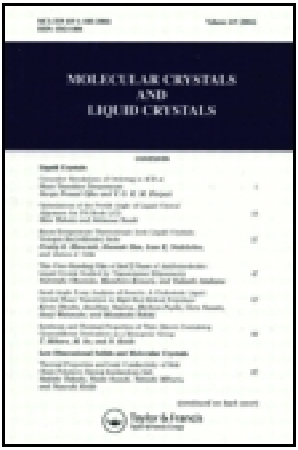

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pVT-Data and Tait-Equation for 4-trans-(4-alkyl)-Cyclohexyl-Benzonitriles

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pVT-Data and Tait-Equation for 4-trans-(4-alkyl)-Cyclohexyl-Benzonitriles

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A high pressure piezometer for density measurement up to 4 kbar is described. The pVT-data are given for three trans-4-R-(cyanophenyl)-cyclohexanes (R = C_3H_7, C_5H_{11} and C_7H_{15}) and for a eutectic mixture of these three compounds.

With $C = 0.2850$ for the four substances the isotherms between 50°C and 90°C can be represented by the Tait-equation in the *isotropic range*.

For the *nematic range* the Tait-equation has to be modified by $C^+ = C\,(V_0/V_1)$ with V_1 as the density at the transition point and V_0 as the fictitious density at 1 bar.

Directly after the isotropic-nematic transition the compressibility in the nematic phase is greater than that in the isotropic phase over a short pressure range.

I INTRODUCTION

For the interpretation of diverse physical properties, the dependence of density on temperature and pressure is required. This represents a scale for the mean distances between the molecules, which is characteristic for the present state of the substance.

With regard to the ordered states of the molecules in the different mesophases, the density step at the transition point and the compressibilities in the isotropic and the ordered state, liquid crystals are of special interest.

For interpretation the actual densities as a function of pressure must be represented by a suitable equation of state. The semi-empirical equation of Tait has turned out to be the most accurate for *n*-alkanes, mono-alcohols and other compounds.[1] In the present paper this equation is applied to the ordered phases of liquid crystals.

II THE HIGH PRESSURE PIEZOMETER

For pVT measurements up to 4 kbar (400 MPa) a high pressure piezometer was designed. The overall arrangement is shown in Figure 1.

The glass piezometer inside the autoclave A is filled with the measuring substance P, sealed off by mercury M. With increasing pressure the volume of the substance P decreases and the mercury level settles down in the internal calibrated tube. The mercury level is scanned by a tungsten single-crystal tip S, which gives electric contact when level is reached.

The self-sealed rotatable shaft B is turned without axial displacement to avoid any influence of pressure on the position of tip S.

Bridgman's "principle of the unsupported area" for high pressure closures[4] is modified for sealing of a rotating shaft.

The long bore inside the shaft B contains the measuring screw spindle C, which is milled plane at two opposite sides. The spindle C is turned together with the shaft B but is moved in axial direction in a screw plate E. With this

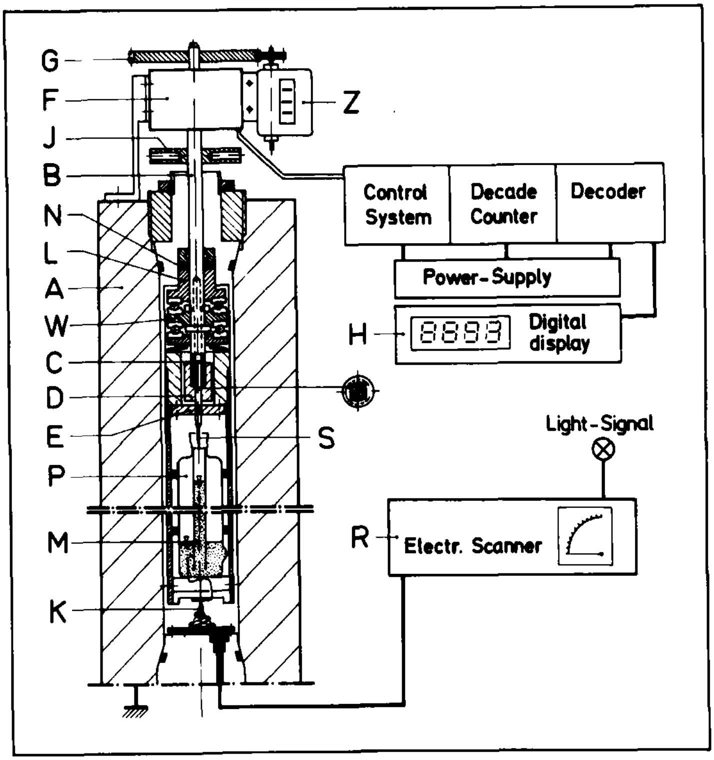


FIGURE 1 The Piezometer-System

design the level indication is no longer influenced by the compression of the sealings.

