

Materials science of organic compounds. Part 2. Thermal studies of acentric (second-harmonic-generative) and centrosymmetric crystals of achiral straight-chain *para*-nitrophenylcarbonyl compounds¹

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Abstract

Straight-chain alkyl and analogous polymethylene *p*-nitrophenylurethanes and ureas yield acentric crystals having nonlinear-optical (NLO) properties. DSC onset points are shown to agree with metal-calibrated capillary melting ranges within experimental error. Heats of fusion and melting/onset points for the alkylurethanes (C₁–C₂₂) show a sharp minimum at C₄–C₅. The high second-harmonic-generation (SHG) maximum at C₆ appears unrelated.

Several of the alkylurethanes (C₂, C₅, C₇ and C₁₆), when crystallized using different solvents or temperatures, yielded SHG-inactive forms differing in heats of fusion, though not in onset points; in other cases lower heats of fusion upon remelting suggested analogous changes. Similar behavior was noted for some ureas and for some omega-substituted polymethylene urethanes.

INTRODUCTION

Nonlinear optics is concerned with intensity-dependent optical phenomena. At the momentarily high radiation flux produced by a laser pulse it becomes possible to combine two photons into a single photon of twice the energy (half the wavelength). This second-harmonic generation (SHG) can only be done in an acentric environment, such as a non-centrosymmetric crystal. These are piezoelectric, examples being quartz, Rochelle salt, and urea. All homochiral compounds must fall in this class, but racemic mixtures and achiral compounds usually form centrosymmetric (SHG-inactive) crystals. The more asymmetric and extended is the electronic potential well, the greater the SHG efficiency; i.e. the lower the laser power required to produce a chosen double-frequency power. Organic molecules having a polar axis of donor and acceptor groups joined by a conjugated

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electron system typically show high SHG efficiencies when they crystallize (acentrally) with axes well aligned. In this study the *p*-nitrophenylcarbonyl group is the donor-acceptor unit and is attached through an oxygen or nitrogen atom to a polymethylene group, $-(\text{CH}_2)_n\text{X}$, which directs/modifies the alignment of the NLO-active moiety [1].

The thermal analyses were done, regrettably as an afterthought, to confirm absence of solvent. Subsequently it was realized that the information contained in the DSC results would have been extremely helpful in conducting the NLO research.

It is generally accepted that the properly calibrated DSC onset point correlates with the true melting point of pure substances, but we know of no systematic comparison with traditional capillary melting points/ranges. The present work represents a first step in that direction.

EXPERIMENTAL

The *p*-nitrophenylurethanes, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCO}_2-(\text{CH}_2)_n\text{X}$, and the *p*-nitrophenylureas, $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHCONH}-(\text{CH}_2)_n\text{X}$, were the exact mate-

TABLE 1

Test of metal-calibrated capillary melting range minus DSC onset point, for *n*-alkyl *p*-nitrophenylurethanes, $\text{R-OCONHC}_6\text{H}_4\text{NO}_2$ (*p*)

Sample number (from ref. 1)	<i>n</i> -Alkyl group, R-	Capillary melting temperature range ^a minus DSC onset point (°C)	Sample number (from ref. 1)	<i>n</i> -Alkyl group, R-	Capillary melting temperature range ^a minus DSC onset point (°C)
1	CH ₃ -	+0.2 to +1.2	8	C ₈ H ₁₇ -	-0.4 to +0.1
2	C ₂ H ₅ -	+0.8 to +1.8	9	C ₉ H ₁₉ -	+1.1 to +1.6
2A	C ₂ H ₅ -	-0.1 to +1.4	10	C ₁₀ H ₂₁ -	-0.2 to +0.8
2B ^b	C ₂ H ₅ -	{ -9.7 to -8.7 } { +4.3 to +5.3 }	11	C ₁₁ H ₂₃ -	+0.7 to +0.7
3	C ₃ H ₇ -	-0.9 to +0.1	12	C ₁₂ H ₂₅ -	+0.1 to +1.1
4	C ₄ H ₉ -	+2.2 to +2.7	13	C ₁₃ H ₂₇ -	-1.1 to -1.1
5	C ₅ H ₁₁ -	+1.2 to +1.2	13A	C ₁₃ H ₂₇ -	-0.5 to +0.5
5A	C ₅ H ₁₁ -	+0.3 to +1.3	^c	C ₁₄ H ₂₉ -	+1.3 to +2.3
6	C ₆ H ₁₃ -	0.0 to +1.0	16	C ₁₆ H ₃₃ -	-0.2 to +0.8
7	C ₇ H ₁₅ -	+1.3 to +2.3	16A	C ₁₆ H ₃₃ -	+0.7 to +0.7
7A	C ₇ H ₁₅ -	+0.8 to +1.8	18	C ₁₈ H ₃₇ -	-1.0 to -0.5
7B	C ₇ H ₁₅ -	+0.4 to +1.4	19	C ₁₉ H ₃₉ -	-0.1 to +0.9
			22	C ₂₂ H ₄₅ -	-1.1 to +0.4

