Supporting Information for:

SYNTHESIS AND MOLECULAR STRUCTURE CHARACTERIZATION OF NOVEL 1,6-DIAZAHEXATRIENES

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1. General Remarks

Melting points were determined using an X-5 apparatus (open capillaries, uncorrected values).

Infrared spectra were recorded on a Bruker VERTEX70 instrument using potassium bromide pellets. All NMR experiments were recorded on a Bruker AV400 spectrometer at 400 MHz for proton NMR and 100 MHz for carbon NMR at ambient temperature (25°C). The ^1H NMR chemical shifts are expressed in ppm relative to tetramethylsilane (TMS), and the ^{13}C NMR chemical shifts were referenced to the triplet of CDCl_3 (δ : 77 ppm). The complete ^1H and ^{13}C NMR chemical shift assignments were obtained using 2D NMR techniques, such as COSY. Mass spectra were recorded on a Bruker Esquire 6000 mass spectrometer. The X-ray data were measured with graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Rigaku RAXIS RAPID IP diffractometer at ambient temperature.

2. Procedures for 1,6-diazahexatriene Synthesis

An ice cooled mixture of activated (heated at 100°C in a hot-air oven for about 24 h) Na_2CO_3 (105.99, 2.12 g, 20.00 mmol), ethyl 3-(2-methyl-2-phenylhydrazinyl)propanoate (222.23, 2.20 g, 10.00 mmol), Na_2SO_4 (142.06, 2.84 g, 20.00 mmol) and 10 ml of dried dioxane in 100 ml, round-bottomed flask was stirred magnetically under nitrogen. The stirring was continued, and the progress of the reaction was monitored by TLC. Most of the reactants had disappeared in about 1 h. However, the reaction mixture was stirred for a total period of 2 h. Then, the precipitated solid was collected by filtration and chromatographed on a silica-gel column by using 1:10, 2:9, and 3:7 mixtures of ethyl acetate and petroleum ether to get 2.66 g of 4.36 g (6.10 mmol, 61%).

By using the above protocol 1,6-diazahexatrienes(**1a-d**) were prepared and their yields were placed in the table-2 in %. The analytical data for all these compounds is depicted bellow.

3. Analytical data of the compounds(**1a-d** and **3d**)

Diethyl (E)-2,3-bis(methylidene-2,2-N-methyl-N-phenylamino)fumarate (1a). Red solid; mp 159.2-160.9 °C; ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.37 (t, J = 7.2 Hz, 6H, -CH₃), 3.40 (s, 6H, -CH₃), 4.38 (m, J = 7.2 Hz, 4H, -CH₂), 6.98 (m, J = 8.0 Hz, 2H, Ar-H), 7.31 (m, J = 8.0 Hz, 8H, Ar-H), 7.63 (s, 2H, -CH); ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 14.3, 33.4, 61.4, 115.9, 121.7, 128.6, 128.9, 131.1, 147.1, 167.3; HRMS (ESI+) m/z calcd 437.2183 for C₂₄H₂₉N₄O₄ [M]⁺, found 437.2178.

Diethyl (E)-2,3-bis(methylidene-2,2-N-ethyl-N-phenylamino)fumarate (1b). Red solid; mp 154.3-156.1 °C; ¹H NMR (400 MHz, δ, ppm): 1.28 (t, J = 8.0 Hz, 6H, -CH₃), 1.36 (t, J = 7.2 Hz, 6H, -CH₃), 3.99 (m, J = 8.0 Hz, 4H, -CH₂), 4.38 (m, J = 7.2 Hz, 4H, -CH₂), 6.98 (t, J = 7.2 Hz, 2H, Ar-H), 7.30 (m, J = 7.2 Hz, 8H, Ar-H), 7.70 (s, 2H, -CH); ¹³C NMR (100 MHz, δ, ppm): 10.0, 14.3, 40.3, 61.3, 115.4, 121.5, 128.1, 129.0, 131.2, 146.1, 167.3; HRMS (ESI+) m/z calcd 465.2496 for C₂₆H₃₃N₄O₄ [M]⁺, found 465.2494.

Diethyl (E)-2,3-bis(methylidene-2,2-diphenylamino)fumarate (1c). Red solid; mp 183.5-185.6 °C; ¹H NMR (400 MHz, δ, ppm): 1.10 (t, J = 8.0 Hz, 6H, -CH₃), 4.15 (m, J = 8.0 Hz, 4H, -CH₂), 7.06 (d, 8H, Ar-H), 7.12 (t, 4H, Ar-H), 7.21 (t, 8H, Ar-H), 7.40 (s, 2H, -CH); ¹³C NMR (100 MHz, δ, ppm): 14.1, 61.3, 122.5, 125.1, 129.7, 132.0, 132.4, 142.7, 166.8; HRMS (ESI+) m/z calcd 561.2493 for C₃₄H₃₃N₄O₄ [M]⁺, found 561.2491.

