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Materials science of organic compounds. Part 3. Glass-formers, vitriphores, T_g, and molecular chirality [1]

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Abstract

Non-centrosymmetric crystals are required for second-harmonic generation (SHG). Homochiral compounds cannot crystallize centrosymmetrically.

Various chiral *p*-nitrophenylurethanes and ureas, useful for SHG, were studied by differential scanning calorimetry (DSC). On quench-cooling from the melt, these compounds invariably formed glasses and gave T_g values on reheating. This behavior was generalized, first to other homochiral compounds, and then to racemic mixtures. For mixtures the T_g values were not strictly linear interpolations.

The rule is proposed that molecular chirality, even when of steric origin and/or rapidly inverting, strongly favors glass formation. An attached dissymmetric group is termed a "vitriphore".

INTRODUCTION

The old term "optically active" takes on new meaning, because enantiomerically pure (homochiral) compounds cannot crystallize centrosymmetrically; the resulting acentric crystals therefore must possess non-linear optical "activity", typically some degree of second-harmonic generation (SHG) capability. A brief account of the significance of good donor-acceptor molecules being properly aligned in the crystal has been given in ref. 1. Numerous chiral *p*-nitrophenylurethanes and ureas, useful for SHG [2], were available for study by differential scanning calorimetry (DSC).

EXPERIMENTAL

A Du Pont 912/2100 DSC apparatus, calibrated with indium and tin, and a Seiko DSC-220c, similarly calibrated, were used. Temperatures are given in kelvins, ±1–2 K. The T_g is here determined as the inflection point (Du Pont) or the T_g but as the transition midpoint (Seiko); the instruments

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TABLE 1

p-Nitrophenylurethanes of homochiral alcohols: thermal data

Homochiral alcohol precursor to urethane	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ (J g^{-1})	T_m (K)	T_g/T_m
(−)Menthol	306	388–389	390	76	389	0.79
(*S*) (−)Methyl lactate	286	395–396	397	94	396	0.72
(*S*) Glycerol acetonide	282	383–386	381	43	384	0.73
"(*S*)" Glycerol (from acetonide)	279	445–446	446	185	446	0.63
(1*R*) Nopol	277	347–349	347	62	348	0.80
(+) Methyl 3-hydroxy-2-methyl propionate	269	375–376	376	94	376	0.72

gave similar results. Possible ageing effects were not considered, nearly all T_g runs being made immediately after a previous melting run. Heating rates were 10 K min^{-1}. Metal-calibrated [3] capillary melting points were averaged with onset points to define T_m. Heats of fusion, ±5–10%, are also reported.

The purities of the organic compounds were attested to by the narrowness of the melting point ranges and by the DSC onset behavior, as well as by agreement with literature values. For the imides, synthesis was by reaction of the corresponding amines (Aldrich) and anhydrides (Eastman and Aldrich) in chlorobenzene, followed by thermal cyclization at 200–250°C and recrystallization from ethanol or ethanol–chlorobenzene. The identities and purities of these and other previously unreported compounds were verified by infrared and NMR spectroscopy (^{1}H and ^{13}C). Homochiral 4-nitrophenyl and related urethanes and ureas [2], numerous chiral imides, and racemic 4-substituted phenols were examined, as were several unrelated homochiral and racemic compounds. Pairs of dissimilar compounds (equal-weight mixtures) having nearly identical T_g and T_m values were used to indicate the effects of mixing. The results are presented in Tables 1–9.

DISCUSSION

Perhaps all melt-stable organic chemicals could be obtained in glassy form by "splat" cooling (as has been done for metal alloys); their glass transition temperatures would then become directly measurable. While that is normally impractical, it has long been known that some organic compounds form glasses upon quench-cooling [4] or slow-cooling from the melt; rates attainable in DSC apparatus (50–100 K min^{-1}) suffice. Indeed, organic-compound glasses were employed almost exclusively by Tammann in his pioneering work on the thermal properties of glass [5].

