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X-ray crystal structure of 2-styrylpyridine

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We have crystallized the 2-styrylpyridine from the condensation reaction between the 2-methylpyridine with benzaldehyde in the formation of the model compound 2-styrylpyridine. The X-ray structure and NMR are currently reported. The main features of the structure is that it shows a localization of the double bonds rather than a delocalization of π electrons in an aromatic fashion.

KEY WORDS: 2-Styrylpyridine; 2-stilbazole; single crystal X-ray structure.

Introduction

While studying polystyrylpyridine polymers based on polymerization reactions of 6-methyl-2-pyridinecarboxaldehyde, as well as terephthalaldehyde with 2,6-dimethylpyridine, some problems arose with the gelation process and the possible structure of the insoluble polymer. It was then decided to undertake a project with model molecules, i.e., two rings and one double bond. One of the rings was a pyridine group and the other was a benzene ring. It was thought that an explanation of the strange behavior of these systems might be possible.

The pyridine derivatives like methylpyridines, dimethylpyridines, and trimethylpyridines can have a large reactivity due to the acidic character of the methyl group caused by the inductive effect and the electronic resonance of the pyridine ring.

Its reactivity can be observed in a typical condensation reaction of methylpyridines in which an easy loss of a proton from the methyl group could make possible the reaction with aromatic aldehydes (e.g., benzaldehyde and terephthalaldehyde), using a catalyst to obtain styrylpyridines also known as stilbazoles.

The 2-styrylpyridine was synthesized for the first time at the beginning of the century[1] and many authors[2–4] have since used different catalysts. The present project made use of no catalyst, or one could call an auto-catalyzed reaction. This made it possible to obtain good enough crystals to solve the crystalline structure.

The literature[3] reports the reaction for the 2-methylpyridine with benzaldehyde using acetic anhydride to obtain the 2-stilbazole. However the crystal structure has not been reported.

Experimental

2-Styrylpyridine

We added 0.05 mol of 2-methylpyridine (Aldrich) and 0.05 mol of benzaldehyde (Productos Químicos Monterrey), freshly distilled, in a 50 ml flask. The mixture was magnetically stirred and refluxed for 39 hr to 120°C. The purification was carried out by distillation at 205°C. The resultant product (dark brown color) was treated with a 2N sodium hydroxide solution, from which several crystals of 2-styrylpyridine were formed. The crystals were washed with a methanol-hexane (9:1) and colorless crystals with a 8.11%

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Table 1. Summary of the crystal and intensity collection data for compound **1**

Formula	$C_{13}H_{11}N$
Color/habit	Colorless, irregular
*F*w	181.2
Space group	$P2_12_12_1$
Temp., °C	25
Cell constants[a]	
a (Å)	7.597(0)
b (Å)	10.425(0)
c (Å)	12.873(0)
Cell volume (Å^3)[a]	1019.55(6)
Z	4
Density (calc.)	1.181
μ(mm^{-1})	0.529
Diffractometer/scan	Siemens P4
Radiation, graphite monochromator	Cu$K\alpha$(λ = 1.54178 Å)
Crystal dimensions (mm)	0.24 × 0.20 × 0.20
2θ range, deg.	3.0 to 110.0
h k l range	$0 \le h \le 8$; $0 \le k \le 11$; $-13 \le l \le 13$
Reflections observed ($F > 4.0\ \sigma\ (F)$)[b]	1427
Solution and refinement	SHELEXTL PLUS (PC version)[4]
Solution	Direct methods
No. of parameters refined	128
Weighting scheme	$w^{-1} = \sigma^2\ (F) + 0.0030F^2$
R(%)	5.72
*R*w(%)	10.13
Goodness-of-fit	1.54
Largest difference peak	0.14eÅ^{-3}

[a] Least-squares refinement of 32 centered reflections ($25.314 < 2\theta < 55.890$).

[b] Corrections: Lorentz-Polarization.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) of 2-styrylpyridine

Atom	*x*	*y*	*z*	*U*(eq)
H(3A)	1046	8051	9861	80)
H(4A)	480	9736	11015	80
H(5A)	−957	9243	12568	80)
H(6A)	−2138	7171	12814	80
H(7A)	968	5796	9334	80)
H(8A)	−963	4177	10621	80
H(10A)	1471	4438	8257	80
H(11A)	1859	2751	7077	80
H(12A)	1107	679	7479	80
H(13A)	−463	300	8989	80
H(14A)	−1123	1940	10144	80
N(1)	−966(9)	6401(4)	11598(4)	84(2)
C(2)	−70(9)	6645(6)	10693(4)	71(2)
C(3)	467(9)	7881(5)	10509(5)	78(2)
C(4)	82(11)	8885(6)	11174(7)	96(3)
C(5)	−761(11)	8602(6)	12044(5)	91(3)
C(6)	−1375(9)	7362(4)	12240(5)	76(2)
C(7)	272(9)	5599(5)	9935(4)	74(2)
C(8)	−263(8)	4399(6)	10026(4)	77(3)
C(9)	151(8)	3364(5)	9300(4)	63(2)
C(10)	1042(9)	3593(4)	8411(4)	68(2)
C(11)	1330(11)	2600(6)	7743(5)	92(3)
C(12)	825(10)	1378(7)	7935(5)	85(3)
C(13)	−93(10)	1160(6)	8837(6)	88(3)
C(14)	−441(10)	2120(6)	9534(5)	91(3)

