Torr) and then further concentrated with an air stream overnight.

The oil was dissolved in a little methanol, and ethereal diazomethane (less than 1 g, from Diazald, following the procedure of de Boer)[13] was added until the yellow color remained. After 1 hr at room temperature the solvents were removed *in vacuo*. The crude products were chromatographed on 75 g of SilicAR CC-7 with 7:3 chloroform–Skellysolve B by the procedure described for the preparation of this compound from methyl methacrylate. Gas chromatography at 190° led to a combination of identical fractions. Crystallization from ether–hexane gave the following physical constants for the two samples of 3-*O*-acetyl-(*R*)-2,3-dihydroxy-2-methylpropanoate. Sample I (derived from (*S*)-atrolactic acid) weighed 0.49 g (52.3%), mp 31–34°. The rotation of sample I (optical purity 77.1%) was determined, $[\alpha]^{23}{}_D$ −7.33° (*c* 6.09, EtOH), from which the rotation of an optically pure sample in ethanol is calculated to be −9.52°.

Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 48.00; H, 7.01.

Sample II (derived from α-methylstyrene) weighed 0.62 g (61.5%), mp 35–36°C, $[\alpha]^{23}{}_D$ −9.18° (*c* 5.07, EtOH). Assuming that sample II is 97.5% optically pure, the rotation for a pure sample should be −9.42°.

Anal. Calcd for $C_7H_{12}O_5$: C, 47.72; H, 6.87. Found: C, 47.49; H, 6.74.

Registry No.—**1**, 35638-89-2; (*R*)-**1**, 35638-90-5; **2**, 4217-66-7; (*R*)-**2**, 35638-92-7; (*S*)-**2**, 2406-22-6; (*R*,*S*)-**3**, 35638-93-8; (*S*,*R*)-**3**, 35638-94-9; (*R*)-**4**, 35638-95-0; (*S*)-**4**, 35638-96-1; **5**, 19860-56-1; **6**, 35638-98-3.

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[13] (a) T. J. deBoer and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **73**, 229 (1954); (b) Technical Information Sheet, D2800-0, Aldrich Chemical Co., Jan 1967.

Mesomorphic Properties of Some Ring-Methylated Phenyl Benzoyloxybenzoates

WILLIAM R. YOUNG,* IVAN HALLER, AND DENNIS C. GREEN

IBM Watson Research Center, P. O. Box 218, Yorktown Heights, N. Y. 10598

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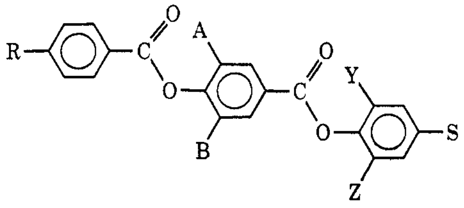
To delineate the role of laterally placed methyl groups upon mesomorphic character, a series of esters of the general formula 1 was prepared, where R and S were ethoxyl and butyl, respectively, and A, B, Y, and Z were the nine independent combinations of methyl and hydrogen. Every derivative exhibited a nematic phase, and the nematic–isotropic transition temperatures decreased as the number of appended methyl groups increased. An investigation of the nematic–isotropic transition by means of differential scanning calorimetry revealed that methylation of the central ring increased the intermolecular interactions and order in the nematic phase, relative to the isotropic phase, while no such effect was apparent upon methylation of the terminal ring. This result demonstrates that the concept of increased intermolecular separation, resulting from laterally placed substituents, is not always sufficient to account for a decrease in nematic–isotropic transition temperatures.

As part of our efforts to obtain stable, low-melting nematic liquids with long mesomorphic ranges and to delineate the effects of symmetry and molecular structure upon mesomorphic properties,[1-3] an investigation was undertaken to uncover the liquid crystalline character of a series of esters derived from phenyl 4-benzoyloxybenzoate.[4] Previous work on more symmetrical esters, *viz.*, the 1,4-phenylene bis(4-*n*-alkoxybenzoates)[5-9] and di-4-*n*-alkoxyphenyl terephthalates,[7] have demonstrated that these esters can exhibit very long nematic ranges (~100°). In addition, Arora, *et al.*, by affixing a methyl group to the central ring of one of their phenylene bisbenzoates, have prepared a material, the lowest melting substance in either series, with a nematic range of 72–156°.[8]



1

For this investigation, compounds of the general formula **1** were prepared, where R and S were selected to be ethoxyl and *n*-butyl, respectively, in analogy with the low melting points and high nematic CMD values (clearing point/melting point differences[2]) for Schiff bases,[10-12] acetylenes,[13] and chlorostilbenes.[1,2] With the aim of understanding the role of laterally placed methyl groups upon mesomorphic properties, nine compounds were prepared corresponding to all independent combinations of methyl and hydrogen in positions A, B, Y, and Z. Two compounds in which R and S were interchanged were also prepared. The pertinent phase transition temperatures of the compounds were determined, and, in addition, the enthalpies and entropies of the mesomorphic transitions were measured by differential scanning calorimetry. The results are presented in the next section.