The number of revolutions needed to get electric contact with the mercury level is measured by the electronic altimeter and the scanning device as indicated in Figure 1. A reproducibility in density of ±0.0003 g/ml is reached.

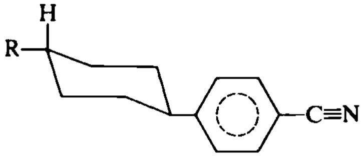
The absolute accuracy of the arrangement was checked with the pVT-data of *n*-hexane. The greatest deviation of density at high pressure between our measurements and those of Mopsik,[5] Landau and Wuerflinger[6] is 0.1 permille.

III RESULTS AND INTERPRETATION

In a preceding paper[7] the pVT-data of MBBA and EBBA were published. The compressibility of these liquid crystals is small compared to that of organic compounds. There is no significant difference between the compressibilities of the isotropic and the nematic phase.

For further investigations a new series of liquid crystals—the trans-1-(4-cyanophenyl)-4-alkylcyclohexanes, developed by E. Merck, Darmstadt—is of special interest for scientific and industrial application concerning pVT-behavior at high pressure, the applicability of the Tait-equation and the influence of the chainlength of the compound.

The molecular structure of the compounds is characterized by:



The structure and the physical properties of the 4-trans-(4-alkyl-cyclohexyl-benzonitriles has been investigated extensively by L. Pohl, R. Eidenschink, J. Krause and D. Erdmann.[8,9]

A survey of these and similar groups of liquid crystals regarding their application in electro-optical displays, watches, electronic calculators and data screens has been given by R. Eidenschink.[10]

The peculiarities of the 4-trans-(4-alkyl)-cyclohexyl-benzonitriles are:

a) Additional to the phenyl-group the compounds contain a cyclohexyl-group.

b) The ring-groups are arranged perpendicular to each other.

c) Compared to other liquid crystals the compounds containing a trans-1,4-substituted cyclohexane ring are very stable even at high temperatures.

Up to six isotherms of the three compounds, R = C_3H_7, C_5H_{11} and C_7H_{15}, and of a eutectic mixture of the three compounds were investigated in the isotropic and the nematic range. At atmospheric pressure the corresponding transition temperatures were 46.3°, 55.3°, 57.7°, and 52.2°C.

The range of the liquid crystal phase, limited by melting and clearing point, differs remarkably with the chainlength of the endgroup. The differences between melting and clearing point for the four substances at 1 bar were 4.3°, 25.3°, 27.7° and 55.2°C.

As example the measured densities of tr.-4-heptyl-(4-cyanophenyl)-cyclohexane are given in Figure 2.

At 60, 70, 80 and 90°C the compound is isotropic in the low pressure range and nematic in the high pressure range. The steps in density of 0.0054 g/ml at