Average of range differences +0.2 to +0.9^d

^a The capillary melting temperatures are in most cases read to the nearest 0.5°C, at 1°C min⁻¹ heating rate. ^b Omitted from average. ^c Not included in Ref. 1. ^d Standard deviation of the average difference ±0.2°C; ±0.9°C per single measurement.

rials used in the previously-reported SHG study [1], and for which the sample numbering is here repeated in the tables. A Du Pont 912/2100 differential scanning calorimeter, calibrated with indium and tin, was used; heating rates were $10^{\circ}\text{min}^{-1}$. Capillary melting ranges were metal-calibrated [2] and averaged 0.5°C higher than the DSC onset points (Table 1), with a per-sample standard deviation of $\pm 0.9^{\circ}\text{C}$. Heats of fusion, as given by the DSC program, were calibrated for each of the two measurement sites in the differential scanning calorimeter using “5N” (99.999%) gallium, indium, tin, and purified samples of biphenyl, stilbene, eicosane and dotriacontane, the standard deviation being under 5%. Reheating was done after cup-quenching with liquid nitrogen; only the C₅ urethane formed a glass ($T_g = -30^{\circ}\text{C}$). The SHG efficiencies are for the same finely crystalline [3] samples, and have been reported [1]; they are expressed relative to urea (taken as unity) when measured under the same conditions.

DISCUSSION AND CONCLUSIONS

It is not altogether surprising that little or nothing has been published linking DSC onset points and traditional capillary melting points/ranges.

TABLE 2

Test of repeatability of DSC onset point upon reheating, for *n*-alkyl *p*-nitrophenylurethanes, R–OCONHC₆H₄NO₂ (*p*)

Sample number (from ref. 1)	<i>n</i> -Alkyl group, R–	Reheat onset point minus initial onset point ($^{\circ}\text{C}$)	Sample number (from ref. 1)	<i>n</i> -Alkyl group, R–	Reheat onset point minus initial onset point ($^{\circ}\text{C}$)
1 ^a	CH ₃ –	(–2.4)	8	C ₈ H ₁₇ –	–0.6
2	C ₂ H ₅ –	+0.5	9	C ₉ H ₁₉ –	+0.5
2A	C ₂ H ₅ –	+0.1	10	C ₁₀ H ₂₁ –	+0.1
2B ^a	C ₂ H ₅ –	(+15.7)	11	C ₁₁ H ₂₃ –	–0.2
3	C ₃ H ₇ –	–0.2	12	C ₁₂ H ₂₅ –	–0.1
4	C ₄ H ₉ –	+1.3	13	C ₁₃ H ₂₇ –	–0.4
5	C ₅ H ₁₁ –	+1.2	13A	C ₁₃ H ₂₇ –	–0.2
5A	C ₅ H ₁₁ –	+0.2	^b	C ₁₄ H ₂₉ –	–0.5
6	C ₆ H ₁₃ –	–0.5	16	C ₁₆ H ₃₃ –	0.0
7	C ₇ H ₁₅ –	–0.7	16A	C ₁₆ H ₃₃ –	+0.7
7A	C ₇ H ₁₅ –	–0.8	18	C ₁₈ H ₃₇ –	–0.2
7B	C ₇ H ₁₅ –	–1.1	19	C ₁₉ H ₃₉ –	0.0
			22	C ₂₂ H ₄₅ –	+0.2

Average change upon reheating $0.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ standard deviation^a

^a Omitted from average; the substantial changes both in onset point and heat of fusion (Table 3) signal a change of crystal form. ^b Not included in ref. 1. ^c Standard deviation of a single measurement is $\pm 0.5^{\circ}\text{C}$.

