The effect of compression on the Frank constants of two nematic liquid crystals

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The effect of compression on the Frank constants of two nematic liquid crystals

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Along lines in the phase diagram of a nematic liquid crystal on which its order parameter (i.e. the degree of alignment of its molecules) is constant, the Frank stiffness constants are expected to increase with pressure. We have sought evidence for this by studying, using an orthodox optical method, a magnetic Fréedericksz transition in thin films of two alkyl cyanobiphenyl compounds inside pressure vessels; our measurements on 5CB extended to 2 kbar and on 6CB to 0·5 kbar. To analyse our data we need to know, though not with great precision, the ordinary refractive index of the nematic, n_o, for each pressure and temperature. We therefore made supplementary measurements of refractive index on 5CB and 6CB (and incidentally on 7CB and 8CB as well) at pressures up to 2·5 kbar. Given n_o we can deduce the extraordinary refractive index n_e from our observations on the Fréedericksz transition. Hence we can deduce values for the quantity $\Sigma (= 3(n_e^2 - n_o^2)/(n_e^2 + 2n_o^2 - 3))$, which we take to be proportional to the order parameter. As for the anisotropy in the magnetic susceptibility, which is also involved in the analysis, we make the assumption that along lines in the phase diagram for which Σ is constant the anisotropy per unit mass, $\Delta\chi^{(m)}$, is constant too, despite the biaxiality effects which are known to prevent $\Delta\chi^{(m)}/\Sigma$ from being quite independent of temperature at atmospheric pressure. Our results suggest that for 5CB the effect of compression on both the bend constant, K_3, and the splay constant, K_1, is about half as great as would be predicted by Maier–Saupe theory in its simplest form. Alternative theories which could be used to explain the difference are outlined in the final section, but we have no explanation for what we observe for 6CB, where the effect of compression seems to be significantly smaller still—too small, indeed, to be detected.

1. Introduction

Previous experiments on nematic liquid crystals under pressure (for example, [1–4] have shown that the temperature $T_{NI}(p)$ at which the nematic phase transforms to the isotropic increases rather rapidly on compression. In terms of the molar volume of the nematic, V_N, one finds

$$T_{NI} \propto V_N^{-\gamma}, \tag{1}$$

with an exponent γ which, at any rate for the two nematics that concern us in this paper, is at least 6. If we are to believe the mean field theory of Maier and Saupe [5], this volume-dependence arises from a volume-dependence of the strength of the anisotropic interaction potentials which are responsible for nematic alignment, and since these potentials determine not only T_{NI} but also the three Frank stiffness constants K_i ($i = 1, 2, 3$) we should expect

$$K_i \propto V_N^{-\gamma} \tag{2}$$

along any line on the phase diagram on which the order parameter S_2, which describes the degree of alignment in the nematic, is constant; such lines are known to run roughly parallel to the clearing curve itself, i.e. to the curve which describes $T_{NI}(p)$. The very different continuum theory of nematic disorder developed by Faber [6] leads to a similar prediction. This paper describes a first attempt to verify it, using the nematic compounds 4-*n*-pentyl-4′-cyanobiphenyl, or 5CB, and its hexyl homologue 6CB.

In planning the experiments we looked for a method which could be applied inside a pressure vessel and which could, in principle, yield results with a relative accuracy of 1 per cent. We decided in favour of the method adopted by Karat and Madhusudana [7] and others, which involves using optical techniques to monitor a Fréedericksz transition in a thin layer of nematic with homeotropic (normal) alignment, when a magnetic field is applied parallel to the layer. The bend constant K_3 is related to the critical field B_0 at which the transition starts by the equation

$$B_0 = (\pi/L)(\mu_0 K_3/4\pi\Delta\chi)^{1/2} \qquad (3)$$

and from observations at higher fields a quantity κ ($= (K_3 - K_1)/K_3$) and hence the splay constant K_1 can be deduced. The successful application of this method in our laboratory to various nematics at atmospheric pressure, including 5CB and 6CB, has been described in two previous papers [8, 9].

The theoretical expressions which relate the quantity which is measured in this method (a difference in optical path for the two principal polarizations) to the strength of the applied field, B, include not only the parameters B_0 and κ, but also the thickness of the nematic layer, L, its ordinary refractive index n_0 and the quantity $v = (n_e^2 - n_0^2)/n_e^2$. When the work was first planned we expected to be able to treat L, n_0 and v as known for all values of pressure, p, and temperature T, since we felt that we could rely on the detailed refractive index data reported by Horn [2]. Subsequently it became clear that Horn's pressure gauge was affected by a temperature dependent zero error [4], more than large enough to obscure the small effects for which we were looking. We therefore developed a fitting procedure which enables v to be estimated from each set of observations at the same time as B_0 and κ are estimated, and the use of this procedure at atmospheric pressure to provide a check on the assumptions concerning L has been described in [8]. We still need to know n_0 as a function of pressure and temperature, of course, so one of us (J. D. B.) set up an independent experiment to measure this. His method is briefly described in §2 of this paper, and his results briefly summarized in §3. In most contexts the results, because of unresolved experimental difficulties, would no doubt seem inadequate, but for our purposes they prove sufficient. Our conclusions are insensitive to the choice of n_0.

We cannot hope to deduce how K_3 and K_1 vary with volume at constant S_2 unless we have some way of estimating relative values of V_N and S_2 for each set of readings. We shall follow Horn and Faber [10] in assuming these quantities to be proportional respectively to

$$\Omega = (n_e^2 + 2n_0^2 + 6)/(n_e^2 + 2n_0^2 - 3) = ((1 - 2v/3)n_0^2 + 2)/((1 - 2v/3)n_0^2 - 1)$$

$$(4)$$

and to

$$\Sigma = 3(n_e^2 - n_0^2)/(n_e^2 + 2n_0^2 - 3) = vn_0^2/((1 - 2v/3)n_0^2 - 1). \qquad (5)$$

Evidently Ω and Σ can both be deduced from v and n_0. The proportionality of S_2 to

Σ has been discussed by Bunning *et al.* [11]. It is clearly not exact, because of local field effects and the influence of off-diagonal elements in the Saupe ordering matrix. According to Bunning *et al.*, however, the corrections needed for these effects are too small to be significant here.

