

Single Crystal X-ray Structure Determination of N,N'-di(9-ethyl-9H-carbazole-3-yl)hydrazine[†]

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Abstract

The structure of N,N'-di(9-ethyl-9H-carbazole-3-yl)hydrazine has been determined by single crystal X-ray crystallography. No $\pi \cdots \pi$ interactions were observed among the molecules. The crystal packing is stabilized only by the weak $\pi \cdots H-C$ interactions. The calculated values of the bond lengths and bond angles have been compared with those obtained from X-ray diffraction analyses. There is a good agreement between experimental and calculated values of the data, except the N1-N1' bond length and the angles around these atoms in the molecule.

Keywords: Dicarbazolyldiazine, X-ray diffraction, AM1 calculations

N,N'-di(9-etil-9H-karbazol-3-il)hidrazinin Tek Kristal X-Işını Yapı Tayini

Özet

N,N'-di(9-etil-9H-karbazol-3-il)hidrazinin yapısı tek kristal X-ışını kristalografisi ile belirlenmiştir. Moleküller arası $\pi \cdots \pi$ etkileşimi gözlenememiştir. Kristal paketlenmesi sadece zayıf $\pi \cdots H-C$ etkileşimleriyle kararlaştırılmıştır. Hesaplanan bağ uzunlukları ve bağ açıları X-ışını kırınım analizinden elde edilen değerlerle karşılaştırılmıştır. Molekülde N1-N1' bağ uzunlukları ve bu atomlar etrafındaki bağ açılarının dışındaki diğer deneysel ve hesaplanan değerler arasında iyi bir uyum görünmektedir.

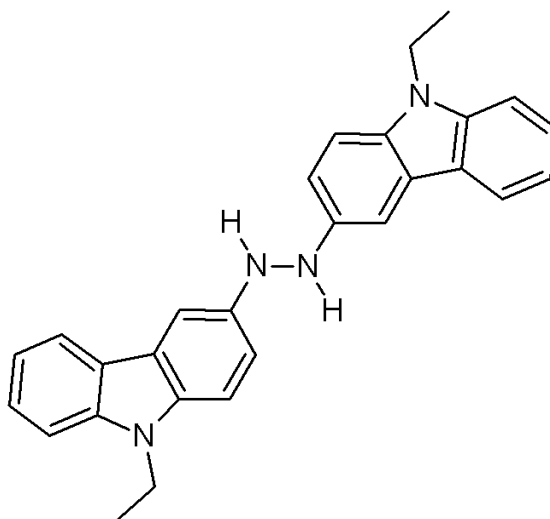
Anahtar kelimeler: Dikarbazolilhidrazin, X-ışını kırınımı, AM1 hesaplamaları.

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1. Introduction

Amine derivatives of carbazoles are important mainly for their biological activities and also for their semiconductor properties. For example 3-amino-9-ethylcarbazole has been widely used as a peroxidase suitable for the colorimetric detection of antibodies for the diagnosis of certain diseases [1-4]. Both polymeric and molecular amorphous derivatives of 3-aminocarbazoles have attracted interest of the researchers due to their semiconductive properties [5-9]. Requirements for a compound to be used as a hole-transporting material includes thermal, physical, and photo stability, ability to form good films and having a low ionization potential [10]. Electron rich aminocarbazole derivatives make good candidates for hole-transporting materials. In low molecular organic molecules with conjugated π -systems geometry of the chromophore groups plays an important role on the electronic and physical properties. Therefore, it is important to understand the molecular structures of these compounds. Our research group particularly interested in synthesizing and determining the thermal and photophysical properties of low molecular weight carbazole based imine compounds. In the progress of our research we have unintentionally obtained *N,N'*-di(9-ethyl-9*H*-carbazole-3-yl)hydrazine (**1**), (Scheme 1). Herein, we report the synthesis and the results of the single crystal X-ray diffraction analysis and AM1 calculations of this compound.



Scheme 1. Molecular structure of *N,N'*-di(9-ethyl-9*H*-carbazole-3-yl)hydrazine

2. Experimental

2.1. Synthesis and characterization

The melting points were determined on a STUART SMP3 melting point apparatus. The UV-vis spectra were recorded on a PG Instruments T70 UV-Visible spectrophotometer. The IR spectra were measured on a PerkinElmer BX 2 FT-IR spectrometer in KBr pellets. ^1H NMR spectra were recorded on a Varian Mercury spectrometer with TMS as the internal standard.

