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Molecular Ordering and Even-Odd Effect in a Homologous Series of Nematic Liquid Crystals*

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ABSTRACT

Order parameters $S = \langle P_2(\cos\theta)\rangle$ have been measured in a homologous series of nematic liquid crystals, p-alkoxyazoxybenzenes, by ^{13}C nmr in a magnetic field of 23 kG. The ordering exhibits an even-odd alternation along the series in agreement with other thermodynamical quantities. A comparison of our data at the isotropic-nematic transition temperatures is made for the first time with a recent theory of Marčelja which explicitly accounts for end chain interactions between the molecules, and agreement is good. Some conclusions are drawn concerning molecular conformational motion and ^{14}N spin relaxation in the nematic phase.

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Although molecular end chains are known to have perceptible and important effects on the properties of liquid crystals, until recently, theories of the liquid crystal phase have not included their effects explicitly. Rather, their influence was taken into account indirectly by assuming simply that they 'take up space' and thus affect the average interaction between essentially rigid molecules.[1] Marčelja has now presented a theory which accounts specifically for the effects of the end chains on the anisotropic interactions between the molecules.[2] This theory provides good agreement with experimental data on isotropic-nematic transition temperatures and entropies, and explains for the first time the 'even-odd' effect in these quantities along a homologous series.[3] A quantity of prime concern in the structure of the nematic phase is the degree of orientational molecular ordering, described by an order parameter[4]:

$$S = \langle P_2(\cos\theta)\rangle \tag{1}$$

where θ is the angle between the long molecular axis and the nematic director. A striking prediction of the theory is that S should depend significantly on the end chains and should also exhibit the even-odd effect in a homologous series. In this letter we present the results of measurements of the order parameter for a homologous series of nematic liquid crystals at the isotropic-nematic transitions and lower in the nematic phase. These data provide the first convincing

manifestation of the even-odd effect for the ordering near the transitions, and a reliable basis for the quantitative examination of microscopic theories of liquid crystal phases. In addition, we present some conclusions regarding conformational motion of the liquid crystal molecules and ^{14}N spin relaxation in the nematic phase.

The technique we have employed for these studies is carbon-13 nuclear magnetic resonance and the liquid crystal series is that of figure 1, p-alkoxyazoxybenzenes, with n + 1 from 1 to 7.[5] Previously, high resolution nmr has not been generally possible in liquid crystals and limited approaches employing wideline nmr, deuterated materials and small probe molecules have been used. In some recent experiments, we demonstrated that with high power proton spin decoupling, high resolution and tractable ^{13}C nmr spectra can be obtained, and that they are sensitive to molecular ordering through the strongly anisotropic ^{13}C chemical shielding tensors.[6] The present experiments were performed on a homebuilt ^{1}H-^{13}C double resonance spectrometer.[7] Proton decoupling fields were provided by a tuned rf amplifier delivering several hundred watts of power into a double coil probe in the bore of a superconducting magnet. The probe was tuned with high voltage capacitors of polished copper tubes with glass impregnated teflon dielectric. Temperature was controlled to 0.2°C with a stream of dry nitrogen gas passing over a feedback regulated tungsten heater near the sample. Samples were obtained commercially from Eastman Kodak Co., checked for purity (m.p. within 1°C of literature values) and then sealed under vacuum in pyrex ampoules after several freeze-thaw cycles.

Figure 1 shows Fourier-transform ^{13}C nmr spectra in the isotropic and nematic phases of series I. The line assignments appear in the caption. In the nematic phase, some of the spectra were acquired with proton-enhancement to improve the signal/noise for the low abundance ($\sim$ 1%) ^{13}C nuclei.[8] Without intense spin decoupling, broad, featureless spectra normally characteristic of the nematic phase were observed. In the isotropic phase, the chemical shifts σ_i for each of the carbon positions in the molecule are given by:

$$\sigma_i = \frac{1}{3} \mathrm{Tr}\, \underset{\sim}{\sigma} \tag{2}$$

where $\underset{\sim}{\sigma}$ are the chemical shielding tensors.[9] In the nematic phase, we assume rapid reorientation of the molecules about their long axes, yielding averaged tensors $\bar{\underset{\sim}{\sigma}}$ with elements $\bar{\sigma}_{\parallel}$ and $\bar{\sigma}_{\perp}$ relative to the long axis. The observed chemical shifts σ are then given by:

$$\sigma = \sigma_i + \frac{2}{3} S \left(\bar{\sigma}_{\parallel} - \bar{\sigma}_{\perp}\right) \tag{3}$$

where S is the order parameter in (1). For the aromatic rings, it has been shown that $\bar{\sigma}_{\parallel} < \bar{\sigma}_{\perp}$[6,8] and thus a downfield shift of the lines is expected in the isotropic-nematic transition, exactly as observed for the whole series in figure 2. Further conclusions are presented from these spectra at the end of this letter.