Results and Discussion

Synthesis.—The esters prepared in this investigation and their physical properties are listed in Tables IA and IB. The sequence of reactions employed in their

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[1] W. R. Young, A. Aviram, and R. J. Cox, *Angew. Chem., Int. Ed. Engl.*, **10**, 410 (1971).

[2] W. R. Young, A. Aviram, and R. J. Cox, *J. Amer. Chem. Soc.*, **94**, 3976 (1972).

[3] W. R. Young, I. Haller, and A. Aviram, *Mol. Cryst. Liquid Cryst.*, **15**, 311 (1972).

[4] Nematic esters of this class have been previously reported. See D. Vorlaender, *Z. Phys. Chem. (Leipzig)*, **105**, 211 (1923)

[5] M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

[6] M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

[7] M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2811 (1970).

[8] S. L. Arora, J. L. Fergason, and T. R. Taylor, *ibid.*, **35**, 4055 (1970).

[9] S. A. Haut, D. C. Schroeder, and J. P. Schroeder, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971, Abstract PHYS 146.

[10] H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *Angew. Chem., Int. Ed. Engl.*, **9**, 962 (1970).

[11] D. L. Fishel and Y. Y. Hsu, *Chem. Commun.*, **1971**, 1557.

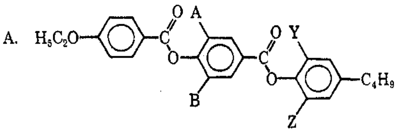
[12] H. J. Dietrich and E. L. Steiger, *Mol. Cryst. Liquid Cryst.*, **16**, 263 (1972).

[13] J. Malthete, M. Leclercq, J. Gabard, J. Billard, and J. Jacques, *C. R. Acad. Sci.*, **273C**, 265 (1971).

TABLE I

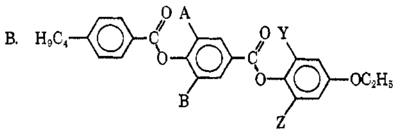
PHYSICAL PROPERTIES OF SOME MESOMORPHIC DERIVATIVES OF PHENYL 4-BENZOYLOXYBENZOATE

A.



No.	A	B	Y	Z	Transition[a]	Temp, °C	ΔH, kcal/mol	ΔS, eu
1a	H	H	H	H	C → N	124	9.15	23.0
					N → I	231	0.39	0.77
1b	H	H	CH_3	H	C → N	113	8.36	21.7
					N → I	188	0.25	0.55
1c	CH_3	H	H	H	C → N	91	7.32	20.1
					N → I	179	0.39	0.87
1d	H	H	CH_3	CH_3	C → N	143	8.82	21.2
					N → I	145	0.29	0.69
1e	CH_3	H	CH_3	H	C → I	160	10.97	25.3
					N → I[b]	143	0.36	0.88
1f	CH_3	CH_3	H	H	C → N	122	9.83	24.9
					N → I	129	0.51	1.26
1g	CH_3	H	CH_3	CH_3	C → I	195	*c*	*c*
					N → I[b]	104	*d*	*d*
1h	CH_3	CH_3	CH_3	H	C → I	138	10.41	25.9
					N → I[b]	103	0.50	1.32
1i	CH_3	CH_3	CH_3	CH_3	C → I	137	*c*	*c*
					N → I[b]	79	*d*	*d*

B.



No.	A	B	Y	Z	Transition[a]	Temp, °C	ΔH, kcal/mol	ΔS, eu
1j	H	H	H	H	C → N	138	7.63	18.6
					N → I	225	0.30	0.61
1k	CH_3	H	H	H	C → N	96	6.28	17.0
					N → I	176	0.40	0.90

[a] C, crystalline; N, nematic; I, isotropic. [b] Monotropic transition. [c] Not measured. [d] Rapid crystallization of supercooled liquid precluded measurement.

preparation is outlined in Scheme I, and the reaction pathways leading to the several key intermediate substances are depicted in Scheme II.

