Supplementary Material

for

The Design of Organic Structures in the Solid State: Hydrogen-Bonded Molecular "Tapes"

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Experimental

General: Melamine, barbituric acid, 5,5-diethylbarbituric acid, and 5,5-dibromobarbituric acid were obtained commercially and used without purification. Syntheses of all substituted melamines were performed according to modifications of published procedures.[1] Synthesis of 5,5-di(*p*-bromobenzyl)barbituric acid was achieved by modifications of published procedures.[2]

X-ray Crystallography for N,N'-diphenylmelamine/5,5-diethylbarbituric acid. A crystal data summary is given in Table 1. X-ray data were collected on a Siemens R3m/V four-circle diffractometer equipped with a LT-1 low-temperature device. Data collection was controlled using the Siemens P3 program.[3] Unit cell symmetry was checked with the program XCELL. Raw diffractometer data was processed with the program XDISK. An empirical absorption correction

was performed with the program PSICORR (public domain). The structure was solved by use of the SHELXTL-PLUS[4] package of programs. Drawings were produced using the Siemens program XP.

The crystals for study were grown by slow evaporation of dichloromethane solvent. A crystal of dimensions 0.21 x 0.15 x 0.13 mm was attached to a 0.30 mm glass fiber with a minimum amount of silicon grease. The fiber was then mounted on a 1/8" diameter brass pin using epoxy glue. The pin was attached to the goniometer head and the head was then transferred to the diffractometer where the crystal was immersed in a cold nitrogen stream (-80(1) °C). The unit cell was indexed using data obtained from a rotation photograph. A lattice determination using both the P3 program and XCELL suggested a primitive orthorhombic cell. Examination of the axial photographs confirmed this assignment. The final unit cell parameters were obtained by a least squares refinement of 25 selected reflections, including six Friedel pairs, in the range $4° < 2\theta < 24°$.

A total of 4845 reflections were collected in the range $4° < 2\theta < 50°$ (0,0,0 to *h, k, l*). The intensities of three check reflections, (0,2,9), (0,7,3), and (2,0,8), were measured after every 60 reflections. The crystal did not decay during the 56 hours of exposure. A semi-empirical absorption correction as well as Lorentz and polarization corrections were applied to the data.

Systematic absences determined the space group to be either $P2_1nb$ or *Pmnb*. The standard setting of *Pnma* was chosen, and successful solution in this space group confirmed its choice. Most of the non-hydrogen atoms were located by the use of direct methods.[5] Standard difference map techniques were used to find the remaining non-hydrogen atoms. After all of the non-hydrogen atoms were located and refined anisotropically, a difference map revealed several of the hydrogen atom positions. The hydrogen atoms were placed in calculated positions ($U_{iso}(H) = 1.2U_{iso}(C)$; $d_{C-H} = 0.96$ Å) for refinement. Refinement was performed to convergence ($\Delta/\sigma(max) < 0.01$) with this model. The weighting scheme was $w = [\sigma^2(F) + gF^2]^{-1}$ (g refined to 0.0). The final difference map contained only peaks that were less than 0.38 eÅ^{-3}.

The semi-empirical absorption correction employed scans near $\chi = 270$, using the program PSICORR, and was based on scans from 3 reflections in the range $10° < 2\theta < 21°$. This procedure yielded a refined structure with no non-positive definite atoms.

Table 1. Crystal data summary for N,N'-diphenylmelamine/5,5-diethylbarbituric acid.

color of crystal	colorless
empirical formula	$(C_{15}H_{14}N_6)(C_8H_{12}N_2O_3)$
crystal dimensions, mm	0.21 x 0.15 x 0.13
space group	*Pnma* (No. 62)
temperature, °C	-80(1)
cell dimensions	
a, Å	12.940(3)
b, Å	9.982(5)
c, Å	17.377(3)
wavelength, Å	0.71073
Z (asymmetric units/cell)[a]	4
volume, Å^3	2245(1)
d_{calcd}, g cm^{-3}	1.369
linear absorption coefficient, cm^{-1}	0.90
scan type	$\theta - 2\theta$
scan speed, deg/min	3 - 30
scan width, deg (+ dispersion)	2.0
background / scan ratio	0.50
2θ range, deg	4 - 50
data collected	*h*, *k*, *l*
F(000)	976
parameters refined	137

Table 1 (continued)

total number of reflections collected	4845
number of unique reflections	1984
R_{int}	0.1121
number with $F_o > 4.00\sigma(F_o)$	933
R^b	0.0654
R_w^c	0.0486
"goodness of fit" for last cycle	1.21
largest Δ/σ for last cycle	0.002
final difference map, eÅ^{-3} (maximum)	0.38
(minimum)	-0.40

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a. Total number of molecules per cell is 4 of diphenylmelamine and 4 of diethylbarbituric acid.