N,N'-Di(9-ethyl-9*H*-carbazole-3-yl)hydrazine (**1**) was obtained as the decomposition product of 3-amino-9-ethylcarbazole (Aldrich) in ethanol/tetrahydrofuran (THF) mixture. Pale yellow prisms, mp. 146 °C.

FT-IR [KBr, ν_{\max} (cm⁻¹): 3443 (ArN–H), 3048 (Ar–H), 2967 (–CH₃), 2929 (–CH₂–), 1626, 1614, 1596 (Ar–N), 1490, 1472, 1447 (Ar C=C), 1132, 1120 (ArN–NAr); ¹H NMR (300 MHz, CDCl₃, ppm): 1.41 (t, $J = 7.0$ Hz, 6H, CH₃), 4.31 (q, $J = 7.0$ Hz, 4H, CH₂ CH₃), 7.20–7.60 (m, 10H, ArH), 8.05–8.25 (m, 4H, ArH), 8.68 (s, NH), 8.81 (s, NH). UV-Vis, [EtOH, λ_{\max} (nm), (ϵ)] = 299 (55100), 352 (40600), 379 (35600).

Single crystals of **1** suitable for the X-ray diffraction studies were grown by recrystallization from benzene by slow evaporation technique at ambient temperature.

2.2. Single crystal X-ray diffraction work.

The single crystal X-ray measurements were carried out on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation with $\lambda = 0.71070$ Å. The structure of **1** was solved using SIR-92 [11] structure solution software with direct methods. The refinement procedure for the structures involved full-matrix least-squares on F^2 using SHELXL-97 [12] embedded in WinGX [13] programs system. All H atoms were fixed geometrically and allowed to ride on their corresponding parent atoms with C–H distances of 0.93 Å (aromatic), 96 Å (methyl) and 0.97 Å (methylene) and N–H distance of 0.86 Å with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ of the parent atom for the methyl groups and $1.2U_{\text{eq}}(\text{C/N})$ for the remainder. The summary of crystal data and the details of data processing are given in Table 1 and the final fractional atomic coordinates in Table 2.

Table 1 Summary of general and crystal data with data collection and structure refinement of **1**.

| Compound | 1 | | |
|--|---|--|---------------------------------------|
| Empirical formula | C ₂₈ H ₂₆ N ₄ 2(C ₆ H ₆) | Absorption coefficient (mm ⁻¹) | 0.069 |
| Formula weight | 574.74 | $F(000)$ | <u>612</u> |
| Temperature (K) | 293(2) | Crystal size (mm) | 0.6 × 0.4 × 0.1 |
| Wavelength (Å) | <u>0.71073</u> | θ range for data collection (°) | 2.76–25.10 |
| Crystal system | Monoclinic | Index ranges | |
| Space group | <u>$P2_1/n$</u> | h | -18–17 |
| Unit cell dimensions | | k | 0–6 |
| a (Å) | <u>15.3311(10)</u> | l | 0–22 |
| b (Å) | <u>5.6760(3)</u> | Reflections collected/unique | 2574/2573 [$R(\text{int}) < 0.001$] |
| c (Å) | <u>19.4249(2)</u> | Refinement method | Full-matrix least squares on F^2 |
| β (°) | <u>105.952(3)</u> | Data/restraints/parameters | 2573/0/89 |
| Volume (Å ³) | <u>1625.25(14)</u> | Goodness-of-fit on F^2 | 1.465 |
| Z | 2 | Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.1221$, $wR_2 = 0.227$ |
| Calculated density (Mg m ⁻³) | <u>1.174</u> | Largest diff. peak and hole (e Å ⁻³) | 0.157 and -0.206 |

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of the non-hydrogen atoms for structure **1**.