For the most part, the syntheses were based on well-known procedures and were routine. It is noteworthy, however, that esterifications employing a hindered 2,6-dimethylphenol derivative, such as **4c** and **7c**, required prolonged heating at reflux (3-4 days) in pyridine–toluene to effect complete reaction. Also, during the isolation of the benzoyloxybenzoic acids, **5**, a period of reflux in aqueous dioxane was sometimes required in order to hydrolyze the undesired carboxylic anhydride by-products.

The esters **1a**–**1k**, which were previously unreported, exhibited satisfactory elemental analyses[14] and consistent spectral properties. In every instance, intense vibrational absorption occurred in the infrared region at 1735 cm^{-1} (carbonyl stretching) and at 1505 and 1606 cm^{-1} (phenyl ring vibrations). In addition, at least five intense vibrational bands were detected in the C–O stretching region (1000–1300 cm^{-1}) for each ester. In the nmr spectra taken in deuteriochloroform, sharp singlets for the absorption of the methyl group on the central aromatic ring (A and/or B of structure **1**) appeared at 2.3 ppm downfield from TMS, while the absorption for methyl groups on the terminal ring (Y and/or Z) appeared as a sharp singlet at about 2.2 ppm.

The esters are colorless materials and, in comparison with the nematic Schiff bases, azobenzenes, azoxybenzenes, nitrones, and stilbenes, are highly transparent in the ultraviolet region.[2,15] For example, in ethanol solution ester **1f** exhibited a λ_{max} at 262 nm (ϵ 34,000) while ester **1a** exhibited λ_{max} at 267 (28,800); neither substance absorbed above 340 nm.

Melting Point Trends.—The melting points for esters **1a**–**1i** are listed in Table IA. They do not vary in any regular fashion as additional lateral methyl groups are affixed to the aromatic rings. Also, the desired low-melting ester, with a long nematic range including room temperature, was not approached; the lowest melting substance of the group exhibited a crystal–nematic transition of 91°.

The lack of a clear-cut trend in melting point as molecular structure is regularly varied is a common occurrence. Similar results have been reported and discussed several times for many series of mesomorphic compounds[15,16] and nonmesomorphic materials.[16] It is important to realize, however, that the addition of several methyl groups to the molecule can grossly affect

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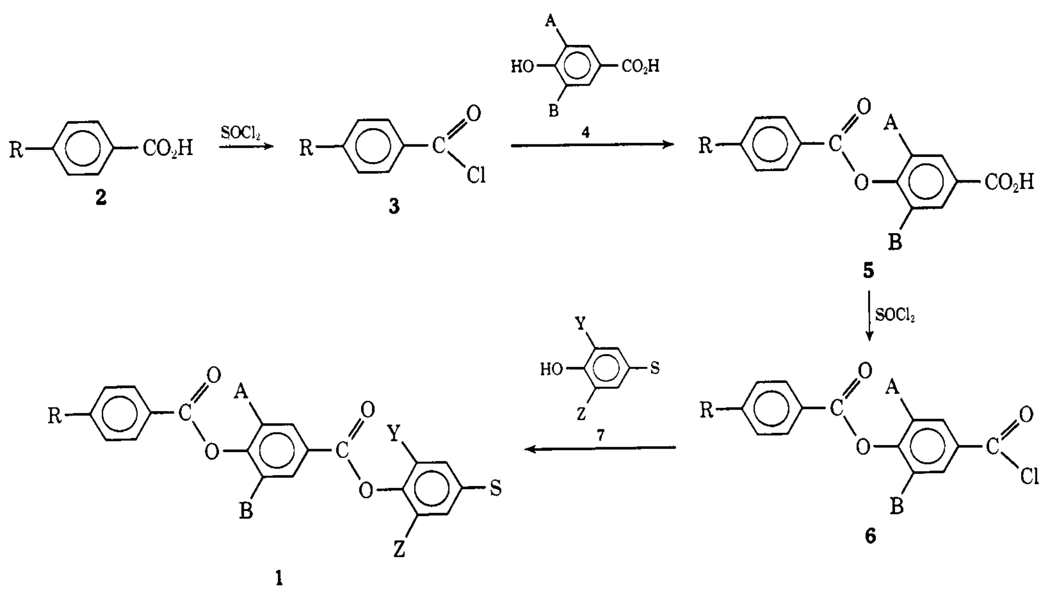
(14) The elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(15) W. R. Young, I. Haller, and A. Aviram, *IBM J. Res. Develop.*, **15**, 41 (1971); *Mol. Cryst. Liquid Cryst.*, **13**, 357 (1971).