b $R = \Sigma|(Fo-Fc)|/\Sigma Fo$

c $R_w = \Sigma(w^{1/2}|(Fo-Fc)|/\Sigma(w^{1/2}Fo)$, $w = [\sigma^2(F)+ gF^2]^{-1}$

Table 2. Fractional atomic coordinates (x 10^4) and equivalent isotropic displacement parameters for N,N'-diphenylmelamine/5,5-diethylbarbituric acid. Atoms numbered according to figure 1.

atom	x	y	z	U(eq)
N(1)	1237(3)	1302(4)	5674(2)	18(1)
N(2)	-181(4)	2500[a]	6223(3)	19(2)
N(3)	2640(4)	2500	5237(3)	24(2)
N(4)	-154(3)	199(4)	6204(2)	19(2)
N(5)	7757(3)	1330(5)	4598(2)	21(1)
O(1)	9212(3)	2500	4311(3)	24(2)
O(2)	6329(2)	116(4)	4845(2)	29(1)
C(1)	1667(5)	2500	5537(4)	16(2)
C(2)	312(3)	1390(6)	6029(3)	19(1)
C(3)	-1057(3)	96(6)	6669(2)	19(1)
C(4)	-1126(4)	727(6)	7375(3)	29(2)
C(5)	-2016(4)	584(6)	7811(3)	34(2)
C(6)	-2822(4)	-181(6)	7566(3)	38(2)
C(7)	-2743(4)	-802(7)	6874(3)	52(3)
C(8)	-1860(4)	-668(7)	6419(3)	40(2)
C(9)	8297(6)	2500	4498(4)	21(3)
C(10)	6720(3)	1214(6)	4769(3)	20(1)
C(11)	6099(5)	2500	4868(4)	18(2)

Table 2 cont'd.

C(12)	5229(5)	2500	4249(4)	22(3)
C(13)	5604(5)	2500	3428(4)	33(2)
C(14)	5602(5)	2500	5676(4)	26(2)
C(15)	6401(6)	2500	6318(4)	45(3)

a. Atom fixed on a special position.

Notes and References

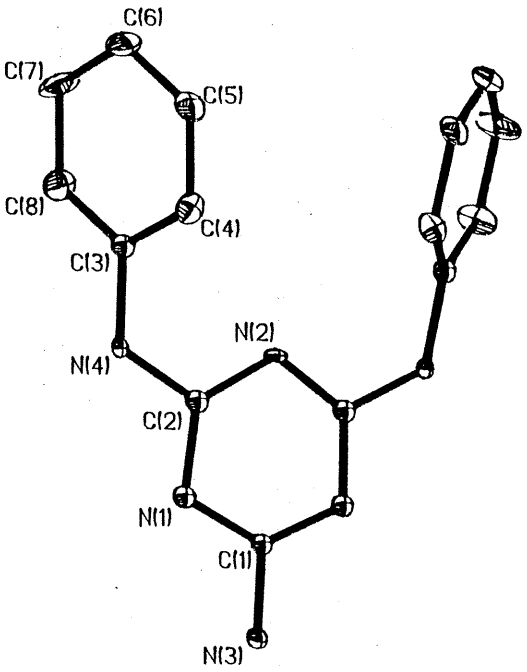
1. Kaiser, D.W.; Thurston, J.T.; Dudley, J.R.; Schaefer, F.C.; Hechenbleikner, I.; Holm-Hansen, D. *J. Am. Chem. Soc.* **1951**, *73*, 2984.

2. *Organic Syntheses Collective Volume 2;* Blatt, A.H., Ed.; Wiley and sons: New York, 1943; p. 60. Diethyl di(*p*-bromobenzyl)malonate prepared from diethyl malonate and *p*-bromobenzyl bromide with NaH in THF.

3. "P3/R3 Data Collection Manual" Siemens Analytical X-Ray Instruments: Madison, Wisconsin (1990).

4. "SHELXTL - PLUS Users Manual" Siemens Analytical X-Ray Instruments: Madison, Wisconsin (1990).

5. Structure factors taken from *International Tables for X-Ray Crystallography;* Kynoch: Birmingham, England, 1974; Vol. IV.



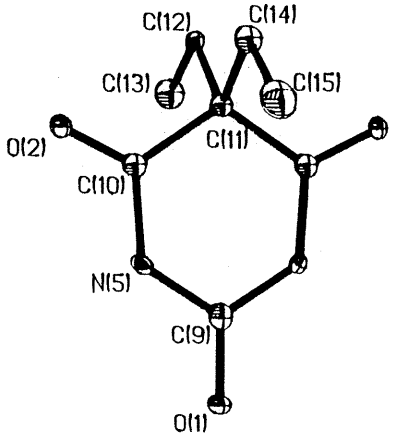


Figure 1. ORTEP plot of N,N'-diphenylmelamine/5,5-diethylbarbituric acid complex showing 30% ellipsoids. Atoms without numbers are symmetry equivalents.