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〈Communication〉

Structural Analysis for the Single Crystal of 2-(4-(9*H*-carbazol-9-yl)benzylidene) based Dye Compound

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Abstract: The designed dye material, namely 2-(4-(9*H*-carbazol-9-yl)benzylidene) compound, was synthesized. After the reaction, the solid was filtered and purified by recrystalization with acetone/water. To confirm and analyze its synthesis and structural formation, the single crystal was prepared and its measurement was carried out. A yellow needle crystal of $C_{22}H_{13}N_3$ were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated CuKα radiation. All details were suggested and introduced to support and communicate this study.

Keywords: *carbazol, benzylidene, malononitrile, $C_{22}H_{13}N_3$, orthorhombic, single crystal*

1. Experimental details

2-(4-(9*H*-carbazol-9-yl)benzylidene) malononitrile was synthesized through the reaction of 4-(9*H*-carbazol-9-yl) benzaldehyde and malononitrile[1-4]. After the reaction, the solid was filtered and purified by recrystalization with acetone/water. Yellow needle single crystals of title compound suitable for X-ray diffraction measurement were grown by solvent diffusion method at 15°C. Dichloromethane and n-hexane were used as a good and a poor solvent, respectively. A yellow needle crystal of $C_{22}H_{13}N_3$ were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated CuKα radiation. All calculations were performed using the Crystal Structure 4.0[5] crystallographic software package except for refinement, which was performed using SHELXL-97[6-10].

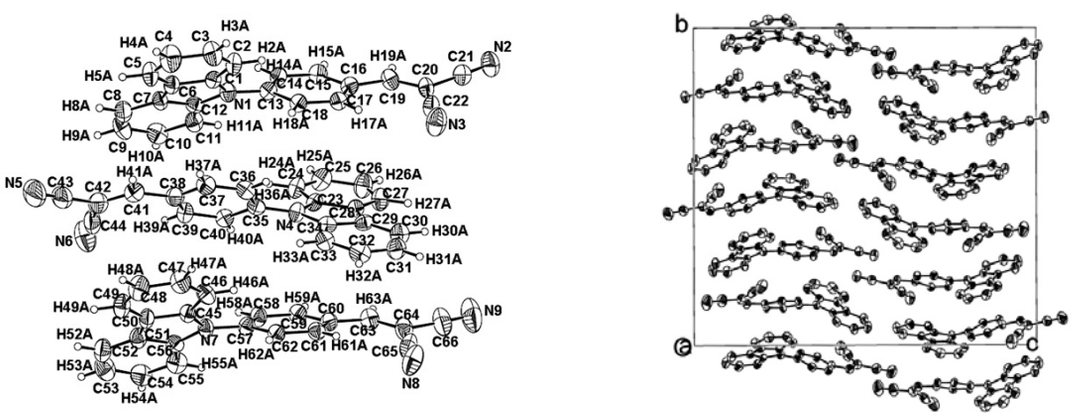

Figure 1. ORTEP diagram of 2-(4-(9*H*-carbazol-9-yl)benzylidene) malononitrile.

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All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $d(Csp^2\text{-}H)$=0.93ÅwithU_{iso}=1.04U_{eq}(parentatom).

2. Discussion and conclusions

The title crystal structure is built up from three $C_{22}H_{13}N_3$ molecules in the asymmetric unit(figure, top), with all the interatomic distances within the molecule being within normal ranges. The crystal structure contains four symmetry-equivalent molecules per unit cell, which are characterized by +X, +Y, +Z', '1/2+X, 1/2-Y, -Z', '-X, 1/2+Y, 1/2-Z' and '1/2-X, -Y, 1/2+Z'. The molecular structure shows the electro-withdrawing(maleonitrile) and electro-donating (carbazole) moieties bridged by almost planar aromatic ring, which is defined by C13, C14, C15, C16, C17, and C18. A carbazole moiety is tilted by 42.6(7)° against the almost planar bridge aromatic ring.

