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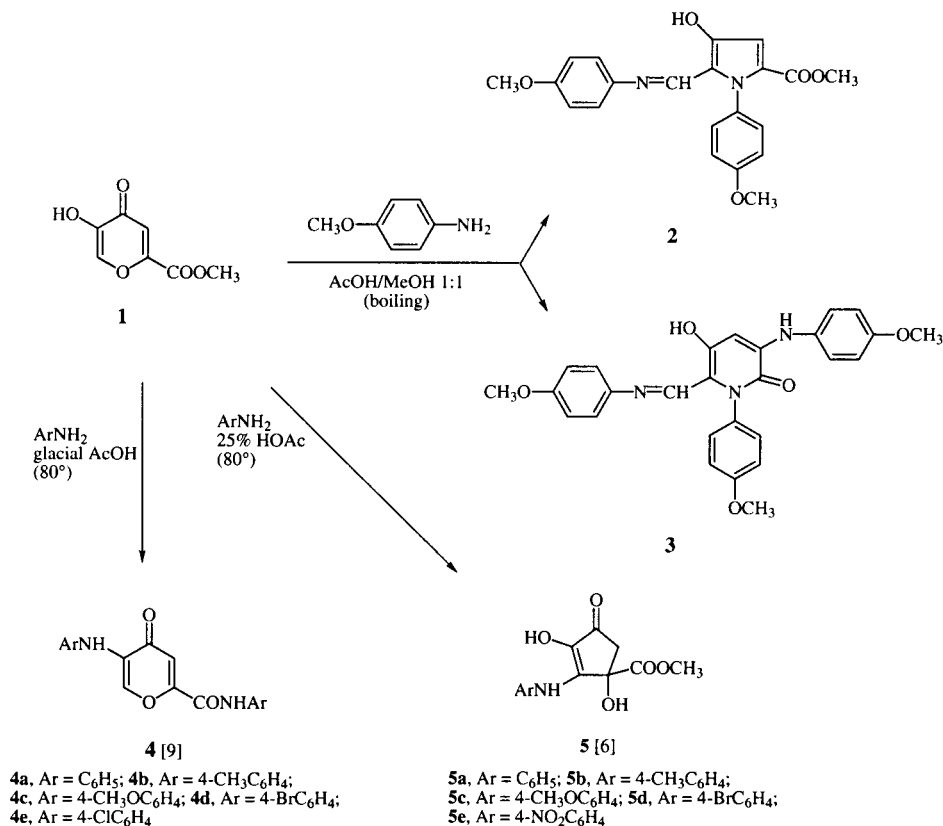
Unlike most of other aromatic amines, 4-methoxyaniline with methyl comenate (**1**) in the mixture of acetic acid and methanol (1:1) gave two unexpected products with azomethyne moiety. The structures of new compounds were determined from their characteristic spectroscopic behaviour and were confirmed by X-ray crystallographic measurements.

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The usual reactions of γ -pyrones with primary aromatic amines [1] involve a nucleophilic attack at α or α' position followed by the ring opening/ring closure sequences and it is often used to prepare the corresponding 4-pyridones [2].

The procedure was adopted in our laboratory [3] to prepare various *N*-aryl or *N*-heteroaryl-4-pyridones with mostly an unsubstituted β -hydroxy group [4] which turned out to be suitable selective extractants for a num-

