

Table S-1. Crystallization results

A 'no' entry means either that the crystals obtained were of the starting materials or else that the crystal quality was too poor to allow their identification.

Solvent	ORTHO	META-I	META-II	PARA-I	PARA-II	PARA-III	PARA-IV
acetonitrile	prisms	needles		needles		needles	
acetone	needles	needles				needles	
benzene	needles	prisms plates	needles prisms			needles plates prisms	
carbon tetrachloride	no	needles	needles	-----no-----			
chloroform	plates	-----no-----			needles	plates	
methylene chloride	no	prisms plates			prisms plates needles	needles plates	needle
diethyl ether	no	needles		-----no-----			

Table S-2 o-TDB/HMB unit cells^a

sample	solvent	temp	a	b	c	α	β	γ	V	type	note
1990	CH ₃ CN	183	15.825(5)	9.142(5)	13.881(9)		102.86(5)		1958	I	a
1992a	(CH ₃) ₂ CO	189	15.85(3)	9.15(8)	13.85(2)		103.5(1)		1951	I	
1992b	C ₆ H ₆	189	15.746(11)	9.131(3)	13.846(8)		102.67		1947	I	
1992c	CHCl ₃	188	15.779(14)	9.144 (11)	13.826(18)		103.1(3)		1943	I	
1992d	CH ₃ CN	189	15.820(5)	9.132(3)	13.896(16)		103.39(6)		1953	I	
1992e	CH ₃ CN	297	15.861(5)	9.196(3)	14.097(4)		102.10(2)		2010	I	
2001	CH ₃ CN	173	15.824(3)	9.150(2)	13.894(2)		102.88(1)		1961	I	a,b

a A structure determination was made from these data.

b. Reported in Table 1.

Table S-3. m-TDB/HMB unit cells

sample	solvent	temp	a	b	c	α	β	γ	V	type	note
1990a	CH ₃ CN	187	7.513(3)	8.615(3)	9.029(2)	113.30(2)	113.30(2)	91.92(3)	476(1)	I	a
1990b	"	297	7.623(8)	9.009(2)	9.066(7)	117.50(5)	110.56(9)	92.84(9)	500(1)	I	b
1990c	CH ₃ CN	297	7.598(4)	8.997(4)	9.093(4)	118.55(3)	109.18(4)	94.45(4)	495(1)	I	c
1990d	"	187	-	-	-	-	-	-	-	I	c,d
1997a	C ₆ H ₆	174	8.960(1)	14.065(1)	15.941(1)	83.43(1)	88.79(1)	76.43(1)	1940(1)	II	a,e
1997b	CH ₃ CN	174	7.541(4)	8.939(11)	9.068(8)	118.46(5)	109.68(6)	94.83(9)	483(1)	I	
1997c	C ₆ H ₆	223	8.999(1)	14.126(1)	16.012(1)	83.41(1)	88.85(1)	76.48(1)	1966(1)	II	a
1997d	C ₆ H ₆	297	7.658(32)	9.003(8)	9.132(8)	118.56(8)	109.61(16)	94.14(17)	500(3)	I	
1998a	CH ₂ Cl ₂	297	7.601	9.042	9.131	118.70	109.02	94.64	499	I	f,g
			7.616	9.023	9.151	118.38	108.97	94.84	501	I	
1998b	CH ₂ Cl ₂	297	7.643	9.015	9.132	118.58	109.26	94.36	500	I	f
1998c	C ₆ H ₆	297	9.002(2)	14.325(3)	15.996(3)	83.01(2)	88.92(1)	75.97(3)	1986(1)	II	h
2001a	C ₆ H ₆	174	8.945	14.021	15.887	83.52	88.80	76.54	1925	II	f
2001b	C ₆ H ₆	297	7.613(3)	9.003(5)	9.109(4)	118.51(3)	109.18(4)	94.43(6)	497	I	
2001c	C ₆ H ₆	174	7.529(1)	8.950(1)	9.051(1)	118.43(1)	109.41(1)	95.14(1)	483	I	a,i
2001d	C ₆ H ₆	297	9.012(8)	14.320(13)	16.011(13)	83.09(11)	88.90(9)	75.94(10)	1990	II	
2001e	"	174	8.922	14.051	15.909	83.37	88.67	76.33	1925	II	f

