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The Frank constants of some nematic liquid crystals

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Résumé. — Nous présentons des résultats concernant les constantes de Frank K_{11} et K_{33} de composés nématiques appartenant à deux séries homologues, les alkyl- et alcoxy-cyanobiphényles et celle du PAA. Ces résultats ont été obtenus dans deux laboratoires par des méthodes différentes. Leur concordance suggère qu'aucun d'entre eux n'est affecté d'erreurs systématiques.

Abstract. — We present results for the splay and bend constants, K_{11} and K_{33}, in two homologous series of nematic compounds, the alkyl- and alkoxy-cyanobiphenyls, and in PAA. They have been obtained in two laboratories using different methods, and the extent to which they agree gives confidence that neither set is significantly affected by systematic error.

1. Introduction.

Measurements of the Frank stiffness constants in nematic liquid crystals have been in progress at our two laboratories for some years. At Malvern the samples have been contained between surfaces treated to ensure homogeneous planar alignment of the director in the absence of any field, and electric fields have been used to tilt the director towards the normal : the progress of this Freedericksz transition has been monitored by measurement of the capacitance across the nematic layer. At Cambridge the samples have had homeotropic alignment initially, and the director has been tilted away from the normal by means of a magnetic field; optical methods have been used to monitor the transition. The critical field at which the transition begins gives the splay constant, K_{11}, in the first case and the bend constant, K_{33}, in the second, but in both cases values for the ratio K_{33}/K_{11} have been obtained by a computer fit to the data for higher fields.

Which method is in principle the more reliable is still open to debate. Some of the arguments which have been put forward in favour of the electrical method are :

(i) The dielectric anisotropy, $\Delta\varepsilon$, which is needed for the interpretation of the results, is measured in the course of the experiment, whereas the magnetic method requires a separate experiment to measure $\Delta\chi$;

(ii) The magnetic method also requires measurement of the thickness of the nematic layer, but when the electrical method is used this quantity is not directly relevant;

(iii) The range that is open to investigation above the critical field is less restricted when the field is electric.

Arguments that have been put forward in favour of the other method are :

(iv) The electrical method can be used only if the nematic material has quite a large positive dielectric anisotropy — $\Delta\varepsilon$ greater than + 1, say — which makes the magnetic method more versatile;

(v) The magnetic method is not open to the criticism [1, 2] that currents and space charges in the nematic may in some materials (though not, we believe, in the ones we have investigated) affect the results obtained;

(vi) It is sometimes easier to obtain homeotropic alignment, and to check that this alignment is truly homogeneous, than to obtain and check planar alignment.

(vii) The computer fit for fields above the critical is in principle more sensitive to the choice of K_{33}/K_{11} when the fields are magnetic [3].

Our purpose in this paper is not to argue the case for or against either method, but simply to bring together the results we have accumulated. The extent to which they agree shows that both methods are capable, with care, of giving good results and makes it seem very unlikely that the results are significantly affected, as has sometimes been suggested [4, 5], by limitations in the assumption that at the surfaces of the nematic film the director is firmly anchored in the preferred direction. For six of the ten nematics we have studied, values of the Frank constants, not entirely consistent with ours, have been published by other authors. For the remaining four no other results seem yet to be available.

2. Experimental details.

2.1 MATERIALS.

— The materials studied were the 4-n-alkyl-4'-cyanobiphenyl compounds,

$$C_nH_{2n+1}(C_6H_4)_2CN ,$$

with $n = 5, 6, 7, 8, 9$; the corresponding alkoxy-compounds $C_nH_{2n+1}O(C_6H_4)_2CN$, with $n = 5, 6, 7, 8$; and p-azoxyanisole. They will be referred to by the commonly used acronyms, nCB, nOCB or PAA as the case may be. The source of supply of cyanobiphenyls was the same for both laboratories (BDH Ltd), but the values we recorded for the temperature, T_c, of the nematic isotropic transition were not identical. For 5OCB, indeed, our values for T_c differed by as much as 2 °C (see Table II below), and they bracket the value suggested by more recent measurements on this substance. The implication seems to be that in neither laboratory were the procedures for measurement of temperature impeccable at the time when the data to be presented were collected. We hope to have removed the worst errors by presenting the data as functions of the temperature difference $(T_c - T)$, but errors in this temperature difference of a few tenths of a degree, systematic within the data for a single substance from one of the laboratories, are not out of the question.