Scheme 1

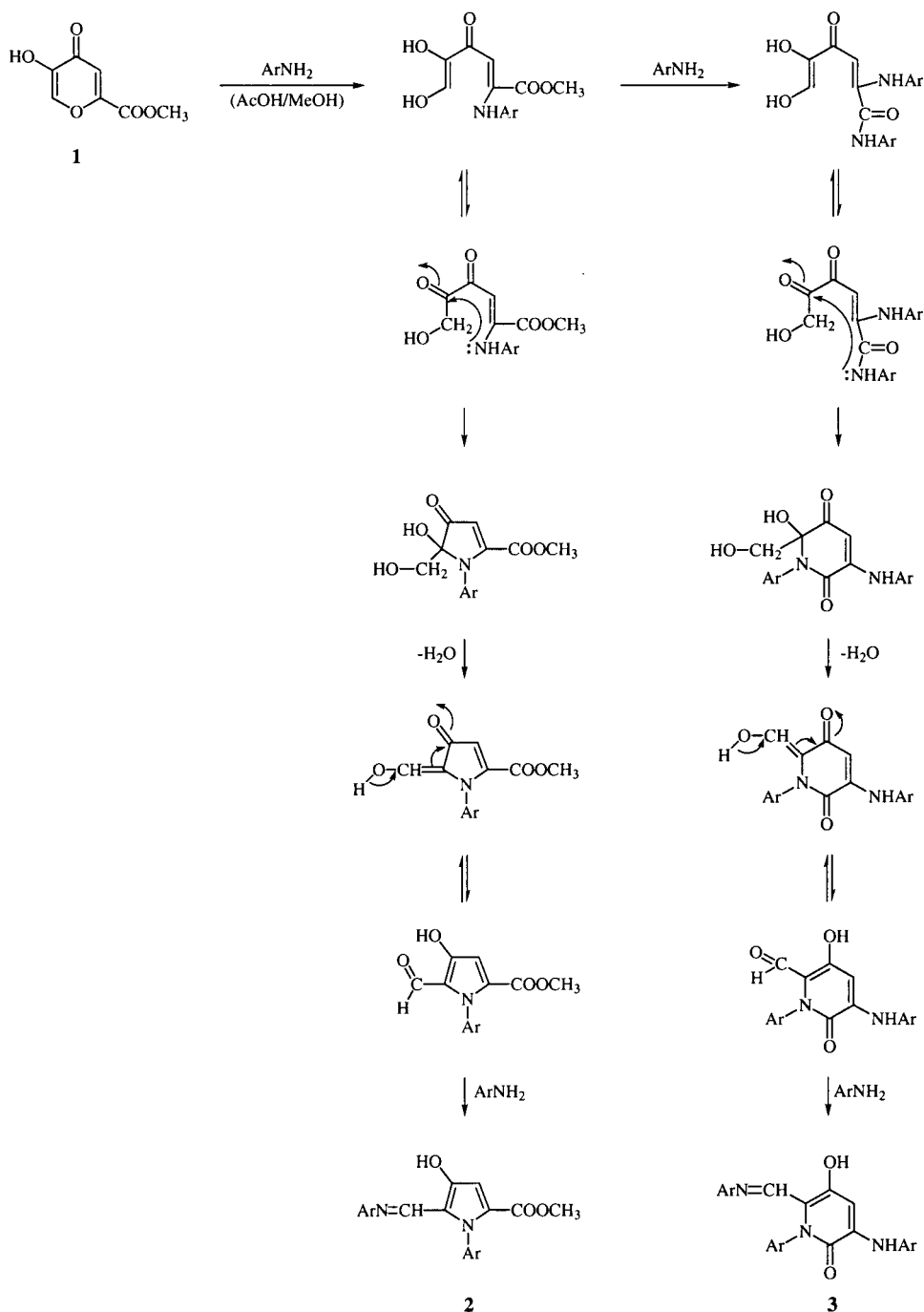


ber of metal ions [5]. Nevertheless, we observed some different reactions, depending on the substituent pattern and reaction conditions applied. Thus, in the reaction of methyl comenate and an aromatic amine in 25% acetic acid or in methanol at 75–80° we found the novel preparatively useful ring contraction of 4-pyrones to substituted cyclopent-2-enone derivatives **5** [6,7] (Scheme 1).