The π···π interaction was found between two head-to-head motif molecules. This interaction displays the usual slipped stacking geometry with the angle between the ring normal and vectors between the ring centroids is 30.32° and 37.52°. The packing schemes of the molecules are characterized a layer-by-layer arrangement, with the shortest distance between layers being about d=3.471(8)Å (figure, bottom), characteristic of a weak interaction.

Table 1. Data collection and handling

Crystal:	yellowish needle, size 0.40 × 0.10 × 0.04 mm
Wavelength:	CuK_αradiation1.54187 Å
μ:	6.00 cm^{-1}
X-ray source:	Rigaku RAXIS-RAPID, ω
2θmax:	136.3°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	47716, 9135
Criterion for I_{obs},$N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 4161
$N(param)_{refined}$:	676
Programs:	Crystal Structure 4.0[5], SIR 2004[6]

Table 2. Atomic coordinates and displacement parameters(in $Å^2$)

Atom	Site	*x*	*y*	*z*	U_{iso}
H2A	4*a*	0.1910	0.2517	0.8248	0.0781
H3A	4*a*	0.2570	0.2832	0.9101	0.0990
H4A	4*a*	0.0832	0.2771	0.9806	0.1179
H5A	4*a*	-0.1580	0.2401	0.9655	0.0943
H8A	4*a*	-0.4238	0.1927	0.9222	0.0890
H9A	4*a*	-0.6042	0.1496	0.8684	0.0977
H10A	4*a*	-0.5531	0.1277	0.7795	0.0880
H11A	4*a*	-0.3206	0.1532	0.7415	0.0790

(continued)

Atom	Site	*x*	*y*	*z*	U_{iso}
H14A	4*a*	-0.1948	0.2313	0.7031	0.0694
H15A	4*a*	-0.0784	0.2285	0.6208	0.0719
H17A	4*a*	0.3029	0.1699	0.6897	0.0649
H18A	4*a*	0.1849	0.1727	0.7727	0.0630
H19A	4*a*	0.1297	0.2193	0.5658	0.0757
H24A	4*a*	-0.1548	0.0668	0.7094	0.0780
H25A	4*a*	-0.1964	0.0792	0.6176	0.0926
H26A	4*a*	-0.0079	0.0589	0.5552	0.1001
H27A	4*a*	0.2259	0.0283	0.5832	0.0875
H30A	4*a*	0.4868	-0.0075	0.6422	0.0821
H31A	4*a*	0.6503	-0.0376	0.7086	0.0921
H32A	4*a*	0.5806	-0.0400	0.7972	0.0875
H33A	4*a*	0.3433	-0.0086	0.8239	0.0777
H36A	4*a*	0.2195	0.0800	0.8390	0.0770
H37A	4*a*	0.1005	0.0980	0.9196	0.0771
H39A	4*a*	-0.2813	0.0278	0.8618	0.0754
H40A	4*a*	-0.1611	0.0079	0.7820	0.0667
H41A	4*a*	-0.1013	0.0948	0.9764	0.0843
H46A	4*a*	0.1583	-0.0696	0.8894	0.0850
H47A	4*a*	0.1916	-0.0324	0.9756	0.0969
H48A	4*a*	0.0066	-0.0424	1.0411	0.1070
H49A	4*a*	-0.2221	-0.0858	1.0208	0.0926
H52A	4*a*	-0.4669	-0.1423	0.9729	0.0974
H53A	4*a*	-0.6295	-0.1900	0.9154	0.1116
H54A	4*a*	-0.5609	-0.2130	0.8286	0.0961
H55A	4*a*	-0.3219	-0.1871	0.7965	0.0852
H58A	4*a*	-0.2099	-0.1115	0.7595	0.0735
H59A	4*a*	-0.0872	-0.1107	0.6790	0.0715
H61A	4*a*	0.3036	-0.1464	0.7547	0.0703
H62A	4*a*	0.1782	-0.1451	0.8358	0.0671
H63A	4*a*	0.1265	-0.1192	0.6256	0.0830

(continued)