2001f	C ₆ H ₆	297	9.091	14.278	15.992	82.98	89.20	75.49	1994	II	f,j
			8.966	14.250	16.001	83.17	88.71	75.47	1965	II	
			9.042	14.309	15.985	83.13	89.14	75.67	1989	II	
2001g	(CH ₃) ₂ O	174	7.538	8.944	9.047	118.31	109.50	95.26	483	I	f,k
			7.538	8.913	9.072	118.33	109.50	95.13	481	I	
2001h	C ₆ H ₆	174	8.926	14.031	15.918	83.49	88.77	76.47	1926	II	f
2001i	C ₆ H ₆	174	8.941(1)	14.025(2)	15.912(2)	83.45(1)	88.81(1)	76.49(1)	1927	II	a
2001j	C ₆ H ₆	174	8.926	14.031	15.918	83.50	88.77	76.47	1926	II	f
2001k	C ₆ H ₆	173	8.955(1)	14.064(2)	15.939(2)	83.40(1)	88.79(1)	76.46(1)	1939	II	a,i,l
2001l	"	174	8.951(1)	14.045(2)	15.928(2)	83.41(1)	88.78(1)	76.48(1)	1934	II	a,l
2001m	"	174	7.543(1)	8.959(2)	9.057(2)	118.36(2)	109.40(2)	95.20(2)	483	I	a,m

a A structure determination was made from these data.

b A quotation mark for the solvent means that the previous crystal has been remeasured.

c Oscillation photographs were taken about all three axes. There was no indication of a larger cell. There were also no apparent disorder streaks.

d The unit cell was not determined,

e This is not the cell reported in the main body of the paper. It is the reduced cell which was routinely found by both SMART and GEMINI. The cell in the main body was chosen to emphasize the similarity between I and II. It is obtained from the Niggli cell with the matrix 0,-1,0/-1,0,0/1,0,-1.

f. If no su's are given, the cell could not be found by SMART but was found by GEMINI

- g This crystal was twinned with the two fragments related by rotation of 180° around 1,7,-7 in reciprocal space.
- h These data were carefully examined for twinning. All of the reflections could be accounted for with the reported, untwinned, cell.
- i. Reported in Table 1.
- j This was a trilling. The rotation axes were not found.
- k This was a twin. The fragments were related by 180° rotation about 010 in reciprocal space.
- l Two data sets were collected on this crystal, first on the Bruker and then on the Siemens.
- m Only those reflections from 20011 that fit the META-I cell were used in the solution and refinement.

Table S-4 p-TDB/HMB unit cells

sample	solvent	temp	a	b	c	α	β	γ	V	type	note
1989a	CH ₃ CN	189	7.513(3)	8.615(3)	9.029(2)	114.24(3)	113.30(2)	91.92(3)	476	I	a,b
1992a	CH ₂ Cl ₂	297	7.622(4)	9.007(3)	9.076(7)	117.47(5)	110.65(5)	92.81(3)	500	II	a,c,
1992b	"	263	7.605(3)	8.968(3)	9.045(9)	117.22(6)	110.96(6)	92.87(3)	495	II	d
1992c	"	233	7.583(5)	8.942(4)	9.051(14)	117.16(9)	111.20(8)	92.70(5)	492	II	
1992d	"	203	7.571(4)	8.921(3)	9.008(8)	116.92(5)	111.61(5)	92.58(4)	488	II	
1992e	"	177	7.552(3)	8.899(2)	8.993(6)	116.76(4)	111.90(4)	92.36(3)	485	II	a
1992f	C ₆ H ₆	297	9.745(5)	15.407(5)	7.545(7)		116.84(5)		1011	III	a
1992g	CH ₃ CN	177	7.528(7)	8.660(8)	9.064(13)	114.32(10)	112.93(10)	92.30(8)	481	I	a,e
1992h	"	189	7.533 (7)	8.670(8)	9.062(13)	114.32(9)	112.89(10)	92.35(7)	482	I	
1192i	"	201	7.547(5)	8.676(7)	9.066(11)	114.24(8)	112.92(8)	92.46(6)	484	I	
1992j	"	215	7.556(5)	8.684(6)	9.067(10)	114.19(7)	112.89(7)	92.58(5)	485	I	
1992k	"	227	7.565(5)	8.694(5)	9.072(9)	114.17(6)	112.85(7)	92.65(5)	486	I	
1992l	"	241	7.581(4)	8.696(4)	9.084(7)	114.04(5)	113.01(6)	92.77(4)	488	I	
1992m	"	268	7.596(6)	8.726(3)	9.092(4)	114.00(3)	112.88(5)	93.00(4)	491	I	f
1992n	CH ₃ CN	297	9.747(4)	15.416(5)	7.548(2)		116.80(5)		1012	III	g
1992o	"	173	7.541(4)	8.666(7)	9.076(7)	114.13(3)	113.20(5)	92.29(5)	483	I	g

