

Crystal structure of a substituted pyranocarbazole alkaloid N-allyl girinimbine

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Abstract. The crystal structure of a substituted pyranocarbazole alkaloid has been determined by X-ray diffraction method on a single crystal using MoK_α radiation. The compound crystallizes in the monoclinic system with the space group $P2_1/c$ and $Z=4$. The unit cell dimensions are $a=5.521(1)$, $b=15.314(2)$, $c=19.989(2)$ Å and $\beta=93.19(1)^\circ$. The structure was solved by direct methods and refined by full-matrix least squares to a final R value of 0.063 with 1551 ‘observed’ reflections. The molecule is not quite planar. The carbazole moiety adopts a slight boat conformation; the dihedral angle between the two six-membered rings is $3.9(2)^\circ$. The pyran ring is not planar and makes an angle of $5.2(3)^\circ$ with the plane of the carbazole moiety. The N(1)–C(19) bond distance is slightly shorter than the single C–N bond value.

Introduction

Substituted Δ^3 -pyran systems, under thermal condition racemise and undergo interesting photochemical rearrangements (Narashimnan and Kelkar, 1976). The title compound was prepared to investigate the photochemical transformations or rearrangements of N-substituted pyranocarbazole ring systems. The lone pair of electrons of the hetero nitrogen

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Table 1. Crystallographic data and experimental parameters for data collection.

Molecular formula	C ₂₁ H ₂₁ NO
<i>M_r</i>	303.40
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	5.521(1)
<i>b</i> (Å)	15.314(2)
<i>c</i> (Å)	19.989(2)
β (deg)	93.19(1)
<i>V</i> (Å ³)	1687.4(4)
<i>Z</i>	4
Density (calculated) (gm · cm ⁻³)	1.206
Density (measured) (gm · cm ⁻³)	1.203
Radiation (λ)	MoK α (0.71073 Å)
μ (MoK α) (cm ⁻¹)	0.68
Temperature (K)	295
Scan type	ω -2 θ
Collection range (deg)	0 \leq 2 θ \leq 45
Standard reflections	102; 024
Number of unique data	2162
Number of data with $I > 3\sigma(I)$	1551
Number of variables	208
<i>R</i>	0.063
<i>R_w</i>	0.063
<i>F</i> (000)	648

atom appears to play some vital role in governing the course of the photorearrangement. The analysis was undertaken to characterize the compound structurally and to investigate the effects of N-substitution on the pyranocarbazole system.

Experimental

Needle shaped crystals were grown from benzene by slow evaporation at room temperature. Preliminary oscillation and Weissenberg photographs indicated a monoclinic system with systematic absences: $0k0:k = \text{odd}$; $h0l:l = \text{odd}$, consistent with the space group *P*2₁/*c*. A crystal of dimensions about 0.16 × 0.20 × 0.30 mm was selected for the intensity data collection on a Enraf-Nonius CAD-4 diffractometer using graphite monochromatized MoK α radiation. The accurate cell parameters were determined by a least-squares refinement of the setting angles of 25 reflections. Intensities of all reflections were measured over the range of 0 \leq 2 θ \leq 45° using ω -2 θ scan technique. A total of 2162 unique reflections were measured of which 1551 had $I > 3\sigma(I)$ and were used for the structure determination and refinement. Corrections for the Lorentz and polarization factors were applied to the intensity values but no absorption correction was made. During the data

