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Jk Swadesh [a a] & Jc Poirier [a]
[a] Department of Chemistry, Duke University, Durham, NC, 27706
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A LINEAR RELATIONSHIP BETWEEN THE ^{13}C ESTER CARBON CHEMICAL SHIFT AND THE MELTING POINT OR S TO N TRANSITION TEMPERATURE OF n-ALKYL ESTERS OF BIPHENYL-4,4'-DICARBOXYLIC ACID

JK Swadesh* and JC Poirier
Department of Chemistry
Duke University
Durham, NC 27706

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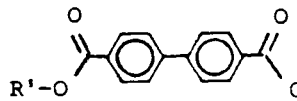
Abstract. We present evidence that the relative electron densities at the ester carbon of the symmetrical n-alkyl diesters of biphenyl-4,4'-dicarboxylic acid may determine the relative melting points of homologs in this series. A similar relationship may determine the relative smectic to nematic transition temperatures of the corresponding monoesters. We present a model to rationalize our observations.

In an earlier work[1], we described the synthesis and characterization of various n-alkyl monoesters R_nBDCA-H, $2 \leq n \leq 15$, and diesters R_nBDCA-R_n, $1 \leq n \leq 15$:



R_nBDCA-R_n: R'=R"=n-alkyl

R_nBDCA-H : R'=n-alkyl, R"=H

* Correspondence should be sent to: Department of Chemistry, Cornell University, Ithaca NY 14853.

The R_nBDCA-R_n exhibited no mesomorphism. Most of the R_nBDCA-H exhibited a nematic mesophase, and all exhibited one or more smectic mesophases. We recorded the solution ^{13}C spectra of seven diesters in $CDCl_3$, and of one monoester in DMSO-d_6. The relevant data, reproduced from earlier works[1,2], are presented in Table 1 and in Figure 1*.

TABLE 1 Thermal transitions and ^{13}C NMR shifts

Number of carbons in alkyl chain	Diester melting point (°C)	Mean S-N monoester transition temp. (°K)	Ester carbon chemical shift (ppm)[a]	Terminal methyl carbon chemical shift (ppm)[a]
1	218	b	52.17	c
2	111.5	540.4(0)	61.09	14.33
3	80	482.5(5)	66.70	10.58
4	45	503.5(5)	64.94	13.75
7	57	515.4(5)	65.28	14.04
8	68	514.0(5)	65.31	14.11
9	71	509.7(5)[d]	65.28	14.09

a: Data from diester in $CDCl_3$, using a TMS internal standard;
b: monoester not synthesized; c: see adjacent column;
d: N not resolved from the overall S-I transition. The value presented is the mean of the S-I transition.

*Weak and probably artifactual NMR signals were observed in the spectra of the heptyl monoester (138.13 ppm) and of the octyl diester (18.89 and 133.76 ppm); these are omitted from the figure. In Table 1, the penultimate transition observed on heating the ethyl monoester to the isotropic liquid is presented as the S-N transition; this identification is tentative.

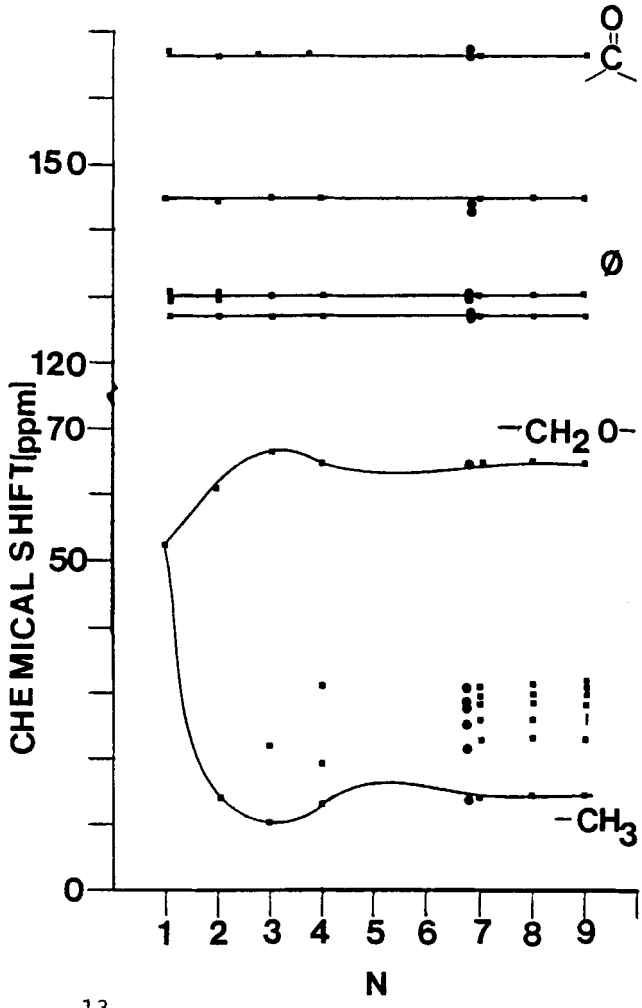


FIGURE 1 The ^{13}C chemical shifts of various esters of biphenyl-4,4'-dicarboxylic acid as a function of the number of carbons, N, in the pendant alkyl chain. The chemical shifts of the heptyl monoester are indicated by large, filled circles offset slightly from N=7. The vertical bar near 26 ppm, N=9, indicates uncertainty in the chemical shift of that carbon. The symbols of the chemical shifts of the methylene carbons internal to the alkyl chain (19-32 ppm) are not explicitly labelled.