2.2 THE ELECTRICAL METHOD.

— Descriptions of this method have been given in several previous publications [6-8]. Briefly, the required alignment was secured by prior evaporation onto the two glass plates which contained the nematic of a 200 Å layer of silicon monoxide at 60° to the normal; the AC voltage used to measure the capacitance could be varied in amplitude so as to provide the aligning field; edge effects were eliminated by use of the guard ring technique; the capacitance was measured with the cell empty and the result used to normalize measurements with the cell full; measurements at low voltages gave $\varepsilon_\perp$ directly, while a first estimate for $\varepsilon_\parallel$ could be obtained from a V^{-1} extrapolation of measurements at high

voltages, up to five times the critical voltage V_c; the sharpness of the transition at V_c was used to check that the initial alignment was indeed parallel to the plates and free of defects. We found that the application of a high voltage sometimes introduced defects which were slow to disappear subsequently, so the high voltage measurements were deferred in all our later experiments, until the range between V_c and say twice V_c had been thoroughly explored.

The computer programme used to fit the capacitance measurements above V_c allowed three parameters to be varied until the mean square deviation from the predicted curve for $C(V)$ was a minimum. These parameters were V_c (from which K_{11} could be calculated once $\Delta\varepsilon$ was known), $(K_{33} - K_{11})/K_{33}$, and also $\Delta\varepsilon/\varepsilon_\perp$. The values determined for $\Delta\varepsilon/\varepsilon_\perp$ in this way were consistent with, but more accurate than, values calculated from $\varepsilon_\perp$ and our first estimates for $\varepsilon_\parallel$. The sort of fit that could be achieved is illustrated by figure 1, where two typical sets of residuals are plotted : they are less than 10^{-4} V and show no systematic behaviour. As figure 1 suggests, the data used for fitting purposes were normally those taken in the range between V_c and $2 V_c$, but we saw no evidence that systematic discrepancies developed at higher voltages.

The results obtained for K_{11} by this method are estimated to be accurate to within $\pm 2 \%$, while the results for K_{33} should be within $\pm 5 \%$. The results were normally repeatable within these limits.

2.3 THE MAGNETIC METHOD.

— This has been described [3] in such detail as to make a further account inappropriate, though it is worth noting that the computer fit, as in the electrical case, was a three-parameter one; it was restricted, by limitations in the magnet available, to fields less than twice the critical value. Although one of the adjustable parameters which could in principle be found from the programme
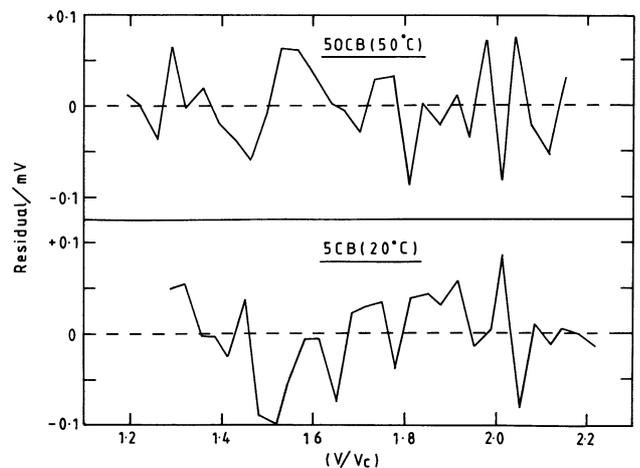
Fig. 1. — The residual discrepancies between measurements made by the electrical method and the best computed curve, in two typical cases. In both cases V_c was about 1 volt.

was the quantity

$$v = (n_e^2 - n_0^2)/n_e^2,\qquad(1)$$

it was desirable to have prior knowledge of this, so the refractive indices n_e and n_0 were measured by one of us (J. D. B.) using a wedge technique [9] with result that will be described elsewhere.

