASE Fellow on leave from Military University of Technology, Warsaw, Poland.

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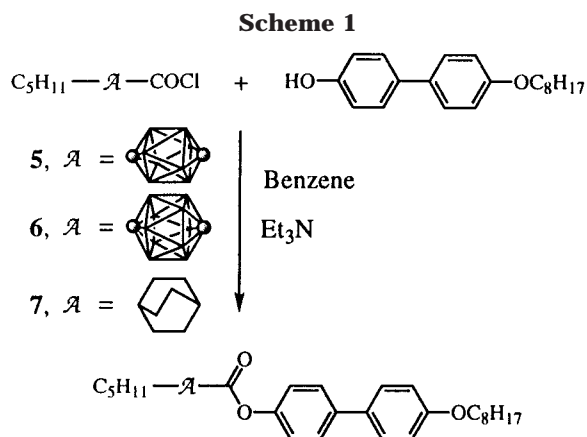
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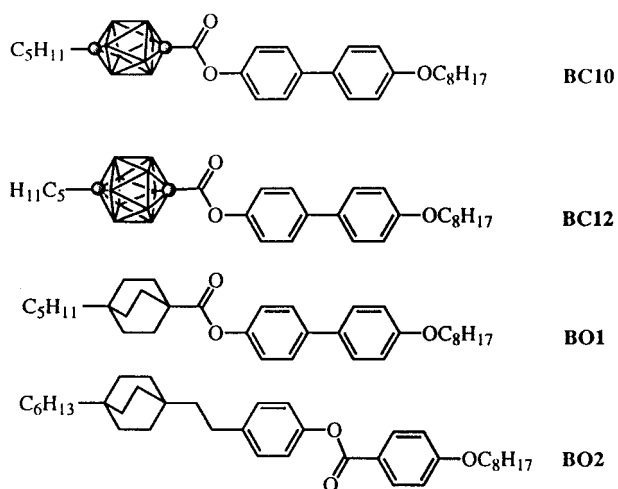
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formulation of binary mixtures of three structurally similar esters, **BC12**, **BC10**, and **BO1**.



Results and Discussion

The esters **BC10**, **BC12**, and **BO1** were synthesized from carbonyl chlorides **5**, **6**, and **7**, respectively, and 4'-octyloxy-4-biphenol according to Scheme 1. The preferred reagent for the preparation of chlorides **5** and **6** from the corresponding carboranylcarboxylic acids is PCl_5 ,¹⁵ while the bicyclo[2.2.2]octane-1-carbonyl chloride (**7**) was prepared using $SOCl_2$.¹⁶ In contrast to the straightforward synthesis of the carborane esters **BC10** and **BC12**, the formation of the bicyclo[2.2.2]octane ester **BO1** required prolonged heating due to low reactivity of the acid chloride **7**.¹⁷

The transition temperatures and transitional enthalpies for **BC10**, **BC12**, **BO1**,¹⁸ and **BO2**¹⁹ are presented in Table 1. Both carborane derivatives form enantiotropic nematic and monotropic smectic C phases. The nematic phases were assigned on the basis of the highly mobile, schlieren textures viewed by polarized light microscopy. The smectic C phases formed only schlieren

textures which are very similar to those for the nematic. Assignment of the smectic C phase for **BC12** has been confirmed by testing miscibility with the known smectic C compound **BO2** (Figure 2) and by mixing with **BO1** (vide infra).

The previously reported transition temperatures and phase assignments for **BO1**¹⁸ are in good agreement with our data, with the exception that we believe that there are highly ordered, tilted smectic phases below the smectic B. The transition at 93.4 °C previously reported as crystal-smectic B exhibits no hysteresis, suggesting that it is actually a smectic-smectic transition (Figure 3). When studied by optical microscopy, the homeotropic texture for the smectic B phase is transformed into a mosaic texture when cooled into the smectic X phase. Microscopic, DSC, X-ray diffraction, and miscibility studies are currently underway to establish the full mesophase and crystal polymorphism for **BO1**, and the results will be published elsewhere.