Bunning *et al.* have also discussed the anisotropy in the magnetic susceptibility of the nematic, $\Delta\chi$, which plays a role in equation (3). They conclude that the off-diagonal elements referred to have an appreciable effect upon it, so that

$$\Delta\chi^{(m)} \propto S_2(1 + \alpha b),$$

and hence

$$\Delta\chi \propto (\Sigma/\Omega)(1 + \alpha b), \tag{6}$$

where $\chi^{(m)}$ is the susceptibility per unit mass, b is a biaxiality ratio defined in the Appendix, and α is a numerical coefficient of order unity. It is known that b varies with temperature at constant pressure, but we argue in the Appendix that at constant S_2 its variation with volume is likely to be negligible. If so, we may assume that along lines in the phase diagram for which Σ, and therefore S_2, is constant K_3 varies like $(L^2 B_0^2/\Omega)$. Since the variation of L is likely to be negligible—the effect of pressure on the spacers that determine L is small and in any case is roughly compensated by their thermal expansion—we may display our results by plotting (B_0^2/Ω) versus Σ. The effect we are looking for should show up on such a plot as a separation between curves obtained in successive runs, for each of which T was varied while p was held more or less fixed, but between which p was increased.

For 5CB we see such a separation (see §4), but it is only about half as much as that predicted; for 6CB it seems wholly absent. In §5 of this paper we recall modifications to the theories mentioned previously which may perhaps serve to explain what we have observed for 5CB, but our negative result for 6CB remains distinctly curious. For one referee who saw an earlier draft of this paper it is so curious as to cast doubt upon our data or upon the assumptions which have been outlined in this Introduction. The data are admittedly incomplete, because our experimental programme was twice interrupted when Drs. Sherrell and Bunning left to work elsewhere. They seem to us reliable as far as they go, however, and having reached the same negative result for 6CB by another method of analysis, involving a different set of assumptions, we have confidence in it. Nevertheless confirmation from further experiments is undoubtedly desirable.

The way in which Σ and Ω (i.e. S_2 and V_N) vary with pressure and temperature for nematics is a topic of some interest in its own right. Such information concerning their variation as can be deduced from our observations will be found in §3. Brief references will be found in that section to two further homologues of 5CB, namely 7CB and 8CB, on which refractive index measurements were made, though shortage of time prevented their use in the Fréedericksz transition work.

2. Experimental details

The pressure vessels used in this work were cylinders about 8 cm long and about 8 cm in external diameter, enclosed by heating coils so that their temperature could be raised by 100°C or more. Temperature was measured by means of chromel–alumel thermocouples with one junction in the interior of the vessel, surrounded by the nematic specimen. Pressure was generated in a separate intensifier, filled with a silicone fluid, and measured with manganin gauges kept at room temperature. The

gauges were calibrated against secondary standard gauges and were also compared with the gauge used by Wallis and Roy [4]. In principle they were accurate to ± 0.01 kbar or less, but zero errors exceeding 0.01 kbar may have crept into the readings sometimes, for example, when the room temperature changed, as we shall see later. The pressure was transmitted from the intensifier to the specimen through Harwood tubing filled with the silicone fluid and then through metal bellows; a preliminary experiment shows the pressure drop across the bellows to be negligible. The pressure-proof seals which were an essential feature of the vessels were of conventional design and will not be described here.

The vessel used for observations on the Fréedericksz transition in 6CB (by J. D. B.) was of non-magnetic stainless steel and had a working chamber, bored out along the axis of the cylinder, with a diameter of about 17 mm. The tube from the intensifier entered through a plug at one end of the cylinder and the bellows were inside the working chamber. The plug at the other end had a hole bored along its axis to allow a He–Ne laser beam to enter the chamber and to emerge again after reflection. An optically flat glass window about 6 mm thick was seated on the flat and polished end of this plug, and the inner face of the window formed one of the surfaces containing the thin layer of nematic on which observations were made. The other containing surface was provided by a glass cover slip, aluminized on its other side, which was pushed towards the window by a loose spring but prevented from touching it by spacers of tungsten wire with a diameter of about $50\,\mu$m. The compressibility and thermal expansion of tungsten are such that changes in the thickness L of the nematic layer should not have exceeded a few parts in 10^4 over the relevant ranges of p and T. The two containing surfaces were treated with surfactant before assembly to ensure homeotropic alignment of the nematic layer. After assembly, which involved filling with nematic liquid the whole of the working space on one side of the bellows, the vessel was set up between the poles of an electromagnet, which could provide fields parallel to the layer of up to 0.3 T, and the Fréedericksz transition was monitored in the way that Bunning *et al.* [8] have described. The apparatus used for 5CB (by P. L. S.) was not identical but it differed in no essential particular.

The vessel designed (by J. D. B.) for refractive index measurements was of beryllium/copper and had a working chamber with a diameter of about 14 mm. A He–Ne laser beam entered the chamber through a window, as with the steel vessels, but instead of being reflected it was allowed to carry on and exit from the other end of the vessel through a second window. The brass bellows were now in a detached separator unit, filled on one side with the silicone fluid and on the other with the nematic specimen; the nematic in the separator communicated directly with the nematic in the working chamber *via* a narrow hole drilled at right angles to the main axis of the pressure vessel.

The face of the plug on which the exit window was set was angled in such a way that this window was inclined to the entry window at about $5°$. Silicone monoxide was evaporated on both windows before assembly, at an angle of $60°$ to the normal, so as to promote homogeneous planar alignment of the wedge of nematic between them, and a magnetic field could be used to improve the alignment if necessary. The wedge was therefore birefringent, and by measuring the deviations of the ordinary and extraordinary rays, using a laser beam polarized at $45°$ to the principal directions, the two principal refractive indices of the nematic, n_o and n_e, could be found. The hole through the exit plug was made conical to allow deviated beams to emerge. The deviations were measured on a graduated scale about 7.5 m from the wedge. Before

and (except in cases where leakage prevented this) after each set of measurements at high pressure they were measured as a function of temperature at atmospheric pressure; from a comparison with the results of previous determinations of n_o and n_e at atmospheric pressure [11] the wedge angle could be deduced.