1992p	CH ₃ CN	297	9.752(6)	15.424(6)	7.558(3)		116.87(3)		1014	III	h
1993a	CH ₂ Cl ₂	297	7.623(2)	9.006(2)	9.067(2)	117.46(3)	110.63(3)	92.84(3)	500	II	a
1997a	(CH ₃) ₂ CO	297	9.769(10)	15.428(15)	7.549(9)		116.93(11)		1014	III	
1997b	CH ₃ CN	297	9.754(5)	15.409(14)	7.554(4)		116.94(4)		1012`	III	
1997c	CH ₂ Cl ₂	297	7.590(5)	9.130(6)	15.612(18)	85.33(4)	81.41(6)	73.13(14)	1023	IV	i
1997d	"	174	7.498(1)	9.037(1)	15.454(1)	85.08(1)	81.80(1)	71.17(1)	980	IV	a,b,i
1998a	(CH ₃) ₂ CO	297	9.744(5)	15.406(5)	7.556(3)		116.90(3)		1012	III	
1998b	CH ₃ CN	297	9.751(2)	15.430(6)	7.555(2)		116.83		1014	III	
1998c	C ₆ H ₆	297	9.757(2)	15.414(5)	7.560(2)		116.90(2)		1014	III	
1998d	CH ₂ Cl ₂	297	7.633(4)	9.009(3)	9.069(6)	117.46(2)	110.83(4)	92.60(4)	500	II	j
1998e	CH ₂ Cl ₂	297	7.630(6)	9.008(6)	9.071(6)	117.44(4)	110.79(6)	92.61(7)	501	II	j
1998f	CH ₂ Cl ₂	297	7.633(2)	9.019(3)	9.066(3)	117.26(2)	110.88(2)	92.71(3)	502	II	j
1998g	CH ₂ Cl ₂	297	7.639(4)	9.004(5)	9.066(5)	117.44(3)	110.84(5)	92.71(7)	500	II	j
1998h	CH ₂ Cl ₂	297	9.752(2)	15.421(6)	7.553(2)		116.87(2)		1013	III	j,k
1998i	"	174	7.555(3)	8.888(2)	8.989(3)	116.62(2)	112.09(2)	92.10(2)	485	II	
1998j	"	297	7.636(3)	9.006(3)	9.067(4)	117.38(2)	110.73(2)	92.63(3)	501	II	
1998k	CH ₃ CN	297	9.747(4)	15.404(4)	7.555(2)		116.86(3)		1012	III	l
1998l	"	174	7.553(2)	8.887(3)	8.979(3)	116.64(2)	112.05(2)	92.15(2)	484	II	

[illegible]

- a A structure determination was made on this crystal.
- b Reported in Table 1.
- c 1992a-e show a regular change in cell constants with temperature.
The unit cell volume is given by $V(\text{\AA}^3) = 499.9 - 0.1288(297 - T)$ where T is the absolute temperature.
- d A quotation mark for the solvent means that the previous crystal has been remeasured.
- e 1992g-m show a regular change in cell constants with temperature.
The unit cell volume is given by $V(\text{\AA}^3) = 493.8 - 0.1046(297 - T)$ where T is the absolute temperature.
- f The warming was continued to 297 where no reasonable cell could be found. It was not obvious from the appearance but the crystal had presumably decomposed.
- g 1992n was cooled to 173 K with no change in appearance to give 1992o. When 1992o was rewarmed to 297 no cell could be obtained.
- h When this crystal was cooled to 173 K no cell could be found.
- i This crystal, a clear needle, transformed on cooling to an obvious twin, with three clear segments bent at about 120° to each other. 1997d corresponds to the terminal fragment.
- j These crystals were taken from seven independent syntheses of the complex in CH₂Cl₂, in a search for another crystal of para-IV.
- k 1998h was cooled to 174 K with no change in appearance to give 1998i. 1998i was then warmed back to 297 K with no change in appearance to give 1998j.
- l 1998k was cooled to 174 K with no change in appearance to give 1998l.
- m On cooling this sample went to two twin fragments, which were indexed using GEMINI. The twins were related by 180° rotation about the direct space axis 0,-1,-2. The transformation occurred between 255 and 297 K.
- n If no su's are given, the cell could not be found by SMART but was found by GEMINI.

- o On cooling this sample went to several fragments, which could not be indexed. The transformation was between 268 and 297 K.
- p. On cooling this sample changed shape abruptly at 291 K. It was cooled to 174 K and indexed as 2001c. A complete data set was collected and solved, verifying that this was II. However, only 38/49 reflections had been indexed successfully. A larger set of 587 reflections was reaped and indexed with GEMINI. 511 reflections gave the 2001c cell. 53 Of the remaining 76 could be indexed as 2001d. When a data set was collected for 2001d, the quality was very poor and it could not be solved. However, when the $\text{Cl}_4\text{C}_6(\text{CN})_2$ atoms were introduced as a trial structure, the difference map showed the HMB molecule in the correct position for I.
- q. This crystal was cooled slowly and transformed into two fragments at 249 K.
- r. This visually appeared to be a twin with two distinct fragments with different orientations. Cell data were collected with the intention of finding the twin law. However GEMINI fit 361/367 reflections as shown. This was not a twin.
- s. Slow cooling showed a transformation at 278 K
- t No cell was determined.
- u Slow cooling showed a transformation at 283 K