An example of the dependence of chemical shifts on temperature for the lines in p-butoxyazoxybenzene (n + 1 = 4) is depicted in figure 3, reflecting the first-order isotropic-nematic transitions and the marked effect of ordering on the chemical shifts. Similar behavior

was observed for the whole series. In order to extract quantitative values of the order parameters for comparison with theory, we make the assumptions that the aromatic $\underset{\sim}{\sigma}$ tensors remain the same and that the geometry of the aromatic region of the molecules is similar throughout the homologous series. The values of σ for the low field lines can then be used to calculate relative values for S from (3). Such values at the isotropic-nematic transitions and 5°C below are shown in figure 4, normalized to 0.43, the Maier-Saupe value for $n + 1 = 1$. The values at the transition temperatures were obtained in a separate set of experiments with ^{13}C spectra displaying two sets of lines from the isotropic and nematic phases in equilibrium. Also shown are the transition values calculated by Marčelja[2]. Although these are not expected to be accurate in a mean field theory near the transitions, the correspondence in general trend and in the even-odd effect is quite remarkable[10]. Values of S over the entire temperature ranges are available from our data and these will be presented in a full description of our work and compared with any forthcoming theoretical calculations.

Finally, it is interesting to comment on some aspects of conformational motion and spin relaxation which can be studied by our technique:

1. Molecular reorientation about the long axes is certainly rapid, but there is a question of conformational rigidity. In particular, are the benzene rings fixed or do they rotate rapidly about the para axes? In PAA, Rowell et al have found that they rotate rapidly, by deuteron magnetic resonance[11]. Similar conclusions

were reached regarding MBBA[6] and the center ring in TBBA[12]. If the rings are fixed for the series I which we have studied, then in the nematic phase we expect a chemical shift difference $\Delta\sigma$ for the two carbon positions ortho to the N = N linkage given by:

$$\Delta\sigma \approx 1.73 \cdot S \cdot \sin\phi \cos\phi \, (\sigma_{22}-\sigma_{11}) \qquad (4)$$

where ϕ is the angle between the long molecular axis and the para axis, σ_{ii} are the low field elements of $\underset{\sim}{\sigma}$ for the benzene ring, one of the rings is assumed not to deviate too markedly from planarity[13], and 120° angles are assumed for the rings. Taking values of $\phi = 8°$, $\sigma_{11} = -98$ ppm, $\sigma_{22} = -13$ ppm[14] and S = 0.6, we see from (4) that $\Delta\sigma \approx 12$ ppm which is clearly within the limits of our resolution. Since no such additional splittings occur in the nematic phase, we conclude that the benzene rings rotate or flip about the para axes at a rate greater than 1 kHz for the whole series throughout the nematic ranges.

2. A striking observation from the spectra in figure 2 is that one set of lines appears to disappear consistently for the whole series in the isotropic-nematic transitions. These are the lines assigned to ^{13}C nuclei bonded to the N = N group and thus coupled to ^{14}N nuclei. A possible explanation for this effect is the combination of ^{13}C-^{14}N magnetic dipolar coupling and ^{14}N spin relaxation by fluctuating electric field gradients. The threefold splitting in ^{13}C lines expected from the coupling is $\sim$ 1 kHz and thus ^{14}N spin relaxation with $T_1 \sim 1$ ms would cause a severe broadening of the

^{13}C lines making the resonance essentially unobservable. Much slower or more rapid ^{14}N spin relaxation would yield three or one sharp lines respectively. ^{14}N spin relaxation has been measured in the isotropic phase of PAA[15], and it would be interesting to check our contention directly in the nematic phases.

We have carried out one set of experiments with results which are consistent with our explanation. Di-ethylazoxybenzoate, the analog of series I (figure 1) with -COO C_2H_5 constituting the side chains, exhibits a smectic A phase. In the isotropic-smectic transition the ^{13}C-^{14}N lines again disappear, but when the sample is rotated by 55° (the magic angle) in the smectic A phase they reappear[16]. This is consistent with our explanation, since at this angle the ^{13}C-^{14}N magnetic dipolar coupling disappears rendering the three ^{13}C transitions degenerate and eliminating the broadening due to ^{14}N spin relaxation.