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	4*a*	-0.0856(6)	0.2042(2)	0.7978(2)	0.056(3)	0.069(4)	0.044(3)	-0.003(3)	-0.001(3)	-0.002(3)
N2	4*a*	0.3989(7)	0.2169(3)	0.4751(2)	0.106(5)	0.121(5)	0.061(4)	-0.002(4)	0.018(4)	0.009(4)
N3	4*a*	0.5507(7)	0.1476(3)	0.6302(2)	0.086(5)	0.152(6)	0.081(5)	0.036(5)	0.002(4)	0.006(4)
N4	4*a*	0.1195(5)	0.0295(2)	0.7525(2)	0.046(3)	0.070(4)	0.049(3)	0.005(3)	-0.003(3)	-0.007(3)
N5	4*a*	-0.349(1)	0.0844(3)	1.0753(3)	0.24(1)	0.135(6)	0.094(5)	-0.041(7)	0.064(6)	-0.024(5)
N6	4*a*	-0.5257(8)	0.0106(4)	0.9281(3)	0.092(6)	0.179(8)	0.117(6)	-0.029(6)	0.019(5)	0.008(5)
N7	4*a*	-0.1057(5)	-0.1265(2)	0.8566(2)	0.053(3)	0.068(4)	0.043(3)	0.008(3)	0.004(3)	0.006(3)
N8	4*a*	0.5467(8)	-0.1858(4)	0.6973(3)	0.078(5)	0.166(7)	0.115(6)	0.024(5)	0.009(5)	-0.038(5)
N9	4*a*	0.4020(9)	-0.1356(4)	0.5371(3)	0.161(7)	0.222(9)	0.095(5)	-0.042(6)	0.048(6)	-0.012(6)
C1	4*a*	-0.0210(6)	0.2261(2)	0.8449(2)	0.041(4)	0.055(4)	0.049(4)	0.005(3)	-0.004(3)	0.000(3)
C2	4*a*	0.1221(7)	0.2491(3)	0.8532(3)	0.050(4)	0.092(5)	0.053(4)	0.002(4)	0.004(4)	-0.008(4)
C3	4*a*	0.1607(8)	0.2679(3)	0.9038(3)	0.068(5)	0.113(6)	0.067(5)	-0.019(4)	-0.003(4)	-0.004(4)
C4	4*a*	0.0560(9)	0.2643(3)	0.9463(3)	0.099(6)	0.139(7)	0.057(5)	-0.018(5)	-0.011(5)	-0.024(5)
C5	4*a*	-0.0876(8)	0.2419(3)	0.9375(3)	0.071(5)	0.111(6)	0.054(4)	-0.006(4)	0.015(4)	-0.004(4)
C6	4*a*	-0.1243(7)	0.2225(3)	0.8872(2)	0.056(4)	0.063(4)	0.046(4)	0.003(4)	0.004(3)	-0.001(3)
C7	4*a*	-0.2608(7)	0.1981(3)	0.8646(3)	0.057(4)	0.066(5)	0.047(4)	0.001(4)	0.007(3)	0.007(3)
C8	4*a*	-0.4023(8)	0.1845(3)	0.8862(3)	0.070(5)	0.085(5)	0.068(4)	0.007(4)	0.011(4)	0.007(4)
C9	4*a*	-0.5096(8)	0.1588(3)	0.8540(3)	0.058(5)	0.104(6)	0.083(5)	-0.022(4)	0.007(4)	0.017(5)
C10	4*a*	-0.4798(7)	0.1461(3)	0.8004(3)	0.051(5)	0.083(5)	0.086(5)	-0.009(4)	-0.015(4)	0.005(4)
C11	4*a*	-0.3410(7)	0.1609(3)	0.7776(3)	0.048(4)	0.080(5)	0.070(4)	0.007(4)	-0.001(4)	0.010(4)
C12	4*a*	-0.2337(7)	0.1874(2)	0.8103(3)	0.048(4)	0.048(4)	0.065(4)	0.002(3)	-0.010(4)	0.011(3)
C13	4a	-0.0178(6)	0.2019(3)	0.7460(2)	0.048(4)	0.058(4)	0.051(4)	0.004(3)	-0.008(3)	0.000(3)
C14	4a	-0.0945(7)	0.2189(3)	0.7005(2)	0.058(4)	0.065(4)	0.051(4)	0.011(4)	0.001(3)	0.003(3)
C15	4a	-0.0237(7)	0.2175(3)	0.6513(2)	0.054(4)	0.076(5)	0.049(4)	0.005(4)	-0.015(3)	0.004(4)