Presented with two discrepant sets of data for the anisotropy in the *mass* susceptibility, $\Delta\chi^{(m)}$, in 5CB, Bunning *et al.* chose to make use of values obtained by Buka and de Jeu [10], largely because for 7CB the results of Buka and de Jeu appeared to be supported by those of Schad, Baur and Meier [11]; Schad *et al.* estimated $\Delta\chi$ from separate measurements of $\Delta\chi/\Delta\varepsilon$ and $\Delta\varepsilon$. Subsequently, however, Schad and Osman [12] presented revised estimates for $\Delta\chi$ in 7CB which were about 5 % higher, and the values we obtain by combining their results for $\Delta\chi/\Delta\varepsilon$ with our own results for $\Delta\varepsilon$ (see Table I) are somewhat higher still. Following this revision, the results of Schad *et al.* for 7CB seem much more consistent with the measurements of Sherrell and Crellin [13] than with those of Buka and de Jeu. Since the Sherrell and Crellin values for the series of cyanobiphenyls are also more easy to reconcile with what is known about the susceptibility of related compounds such as biphenyl in the crystalline form, we prefer to trust these values in what follows, and to supplement them where necessary (e.g. for the alkoxy compounds) with unpublished data obtained using the same apparatus by Crellin. Crellin's data will be presented and discussed along with the refractive index data mentioned above.

Because the critical field depends upon $\Delta\chi$ rather than $\Delta\chi^{(m)}$ we also need to know the density. So far as the alkyl-cyanobiphenyls are concerned we have relied on the density measurements of Dunmur and Miller [14], extrapolating to lower temperatures where necessary. Dr. Dunmur has kindly supplied us with unpublished density data for 5OCB and 6OCB, while density measurements have been made on 5CB, 7OCB and 8OCB at Malvern by Mrs. J. Constant.

We believe the overall accuracy achievable by the magnetic method to be similar to that achieved by the electrical method i.e. ± 2 % for K_{33} and ± 5 % for K_{11}, though the possibility that some additional systematic error creeps in through the susceptibility cannot be ruled out. Note that of the two Frank constants determined the more accurate one is here K_{33}, whereas for the electrical method it is K_{11}.

3. Results.

According to Bunning, Faber and Sherrell [3] the two methods give distinctly different results in the case of 5CB. The discrepancies suggested by their figure 4 have been removed, however, (a) by the use of different values for $\Delta\chi^{(m)}$ for reasons discussed above, and (b) by refinement of the techniques and apparatus used at Malvern since the preliminary results on 5CB,

quoted in [3], were obtained; the most significant refinement, that of deferring the high voltage measurements, has been described in section 2.2. The revised results are compared in figure 2. Although small systematic differences between the two sets of points for both K_{11} and K_{33} are apparent for values of $(T_c - T)$ around 3 K, these may be accounted for by systematic errors in $(T_c - T)$ and the agreement overall is gratifyingly close. Dashed lines in this figure represent results obtained for 5CB by Madhusudana and Pratibha [15]. These authors used the earlier measurements, made by the magnetic method, of Karat and Madhusudana [16] and like them they estimated $\Delta\chi^{(m)}$ from the birefringence. We attribute much of the difference between their results and ours to the limitations inherent in such an indirect procedure.

It is evident from figure 2 that the electric and magnetic methods give virtually identical results for the ratio K_{33}/K_{11} in the case of 5CB. The temperature dependence of this ratio for four nCB compounds is shown in figure 3, and four nOCB compounds in figure 4. The agreement is satisfactory for all of these, with the obvious exception of 5OCB, but we differ somewhat from Schad and Osman's tabulated results for 7CB [12] which are indicated by crosses in figure 3.
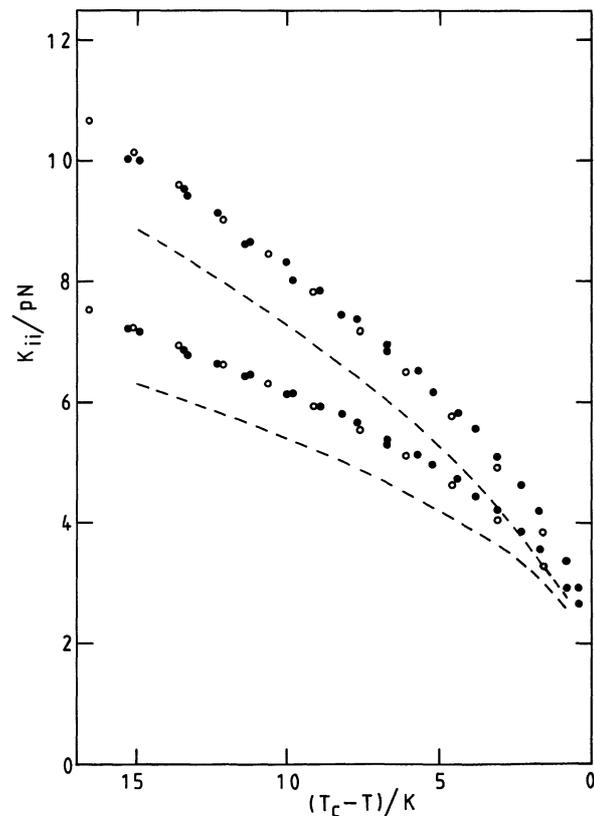