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References and Footnotes

1. K. K. Kobayashi, J. Phys. Soc. Japan, 29, 101 (1970); W. L. Mc Millan, Phys. Rev. A, 4, 1238 (1971); 6, 936 (1972); F. T. Lee, H. T. Tom, Y. M. Shih and C-W. Woo, Phys. Rev. Lett., 31, 1117 (1973); H. Schroder, private communication.
2. S. Marčelja, Sol. St. Comm., 13, 759 (1973); J. Chem. Phys., 60, 3599 (1974).
3. H. Arnold, Z. Phys. Chem. (Leipzig), 226, 146 (1964); J. van der Veen, W. H. de Jeu, M. W. M. Wanninkhof and C. A. M. Tienhoven, J. Phys. Chem., 77, 17 (1973); W. H. de Jeu, J. van der Veen and W. J. A. Goossens., Sol. St. Comm., 12, 405 (1973).
4. W. Maier and A. Saupe, Z. Nat., A14, 882 (1959).
5. C. Weygand and R. Gabler, J. Prakt. Chem., 155, 332 (1940).
6. A. Pines and J. J. Chang, Phys. Rev. A, in press, J. Am. Chem. Soc., in press; A. Pines, presented at the 15th Experimental NMR Conference, Raleigh, N.C., April, 1974.
7. A. Pines, J. J. Chang and R. G. Griffin, J. Chem. Phys, in press.
8. A. Pines, M. G. Gibby and J. S. Waugh, J. Chem. Phys., 59, 569 (1973).
9. N. F. Ramsey, Phys. Rev., 78, 699 (1950).
10. An even-odd variation has previously been observed by I. G. Chistyakov and V. M. Chaikovskii, Kristallographiya, 18, 293 (1973), using X-rays. However, these authors report single temperature values at equal points above the solid-nematic

transition. They thus contain inherently the variations in nematic range and are not useful for comparison with theory relative to the isotropic-nematic transitions.

11. J. C. Rowell, W. D. Phillips, L. R. Melby and M. Panar, J. Chem. Phys., 43, 3442 (1965).

12. Z. Luz and S. Meiboom, to be published. We are grateful to Dr. Meiboom for sending us a preprint describing this work.

13. W. R. Krigbaum, Y. Chatani and P. G. Barker, Act. Cryst., B26, 97 (1970); W. R. Krigbaum and P. G. Barker, Act. Cryst., B27, 1884 (1971).

14. A. Pines, M. G. Gibby and J. S. Waugh, Chem. Phys. Lett., 15, 373 (1972).

15. B. Cabane and W. G. Clarke, Phys. Rev. Lett., 25, 91 (1970).

16. A. Pines and S. Allison, to be published.

Figure Captions

Figure 1. p-Alkoxyazoxybenzenes, series I. D represents the long molecular axis and ϕ is the angle between this axis and the benzene 'para' axes.

Figure 2. Fourier transform ^{13}C nmr spectra of the series in figure 1 with high power proton spin decoupling. Assignments in the isotropic phase are: $\sim$ -40 ppm, aromatic C-O; $\sim$ -20 ppm, C-N; $\sim$ -10 to 10 ppm, remaining 'ortho' aromatic carbons; $\sim$ 50 - 70 ppm, aliphatic C-O. In the nematic phase the assignment order remains the same but the lines assigned to ^{13}C coupled to ^{14}N nuclei (C-N) appear to broaden and are unobservable, as discussed in the text. The nematic phase spectra were taken at various temperatures.

Figure 3. Dependence of chemical shifts σ on temperature for p-butoxyazoxybenzene, $n + 1 = 4$. T_c is the isotropic-nematic transition temperature; $T_c = 136°C$.

Figure 4. Relative order parameters calculated from the aromatic chemical shifts at T_c (normalized to 0.43 for $n + 1 = 1$) and 5°C below T_c in the nematic phase. The vertical bars depict the typical range of values from the different aromatic lines. The theoretical data are taken from the mean field calculation of Marčelja, reference 2.