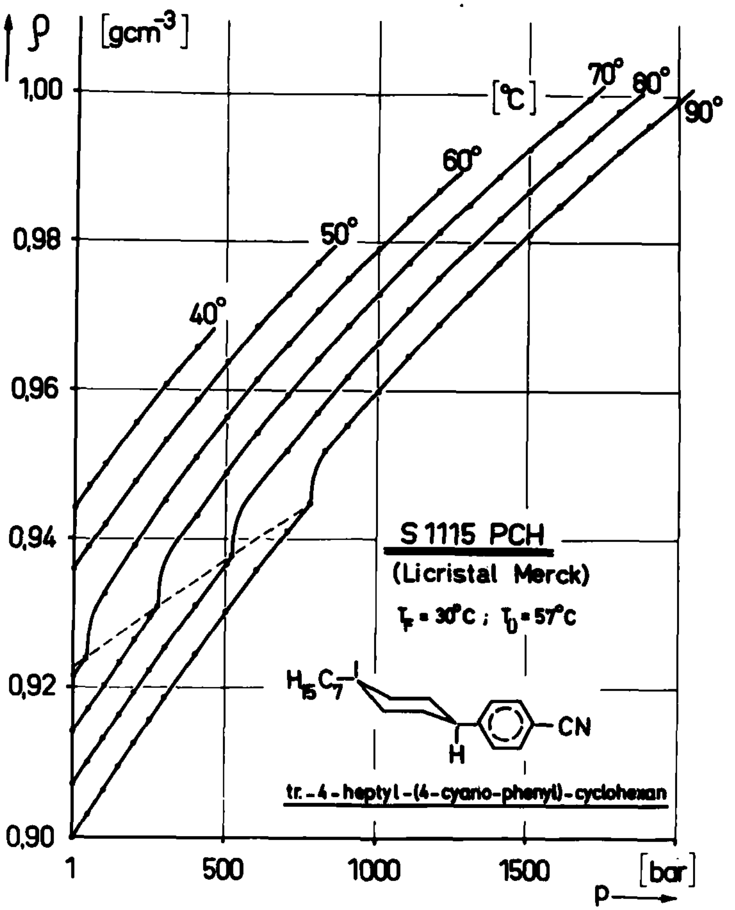


FIGURE 2 The ρ-p-T Diagram of tr.-4-heptyl-(4-cyanophenyl)-cyclohexane in the isotropic and the nematic range.

the transition point are greater than these of other liquid crystals like MBBA (0.0021 g/ml) or EBBA.

With increasing temperature the transition-pressure is shifted by about 24 bar/°C for S 1115 and 28 bar/°C for MBBA. These values are marginally increasing with temperatures, which means, that the transition-curve isotropic/nematic given in the/*p-T* diagram is not exactly straight. A similar behavior was found in an earlier investigation[11] on melting- and clearing-curves of azo- and azoxy-benzenes.

The densities of the three 4-trans-(4-alkyl)-cyclohexylbenzonitriles and of the eutectic mixtures are tabulated in the Tables I–IV as a function of pressure

TABLE I

Density of Trans-4-Propyl-(4-cyanophenyl)-Cyclohexane.
S 1103 PCH, Licristal Merck, in kg·m^{-3}

______ indicates the transition from the isotropic to the nematic phase

bar	50	60	70	80	90°C
1	952.2	945.3	938.6	932.1	925.7
50	955.2	948.3	941.7	935.3	928.9
100	965.0	951.2	944.7	938.3	931.9
200	971.9	957.3	950.7	944.5	938.1
300	978.7	(969.3)	956.6	950.5	944.2
400	—	975.9	962.4	956.3	950.2
500		981.8	968.0	962.0	956.1
600		987.3	980.0	967.4	961.7
700		992.5	985.6	972.7	967.0
800		997.4	990.8	984.5	972.1
900		—	995.6	989.8	977.1
1000			1000.2	994.8	988.1
1100			1004.6	999.4	993.1
1200			1008.8	1003.8	997.9
1300			1012.8	1008.1	1002.4
1400			—	1012.1	1006.6
1500				1016.1	1010.7
1600				1019.9	1014.7
1700				1023.5	1018.5
1800				1027.0	1022.2
1900				—	1025.7
2000					1029.1

Density of the isotropic phase at the transition point:

80	957.4				
290		963.1			
505			968.6		
726				974.1	
955					979.4

TABLE II

The Density of Trans-4-Pentyl-(4-cyanophenyl)-Cyclohexane.
S 1114 PCH, Licristal Merck; in kg·m^{-3}