In contrast to **BO1**, which has a rich smectic polymorphism below its nematic phase, the carboranes **BC12** and **BC10** each exhibit only the smectic C phase below the nematic. The nematic phase for **BC12** has greater thermal stability than that for **BC10**, which is consistent with the general trend in other pairs of mesogens containing either the 10- or 12-vertex carboranes.⁶ In contrast to the relative nematic phase stabilities, the smectic C phase for **BC12** has lower thermal stability than that for **BC10** (Table 1). The mesophase transition temperatures for the two carborane-containing compounds are significantly lower than those for comparable transitions in **BO1**. This suppression of smectic properties and depression of T_{NI} that occurs when substituting a carborane unit into a liquid crystal core is in general accord with our other observations for 12-vertex carborane derivatives^{1,4,5} and is now demonstrated for a 10-vertex carborane compound.

The phase diagrams for binary mixtures of **BO1**-**BC10** and **BO1**-**BC12** (Figure 4) show that the nematic phases exhibit ideal mixing in both cases while the smectic C curves exhibit positive deviations. The **BO1**-**BC10** equimolar mixture shows the greatest enhancement in smectic C stability, estimated to be 22 °C (Figure 4a), while the maximal deviation for the **BO1**-**BC12** system is estimated to be 13 °C at 50 mol % **BC12** (Figure 4b). The smectic A, smectic B, and smectic X phases for **BO1** are all destabilized when the concentration of either carborane is increased. This suppression is most marked for the 12-vertex carborane; the smectic A and smectic X phases are both strongly destabilized above 20 mol % **BC12** and the smectic B phase is not observed for concentrations of **BC12** above 10 mol %. Above 40 mol % **BC12**, only the nematic and smectic C phases are observed. By comparison, the smectic A and smectic X phases for **BC10**-**BO1** exhibit a linear decrease in stability with respect to concentration and the smectic X phase is observed for mixtures containing up to 70 mol % **BC10**.

The destabilization of smectic phases induced by the **BC12** additive is greater than that observed for **BC10**. This is in accord with the lower smectic C-nematic transition temperature for the pure **BC12** than the analogous transition for the 10-vertex derivative **BC10** and can be rationalized on the basis of the relative steric

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Table 1. Phase Transition Temperatures and Transitional Enthalpies for BC10, BC12, BO1, and BO2^a

compd		C ^b	S _G	S _X	S _B	S _C	S _A	N	I
BC10	T/°C	•58.5				(•46.0)		•153.0	•
	ΔH/kcal mol ⁻¹	•3.98				•0.06		•0.22	•
BC12	T/°C	•80.3				(•40.0)		•167.3	•
	ΔH/kcal mol ⁻¹	•5.28				•0.09		•0.20	•
BO1^c	T/°C	•67.8		•93.4	•129.8	•143.7	•185.3	•219.1	•
	ΔH/kcal mol ⁻¹	•4.42		•0.28	•0.41	• ^d	•0.11	•0.19	•
BO2^e	T/°C	•75.5	(•70)			•90		•196	•

^a Observed phases are denoted by bullets and monotropic transitions are in parentheses. C, crystal; S, smectic; N, nematic; and I, isotropic. ^b Melting points were determined on first heating. ^c Literature values:¹⁸ C 95.6 S_B 128.8 S_C 144.7 S_A 185.8 N 220.9 I. ^d Second order transition. ^e Reference 19.

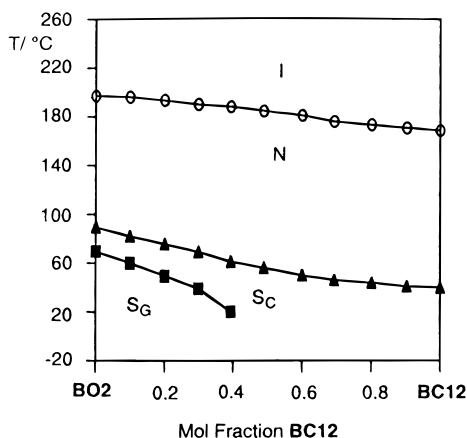


Figure 2. Binary phase diagram for **BO2**–**BC12**. The lines are guides to the eye.

