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structures, high melting points, and ir spectra strongly indicate exclusively intermolecular H bonding,[8] and yet both exhibit very stable mesophases.

The diamine was prepared by hydrogenation of p-phenylene di-p-nitrobenzoate (3, Z = NO_2)[9,10] with Adams catalyst in dioxane. *Anal.*[11] Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.80; H, 4.49; N, 7.84. It melts at 322.5° to a peculiar nematic[12] mesophase consisting of birefringent, schlieren-textured or striated zones in a predominantly homeotropic (pseudoisotropic) matrix. The compound's ir spectrum (KBr pellet) shows strong absorption bands at 3360 and 3380 cm^{-1} (N–H stretch, intermolecular H bonding) and at 3433 and 3480 cm^{-1} (N–H stretch, free NH_2). On cooling the nematic melt, crystallization occurs at about 275°.

The diphenol was first synthesized from the diamine by tetrazotization followed by acid hydrolysis (transition temperatures: solid–nematic, 339°; nematic–smectic, 248°). *Anal.*[11] Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03. Found: C, 68.41; H, 4.10. The product is soluble in cold 5% aqueous NaOH solution and is converted to the known di-n-hexyloxy ether (3, Z = n-$C_6H_{13}O$) by reaction with n-hexyl bromide in the presence of K_2CO_3 (transition temperatures: solid–nematic, 123°; nematic–isotropic, 211° (lit.[13] 124°, 213°)). A purer product was recently obtained in better yield by hydrogenolysis of p-phenylene di-p-benzyloxybenzoate (3, Z = $C_6H_5CH_2O$) in dioxane over palladium on charcoal. This material melts at 340° to a nematic mesophase identical in appearance with that of the diamine. Its ir spectrum (KBr pellet) has a very strong absorption band at 3390 cm^{-1} (O–H stretch, intermolecular H bonding). The melt supercools phenomenally. At 267°, there is a thermally reversible transition to a smectic[12] mesophase, unmistakable from its focal-conic texture. Crystallization does not commence until about 215°.

The thermal stabilities of the nematic mesophases are remarkable. Neither shows evidence of transition to isotropic liquid on heating to 360°, where marked decomposition (gas evolution) occurs. The stability of the diphenol's mesophases is further demonstrated by their resistance to crystallization on cooling over 120° below the melting point.[14] Our conclusion is that intermolecular H bonding is not a deterrent to mesomor-

(8) Molecular models of the compounds can be manipulated to allow intramolecular H bonding between the amino or hydroxy groups. However, these cyclic, nonlinear structures are not consistent with the observed mesomorphism.
(9) M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970).
(10) J. P. Schroeder and D. W. Bristol, *J. Org. Chem.*, **38**, 3160 (1973).
(11) Galbraith Laboratories, Inc., Knoxville, Tenn.
(12) In a nematic mesophase, the only constraint on the rod-shaped molecules is that their long axes be parallel. In a smectic mesophase, the molecules are not only parallel but are also in layers with their long axes more or less perpendicular to the planes of the strata.
(13) S. L. Arora, J. L. Fergason, and T. R. Taylor, *J. Org. Chem.*, **35**, 4055 (1970).
(14) In these determinations, the sample was cooled immediately after melting. The low freezing point may be due, in part, to decomposition products resulting from the high temperature required for fusion. However, this effect is believed to be small inasmuch as there was only slight discoloration and little or no gas evolution.

phism in these compounds and, in consideration of the high mesophase stabilities, may even encourage it. We propose that this unusual behavior is associated with the particularly strong tendency of the p-phenylene dibenzoates (3) to be mesomorphic.[10] This propensity undoubtedly carries over to the diamine and diphenol. Under these circumstances, with the long molecular axes tending to be parallel, there are two available modes of intermolecular H bonding between NH_2 or OH groups that are compatible with mesomorphism. Lengthwise head-to-tail bonding would result in linear chains of molecules that are consistent with nematic mesomorphism. Sidewise bonding between adjacent parallel molecules is consistent with smectic mesomorphism. Molecular models indicate that lengthwise bonding is entirely reasonable but that sidewise bonding gives a crowded arrangement with aromatic rings on adjacent molecules facing one another in very close proximity. X-Ray diffraction data for the solids and the smectic mesophase would be helpful in appraising the validity of these hypothetical molecular arrangements, and we intend to obtain such information.

If this view is generally correct, other compounds with terminal NH_2 and OH groups should be mesomorphic. However, it appears that a backbone structure which is especially prone to give a parallel molecular alignment may be necessary; e.g., although the p,p'-di-n-alkoxyazoxybenzenes (4, Z = n-alkoxy) are mesomor-

4
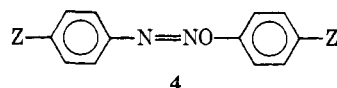
phic,[2] the corresponding diphenol (4, Z = OH) is not.[15,16]

(15) D. Bigiavi and G. Carrara, *Gazz. Chim. Ital.*, **53**, 285 (1923).
(16) R. A. Raphael and E. Vogel, *J. Chem. Soc.*, 1958 (1952).