Table 2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) with their e.s.d's in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
O(1)	0.4779(6)	0.4199(2)	0.3228(2)	47(1)
N(1)	-0.1665(7)	0.4123(3)	0.1426(2)	40(1)
C(1)	-0.2096(9)	0.3503(3)	0.0924(2)	40(1)
C(2)	-0.3944(9)	0.3478(4)	0.0423(3)	41(1)
C(3)	-0.3959(10)	0.2787(4)	-0.0013(3)	45(1)
C(4)	-0.2192(11)	0.2137(4)	0.0034(3)	45(1)
C(5)	-0.0370(10)	0.2162(3)	0.0536(3)	42(1)
C(6)	-0.0320(9)	0.2847(3)	0.0998(2)	48(1)
C(7)	0.1221(9)	0.3078(3)	0.1577(2)	44(1)
C(8)	0.3185(9)	0.2666(3)	0.1905(2)	56(2)
C(9)	0.4333(9)	0.3025(3)	0.2473(2)	48(1)
C(10)	0.3455(8)	0.3830(3)	0.2696(2)	47(1)
C(11)	0.1534(8)	0.4291(3)	0.2375(2)	56(2)
C(12)	0.0378(8)	0.3873(3)	0.1819(2)	60(2)
C(13)	0.1119(10)	0.5179(4)	0.2608(3)	47(1)
C(14)	0.2097(9)	0.5444(3)	0.3192(3)	59(2)
C(15)	0.3531(9)	0.4819(3)	0.3642(3)	53(2)
C(16)	0.1898(10)	0.4314(4)	0.4087(3)	70(2)
C(17)	0.5563(9)	0.5279(3)	0.4038(3)	47(1)
C(18)	0.6479(9)	0.2597(3)	0.2841(3)	54(1)
C(19)	-0.3239(9)	0.4864(4)	0.1526(3)	59(2)
C(20)	-0.2488(12)	0.5677(4)	0.1171(3)	54(2)
C(21)	-0.0704(13)	0.5764(4)	0.0799(3)	80(2)

collection two standard reflections (Table 1) were used to monitor the centering and the stability of the crystal. No significant change in intensity (maximum variation $\pm 1\%$) was observed. Table 1 shows the crystallographic data and experimental parameters for data collection.

Structure determination and refinement

The structure was solved by direct methods using the program SHELX 86 (Sheldrick, 1985). All the non-hydrogen atoms were obtained from the E-map. Full-matrix least-squares refinement (SHELX 76; Sheldrick, 1976), first using isotropic and then anisotropic thermal parameters gave a *R* value of 0.086. An attempt was made to locate the hydrogen atom positions through a difference electron density synthesis. Only 12 hydrogen atoms were located from the difference Fourier map. Other hydrogen atom positions were calculated from the geometrical considerations. These hydrogen atom positions were included in the subsequent cycles of refinement with their coordinates held invariant and with $U_{\text{iso}} = 0.05 \text{ \AA}^2$ assigned to each hydrogen atom. The refinement was stopped at $R = 0.063$ when all the least-

Table 3. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters of hydrogen atoms, $U_{\text{iso}} = 0.05 \text{ \AA}^2$ for all H atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	-0.5195	0.3935	0.0382
H(3)	-0.5244	0.2738	-0.0364
H(4)	-0.2212	0.1660	-0.0292
H(5)	0.0894	0.1701	0.0573
H(8)	0.3770	0.2109	0.1735
H(13)	0.0092	0.5574	0.2335
H(14)	0.1893	0.6047	0.3334
H(16)1	0.0530	0.4074	0.3825
H(16)2	0.1214	0.4693	0.4417
H(16)3	0.2679	0.3845	0.4323
H(17)1	0.6922	0.5557	0.3762
H(17)2	0.6365	0.4873	0.4345
H(17)3	0.4927	0.5740	0.4302
H(18)1	0.8145	0.2988	0.2802
H(18)2	0.6082	0.2449	0.3353
H(18)3	0.6619	0.1961	0.2823
H(19)1	-0.4887	0.4718	0.1377
H(19)2	-0.3277	0.4990	0.2000
H(20)	-0.3482	0.6195	0.1220
H(21)1	-0.0301	0.6437	0.0566
H(21)2	0.0592	0.5150	0.0675

squares shifts were less than the corresponding standard deviations (shift/ $\sigma < 0.08$). The function minimized was $\Sigma \omega (|F_o| - |F_c|)^2$ with $\omega = 1/(\sigma^2 |F_o|)$. A final difference Fourier synthesis showed peaks lying between -0.27 to 0.19 e\AA^{-3} . The geometrical parameters of the molecule were computed with the program PARST (Nardelli, 1983).¹

