

Thermodynamic properties of *trans*-azobenzene and *trans*-stilbene

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(Received 27 June 1983)

Molar heat capacities obtained by adiabatic calorimetry are presented for *trans*-azobenzene and *trans*-stilbene. For *trans*-azobenzene the measuring range was from 83 K to 356 K, for *trans*-stilbene from 8 K to 348 K. Molar enthalpies of fusion $\Delta_f H_m^\circ$ and the corresponding temperatures are: $C_6H_5-N=N-C_6H_5$, 22.52 kJ·mol⁻¹, 341.03 K; $C_6H_5-CH=CH-C_6H_5$, 27.4 kJ·mol⁻¹, 398 K. Apart from fusion no phase transition was detected in these compounds.

1. Introduction

The formation of solid solutions of binary organic systems is subject to several conditions: the components must be similar in shape, they must have an identical space-group with the same number of molecules in the unit cell, and moreover the unit cells must show a similar packing of the molecules.⁽¹⁾ Preparing mixed crystals by rapid cooling of the liquid mixture produces inhomogeneous crystals. In principle these crystals can be homogenized by annealing. The diffusion rate in the solid phase is, however, too low (except in plastic crystals) to achieve a homogeneous crystal within an acceptable time.

In our laboratory an apparatus has been developed⁽²⁾ to prepare homogeneous organic mixed crystals by the zone-levelling technique.⁽³⁾ In this paper we report on the thermodynamic properties of *trans*-azobenzene and of *trans*-stilbene, which are known to mix with complete solid-solution formation.⁽⁴⁾ Detailed studies of the crystal structures of the mixed crystals and of the excess thermodynamic properties are in progress.

2. Experimental

Trans-azobenzene (B.D.H.) was purified by slow vacuum sublimation.⁽⁵⁾ The purity was determined by fractional melting (see later) and found to be (99.87 ± 0.03) moles per cent. *Trans*-stilbene, which was purified by counter-current crystallization, was supplied by the Physical-Chemical Laboratory of TNO, Zeist, the Netherlands. The purity of the sample was established by g.l.c. and found to be (99.8 ± 0.05) moles per

cent. A detailed description of the calorimeter in which *trans*-azobenzene was measured is given in reference 6. *Trans*-stilbene was measured in a new calorimeter which was calibrated with sapphire (N.B.S. standard reference material). Above 40 K the deviations from the standard were within 0.1 per cent. Sample masses were 11.8 g for *trans*-azobenzene and 6.7 g for *trans*-stilbene. About 1000 Pa of helium was admitted to the sample container to enhance heat conductivity. Measurements were made fully automatically using, above 90 K, a heater-on time of 1500 s and a heater-off time between 1000 and 2000 s.

3. Results and discussion

In table 1 the experimental molar heat capacities of *trans*-azobenzene are given. Smoothed molar heat capacities at round temperatures are given in table 2. In table 3 the equilibrium temperatures measured in the fusion range are given together with the reciprocals of the melted fraction. From these results the triple-point temperature was found to be 341.03 K and the purity 99.87 moles per cent. The start of the fusion process was sharp and no difficulties were encountered in

TABLE 1. Experimental molar heat capacities $C_{p,m}$ of $C_6H_5-N=N-C_6H_5$

T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$
83.51	80.21	172.03	135.15	239.23	182.28	301.19	230.27
91.37	84.70	177.30	138.65	243.58	185.64	305.84	233.97
98.84	88.73	182.49	142.06	247.87	188.86	310.44	237.67
105.99	93.01	187.60	145.58	252.12	192.09	314.99	241.24
112.85	97.92	192.62	148.99	256.32	195.27	319.50	245.02
119.47	101.94	197.58	152.40	260.48	198.49	323.96	249.17
125.89	105.88	202.46	155.81	264.59	201.73	328.36	254.49
132.12	109.73	207.27	159.26	268.66	204.93	332.68	263.54
138.20	113.50	212.01	162.56	277.18	211.26	336.74	307.87
144.14	117.22	216.69	165.93	282.10	215.32	344.61	301.37
149.94	120.91	221.31	169.24	286.95	219.19	348.50	303.43
155.62	124.51	225.88	172.40	291.75	222.91	352.38	305.35
161.19	128.09	230.38	175.56	296.49	226.24	356.24	307.22
166.66	131.64	234.84	178.95				

TABLE 2. Smoothed molar heat capacities of $C_6H_5-N=N-C_6H_5$ at round temperatures

T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$
90	83.9	150	121.0	210	161.1	270	205.7
100	89.4	160	127.3	220	168.3	280	213.6
110	95.9	170	133.8	230	175.3	290	221.6
120	102.3	180	140.4	240	182.9	300	229.3
130	108.4	190	147.2	250	190.5	310	237.5
140	114.6	200	154.1	260	198.1	320	246.1

TABLE 3. Equilibrium temperatures in the fusion process against the reciprocal of the melted fraction F for $C_6H_5-N=N-C_6H_5$

