

Vitrigens. I

Synthesis and Characterization of Low Molecular Weight Organic Glasses

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Received February 6th, 1998, respectively November 5th, 1998

Keywords: Amorphous materials, Glasses, Carbazole, Twin molecules, Vitrigens

Abstract. New low molecular weight organic materials with a strong tendency towards glass formation and glass temperatures above room temperature were synthesized. These materials consist of twin molecules where two bulky groups, *i.e.* carbazole (**Ca**), 3,6-dibromocarbazole (**DBrCa**), 2,3-benzocarbazole (**BC**), 1,2-benzo-3,4-dihydrocarbazole (**BCDH**),

phenothiazine (**Ph**), 1,8-naphthalic acid anhydride (**NI**), and pyrene-1-aldehyde (**PY**) have been linked by flexible or semi-flexible aliphatic or aromatic central units. Their structure-glass temperature relationship and some relations between thermodynamic parameters and amorphous properties are discussed.

Low molecular weight organic compounds which are able to form stable glasses are a new class of materials and have recently found interest for optical and/or electric devices [1, 2]. Generally, such devices require thin organic films with a good film homogeneity. Monocrystalline thin films without any structural imperfections are thus considered to be ideal. However, it is very difficult to form monocrystalline thin films of complex organic functional molecules with a thickness less than 100 nm. Moreover, polycrystalline films always have grain boundaries of various sizes, which cause serious structural defects. An alternative approach to form uniform organic films are amorphous (glassy) organic thin films.

The glassy state of low molecular weight organic compounds was first described by Tammann at the end of the 19th century [3]. In the following years many studies have been carried out on glasses that also included some organic materials [4, 5]. However, only few groups of nonpolymeric amorphous molecules with glass transition temperatures higher than room temperature are known.

Systematic studies on such stable low molecular weight organic glasses presenting a new class of amorphous materials began since 1990 by Wirth [6], Shirota [7, 8] *et al.* and Naito [9]. The molecular design of such molecules includes above all star-shaped and twin molecules.

Synthesis of Twin Molecules

The concept used in this investigation includes twin mol-

ecules of the type Q–Y–Q where two identical bulky groups Q were linked by a central group Y (symmetric twins), which can be selected to be flexible or semi-flexible. This type of molecules allows to introduce a broad range of further modifications by length, flexibility and shape of the central link.

The following bulky groups were used: Carbazole, 3,6-dibromocarbazole, 1,2-benzo-3,4-dihydrocarbazole, 2,3-benzocarbazole, phenothiazine, 1,8-naphthalic anhydride and pyrene-1-aldehyde.

Carbazole-, 3,6-dibromocarbazole-, 1,2-benzo-3,4-dihydrocarbazole-, 2,3-benzocarbazole- and phenothiazine-twins were synthesized by deprotonation of the N-H-bond with sodium hydride in *N*-methyl-pyrrolidone as solvent in the first step. The so formed anions can react with various α,ω -dihalogen compounds in a nucleophilic substitution to give the twin molecules.

Pyrene-1-aldehyde- and 1,8-naphthalic anhydride-twins were synthesized by a condensation reaction with α,ω -diamino compounds under water separation. Table 1 gives an overview of the synthesized products.

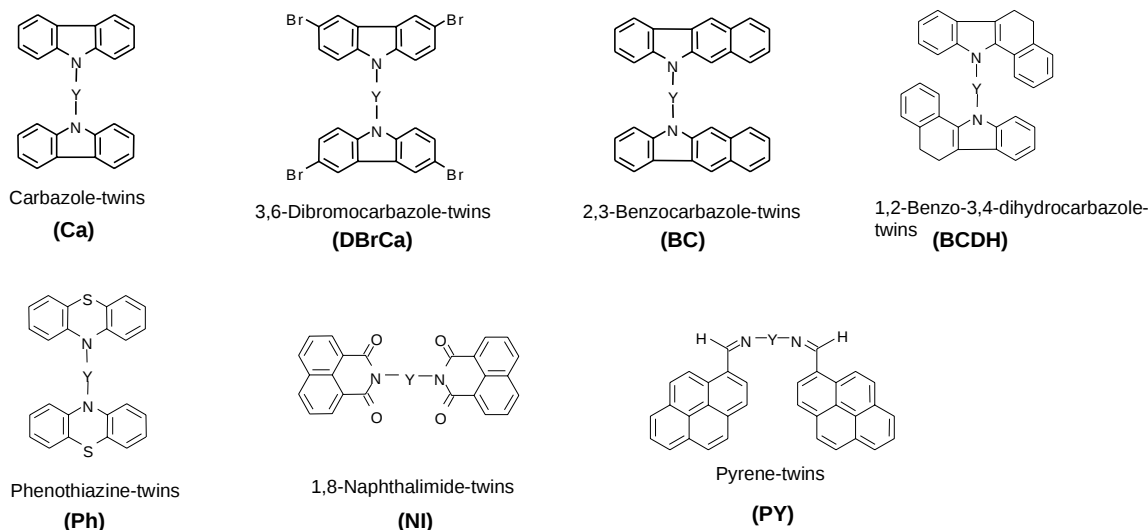
The melting points (T_m) and glass transition temperatures (T_g) of the synthesized products are shown by the following tables 2–8.

Comparative View of the Synthesized Compounds

Relation between Melting Point and Glass Transition Temperature

It is known from polymers that the factors which determine the melting temperature, *e.g.* rigidity of the polymer chain, polar groups and substituents on the main chain also influence the glass transition temperature [10].

General structures of the synthesized compounds:



This behaviour can be described roughly by the well-known Beaman-Boyer rule [11].

$$T_g/T_m \approx 2/3$$

Fig. 1 shows the dependence of T_g on T_m for some low molecular weight organic glasses of this paper. The ratio $T_g/T_m \approx 2/3$ is nearly confirmed, but a general statement is not possible, because the scattering of the values in all series of compounds is relatively high.

Comparison of the Twins with Aliphatic Bridges

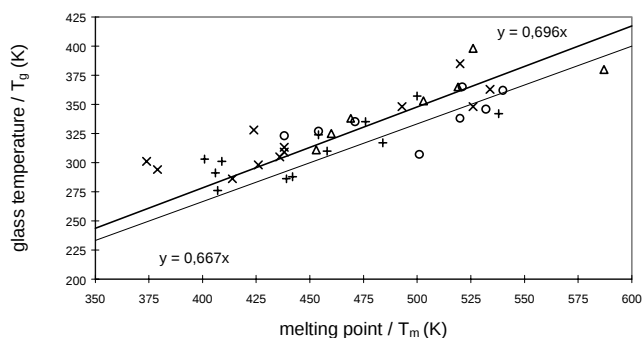


Fig. 1 Glass transition temperature of (T_g) and melting point (T_m) of carbazole- (+), 3,6-dibromocarbazole- (x), 2,3-benzocarbazole- (Δ) and 1,2-benzo-3,4-dihydrocarbazole-twins (o).