TABLE 2

Homochiral (*R*-1-phenylethyl)ureas from various arylamines: thermal data

Arylamine precursor to (*R*-1-phenylethyl)ureas	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\,g^{-1}$)	T_m (K)	T_g/T_m
2-Methoxy-4-nitroaniline	331 [a]		457 [a]	91 [a]		
	330 [b]	456–457	457 [b]	86 [b]	457	0.72
2-chloro-4-nitroaniline	324 [a]	441–442	440 [a]	89 [a]	441	0.73
4-Nitroaniline	318 [a]	451–452	452 [a]	122 [a]	452	0.70
4-Cyanoaniline	314 [a]	464–465	465 [a]	129 [a]	465	0.68
1-Naphthylamine	306 [b]	497–499	501 [b]	113 [b]	500	0.61
4-Nitro-1-naphthylamine	305 [b]	450	445 [b]	107 [b]	448	0.68
2-Naphthylamine	304 [b]	458–459	457 [b]	115 [b]	458	0.66
2-Nitroaniline	299 [a]	456–457	450 [a]	139 [a]	454	0.66
3-Nitroaniline	301 [a]	431–433	431 [a]	113 [a]	431	0.70
4-Chloroaniline	297 [b]	462–463	463 [b]	116 [b]	463	0.64
3,4-Dichloroaniline	296 [a]	443–444	441 [a]	94	443	0.67
2-Chloroaniline	292 [b]	435–436	434 [b]	108 [b]	435	0.67
4-Methoxyaniline	287 [b]	453–454	453 [b]	135 [b]	453	0.63
3-Chloroaniline	286 [b]	416–417	415 [b]	95 [b]	416	0.69
3-Trifluoromethylaniline	280 [b]	397–398	396 [b,c]	69 [b]	397	0.71

[a] Du Pont DSC. [b] Seiko DSC. [c] Also had onset point at 381 K; some of the other samples had lower onset points, though less clearly defined.

TABLE 3

Homochiral *N*-(1-arylethyl) imides: thermal data

Homochiral imide	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\,g^{-1}$)	T_m (K)	T_g/T_m
N-(*R*-1-Phenylethyl)-tetraiodophthalimide	370	544–545	540	38	543	0.68
N-(*S*-1-Naphthylethyl)-tetrachlorophthalimide	362	462–463	462	50	462	0.78
N-(*S*-1-Naphthylethyl)-2,2′-diphenic imide	356	470–472	466	83	469	0.76
N-(*R*-1-Phenylethyl)-2,2′-diphenic imide	333	483–484	483	122	483	0.69
N-(*R*-1-Phenylethyl)-tetrabromophthalimide	330	501–502	500	59	501	0.66
N-(*R*-1-Phenylethyl)-4-nitro-1,8-naphthalimide	320	402–404	396	56	401	0.80
N-(*R*-1-Phenylethyl)-1,8-naphthalimide	319 [a]	435–436	434 [a]	61 [a]	435	0.73
N-(*R*-1-Phenylethyl)-tetrachlorophthalimide	313	456–457	457	76	457	0.68
N-(*R*-1-Phenylethyl)-3-nitrophthalimide	289	396–397	393	65	395	0.73

[a] Du Pont DSC; remainder Seiko DSC.

TABLE 4

Racemic *N*-substituted imides and *para*-substituted phenols: thermal data

Racemic imide or phenol	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\,g^{-1}$)	T_m (K)	T_g/T_m
4-Acetamido-*N*-(2′,4′-dimethylphenyl)-1,8-naphthalimide	401	565–566	562	105	564	0.71
N-(1,2,3,4-Tetrahydro-1-naphthyl)-tetrachlorophthalimide	343	500–501	501	90	501	0.68
N-(1-Phenylethyl)-2′,2″-diphenic-imide	333	475–477	473	123	475	0.70
N-(1-Phenylethyl)-tetrachlorophthalimide	312	435–436	435	64	435	0.72
2,2,4-Trimethyl-4-(*p*-hydroxyphenyl) chroman (Dianin's compound)	299[a]	428–433	430[a]	132[a]	430	0.70
1-Methyl-1-(p-hydroxyphenyl)-1,2,3,4-tetrahydronaphthalene	283[a]	393–394	393[a]	113[a]	393	0.72
1-(*p*-Hydroxyphenyl)indane	269[a]	362–364	363[a]	102[a]	363	0.74
2-(*p*-Hydroxyphenoxy)tetrahydropyran	255[a]	358–360	356[a]	114[a]	358	0.71

[a] Du Pont DSC; remainder Seiko DSC.