Both types of experiment were conducted by setting the pressure to a more or less fixed value and then varying the temperature. Such a procedure is more time consuming than the alternative adopted in previous work [4, 10] of setting the temperature and varying the pressure: the large thermal capacity of the pressure vessels slows down the process of temperature adjustment. It reduces the risk of failure due to leakage, however, and it generates results that are easier to present in meaningful form. At each setting of the pressure p the temperature $T_{NI}(p)$ of the transition to the isotropic phase was normally determined, so the results could be plotted against $(T_{NI}(p) - T)$ as is customary at atmospheric pressure. The clearing temperature at atmospheric pressure, $T_{NI}(0)$, was liable to be lower at the end of a high pressure run than at the beginning by about $0.2°C$, perhaps due to chemical changes in the specimen, and $T_{NI}(p)$ for nominally fixed p was not wholly reproducible for different specimens, perhaps because of zero errors in the pressure gauges. But changes in T_{NI} should be of relatively little importance if one concentrates upon the difference, $(T_{NI} - T)$.

The results presented later show that B_0 could be measured under pressure with an accuracy no less than that achieved at atmospheric pressure. The same cannot be said of the refractive indices. At atmospheric pressure the relative accuracy of values of n_o and n_e obtained by the wedge technique is of order ± 0.0003, but under pressure errors as large as ± 0.01 sometimes occurred; this statement is based on a comparison of the results obtained for a single specimen at different pressures and for different specimens at a single pressure. The errors seemed usually to be systematic while the pressure remained unchanged but were not invariably so. Imperfect alignment of the nematic was no doubt partly to blame, but changes in the wedge angle presumably due to displacement or distortion of the windows were also a serious problem. The fact that the measured value of the wedge angle was sometimes different before and after a run provided evidence for displacement. Evidence that elastic distortion occurred was provided by observations at pressures greater than about 2·5 kbar. Here the two spots of light on the graduated scale invariably became too diffuse for measurements to be possible, though they improved when the pressure was lowered again; since the single spot observed when the specimen was heated above $T_{NI}(p)$ was equally diffuse, the diffuseness could not be blamed upon poor alignment.

The data for the Fréedericksz transition which we present later were obtained at pressures not exceeding 2·1 kbar for 5CB, while for 6CB the maximum pressure used was only about 0·5 kbar. While it is possible that these pressures were sufficient to move the windows on the steel vessels, we presume that, if so, the cover slips moved with them. Had the thickness of the nematic layer between window and cover slip become significantly non-uniform under pressure the data would have been affected; for example, the transition curve would have developed a tail [8]. We saw no evidence of this.

It should be said that although the 6CB transition data span a smaller pressure range than the 5CB data they are in some respects of superior quality, since between the two sets of measurements our methods for preparing well-aligned specimens improved.

3. Experimental results: refractive indices, order parameter and volume
3.1. *The clearing curve*

Previous authors have found that the clearing curve for cyanobiphenyls may be described by the equation

$$T_{NI}(p) = T_{NI}(0) + Ap - Bp^2. \tag{7}$$

We have fitted this equation to our observations using the coefficients listed in the table, but it should be repeated that measurements of $T_{NI}(p)$ are not quite as reproducible as could be wished; an individual measurement may differ from the value corresponding to equation (7) by as much as 1 K at a pressure of 2 kbar. Within such limits our results are in satisfactory agreement with those reported by Wallis and Roy [4] for the same compounds. In particular, they confirm the results reported by Wallis and Roy for 7CB, rather than the somewhat different results of Shashidhar and Venkatesh [3].

Coefficients in equation (7).

Mesogen	$T_{NI}(0)/K$	$A/K\,kbar^{-1}$	$B/K\,kbar^{-2}$
5CB	308·7	39·0	1·2
6CB	302·8	37·8	1·2
7CB	316·0	34·5	0·45
8CB	314·1	36·3	1·6

From the coefficients in the table we deduce that $T_{NI}^{-1}(dT_{NI}/dp)$ is $0·126\,kbar^{-1}$ for 5CB at low pressures, and 0·125 for 6CB.

3.2. *Refractive indices*

The refractive indices of 5CB were measured using only one specimen, and this was a case in which the wedge angle changed slightly during the run. The run covered five values of p, for each of which the results for n_o lay on a smooth curve when plotted against ΔT, where

$$\Delta T = (T_{NI}(p) - T). \tag{8}$$

In figure 1 we plot the values of n_o corresponding to $\Delta T = 5\,K$ which are indicated by these curves, with error bars which reflect only the scatter in each set of readings. One way to interpret these results would be to fit some sort of curve through them and through the point at $p = 0$ which represents the atmospheric pressure observations on which the wedge angle calibration is based. We prefer to believe, however, that n_o is a more or less linear function of p for fixed ΔT and to fit through the points the straight line which is drawn in figure 1, with a slope

$$(\partial n_o/\partial p)_{\Delta T} = 0·011\,kbar^{-1}. \tag{9}$$

We attribute the fact that this line does not pass through the point at $p = 0$ to a small change in wedge angle under pressure which relaxed when the pressure was released.

The crosses in figure 1 represent our results for n_o at $\Delta T = 5\,K$ in 6CB, of which three different specimens were investigated. The scatter is large and implies significant calibration errors in at least two of the runs, but the general trend of the points seems to be consistent with equation (9), as in 5CB. Similar plots for other values of ΔT show
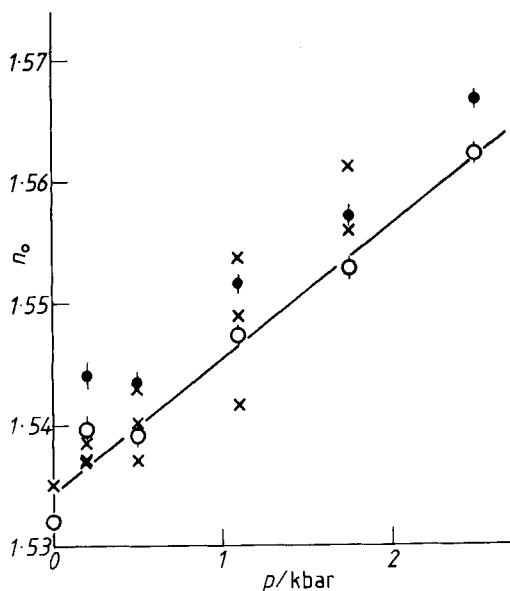
Figure 1.   Values of n_o at $\lambda = 632 \cdot 8$ nm and $\Delta T = 5$ K observed for 5CB (circles) and 6CB (crosses) at different pressures. The filled and open circles represent results calculated using the wedge angle observed before and after, respectively, the 5CB specimen was subjected to pressure.

no evidence of any temperature dependence of $(\partial n_o/\partial p)_{\Delta T}$ for 6CB, but for 5CB it seems to decrease slightly as ΔT increases.