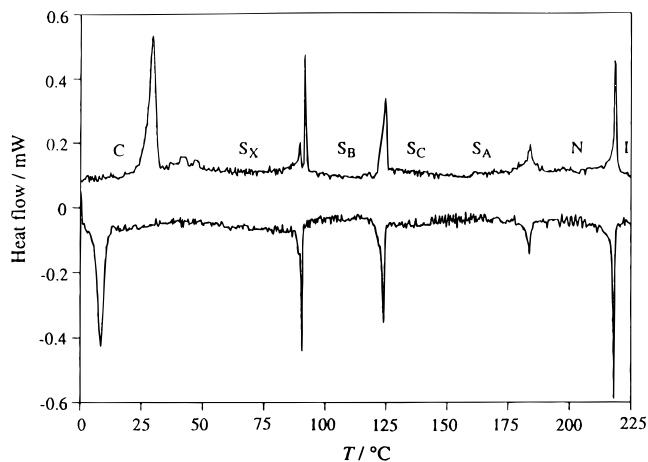


Figure 3. DSC traces for **BO1** on cooling (lower) and on subsequent heating (upper) recorded at 2 °C min⁻¹.

effects of the two carboranes. Substitution with bicyclo[2.2.2]octane, 10- or 12-vertex carborane rings has a minimal effect on overall molecular length but a marked effect on the molecular width. Bicyclo[2.2.2]octane (**3**) and benzene (**4**) have similar diameters which are smaller than those for the carboranes (Figure 1). It is known that the addition of a lateral group to a mesogen suppresses smectic phases, presumably by reducing the ability of molecules to pack efficiently in lamellar arrangements.²⁰ By analogy, the broader 12-vertex carborane might be expected have a greater disruptive effect on lamellar organization than the 10-vertex carborane, causing a greater suppression in smectic behavior. It is possible that other molecular influences

may be responsible for, or contribute to, the smectic destabilization, but certainly the results are consistent with this rationalization. Similarly, the stabilization of the smectic C phase that occurs for equimolar mixtures is most pronounced for the 10-vertex carborane, although the reason for this stabilization is not clear. This observation of smectic phase stabilization is not unique and we have noted the enhanced stability of the smectic E phase for a binary mixture of a similar carborane-containing system.⁴

With respect to potential commercial application, the results indicate that the carborane-containing compounds are compatible with bicyclo[2.2.2]octane-containing compounds and that they are potentially useful additives. For example, a 3:2 mixture of **BO1** in **BC12** has a short-range smectic A phase and a wide-range smectic C phase and the highly ordered smectic phase is suppressed to below room temperature, which is desirable for smectic C device technologies.²¹

Conclusions

The 10- and 12-vertex carborane-containing compounds **BC10** and **BC12** exhibit similar mesogenic properties. Both compounds form nematic and smectic C phases and both have mesophase transition temperatures that are lower than the analogous bicyclo[2.2.2]octane ester **BO1**. Compounds **BC10** and **BC12** show good miscibility with all-organic mesogens, and the smectic C phase assignments are confirmed by miscibility studies. Binary mixtures of **BO1** with both **BC10** and **BC12** exhibit the greatest enhancement of the smectic C phase stability at equimolar concentrations, while the suppression of the smectic B and smectic X phases for **BO1** is most pronounced when **BC12** is the additive. The effects of the carboranes on smectic phase stabilities in their pure compounds and in mixtures with **BO1** are consistent with their relative molecular sizes.

Experimental Section

The phase transition points of the compounds and their mixtures were determined using a PZO "Biolar" polarized light microscope equipped with an HCS250 Instec hot stage. Thermal analysis was obtained using a Mettler DSC 30 instrument. Transition temperatures were ascertained using small samples (1–2 mg) and a heating rate of 1 °C min⁻¹, while for the transition enthalpies large samples (10–15 mg) and fast heating (10 °C min⁻¹) were used. Melting points are those for first heating. The phase diagrams were determined by the