All investigated series of twins with aliphatic bridges show a similar dependence between glass transition temperature and length of the bridge. With increasing bridge length the glass transition temperature is decreasing. In the examined regions the dependence is nearly linear (Fig. 2).

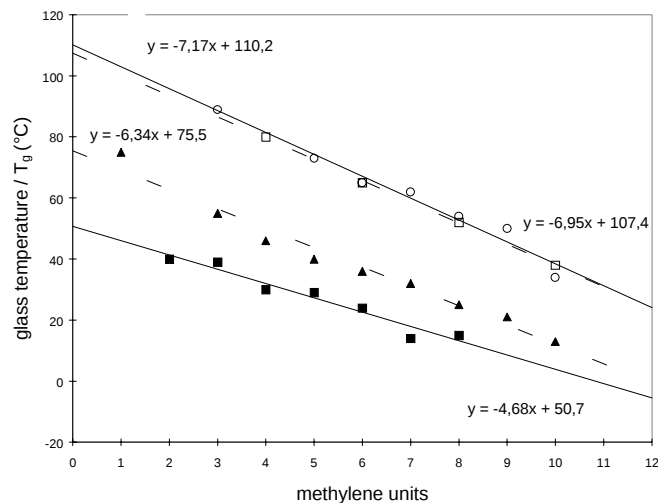


Fig. 2 Glass transition temperature and length of the aliphatic bridge of 3,6-dibromo-carbazole-twins (o), 2,3-benzocarbazole-twins ($\square$), 1,2-benzo-3,4-dihydrocarbazole-twins ($\blacktriangle$) and pyrene-twins ($\blacksquare$).

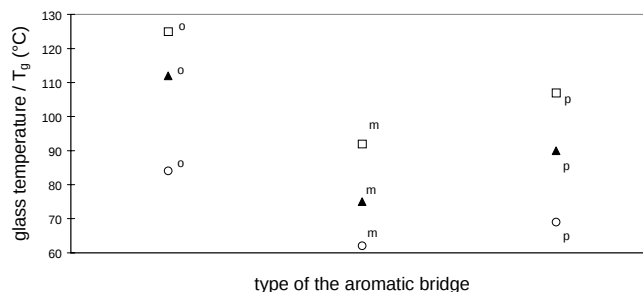


Fig. 3 Dependence between glass transition temperature and type of the aromatic bridge (o = ortho, m = meta, p = paraphenylene) for carbazole- (o), 2,3-benzocarbazole- ($\square$) and 1,2-benzo-3,4-dihydrocarbazole- ($\blacktriangle$) twins.

Bridge Y	Ca	DBrCa	BC	BCDH	Ph	NI	PY
-	-	-	-	-	-	-	PY-0
-(CH ₂) ₂ -	Ca-1	DBrCa-1	-	BCDH-1	Ph-1	NI-2	PY-2
-(CH ₂) ₃ -	Ca-3	DBrCa-3	-	BCDH-3	Ph-3	NI-3	PY-3
-(CH ₂) ₄ -	Ca-4	DBrCa-4	BC-4	BCDH-4	Ph-4	NI-4	PY-4
-(CH ₂) ₅ -	Ca-5	DBrCa-5	-	BCDH-5	Ph-5	NI-5	PY-5
-(CH ₂) ₆ -	Ca-6	DBrCa-6	BC-6	BCDH-6	Ph-6	NI-6	PY-6
-(CH ₂) ₇ -	Ca-7	DBrCa-7	-	BCDH-7	Ph-7	NI-7	PY-7
-(CH ₂) ₈ -	Ca-8	DBrCa-8	BC-8	BCDH-8	Ph-8	NI-8	PY-8
-(CH ₂) ₉ -	Ca-9	DBrCa-9	-	BCDH-9	Ph-9	NI-9	-
-(CH ₂) ₁₀ -	Ca-10	DBrCa-10	BC-10	BCDH-10	Ph-10	NI-10	-
-(CH ₂) ₁₂ -	-	-	-	-	-	NI-12	PY-12
	Ca-O	-	-	BCDH-O	-	-	-
	Ca-OX	DBrCa-OX	BC-OX	BCDH-OX	Ph-OX	-	-
	Ca-MX	DBrCa-MX	BC-MX	BCDH-MX	Ph-MX	NI-MX	PYDAMX
	Ca-PX	DBrCa-PX	BC-PX	BCDH-PX	Ph-PX	NI-PX	PYDAPX
	-	-	-	-	-	NI-MP	-
	-	-	-	-	-	NI-PP	-
	-	-	-	-	-	NI-ME	PYDADPM
	-	-	-	-	-	NI-ET	PYDADB
	-	-	-	-	-	-	PYDADC
	-	-	-	-	-	-	PYDADPE
	-	-	-	-	-	-	PYDANA

The search for low molecular weight organic glasses with high glass transition temperatures would be simplified when rules were known for suitable molecular structures obtained by theoretical considerations. The melting points (T_m) and glass transition tempera-

In this equation h_g stands for a material family constant corresponding to the activation energy for heavy atom rearrangements; $\sum \Delta S_{tr,m}$ means the sum of all entro-

pies of fusion and of phase transition for a crystalline sample between T_g and T_m , and N is the number of heavy atom per molecule except hydrogen atoms.

Table 2 Melting points and glass transition temperatures of the synthesized 3,6-carbazole-twins (**Ca**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
Bis(carbazol-9-yl)methane	Ca-1	325	–
1,3-Bis(carbazol-9-yl)propane	Ca-3	185	37
1,4-Bis(carbazol-9-yl)butane	Ca-4	211	44
1,5-Bis(carbazol-9-yl)pentane	Ca-5	181	51
1,6-Bis(carbazol-9-yl)hexane	Ca-6	128	30
1,7-Bis(carbazol-9-yl)heptane	Ca-7	136	28
1,8-Bis(carbazol-9-yl)octane	Ca-8	169	15
1,9-Bis(carbazol-9-yl)nonane	Ca-9	166	13
1,10-Bis(carbazol-9-yl)decane	Ca-10	134	3
1,8-Bis(carbazol-9-yl)-3,6-dioxaoctane	Ca-O	133	18
1,2-Bis[(carbazol-9-yl)methyl]benzene	Ca-OX	227	84
1,3-Bis[(carbazol-9-yl)methyl]benzene	Ca-MX	203	62
1,4-Bis[(carbazol-9-yl)methyl]benzene	Ca-PX	265	69