T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}	T/K	F^{-1}
340.6233	7.82	340.8242	3.62	340.9049	2.34	340.9345	1.73	340.9546	1.37	340.9742	1.14
340.7576	4.97	340.8729	2.85	340.9224	1.99	340.9452	1.53	340.9601	1.24		

TABLE 4. Experimental molar heat capacities $C_{p,m}$ of $C_6H_5-CH=CH-C_6H_5$

T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$	T K	$C_{p,m}$ $J \cdot K^{-1} \cdot mol^{-1}$
8.12	2.22	72.24	73.28	163.97	129.94	249.47	194.42
8.86	2.74	74.19	74.64	167.20	132.32	252.02	196.40
9.38	2.91	76.09	75.94	168.09	133.66	254.57	198.45
9.78	3.14	77.94	77.20	170.38	135.31	257.09	200.37
10.12	3.88	79.75	78.40	173.52	137.89	259.60	202.31
10.45	3.47	81.53	79.56	174.40	138.72	262.10	204.10
10.71	4.55	83.27	80.68	176.63	140.28	264.59	205.80
10.82	3.72	84.64	81.39	179.71	142.52	267.06	207.35
11.29	4.35	84.98	81.78	180.58	143.08	269.52	209.90
11.66	4.85	86.66	82.72	182.76	144.63	271.96	212.35
11.98	5.65	88.31	83.87	185.79	146.75	274.39	214.38
12.29	5.36	89.94	84.91	186.65	147.30	276.81	216.25
13.02	6.76	91.54	85.89	188.79	148.82	279.21	218.35
14.85	9.01	93.12	86.85	191.76	150.90	281.60	220.29
15.52	9.51	94.21	87.35	192.61	151.53	283.99	222.24
16.11	10.17	94.68	87.80	194.71	153.03	286.35	224.16
19.77	15.51	96.22	88.67	197.64	155.17	288.71	226.16
22.77	19.91	97.75	89.60	198.48	155.73	291.05	228.42
25.09	23.12	101.93	92.10	200.55	157.27	293.38	229.93
28.74	28.55	103.05	92.69	203.43	159.36	295.70	231.97
30.26	30.85	106.16	94.71	204.26	159.95	298.01	234.60
31.64	32.55	110.28	97.34	206.29	161.45	302.51	237.62
34.66	36.78	111.37	97.92	209.13	163.53	304.80	239.47
36.79	39.68	114.29	99.79	209.95	164.09	307.07	241.36
38.72	42.40	118.22	102.13	211.95	165.61	309.33	243.11
40.51	44.45	119.28	102.71	214.74	167.72	311.58	245.05
42.19	46.53	122.07	104.38	215.56	168.29	313.82	246.81
43.76	48.31	125.84	106.61	217.52	169.80	316.05	248.61
45.25	49.91	126.88	107.19	220.28	171.84	318.26	250.50
46.67	51.47	129.56	108.81	221.09	172.47	320.47	252.33
48.03	52.91	133.21	111.01	223.02	173.89	322.67	254.05
49.32	54.25	134.22	111.59	225.74	176.05	324.87	255.87
50.57	55.35	136.80	113.20	226.55	176.61	327.05	257.71
51.78	56.55	140.34	115.35	228.45	178.09	329.22	259.41
52.95	57.61	141.33	115.91	231.13	180.12	331.38	261.22
54.08	58.65	143.84	117.47	231.93	180.76	333.54	263.02
55.19	59.62	147.29	119.61	233.80	182.16	335.68	264.78
56.26	60.56	148.26	120.17	236.45	184.24	337.82	266.59
59.07	62.95	150.70	121.72	237.25	184.87	339.95	268.38
61.49	65.08	154.06	123.84	239.09	186.33	342.07	270.16
63.81	66.94	155.02	124.40	241.71	188.35	344.18	271.93
66.03	68.66	157.40	125.91	244.31	190.34	346.29	273.68
68.17	70.35	160.70	127.94	246.90	192.46	348.38	275.85
70.23	71.88	161.63	128.40				

subtracting the base value for the heat capacity of the solid and the liquid phase. For the solid phase a linear fit between 290 to 320 K was used. The molar enthalpy of fusion is (22.52 ± 0.02) kJ · mol⁻¹.