(continued)

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C16	4a	0.1282(7)	0.2001(3)	0.6451(2)	0.064(4)	0.060(4)	0.042(3)	0.002(4)	-0.006(3)	-0.003(3)
C17	4a	0.2029(6)	0.1827(2)	0.6920(2)	0.047(4)	0.060(4)	0.055(4)	0.002(3)	-0.005(3)	0.002(3)
C18	4a	0.1319(6)	0.1840(2)	0.7419(2)	0.058(4)	0.060(4)	0.039(3)	0.009(3)	-0.007(3)	0.004(3)
C19	4a	0.1948(7)	0.2048(3)	0.5922(2)	0.064(4)	0.083(5)	0.043(3)	-0.010(4)	-0.007(3)	0.006(4)
C20	4a	0.3359(7)	0.1916(3)	0.5742(2)	0.057(4)	0.076(5)	0.044(4)	-0.008(4)	0.006(3)	-0.002(3)
C21	4a	0.3732(7)	0.2051(3)	0.5190(3)	0.060(4)	0.078(5)	0.064(4)	-0.001(4)	-0.002(4)	-0.001(4)
C22	4a	0.4542(8)	0.1672(3)	0.6060(3)	0.068(5)	0.093(6)	0.058(4)	0.006(5)	0.012(4)	-0.003(4)
C23	4a	0.0640(7)	0.0394(3)	0.7005(2)	0.045(4)	0.056(4)	0.052(4)	0.000(3)	-0.003(3)	-0.011(3)
C24	4a	-0.0787(7)	0.0589(3)	0.6843(3)	0.055(4)	0.080(5)	0.061(4)	0.006(4)	0.003(4)	-0.014(4)
C25	4a	-0.1024(8)	0.0661(3)	0.6296(3)	0.067(5)	0.091(5)	0.073(5)	0.011(4)	-0.011(4)	-0.013(4)
C26	4a	0.0116(8)	0.0541(3)	0.5919(3)	0.080(6)	0.114(6)	0.057(4)	0.007(5)	0.002(4)	-0.011(4)
C27	4a	0.1500(7)	0.0357(3)	0.6084(3)	0.056(5)	0.094(5)	0.069(5)	0.000(4)	0.004(4)	-0.004(4)
C28	4a	0.1791(7)	0.0278(3)	0.6635(3)	0.058(4)	0.055(4)	0.056(4)	-0.003(4)	0.008(4)	-0.002(3)
C29	4a	0.3105(7)	0.0099(3)	0.6936(3)	0.051(4)	0.043(4)	0.070(4)	-0.002(3)	-0.013(4)	-0.006(3)
C30	4a	0.4567(7)	-0.0079(3)	0.6783(3)	0.054(4)	0.083(5)	0.068(4)	0.002(4)	-0.007(4)	0.001(4)
C31	4a	0.5529(7)	-0.0257(3)	0.7180(3)	0.052(4)	0.084(5)	0.094(6)	0.002(4)	0.005(4)	-0.002(5)
C32	4a	0.5119(7)	-0.0266(3)	0.7715(3)	0.052(5)	0.084(5)	0.083(5)	-0.001(4)	-0.020(4)	0.009(4)
C33	4a	0.3709(7)	-0.0081(3)	0.7876(3)	0.054(4)	0.075(5)	0.064(4)	-0.004(4)	-0.007(4)	0.002(4)
C34	4a	0.2707(7)	0.0115(3)	0.7484(3)	0.053(4)	0.051(4)	0.054(4)	-0.002(3)	-0.012(4)	0.001(3)
C35	4a	0.0449(7)	0.0418(3)	0.8015(3)	0.056(4)	0.053(4)	0.058(4)	-0.004(3)	-0.007(4)	0.005(3)
C36	4a	0.1187(7)	0.0689(3)	0.8434(3)	0.062(4)	0.067(5)	0.064(4)	-0.007(4)	-0.007(4)	0.006(4)
C37	4a	0.0472(8)	0.0799(3)	0.8918(3)	0.075(5)	0.067(5)	0.050(4)	-0.011(4)	-0.010(4)	-0.008(3)
C38	4a	-0.1042(8)	0.0641(3)	0.8997(3)	0.077(5)	0.066(5)	0.051(4)	-0.000(4)	-0.000(4)	-0.002(3)
C39	4a	-0.1796(7)	0.0379(3)	0.8576(2)	0.056(4)	0.077(5)	0.056(4)	0.006(4)	0.004(4)	-0.003(4)