Table 3 Melting points and glass transition temperatures of the synthesized 3,6-dibromocarbazole-twins (**DBrCa**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
Bis(3,6-dibromocarbazol-9-yl)-methane	DBrCa-1	350 (dec.)	–
1,3-Bis(3,6-dibromocarbazol-9-yl)-propane	DBrCa-3	267	89
1,4-Bis(3,6-dibromocarbazol-9-yl)-butane	DBrCa-4	329 (dec.)	–
1,5-Bis(3,6-dibromocarbazol-9-yl)-pentane	DBrCa-5	259	73
1,6-Bis(3,6-dibromocarbazol-9-yl)-hexane	DBrCa-6	247	65
1,7-Bis(3,6-dibromocarbazol-9-yl)-heptane	DBrCa-7	198	62
1,8-Bis(3,6-dibromocarbazol-9-yl)-octane	DBrCa-8	181	54
1,9-Bis(3,6-dibromocarbazol-9-yl)-nonane	DBrCa-9	165	50
1,10-Bis(3,6-dibromocarbazol-9-yl)-decane	DBrCa-10	228	34
1,2-Bis[(3,6-dibromocarbazol-9-yl)methyl]-benzene	DBrCa-OX	dec.	–
1,3-Bis[(3,6-dibromocarbazol-9-yl)methyl]-benzene	DBrCa-MX	248	92
1,4-Bis[(3,6-dibromocarbazol-9-yl)methyl]-benzene	DBrCa-PX	dec.	–

Table 4 Melting points and glass transition temperatures of the synthesized 2,3-benzocarbazole-twins (**BC**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
1,4-Bis(2,3-benzocarbazol-9-yl)-butane	BC-4	230	80
1,6-Bis(2,3-benzocarbazol-9-yl)-hexane	BC-6	196	65
1,8-Bis(2,3-benzocarbazol-9-yl)-octane	BC-8	187	52
1,10-Bis(2,3-benzocarbazol-9-yl)-decane	BC-10	180	38
1,2-Bis[(2,3-benzocarbazol-9-yl)methyl]benzene	BC-OX	253	125
1,3-Bis[(2,3-benzocarbazol-9-yl)methyl]benzene	BC-MX	246	92
1,4-Bis[(2,3-benzocarbazol-9-yl)methyl]benzene	BC-PX	314	107

Table 5 Melting points and glass transition temperatures of the 1,2-benzo-3,4-dihydrocarbazole-twins (**BCDH**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-methane	BCDH-1	220	75
1,3-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-propane	BCDH-3	151	55
1,4-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-butane	BCDH-4	242	46
1,5-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-pentane	BCDH-5	165	40
1,6-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-hexane	BCDH-6	165	36
1,7-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-heptane	BCDH-7	163	32
1,8-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-octane	BCDH-8	153	25
1,9-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-nonane	BCDH-9	106	21
1,10-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-decane	BCDH-10	141	13
1,8-Bis(1,2-benzo-3,4-dihydrocarbazol-9-yl)-3,6-dioxaoctane	BCDH-O	101	28
1,2-Bis[(1,2-benzo-3,4-dihydrocarbazol-9-yl)methyl]benzene	BCDH-OX	247	112
1,3-Bis[(1,2-benzo-3,4-dihydrocarbazol-9-yl)methyl]benzene	BCDH-MX	253	75
1,4-Bis[(1,2-benzo-3,4-dihydrocarbazol-9-yl)methyl]benzene	BCDH-PX	261	90

Table 6 Melting points and glass transition temperatures of the phenothiazine-twins (**Ph**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
Bis(phenothiazin-10-yl)methane	Ph-1	243	70
1,3-Bis(phenothiazin-10-yl)propane	Ph-3	161	48
1,4-Bis(phenothiazin-10-yl)butane	Ph-4	187	34
1,5-Bis(phenothiazin-10-yl)pentane	Ph-5	97	24
1,6-Bis(phenothiazin-10-yl)hexane	Ph-6	163	20
1,7-Bis(phenothiazin-10-yl)heptane	Ph-7	92	17
1,8-Bis(phenothiazin-10-yl)octane	Ph-8	144	11
1,9-Bis(phenothiazin-10-yl)nonane	Ph-9	78	8
1,10-Bis(phenothiazin-10-yl)decane	Ph-10	91	4
1,2-Bis[(phenothiazin-10-yl)methyl]-benzene	Ph-OX	225	61
1,3-Bis[(phenothiazin-10-yl)methyl]-benzene	Ph-MX	207	48
1,4-Bis[(phenothiazin-10-yl)methyl]-benzene	Ph-PX	245	54

Table 7 Melting points and glass transition temperatures of the 1,8-naphthalimide-twins (**NI**)

Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
1,2-Bis(1,8-naphthalimido)ethane	NI-2	375	–
1,3-Bis(1,8-naphthalimido)propane	NI-3	319	–
1,4-Bis(1,8-naphthalimido)butane	NI-4	346	–
1,5-Bis(1,8-naphthalimido)pentane	NI-5	274	67
1,6-Bis(1,8-naphthalimido)hexane	NI-6	262	59
1,7-Bis(1,8-naphthalimido)heptane	NI-7	191	42
1,8-Bis(1,8-naphthalimido)octane	NI-8	206	37
1,9-Bis(1,8-naphthalimido)nonane	NI-9	175	30
1,10-Bis(1,8-naphthalimido)decane	NI-10	173	29
1,12-Bis(1,8-naphthalimido)dodecane	NI-12	166	25
1,3-Bis(1,8-naphthalimido)benzol	NI-MP	371	161
1,4-Bis(1,8-naphthalimido)benzol	NI-PP	dec.	–
1,3-Bis[(1,8-naphthalimido)methyl]-benzol	NI-MX	327	–
1,4-Bis[(1,8-naphthalimido)methyl]-benzol	NI-PX	423	–
4,4'-Bis(1,8-naphthalimido)diphenylmethane	NI-ME	427	170
4,4'-Bis(1,8-naphthalimido)-1,2-diphenylethane	NI-ET	454 (dec.)	–

Table 8 Melting points and glass transition temperatures of the pyrene-twins (PY)

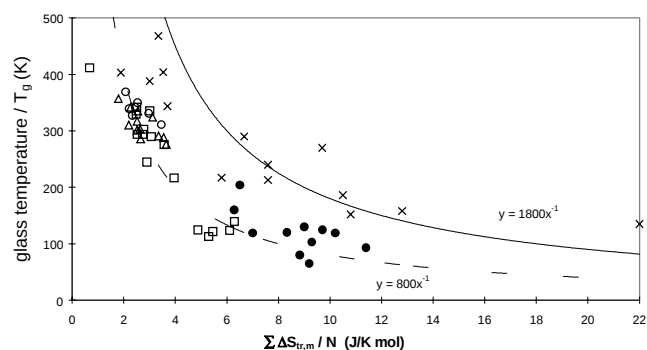
Name	Abbrev.	$T_m(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$
Pyren-1-aldehydazine	PY-0	311	100
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,2-ethylenediamine	PY-2	238	40
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,3-propylenediamine	PY-3	189	39
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,4-butylenediamine	PY-4	230	30
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,5-pentylenediamine	PY-5	141	29
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,6-hexylenediamine	PY-6	150	24
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,7-heptylenediamine	PY-7	134	14
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,8-octylenediamine	PY-8	167	15
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,12-dodecylenediamine	PY-12	131	8
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-a,a'-diamino-m-xylylene	PYDAMX	168	79
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-a,a'-diamino-p-xylylene	PYDAPX	209	95
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-4,4'-diaminocyclohexylmethane	PYDADC	246	81
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-4,4'-diaminodiphenylether	PYDADPE	212	83
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-4,4'-diaminodiphenylmethane	PYDADPM	232	86
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-4,4'-diaminodibenzyl	PYDADB	293 (dec.)	–
<i>N,N'</i> -Bis[(pyren-1-yl)methylidene]-1,5-naphthylendiamine	PYDANA	345 (dec.)	–