Measurements of n_e are more likely to be affected by misalignment of the nematic director than are measurements of n_o, and perhaps that is why our n_e results for 5CB are too erratic for us to be able to deduce a value of $(\partial n_e/\partial p)_{\Delta T}$ with conviction. But for 6CB $(\partial n_e/\partial p)_{\Delta T}$ seems to be $0 \cdot 013$ kbar^{-1}, effectively independent of temperature. This figure is consistent with what may be inferred about n_e from the data for v to be discussed later.

Similar results are available for 7CB and 8CB, but they are not needed for the analysis that follows and do not seem worth quoting here. Such figures as we have quoted apply, of course, at the He–Ne wavelength, $\lambda = 632 \cdot 8$ nm.

3.3. *The order parameter*

From each set of observations on a Fréedericksz transition at given T and p we obtain, using a three-parameter computer fit which is explained in greater detail in [8], values for B_0, κ and v. Here we are concerned only with the results for v, and with what may be deduced from them concerning the pressure dependence of Σ (and hence of the order parameter S_2).

It should first be explained that the values generated for v depend to some extent on the values assumed for n_o and L, which are necessary inputs for the computer program. It has been established, however, [8], that replacement of the true values for these quantities by slightly different values n_o' and L' changes the output of the program from v to v', where

$$(n_o L/n_o' L') = ((1 - v')^{-1/2} - 1)/((1 - v)^{-1/2} - 1). \tag{10}$$

At atmospheric pressure, where n_o, n_e and v are known but where our estimate for the layer thickness—say L'—is initially a little uncertain, we use equation (10) to establish a correction factor, (L/L'). This turns out to be independent of temperature, as expected; for 6CB it was 1·015 and for 5CB it was 0·937, the difference reflecting a difference between the methods used by J. D. B. and P. L. S. for the estimation of L'. At high pressures we use the same correction factor for the layer thickness, for reasons stated previously, and equation (10) then enables us to establish v, from results for v' which were originally computed without allowance for this correction and using values for n_o' which we now believe to be erroneous. For n_o we use

$$n_o(\Delta T, p) = n_o(\Delta T, 0) + p(\partial n_o/\partial p)_{\Delta T}, \qquad (11)$$

both for estimating v from v', and for calculating Σ from v with the aid of equation (5). The errors in our estimates of $(\partial n_o/\partial p)_{\Delta T}$ may be as much as 20 per cent (see figure 1) but the corresponding errors in v and Σ should not exceed 0·2 per cent, such is the insensitivity of v to the choice of n_o.

It has been shown by Wallis and Roy [4], who measured proton N.M.R. line-widths under pressure, that S_2 is constant along the clearing curve for 6CB, and the refractive index measurements of J. D. B. confirm that Σ is likewise constant for this substance. For 5CB, however, S_2 is clearly not constant along the clearing curve: it falls between atmospheric pressure and 2 kbar by about 10 per cent. This has been shown in different ways by both Horn and Faber [10] and Wallis and Roy [4], and the refractive index measurements of J. D. B. again provide confirmation. They also confirm, incidentally, the similar fall along the clearing curve reported by Wallis and Roy [4] for 7CB and 8CB.

Figure 2 shows our limited results for Σ in 6CB at three different pressures, plotted against ΔT. The points for atmospheric pressure and for 0·5 kbar lie on much the same curve, but those for 0·2 kbar are well to the left of this curve. During the 0·2 kbar run, however, the zero on the pressure gauge drifted, and we have independent evidence that the true pressure had fallen to 0·17 kbar by the time that T_{NI} was measured. Consequently we believe the recorded values for ΔT for the early readings in this run to be too low by about 1 K. Corrected by that amount the points for 0·2 kbar would come into coincidence with the other two sets of points in figure 2. Hence it seems that, up to 0·5 kbar at any rate, the lines of constant S_2 run closely parallel to the clearing curve for 6CB.

Figure 3 is a similar plot of Σ versus ΔT for 5CB. The data come from a sequence of runs on a single specimen. Other specimens gave similar results, but it would confuse the diagram if we tried to show these. The sets of points we have chosen to include in figure 3 display various irregularities, which may well be due to zero errors in the pressure gauge, undetected at the time the data were recorded. These irregularities make it hard to draw firm conclusions from the figure, but it looks as though for 5CB the lines of constant S_2 are diverging slightly from one another at pressures of around 2 kbar.