Prior to the development of metal-calibration [2] the capillary technique lacked a firm link to the International Temperature Scale (which anchors DSC measurements); hence precise comparisons would have been meaningless. In Table 1 we show that the methods are indeed equivalent within experimental error. This does not mean that literature capillary melting point values, lacking such metal-calibration, are to be pronounced equally reliable.

TABLE 3

Comparisons of heats of fusion, measured initially and upon reheating, for samples of *n*-alkyl *p*-nitrophenylurethanes, R–OCONHC₆H₄NO₂ (*p*)

Sample number (from ref. 1)	<i>n</i> -Alkyl group, R–	Initial onset point (°C)	SHG ^a efficiency	Heat of fusion (J g ⁻¹)	
				Initial	Reheat
1	CH ₃ –	177.8	0.001	161	145
2	C ₂ H ₅ –	126.2	23.	129	121
2A	C ₂ H ₅ –	128.6	5.5	138	133
2B	C ₂ H ₅ –	{123.7} ^b {108.0}	(0.000) ^c	123	115
3	C ₃ H ₇ –	116.9	0.000	125	120
4	C ₄ H ₉ –	90.8	85.	91	71
5	C ₅ H ₁₁ –	90.6	46.	97	103
5A	C ₅ H ₁₁ –	91.7	0.03	103	100
6	C ₆ H ₁₃ –	103.5	154.	123	120
7	C ₇ H ₁₅ –	101.7	110.	112	107
7A	C ₇ H ₁₅ –	102.2	0.007	118	109
7B	C ₇ H ₁₅ –	103.6	0.4	120	108
8	C ₈ H ₁₇ –	110.4	62.	132	126
9	C ₉ H ₁₉ –	105.4	80.	120	118
10	C ₁₀ H ₂₁ –	111.2	99.	141	136
11	C ₁₁ H ₂₃ –	112.3	20.	137	132
12	C ₁₂ H ₂₅ –	109.9	8.0	138	127
13	C ₁₃ H ₂₇ –	116.1	7.6	150	140
13A	C ₁₃ H ₂₇ –	116.0	7.1	155	154
^d 14	C ₁₄ H ₂₉ –	115.7	(>1) ^e	160	159
16	C ₁₆ H ₃₃ –	120.2	60.	182	168
16A	C ₁₆ H ₃₃ –	119.3	2.9	172	169
18	C ₁₈ H ₃₇ –	122.5	14.	192	188
19	C ₁₉ H ₃₉ –	119.1	0.5	166	164
22	C ₂₂ H ₄₅ –	123.6	0.6	192	180

^a Second-harmonic generation (SHG) efficiencies (from ref. 1) are relative to that for urea, taken as unity. For these compounds it is evident that SHG lacks correlation with the thermal data. ^b Capillary melting range 114–115°C; then crystallized upon being seeded with sample 2A and melted again at 128–129°C. ^c The X-ray crystal structure was centrosymmetric, rigorously requiring zero SHG efficiency; there was insufficient sample for the SHG test. ^d Not included in ref. 1. ^e SHG observed visually; >>1 implied (see ref. 1).

DSC work says nothing about SHG activity. There is neither theoretical nor experimental correlation. However, when examining crystallization conditions to discover how they may alter crystal structure, changes in onset point upon reheating the sample may be helpful (Tables 2 and 5). For sample 2B, melting, followed by seeded crystallization and a second melting point, was observed cleanly in the capillary determination (at $1^{\circ}\text{C min}^{-1}$) but was somewhat scrambled in the DSC, doubtless owing to the $10^{\circ}\text{C min}^{-1}$ sweep rate. When such melting points are more closely spaced, neither the capillary melting point nor the DSC onset point prove the existence of a second form; however there will often be significant differences in heats of fusion between samples, or upon reheating the crystallized melt. Examples are (Table 3) numbers 1, 2, 2A, 2B, 4, 7, 7A, 7B, 12, 13, 16, 16A and 22; (Table 4) 32–32A, 36, 36A, 36B and 37; (Table 5) 15, 25, 28, 29, 40 and 41. These (and perhaps others) indicate differentiated (metastable) crystals, a conclusion validated in certain cases by the SHG efficiency values, and by powder X-ray data [1]. The DSC method is faster and simpler than others for powder characterization (such as X-ray), and provides additional useful information, for example when compared to capillary melting-point determination.