Table 9 Experimental and calculated values and numbers N of non-hydrogen atoms for carbazole- and 3,6-dibromocarbazole-twins

Compound	$\sum \Delta H_{tr,m}$ (kJ/mol)	N	$\sum \Delta S_{tr,m}/N$ (J/K/mol)
Ca-3	29.2	29	2.20
Ca-4	36.5	30	2.52
Ca-5	43.9	31	3.12
Ca-6	37.7	32	2.63
Ca-7	34.0	33	2.52
Ca-8	53.4	34	3.55
Ca-9	40.8	35	2.66
Ca-10	53.4	36	3.65
Ca-O	46.2	34	3.35
Ca-OX	30.4	34	1.79
Ca-MX	41.1	34	2.54
Ca-PX	41.5	34	2.27
DBrCa-3	43.5	33	2.44
DBrCa-5	47.4	35	2.55
DBrCa-6	46.1	36	2.46
DBrCa-7	38.8	37	2.23
DBrCa-8	51.7	38	3.00
DBrCa-9	40.3	39	2.36
DBrCa-10	70.2	40	3.50
DBrCa-MX	41.4	38	2.09

The necessary data for the examination of equation 1 can be obtained from DSC-measurements. The values for $\sum \Delta S_{tr,m}$ can be calculated from

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$$

**Fig. 4** Glass temperature (T_g) and transition entropies ($\sum \Delta S_{tr,m}/N$) for carbazole-twins (Δ) and 3,6-dibromocarbazole-twins ($\circ$) and for some aromatic ($\square$) and aliphatic ($\bullet$) systems and polyhydroxy ($\times$) compounds examined by Naito and Miura [9, 12].

with the enthalpy of phase transition ΔH_{tr} and the phase transition temperature T_{tr} . Table 9 shows the calculated entropy values and the other necessary data for the examination of equation 1 for carbazole- and 3,6-dibromocarbazole-twins.

Fig. 4 shows the relation between glass transition temperature and transition entropies for carbazole- and 3,6-dibromocarbazole-twins and the values for some aromatic, aliphatic and polyhydroxy compounds investigated by Naito and Miura.

As can be seen, equation 1 describes approximately the behaviour of carbazole- and 3,6-dibromocarbazole-twins. The glass transition temperatures of the carbazole- and the 3,6-dibromocarbazole-twins fulfil equa-

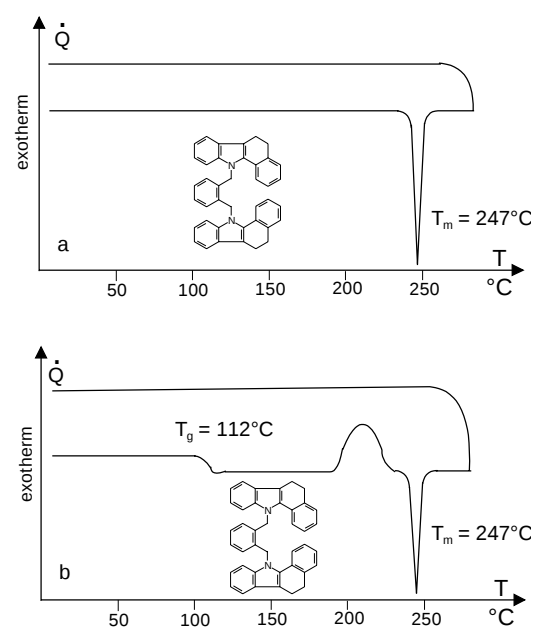
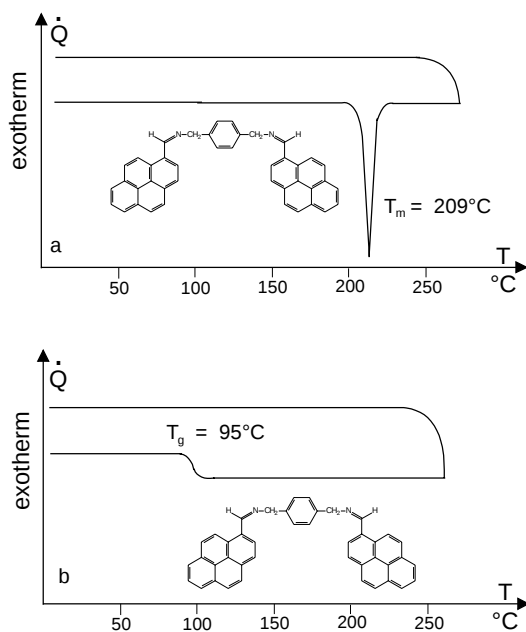
**Fig. 5** DSC-curves from BCDH-OX; (a) first heating, (b) second heating (heating rate: 10 °C/min)

Table 10 Carbazole-twins (Ca)