Results and discussions

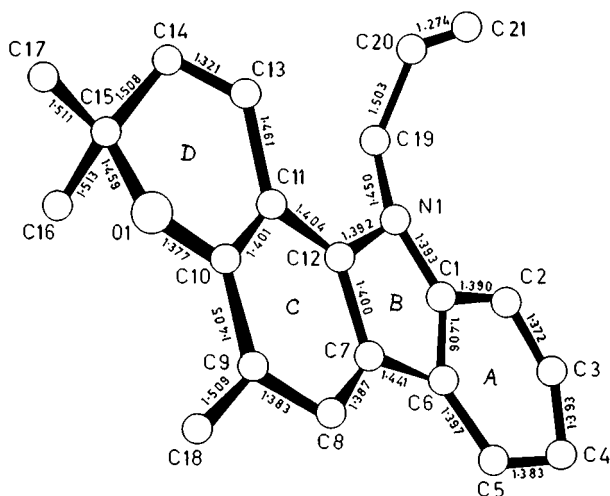
The final positional and thermal parameters are listed in Tables 2, 3 and 4. Figure 1 represents a perspective view of the molecule with the atom numbering scheme. Interatomic bond distances and angles are shown in Figures 1 and 2 respectively.

The four rings form a conjugated system. The bond lengths within the six-membered benzene rings are in the range $1.372(9) \text{ \AA}$ to $1.406(7) \text{ \AA}$ whereas the $C(sp^2) - C(sp^2)$ single bond [C(6)–C(7)] is $1.441(6) \text{ \AA}$. These

¹ Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference No. CSD 54368, the names of the authors and the title of the paper.

Table 4. Anisotropic thermal parameters [U(L,J) × 10³] for non-hydrogen atoms with their e.s.d's in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	46(2)	46(1)	47(2)	-7(1)	0(1)	4(1)
N(1)	47(2)	44(2)	44(2)	4(2)	0(2)	5(2)
C(1)	53(3)	50(3)	38(2)	0(2)	6(2)	-7(2)
C(2)	49(3)	58(3)	52(3)	2(3)	-6(2)	1(2)
C(3)	60(3)	67(4)	50(3)	4(3)	-12(2)	-11(3)
C(4)	74(4)	55(3)	48(3)	-5(2)	-2(3)	-13(3)
C(5)	62(3)	45(3)	53(3)	0(2)	5(2)	0(2)
C(6)	50(3)	41(3)	43(3)	3(2)	5(2)	-2(2)
C(7)	46(3)	40(2)	39(3)	0(2)	2(2)	-2(2)
C(8)	54(3)	38(2)	52(3)	-1(2)	8(2)	4(2)
C(9)	50(3)	41(2)	43(3)	1(2)	7(2)	1(2)
C(10)	45(2)	41(2)	35(2)	-1(2)	7(2)	-2(2)
C(11)	45(3)	39(2)	37(2)	3(2)	4(2)	0(2)
C(12)	44(2)	41(3)	40(2)	4(2)	4(2)	0(2)
C(13)	52(3)	41(3)	47(3)	6(2)	0(2)	7(2)
C(14)	52(3)	40(2)	53(3)	-5(2)	1(2)	5(2)
C(15)	50(3)	50(3)	42(3)	-6(2)	5(2)	1(2)
C(16)	54(3)	71(3)	53(3)	7(3)	9(2)	1(3)
C(17)	53(3)	55(3)	60(3)	-14(2)	-6(2)	0(2)
C(18)	57(3)	46(3)	63(3)	9(2)	-4(2)	10(2)
C(19)	45(3)	60(3)	56(3)	1(2)	4(2)	5(2)
C(20)	89(4)	55(3)	67(4)	11(3)	2(3)	23(3)
C(21)	91(5)	70(4)	81(4)	25(3)	13(3)	-2(4)