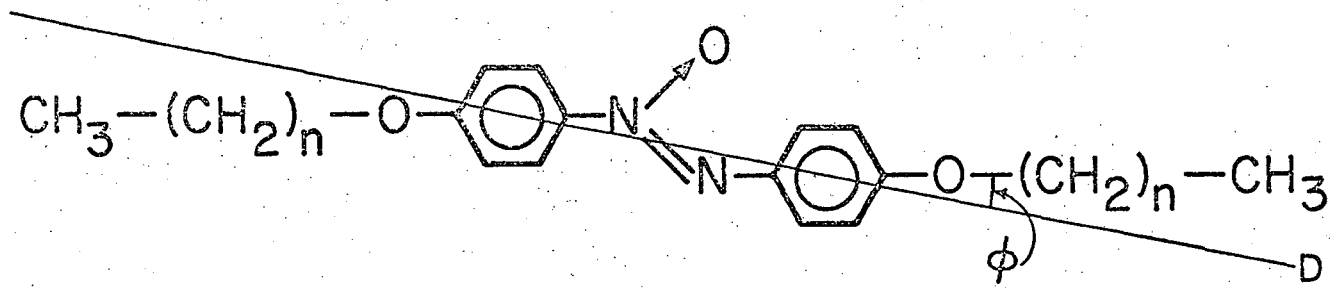

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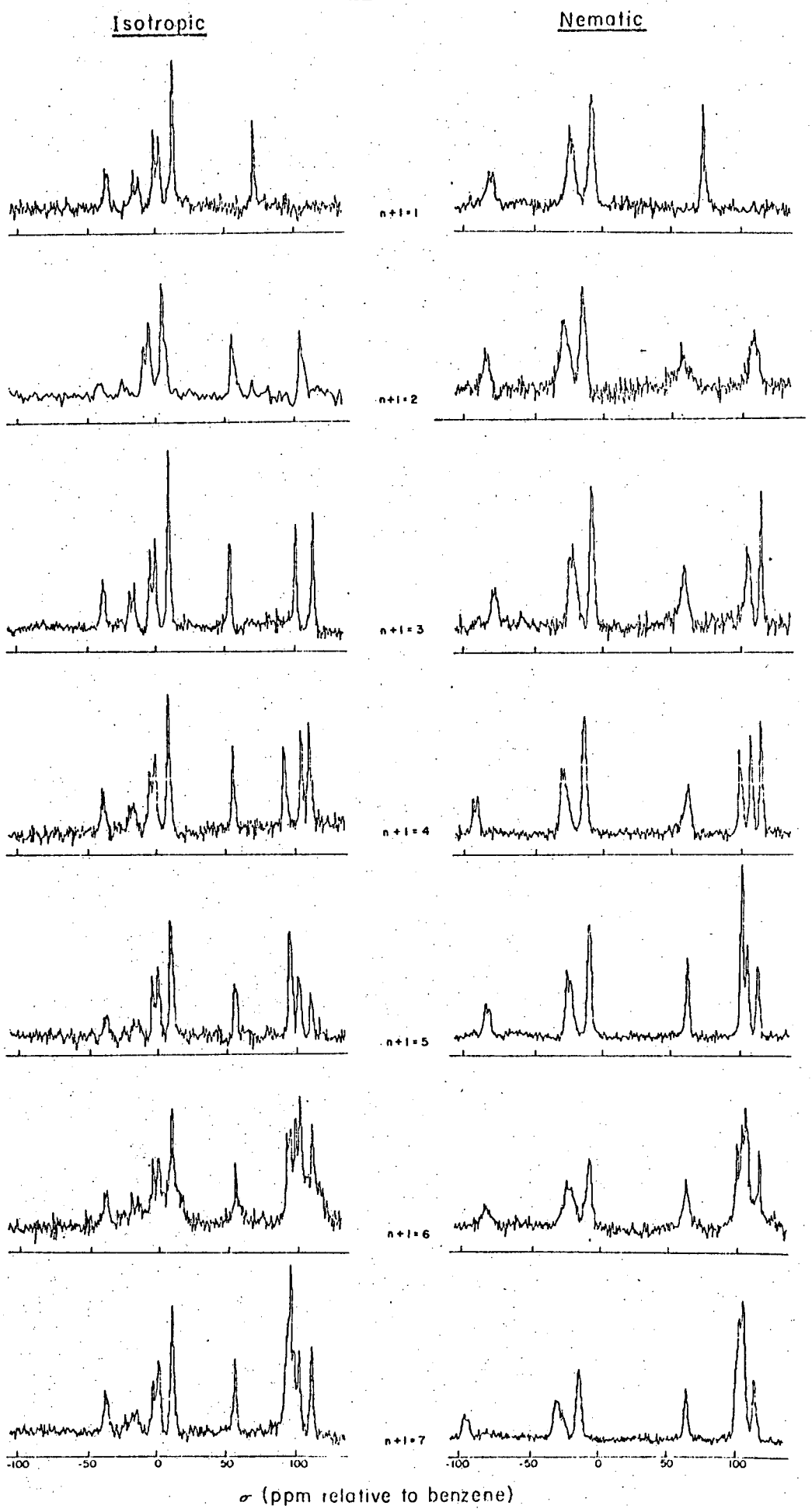
Fig. 1