Compound	yield (%)	T_m (°C)	MS	NMR
Ca-1	70	325 lit. [13] 314–315	$C_{25}H_{18}N_2$ (346,4) $m/z = 346$ (M^+)	1H NMR (300 MHz, DMSO- d_6): δ (ppm) = 7.13 (s, 2H, $-CH_2-$), 7.20–7.25 (t, 4H, Ar-H), 7.38–7.43 (t, 4H, Ar-H), 7.67–7.70 (d, 4H, Ar-H), 8.17–8.19 (d, 4H, Ar-H).
Ca-3	32	185 lit. [14]: 186	$C_{27}H_{22}N_2$ (374,5) $m/z = 374$ (M^+)	1H NMR (300 MHz, DMSO- d_6): δ (ppm) = 2.23–2.28 (quin, 2H, $N-CH_2-CH_2-$), 4.46–4.51 (t, 4H, $N-CH_2-$), 7.16–7.21 (t, 4H, Ar-H), 7.37–7.42 (t, 4H, Ar-H), 7.48–7.51 (d, 4H, Ar-H), 8.13–8.16 (d, 4H, Ar-H).
Ca-4	57	211 lit. [14]: 208	$C_{28}H_{24}N_2$ (388,5) $m/z = 388$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.91–1.98 (m, 4H, $N-CH_2-CH_2-$), 4.17–4.23 (m, 4H, $N-CH_2-$), 7.20–7.28 (m, 8H, Ar-H), 7.40–7.46 (t, 4H, Ar-H), 8.07–8.10 (d, 4H, Ar-H).
Ca-5	71	181 lit. [14]: 184	$C_{28}H_{26}N_2$ (402,5) $m/z = 402$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.39 (m, 2H, $-CH_2-$), 1.78 (m, 4H, $N-CH_2-CH_2-$), 4.32 (m, 4H, $N-CH_2-$), 7.18 (m, 4H, Ar-H), 7.41–7.50 (m, 8H, Ar-H), 8.12–8.14 (d, 4H, Ar-H).
Ca-6	83	128 lit. [14]: 128	$C_{30}H_{28}N_2$ (416,6) $m/z = 416$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.22–1.27 (m, 4H, $-CH_2-$), 1.67–1.72 (m, 4H, $-CH_2-$), 4.08–4.12 (t, 4H, $N-CH_2-$), 7.15–7.25 (m, 8H, Ar-H), 7.35–7.41 (t, 4H, Ar-H), 8.04–8.06 (d, 4H, Ar-H).
Ca-7	71	136	$C_{31}H_{30}N_2$ (430,6) $m/z = 430$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.32(s, 6H, $-CH_2-$), 1.79–1.84 (m, 4H, $N-CH_2-CH_2-$), 4.21–4.26 (t, 4H, $N-CH_2-$), 7.19–7.24 (t, 4H, Ar-H), 7.34–7.36 (d, 4H, Ar-H), 7.42–7.47 (t, 4H, Ar-H), 8.08–8.11 (d, 4H, Ar-H).
Ca-8	75	169	$C_{32}H_{32}N_2$ (444,6) $m/z = 444$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.27–1.33 (m, 8H, $-CH_2-$), 1.76–1.85 (quin, 4H, $N-CH_2-CH_2-$), 4.22–4.27 (t, 4H, $N-CH_2-$), 7.19–7.24 (t, 4H, Ar-H), 7.35–7.38 (d, 4H, Ar-H), 7.42–7.47 (t, 4H, Ar-H), 8.08–8.10 (d, 4H, Ar-H).
Ca-9	79	166	$C_{33}H_{34}N_2$ (458,7) $m/z = 458$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.22–1.33 (m, 10H, $-CH_2-$), 1.78–1.87 (m, 4H, $N-CH_2-CH_2-$), 4.23–4.28 (t, 4H, $N-CH_2-$), 7.19–7.24 (t, 4H, Ar-H), 7.36–7.47 (m, 8H, Ar-H), 8.08–8.11 (d, 4H, Ar-H).
Ca-10	78	134	$C_{34}H_{36}N_2$ (472,7) $m/z = 472$ (M^+)	1H NMR (300 MHz, DMSO- d_6): δ (ppm) = 1.10–1.20 (m, 12H, $-CH_2-$), 1.72 (m, 4H, $N-CH_2-CH_2-$), 4.34–4.38 (t, 4H, $N-CH_2-$), 7.14–7.19 (t, 4H, Ar-H), 7.40–7.45 (t, 4H, Ar-H), 7.55–7.58 (d, 4H, Ar-H), 8.11–8.13 (d, 4H, Ar-H).
Ca-O	64	133	$C_{30}H_{28}N_2O_2$ (448,6) $m/z = 448$ (M^+)	1H NMR (300 MHz, DMSO- d_6): δ (ppm) = 3.27 (s, 4H, $-CH_2-$), 3.56–3.59 (t, 4H, $O-CH_2$), 4.33–4.37 (t, 4H, $N-CH_2-$), 7.14–7.20 (t, 4H, Ar-H), 7.36–7.41 (t, 4H, Ar-H), 7.47–7.49 (d, 4H, Ar-H), 8.11–8.13 (d, 4H, Ar-H).
Ca-OX	73	227	$C_{33}H_{24}N_2$ (446,6) $m/z = 446$ (M^+)	1H NMR (300 MHz, DMSO- d_6): δ (ppm) = 5.99 (s, 4H, $-CH_2-$), 6.06–6.11 (m, 2H, Ar-H), 6.85–6.90 (m, 2H, Ar-H), 7.24–7.29 (t, 4H, Ar-H), 7.44–7.49 (t, 4H, Ar-H), 7.63–7.65 (d, 4H, Ar-H), 8.25–8.27 (d, 4H, Ar-H).
Ca-MX	73	203	$C_{32}H_{24}N_2$ (446,6) $m/z = 446$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.39 (s, 4H, $-CH_2-$), 6.92–7.00 (t, 2H, Ar-H), 7.06–7.11 (t, 2H, Ar-H), 7.22–7.27 (t, 8H, Ar-H), 7.36–7.42 (t, 4H, Ar-H), 8.11–8.14 (d, 4H, Ar-H).
Ca-PX	83	265	$C_{32}H_{24}N_2$ (446,6) $m/z = 446$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 5.44 (s, 4H, $-CH_2-$), 7.01 (s, 4H, Ar-H), 7.20–7.25 (t, 4H, Ar-H), 7.28–7.31 (d, 4H, Ar-H), 7.37–7.42 (t, 4H, Ar-H), 8.09–8.11 (d, 4H, Ar-H).

**Fig. 6** DSC-curves from PYDAPX; (a) first heating, (b) second heating (heating rate: 10 °C/min)**Table 11** 3,6-Dibromocarbazole-twins (DBrCa)

Compound	Yield (%)	T_m (°C)	Elemental analyses		
			calcd./	found:	
			C	H	N
DBrCa-1	53 (dec.)	350	45.36	2.13	4.23
			45.40	1.94	4.29
DBrCa-3	58	267	47.00	2.63	4.06
			47.05	2.37	4.12
DBrCa-4	62 (dec.)	329	47.76	2.86	3.98
			48.03	2.64	3.97
DBrCa-5	67	259	48.50	3.09	3.90
			48.83	2.99	3.84
DBrCa-6	67	247	49.22	3.30	3.83
			49.11	3.21	3.83
DBrCa-7	77	198	49.90	3.51	3.75
			50.05	3.31	3.77
DBrCa-8	75	181	50.56	3.71	3.68
			50.66	3.62	3.71
DBrCa-9	71	165	51.19	3.91	3.62
			51.26	3.74	3.64
DBrCa-10	70	228	51.82	4.09	3.56
			52.15	3.84	3.59
DBrCa-OX	68	dec.	51.11	2.68	3.73
			51.43	2.46	3.79
DBrCa-MX	64	248	51.11	2.68	3.73
			51.41	2.49	3.75
DBrCa-PX	71	dec.	51.11	2.68	3.73
			51.39	2.49	3.77

Table 12 2,3-Benzocarbazole-twins (BC)

Com-pound	Yield (%)	T_m (°C)	MS	Elemental analyses calcd./found:		
				C	H	N
BC-4	78	230	$C_{36}H_{28}N_2$ (488,7) $m/z = 488$ (M^+)	88.49	5.78	5.73
BC-6	80	196	$C_{38}H_{32}N_2$ (516,7) $m/z = 516$ (M^+)	88.65	5.74	5.61
BC-8	78	187	$C_{40}H_{36}N_2$ (544,7) $m/z = 544$ (M^+)	88.34	6.24	5.42
BC-10	82	180	$C_{42}H_{40}N_2$ (572,8) $m/z = 572$ (M^+)	88.45	6.25	5.30
BC-OX	91	253	$C_{40}H_{28}N_2$ (536,7) $m/z = 536$ (M^+)	88.20	6.66	5.14
BC-MX	91	246	$C_{40}H_{28}N_2$ (536,7) $m/z = 536$ (M^+)	88.22	6.68	5.10
BC-PX	75	314	$C_{40}H_{28}N_2$ (536,7) $m/z = 536$ (M^+)	88.07	7.04	4.89
				88.16	7.05	4.79
				89.52	5.26	5.22
				89.53	5.36	5.11
				89.52	5.26	5.22
				89.56	5.40	5.04
				89.52	5.26	5.22
				89.63	5.21	5.16

tion 1 with $h_g = 800$ J/mol and show an analogous dependence of the glass transition temperature from the transition entropy as the aromatic compounds examined by Naito and Miura.

