Crystal structure of 3-diphenylamino-benzo[de]anthracen-7-one, $C_{29}H_{19}NO$

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Abstract

$C_{29}H_{19}NO$, monoclinic, $P12_1/c1$ (no. 14),
 $a = 23.218(4)$ Å, $b = 14.748(2)$ Å, $c = 12.094(2)$ Å,
 $\beta = 90.986(4)^\circ$, $V = 4140.6$ Å³, $Z = 8$,
 $R_{gt}(F) = 0.045$, $wR_{ref}(F^2) = 0.085$, $T = 293$ K.

Source of material

To a 25-mL sidearm flask in a dry nitrogen box were added 3-bromo-benzo[de]anthracen-7-one (2.5 mmol), diphenyl-amine (2.50 mmol), $Pd(CH_3COO)_2$ (0.025 mmol, $Pd/Br = 1\%$), tri-*tert*-butylphosphine (0.03 mmol), and sodium *tert*-butoxide (3.0 mmol). The flask was sealed with a septum and was then moved out of the nitrogen box. *o*-xylene (10 mL) was injected via a syringe. The reaction mixture was heated and stirred at 120 °C under nitrogen until the reaction was completed. The reaction mixture was then cooled to room temperature, filtered through a mixture of celite and silica gel pad, and washed with dichloromethane. The filtrate was then washed with water and dried by $MgSO_4$. Concentration of the filtrate on a rotary evaporator followed by washing of the solid material with methanol afforded the desired crude product. The crude product was then dried at 120 °C in a vacuum and further purified by sublimation. Red crystals were obtained by sublimation at $(4\ldots6) \cdot 10^{-3}$ Pa for 16 h.

Discussion

Aromatic amines play a central role in many areas of modern day organic chemistry, including such diverse fields as polymers, photography, medicine and materials [1–3]. Arylamines can be obtained either by the copper-catalyzed Ullmann condensation or palladium-catalyzed cross-coupling reactions [4–9]. Ullmann reactions involve rather high temperatures and prolonged reaction times and are limited to aryl iodides. Palladium-catalyzed *N*-arylation reaction has opened up the possibility of producing a wide variety of arylamines.

In the crystal structure there are two independent molecular units with similar bond lengths and angles (figure, top & middle). The planes C17/C18/C24 and C46/C47/C53 related to the amine geometry are all perfectly planar, indicating nitrogen atoms have a sp^2 hybridization. The benzo[de]anthracen-7-one ring systems are co-planar. Dihedral angles among planes of three substituted groups attached atoms of N1 and N2 are 60.44°, 72.57°, and 83.44°, as well as 68.02°, 78.47° and 82.00°. Therefore such arrangements have little steric crowding. All bond lengths in the compound are in the normal range, though disorder around C55–C57 appeared due to the loose packing of the concerning phenyl ring (s. arrow in figure, bottom). In the cell projection along *c* the connected molecular units I are located along the border and units II in the centre. The two molecular units greatly differ in their packing. The shortest intermolecular contacts thereby are 2.52 Å, (C11–)H11A...O1', and 2.38 Å, (C54–)H54A...O2' (s. figure).

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Table 1. Data collection and handling.

Crystal:	red columnar, size 0.2 × 0.3 × 0.4 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.77 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\max}$:	50.5°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	18154, 6699
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2724
$N(\text{param})_{\text{refined}}$:	560
Programs:	SHELX-97 [10], ORTEP-3 [11], WinGX [12]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(3A)	4e	0.1895	0.4957	0.2611	0.08
H(4A)	4e	0.1792	0.6306	0.3655	0.08
H(5A)	4e	0.1174	0.6311	0.5181	0.08
H(9A)	4e	-0.0083	0.4774	0.7669	0.08
H(10A)	4e	-0.0630	0.3466	0.8242	0.08
H(11A)	4e	-0.0599	0.2129	0.7152	0.08
H(12A)	4e	-0.0033	0.2106	0.5582	0.08
H(15A)	4e	0.0523	0.2083	0.4274	0.08
H(16A)	4e	0.1124	0.2061	0.2735	0.08
H(19A)	4e	0.2357	0.3779	0.0212	0.08
H(20A)	4e	0.2119	0.4691	-0.1320	0.08
H(21A)	4e	0.1175	0.5318	-0.1415	0.08
H(22A)	4e	0.0550	0.5092	-0.0062	0.08
H(23A)	4e	0.0746	0.4166	0.1481	0.08
H(25A)	4e	0.2495	0.2846	0.3380	0.08
H(26A)	4e	0.3132	0.1617	0.3347	0.08
H(27A)	4e	0.3155	0.0645	0.1723	0.08
H(28A)	4e	0.2487	0.0919	0.0222	0.08
H(29A)	4e	0.1848	0.2162	0.0319	0.08