XBL 747-6739

Fig. 2

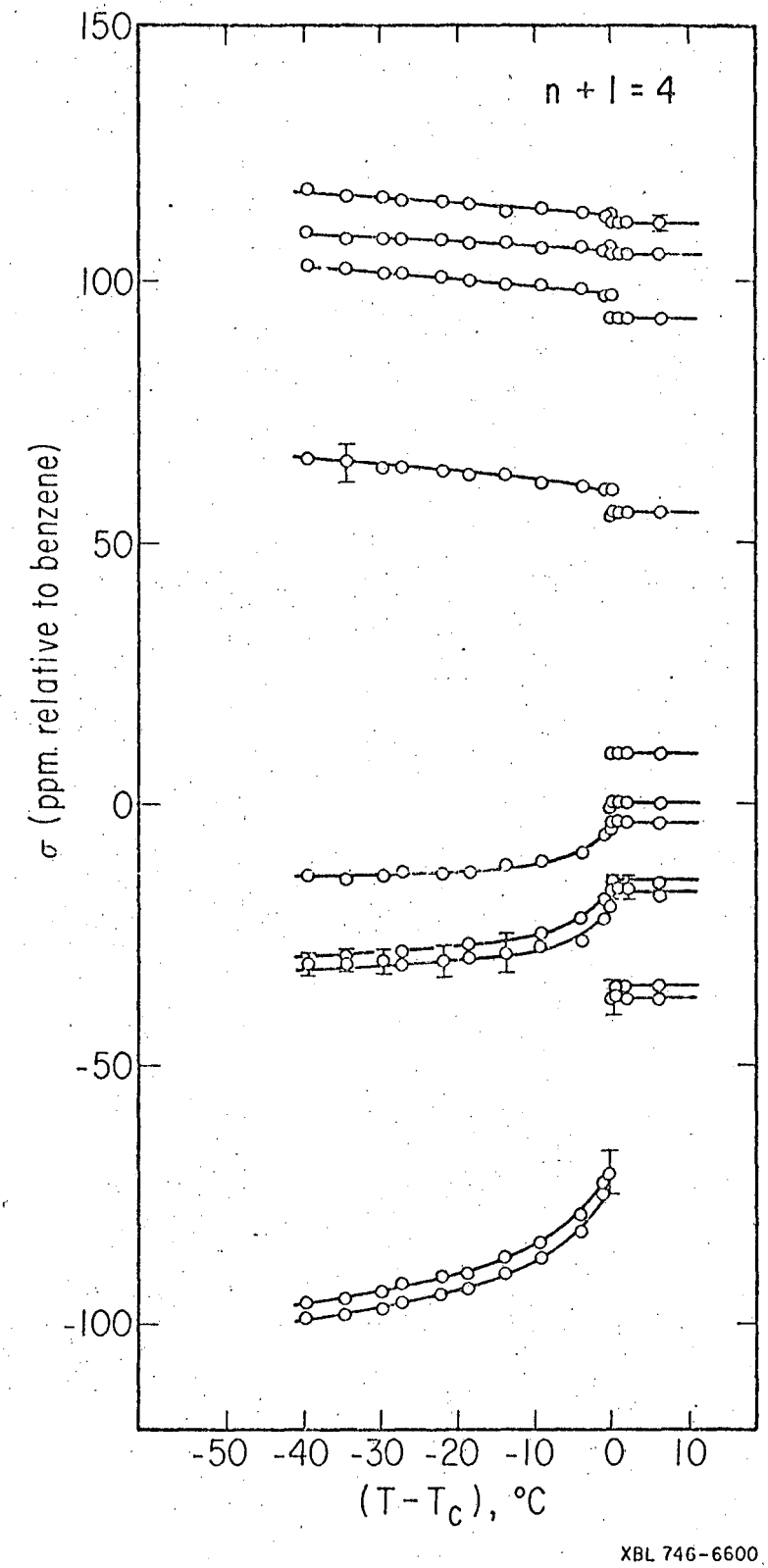

n + l = 4
150
100
50
0
-50
-100
σ (ppm. relative to benzene)
-50 -40 -30 -20 -10 0 10
(T - T_C), °C
XBL 746-6600