Table 13 1,2-Benzo-3,4-dihydrocarbazole-twins (BCDH)

Compound	Yield (%)	T_m (°C)	MS	NMR
BCDH-1	68	220	$C_{33}H_{26}N_2$ (450,6) $m/z = 450$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.82–2.97 (m, 8H, $-CH_2-$), 6.88–6.90 (d, 4H, Ar-H), 6.97 (s, 2H, $-CH_2-$), 6.99–7.05 (m, 2H, Ar-H), 7.15–7.22 (m, 4H, Ar-H), 7.32–7.37 (m, 2H, Ar-H), 7.46–7.51 (m, 4H, Ar-H).
BCDH-3	50	151	$C_{35}H_{30}N_2$ (478,6) $m/z = 478$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.43–2.53 (quin, 2H, $-CH_2-$), 2.84–2.94 (m, 8H, $-CH_2-$), 4.40–4.45 (t, 4H, $N-CH_2-$), 7.08–7.21 (m, 10H, Ar-H), 7.25–7.30 (m, 4H, Ar-H), 7.54–7.57 (d, 2H, Ar-H).
BCDH-4	64	242	$C_{36}H_{32}N_2$ (492,7) $m/z = 492$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.91–1.96 (m, 4H, $-CH_2-$), 2.84–2.96 (m, 8H, $-CH_2-$), 4.36–4.38 (m, 4H, $N-CH_2-$), 7.09–7.25 (m, 10H, Ar-H), 7.30–7.33 (d, 2H, Ar-H), 7.41–7.44 (d, 2H, Ar-H), 7.54–7.56 (d, 2H, Ar-H).
BCDH-5	70	165	$C_{37}H_{34}N_2$ (506,7) $m/z = 506$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.37–1.45 (m, 2H, $-CH_2-$), 1.88–1.98 (m, 4H, $-CH_2-$), 2.85–2.98 (m, 8H, $-CH_2-$), 4.32–4.37 (t, 4H, $N-CH_2-$), 7.09–7.32 (m, 12H, Ar-H), 7.46–7.49 (d, 2H, Ar-H), 7.55–7.57 (d, 2H, Ar-H).
BCDH-6	74	165	$C_{38}H_{36}N_2$ (520,7) $m/z = 520$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.37–1.41 (m, 4H, $-CH_2-$), 1.83–1.88 (m, 4H, $-CH_2-$), 2.84–2.96 (m, 8H, $-CH_2-$), 4.29–4.34 (t, 4H, $N-CH_2-$), 7.08–7.30 (m, 12H, Ar-H), 7.46–7.49 (d, 2H, Ar-H), 7.53–7.56 (d, 2H, Ar-H).
BCDH-7	70	163	$C_{39}H_{38}N_2$ (534,7) $m/z = 534$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.39 (m, 6H, $-CH_2-$), 1.87–1.94 (m, 4H, $-CH_2-$), 2.86–2.99 (m, 8H, $-CH_2-$), 4.33–4.38 (t, 4H, $N-CH_2-$), 7.09–7.34 (m, 12H, Ar-H), 7.49–7.52 (d, 2H, Ar-H), 7.55–7.58 (d, 2H, Ar-H).
BCDH-8	18	153	$C_{40}H_{40}N_2$ (548,8) $m/z = 548$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.32 (m, 8H, $-CH_2-$), 1.87 (m, 4H, $-CH_2-$), 2.88–2.94 (m, 8H, $-CH_2-$), 4.30–4.35 (t, 4H, $N-CH_2-$), 7.08–7.33 (m, 12H, Ar-H), 7.48–7.56 (m, 4H, Ar-H).
BCDH-9	69	106	$C_{41}H_{42}N_2$ (562,8) $m/z = 562$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.27–1.34 (m, 10H, $-CH_2-$), 1.83–1.93 (quin, 4H, $-CH_2-$), 2.85–2.97 (m, 8H, $-CH_2-$), 4.30–4.36 (t, 4H, $N-CH_2-$), 7.08–7.34 (m, 12H, Ar-H), 7.49–7.56 (m, 4H, Ar-H).
BCDH-10	56	141	$C_{42}H_{44}N_2$ (576,8) $m/z = 576$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.25–1.34 (m, 12H, $-CH_2-$), 1.85–1.95 (quin, 4H, $-CH_2-$), 2.85–2.98 (m, 8H, $-CH_2-$), 4.32–4.37 (t, 4H, $N-CH_2-$), 7.08–7.35 (m, 12H, Ar-H), 7.50–7.57 (m, 4H, Ar-H).
BCDH-O	81	101	$C_{38}H_{36}N_2O_2$ (552,7) $m/z = 552$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.85–2.96 (m, 8H, $-CH_2-$), 3.52 (s, 4H, $O-(CH_2)_2-O$), 3.87–3.91 (t, 4H, $N-CH_2-CH_2-O$), 4.50–4.55 (m, 4H, $N-CH_2-$), 7.08–7.27 (m, 8H, Ar-H), 7.29–7.31 (d, 2H, Ar-H), 7.35–7.38 (d, 2H, Ar-H), 7.53–7.56 (d, 2H, Ar-H), 7.66–7.69 (d, 2H, Ar-H).
BCDH-OX	65	247	$C_{40}H_{32}N_2$ (540,7) $m/z = 540$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.96 (m, 8H, $-CH_2-$), 5.43 (s, 4H, $N-CH_2-$), 6.99–7.03 (m, 2H, Ar-H), 7.10–7.22 (m, 14H, Ar-H), 7.30–7.32 (m, 2H, Ar-H), 7.59–7.61 (d, 2H, Ar-H).
BCDH-MX	82	253	$C_{40}H_{32}N_2$ (540,7) $m/z = 540$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.94–2.96 (m, 8H, $-CH_2-$), 5.53 (s, 4H, $N-CH_2-$), 7.00–7.31 (m, 18H, Ar-H), 7.59–7.62 (m, 2H, Ar-H).
BCDH-PX	22	261	$C_{40}H_{32}N_2$ (540,7) $m/z = 540$ (M^+)	1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.93–2.98 (m, 8H, $-CH_2-$), 5.57 (s, 4H, $N-CH_2-$), 7.10–7.32 (m, 18H, Ar-H), 7.59–7.62 (m, 2H, Ar-H).

