Crystal structure of 4-(diisopropylamino)benzonitrile, $C_{13}H_{18}N_2$

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Abstract

$C_{13}H_{18}N_2$, monoclinic, $C12/c1$ (no. 15),
 $a = 16.657(3)$ Å, $b = 14.714(3)$ Å, $c = 20.725(3)$ Å,
 $\beta = 92.73(1)^\circ$, $V = 5073.7$ Å³, $Z = 16$,
 $R_{\text{gt}}(F) = 0.065$, $wR_{\text{ref}}(F^2) = 0.199$, $T = 293$ K.

Source of material

4-(diisopropylamino) benzonitrile (DIABN) was supplied by Dr. Christoph Mark, Chemische Laboratorien Worms, and used without further purification for crystal growth. Crystals were grown from solution and also by slow sublimation at 323 K in a tubular furnace. By both methods good quality single crystals were obtained with identical unit cells. The data presented here was obtained from solution grown crystals. 1.1 g of DIABN powder was dissolved in 120 ml of cyclopentane and filtrated. The clear solution was allowed to stand at room temperature in an exsiccator under low nitrogen flow for 2 weeks. Slow evaporation of the solvent led to the formation of colorless plate-like crystals.

Discussion

The crystal structure consists of layers of DIABN molecules in the ab plane (figure, top). We found two crystallographically independent molecules with a nearly parallel orientation in the unit cell (figure, bottom). DIABN belongs to a class of molecules that undergo intramolecular charge transfer (ICT) upon photo-excitation. The structural changes associated with this ICT have been debated for the last 40 years. DIABN is particularly interesting since here the ICT process and the concomitant structural changes occur in solution and in the crystalline state [1]. Therefore it could be possible to trace these structural changes by time-resolved X-ray diffraction. The structure presented here lays the basis for such studies.

Table 1. Data collection and handling.

Crystal:	colorless block, size $0.6 \times 1.0 \times 1.5$ mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	0.63 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	6016, 5819
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3978
$N(\text{param})_{\text{refined}}$:	272
Programs:	SHELXS-97 [2], SHELXL-97 [3]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(2A)	8f	0.5979	−0.0249	0.6164	0.077
H(3A)	8f	0.7099	−0.1153	0.6269	0.093
H(5A)	8f	0.8510	0.0975	0.5976	0.086
H(6A)	8f	0.7411	0.1888	0.5846	0.075
H(8A)	8f	0.5115	0.0457	0.5781	0.077
H(9A1)	8f	0.5097	0.0854	0.6865	0.140
H(9A2)	8f	0.4223	0.0822	0.6551	0.140
H(9A3)	8f	0.4648	0.1760	0.6679	0.140
H(10A)	8f	0.4744	0.1487	0.4966	0.131
H(10B)	8f	0.4412	0.2149	0.5483	0.131
H(10C)	8f	0.4003	0.1201	0.5359	0.131
H(11A)	8f	0.5365	0.2687	0.6003	0.076
H(12A)	8f	0.6136	0.2482	0.6952	0.133
H(12B)	8f	0.6263	0.3446	0.6652	0.133
H(12C)	8f	0.6914	0.2688	0.6581	0.133
H(13A)	8f	0.5910	0.2768	0.4997	0.128
H(13B)	8f	0.6772	0.2861	0.5330	0.128
H(13C)	8f	0.6130	0.3625	0.5419	0.128

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(2B)	8f	0.2603	−0.0184	0.7329	0.066
H(3B)	8f	0.3700	−0.1111	0.7424	0.072
H(5B)	8f	0.3845	−0.1115	0.5501	0.076
H(6B)	8f	0.2761	−0.0174	0.5399	0.067
H(8B)	8f	0.1255	0.1529	0.6624	0.085
H(9B1)	8f	0.0673	0.0229	0.7028	0.156
H(9B2)	8f	0.0840	0.0959	0.7569	0.156
H(9B3)	8f	0.1407	0.0114	0.7522	0.156
H(10D)	8f	0.2578	0.1942	0.6864	0.147
H(10E)	8f	0.2628	0.1218	0.7420	0.147
H(10F)	8f	0.2044	0.2049	0.7462	0.147
H(11B)	8f	0.1708	0.0297	0.5344	0.076
H(12D)	8f	0.0435	0.0212	0.5756	0.134
H(12E)	8f	0.0442	0.0886	0.5171	0.134
H(12F)	8f	0.0447	0.1264	0.5878	0.134
H(13D)	8f	0.2480	0.1615	0.5438	0.134
H(13E)	8f	0.1738	0.2148	0.5681	0.134
H(13F)	8f	0.1721	0.1770	0.4973	0.134