Fig. 2. — The splay and bend constants for 5CB : open circles, electrical measurements; filled circles, magnetic measurements; broken lines, reference [15]. The lower points and curve describe K_{11} and the upper ones describe K_{33}.

Table I.

$(T_c - T)$ K	$\Delta\varepsilon$	K_{11} pN	K_{33} pN	$10^{-3}\rho$ kg m^{-3}	$10^{12}\Delta\chi^{(m)}$ (kg m^{-3})$^{-1}$	K_{11} pN	K_{33} pN
5CB		$T_c = 35.1$ °C			$T_c = 35.6$ °C		
0.5	—	—	—	1.013	80	2.75	3.05
1	—	—	—	1.013	85	3.1	3.6
2	10.0	3.5	4.15	1.014	92	3.75	4.4
3	10.7	4.0	4.85	1.016	96.5	4.2	5.1
4	11.25	4.45	5.5	1.017	100.5	4.55	5.65
6	12.1	5.1	6.5	1.019	106.5	5.2	6.6
8	12.75	5.65	7.4	1.021	110.5	5.75	7.5
10	13.3	6.2	8.25	1.022	113.5	6.2	8.2
12	13.75	6.65	8.95	1.024	116	6.6	9.0
14	14.15	7.05	9.75	1.026	118.5	7.0	9.7
16	14.55	7.4	10.45	—	120.5	7.35	10.3
18	14.85	7.8	11.15	—	—	—	—
6CB		$T_c = 29.2$ °C			$T_c = 29.6$ °C		
0.5	—	—	—	1.004	69	2.4	2.6
1	—	—	—	1.005	75.5	2.75	3.05
2	8.3	2.85	3.2	1.006	81.5	3.35	3.75
3	8.95	3.3	3.75	1.007	85.5	3.85	4.3
4	9.45	3.75	4.3	1.008	89	4.25	4.75
6	10.2	4.4	5.05	1.010	94	4.9	5.5
8	10.75	4.95	5.8	1.011	98.5	5.35	6.15
10	11.2	5.4	6.4	—	101.5	5.65	6.75
12	11.6	5.8	6.95	—	—	—	—
14	11.95	6.15	7.5	—	—	—	—
7CB		$T_c = 42.3$ °C			$T_c = 43.0$ °C		
0.5	—	—	—	0.987	70	2.9	3.1
1	—	—	—	0.988	75.5	3.65	3.95
2	—	—	—	0.990	82	4.45	4.8
3	9.0	4.65	5.0	0.991	86.5	5.0	5.45
4	9.4	5.15	5.6	0.992	89.5	5.5	6.05
6	10.05	5.95	6.6	0.994	95	6.35	7.05
8	10.5	6.6	7.45	0.997	98.5	7.05	8.0
10	10.85	7.2	8.25	0.999	102	7.65	8.85
12	11.15	7.75	9.0	—	105	8.2	9.65
14	11.4	8.25	9.7	—	107.5	8.7	10.4
16	11.6	8.75	10.4	—	109.5	9.25	11.15
18	11.8	9.2	11.1	—	111.5	9.75	11.9
20	11.95	9.65	11.8	—	—	10.25	12.6
22	12.1	10.05	12.55	—	—	10.75	13.3
24	—	—	—	—	—	11.25	14.05
8CB		$T_c = 39.8$ °C			$T_c = 41.2$ °C		
0.5	—	—	—	0.981	60	2.85	2.8
1	6.75	2.95	2.7	0.982	68	3.5	3.5
2	7.65	4.0	3.75	0.983	74	4.35	4.35
3	8.2	4.7	4.6	0.985	78	5.0	5.05
4	8.6	5.4	5.5	0.986	81	5.65	5.8
5	8.9	6.0	6.4	0.987	84	6.25	7.1
6	9.15	6.7	8.1	0.988	87	6.75	9.7
6.2	9.2	6.8	8.7	0.988	88	—	10.5
6.4	9.25	6.95	9.3	0.988	88	—	12.65