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(32A)	4e	0.3803	0.7035	0.1262	0.08
H(33A)	4e	0.4379	0.7384	-0.0233	0.08
H(34A)	4e	0.4684	0.6241	-0.1477	0.08
H(38A)	4e	0.4784	0.3058	-0.2536	0.08
H(39A)	4e	0.4587	0.1515	-0.2141	0.08
H(40A)	4e	0.4053	0.1081	-0.0538	0.08
H(41A)	4e	0.3721	0.2213	0.0642	0.08
H(44A)	4e	0.3420	0.3217	0.1604	0.08
H(45A)	4e	0.3094	0.4382	0.2722	0.08
H(48A)	4e	0.2524	0.6108	0.1102	0.08
H(49A)	4e	0.1822	0.7114	0.0730	0.08
H(50A)	4e	0.1710	0.8430	0.1877	0.08
H(51A)	4e	0.2357	0.8664	0.3304	0.08
H(52A)	4e	0.3078	0.7651	0.3670	0.08
H(54A)	4e	0.4360	0.5781	0.3219	0.08
H(55A)	4e	0.4767	0.5725	0.4814	0.08
H(56A)	4e	0.4183	0.5822	0.6513	0.08
H(57A)	4e	0.3260	0.6060	0.6396	0.08
H(58A)	4e	0.2822	0.6167	0.4611	0.08