TABLE 5

Various homochiral vitrigens: thermal data

Homochiral vitrigen	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\,g^{-1}$)	T_m (K)	T_g/T_m
Cinchonine (Am. Quinine)	395[b]	521–526	517[b]	127[b]	522	0.76
Brucine (M, C&B)	371[a]	449–451	451[a]	67[a]	451	0.82
Cinchonidine (Aldrich)	377[b]	477–478	476[b]	133[b]	476	0.71
Salicin (Aldrich)	334[b]		471[b]	184[b]		
	333[a]	468–471	471[a]	185[a]	471	0.71
Cholesterol[c]	332[b]	(422)[c]	–	–	422	0.79
Sucrose	319[b]	455–457	459[b]	128[b]	458	0.70
1,3-Dinitro-4,6-bis-(*R*-1′-phenylethylamino)benzene	316[b]	468–470	469[b]	84[b]	469	0.67
N-(*R*-1-Phenylethyl)-*N*′-(*p*-nitrophenyl)thiourea	313[a]	386–387	386[a]	74[a]	386	0.81
β-D-Glucose pentaacetate	296[a]	404–405	405[a]	82[a]	405	0.73
α-D-Glucose pentaacetate	291[a]	385–386	386[a]	87[a]	386	0.75
l-Menthyl-3-nitrophenylurethane	288[a]	356	353[a]	70[a]	354	0.81
1′-(Ethoxycarbonyl)ethyl-2-methyl-4-nitrophenylurethane	273[a]	344	342[a]	76[a]	343	0.80

[a] Du Pont DSC. [b] Seiko DSC. [c] The sample (age 40+ years) was glassy and failed to show a distinct onset point; the literature melting point is used.

TABLE 6

Various racemic vitrigens: thermal data

Racemic vitrigen	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\ g^{-1}$)	T_m (K)	T_g/T_m
1,1,3-Trimethyl-3-(*p*-carboxyphenyl)-indan-5-carboxylic acid	402	566–567	563	162	565	0.71
2-Benzyl-(3,3′)spirobi-(benzo[f]chroman)	339	483–484	482	99	483	0.70
N-(1-Phenylethyl)-*N*′-(*p*-nitrophenyl)urea	305 [a]	443–444	444 [a]	96 [a]	444	0.69
N-(1-Phenylethyl)-2,4-dinitroaniline	283	387–389	387	81	387	0.73
N-(2-Tetrahydropyryl)saccharin	279 [a]	409–410	407 [a]	140 [a]	409	0.68
3-Pentadecyl-cyclohexanone	225	314–315	311	184	313	0.72

[a] Du Pont DSC; remainder Seiko DSC.

TABLE 7

Formally achiral vitrigens: thermal data

Formally achiral vitrigen	T_g (K)	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ ($J\ g^{-1}$)	T_m (K)	T_g/T_m
9,9-Bis(*p*-hydroxyphenyl)fluorene	372	496–497	479	99	497	0.75
Phenolphthalein	265 [a]	535–536	535 [a]	149 [a]	535	0.68
9,9-Bis(*p*-aminophenyl)fluorene	360	501–504	500	101	501	0.72
Anilinephthalein	353 [a]	475–476	475 [a]	101 [a]	475	0.74
4,4′-Dimethoxytetraphenylmethane	297	453	452	104	452	0.66
2,2,2-Tris(chloromethyl)ethyl-*p*-nitrophenylurethane	293	428–429	429	108	429	0.68
Piperine (Aldrich)	284 [a]	400–402	401 [a]	96 [a]	401	0.71
2,2,3,3-Tetrafluoropropyl-*p*-nitrophenylurethane	261	347–353	348	91	348	0.75
n-Pentyl-*p*-nitrophenylurethane	243	365–366	365	94	365	0.67
o-Terphenyl	245 [b]	–	329	73.6 [b]		
	243 [c]	329.35 [c]	–	74.6 [c]	329	0.74
	243 [d]	–	329	79.9 [d]		

[a] Seiko DSC; remainder Du Pont DSC. [b] Data of ref. 6. [c] Data of ref. 7; this is presumed to be the most accurate measurement. [d] Data of ref. 8.