The respective data for 1,2-benzo-3,4-dihydrocarbazole- and phenothiazine-twins fulfil equation 1 with $h_g = 850$ J/mol resp. 700 J/mol.

Experimental

Differentialcalorimetric Measurements

Melting points and glass transitions were determined by differential scanning calorimetry (DSC) using a Du Pont 912 thermal analyzer. Samples of 5–10 mg as obtained from synthesis were heated in aluminium pans at a scan rate of 10 K/min under a nitrogen flow. Indium metal was used as a standard. During the first heating the melting points and their enthalpy changes were measured. After melting, the samples were cooled with a cooling rate of approximately 20 K/min. Products which underwent crystallization in this process were cooled rapidly after melting, with liquid nitrogen to form glasses. The resulting glasses were heated again under the same conditions to measure the glass transitions. Fig. 5 and 6 show two typical DSC-curves with and without recrystallization during the second heating.

Characterization of the Products

^1H NMR spectra were obtained with a Bruker WM-300 instrument and chemical shifts are given in parts per million downfield from Me_4Si . Mass spectra (MS) were obtained with a Varian 311A instrument in the field-desorption modus. Elemental analyses were performed with a Perkin Elmer 240 element analyzer.

Carbazole- (Ca), 3,6-Dibromocarbazole- (DBrCa), 2,3-Benzo-carbazole- (BC), 1,2-Benzo-3,4-dihydrocarbazole- (BCDH) and Phenothiazine-twins (Ph) (General Procedure)

In a 100 ml three necked round bottomed flask equipped with a reflux condenser and a dropping funnel 10 mmol starting compound were dissolved in 30 ml of 1-methyl-2-pyrrolidinone under a stream of nitrogen. Then the mixture was heated to 80 °C, and 12.5 mmol (0.7 g) potassium hydroxide were added. After 4 hours 5 mmol of the dihalogen compound dissolved in 20 ml 1-methyl-2-pyrrolidinone were added during 30 minutes. The reaction was stopped after 10 hours. After evaporation of the solvent the crude product was crystallized from toluene or a mixture of toluene and methanole. The isolated crystals were filtered and dried *in vacuo*.

The following dihalogen compounds were used: Dibromomethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane, 1,8-dibromooctane, 1,9-dibromononane, 1,10-dibromodecane, 1,2-bis(2-chlorethoxy)ethane, 1,2-bis(chloromethyl)benzene, 1,3-bis(chloromethyl)benzene, 1,4-bis(chloromethyl)benzene

In the following tables 10 to 16 the obtained products are characterized.

Synthesis of 1,8-Naphthalimide-Twins (NI)

In a 500 ml three necked round-bottomed flask equipped with a water separator, reflux condenser and a dropping funnel were placed 3.96 g (20 mmol) 1,8-naphthalic anhydride dissolved in 200 ml Shellsol A® (high boiling hydrocarbon-mixture of Shell company; *b.p.* 160–175 °C). The reaction mixture was heated to reflux followed by addition of a solution of 10 mmol of the diamino compound dissolved in 50 ml Shellsol A® during a period of 1 hour. Then the solution was refluxed for 3 hours. After evaporation of the solvent the crude product was crystallized from dimethylsulfoxide. The isolated crystals were filtered and dried *in vacuo*.

The following diamino compounds were used: 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,9-diaminononane, 1,10-diaminodecane, 1,12-diaminododecane, 1,3-diaminobenzene, 1,4-diaminobenzene, 1,3-bis(aminomethyl)benzene, 1,4-bis(aminomethyl)benzene, bis(4-aminophenyl)methane, 1,2-bis(4-aminophenyl)ethane.

Synthesis of Pyrene-Twins (PY)

In a 500 ml three necked round-bottomed flask equipped with a water separator, reflux condenser and a dropping funnel were placed 2.30 g (10 mmol) pyrene-1-aldehyde dissolved in 100 ml toluene. The reaction mixture was heated to reflux followed by addition of a solution of 5 mmol of the diamino compound dissolved in 50 ml toluene over a period of 1 hour. Then the solution was refluxed for 3 hours. After cooling to room temperature the precipitated crystals were filtered, and the crude product was recrystallized from toluene and dried *in vacuo*.

Table 14 Phenothiazine-twins (Ph)

Compound	Yield (%)	T_m (°C)	MS	Elemental analysis		
				calcd.: C	H	N
				found: C	H	N
Ph-1	67	243	$\text{C}_{25}\text{H}_{18}\text{N}_2\text{S}_2$ (410,6) $m/z = 410$ (M^+)	73.14 73.07	4.42 4.39	6.82 6.89
Ph -3	63	161	$\text{C}_{27}\text{H}_{22}\text{N}_2\text{S}_2$ (438,6) $m/z = 438$ (M^+)	73.94 73.82	5.06 4.99	6.39 6.43
Ph -4	49	187	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{S}_2$ (452,6) $m/z = 452$ (M^+)	74.30 74.21	5.34 5.26	6.19 6.20
Ph -5	42	97	$\text{C}_{29}\text{H}_{26}\text{N}_2\text{S}_2$ (466,7) $m/z = 466$ (M^+)	74.64 74.59	5.62 5.60	6.00 6.05
Ph -6	41	163	$\text{C}_{30}\text{H}_{28}\text{N}_2\text{S}_2$ (480,7) $m/z = 480$ (M^+)	74.96 74.88	5.87 5.78	5.83 5.91
Ph -7	42	92	$\text{C}_{31}\text{H}_{30}\text{N}_2\text{S}_2$ (494,7) $m/z = 494$ (M^+)	75.26 75.21	6.11 6.09	5.66 5.66
Ph -8	36	144	$\text{C}_{32}\text{H}_{32}\text{N}_2\text{S}_2$ (508,7) $m/z = 508$ (M^+)	75.55 75.49	6.34 6.22	5.51 5.59
Ph -9	51	78	$\text{C}_{33}\text{H}_{34}\text{N}_2\text{S}_2$ (522,8) $m/z = 522$ (M^+)	75.82 75.78	6.56 6.47	5.36 5.43
Ph -10	52	91	$\text{C}_{34}\text{H}_{36}\text{N}_2\text{S}_2$ (536,8) $m/z = 536$ (M^+)	76.08 75.95	6.76 6.70	5.22 5.30
Ph -OX	60	225	$\text{C}_{32}\text{H}_{24}\text{N}_2\text{S}_2$ (500,7) $m/z = 500$ (M^+)	76.77 76.67	4.83 4.78	5.60 5.52
Ph -MX	57	207	$\text{C}_{32}\text{H}_{24}\text{N}_2\text{S}_2$ (500,7) $m/z = 500$ (M^+)	76.77 76.69	4.83 4.79	5.60 5.59
Ph -PX	62	245	$\text{C}_{32}\text{H}_{24}\text{N}_2\text{S}_2$ (500,7) $m/z = 500$ (M^+)	76.77 76.68	4.83 4.82	5.60 5.51