_____ signifies the transition from the isotropic to the nematic range

bar	40	50	60	70	80	90°C
1	953.7	944.9	932.3	925.6	919.0	912.5
50	956.7	948.0	935.4	928.5	922.1	915.7
100	959.5	951.1	938.4	931.5	925.2	918.8
150	962.3	954.0	946.4	934.5	928.3	921.9
200	964.9	956.9	949.6	937.6	931.4	925.0
300	970.3	962.4	955.8	943.6	937.5	931.0
400	975.6	967.8	961.6	954.8	943.2	936.8
500	—	973.1	967.1	960.8	948.8	942.6
600		978.1	972.2	966.2	959.5	948.3
700		982.7	977.1	971.4	965.0	953.8
800		986.8	981.8	976.4	970.2	959.0
900		—	986.2	981.1	975.2	968.8
1000			990.3	985.5	980.0	973.8
1100			994.3	989.7	984.5	978.5
1200			998.2	993.7	988.8	983.1
1300			—	997.6	993.0	987.4
1400				1001.3	996.9	991.6
1500				1004.9	1000.6	995.5
1600				1008.4	1004.2	999.3
1700				—	1007.7	1003.0
1800					1011.2	1006.6
1900					1014.6	1010.1
2000					1017.9	1013.5
Density of the isotropic phase at the transition point:						
110			938.6			
335				945.5		
560					952.3	
800						959.0

and temperature. Above the horizontal lines, the substance is in the isotropic, below in the nematic phase.

The density of the isotropic phase at the transition point, given at the end of the tables, is obtained experimentally with good accuracy (sudden high increase of density with increase of pressure). In contrast to this the corresponding density of the nematic phase is not well defined because of the normally observed curvatures of the isotherm at the end of the transition.

The isobars are bent slightly convex against the T-axis.

A theoretical equation of state for nematic liquid crystals was set up by J. G. J. Ypma and G. Vertigen.[2] Furthermore, a theory of the density step at

TABLE III

The Density of Trans-4-Heptyl-(4-cyanophenyl)-Cyclohexane.
[S 1115 PCH, Licristal Merck;] in kg·m^{-3}

______ signifies the transition from the isotropic to the nematic range

bar	40	50	60	70	80	90°C
1	944.1	935.9	921.5	914.2	907.0	899.9
50	947.1	939.0	929.1	917.3	910.2	903.2
100	950.0	941.9	932.6	920.4	913.4	906.4
200	955.6	947.7	939.1	926.5	919.6	912.6
300	960.8	953.3	945.1	937.3	925.5	918.7
400	965.8	958.7	950.9	943.2	931.1	924.5
500	—	963.8	956.2	948.9	936.7	930.2
600		968.6	961.3	954.3	946.8	935.7
700		973.0	966.1	959.5	952.1	941.0
800		977.3	970.6	964.3	957.2	950.2
900		—	975.0	968.9	962.1	955.3
1000			979.2	973.2	966.7	960.1
1100			983.2	977.5	971.1	964.7
1200			987.0	981.5	975.4	969.2
1300			—	985.4	979.5	973.4
1400				989.2	983.4	977.6
1500				992.8	987.2	981.5
1600				996.4	990.8	985.3
1700				999.7	994.4	989.0
1800				—	997.9	992.6
1900					—	996.1
2000						999.4
Density of the isotropic phase at the transition point:						
40			923.9			
275				930.9		
520					937.8	
777						944.7

atmospheric pressure was set up and proved on *p*-azoxyanisole by S. Chandrasekhar and N. V. Madhusudana.[3]

For the ***mathematical representation*** of the pVT-data several equations of state were tested for diverse groups of compounds in an earlier paper.[1] It was found that

the TAIT-equation
$$\frac{V_0 - V}{V_0} = C \lg\left(\frac{B + p}{B + p_0}\right)$$

is the most suitable correlation for molecular interpretations, since

a) a very good representation of the measured densities is attainable

TABLE IV

PVT-Behavior of the eutectic Mixture: 30% (S1103) + 40% (S1114) + 30% (S1115); Merck NP 1083