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Nuclear Magnetic Resonance Spectroscopy. Carbon-13 T_1 Measurements of Cycloalkanes[1]

Sir:

The recent increase of interest in ^{13}C spin–lattice relaxation times[2,3] prompts us to report data on ^{13}C T_1's of cycloalkanes. These compounds have been chosen because (i), with only one nmr signal, they are ideal to study the reproducibility and the systematic

(1) Supported by the National Science Foundation and by the Public Health Service, Research Grant No. GM-11072, from the Division of General Medical Sciences.
(2) G. C. Levy, *Accounts Chem. Res.*, **6**, 161 (1973).
(3) (a) N. J. M. Birdsall, A. G. Lee, Y. K. Levine, J. C. Metcalfe, P. Partington, and G. C. K. Roberts, *J. Chem. Soc., Chem. Commun.*, 757 (1973); (b) G. A. Gray and S. E. Cremer, *J. Magn. Resonance*, **12**, 5 (1973); (c) C. F. Brewer, H. Sternlicht, D. M. Marcus, and A. P. Grollman, *Biochemistry*, **12**, 4448 (1973); (d) A. Allerhand and R. A. Komoroski, *J. Amer. Chem. Soc.*, **95**, 8228 (1973); (e) H. Saito, H. H. Mantsch, and I. C. P. Smith, *ibid.*, **95**, 8453 (1973); (f) D. M. Grant, R. J. Pugmire, E. P. Black, and K. A. Christensen, *ibid.*, **95**, 8465 (1973).

errors involved in relaxation-time measurements and (ii), with their expected differences in motional behavior, a considerable change of relaxation mechanisms could well take place in the series.

The relaxation data were determined using the progressive saturation method[4] with our Brukerian DFS-60[5] at a resonance frequency of 15.09 MHz. The solutions (50% w/w in $CDCl_3$) were degassed by three freeze–thaw cycles and were contained in special bulbs which matched the geometry of the rf signal coil in order to avoid diffusion effects within the liquid sample and the effect of gas–liquid exchange. The probe temperature was 30°. A spectral width of 200 Hz was used giving 2050 data points (acquisition time, 5 sec) to monitor the free–induction decay. An 8 K Fourier transform provided a resolution of 0.05 Hz/point, which seemed desirable for accurate integration. Of the various methods commonly tried to evaluate peak integrals, the most convenient method proved to be the application of a very small exponential weighting factor to the free-induction decay which produced broad symmetrical peaks with intensities directly proportional to their integrals.[6]

Nuclear Overhauser enhancement (NOE) measurements were made using a gating technique. During a delay time in the order of five times T_1, the proton decoupling frequency synthesizer was electronically switched to a position far from resonance. The ^{13}C T_1 data obtained are given in Table I. For factorization into the spin rotation and dipole–dipole contribution to the overall relaxation mechanism, the usual equations were used,[2] assuming the absence of other relaxation mechanisms for these compounds.

The major systematic error, using the progressive saturation method, proved to be the accuracy of determining the flip angle.[4] Because the common, small data-processing computers allow changes in the pulse width only in integer steps of microseconds, the method can hardly be more accurate than 10%, especially on a single-coil instrument with a typical 90° pulse within the

Table I. Relaxation Times, Nuclear Overhauser Enhancements for ^{13}C in Cycloalkanes $(CH_2)_n$

n	T_1, sec	NOE	T_{1D},^{a} sec	T_{1SR},^{b} sec
3	36.7	2.0	72.2	74.6
4	35.7	2.4	50.7	121
5	29.2	2.52	38.2	124
6	19.6	2.9	20.5	447
7	16.2	2.96	16.4	>1000
8	10.3	3.0	10.3	>1000
10	4.7	3.0	4.7	>1000

^{a} Contribution to the overall T_1 of dipolar relaxation. ^{b} Contribution to the overall T_1 of spin-rotation relaxation.

order of 12 μsec. The random error of our measurements was close to 5%. To our knowledge, the only other reported data on cycloalkanes is that of Alger and Grant[7] who reported a T_1 for cyclohexane of 17.5 ± 2 sec, well in agreement with our results.

The data in Table I clearly show that for the larger molecules (cyclohexane to cyclodecane) the dipolar mechanism is the only effective relaxation mechanism whereas, for the smaller molecules, spin rotation is competitive. In cyclopropane, both mechanisms are equally important. Preliminary results in this laboratory showed that there is no significant concentration dependence of the relaxation time of cyclohexane. The macroscopic viscosities of 50% solutions of cyclopentane to cyclooctane show a surprisingly good correlation to the measured relaxation time. However, the physical significance of this is not wholly clear at this point. We are currently investigating the temperature dependence of the relaxation times of these molecules and will report later studies with substituted cycloalkanes and bridged cycloaliphatic compounds.

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(7) T. D. Alger and D. M. Grant, *J. Phys. Chem.,* 75, 2538 (1971).

(8) (a) Postdoctoral Research Fellow, Deutsche Forschungsgemeinschaft, 1973–1974; (b) Postdoctoral Research Fellow, Deutscher Akademischer Austauschdienst, 1973–1974.

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Book Reviews*

Annual Review of Materials Science. Volume 3. Edited by R. A. HUGGINS, R. H. BUBE, and R. W. ROBERTS. Annual Reviews Inc., Palo Alto, Calif. 1973. 483 pp. Price ?

This volume is a compilation of fifteen reviews in the general area of physics and physical chemistry of solid materials, from elements, such as carbon, to complex mixtures such as concrete. More general topics, such as crystallization, mass transport in solids, liquid crystals, etc., constitute other chapters. The reviews appear to be comprehensive, with substantial bibliographies, but unfortunately it is not made clear up to what date the literature was

surveyed. Substantial author and subject indexes are a welcome feature.

Bibliography of Column Chromatography 1967–1970. Supplementary Volume No. 3 of the Journal of Chromatography. Edited by Z. DAYL, J. ROSMUS, M. JURICOVA, and J. KOPECKY. Elsevier, New York, N. Y. 1973. xix + 1067 pp. $68.50.

This fat and expensive paperback consists of a carefully organized bibliography which gives full titles of all citations (translated into English where necessary). The Table of Contents is a detailed guide of thirteen pages to the many subdivisions. There is also a 160-page author index and a 137-page list of compounds chromatographed. This work is obviously indispensable to libraries

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