Fig. 3. — The ratio between Frank constants for nCB compounds : open circles, electrical measurements; filled circles, magnetic measurements; crosses, reference [12].

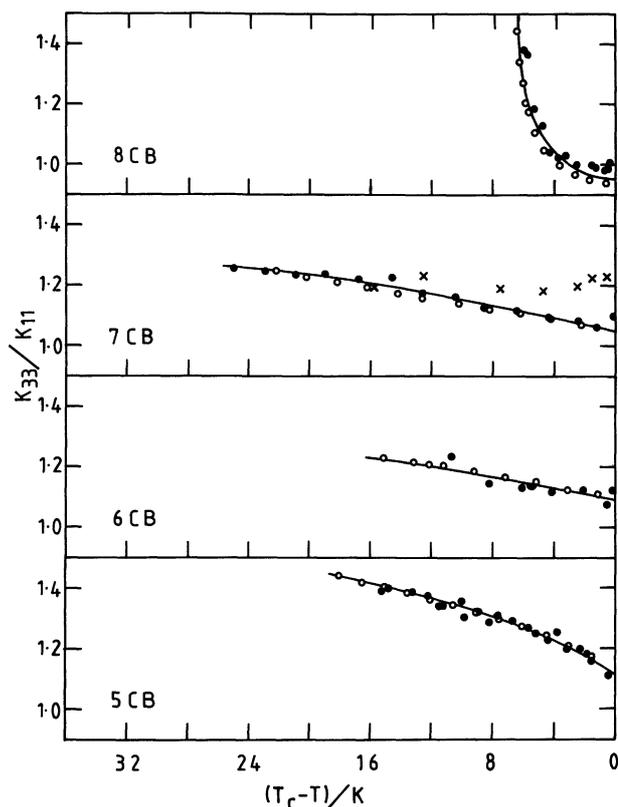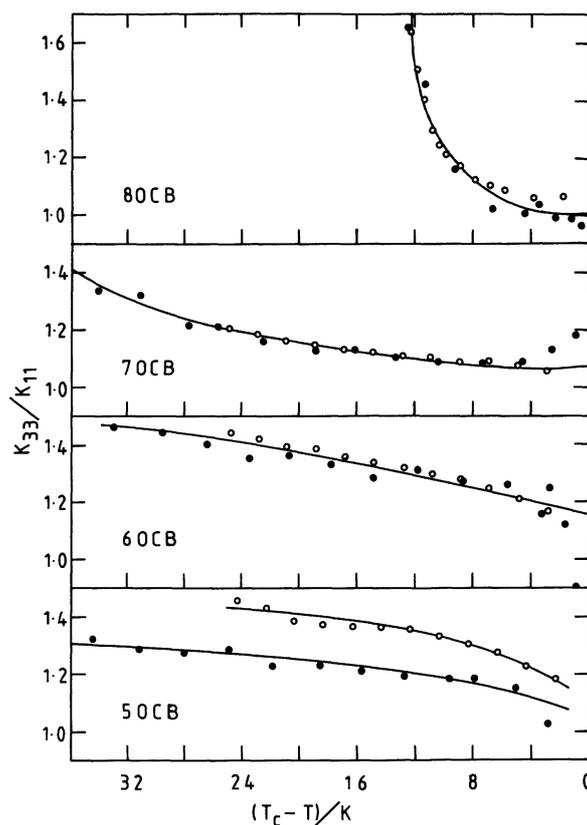Fig. 4. — The ratio between Frank constants for nOCB compounds : open circles, electrical measurements; filled circles, magnetic measurements.