TABLE 8

Non-vitrigens: compounds failing to vitrify upon rapid cooling

Non-vitrigen	Melting range (K)	Onset point (K)	$\Delta_{fus}H$ (J g^{-1})
N-(*R*-1-Phenylethyl)-2′,3′-naphthalimide	448–450	448[a] 446	79[a] 84
N-2-Butyl-tetrachlorophthalimide	460–461	460	60[b] 52[c]
N-2-Methyl-1-butyl-tetrachlorophthalimide	418–419	417[d]	80[b] 54[c,d]
N-(*p*-2-Pentylphenyl)-tetrachlorophthalimide	457–458		64[b] 56[c]
p-(2-Methyl-2-butyl)phenol	366–368	365[a]	97[a]
p-Cyclohexylphenol	391–397	394[a]	123[a]
N,*N*′-Bis-(*R*-1-phenylethyl)urea	478–481	479[a]	132[a]
(+)Camphor (Aldrich 99%)	452–454		
(±)Camphor (Aldrich 96%)	435–441		
6′-Chlorohexyl-2-methyl-4-nitrophenylurethane	373–374	374[a]	128[a]
6′-Chlorohexyl-2-methoxy-4-nitrophenylurethane	363–364	359[a]	115[a]
Hexaethylbenzene	401	402	128
Cyclotetradecadiyne-1,8	369–371	370	112
2,2′-Dinitrobiphenyl	396–397	396	99

p-Nitrophenylurethanes, X-$(CH_2)_nOCONH$-$C_6H_4NO_2$, of ref. 1, specifically; if X is H, $n = 1, 3, 6, 7, 9, 10, 16$, and 22; if X is Cl, $n = 6$; if X is Br, $n = 11$; if X is I, $n = 11$; and if X is OH, $n = 8$.

[a] Du Pont DSC; remainder Seiko DSC. [b] Initial fusion in hermetic pan. [c] Reproducible heats of fusion upon remelting in hermetic pan; no change in onset point or slope, no T_g, no significant weight loss. [d] After the initial fusion there were two endotherms, at 405 and 417 K, of similar size, connected by a moderate unresolved exotherm; the reproducible combined (net) heat is listed.

TABLE 9

Glass transition and melting behavior of previously fused mixtures: thermal data

Components and equal-weight mixtures	T_g (K)	Onset point (K)	$\Delta_{fus}H$ (K)
(*S*-Methyl lactate)-*p*-nitrophenylurethane (A)	286.5	397	94
1-Methyl-1-(*p*-hydroxyphenyl)-1,2,3,4-tetrahydronaphthalene (B)	283.5	393	113
N-(*R*-1-Phenylethyl)-3-nitrophthalimide (C)	290.2	393	63
Equal-weight mixture: (A) + (B)	287.3	365	81
Equal-weight mixture: (A) + (C)	280.1	365	96
Equal-weight mixture: (B) + (C)	282.2	359	79
2,2,4-Trimethyl-4-(*p*-hydroxyphenyl)chroman (D)	298.8	430	132
2,2,2-Tris(chloromethyl)ethyl-*p*-nitrophenylurethane (E)	293.5	429	108
Equal-weight mixture: (D) + (E)	291.8	411	110

Unfortunately, organic chemists are taught little or nothing about materials science, and are generally unaware of the "materials" properties of organic chemicals, especially their glassy behavior. Thus far I have found no references to any explicit attempts to rationalize or predict glass formation in organic compounds, although it is widely known that "sugars are hard to crystallize", and, closer to the present work, "simple ... unassociated molecules ... asymmetric in structure" [6] can form glasses.

Here an apparently novel general rule is proposed that molecular chirality strongly favors vitrification, even at cooling rates much slower than quench-cooling. In the necessarily limited tests carried out so far the positive predictive success rate is excellent, and the negative rate, though lower, is quite good. The results of Tammann [4] support this rule, although he drew no such correlation; his "glass-formers" were derived from chiral natural products, while his "crystallizers" were achiral, synthetic, principally aromatic molecules.

The present author has also established that racemic mixtures, sterically chiral molecules, and/or "rapidly" inverting ones, all favor glass formation. An interesting example is the seemingly symmetric nitrophenylurethane $4\text{-}NO_2C_6H_4NHCO_2CH_2C(CH_2Cl)_3$ (Table 7). The bulky $-C(CH_2Cl)_3$ group takes up right- and left-handed conformations, as may be seen by molecular modeling [9] or even by use of space-filling atom models.