(continued)

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C40	4a	-0.1079(7)	0.0262(3)	0.8095(2)	0.056(4)	0.059(4)	0.052(4)	-0.000(3)	-0.007(3)	-0.003(3)
C41	4a	-0.1665(8)	0.0751(3)	0.9531(3)	0.076(5)	0.072(5)	0.063(4)	0.008(4)	-0.008(4)	-0.000(4)
C42	4a	-0.304(1)	0.0617(3)	0.9748(3)	0.092(6)	0.079(6)	0.069(5)	0.002(5)	0.005(5)	-0.001(4)
C43	4a	-0.3319(9)	0.0747(3)	1.0310(3)	0.139(7)	0.089(6)	0.076(5)	-0.017(5)	0.025(6)	-0.005(5)
C44	4a	-0.424(1)	0.0328(4)	0.9477(3)	0.069(6)	0.112(7)	0.086(6)	0.012(5)	0.026(5)	0.013(5)
C45	4a	-0.0543(7)	-0.1014(3)	0.9051(2)	0.057(4)	0.063(4)	0.040(4)	0.010(4)	-0.002(3)	0.009(3)
C46	4a	0.0833(8)	-0.0733(3)	0.9156(3)	0.071(5)	0.080(5)	0.062(4)	-0.008(4)	-0.003(4)	0.018(4)
C47	4a	0.1016(8)	-0.0514(3)	0.9670(3)	0.089(6)	0.099(6)	0.055(4)	-0.004(5)	-0.012(4)	0.001(4)
C48	4a	-0.0108(9)	-0.0568(3)	1.0065(3)	0.097(6)	0.120(7)	0.050(4)	0.009(5)	-0.011(5)	-0.007(4)
C49	4a	-0.1461(8)	-0.0830(3)	0.9948(3)	0.068(5)	0.110(6)	0.054(4)	0.016(5)	0.004(4)	0.002(4)
C50	4a	-0.1681(7)	-0.1055(3)	0.9432(3)	0.061(4)	0.073(5)	0.048(4)	0.013(4)	0.011(4)	0.004(4)
C51	4a	-0.2948(7)	-0.1349(3)	0.9186(3)	0.057(5)	0.083(5)	0.062(4)	0.016(4)	0.007(4)	0.014(4)
C52	4a	-0.4375(8)	-0.1508(3)	0.9377(3)	0.069(5)	0.105(6)	0.070(5)	0.019(5)	0.014(4)	0.008(4)
C53	4a	-0.5334(8)	-0.1795(3)	0.9031(4)	0.058(5)	0.117(7)	0.104(6)	-0.001(5)	0.003(5)	0.022(5)
C54	4a	-0.4931(8)	-0.1932(3)	0.8508(3)	0.049(5)	0.084(5)	0.107(6)	-0.005(4)	-0.013(5)	0.007(5)
C55	4a	-0.3513(7)	-0.1776(3)	0.8315(3)	0.059(5)	0.083(5)	0.071(4)	0.011(4)	-0.016(4)	0.005(4)
C56	4a	-0.2545(7)	-0.1476(3)	0.8655(3)	0.055(4)	0.057(4)	0.053(4)	0.004(4)	-0.009(4)	0.014(3)
C57	4a	-0.0305(7)	-0.1277(3)	0.8064(2)	0.056(4)	0.064(4)	0.046(4)	0.009(4)	-0.002(3)	-0.003(3)
C58	4a	-0.1058(7)	-0.1183(3)	0.7588(2)	0.068(4)	0.074(5)	0.042(4)	0.009(4)	0.003(4)	0.007(3)
C59	4a	-0.0324(7)	-0.1186(3)	0.7103(2)	0.069(5)	0.071(5)	0.039(3)	0.004(4)	-0.007(3)	0.004(3)
C60	4a	0.1230(7)	-0.1303(3)	0.7064(3)	0.064(5)	0.062(4)	0.046(4)	0.001(4)	-0.001(4)	-0.000(3)
C61	4a	0.1995(7)	-0.1395(2)	0.7552(2)	0.058(4)	0.058(4)	0.060(4)	-0.005(3)	0.000(4)	-0.002(3)
C62	4a	0.1244(7)	-0.1385(3)	0.8041(2)	0.065(4)	0.063(4)	0.039(3)	0.007(3)	-0.003(3)	0.007(3)
C63	4a	0.1902(7)	-0.1311(3)	0.6534(3)	0.064(5)	0.085(5)	0.058(4)	-0.010(4)	-0.006(4)	-0.004(4)
C64	4a	0.3302(9)	-0.1462(3)	0.6383(3)	0.063(5)	0.091(6)	0.077(5)	-0.021(5)	0.011(5)	-0.012(4)
C65	4a	0.449(1)	-0.1677(4)	0.6714(3)	0.068(6)	0.109(7)	0.092(6)	-0.007(5)	0.021(5)	-0.039(5)
C66	4a	0.3724(9)	-0.1411(4)	0.5815(4)	0.096(6)	0.147(8)	0.085(6)	-0.035(6)	0.024(5)	-0.009(6)