Recently we reported about the synthesis of 5-aryl-amino-4-pyrone-2-carboxanilides **4** by heating of a

4-pyronecarboxylate (methyl comenate) with an excess of 4-substituted anilines in glacial acetic acid [9]. It is known that the reaction of 4-pyrones with amines is dependent on the nucleophilicity of an aromatic amine [2]. Thus, in our case, the reaction with 4-nitroaniline failed due to the electron withdrawing nitro group. In contrast, the activation effect of the 4-methoxy group of 4-anisidine enhances the reactivity greatly, but the consequence was substantial polymerization, which lowers the yield of

Scheme 2



expected 5-(4-methoxyphenyl)amino-4-pyronyl-2-(*N*-4-methoxyphenyl)carboxamide (**4c**) profoundly [9]. Besides, we detected the formation of minor quantities of some new coloured compounds. These new products attracted our attention, and in the present paper we wish to report on the formation and structure of two new compounds obtained in the reaction of methyl comenate with an excess of 4-methoxyaniline (4-anisidine).

The mixture of acetic acid and methanol (1:1) was found to be the reaction media of choice giving under reflux isolable quantities of **2** and **3** (Scheme 1) but no carboxamide **4** [10].

Tentatively, we suggest that similar to the usual mechanism of 4-pyrone to 4-pyridone transformations, the initial attack of 4-anisidine should appear at the α -position next to the methyl carboxylate group of methyl comenate (**1**). Intermediate "open-chain" product seems to be susceptible to different types of ring closure steps leading, in the present example, to **2** and **3** (Scheme 2).

The structures of **2** and **3** were deduced from their spectroscopic characteristics and were confirmed by X-ray crystallographic analyses.

The ir spectrum of **2** showed an ester carbonyl and an azomethyne absorption at 1710 and 1590 cm^{-1} respectively.

In the ^1H nmr of compound **2** signals at 7.96 ppm (s, 1H) and 6.54 ppm (s, 1H) were assigned to azomethyne and pyrrole protons respectively. The broad signal centered at 4.2 ppm (bs, 1H, disappeared on treatment with deuterium oxide) was assigned to the hydroxy group situated in position 4 of the pyrrole ring. The other signals could be easily assigned for two *p*-methoxyphenyl substituted aryl groups.

The ^{13}C nmr spectra conformed to the suggested structure of compound **2**.

Final proof of the structure was performed by X-ray diffraction measurement on a single crystal of **2**. The structure of **2** was solved by direct methods [11] and refined by bloc matrix least-squares technique [12]. The hydrogen atoms were generated and were at a fixed distance from the attached carbon atoms with a fixed isotropic temperature factor for two groupings according to the stereochemical rules for sp^2 and sp^3 hybridized carbon atoms. The location of H atoms of the hydroxy groups are not found in different Fourier maps. The final R-value was 0.078 for 246 parameters, $(\Delta/\sigma)_{\text{max}} = 0.001$, with the largest peaks in the final difference map of 0.97 and $-0.22 \text{ e}\text{\AA}^{-3}$. The final atomic coordinates and equivalent isotropic temperature factors for the nonhydrogen atoms are given in Table I. Bond lengths and bond angles are presented in Table II.

Crystals of **2** were observed to contain two fully independent molecules in the unit cell that are structurally similar.

Table I

Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Compound **2** (estimated standard deviations are in parentheses)