Table 15 1,8-Naphthalimide-twins (NI)

Compound	Yield (%)	T_m (°C)	MS	Elemental analysis		
				calcd.: C found: C	H H	N N
NI-2	74	375	$C_{26}H_{16}N_2O_4$ (420,4) $m/z = 420$ (M ⁺)	74.28 73.98	3.84 3.81	6.66 6.60
NI-3	58	319	$C_{27}H_{18}N_2O_4$ (434,5) $m/z = 434$ (M ⁺)	74.65 74.36	4.18 4.11	6.45 6.34
NI-4	63	346	$C_{28}H_{20}N_2O_4$ (448,5) $m/z = 448$ (M ⁺)	74.99 74.77	4.49 4.41	6.25 6.30
NI-5	80	274	$C_{29}H_{22}N_2O_4$ (462,5) $m/z = 462$ (M ⁺)	75.31 75.00	4.79 4.67	6.06 6.01
NI-6	74	262	$C_{30}H_{24}N_2O_4$ (476,5) $m/z = 476$ (M ⁺)	75.62 75.35	5.08 4.93	5.88 5.89
NI-7	70	191	$C_{31}H_{26}N_2O_4$ (490,6) $m/z = 490$ (M ⁺)	75.90 75.77	5.34 5.34	5.71 5.79
NI-8	66	206	$C_{32}H_{28}N_2O_4$ (504,6) $m/z = 504$ (M ⁺)	76.17 75.83	5.59 5.50	5.55 5.42
NI-9	71	175	$C_{33}H_{30}N_2O_4$ (518,6) $m/z = 518$ (M ⁺)	76.34 76.28	5.83 5.85	5.40 5.49
NI-10	77	173	$C_{34}H_{32}N_2O_4$ (532,6) $m/z = 532$ (M ⁺)	76.67 76.49	6.06 6.12	5.26 5.30
NI-12	80	166	$C_{36}H_{36}N_2O_4$ (560,7) $m/z = 560$ (M ⁺)	77.12 76.73	6.47 6.49	5.00 5.03
NI-MP	35	371	$C_{30}H_{16}N_2O_4$ (468,5) $m/z = 468$ (M ⁺)	76.92 76.68	3.44 3.47	5.98 6.05
NI-PP	57	dec.	$C_{30}H_{16}N_2O_4$ (468,5) $m/z = 468$ (M ⁺)	76.92 76.73	3.44 3.45	5.98 6.10
NI-MX	60	327	$C_{32}H_{20}N_2O_4$ (496,5) $m/z = 496$ (M ⁺)	77.41 77.23	4.06 3.97	5.64 5.71
NI-PX	40	423	$C_{32}H_{20}N_2O_4$ (496,5) $m/z = 496$ (M ⁺)	77.41 77.19	4.06 4.01	5.64 5.74
NI-ME	51	427	$C_{37}H_{22}N_2O_4$ (558,6) $m/z = 558$ (M ⁺)	79.56 79.40	3.97 4.05	5.01 5.12
NI-ET	56	454 (dec.)	$C_{38}H_{24}N_2O_4$ (572,6) $m/z = 572$ (M ⁺)	79.71 79.60	4.22 4.09	4.89 4.92

Table 16 Pyrene-twins (PY)

Compound	Yield (%)	T_m (°C)	MS	Elemental analysis		
				calcd.: C found: C	H H	N N
PY-0	86	311	$C_{34}H_{20}N_2$ (456,6) $m/z = 456$ (M ⁺)	89.45 89.64	4.41 4.33	6.14 6.03
PY-2	84	238	$C_{36}H_{24}N_2$ (484,6) $m/z = 484$ (M ⁺)	89.23 89.34	4.99 4.96	5.78 5.70
PY-3	94	189	$C_{37}H_{26}N_2$ (498,6) $m/z = 498$ (M ⁺)	89.13 89.14	5.25 5.09	5.62 5.58
PY-4	89	230	$C_{38}H_{28}N_2$ (512,7) $m/z = 512$ (M ⁺)	89.03 89.01	5.51 5.48	5.46 5.49
PY-5	73	141	$C_{39}H_{30}N_2$ (526,7) $m/z = 526$ (M ⁺)	88.94 88.85	5.74 5.71	5.32 5.41
PY-6	93	150	$C_{40}H_{32}N_2$ (540,7) $m/z = 540$ (M ⁺)	88.85 88.99	5.97 5.84	5.18 5.17
PY-7	95	134	$C_{41}H_{34}N_2$ (554,7) $m/z = 554$ (M ⁺)	88.77 88.79	6.18 6.10	5.05 4.97
PY-8	93	167	$C_{42}H_{36}N_2$ (568,8) $m/z = 568$ (M ⁺)	88.69 88.74	6.38 6.41	4.93 4.89
PY-12	81	131	$C_{46}H_{44}N_2$ (624,9) $m/z = 624$ (M ⁺)	88.42 88.66	7.10 6.98	4.48 4.36
PYDAMX	72	168	$C_{42}H_{28}N_2$ (560,7) $m/z = 560$ (M ⁺)	89.97 90.04	5.03 5.06	5.00 4.87
PYDAPX	75	209	$C_{42}H_{28}N_2$ (560,7) $m/z = 561$ (M ⁺)	89.97 90.05	5.03 5.04	5.00 4.91
PYDADC	66	246	$C_{47}H_{42}N_2$ (634,9) $m/z = 635$ (M ⁺)	88.92 89.00	6.67 6.62	4.41 4.30
PYDADPE	75	212	$C_{46}H_{28}N_2O$ (624,7) $m/z = 624$ (M ⁺)	88.44 88.40	4.53 4.60	4.48 4.42
PYDADPM	83	232	$C_{47}H_{30}N_2$ (622,8) $m/z = 622$ (M ⁺)	90.64 90.60	4.86 4.89	4.50 4.41
PYDADB	78	293 (dec.)	$C_{48}H_{32}N_2$ (636,8) $m/z = 636$ (M ⁺)	90.53 90.38	5.07 5.18	4.40 4.37
PYDANA	63	345 (dec.)	$C_{44}H_{26}N_2$ (582,7) $m/z = 582$ (M ⁺)	90.70 90.61	4.50 4.60	4.81 4.75

The following diamino-compounds were used: hydrazine sulfate, 1,2-diaminoethane, 1,3-diamino-propane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane, 1,7-diaminooheptane, 1,8-diaminooctane, 1,12-diaminododecane, 1,3-bis(aminomethyl)benzene, 1,4-bis(amino-methyl)benzene, bis(4-aminophenyl)methane, 1,2-bis(4-aminophenyl)-ethane, 4,4'-methylenedicyclohexylamin, 4,4'-diaminodiphenylether, 1,5-diaminonaphthalin.

The authors thank Dr. H. O. Wirth for stimulating discussion and the Fonds der Chemischen Industrie for financial support.

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