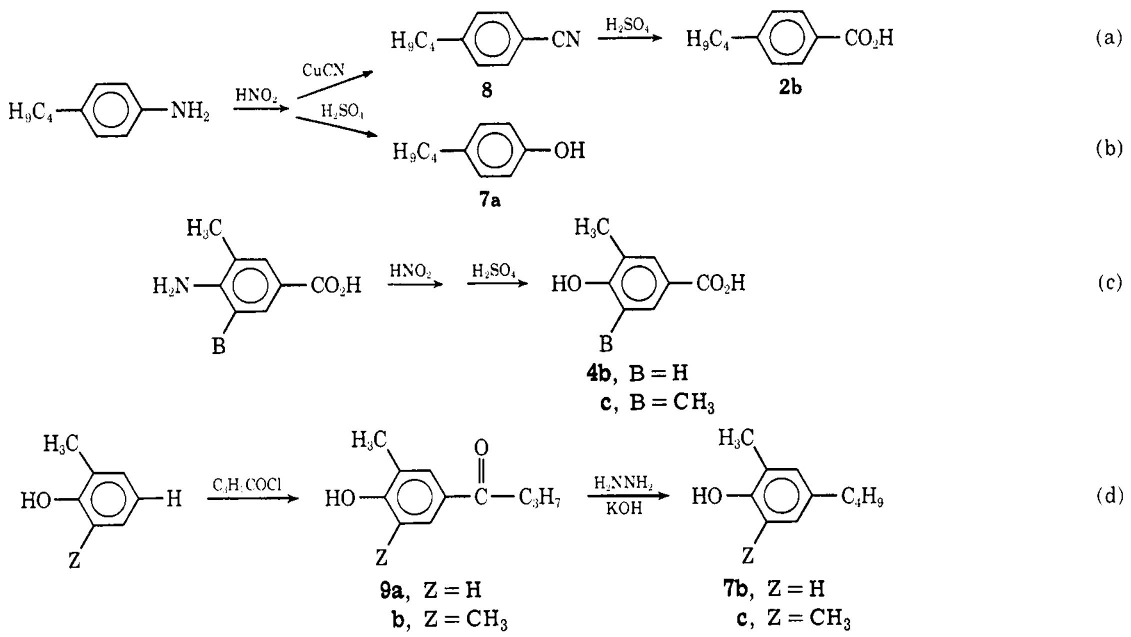
(16) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

SCHEME I



R, S = C_2H_5O, n-C_4H_9; A, B, Y, Z = CH_3 or H

SCHEME II



the molecular shape, and, as a direct consequence, the intermolecular interactions in the crystalline state. Hence the large variation in melting point with methyl substitution is not unreasonable.

It is interesting to compare the effect of a single aromatic methyl substituent upon melting point for a few different mesomorphic materials.[17-19] The results, shown in Table II, indicate that the addition of a lone methyl group tends to lower the melting point of a nematogenic compound, when placed ortho to the linkage group. Although the magnitude of this effect varies greatly with molecular features, *o*-methyl substitution appears to offer promise as a method of lowering C → N transition temperatures.[20]

Nematic–Isotropic Transition Temperatures.—The data in Table IA indicate that the nematic–isotropic transition temperatures decrease systematically as the number of aromatic methyl group appendages increases. Analogous results in polysubstituted nematogenic materials have been previously reported.[16,17,21] This result is usually explained in terms of increased molecular broadening with increased methyl substitution, such that intermolecular interactions that are responsible for mesomorphism are decreased as the intermolecular separation increases. As will be discussed in the section on calorimetry, this explanation is too simple and can only accommodate part of the experimental findings.

In considering positional effects of methyl substitution, the following observations can be made. The nematic–isotropic transition temperature, T_{NI}, is lowered by about the same amount when a *single*

(17) R. J. Cox, *Mol. Cryst. Liquid Cryst.*, in press.

(18) W. Leister, Dissertation, Universitaet Halle, Germany, 1920.