| <i>Structure 1</i> | | | | |
|--------------------|-----------|-------------|-------------|-------------------|
| Atom | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{(eq)}}$ |
| N1 | 0.9707(3) | -0.0111(9) | 0.97080(19) | 0.0869(13) |
| N9 | 0.6578(2) | 0.5203(7) | 0.86495(19) | 0.0652(10) |
| C1 | 0.8058(3) | 0.4843(9) | 0.9594(2) | 0.0695(12) |
| C2 | 0.8819(3) | 0.3440(9) | 0.9823(2) | 0.0702(13) |
| C3 | 0.8926(3) | 0.1386(8) | 0.9463(2) | 0.0626(11) |
| C4 | 0.8276(3) | 0.0729(8) | 0.8854(2) | 0.0652(12) |
| C4A | 0.7497(3) | 0.2106(8) | 0.8613(2) | 0.0602(11) |
| C4B | 0.6685(3) | 0.1901(8) | 0.8014(2) | 0.0595(11) |
| C5 | 0.6390(3) | 0.0277(9) | 0.7465(2) | 0.0713(13) |
| C6 | 0.5561(3) | 0.0581(10) | 0.6985(3) | 0.0808(14) |
| C7 | 0.5020(3) | 0.2483(10) | 0.7042(3) | 0.0821(15) |
| C8 | 0.5292(3) | 0.4135(9) | 0.7575(2) | 0.0721(13) |
| C8A | 0.6137(3) | 0.3832(8) | 0.8067(2) | 0.0615(11) |
| C9A | 0.7392(3) | 0.4139(8) | 0.8986(2) | 0.0579(11) |
| C10 | 0.6164(3) | 0.7085(9) | 0.8960(3) | 0.0739(13) |
| C11 | 0.5699(4) | 0.6180(12) | 0.9499(3) | 0.1047(19) |
| C12 | 0.7478(8) | 0.0228(18) | 1.0922(4) | 0.138(3) |
| C13 | 0.6676(6) | 0.0455(14) | 1.1076(5) | 0.137(3) |
| C14 | 0.6425(5) | -0.1116(17) | 1.1503(4) | 0.122(2) |
| C15 | 0.6977(7) | -0.2868(15) | 1.1783(4) | 0.128(3) |
| C16 | 0.7780(7) | -0.3103(16) | 1.1635(5) | 0.139(3) |
| C17 | 0.8036(6) | -0.153(2) | 1.1203(5) | 0.132(3) |

2.3. Theoretical calculations.

The geometries of **1** were initially pre-optimized by applying molecular-mechanics method [14] using MM+ force field [15]; fully optimization was performed using semi-empirical Austin Model 1 (AM1) methods [16] implemented in the HyperChem 8.02 molecular modeling software [17]. The Polak-Ribiere conjugated gradient algorithm was used for the energy minimizations. Convergence to a local minimum was achieved when the energy gradient was $\leq 0.01 \text{ kcal.mol}^{-1}$.

3. Results and Discussion

The structure of **1** (Figure I) was solved in the monoclinic space group $P2_1/n$. The asymmetric unit contains one benzene and one-half N,N'-di(9-ethyl-9*H*-carbazole-3-yl)hydrazine molecules in the structure of **1** where the other half is generated by a center of inversion, which lies at the midpoint of N1–N1ⁱ bond. The selected bond lengths, bond angles and torsion angles are given in Table 3. The bond lengths and angles of the carbazole skeletons are comparable to those of related molecules reported in the literature [18,19] The shortest bonds in the six-membered rings of the carbazole units were C1–C2 and C7–C8. This was attributed to the electron releasing ability of hydrazine nitrogen. The C4a–C4b bond of the pyrrolic ring is longest [1.446(8) Å in **1**]. The N1–N1ⁱ bond length of 1.253(10) Å is found to be ~ 0.1 Å shorter than regular hydrazines [20-22].

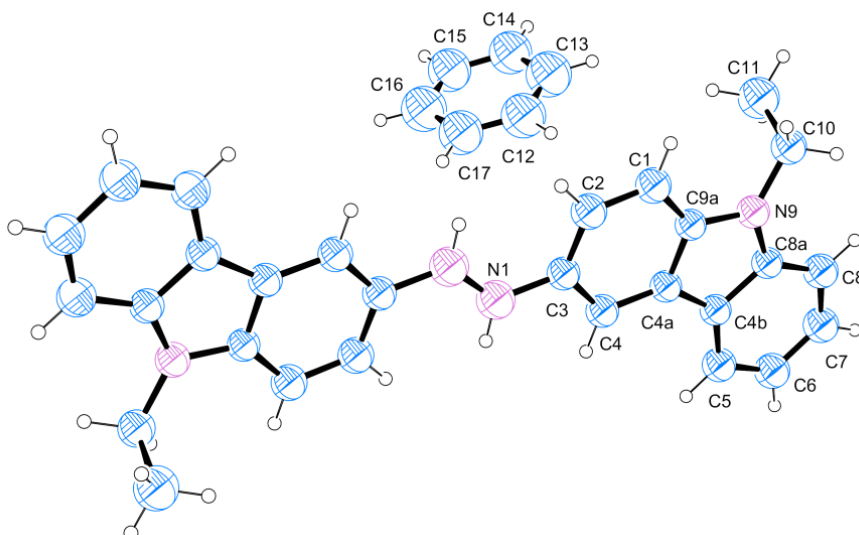


Fig 1. ORTEP drawing of the structure of **1** with atom numbering scheme (displacement ellipsoids drawn at the 35% probability level; arbitrary spheres for the H atoms; unlabeled atoms are related to labeled atoms by $(-x+2, -y, -z+2)$).