The compounds 8CB and 8OCB transform to the smectic A phase, of course, when $(T_c - T)$ reaches about 7 K and about 13 K respectively. Pretransitional effects in K_{33} are clearly visible for these two compounds in figures 3 and 4.

As far as the absolute magnitude of K_{11} and K_{33} in compounds other than 5CB is concerned, we think it may be more helpful to present our data in tabular rather than graphical form, though the tables are based on smoothed curves and so cannot illustrate the scatter in the raw data points. Table I contains smoothed results, obtained by both methods, for nCB compounds, and table II contains similar results for nOCB compounds. Both the electrical results on the left of these tables and the magnetic results on the right have been rounded off to the nearest 0.05 pN, since the data do not justify greater precision. We include smoothed values (similarly rounded off) for $\Delta\varepsilon$, density ρ and $\Delta\chi^{(m)}$. If later work suggests that any of these are wrong, then the corresponding values for K_{11} and K_{33} will need to be scaled, like $\Delta\varepsilon$ or like $\rho \, \Delta\chi^{(m)}$ as the case may be. (It may help to prevent confusion in the future if we stress that, like all previous workers in this field, we use unrationalized units for the magnetic susceptibility : our χ is $(\mu - 1)/4\pi$ rather than $(\mu - 1)$). No values for ρ or $\Delta\chi^{(m)}$ are listed for temperatures below the limits to which

measurements of density or susceptibility have so far extended; we used graphical methods to extrapolate beyond these limits when analysing some of the magnetic results. The substances 9CB and PAA were studied by the magnetic method only, and unsmoothed results for these are presented in table III. In the case of PAA, for which Sherrell and Crellin [13] made no susceptibility measurements, we list $(K_{11}/\Delta\chi)$ and $(K_{33}/\Delta\chi)$, to facilitate comparison with previous work. Values for $\Delta\chi$ can be found, if required, in reference [4].

Examination of tables I and II will show that 5CB is not the only cyanobiphenyl for which the electrical and magnetic methods have yielded essentially identical results : for 6OCB, for example, the agreement is almost equally close. For 7CB and 7OCB, however, the electrical results are systematically lower than the magnetic ones, by about 7 %. For 6CB the discrepancy is about 5 % at the lower temperatures but seems to increase on heating, which may indicate error in one set of values for $(T_c - T)$. For 5OCB it is about 4 % in the case of K_{11} but as high as 10 %, and of opposite sign, in the case of K_{33}. Overall, we regard the consistency between the two sets of results as satisfactory, though no doubt it could be further improved by patient repetition of the measurements, with more care being paid to the measurement of temperature. Larger differences exist, as has already been indicated, between

Table II.