Table 3. Bond lengths (Å) and angles (°)

Bond	Length	Bond angle	Angle
N(1)−C(6)	1.335(8)	C(2)−N(1)−C(6)	120.1(5)
C(2)−C(7)	1.486(8)	N(1)−C(2)−C(7)	120.5(5)
C(4)−C(5)	1.324(12)	C(2)−C(3)−C(4)	122.7(6)
C(7)−C(8)	1.321(8)	C(4)−C(5)−C(6)	121.3(6)
C(9)−C(10)	1.350(8)	C(2)−C(7)−C(8)	125.7(5)
C(10)−C(11)	1.363(8)	C(8)−C(9)−C(10)	121.3(5)
C(12)−C(13)	1.373(10)	C(10)−C(9)−C(14)	120.3(5)
N(1)−C(2)	1.373(8)	C(10)−C(11)−C(12)	123.7(6)
C(2)−C(3)	1.372(8)	C(12)−C(13)−C(14)	122.1(6)
C(3)−C(4)	1.384(9)	N(1)−C(2)−C(3)	117.9(5)
C(5)−C(6)	1.398(8)	C(3)−C(2)−C(7)	121.6(5)
C(8)−C(9)	1.462(8)	C(3)−C(4)−C(5)	117.3(6)
C(9)−C(14)	1.405(8)	N(1)−C(6)−C(5)	120.3(6)
C(11)−C(12)	1.353(9)	C(7)−C(8)−C(9)	125.2(5)
C(13)−C(14)	1.370(9)	C(8)−C(9)−C(14)	118.4(5)
		C(9)−C(10)−C(11)	118.7(5)
		C(11)−C(12)−C(13)	117.0(6)
		C(9)−C(14)−C(13)	118.2(6)

yield were obtained. Final elucidation of the molecular structure was performed by X-ray diffraction analysis (Tables 1–3) and ^{1}H NMR ($CDCl_3$, 400 MHz) (Table 4).

Results and discussion

Several authors have studied the reactions[2–4] to obtain styrylpyridines using different catalysts, e.g., bases (piperidine, sodium hydroxide), acids (acetic

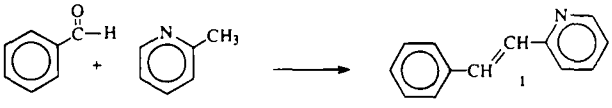


Fig. 1. Reaction to obtain the model compound 2-styrylpyridine.

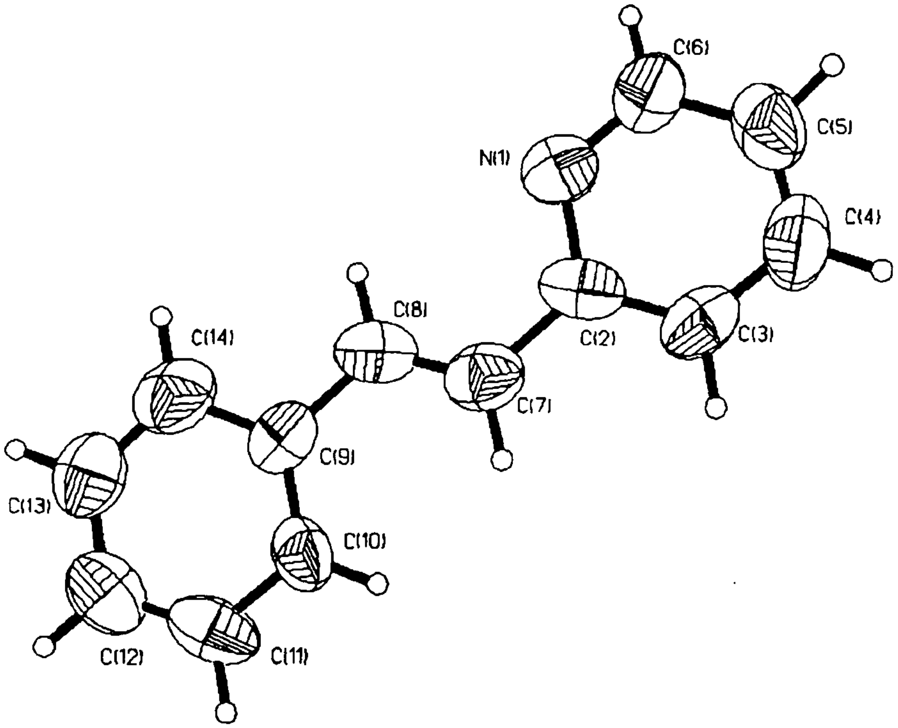


Fig. 2. Molecular structure of 2-styrylpyridine.