Wallis and Roy [4] have provided polynomial expressions for the N.M.R. line-width, ΔH, in 6CB and 7CB as a function of T and p. From these it should be possible to calculate curves to superimpose for comparison purposes on figure 2; the necesary assumption that ΔH and Σ are proportional to one another has been verified to within 1 per cent for 6CB at atmospheric pressure in separate experiments by Roy [12]. Unfortunately, the polynomial proves to be unreliable at the relatively low pressures in which we are most interested. We have referred instead to the detailed results which
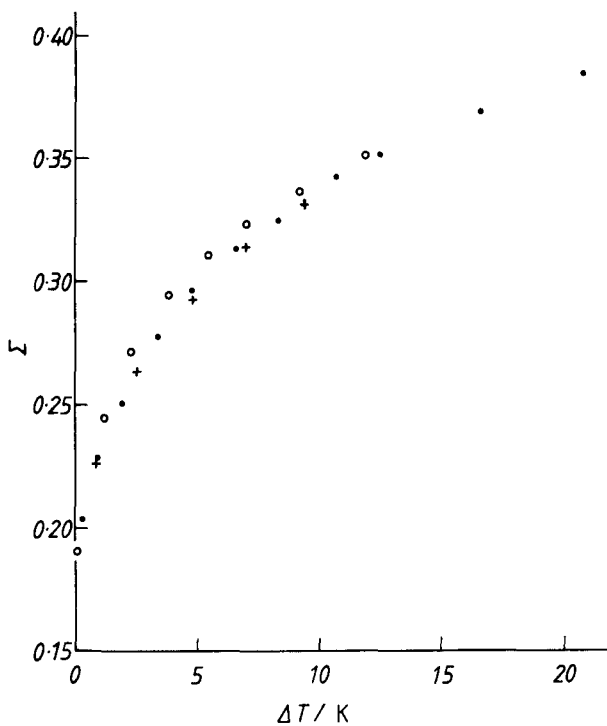
Figure 2. 6CB: values of Σ, deduced from observations on the Fréedericksz transition, plotted against ΔT: $+$, atmospheric pressure; $\bigcirc$, $p = 0.20$ kbar; $\bullet$, $p = 0.50$ kbar. The displacement of the open circles relative to the two other sets of points is attributed to an error in the identification of T_{NI} at 0.20 kbar.
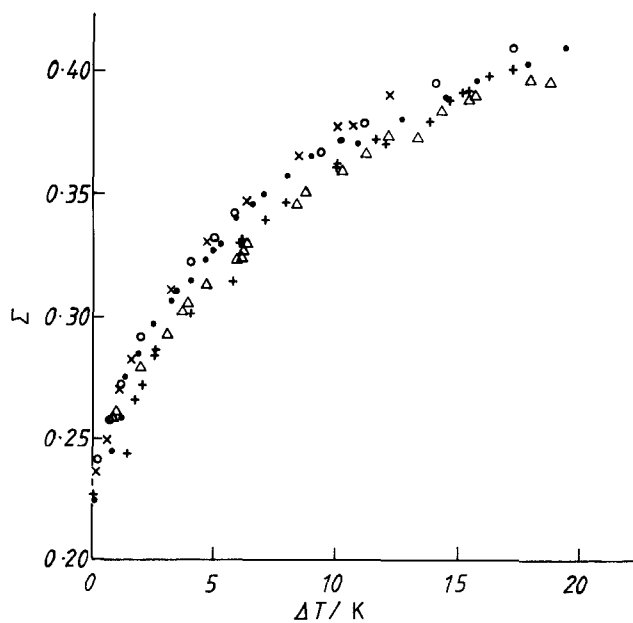

Figure 3. 5CB: values of Σ plotted against ΔT: $\times$, atmospheric pressure; $\bigcirc$, $p = 0.69$–0.71 kbar; $\bullet$, $p = 1.01$–1.05 kbar; $+$, $p = 1.52$–1.56 kbar; $\triangle$, $p = 2.03$–2.07 kbar.

Roy [12] has recorded, but the fact that he collected data while varying p at constant T while we did the reverse introduces too many ambiguities into the comparison to make it useful. Comparison of the data in figure 3 with Horn's refractive index measurements for 5CB [2] is equally unrewarding.

3.4. *Compressibility*

To go with each value of Σ we have, of course, a value of Ω deduced from n_o and v with the aid of equation (4). The results for 6CB are plotted against ΔT in figure 4. Here we have chosen to correct the set of readings corresponding to a pressure of 0.20 kbar for drift in the pressure gauge, using figure 2 as a guide. The correction brings these readings into line with the other two sets, and collectively they imply that for 6CB

$$V_N^{-1}(\partial V_N/\partial p)_\Sigma \simeq \Omega^{-1}(\partial \Omega/\partial p)_{\Delta T} = -0.018 \text{ kbar}^{-1}, \qquad (12)$$

effectively independent of ΔT. The exponent defined by equation (1) is therefore

$$\gamma = T_{NI}^{-1}(dT_{NI}/dp)/\Omega^{-1}(\partial \Omega/\partial p)_{\Delta T=0} \simeq 7 \pm 1. \qquad (13)$$

The estimated limits of error attached to this figure reflect the fact that Ω is more sensitive than Σ is to errors in $(\partial n_o/\partial p)_{\Delta T}$. For 5CB we estimate in the same way that

$$\gamma \simeq 8.5 \pm 1.5; \qquad (14)$$

this may be compared with the figure of 6 quoted for γ in 5CB by Horn and Faber [10].

Measurements of refractive index made just above T_{NI} suggest that in the isotropic phase of 6CB

$$V^{-1}(\partial V/\partial p)_{T=T_{NI}} = 0.020(\pm 0.002) \text{ kbar}^{-1}, \qquad (15)$$

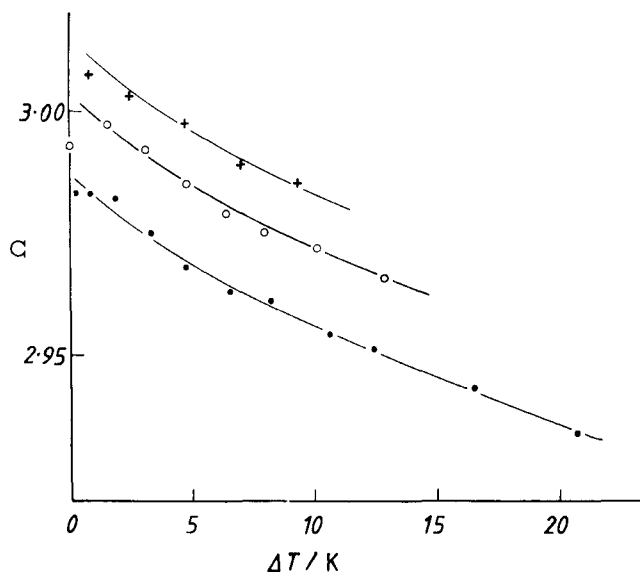with similar results for the other cyanobiphenyls.

Figure 4. 6CB: values of Ω plotted against ΔT: $+$, atmospheric pressure; $\bigcirc$, $p = 0.20$ kbar; $\bullet$, $p = 0.50$ kbar. A correction has been applied for the suspected error in T_{NI} at 0.20 kbar.