2'-substituted 3-(2,2-dimethylhydrazinyl)propanenitrile (3d). Red solid; mp 186.6-187.3 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.82 (s, 6H), 3.30 (d, J = 4.4 Hz, 2H), 3.30 (t, J = 4.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 21.9, 42.6, 117.0, 121.2.

2,3-Bis((E)-(2,2-dimethylhydrazono)methyl)fumaronitrile (1d).

Red solid; mp 204.2-206.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 3.17 (s, 12H), 7.11 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 42.8, 114.5, 116.4, 124.2; HRMS (ESI+) m/z calcd 218.1280 for C₁₀H₁₄N₆ [M]⁺, found 218.1267.

4. ¹H NMR and ¹³C NMR spectra of the compounds 1a-d and 3d:

Figure 1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **1a**

Figure 2. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **1a**

Figure 3. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **1b**

Figure 4. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **1b**

Figure 5. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **1c**

Figure 6. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **1c**

Figure 7. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **3d**

Figure 8. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **3d**

Figure 9. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **1d**

Figure 10. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **1d**

5. X-ray diffraction data

The X-ray data were measured with graphite-monochromatized Mo $k\alpha$ radiation ($\lambda = 0.71073$ Å) on a Rigaku RAXIS RAPID IP diffractometer at ambient temperature. The structure was solved by direct methods (SHELXS-97). The structure refinement employed a full-matrix least-squares refinement on F² using SHELXL-97. All of the non-hydrogen atoms were refined with anisotropic displacement parameters. All of the hydrogen atoms were fixed in positions of ideal geometry and refined isotropically based on the corresponding C atoms [$U(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$]. The structure refinement parameters for **1a** are provided in Table 1. The crystallographic data for **1a** were deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 775905. The structure refinement parameters for **1d** are provided in Table 2. The crystallographic data for **1d** were deposited with the Cambridge Crystallographic Data Centre under deposition number CCDC 935136 and 920466.

Table 1. Crystal data and structure refinement of **1a**.

Crystal	1a
Empirical formula	C ₂₄ H ₂₈ N ₄ O ₄
Formula weight	436.50
Temperature	113(2)K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 15.922(3) Å b = 8.0335(16) Å c = 18.655(4) Å
	$\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$
Volume	2386.2(8) Å ³
Z	4
Calculated density	1.215 Mg m ⁻³
Absorption coefficient	0.084 mm ⁻¹
F(000)	928
Crystal size	0.20×0.10×0.08 mm ³
θ range for data collection	2.53 - 25.01°
Index ranges	-15 ≤ h ≤ 18, -9 ≤ k ≤ 9, -22 ≤ l ≤ 22
Reflections collected/unique	14849/2093
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2093/64/165
Goodness of fit on F ²	1.068
Final R indices I>2σ(I)	R ⁱ =0.0578, wR ² =0.1644
R indices (all data)	R ⁱ =0.0546, wR ² =0.1644
Extinction coefficient	0.045(6)
Largest diff. peak and hole	0.516 and -0.514 eÅ ⁻³

Table 2. Crystal data of **1d-E** and **1d-Z**

Crystal	1d-E	1d-Z
Empirical formula	C ₁₀ H ₁₄ N ₆	C ₁₀ H ₁₄ N ₆
Formula mass	218.27	218.27
Colour, habit	Colorless, Prism	Colorless, Prism
Crystal dimensions (mm)		
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ /c	<i>Pbca</i>
<i>Z</i>	2	8
<i>a</i> (Å)	14.514(5)	14.161(4)
<i>b</i> (Å)	11.219(4)	7.870(2)
<i>c</i> (Å)	7.357(2)	20.497(6)
α (°)	90.00	90.00
β (°)	101.164(5)	90.00
γ (°)	90.00	90.00
Collection ranges	-19 ≤ <i>h</i> ≤ 19, -14 ≤ <i>k</i> ≤ 14, -9 ≤ <i>l</i> ≤ 9	-18 ≤ <i>h</i> ≤ 17, -10 ≤ <i>k</i> ≤ 10, -26 ≤ <i>l</i> ≤ 26
Temp (K)	113(2)	113(2)
Volume (Å ³)	1175.2(7)	2284.3(11)
<i>D</i> _{calc} (Mg m ⁻³)	1.234	1.269
Radiation	Mo Kα (<i>λ</i> =0.71073 Å)	Mo Kα (<i>λ</i> =0.71073 Å)
Absorption coeff. (μ) (mm ⁻¹)	0.082	0.085
Absorption correction	MULTI-SCAN	MULTI-SCAN
<i>F</i> (000)	464	928
θ range for data collection (°)	2.3–27.9	1.7–27.9
Observed reflections	12004	21645
Independent reflections	2804	2715
Data/restraints/parameters	2804/0/149	2715/2/155
Goodness-of-fit on <i>F</i> ²	1.037	1.043
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ =0.0715, <i>wR</i> ₂ =0.1114	<i>R</i> ₁ =0.0440, <i>wR</i> ₂ =0.1000
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0514, <i>wR</i> ₂ =0.1026	<i>R</i> ₁ =0.0355, <i>wR</i> ₂ =0.0956