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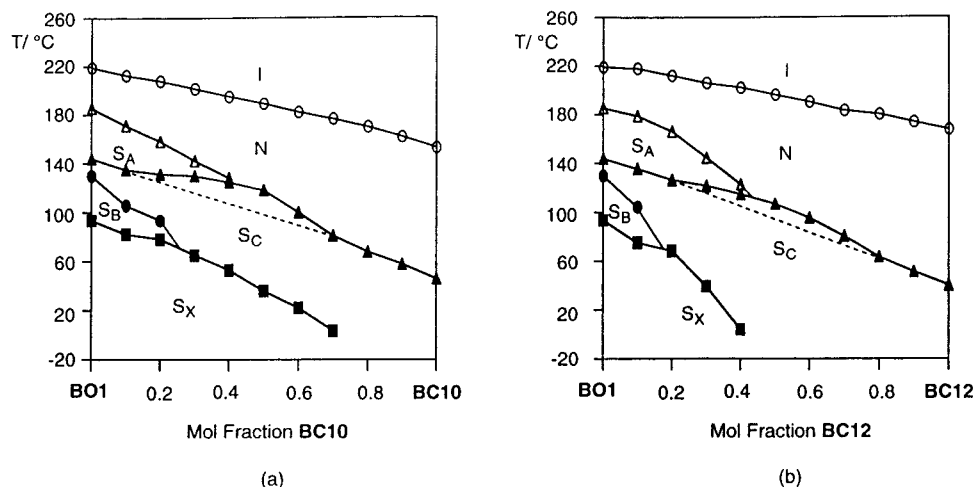


Figure 4. Binary phase diagrams for **BO1-BC10** (a) and **BO1-BC12** (b). The lines are guides to the eye. The dashed lines indicate the transition points expected for ideal mixing.

single concentration method. ^1H and ^{13}C NMR spectra were obtained on a Bruker 300 MHz instrument in CDCl_3 referenced to the solvent. ^{11}B NMR spectra were obtained using a Bruker 200 MHz spectrometer and referenced to $\text{B}(\text{OMe})_3$. IR spectra were recorded using an ATI Mattson Genesis FT-IR by deposition of a thin film from solution onto sodium chloride disks. Mass spectrometry was performed using a Hewlett-Packard 5890 instrument (GCMS). Elemental analysis was provided by Atlantic Microlab, Norcross, GA. Benzene was dried by distillation from calcium hydride and triethylamine by standing over potassium hydroxide. 10-Pentyl-1,10-dicarbadecaborane(8)-1-carboxylic acid was purchased from Katchem.

10-Pentyl-1,10-dicarbadecaborane(8)-1-carboxylic Acid 4'-Octyloxybiphenyl-4-yl Ester (BC10). 10-Pentyl-1,10-dicarbadecaborane(8)-1-carboxylic acid (100 mg, 0.426 mmol) and PCl_5 (193 mg, 0.447 mmol) were placed in a dry flask, and dry benzene (3 mL) was added. The reaction was stirred under nitrogen for 20 min at 40 °C, forming a clear solution. The solvent was removed to yield a colorless oil and after flushing with nitrogen, dry benzene (3 mL) was added to dissolve the acid chloride **5**. This solution was added dropwise to a stirred solution of 4'-octyloxybiphen-4-ol (135 mg, 0.447 mmol) and triethylamine (0.062 mL, 0.447 mmol) in dry benzene (2 mL) and the mixture stirred overnight at room temperature under nitrogen. The solution was then filtered through a silica gel plug eluted with benzene and the solvent removed. The product was purified by chromatography (methylene chloride:hexanes, 1:4) to give 188 mg (80% yield), followed by repeated recrystallization from pentane, giving 119 mg (54% yield): mp 58.5 °C; ^1H NMR δ 1.0–3.2 (br m), 0.92 (t, $J = 6.9$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H), 1.20–1.60 (m, 14H), 1.77–1.86 (m, 2H), 1.93–2.04 (m, 2H), 3.24 (t, $J = 8.4$ Hz, 2H), 4.00 (t, $J = 6.5$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 8.6$ Hz, 2H), 7.52 (d, $J = 8.7$ Hz, 2H), 7.62 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR δ 14.00, 14.07, 22.45, 22.63, 26.04, 29.23, 29.35, 29.68, 31.54, 31.69, 31.80, 35.12, 68.04, 105.86, 114.80, 121.47, 127.69, 128.05, 129.34, 132.41, 139.19, 149.71, 158.87, 163.56; ^{11}B NMR δ -11.54 ($J_{\text{BH}} = 147$ Hz); IR 2928, 2857, 2606, 1761, 1606, 1498, 1467, 1245, 1203, 1168, 1138 cm^{-1} ; EIMS m/e 517–512 (max at 515, 75, M), 219–215 (max at 218, 100), 185 (48), 157 (22). Anal. Calcd for $\text{C}_{28}\text{H}_{44}\text{B}_8\text{O}_3$: C, 65.29; H, 8.61. Found: C, 65.13; H, 8.55.