Density in kg·m^{-3}

bar	25	40	60	70	80	90°C
1	966.8	953.8	932.5	925.6	919.3	912.9
50	969.5	956.7	935.6	928.7	922.5	916.1
100	972.2	959.8	938.7	931.7	925.6	919.3
200	977.7	965.7	944.7	937.8	931.7	925.5
300	982.7	971.1	955.2	943.7	937.6	931.6
400	987.5	976.1	960.9	949.5	943.4	937.6
500	992.1	981.0	966.4	959.9	949.2	943.5
600	996.4	985.6	971.6	965.4	954.6	949.1
700	1000.6	990.1	976.5	970.7	(964.2)	954.4
800	1004.6	994.3	981.3	975.6	969.5	959.5
900	—	998.2	985.9	980.3	974.5	964.4
1000		1001.9	990.2	984.8	979.2	973.4
1100		1005.5	994.3	989.1	983.8	978.2
1200		—	998.2	993.2	988.1	982.7
1300			1001.9	997.2	992.3	987.1
1400			1005.4	1001.0	996.3	991.2
1500			—	1004.6	1000.1	995.2
1600				1008.1	1003.8	999.1
1700				1011.5	1007.4	1002.8
1800				—	1010.8	1006.4
1900					1014.2	1009.9
2000					1017.4	1013.3
Density of the isotropic phase at the transition point:						
210			945.2			
440				951.8		
670					958.2	
903						964.3

TABLE V

Tait parameter for the isotropic range, B·[bar]
$C = 0.2850$ for all compounds and temperatures

Formula of page 202	60°	70°	80°	90°C
a) R = C_3H_7	1867	1812	1756	1701 bar
b) R = C_5H_{11}	1847	1793	1738	1683 bar
c) R = C_7H_{15}	1822	1767	1713	1657 bar
d) eutectic mixture (*a*, *c* 30%; *b* 40%)	1834	1779	1724	1670 bar

b) it contains only two material constants

c) C can be adapted as independent of temperature and B shows correlations to the molecular structure of the substance.

For most isotherms the transition isotropic/nematic of liquid crystals occurs at high pressures. For that reason V_0 of the Tait-equation for the nematic phase is not known with sufficient accuracy.

For isotherms beginning at the transition point p_1, V_1, the Tait-equation is modified to:

starting from: $$\mathcal{K} = -\frac{1}{V_0}\left(\frac{\partial V}{\partial p}\right)_T = \frac{C}{B+p}$$

$$\frac{V_1 - V}{V_1} = \frac{C \cdot V_0}{V_1} \lg\left(\frac{B+p}{B+p_1}\right) = C^* \lg\left(\frac{B+p}{B+p_1}\right)$$

The type of the Tait-equation is not altered, but $C^* = C \cdot V_0/V_1$ is no longer independent of temperature since V_1—the starting point of the nematic isotherm—is shifted considerably with temperature.

Together with the chosen value V_1, which can be a value after transition to nematic phase, the corresponding p_1 is inserted into the above formula.

For the *isotropic range* the same general value $C = 0.2850$ was found for all compounds independent of temperature. The constants B, which were calculated from the measured densities by computer evaluation are listed in Table V. With these constants the isotherms are reproduced within the experimental accuracy.

The constant B decreases with increasing chainlength of the endgroup R. It decreases for all compounds linearly by about 5.54 units/°C with increasing temperature. In approximation B of the mixture can be evaluated linearly from the constants of the pure components.

The *nematic range* proves to be more difficult. The constants C^+ and B are reproduced in Figure 3.

C^+ changes within the homologeous series from one compound to the other. It increases linearly with temperature and with chainlength. B decreases with increasing temperature. In first approximation B of the mixture can be evaluated again linearly from the B's of the pure components.

The constants C^+ yield no uniform C for the four compounds. It is a further advantage of the Tait-equation, that C can be varied within a certain range without noticable loss in accuracy, if B is adapted to the new value of C. With $C = 0.1800$ and a new set of adapted B-values a satisfactory reproduction of the isotherms can be achieved. These values are tabulated in Table VI.

It should be remarked, that in the interpretation of R. J. Ginell[12] constant C is a scale for the free volume of the liquid. In this sense it is understandable, that C changes drastically at the transition isotropic/nematic.