Attachment of a chiral group thus typically produces a "vitrigen" (a glass-forming molecule); the group perceived as conferring this property is suitably referred to as a "vitriphore". While current exceptions to the rule (Table 8) may be resolved by subsequent successful vitrification (several of the tabulated vitrigens were initially "exceptions"), nevertheless it is reasonable that vitriphores differ in effectiveness. It is obvious that the rule represents an arbitrary though convenient point in a continuous scale of tendencies toward vitrification. Wunderlich has suggested that this represents an increasing inhibition of crystallization [10].

Boyer [11] has proposed a plausible "reduced" glass transition temperature, $T_g^* = T_g/T_m = 2/3$; an attempt to improve it [12] by adding the substance's boiling-point temperature to both numerator and denominator merely serves to conceal whatever genuine variability may exist. Molecular shape and polar character appear to influence the T_g/T_m ratio. Hydrogen-bonding hydroxyl groups (Tables 1 and 4) raise T_g less than T_m, giving ratios as low as 0.6. While strongly polarizable/polar polyhalo and nitro aromatic groups tend to produce ratios between 0.6 and 0.7, most of the examples in the tables have ratios above 0.7. It has been asserted that "the glass transition of *o*-terphenyl is abnormally high" [6], the ratio being 0.74 [7]. It is thus of particular interest that the cycloaliphatic, though polar, cholesterol, brucine, and menthyl and nopyl urethanes of Tables 1 and 5 show $T_g/T_m \approx 0.8$.

While the T_g values reported here are (as are nearly all such in the DSC literature) too high due to well-known kinetic effects which could be, but have not been, corrected for in the commercial DSC software [13], the T_g/T_m ratio is unlikely to be in error by more than +0.01 to +0.03. Further but normally much smaller positive errors will result from a low purity sample. "Mixed-melting-points" of dissimilar but like-melting compounds are normally strongly depressed; this is not true for "mixed-T_g" values, which may fall a little below or above those of the pure materials, these having been chosen to be nearly equal (Table 9). Non-linear but monotonic dependence of T_g upon composition is known [5, 14]. Three racemic mixtures, two imides (Table 4) and a urea (Table 6), when compared to their homochiral components (Tables 3 and 2), show significant depressions of T_m relative to T_g. Elevation of T_g upon mixing, when it occurs, indicates complex formation [14].

The T_g/T_m ratio may reveal more about melting behavior than about vitrification. Because T_g values differ little among isomers and structurally related compounds, and T_m varies markedly (see for example Table 2), it follows that T_g/T_m will not be a true constant. Correlations of T_g with structural features, as has been done for polymers [15], should be more fruitful than attempts involving T_m.

REFERENCES

1 G.V.D. Tiers and C.V. Francis, Thermochim. Acta, 226 (1993) 311.
2 G.V.D. Tiers, US Patent 4,818,899 (1989).
3 G.V.D. Tiers, Anal. Chim. Acta, 237 (1990) 241.
4 G. Tammann, Z. Phys. Chem., 25 (1898) 472.
5 G. Tammann, Der Glaszustand, L. Voss, Leipzig, 1933.
6 R. J. Greet and D. Turnbull, J. Chem. Phys., 46 (1967) 1243.
7 S.S. Chang and A.B. Bestul, J. Chem. Phys., 56 (1972) 503.
8 R.J. Greet and D. Turnbull, J. Chem. Phys., 47 (1967) 2185.
9 J. Stevens and G.V.D. Tiers, in preparation.
10 B. Wunderlich, comment made at 21st NATAS conference, Atlanta, GA, September 1992.
11 R.F. Boyer, J. Appl. Phys., 25 (1954) 825.
12 R.F. Fedors, J. Polym. Sci. Polym. Lett., 17 (1979) 719.
13 L. Aras and M.J. Richardson, Polymer, 30 (1989) 2246.
14 A.V. Lesikar, Phys. Chem. Glasses, 16 (1975) 83; J. Chem. Phys., 68 (1978) 3325.
15 D.W. Van Krevelen, Properties of Polymers: Their Estimation and Correlation with Chemical Structure, Elsevier, New York, 1976, Chapt. 6.