4. Experimental results: stiffness constants

4.1. *The bend constant for 6CB*

In figure 5 we present our results for the critical field at which the Fréedericksz transition begins in the manner suggested in the Introduction, i.e. by plotting (B_0^2/Ω) versus Σ. It should be noted that the errors which may have crept into some of our estimates of ΔT as a result of pressure gauge problems are of no relevance here. They affect our evaluation of n_0 a little, but by too little to have any significant effect upon either Ω or Σ, while the value of B_0 generated by our fitting procedure is essentially independent of n_0. Thus it makes no visible difference in figure 5 to the points for 6CB at 0·2 kbar whether the ΔT values are corrected by 1 K (see §3.3) or not.

Of the four sets of points in figure 5, three were obtained using the single 6CB specimen for which Σ was plotted against ΔT in figure 2. The fourth set represents the
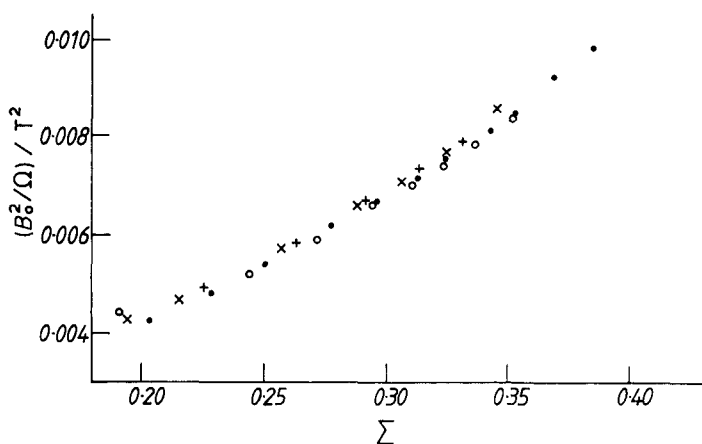
Figure 5. 6CB: (B_0^2/Ω) plotted against Σ: ×, previous experiments at atmospheric pressure; +, atmospheric pressure; ○, $p = 0·20$ kbar; ●, $p = 0·50$ kbar.
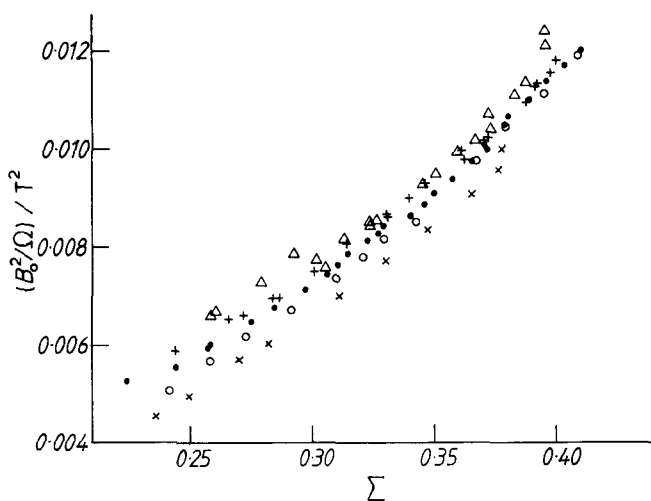

Figure 6. 5CB: (B_0^2/Ω) plotted against Σ: ×, atmospheric pressure; ○, $p = 0·69$–$0·71$ kbar; ●, $p = 1·01$–$1·05$ kbar; +, $p = 1·52$–$1·56$ kbar; △, $p = 2·03$–$2·07$ kbar.

results of previous experiments on 6CB at atmospheric pressure [9], normalized to reflect the fact that in that previous work L was slightly different. The agreement with previous work is evidently very close, but in fact all four sets of points in the figure lie quite close to one another. Between 0 and 0·5 kbar, $T_{NI}(p)$ for 6CB rises by 6·1 per cent (see the table) and according to the theories outlined in the Introduction (B_0^2/Ω) should rise by the same amount. Such an increase should be sufficient to show up quite clearly in figure 5 but in fact there is no sign of it: if anything, the points for 0·2 and 0·5 kbar lie below the atmospheric pressure points.

4.2. *The bend constant for 5CB*

Figure 6 is a plot of (B_0^2/Ω) versus Σ for the sequence of runs on a single specimen of 5CB, of fixed L, which provided the data for figure 3. Despite some irregularity in the set of results obtained above 2 kbar, the points provide clear evidence for an increase of (B_0^2/Ω), and therefore of K_3, on compression at constant Σ. The rate of increase, and the way in which it seems to vary with Σ (i.e. with ΔT) is indicated in figure 7. A dotted line in this figure represents the rate of increase to be expected at low pressures in 5CB if the theories outlined in the Introduction are to be believed.
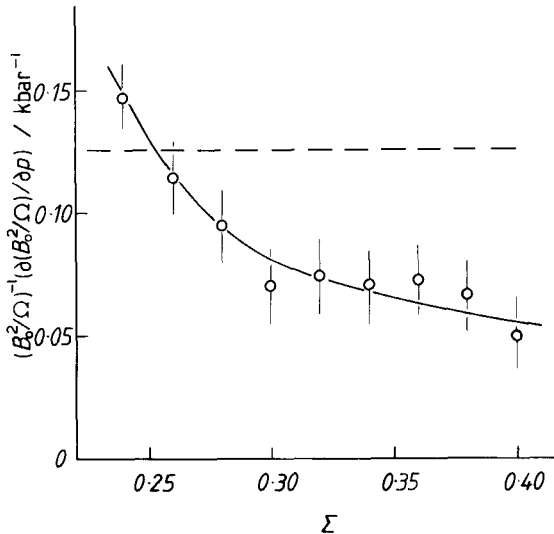

Figure 7.   5CB: the relative rate of increase in (B_0^2/Ω), and hence in K_3, on compression at constant Σ.

4.3. *The splay constant*

The ratio between K_1 and K_3 is given by the parameter κ referred to in the Introduction. Results for the specimens of 6CB and 5CB to which figures 5 and 6 respectively refer are plotted against Σ in figures 8 and 9. The curves drawn in these figures represent the best available values for the ratio at atmospheric pressure, taken from the work of Bradshaw *et al.* [9].