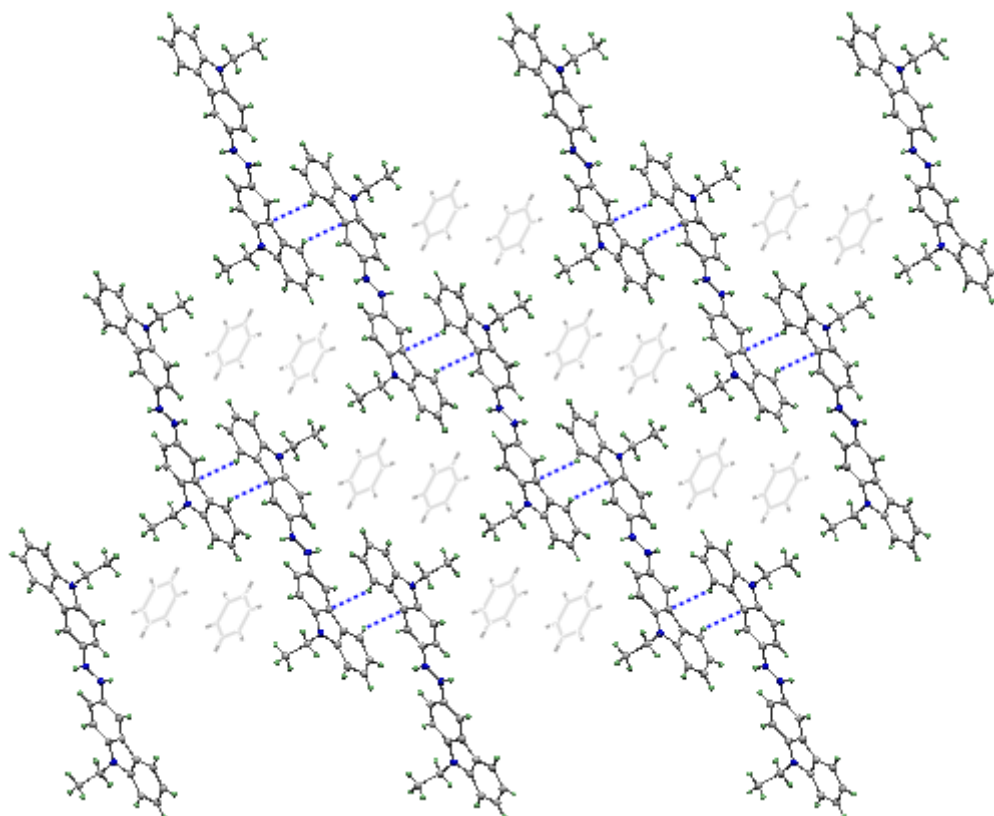


Fig 2. Molecular packing diagram of structure **1** (dashed cyan lines represent C–H \cdots π bonds).

The carbazole and benzene skeletons are essentially planar with r.m.s deviations of 0.018Å (labeled carbazole ring), 0.019Å (unlabeled carbazole ring) and 0.009Å (benzene ring) in structure **1**. The dihedral angle of 0.01(20)° between the planes of the carbazole groups in **1** is a clear indication of the coplanar geometry; the benzene ring is

almost perpendicular to the neighboring carbazole ring as indicated by the dihedral angle of $89.24(22)^\circ$ between their respective planes. The ethyl groups stay out of the planes of the carbazole groups and point opposite directions as indicated by the $C8a-N9-C10-C11$ and $C9a-N9-C10-C11$ torsion angles (Table 3). Protrusion of the ethyl groups is also observed in **1** and other N-ethylcarbazole derivatives reported in the literature, possibly, to avoid any short contacts among hydrogens of ethyl group and H1 and H8 of the carbazole ring. Unsurprisingly, there is no significant overlap of the π -rings observed, since the lone pair electrons of the connector N-atoms are contributed to the related π -systems. The only force that stack the molecules appears to be weak intermolecular $C-H\cdots\pi$ interactions (Figure 2) between C4a–H5 with the inter-atomic distance of $2.785(6)\text{\AA}$.