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References

1. X. Li, S. H. Kim, and Y. A. Son, Optical Properties of Donor-π-(accepter)n Merocyanine Dyes with Dicyanovinylindane as Acepter Group and Triphenylamine as Donor Unit, *Dyes and Pigments*, **82**, 293(2009).
2. S. Horie, M. Nagata, and J. Nakano, Electrophorographic Light-sensitive Materials, United States Patent, US 4469678, 1984.
3. M. Murakami, M. Fukuyama, M. Suzuki, and M. Hashimoto, Electroluminescent Device Containing Anthraquinone Derivative or Indandione Derivative, Japanese Kokai Tokkyo Koho JP 08097465, 1996.
4. E. Kato, Cellulose Acylate Films, their Manufacture, Optical Films, Liguid-crystal Displays, and Silver Halide Photographic Materials, Japanese Kokai Tokkyo Koho, JP 2004042381, 2004.
5. Crystal Structure 4.0, "Crystal Structure Analysis Package", Rigaku Corporation, Tokyo pp.196-8666, 2000-2010.
6. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. D. Caro, C. Giacovazzo, G. Polidori, and R. Spagna, An Improved Tool for Crystal Structure Determination and Refinement, *J. of Applied Crystallography*, **38**, 381(2005).
7. G. M. Sheldrick, A Short History of SHELX, *Acta Crystallographica Section A*, **64**, 112(2008).
8. V. V. Nesterov, M. Y. Antipin, V. N. Nesterov, and T. V. Timofeeva, Search for New Potential NLO Crystalline Materials: Chiral Derivatives of (2S)-2-(methoxymethyl)pyrrolidine, *J. of Molecular Structure*, **831**, 18(2007).
9. Crystal Structure 3.8, "Crystal Structure Analysis Package", Rigaku and Rigaku/MSC, The Woodlands, TX(USA), 1998-2007.
10. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, and M. Camalli, A Program for Automatic Solution of Crystal Structures by Direct Methods optimized for Powder Data, *J. of Applied Crystallography*, **27**, 435(1994).