Aberrant results for κ are not uncommon, and points which are far from the curve, in figure 9 especially, should be ignored. Apart from these, the points seem to follow the atmospheric pressure curves in both figures, but are, on average, about 3 per cent high for 6CB and 5 per cent high for 5CB. One interpretation for such discrepancies
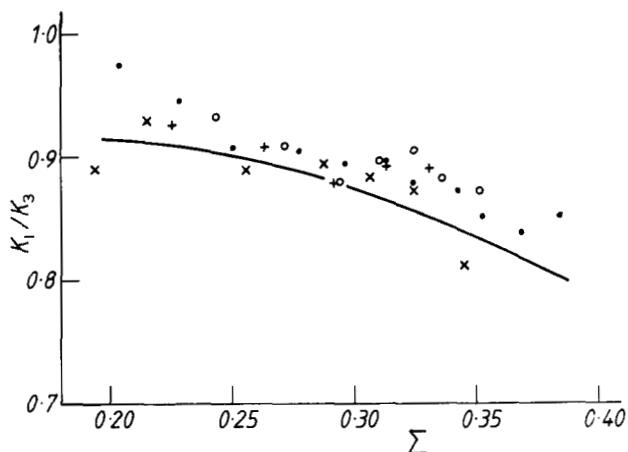
Figure 8. 6CB: the ratio K_1/K_3 versus Σ: $\times$, previous experiments at atmospheric pressure; $+$, atmospheric pressure; $\bigcirc$, $p = 0\cdot20$ kbar; $\bullet$, $p = 0\cdot50$ kbar. The curve is taken from results quoted by Bradshaw *et al.* [9].
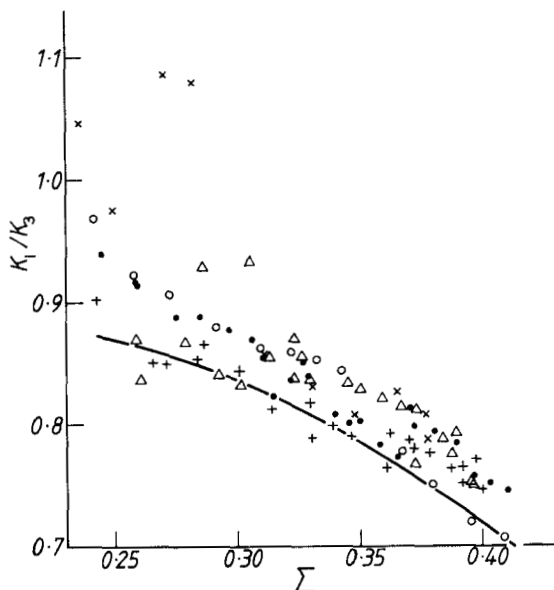

Figure 9. 5CB: the ratio K_1/K_3 versus Σ: $\times$, atmospheric pressure; $\bigcirc$, $p = 0\cdot69$–$0\cdot71$ kbar; $\bullet$, $p = 1\cdot01$–$1\cdot05$ kbar; $+$, $p = 1\cdot52$–$1\cdot56$ kbar; $\triangle$, $p = 2\cdot03$–$2\cdot07$ kbar. The curve is taken from results quoted by Bradshaw *et al.* [9].

is that the magnetic field was not quite parallel to the nematic layers; according to Bunning *et al.* [8] an error in alignment of only $0\cdot004$ radians ($\frac{1}{4}^\circ$) increases the apparent value of K_1/K_3 by 4 per cent. Such misalignment would have tended to decrease the apparent values of B_0 by about 1 per cent. However, during the two sequences of experiments upon which we have relied in plotting figures 2–9 the apparatus remained undisturbed, so within each sequence the effects of misalignment should have been systematic and therefore essentially irrelevant to our argument. Misalignment does not affect the apparent values of v.

Figures 8 and 9 seem to provide no evidence that K_1/K_3 changes on compression at constant Σ. Provisionally, therefore, our conclusions about the effect of compression on K_3 apply equally to K_1.

5. Discussion

We start this section by amplifying remarks in the Introduction about the theories of Maier and Saupe and of Faber.

In its simplest version the Maier–Saupe theory leads to an expression for the molar Gibbs free energy of the nematic phase of the form

$$G_{\mathrm{N}}(V_{\mathrm{N}}) = G_1(V_N) - CS_2^2 + T\Delta S_{\mathrm{m}}, \tag{16}$$

where G_1 is the free energy of the isotropic phase and ΔS_{m} (a function of S_2 only) is the amount by which the entropy of misalignment in the isotropic phase exceeds that in the nematic phase. The term $-CS_2^2$ represents a reduction in the internal energy of the nematic, attributed to anisotropy in the intermolecular van der Waals potential. The theory evidently predicts a transition temperature

$$
\begin{aligned}
T_{\mathrm{NI}} &= (G_1(V_1) - G_1(V_{\mathrm{N}}) + CS_2^2)/\Delta S_{\mathrm{m}} \\
&= (\tfrac{1}{2}(\partial^2 G_1/\partial V^2)\Delta V^2 + CS_2^2)/\Delta S_{\mathrm{m}} \\
&= ((\Delta V^2/2\beta_1 V_1) + CS_2^2)/\Delta S_{\mathrm{m}},
\end{aligned}
\tag{17}
$$

where $\Delta V = (V_1 - V_{\mathrm{N}})$ and β_1 is the isothermal compressibility of the isotropic phase. Equation (17) should be valid at any pressure. The term in ΔV^2 turns out to be negligible in practice, so equation (17) reduces to

$$T_{\mathrm{NI}} \simeq CS_2^2/\Delta S_{\mathrm{m}}. \tag{18}$$

But the equilibrium value of S_2 is a unique function of (T/C)—this follows from the condition that the right-hand side of equation (16) must be a minimum with respect to variations of S_2 at constant V_{N}—which means, in view of equation (17), that it takes a unique value on the clearing curve. Hence at all points on this curve

$$T_{\mathrm{NI}} \propto C. \tag{19}$$

Any pressure dependence of T_{NI} must therefore be attributed to a volume dependence of the interaction coefficient C. It follows from the discussion of the Frank constants given by Saupe [13] and Nehring and Saupe [14] that these must vary with pressure or volume in the same fashion.