Table 3 Selected experimental and calculated (AM1) bond lengths (\AA), bond and torsion angles ($^\circ$) for structure of **1**.

| Structure of 1 | X-ray | AM1 | | X-ray | AM1 |
|---------------------------|-----------|--------|---------------------------|-----------|-------|
| N1–N1 ⁱ | 1.245(7) | 1.398 | N1–C3 | 1.438(6) | 1.441 |
| N9–C8a | 1.387(5) | 1.415 | N9–C9a | 1.379(5) | 1.415 |
| C4a–C9a | 1.395(6) | 1.444 | C4b–C8a | 1.402(6) | 1.446 |
| C7–C8 | 1.374(7) | 1.393 | C1–C2 | 1.380(6) | 1.391 |
| C4a–C4b | 1.456(6) | 1.453 | N9–C10 | 1.456(6) | 1.438 |
| N1 ⁱ –N1–C3 | 124.6(6) | 114.4 | C4–C3–N1 | 117.7(4) | 120.1 |
| C1–C2–C3 | 121.8(4) | 121.8 | C2–C3–N1 | 122.1(4) | 119.9 |
| C8–C7–C6 | 121.9(5) | 121.7 | C2–C3–C4 | 120.2(4) | 119.7 |
| C9a–N9–C10 | 124.5(4) | 122.9 | C8a–N9–C10 | 125.4(4) | 123.0 |
| C1–C2–C3–N1 | –178.6(4) | –173.8 | N1 ⁱ –N1–C3–C4 | –171.2(6) | 124.9 |
| N1 ⁱ –N1–C3–C2 | 8.8(9) | –60.8 | C10–N9–C9a–C4a | 167.5(4) | 156.4 |
| C9a–N9–C10–C11 | –78.3(6) | –72.8 | C8a–N9–C10–C11 | 85.2(5) | 73.5 |

Symmetry code: (i) $-x+2, -y, -z+2$.

The experimentally obtained bond lengths, angles and torsion angles were compared to those obtained by AM1 theoretical calculations [16] (Table 3). The largest differences observed between experimental and calculated bond lengths in **1** were N1–N1ⁱ (0.153\AA), C4a–C9a (0.049\AA), C4b–C8a (0.044\AA), and N9–C9a (0.036\AA). The calculated value of N1–N1ⁱ bond length [$1.245(7)\text{\AA}$] and N1ⁱ–N1–C3 bond angle [$124.6(6)^\circ$] indicate that hydrazine nitrogens are sp^2 hybridized; the calculated values for the same bond length and angle suggest that these atoms are sp^3 hybridized. This notion was also supported by N1ⁱ–N1–C3–C2 measured torsion angle of $8.8(9)^\circ$ compared to the calculated angle of -60.8° . The simple linear regression analysis between X-ray and AM1 data for the bond lengths of structure **1** generated a correlation coefficient of $r = 0.926$ (N1–N1ⁱ bond excluded). The correlation coefficients between X-ray and AM1 data for the bond angles were found to be $r = 0.934$. These correlation coefficients indicate that the experimental and theoretical values of the bond lengths and angles are in a fairly good agreement. In the crystal structure the benzene molecules crystallized

with N,N'-di(9-ethyl-9H-carbazole-3-yl)hydrazine did not cause major changes in the molecular geometry, since they did not involve very much in the crystal packing.

In dimeric N-ethyl carbazoles there are two possible conformational isomers available based on the position of the ethyl substituents. The methyl ends of the ethyl substituents may point the same [23a] or the opposite [23b] directions (as in structure 1). The binding energies calculated for both of these conformations indicate that there is only a slight energy difference (0.02 kcal.mol⁻¹) favoring the opposite directional alignment of ethyl substituents.

4. Conclusion

The comparison of the experimentally obtained data with the calculated data reveals that the solvent (benzene) molecules crystallized with N,N'-di(9-ethyl-9H-carbazole-3-yl)hydrazine did not cause major changes in the bond lengths and angles of carbazole skeletons. The most notable difference between the calculated (AM1) and experimental (X-ray) values of the bond length and angles are the ones involving the hydrazinic nitrogen atoms.

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