The carbon chemical shift is generally regarded to be a function of a number of factors, including the local electron density, currents in the local or neighboring electronic distribution, and solvent effects[3]. Although it is often difficult to determine the cause of chemical shift differences in structurally related compounds[3,4], the data presented in Figure 1 suggest that the electronic environments of the aromatic and carbonyl carbons of the R_nBDCA-R_n are essentially independent of the alkyl chain length. The carbonyl carbon of the ethyl ester is shifted about .5 ppm upfield of that of the methyl ester (and there is a compensating downfield shift of one of the aromatic carbons), but a similar carbonyl shift is observed in the alkyl formates[5,6], and all of the remaining aromatic and carbonyl carbons of the R_nBDCA-R_n exhibit chemical shifts that are essentially constant along the homologous series. The chemical shift differences of the ester carbons of the R_nBDCA-R_n, $1 \leq n \leq 4$, are almost identical to those of the n-alkyl formates, which supports the hypothesis that the influences of the aromatic ring and carbonyl carbons on the chemical shifts of the aliphatic carbons are constant along the homologous series. This implies that the chemical shift differences of the ester carbons of two homologs may be due to an inductive effect within the aliphatic chain.

Evidence that this is the case is found by comparing the charge densities of alkane carbons, computed by Gasteiger and Marsili[7] by the method of Mulliken population analysis, with the chemical shifts presented in Table 1.

Gasteiger and Marsili list the charge, q_c, for the carbons of methane, ethane, and the 1-carbon of n-propane as -77.6, -68.1, and -65.5 millielectrons, respectively. Correlation of these values with the corresponding ester carbon chemical shifts, s, by linear regression results in the equation $s = 139.56 + 1.130q_c$, with a confidence level of 88% by the F-test[8,9]; the F-test confidence level represents the probability that two quantities are indeed linearly related. The level of correlation of q_c with the chemical shift of the terminal methyl carbon is 92%, with the relation $s = -226.63 - 3.584q_c$.

If, as seems probable, aliphatic chemical shift differences directly reflect changes in local electron density, the largest differences in the electron density distributions of corresponding carbons of two homologs would be found at the ester carbon and at the terminal methyl group. We correlated the melting points and ester carbon chemical shifts of the seven diesters presented in Table 1. The analysis indicated that the diester melting point (in $^{\circ}K$) can be written as $T_m = 1068.95 - 11.162s$; the F-level is greater than 99.9% certainty. A similar correlation of T_m with the chemical shift of the terminal methyl carbon had a confidence level greater than 99.5%. As further evidence that electron density at the ester or methyl carbon determines the melting point, correlation of q_c with T_m gave the linear relation $T_m = -389.57 - 11.352q_c$, at an F-level exceeding 99.9%.

If it is assumed that the chemical shifts of the ester carbons of the R_nBDCA-H are essentially the same as those of the R_nBDCA-R_n, an assumption that seems to be supported by the NMR spectral data of R_7BDCA-R_7 presented in Figure 1,

a correlation of the ester carbon chemical shifts to the mean S to N transition temperature results in the least squares equation T_{SN} = 1087.12 - 8.896s, with an F-level greater than 97.5%. A similar correlation of T_{SN} to the chemical shift of the terminal methyl carbon has a confidence level of greater than 95%.

One can rationalize the statistical relationships we have presented according to a simple physical model. In the smectic mesophase, rod-like molecules are believed[10] to be arranged in layers, long molecular axes approximately parallel, and molecular centers of gravity lying in or near a single plane. In such a lattice, if one region of a molecule bears a partial charge, that molecular region would repel a similar region in a neighboring molecule. If the long molecular axes are tilted with respect to the layer plane, the repulsion would decrease, because the perpendicular distance between two regions in neighboring molecules would increase. Such a repulsion would force apart the long molecular axes, destabilizing the smectic mesophase. A similar argument would apply to the destabilization of the solid relative to the liquid for a non-mesogenic compound that forms a layer lattice such as we have described. Although our statistical analysis indicates that either the ester or the terminal methyl carbon could be the locus of partial charge, we suggest that the methyl group donates electron density to the electron-deficient ester carbon, producing various charge densities at the ester carbons of various homologs, and that the magnitude of the ester carbon charge density determines the magnitude of the lateral repulsions. Gray[11] and Gray and Worrall[12] have used an argument similar to that presented in this work to rationalize the

destabilization of the smectic and nematic mesophases of 4'-octyloxybiphenyl-4-carboxylic acids by the introduction of a 3'-substituent; these authors found that a linear relationship exists between the molecular diameter of the substituent and the decrease in transition temperature. The feature common to the work of Gray and Worrall and the present work is the identification of a physical property of a functional group that varies linearly with crystal or mesophase stability. This suggests that it may be possible to analyze the thermal behavior of complex molecules according to substituent properties. Our work further suggests that indirect measures of the molecular electron distribution, such as the NMR chemical shift, can serve as predictors of phase transitions.

Finally, we note that other factors presumably also influence crystal or smectic stability within a homologous series. For the R_nBDCA-R_n, T_m rises for $9<n$, but for the R_nBDCA-H, T_{SN} apparently falls. Because the chemical shifts of the ester and methyl carbons are apparently approximately constant for $7 \leq n$, our analysis presumably will not be valid for R_nBDCA-R_n or R_nBDCA-H with very long alkyl chains. Also, the differences in the thermal properties of mesogens with odd or even numbers of carbons in the pendant n-alkyl chain are well-documented, but we have not considered this in our analysis. It is our position that the analysis that we have presented accounts for the bulk of the variation of T_m and T_{SN} for homologs with $n \leq 9$, and that the effects of other factors are

minor, relative to the effect that we have described.

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