Fig. 3

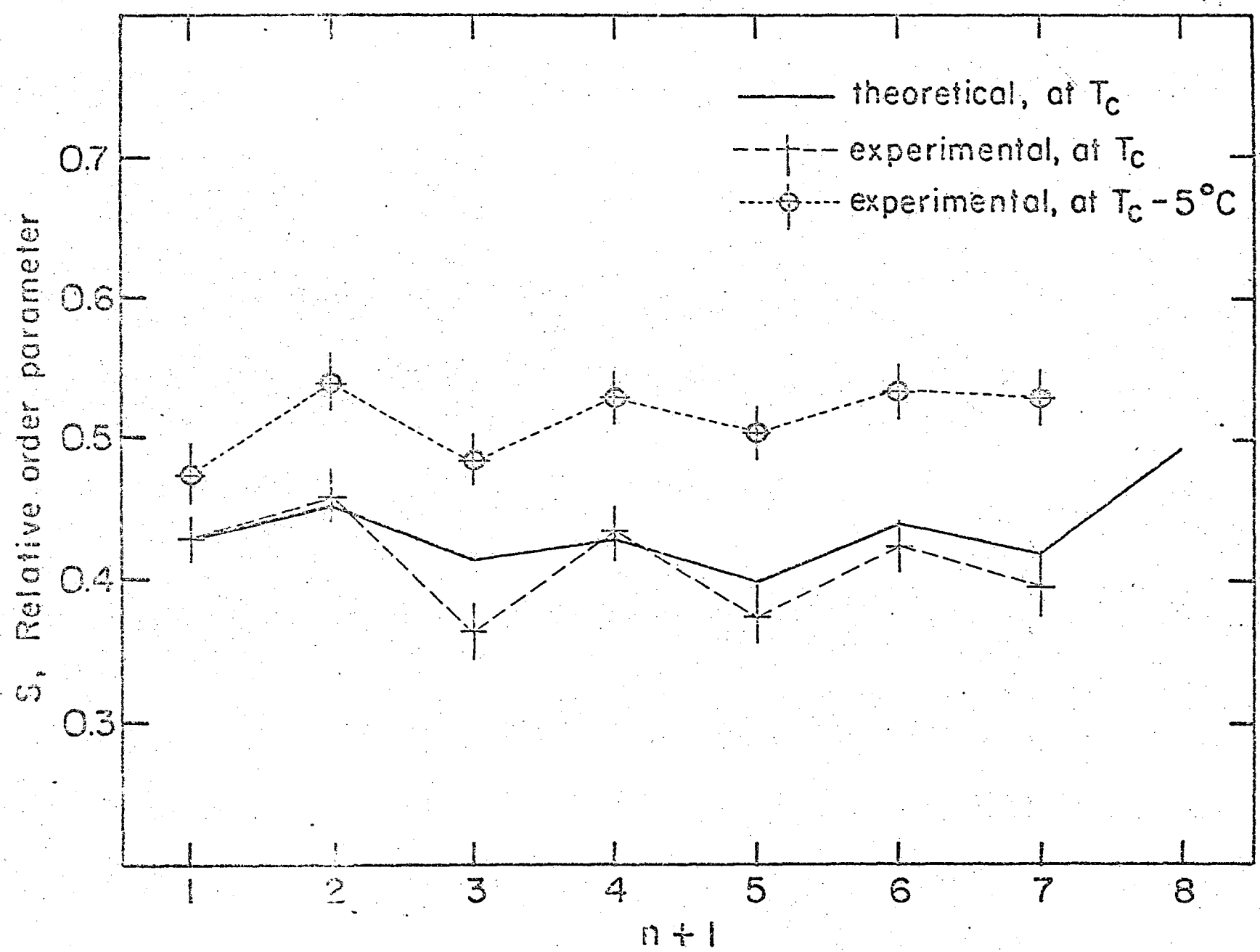


Fig. 4

XBL 747-6740

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