Faber [6] starts from the position that no mean field theory of the Maier–Saupe type can be valid, because the correlations of orientation between adjacent molecules are too strong. The nematic is pictured instead as a medium in which the molecules would be perfectly aligned, but for the thermal excitation of a spectrum of $2N$ distortion modes involving splay, twist and bend in the director field. This picture suggests that

$$\ln(S_2(0)/S_2(T)) \propto T/V_{\mathrm{N}}^{1/3}K, \tag{20}$$

where K is an appropriate average of K_1, K_2 and K_3, and where $S_2(0)$ is unity. It also suggests [15] that at constant volume

$$K(T) = K(0)f(S_2(T)/S_2(0)), \tag{21}$$

where the function f describes a reduction in the stiffness of the nematic due to the misalignment of its molecules at temperatures above zero. The order parameter $S_2(T)$ is to be thought of as determined by a self-consistency condition involving equations (20) and (21).

The theory is not expected to be reliable close to the clearing curve, but comparison with results generated for lattice models by computer simulation suggests that it should be useful at low temperatures, say when $S_2 > 0.5$. Evidently it implies that along any line in the phase diagram for which Σ (> 0.3, say) is constant,

$$K \propto T/V_N^{1/3}.$$

It follows that at low pressures

$$K^{-1}(\partial K/\partial p)_\Sigma = (T_{NI}/T)(T_N^{-1}(\partial T_{NI}/\partial p)_\Sigma) - T^{-1}(\partial \Delta/\partial p)_\Sigma - (3V_N)^{-1}(\partial V_N/\partial p)_\Sigma.$$

(22)

The factor (T_{NI}/T) differs from unity by 5 per cent or less, and the final term on the right-hand side of equation (22) constitutes another correction of only about 5 per cent. For 6CB, in which lines of constant Σ run parallel to the clearing curve, the middle term should vanish and for 5CB it should be small. Hence we could not hope to distinguish between this prediction and one based upon Maier–Saupe theory, viz.

$$K^{-1}(\partial K/\partial p)_\Sigma = T_{NI}^{-1}(\partial T_{NI}/\partial p)_\Sigma. \tag{23}$$

Figure 7 suggests that in 5CB the effect of compression on K_3 is about half as big as equation (23) would suggest, at any rate for temperatures some way below T_{NI}. How might the theories be modified so as to remove this discrepancy?

Many empirical modifications of Maier–Saupe theory have been put forward, involving additional terms in the basic equation for $G_N(V_N)$. They have been used to explain why at atmospheric pressure the order parameter S_2 does not always vary with temperature in the way that Maier–Saupe theory predicts, and in particular to explain why S_2 at $T = T_{NI}$ is often significantly different from the Maier–Saupe value of about 0.43; in 5CB, for example, it is known [16] that S_2 at $T = T_{NI}$ is only 0.39. These modifications have been reviewed by Horn and Faber [10], who attempted (without success) to find one that could be fitted to Horn's data [2] for 5CB over the whole range of temperature and pressure which he investigated. As Horn and Faber showed, some of these modifications imply a distinction between the γs of equations (1) and (2); they admit the possibility that if

$$T_{NI} \propto V_N^{-\gamma}, \quad K_1 \propto C \propto V_N^{-\gamma'}, \tag{24}$$

then γ' may be less than γ by a factor that could in principle be only $\frac{1}{2}$.

As for the continuum theory of Faber, this too seems unable, in its simplest form, to match exactly the temperature dependence of S_2 at atmospheric pressure for 5CB [8]; discrepancies exist not only near T_{NI}, where the theory is known to fail, but also at temperatures such that $S_2 > 0.5$, where it describes the behaviour of artificial nematics, as explored by computer simulation techniques, rather well. It looks as though [17] we need for 5CB to adopt a value for $S_2(0)$ in equations (20) and (21) which is less than unity, and at the same time to allow for thermal excitation of less than $2N$ modes. Modified in this way continuum theory could be consistent with a less rapid variation of K along lines of constant S_2 than equation (22) would require, provided that both $S_2(0)$ and $K(0)$ could be supposed to increase on compression. Such a supposition would not seem implausible on physical grounds.

Alternative explanations for what we have observed using 5CB are therefore available. But why should the behaviour of 6CB be different? The two nematics are close enough in structure for observable properties such as Σ, $\Delta\chi$ and N.M.R. linewidth to vary with temperature at atmospheric pressure in very much the same way for both [11, 12] and although we have noted, in §3.3, one difference in their behaviour under pressure—the fact that S_2 is constant along the clearing curve for 6CB but decreases slowly for 5CB—it seems a rather subtle difference of no obvious relevance to our principal results. The rhetorical question at the start of this paragraph must remain unanswered.

Appendix
The biaxiality correction

Molecules of 5CB and 6CB do not have rotational symmetry about their long axes. Thus if we define the orientation of the director with respect to (x, y, z) axes set in an individual molecule by Euler angles (α, β, γ) and define an order parameter in the usual way by means of an ensemble average,

$$S_2 = \tfrac{1}{2}\langle 3\cos^2\beta - 1\rangle,$$

we can assume (given that the nematic displays no observable biaxiality in the bulk) that averages over α vanish but we cannot make the same assumption about averages over γ. The Saupe ordering matrix, of which S_2 ($\equiv S_{zz}$) is one component, is defined in such a way that

$$S_{xx} - S_{yy} = \tfrac{1}{2}\langle 3\sin^2\beta\cos^2\gamma\rangle,$$

and the biaxiality ratio is then

$$b = (S_{xx} - S_{yy})/S_{zz}.$$

In [11], which may be consulted for further details, it was labelled B; we have changed our notation to avoid confusion with the magnetic field.

It is probable that the magnitude of b has some effect on the ratio (K_1/K_3), and the apparent insensitivity of that ratio to compression along lines of constant S_2 suggests a similar insensitivity on the part of b. That argument is too qualitative, however, to be relied upon. We prefer to note that for 5CB—and in this respect 6CB is probably much the same [11]—b is only about 0·15 or so. Changes in b should be negligible in the context of the present paper provided that

$$\frac{\alpha(\partial b/\partial p)_{S_2}}{(1 + \alpha b)} \ll \gamma.$$

This inequality corresponds roughly to

$$\left(\frac{\partial\langle\sin^2\beta\cos^2\gamma\rangle}{\partial V_{\mathrm{N}}}\right)_{S_2} \ll 50\,\frac{\langle\sin^2\beta\cos^2\gamma\rangle}{V_{\mathrm{N}}}.$$

It would require a remarkable sensitivity to compression of averages over γ for it to fail.

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