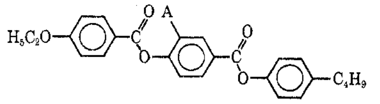
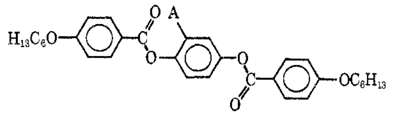
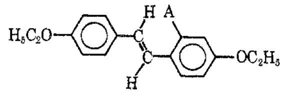
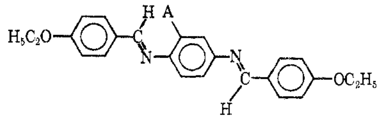
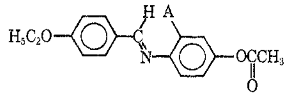
(19) J. v. d. Veen and A. H. Grobben, *Mol. Cryst. Liquid Cryst.*, **15**, 239 (1971).

(20) See ref 19 for several additional examples.

(21) C. Wiegand, *Z. Naturforsch. B*, **6**, 240 (1951).

TABLE II

TRANSITION TEMPERATURES OF SOME NEMATOGENIC COMPOUNDS

		Temp, °C		
Compound	Transition	A = H	A = CH$_3$	Difference
	C → N N → I	124 231	91 179	33 52
	C → N[a] N → I	124 213	88 172	36 41
	C → I[b] N → I	209 189	110 105	99 84
	C → N[c] N → I	203 >330	143 272	60 >58
	C → N[d] N → I	112 134	89[e] 66	23 68

[a] Reference 8. [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] C → I transition.

methyl group is placed in either of positions A or Y. Placing *two* methyl groups on the *same* ring results in approximately twice the lowering of T_{NI} *vs.* that obtained by substitution with a single methyl group. However, when two methyls are affixed to *different* rings, the depression of T_{NI} is somewhat lower. Finally, when the molecule contains three or four methyl groups, the transition temperature drops more slowly with each additional methyl, owing in part, perhaps, to the fact that molecule was already broadened by two or more methyl groups and the addition of further methyls cannot have as much of an effect.

A comparison of the effect of methyl substitution upon the nematic–isotropic transition temperatures of nematogenic materials is presented in Table II. There appears to be little regularity in the magnitude of the effect of *o*-methyl groups upon nematic clearing points as the linkage group and molecular length/breadth ratio vary, although in every case the clearing point is lowered by about 40 to 80°. It is hoped, however, that the data in Table II may prove useful in making crude estimations of the clearing point for a methylated derivative once the nor-methyl compound has been prepared. Such predictions should be limited to pairs of compounds that belong to one of the classes in Table II, with structural changes limited to wing group variations. Although preliminary work in our laboratory and some results reported elsewhere[19] support this conjectural concept, additional experimental corroboration is required.

Reversal of the wing groups in esters such as **1a** and **1c** should have a minimal effect upon molecular geometry, although it would alter the electronic distribution somewhat due to a loss of direct mesomeric interaction between the ethoxyl and carbonyl groups in these materials. The resulting compounds, **1j** and **1k** (Table IB), however, exhibit transition temperatures that are very similar to those of **1a** and **1c**. These facts underscore[3] the dominant role played by the central part of the molecule in affecting transition temperatures.

Entropies and Enthalpies of the Nematic–Isotropic Transition.—Two facts stand out on inspection of the calorimetric data of Tables IA and IB. (1) Substitution of the central ring by one, and even more so by two methyl groups results in a significant increase in the entropy of the nematic–isotropic phase transition. Central ring substitution affects the heat of transition in the same direction, but to a smaller extent. (2) Substitution on the end ring has no comparable effect.

These data are pertinent to the reduction in the transition temperature upon methyl substitution on the central ring. The transition temperature is determined by the heat and the entropy of the transition, two more fundamental quantities that are representative of the change in the interaction energy and in the order when the transition takes place. The decrease

$$T_{NI} = \Delta H_{NI}/\Delta S_{NI}$$

in T_{NI} upon methyl substitution is usually ascribed to a reduction in the energy of intermolecular interactions in the nematic phase, *i.e.*, a lower value for ΔH_{NI}. In particular, this result has been attributed to either increased intermolecular separation due to lateral substitution[16] or to decreased molecular polarizability resulting from a steric loss of conjugation.[8] While in some instances the experimentally measured ΔH_{NI} is smaller for methyl-substituted derivatives than for the parent compound,[22,23] in accord with previous postulates, this trend cannot be universally true. Methyl substitution in the A and B positions of the compounds reported here *increases* ΔH_{NI}; hence the decrease in transition temperature is due to an even larger increase in ΔS_{NI}.