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	4e	0.05772(9)	0.5694(1)	0.6685(2)	0.119(2)	0.085(2)	0.068(2)	0.013(1)	0.005(2)	-0.025(1)
O(2)	4e	0.48112(9)	0.4687(1)	-0.2217(2)	0.095(2)	0.103(2)	0.068(1)	0.013(1)	0.026(2)	0.005(1)
N(1)	4e	0.1727(1)	0.3347(1)	0.1910(2)	0.066(2)	0.062(2)	0.049(2)	0.016(1)	0.010(2)	0.005(1)
N(2)	4e	0.3284(1)	0.6089(1)	0.2697(2)	0.068(2)	0.068(2)	0.050(2)	0.025(1)	-0.004(2)	-0.002(1)
C(1)	4e	0.0973(1)	0.4182(2)	0.4454(2)	0.046(2)	0.050(2)	0.045(2)	0.006(1)	-0.007(2)	-0.001(1)
C(2)	4e	0.1335(1)	0.4178(2)	0.3505(2)	0.049(2)	0.048(2)	0.050(2)	0.001(1)	-0.007(2)	0.003(1)
C(3)	4e	0.1643(1)	0.4971(2)	0.3255(2)	0.059(2)	0.057(2)	0.058(2)	-0.001(2)	-0.003(2)	-0.000(2)
C(4)	4e	0.1585(1)	0.5743(2)	0.3853(2)	0.064(2)	0.062(2)	0.066(2)	-0.010(2)	-0.010(2)	0.002(2)
C(5)	4e	0.1231(1)	0.5752(2)	0.4768(2)	0.069(2)	0.055(2)	0.061(2)	0.003(2)	-0.017(2)	-0.009(2)
C(6)	4e	0.0939(1)	0.4988(2)	0.5085(2)	0.055(2)	0.056(2)	0.046(2)	0.007(2)	-0.007(2)	-0.002(2)
C(7)	4e	0.0589(1)	0.5011(2)	0.6093(2)	0.070(2)	0.070(2)	0.053(2)	0.019(2)	-0.013(2)	-0.005(2)
C(8)	4e	0.0264(1)	0.4189(2)	0.6375(2)	0.053(2)	0.076(2)	0.048(2)	0.016(2)	-0.002(2)	0.001(2)
C(9)	4e	-0.0082(1)	0.4195(2)	0.7317(2)	0.071(3)	0.103(3)	0.057(2)	0.024(2)	0.006(2)	0.003(2)
C(10)	4e	-0.0398(2)	0.3453(3)	0.7595(3)	0.076(3)	0.135(3)	0.066(2)	0.020(2)	0.018(2)	0.018(2)
C(11)	4e	-0.0377(1)	0.2685(2)	0.6955(3)	0.075(3)	0.100(3)	0.084(3)	0.005(2)	0.020(2)	0.026(2)
C(12)	4e	-0.0037(1)	0.2658(2)	0.6031(2)	0.061(2)	0.080(2)	0.074(2)	0.006(2)	0.011(2)	0.009(2)
C(13)	4e	0.0294(1)	0.3406(2)	0.5722(2)	0.049(2)	0.062(2)	0.055(2)	0.010(2)	-0.003(2)	0.008(2)
C(14)	4e	0.0665(1)	0.3384(2)	0.4742(2)	0.050(2)	0.057(2)	0.047(2)	0.005(2)	-0.004(2)	0.001(2)
C(15)	4e	0.0729(1)	0.2619(2)	0.4113(2)	0.058(2)	0.054(2)	0.058(2)	-0.001(1)	-0.002(2)	0.000(2)
C(16)	4e	0.1081(1)	0.2614(2)	0.3183(2)	0.065(2)	0.056(2)	0.051(2)	0.002(2)	0.002(2)	-0.008(1)
C(17)	4e	0.1374(1)	0.3370(2)	0.2867(2)	0.053(2)	0.055(2)	0.051(2)	0.004(2)	0.001(2)	0.002(2)
C(18)	4e	0.1575(1)	0.3888(2)	0.0985(2)	0.062(2)	0.054(2)	0.049(2)	0.006(2)	-0.002(2)	-0.003(2)
C(19)	4e	0.1973(1)	0.4052(2)	0.0163(2)	0.070(2)	0.071(2)	0.059(2)	0.010(2)	0.009(2)	0.007(2)
C(20)	4e	0.1827(2)	0.4586(2)	-0.0739(3)	0.105(3)	0.075(2)	0.067(2)	0.008(2)	0.017(3)	0.011(2)
C(21)	4e	0.1298(2)	0.4987(2)	-0.0814(3)	0.121(4)	0.073(2)	0.066(2)	0.016(2)	-0.004(3)	0.017(2)
C(22)	4e	0.0906(1)	0.4838(2)	0.0006(3)	0.076(3)	0.084(2)	0.078(2)	0.018(2)	-0.014(2)	0.005(2)
C(23)	4e	0.1035(1)	0.4287(2)	0.0891(2)	0.068(3)	0.068(2)	0.060(2)	0.009(2)	-0.003(2)	0.005(2)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(24)	4e	0.2112(1)	0.2598(2)	0.1837(2)	0.054(2)	0.057(2)	0.052(2)	0.003(2)	0.005(2)	0.001(2)
C(25)	4e	0.2484(1)	0.2427(2)	0.2716(2)	0.059(2)	0.065(2)	0.058(2)	−0.003(2)	−0.002(2)	0.002(2)
C(26)	4e	0.2857(1)	0.1699(2)	0.2668(3)	0.063(2)	0.090(2)	0.070(2)	0.009(2)	−0.004(2)	0.018(2)
C(27)	4e	0.2867(2)	0.1149(2)	0.1763(3)	0.082(3)	0.080(2)	0.101(3)	0.031(2)	0.017(3)	0.009(2)