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1A)	8f	0.58852(9)	0.1492(1)	0.58936(8)	0.0541(8)	0.0449(8)	0.0692(9)	0.0024(6)	0.0043(7)	0.0047(7)
C(1A)	8f	0.6548(1)	0.0947(1)	0.59843(8)	0.059(1)	0.0508(9)	0.0441(8)	0.0062(8)	0.0028(7)	0.0000(7)
C(2A)	8f	0.6484(1)	0.0007(1)	0.6119(1)	0.077(1)	0.051(1)	0.064(1)	0.0057(9)	0.0024(9)	0.0022(8)
N(2A)	8f	0.9177(2)	−0.1208(2)	0.6278(2)	0.136(2)	0.156(3)	0.125(2)	0.096(2)	−0.013(2)	−0.024(2)
C(3A)	8f	0.7161(2)	−0.0537(2)	0.6185(1)	0.114(2)	0.052(1)	0.066(1)	0.023(1)	−0.003(1)	−0.0043(9)
C(4A)	8f	0.7924(2)	−0.0192(2)	0.6130(1)	0.082(2)	0.083(2)	0.053(1)	0.034(1)	−0.002(1)	−0.010(1)
C(5A)	8f	0.8001(1)	0.0725(2)	0.6008(1)	0.061(1)	0.093(2)	0.062(1)	0.016(1)	0.0031(9)	0.003(1)
C(6A)	8f	0.7337(1)	0.1275(2)	0.5933(1)	0.060(1)	0.064(1)	0.064(1)	0.0053(9)	0.0038(8)	0.0083(9)
C(7A)	8f	0.8626(2)	−0.0764(2)	0.6214(1)	0.109(2)	0.114(2)	0.072(2)	0.057(2)	−0.005(1)	−0.019(1)
C(8A)	8f	0.5066(1)	0.1102(1)	0.5892(1)	0.055(1)	0.059(1)	0.080(1)	−0.0044(9)	0.0053(9)	−0.000(1)
C(9A)	8f	0.4727(2)	0.1138(2)	0.6558(1)	0.085(2)	0.104(2)	0.093(2)	−0.019(2)	0.027(1)	0.003(2)
C(10A)	8f	0.4505(1)	0.1523(2)	0.5378(1)	0.062(1)	0.099(2)	0.100(2)	−0.008(1)	−0.011(1)	0.002(1)
C(11A)	8f	0.5925(1)	0.2495(1)	0.5970(1)	0.062(1)	0.0444(9)	0.083(1)	0.0048(8)	0.0009(9)	0.0022(9)
C(12A)	8f	0.6348(2)	0.2807(2)	0.6596(1)	0.096(2)	0.066(1)	0.102(2)	−0.004(1)	−0.010(1)	−0.018(1)
C(13A)	8f	0.6211(2)	0.2982(2)	0.5374(1)	0.087(2)	0.063(1)	0.105(2)	−0.003(1)	−0.001(1)	0.029(1)
N(1B)	8f	0.18888(9)	0.0521(1)	0.62899(7)	0.0548(8)	0.0581(9)	0.0505(8)	0.0119(7)	0.0005(6)	−0.0018(6)
C(1B)	8f	0.2543(1)	−0.0043(1)	0.63505(8)	0.0473(8)	0.0441(8)	0.0494(8)	−0.0007(6)	0.0013(7)	0.0009(7)
C(2B)	8f	0.2854(1)	−0.0360(1)	0.69575(8)	0.057(1)	0.060(1)	0.0476(9)	0.0066(8)	0.0078(7)	0.0043(8)
N(2B)	8f	0.5232(2)	−0.2110(2)	0.6573(1)	0.117(2)	0.134(2)	0.135(2)	0.078(2)	−0.002(2)	−0.010(2)
C(3B)	8f	0.3513(1)	−0.0919(1)	0.70161(9)	0.064(1)	0.060(1)	0.056(1)	0.0072(9)	−0.0016(8)	0.0097(8)
C(4B)	8f	0.3904(1)	−0.1202(1)	0.6474(1)	0.063(1)	0.054(1)	0.071(1)	0.0151(9)	0.0019(9)	−0.0021(9)
C(5B)	8f	0.3600(1)	−0.0919(1)	0.5870(1)	0.068(1)	0.064(1)	0.059(1)	0.0133(9)	0.0089(9)	−0.0095(9)
C(6B)	8f	0.2946(1)	−0.0356(1)	0.58093(9)	0.060(1)	0.059(1)	0.0470(9)	0.0063(8)	0.0003(7)	−0.0015(8)
C(7B)	8f	0.4637(2)	−0.1725(2)	0.6534(1)	0.089(2)	0.081(2)	0.088(2)	0.033(1)	0.002(1)	−0.004(1)
C(8B)	8f	0.1613(1)	0.1074(2)	0.6828(1)	0.070(1)	0.082(1)	0.061(1)	0.028(1)	−0.0014(9)	−0.016(1)
C(9B)	8f	0.1084(2)	0.0545(2)	0.7279(1)	0.079(2)	0.165(3)	0.071(2)	0.026(2)	0.023(1)	0.001(2)
C(10B)	8f	0.2277(2)	0.1621(2)	0.7175(1)	0.118(2)	0.087(2)	0.088(2)	0.021(2)	−0.023(2)	−0.034(1)
C(11B)	8f	0.1545(1)	0.0772(1)	0.56426(9)	0.070(1)	0.062(1)	0.056(1)	0.0130(9)	−0.0094(8)	−0.0005(8)
C(12B)	8f	0.0634(1)	0.0785(2)	0.5609(1)	0.077(2)	0.097(2)	0.090(2)	0.007(1)	−0.028(1)	−0.012(1)
C(13B)	8f	0.1904(2)	0.1658(2)	0.5413(1)	0.104(2)	0.078(2)	0.085(2)	0.001(1)	−0.006(1)	0.024(1)

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