(22) W. R. Young, I. Haller, and A. Aviram, submitted for publication.

(23) G. W. Gray and K. J. Harrison, Faraday Symposium on Liquid Crystalline Properties, Dec 1971.

There is insufficient evidence to provide a definitive explanation as to why methyl substitution on the central ring should result in the unusually large increase in ΔS_{NI}. There are a large number of degrees of freedom, both internal and external, that contribute to the entropy, and subtle changes in the restrictions that these experience in the two phases may result in a nonsystematic variation of ΔS_{NI} with substitution. For example, the barriers to internal rotation about the ester linkages are undoubtedly influenced by the steric repulsions of both the methyl groups and the neighboring molecules. Any nonsystematic change in ΔS_{NI} with substitution could be rationalized on this basis.

If it is assumed that the observed systematic changes in ΔS_{NI} are dominated by external, *i.e.*, intermolecular, degrees of freedom, the data imply that at the clearing point there is a larger change in positional correlation of molecules methylated at the central ring than of molecules methylated at the end ring. That is to say, methylation of the center of the molecule increases the coupling between orientational and translational degrees of freedom. The possibility of enhanced positional correlation, or short-range order, in the nematic phase, relative to the isotropic phase, due to a central bulge in the repulsion envelope of the molecules, is consistent with the large value of ΔS_{NI} for compounds **1f** and **1h**. It is also compatible with X-ray observations of the nematic phase of a diester, which was broadened by chlorination, rather than methylation, of the central ring.[24] Also, enhanced short-range order in the nematic phase has been suggested by other investigators.[25-27]

Experimental Section

All of the new compounds exhibited satisfactory spectral properties and elemental analyses.[14] Infrared spectra were recorded on a Perkin-Elmer 137B Infracord spectrometer. Nmr spectra were obtained on a Jeolco Minimar 60 spectrometer. Ultraviolet spectra were taken on a Cary 14 spectrophotometer.

4-Substituted Benzoic Acids (2).—4-Ethoxybenzoic acid (**2a**) was obtained commercially (Aldrich Chemical Co.). 4-*n*-Butylbenzoic acid (**2b**), mp 102°, T_{NI} 112° (lit.[28] mp 99.5°, T_{NI} 113°), was prepared by hydrolysis[29] of 4-*n*-butylbenzonitrile (**8**), bp 122° (6 mm), obtained from 4-*n*-butylaniline (Aldrich) by the method of Clarke and Read.[30]

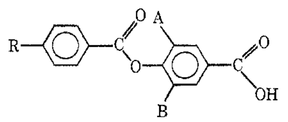
4-Substituted Benzoyl Chlorides (3).—4-Ethoxybenzoyl and 4-*n*-butylbenzoyl chlorides were prepared by refluxing the corresponding acids in thionyl chloride and isolating the products by distillation.

4-Hydroxybenzoic Acids (4).—4-Hydroxybenzoic acid was obtained from Aldrich Chemical Co. 4-Hydroxy-3-methylbenzoic acid (**4b**), mp 172° (lit.[31] 174–175°), and 4-hydroxy-3,5-dimethylbenzoic acid (**4c**), mp 216–217° (lit.[32] 218°), were prepared from 4-amino-3-methylbenzoic acid (Aldrich) and 4-amino-3,5-dimethylbenzoic acid (Aldrich), respectively, by means of diazotization and sulfuric acid hydrolysis.

4-(4′-Substituted benzoyloxy)benzoic Acids (5).—The key intermediate acids of type **5** prepared in this investigation are listed in Table III. They were prepared by reaction of the appropriate acid chloride (**3**) with the appropriate hydroxybenzoic acid (**4**) under reflux in toluene–pyridine solvent for 12–16 hr. After removal of the solvents in the rotary evaporator, the residue was dissolved in ether and washed with dilute HCl and water. Evaporation of the ether yielded an oily or gummy residue which generally contained the desired product plus some anhydride byproduct. The residue was allowed to reflux in aqueous dioxane for 4 hr to hydrolyze any anhydride which was present. The dioxane was removed by azeotropic distillation, and the product was isolated by filtration of the hot, aqueous mixture. Recrystallization from a suitable solvent afforded the desired white, crystalline products in 50–80% yield.