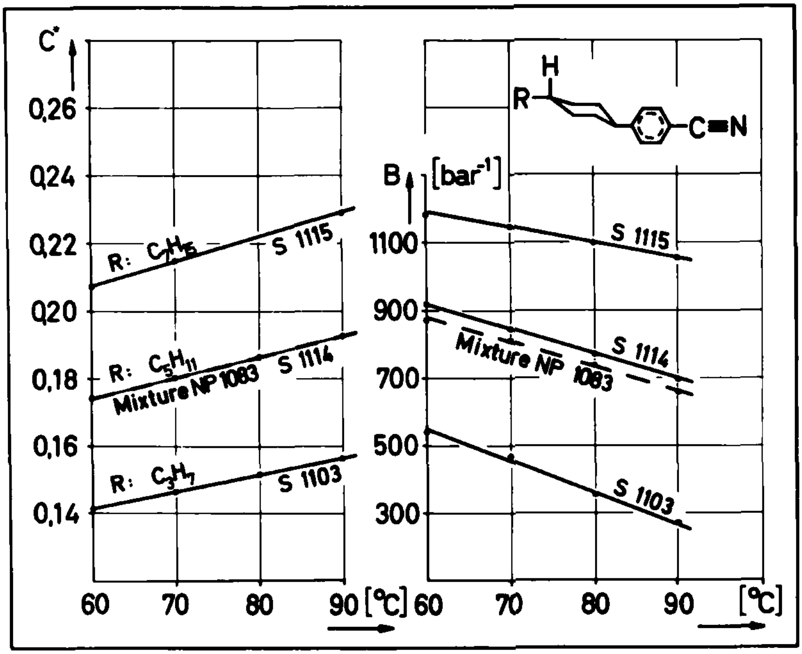


FIGURE 3 The Tait-Constants C^* and B of the three Benzonitriles and the eutectic mixture in the nematic range.

Constant B is the characteristic scale for the special compound of the homologeous series. It changes systematically with the chainlength of the molecule and decreases nearly linearly with increasing temperature. This enables the comparison of different substances and the performance of interpolations and of limited extrapolations.

Finally the ***compressibility*** as a function of pressure is obtained from the above representation. The compressibility curve of S 1115 is reproduced in Figure 4 as an example.

TABLE VI

Tait parameter for the nematic range $C = 0.1800$ for all compounds and temper.

Formula page 202	$C^* \cdot 10^4$				$B \cdot$(bar)			
	60°	70°	80°	90°	60°	70°	80°	90°
a) C_3H_7	1834	1862	1889	1917	890	814	715	622
b) C_5H_{11}	1818	1845	1872	1899	969	865	761	657
c) C_7H_{15}	1807	1834	1861	1889	984	879	774	669
d) mixture	1827	1854	1882	1907	959	855	751	647

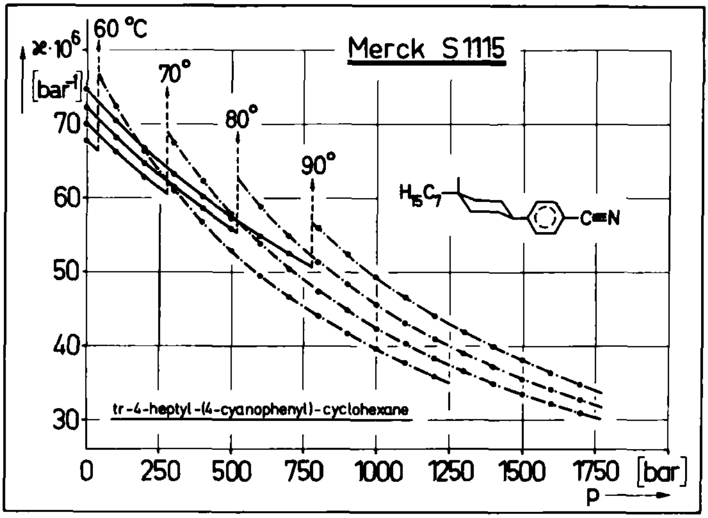


FIGURE 4 The Compressibility of S 1115 in the isotropic and the nematic phase.

The numerical values of the initial compressibility are similar to those of higher molecular alkanes and oils, the decrease with temperature somewhat weaker.

It may be of special interest, that the compressibility after the transition isotropic/nematic is remarkably greater than just before the transition. This means, that the ordered state is more compressible than the isotropic one. To higher pressures the compressibility in the nematic range decreases more rapidly than the extrapolated values of the isotropic phase.

Of course it should be considered, that the step in compressibility at the transition point is idealized by evaluating the compressibility of the two stages separately with the *B* and *C* of the Tables V and VI.

Figure 2 shows that the measured transition is extended over a certain range of about 50–70 bar. Therefore, instead of a sharp peak of infinite height—indicated in Figure 4 only by the arrows—a broader peak with greater compressibility values in the transition range would result from the experimental data.

Acknowledgments

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