TABLE 4

Comparison of initial onset points and heats of fusion to values found upon reheating, for *n*-alkyl *p*-nitrophenylureas, R-NHCONHC₆H₄NO₂ (*p*)

Sample number (from ref. 1)	<i>n</i> -Alkyl group, R-	Initial onset point (°C)	Reheat onset point (°C)	SHG ^a efficiency	Heat of fusion (J g ⁻¹)	
					Initial	Reheat
30	C ₅ H ₁₁ -	131.0	131.0	0.001	79	79
30A	C ₅ H ₁₁ -	131.6	131.8	0.003	80	79
31	C ₆ H ₁₃ -	111.2	108.1	0.9	96	91
32	C ₁₀ H ₂₁ -	115.8	114.4	38.	112	107
32A	C ₁₀ H ₂₁ -	117.4	116.7	3.0	118	111
33	C ₁₂ H ₂₅ -	117.6	116.1	8.0	117	116
34	C ₁₄ H ₂₉ -	119.7	118.6	11.	132	125
35	C ₁₆ H ₃₃ -	119.4	119.2	6.	133	128
36	C ₁₈ H ₃₇ -	122.6	122.3	5.	153	128
36A	C ₁₈ H ₃₇ -	118.9	119.3	0.000	172	129
36B	C ₁₈ H ₃₇ -	119.9	119.7	0.9	146	125
37	Oleyl- ^b	101.6	100.2	1.6	97	79

^a Second-harmonic generation (SHG) efficiencies (from ref. 1) are relative to that for urea, taken as unity. ^b The oleyl group, C₁₈H₃₅-, is *cis*-C₈H₁₇CH=CH(CH₂)₈-, and thus is an alkylene group.

TABLE 5

Comparison of initial onset points and heats of fusion to values found upon reheating, for terminally substituted polymethylene *p*-nitrophenylurethanes, $X(\text{CH}_2)_n\text{-OCONHC}_6\text{H}_4\text{NO}_2$ (*p*)

Sample number (from ref. 1)	Substituted polymethylene group, $X(\text{CH}_2)_n\text{-}$	Straight chain carbon number ^a	Initial onset point (°C)	Reheat onset point (°C)	SHG ^b efficiency	Heat of fusion (J g^{-1})	
						Initial	Reheat
29	$\text{CH}_3\text{S}(\text{CH}_2)_2\text{-}$	2	76.2	74.8	18.	122	115
(40) ^c	$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_2\text{-}$	2	101.8	96.7	1.3	104	81
23	$\text{Cl}(\text{CH}_2)_6\text{-}$	6	87.6	86.6	24.	90	89
28	$\text{HO}(\text{CH}_2)_8\text{-}$	8	113.7	110.5	10.0	142	149/126
(41) ^c	$\text{CH}_3\text{CO}_2(\text{CH}_2)_8\text{-}$	8	126.0	118.0	0.002	150	136
14	$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{-}$	9	103.2	102.9	0.8	131	132
15	$\text{HC}\equiv\text{C}(\text{CH}_2)_9\text{-}$	9	112.2	111.9	32.	160	148
27	$\text{I}(\text{CH}_2)_{11}\text{-}$	11	126.4	126.7	17.	137	132
24	$\text{Br}(\text{CH}_2)_{11}\text{-}$	11	122.4	121.3	67.	141	138
25	$\text{Br}(\text{CH}_2)_{12}\text{-}$	12	100.3	99.7	44.	114	106
26	$\text{Br}(\text{CH}_2)_{16}\text{-}$	16	109.7	109.4	23.	129	123

^a Thermal effects result in part from the length and odd/even count of the polymethylene chain. At constant X (=Br, samples 24–26) these factors become discernible. ^b Second-harmonic generation (SHG) efficiencies (from ref. 1) are relative to that for urea, taken as unity. ^c Samples 40 and 41 were not included in ref. 1.

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