TABLE III

TRANSITION TEMPERATURES OF SOME SUBSTITUTED BENZOYLOXYBENZOIC ACIDS



No.	R	A	B	Temp, °C[a]	
				C → N	N → I
5a	C_2H_5O	H	H	198	>300
5b	C_2H_5O	CH_3	H	230	233
5c	C_2H_5O	CH_3	CH_3	272[b]	
5d	*n*-C_4H_9	H	H	182	250
5e	*n*-C_4H_9	CH_3	H	173	214

[a] These intermediates were not purified so rigorously as the final esters. [b] C → I transition temperature.

4-(4′-Substituted benzoyloxy)benzoyl Chlorides (6).—These acid chlorides were prepared by allowing the corresponding acids (**5**) to reflux in an excess of thionyl chloride and removing the volatile materials by vacuum distillation. The residual products were employed for esterification reactions without additional purification.

4-Substituted Phenols (7 and 9).—4-*n*-Butylphenol (**7a**), mp 22° (lit.[33] 22°), was prepared from 4-*n*-butylaniline by diazotization and sulfuric acid hydrolysis.

4-Hydroxy-3-methylbutyrophenone (**9a**), mp 130–133° (lit.[34] 132–133°), and 4-hydroxy-3,5-dimethylbutyrophenone (**9b**), mp 123–125° (lit.[35] 124–125°), were prepared by the standard Friedel–Crafts acylation of 2-cresol and 2,6-dimethylphenol, respectively, with butyryl chloride in nitrobenzene with aluminum chloride.

4-*n*-Butyl-2-methylphenol (**7b**), bp 130–132° (16 mm) [lit.[34] 127–129° (15 mm)], and 4-*n*-butyl-2,6-dimethylphenol (**7c**), bp 107° (2.5 mm) [lit.[35] 138–146° (20 mm)], were prepared from the corresponding butyrophenones **9a** and **9b** by means of the Huang-Minlon modification of the Wolff–Kishner reduction.[36]

Substituted Phenyl Benzoyloxybenzoates (1).—The esters listed in Table I were all prepared by the following general procedure. An appropriate phenol (**7**) was dissolved in pyridine. An equivalent amount of an acid chloride (**6**) was dissolved in toluene and added to the pyridine solution. Following an overnight reflux period, the solvents were removed and the residue was taken up in ether. Following washes with water, 10% HCl, 10% NaOH, and water, the ether layer was dried and evaporated. The residual product was chromatographed through a column of silica gel with chloroform. The product was then repeatedly crystallized from alcohol or methylcyclohexane and, in some cases, sublimed under high vacuum. The yields of the purified, white products ranged from 20 to 50%.

Microscopy and Calorimetry.—The mesophases were identified and the transition temperatures were determined as described previously.[3] The heats of transition were determined as before,[1] with the exception that the peak areas were determined by means of an on-line IBM 1800 computer. The base-line sections (two for each transition) required for integration were computed by

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(24) A. de Vries, *Mol. Cryst. Liquid Cryst.*, **10**, 219 (1970).

(25) Reference 16, p 85.

(26) L. Pohl and R. Steinstraesser, *Z. Naturforsch. B*, **26**, 26 (1971).

(27) H. Gruler, personal communication.

(28) C. Weygand and R. Gabler, *Z. Physik. Chem., Abt. B*, **46**, 270, 272 (1940).

(29) H. T. Clarke and E. R. Taylor, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 588.

(30) H. T. Clarke and R. R. Read, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 514.

(31) I. Remsen and J. Kuhara, *Amer. Chem. J.*, **3**, 428 (1881).

(32) O. Jacobsen, *Chem. Ber.*, **12**, 606 (1879).

(33) G. Sandulesco and A. Girard, *Bull. Soc. Chem. Fr.*, **47**, 1300 (1930).

(34) C. E. Coulthard, J. Marshall, and F. Pyman, *J. Chem. Soc.*, **1930**, 291.

(35) K. v. Auwers and E. Janssen, *Justus Liebigs Ann. Chem.*, **483**, 44 (1930).

(36) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).

least-squares fits from visually determined start and end points, and are extrapolated to the center of the peak.

Registry No.—**1a**, 35619-91-1; **1b**, 35619-92-2; **1c**, 35619-93-3; **1d**, 35619-94-4; **1e**, 35619-95-5; **1f**, 35619-96-6; **1g**, 35619-97-7; **1h**, 35619-98-8; **1i**, 35619-99-9; **1j**, 35620-00-9; **1k**, 35620-01-0; **5a**, 35620-02-1; **5b**, 35620-03-2; **5c**, 35620-04-3; **5d**, 35620-05-4; **5e**, 35620-06-5.