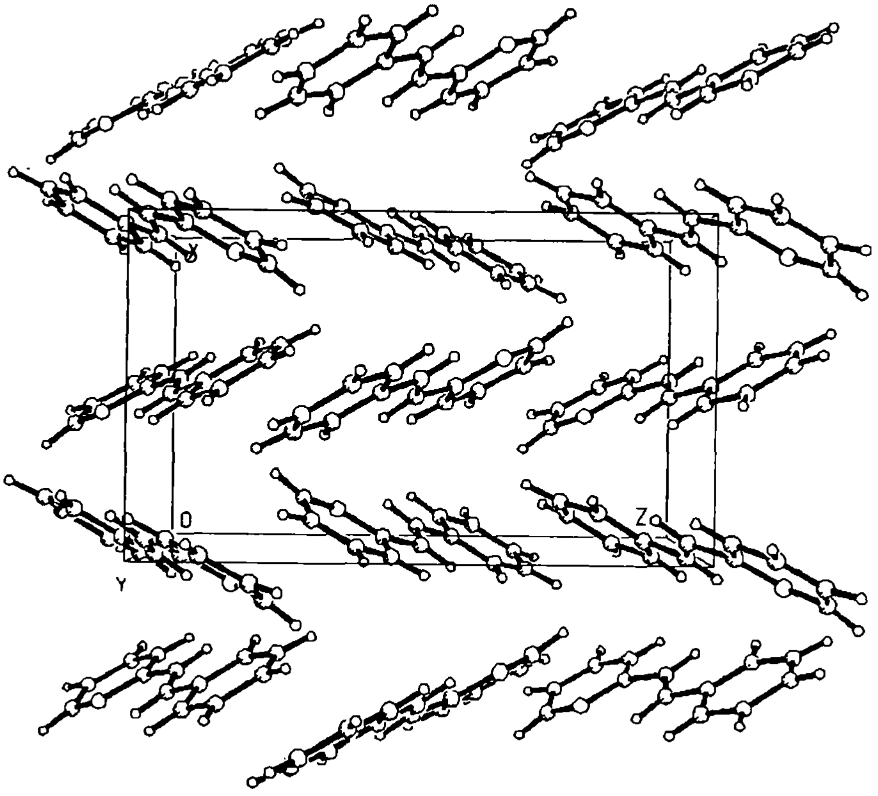
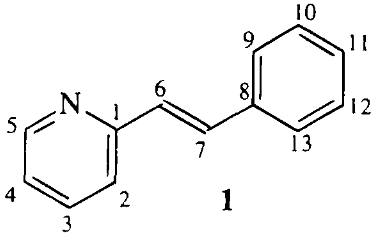


Fig. 3. Molecular packing of 2-styrylpyridine.

Table 4. Summary of structural data for the compound **1**



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Chemical shift(δ)	Integrated intensity	Multiplicity	J_{H-H} Hz	Assignment
8.63	1	Doublet	4.8	H^5
7.68, 7.60	2,1	Multiplet	7.7 15.5 8	H^{13} H^9 H^7
7.57	1	Triplet	4.8	H^4
7.35	3	Multiplet	7.8	H^{10} H^{11} H^{12}
7.2, 7.09	1,1	Multiplet	16.0 4.8	H^6 H^4

anhydride/acetic acid), and Lewis acids (zinc chloride). 2-Styrylpyridine, as reported in the present study, was obtained during the preparation of the model compound. The reaction was performed according to the following condensation reaction of the 2-methylpyridine with benzaldehyde and without catalyst (Fig. 1).

Determination of the crystal structure of 2-styrylpyridine was undertaken in connection with the above project. The molecular structure of the title compound is shown in Fig. 2. From the structure one can observe that the phenyl ring is located *trans* to the pyridine ring in relation to the double bond. The bond lengths between C(8)−C(9) [1.462 (8)Å] and C(2)−C(7) [1.486 (8)Å]; as well as C(7)−C(8) [1.321 (8)Å] show typical double bond values, not indicating a delocalization of the π electrons of the two six-membered rings through the C(7)−C(8) bond but a localization of the π electrons over determined bonds across the rings. According to the carbon–carbon distances observed for the solved structure one may think that the N(1)−C(6) [1.335 (8)Å], C(5)−C(4) [1.324 (12)Å], C(9)−C(10) [1.350 (8)Å] and C(11)−C(12) [1.353 (9)Å] are localized double bonds; Meanwhile C(14)−C(9) [1.405 (8)Å], C(8)−C(9) [1.462 (8)Å], C(7)−C(2) [1.486 (8)Å] have typical carbon–carbon distance values that can be assigned to single bonds.

Conclusion

The conclusion which comes from analyzing the data is that even in a simplified general picture, which is shown in Fig. 3, the molecule is flat would not warrant full aromaticity or full electron delocalization. It seems that delocalization of the π electrons of the two six-membered rings can be seen more as a hyperconjugation with localization of the double bonds and the single bonds which does not show a very systematic pattern. In a recent publication[5] for a similar molecular structure, delocalization of the π electrons of the two six-membered rings through the vinyl group was found.

The NMR results confirm the formation of the compound 2-styrylpyridine as previously reported.[2]

Supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1003/5226. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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