C(28)	4e	0.2496(2)	0.1312(2)	0.0898(3)	0.096(3)	0.075(2)	0.080(3)	0.019(2)	0.011(3)	−0.013(2)
C(29)	4e	0.2117(1)	0.2034(2)	0.0918(2)	0.069(2)	0.069(2)	0.060(2)	0.009(2)	−0.005(2)	−0.006(2)
C(30)	4e	0.3968(1)	0.4950(2)	0.0264(2)	0.044(2)	0.051(2)	0.044(2)	0.003(1)	−0.005(2)	0.002(1)
C(31)	4e	0.3777(1)	0.5652(2)	0.0976(2)	0.052(2)	0.050(2)	0.050(2)	0.005(1)	−0.005(2)	0.005(2)
C(32)	4e	0.3938(1)	0.6555(2)	0.0758(2)	0.071(2)	0.054(2)	0.064(2)	0.008(2)	0.001(2)	−0.000(2)
C(33)	4e	0.4265(1)	0.6764(2)	−0.0132(3)	0.087(3)	0.055(2)	0.079(2)	−0.007(2)	0.004(2)	0.008(2)
C(34)	4e	0.4444(1)	0.6084(2)	−0.0842(2)	0.068(2)	0.069(2)	0.060(2)	−0.001(2)	0.006(2)	0.011(2)
C(35)	4e	0.4302(1)	0.5192(2)	−0.0658(2)	0.050(2)	0.059(2)	0.048(2)	0.005(1)	−0.001(2)	0.005(2)
C(36)	4e	0.4518(1)	0.4483(2)	−0.1414(2)	0.052(2)	0.080(2)	0.051(2)	0.008(2)	−0.000(2)	0.003(2)
C(37)	4e	0.4373(1)	0.3533(2)	−0.1168(2)	0.048(2)	0.067(2)	0.057(2)	0.006(2)	−0.004(2)	−0.011(2)
C(38)	4e	0.4568(1)	0.2847(2)	−0.1871(2)	0.070(3)	0.088(2)	0.075(2)	0.003(2)	−0.003(2)	−0.019(2)
C(39)	4e	0.4451(1)	0.1958(2)	−0.1654(3)	0.087(3)	0.094(3)	0.099(3)	0.014(2)	−0.002(3)	−0.044(2)
C(40)	4e	0.4139(2)	0.1727(2)	−0.0739(3)	0.094(3)	0.058(2)	0.109(3)	0.005(2)	−0.006(2)	−0.017(2)
C(41)	4e	0.3941(1)	0.2388(2)	−0.0034(2)	0.080(3)	0.056(2)	0.081(2)	0.005(2)	0.000(2)	−0.007(2)
C(42)	4e	0.4053(1)	0.3310(2)	−0.0240(2)	0.050(2)	0.054(2)	0.060(2)	0.006(2)	−0.009(2)	−0.005(2)
C(43)	4e	0.3836(1)	0.4029(2)	0.0492(2)	0.045(2)	0.050(2)	0.052(2)	0.003(1)	−0.004(2)	−0.001(2)
C(44)	4e	0.3510(1)	0.3839(2)	0.1396(2)	0.068(2)	0.050(2)	0.066(2)	−0.001(2)	0.010(2)	0.004(2)
C(45)	4e	0.3322(1)	0.4524(2)	0.2102(2)	0.067(2)	0.066(2)	0.062(2)	0.006(2)	0.015(2)	0.005(2)
C(46)	4e	0.3448(1)	0.5414(2)	0.1912(2)	0.060(2)	0.056(2)	0.052(2)	0.011(2)	0.003(2)	0.001(2)
C(47)	4e	0.2858(1)	0.6739(2)	0.2443(3)	0.060(3)	0.066(2)	0.048(2)	0.015(2)	−0.002(2)	0.003(2)
C(48)	4e	0.2481(2)	0.6604(2)	0.1565(3)	0.077(3)	0.083(2)	0.062(2)	0.020(2)	0.007(2)	0.002(2)
C(49)	4e	0.2052(2)	0.7244(3)	0.1340(3)	0.085(3)	0.134(3)	0.062(2)	0.030(2)	−0.018(2)	−0.001(2)
C(50)	4e	0.1993(2)	0.7987(3)	0.1988(4)	0.113(4)	0.122(3)	0.087(3)	0.063(3)	−0.001(3)	0.013(3)
C(51)	4e	0.2371(2)	0.8129(2)	0.2843(3)	0.120(4)	0.081(3)	0.084(3)	0.043(2)	−0.007(3)	−0.003(2)
C(52)	4e	0.2805(1)	0.7516(2)	0.3073(2)	0.086(3)	0.068(2)	0.069(2)	0.020(2)	−0.002(2)	−0.005(2)
C(53)	4e	0.3532(1)	0.6011(2)	0.3770(3)	0.055(2)	0.046(2)	0.064(2)	0.007(2)	−0.002(2)	0.001(2)
C(54)	4e	0.4113(2)	0.5849(2)	0.3878(3)	0.059(3)	0.056(2)	0.099(3)	0.009(2)	−0.024(3)	−0.013(2)
C(55)	4e	0.4362(2)	0.5767(2)	0.4918(5)	0.085(3)	0.062(2)	0.175(5)	0.021(2)	−0.049(4)	−0.032(3)
C(56)	4e	0.4052(3)	0.5858(3)	0.5835(4)	0.203(6)	0.063(3)	0.108(4)	0.020(4)	−0.098(5)	−0.001(3)
C(57)	4e	0.3475(2)	0.6012(2)	0.5742(3)	0.173(5)	0.074(3)	0.053(3)	−0.008(3)	−0.009(4)	0.008(2)
C(58)	4e	0.3209(1)	0.6074(2)	0.4725(3)	0.078(3)	0.076(2)	0.063(2)	−0.006(2)	−0.002(2)	0.002(2)

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