Trans-stilbene was measured between 8 and 350 K. The experimental results are given in table 4. In this temperature region no phase transition was found. The fusion temperature of *trans*-stilbene is too high for the calorimeter used. We measured the enthalpy of fusion using a Setaram DSC 111, which had been calibrated by the manufacturer. The calibration was checked between 370 and 770 K by measuring the heat capacity of standard sapphire. The largest deviation was 1 per cent at the higher temperatures. An overall analysis of the calibration factor reveals a standard deviation of 0.5 per cent. Three samples of about 0.04 g of *trans*-stilbene were measured. The molar enthalpy of fusion is

TABLE 5. Smoothed molar heat capacities and derived thermodynamic functions of
C₆H₅-CH=CH-C₆H₅

$\frac{T}{K}$	$\frac{C_{p,m}}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{H_m^{\circ}(T) - H_m^{\circ}(0)}{J \cdot mol^{-1}}$	$\frac{S_m^{\circ}(T) - S_m^{\circ}(0)}{J \cdot K^{-1} \cdot mol^{-1}}$	$\frac{-G_m^{\circ}(T) + H_m^{\circ}(0)}{J \cdot mol^{-1}}$
10	3.22	9.6	1.29	3.3
20	15.8	101.2	7.2	42.8
30	30.5	332	16.3	157
40	43.8	704	26.9	372
50	54.9	1199	38.0	701
60	63.8	1793	48.8	1135
70	71.7	2472	59.2	1672
80	78.4	3224	69.2	2312
90	84.9	4041	78.8	3051
100	91.0	4921	88.1	3889
110	97.2	5860	97.1	4821
120	103.1	6862	105.8	5834
130	109.1	7923	114.3	6936
140	115.2	9044	122.6	8120
150	121.3	10226	130.7	9379
160	127.6	11470	138.7	10722
170	135.2	12779	146.7	12160
180	142.7	14169	154.6	13659
190	149.6	15631	162.5	15244
200	156.9	17164	170.4	16916
210	164.1	18769	178.2	18653
220	171.7	20448	186.0	20472
230	179.2	22202	193.8	22372
240	187.1	24033	201.6	24351
250	194.8	25943	209.4	26407
260	202.6	27930	217.2	28542
270	210.5	29992	224.9	30731
280	219.1	32140	232.8	33044
290	227.4	34371	240.6	35403
298.15	235.0	36250	247.0	37393
300	236.7	36687	248.5	37863
310	243.6	39084	256.3	40369
320	252.0	41562	264.2	42982
330	260.1	44122	272.1	45671
340	268.4	46751	279.9	48415

TABLE 6. Molar enthalpies of fusion and triple-point temperatures of $C_6H_5-N=N-C_6H_5$ and $C_6H_5-CH=CH-C_6H_5$

<i>Trans</i> -azobenzene						
Reference	7	8	9	10	11	12
$\Delta_f^0 H_m / (kJ \cdot mol^{-1})$	22.1	21.3	20.3	24.7	22.4	22.65 ± 0.12
T_{fus} / K	—	—	—	341.7	340.5	—
This work						
						22.52 ± 0.02
						341.03
<i>Trans</i> -stilbene						
Reference	13	This work				
$\Delta_f^0 H_m / (kJ \cdot mol^{-1})$	30.1	27.4				
T_{fus} / K	397	398 ± 0.5				

$(27.37 \pm 0.03) kJ \cdot mol^{-1}$, the melting temperature is $(398.0 \pm 0.5) K$. In table 5 the thermodynamic properties of *trans*-stilbene are given between 10 and 350 K. Below 8 K the molar heat capacity was extrapolated using a linear relation between C_p/T and T^2 .

In table 6 the molar enthalpy of fusion and the triple-point temperatures of both compounds are compared with the values found in the literature. The more recent values for *trans*-azobenzene^(11,12) correspond very well with our values. For *trans*-stilbene the literature cites older work;⁽¹³⁾ the original results, however, were not available to us.

REFERENCES

1. Kitaigorodsky, A. I. *Molecular crystals and molecules*. Loubl, E. M.: editor. Academic Press: New York and London. 1973.
2. Kolkert, W. J. Thesis, University of Utrecht, The Netherlands, 1974.
3. Pfann, W. G. *Zone melting*. Second edition. Wiley: New York, London. 1959.
4. Vetter, H.; Rössler, S.; Schildknecht, H. *Symposium über Zoneschmelzen und Kolonnenkristallisieren*. Schildknecht, H.: editor. Kernforschungsanstalt: Karlsruhe, Germany. 1963, p. 57.
5. Kruif, C. G. de; Miltenburg, J. C. van; Blok, J. G. *J. Chem. Thermodynamics* 1983, 15, 129.
6. Schaake, R. C. F.; Offringa, J. C. A.; Berg, G. J. K. van den; Miltenburg, J. C. van. *Rec. Trav. Chim. Pays-Bas* 1979, 98, 408.
7. Eykman, J. I. *Z. Physik. Chem.* 1889, 4, 518.
8. Bruner, L. *Chem. Ber.* 1894, 27, 2102.
9. Bogojawlenski, A.; Windogradow, N. *Z. Physik. Chem.* 1908, 64, 251.
10. Padoa, M. *Atti Linc* 1919, (5), 28(2), 239.
11. Cingolani, A.; Berchiesi, G. *J. Thermal Analysis* 1974, 6, 87.
12. Schulze, F. W.; Petrick, H. J.; Cammenga, H. K.; Klinge, H. *Z. Physik. Chem. Neue Folge* 1977, 107, 1.
13. Parks, G. S.; Huffman, H. M. *Ind. Eng. Chem.* 1931, 23, 1138.