12-Pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic Acid 4'-Octyloxybiphenyl-4-yl Ester (BC12). The ester was prepared and purified in a manner analogous to that for **BC10** using 12-pentyl-1,12-dicarbadodecaborane(10)-1-carboxylic acid⁵ to give 54% yield after chromatography and 37% yield of white crystals after repeated recrystallization from pentane: mp 80.3 °C; ^1H NMR δ 1.0–3.5 (br m), 0.86 (t, $J =$

7.3 Hz, 3H), 0.90 (t, $J = 6.2$ Hz, 3H), 1.05–1.55 (m, 16H), 1.60–1.70 (m, 2H), 1.75–1.85 (m, 2H), 3.97 (t, $J = 6.5$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.7$ Hz, 2H), 7.48 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR δ 13.83, 14.09, 22.17, 22.64, 26.03, 28.98, 29.23, 29.34, 31.11, 31.80, 38.37, 68.02, 74.12, 84.45, 114.75, 120.92, 127.56, 128.01, 132.23, 139.24, 149.23, 158.85, 161.31; ^{11}B NMR δ -14.10 ($J_{\text{BH}} = 165$ Hz); IR 2953, 2925, 2856, 2613, 1761, 1607, 1496, 1467, 1250, 1202, 1166 cm^{-1} ; EIMS m/e 541–535 (max at 538, 94, M), 243–239 (max at 241, 100), 185 (95), 157 (40). Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{B}_{10}\text{O}_3$: C, 62.42; H, 8.61. Found: C, 62.32; H, 8.62.

4-Pentylbicyclo[2.2.2]octane-1-carboxylic Acid 4'-Octyloxybiphenyl-4-yl Ester (BO1). 4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid (220 mg, 1 mmol) and freshly distilled thionyl chloride (4 mL) were stirred and refluxed for 4 h under nitrogen. The excess thionyl chloride was distilled off and to the resultant acid chloride **7** was added a solution of 4'-octyloxybiphen-4-ol (318 mg, 1.05 mmol) and triethylamine (0.145 mL, 1.05 mmol) in dry benzene (8 mL). The solution was stirred and refluxed for 48 h and then filtered through a silica gel plug eluted with methylene chloride. The product was purified by column chromatography (methylene chloride:hexanes, 1:4), giving 323 mg (62% yield) of white solid. Recrystallization from ethanol (twice) and hexanes (once) produced pure product as white crystals (120 mg, 24% yield): mp 67.8 °C; ^1H NMR δ 0.87 (t, $J = 6.9$ Hz, 6H), 1.05–1.50 (m, 24H), 1.72–1.83 (m, 2H), 1.85–2.00 (m, 6H), 3.97 (t, $J = 6.6$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 7.04 (d, $J = 8.6$ Hz, 2H), 7.45 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR δ 14.11, 22.69, 23.37, 26.06, 28.62, 29.26, 29.37, 30.37, 30.49, 31.82, 32.80, 39.85, 41.33, 68.07, 114.74, 121.72, 127.55, 128.04, 132.75, 138.34, 149.95, 158.69, 176.88; IR 2953, 2921, 2856, 1744, 1607, 1499, 1464, 1207 cm^{-1} ; EIMS m/e 505 (15, M + 1), 504 (40, M), 186 (27), 185 (31), 179 (100), 123 (26), 109 (32), 95 (39). Anal. Calcd for $\text{C}_{34}\text{H}_{48}\text{O}_3$: C, 80.91; H, 9.59. Found: C, 80.68; H, 9.44.

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