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2,3-Di(2-pyridyl)-2,3-butanediol. A Crystal and Molecular Structure Study of the Meso Form with Ancillary Proton Magnetic Resonance Data

J. N. BROWN, R. M. JENEVEIN, J. H. STOCKER,*[1] AND L. M. TREFONAS*[1]

Department of Chemistry, Louisiana State University in New Orleans, New Orleans, Louisiana 70122

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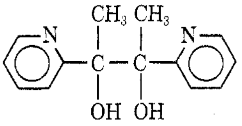
The crystal and molecular structure of 2,3-di(2-pyridyl)-2,3-butanediol ($C_{14}H_{16}N_2O_2$) has been determined by a single-crystal, X-ray diffraction study. The compound crystallizes with four molecules in a monoclinic cell ($P2_1/c$) of dimensions $a = 9.293$, $b = 11.885$, $c = 13.615 \pm 0.001$ Å, and $\beta = 123.98 \pm 0.01°$. The structure was solved by direct methods and the 1097 statistically significant reflections were refined to a final value of $R = 0.05$. Estimated standard deviations were less than 0.008 Å for bond distances and 0.5° for bond angles for those bonds not involving hydrogen atoms. The configuration was established as the meso compound, and, furthermore, the conformation was shown to be that involving hydrogen bridging between each of the pyridyl nitrogens and the more distant oxygen forming additional six-membered rings. Although not required by crystallographic symmetry, the molecule possesses a center of symmetry well within the estimated standard deviation. Pmr data for an additional ten compounds with analogous five-, six-, and seven-membered hydrogen-bonded ring possibilities are given and evaluated, and effectively underscore the uniqueness of the title compound. A comparison of the pmr data with a limited set of corresponding infrared data casts doubt on the reliability of the predictions from the infrared data regarding intramolecular hydrogen bonding.

Unequivocal assignment of the stereochemical identities of the two diastereomeric pinacols (I) resulting from the electropinacolization of 2-acetylpyridine was necessary as part of a continuing study[2] of the stereochemical consequences of this type of electrochemical bimolecular reduction. Such assignments may be made by the tedious and often unsuccessful procedures of absolute synthesis or enantiomeric resolution. More equivocal but often adequate approaches include differences in gross crystal structure, melting point comparisons, and infrared and pmr analysis of the hydroxyl group, particularly where several of these methods reinforce each other. In the present case, these convenient techniques were precluded; the two diastereomers have identical melting points, no free hydroxyl stretching bands in the infrared, and essentially identical hydroxylic proton resonances buried in the aromatic area.[3] A tentative assignment was made, however, on the basis of the degree of shielding encountered by the methyl groups as based on the apparent most favorable conformations for the several different forms possible for each diastereomer as determined from molecular models.[2] To establish this assignment unequivocally, an X-ray crystallographic study was undertaken on the diastereomer that had tentatively been assigned the meso form. Additional pmr studies of related compounds were also undertaken to consider the relative degrees of hydrogen bonding encountered in such compounds. The data are brought together and evaluated in this report.



I (meso, *dl* forms)

Crystallographic Studies

Obtaining crystals of suitable quality for an X-ray structure study proved to be exceedingly difficult and time consuming. First, the compound crystallized in more than one space group, depending on solvent and experimental conditions; *i.e.*, monoclinic crystals in space group $P2_1$ (or $P2_1/m$) were obtained from hot carbon tetrachloride, while crystals in space group $P2_1/c$ were obtained from warm hexane solutions. Second, all of the crystals exhibited extreme layering perpendicular to the b axis. Intensity differences of 5:1 (or greater) in a φ scan at $\chi = 90°$ on a General Electric XRD-5 diffractometer were obtained repeatedly. Finally, a crystal of dimensions 0.10 × 0.15 × 0.23 mm was recrystallized from one of the hexane solutions and exhibited an intensity ratio of 1.13:1.00. Extinctions [$k = 2n + 1$ for the ($0k0$) reflections and $l = 2n + 1$ for the ($h0l$) reflections] uniquely characterized the space group as $P2_1/c$.

Lattice constants were determined by a least-squares fit of 16 carefully measured 2θ values (1° take-off angle

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[1] (a) Address pmr inquiries to J. H. S., crystallographic inquiries to L. M. T. (b) Tables of structure factor data and refined coordinates and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-3712. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[2] J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **34**, 2807 (1969).

[3] For a more detailed discussion of these several approaches, with suitable references, see ref 2.