**Fig. 1.** Bond lengths (Å) involving non-hydrogen atoms.

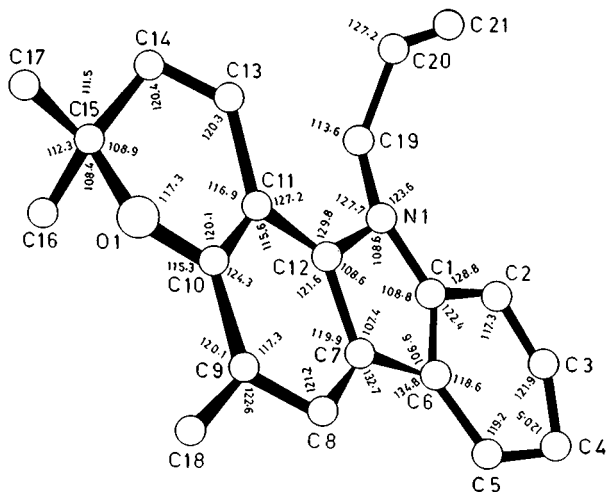


Fig. 2. Bond angles ($^{\circ}$) involving non-hydrogen atoms.

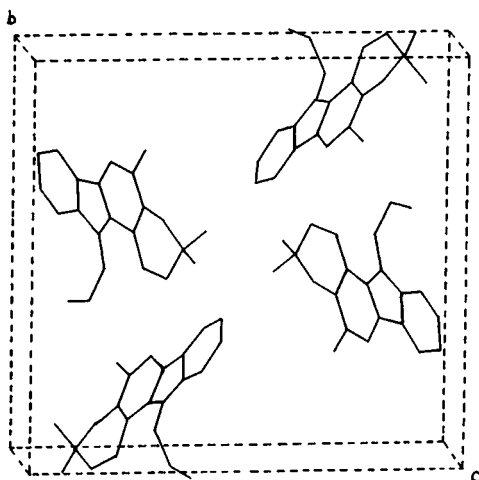


Fig. 3. Packing of the molecule in the unit-cell viewed down the a axis.

values are in accordance with those of other compounds containing carbazole moiety (Kurahashi et al., 1969; Lahiri, 1968; Gerkin and Reppart, 1986). The N(1)–C(19) bond distance [1.450(7) Å] is slightly shorter than C–N single bond value and may involve little π interaction.

The six-membered ring (A) and the five-membered ring (B) of the molecule are nearly planar whereas the other six-membered ring (C) is

not strictly planar within experimental errors. But the carbazole moiety consisting of these three rings is not planar. The non-planarity of the system is probably influenced by the carbazole moiety itself appearing to have a slightly but significantly boat shape; the mean plane of the six-membered rings (A and C) being inclined with respect to the mean plane of the five-membered ring (B) at different angles. The dihedral angle between the ring A and B is 1.2(3)°, between B and C is 2.8(2)° and between A and C is 3.9(2)°. The extent of bowing is indicated by the torsion angles calculated around the inner core of the molecule [i.e., the bonds C(5)–C(6), C(6)–C(7), C(7)–C(8)]; these are 178.9(5)°, –3.71(9)° and –178.2(5)° respectively. In other closely related structures, similar effects have also been observed (Karlsson et al., 1983; Berg et al., 1978; Banerjee, 1974). The plane containing the atoms N(1), C(19), C(20) and C(21) is perfectly planar and is nearly at right angles [90.3(2)°] with the plane of the carbazole moiety.

The pyran ring (D) is not planar and makes an angle of 5.2(3)° with the plane of the carbazole moiety. The substituents at C(15) are in staggered conformation.

The arrangement of the molecules in the unit cell is shown in Figure 3. There are no intermolecular distances shorter than the sum of the relevant van der Waals radii; the shortest non-hydrogen distance is C(10)...C(19) = 3.433(7) Å.

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