(T_c-T) K	$\Delta\varepsilon$	K_{11} pN	K_{33} pN	$10^{-3}\,\rho$ kg m^{-3}	$10^{12}\,\Delta\chi^{(m)}$ (kg m^{-3})$^{-1}$	K_{11} pN	K_{33} pN
5OCB		$T_c = 68.3\,°C$			$T_c = 66.3\,°C$		
2	—	—	—	—	68	—	2.85
4	8.85	3.0	3.85	1.030	77	3.3	3.8
6	9.85	3.75	4.8	1.032	82.5	3.95	4.6
8	10.55	4.3	5.55	1.034	87	4.5	5.25
10	11.15	4.7	6.25	1.036	90.5	4.9	5.8
12	11.65	5.1	6.9	1.038	93.5	5.3	6.3
14	12.15	5.45	7.45	1.039	96	5.65	6.8
16	12.55	5.8	7.95	1.041	98	6.05	7.3
18	12.9	6.1	8.4	1.042	100.5	6.35	7.75
20	13.25	6.4	8.9	1.044	102.5	6.65	8.2
24	13.85	6.95	10.05	—	106	7.25	9.1
28	—	—	—	—	109	7.75	9.95
32	—	—	—	—	111.5	8.25	10.75
36	—	—	—	—	114	8.7	11.55
6OCB		$T_c = 76.8\,°C$			$T_c = 77.3\,°C$		
2	—	—	—	1.013	67.5	3.05	3.5
4	8.4	3.7	4.35	1.015	75	3.9	4.8
6	9.25	4.4	5.45	1.017	80	4.5	5.7
8	9.9	5.05	6.35	1.019	84.5	5.1	6.5
10	10.4	5.55	7.2	1.022	88	5.6	7.2
12	10.8	6.0	7.9	1.023	90.5	6.1	7.9
14	11.2	6.5	8.55	1.025	92.5	6.5	8.5
16	11.5	6.9	9.25	—	94.5	6.9	9.1
18	11.8	7.3	9.9	—	96	7.25	9.7
20	12.1	7.65	10.6	—	97.5	7.6	10.25
24	12.6	8.3	11.9	—	100	8.25	11.4
28	—	—	—	—	102.5	8.85	12.55
32	—	—	—	—	104.5	9.35	13.65
36	—	—	—	—	—	9.8	14.8
7OCB		$T_c = 74.9\,°C$			$T_c = 74.1\,°C$		
2	—	—	—	1.003	63	3.0	3.4
4	7.45	3.4	3.65	1.006	71	4.05	4.4
6	8.25	4.2	4.6	1.008	76	4.8	5.2
8	8.8	4.9	5.35	1.009	80	5.4	5.9
10	9.25	5.5	6.0	1.011	83	5.95	6.5
12	9.6	6.0	6.6	1.014	85.5	6.45	7.05
14	9.9	6.5	7.2	1.016	87.5	6.9	7.7
16	10.15	6.95	7.8	1.017	89.5	7.35	8.25
18	10.4	7.4	8.4	1.019	91.5	7.8	8.8
20	10.6	7.8	9.0	—	93	8.2	9.4
24	10.95	8.55	10.25	—	96	9.0	10.6
28	—	—	—	—	98.5	9.7	12.0
32	—	—	—	—	101	10.3	13.7
36	—	—	—	—	103	10.9	15.7

Table II (continued)

8OCB	$T_c = 79.8$ °C				$T_c = 81.6$ °C		
1	—	—	—	0.988	57.5	3.0	2.95
2	6.2	3.0	3.3	0.990	63.5	3.8	3.8
3	6.85	3.75	4.05	0.991	67.5	4.45	4.45
4	7.35	4.5	4.75	0.992	70.5	5.05	5.05
6	7.95	5.55	6.05	0.994	74	6.05	6.15
8	8.35	6.4	7.35	0.996	77	6.9	7.3
10	8.7	7.3	9.0	0.998	81	—	9.0
11	8.8	7.75	10.5	0.999	83	—	10.4
12	8.95	8.25	13.3	1.000	84.5	—	13.2

our results and those of Schad and Osman [12] for 7CB or of Madhusudana and Pratibha [15] for not only 5CB but also 6CB and 7CB. We seem to agree with Madhusudana and Prathiba, however, concerning 8CB and 8OCB.

As regards table III, the figures quoted there for $(K_{11}/\Delta\chi)$ in PAA are systematically lower by 10 % than the most recent of the previously published sets of values [5]. Since our values for (K_{33}/K_{11}) are also rather lower than the previous ones, especially at low temperatures, the discrepancies reach 20 % in the case of $(K_{33}/\Delta\chi)$. We quote no value for T_c in PAA because it drifted during the course of the experiment. The drift was, of course, allowed for in the calculation of $(T_c - T)$ and we saw no evidence that the chemical changes responsible for it were simultaneously affecting the Frank constants.

Table III.

9CB		$T_c = 50.1$ °C		
$(T_c - T)$	$10^{-3}\,\rho$	$10^{12}\,\Delta\chi^{(m)}$	K_{11}	K_{33}
K	kg m^{-3}	(kg m$^{-3})^{-1}$	pN	pN
0.2	0.969	76	4.55	4.4
0.4	0.969	79	4.9	4.7
0.8	0.970	84.5	5.85	5.95
1.2	0.971	88.5	6.45	7.35

PAA		
$(T_c - T)$	$(K_{11}/\Delta\chi)$	$(K_{33}/\Delta\chi)$
K	μN	μN
0.9	33	51.5
2.3	38	58.5
2.4	35	57
3.3	38	60
4.8	40	65.5
8.0	41	72
10.6	45	76.5
13.1	46	80.5
15.7	47.5	84
18.3	48.5	88
20.6	49	91.5
23.0	51	94.5
26.3	51.5	98.5

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