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{eq}
C3A	8035(15)	-567(12)	597(7)	60(4)
N1A	8749(12)	-1593(10)	367(5)	60(3)
O1A	7909(11)	-867(8)	-826(4)	74(3)
O2A	10453(12)	-5125(9)	2158(5)	89(3)
O3A	6338(11)	2892(9)	2873(4)	79(3)
O4A	4275(12)	3561(9)	391(5)	86(3)
O5A	4456(12)	3394(8)	-687(4)	81(3)
C1A	7233(15)	116(12)	-483(6)	59(4)
C2A	7350(15)	277(11)	153(6)	53(4)
N2A	6471(12)	1364(9)	365(5)	54(3)
C4A	5838(15)	1883(12)	-158(6)	54(4)
C5A	6288(15)	1129(12)	-685(6)	62(4)
C6A	9215(16)	-2466(11)	844(7)	56(4)
C7A	10536(17)	-3333(13)	640(7)	69(4)
C8A	10986(17)	-4241(12)	1075(7)	71(4)
C9A	10129(18)	-4272(14)	1689(8)	71(5)
C10A	8816(17)	-3433(13)	1903(6)	66(4)
C11A	8363(16)	-2544(12)	1475(7)	64(4)
C12A	11745(18)	-6048(13)	1980(8)	100(5)
C13A	6435(17)	1822(11)	1001(6)	55(4)
C14A	7774(16)	2196(11)	1125(7)	58(4)
C15A	7766(17)	2578(12)	1750(7)	65(4)
C16A	6417(17)	2560(11)	2242(6)	58(4)
C17A	5078(15)	2196(11)	2112(6)	55(4)
C18A	5078(16)	1831(10)	1484(7)	55(4)
C19A	7663(18)	3306(16)	3054(7)	102(6)
C20A	4793(16)	3013(12)	-102(7)	59(4)
C21A	3423(18)	4514(12)	-701(7)	84(5)
C3B	3065(13)	1128(11)	5297(6)	57(4)
N1B	3447(12)	529(9)	5815(5)	60(3)
O1B	2856(11)	-1434(8)	5302(5)	81(3)
O2B	5867(12)	2259(10)	7791(4)	87(3)
O3B	1249(12)	5894(9)	3775(5)	83(4)
O4B	1285(12)	1236(9)	2974(5)	83(3)
O5B	621(12)	-587(9)	3112(5)	86(3)
C1B	2417(15)	-682(13)	4830(7)	65(4)
C2B	2547(14)	532(11)	4831(6)	56(4)
N2B	2045(12)	1033(9)	4253(5)	55(3)
C4B	1609(15)	154(13)	3939(7)	59(4)
C5B	1827(15)	-893(12)	4274(6)	59(4)
C6B	4025(15)	1037(13)	6297(6)	58(4)
C7B	4302(16)	332(12)	6837(6)	63(4)
C8B	4901(17)	781(13)	7326(7)	67(4)
C9B	5228(16)	1915(14)	7282(6)	63(4)
C10B	4991(16)	2638(12)	6736(6)	66(4)
C11B	4365(15)	2203(13)	6259(6)	61(4)
C12B	6356(20)	3408(16)	7756(7)	100(6)
C13B	1798(17)	2261(11)	4135(6)	53(4)
C14B	3068(17)	2817(12)	3911(7)	67(4)
C15B	2870(19)	4029(15)	3798(7)	84(5)
C16B	1331(18)	4694(12)	3911(6)	62(4)
C17B	63(16)	4122(12)	4128(6)	63(4)
C18B	307(16)	2894(13)	4237(6)	64(4)
C19B	-295(19)	6520(13)	3803(8)	100(6)
C20B	1133(16)	359(14)	3299(7)	62(4)
C21B	270(19)	-509(13)	2468(8)	97(6)

Table II

Table II (continued)

Bond Distances (Å) and Angles (°) in Compound **2** (C₂₁H₂₀N₂O₅)

A		B	
C3A-N1A	1.30(2)	C3B-N1B	1.32(2)
C3A-C2A	1.44(2)	C3B-C2B	1.39(2)
N1A-C6A	1.44(2)	N1B-C6B	1.39(2)
O1A-C1A	1.35(2)	O1B-C1B	1.34(2)
O2A-C9A	1.38(2)	O2B-C9B	1.39(2)
O2A-C12A	1.42(2)	O2B-C12B	1.44(2)
O3A-C16A	1.37(2)	O3B-C16B	1.38(2)
O3A-C19A	1.43(2)	O3B-C19B	1.40(2)
O4A-C20A	1.20(2)	O4B-C20B	1.19(2)
O5A-C20A	1.34(2)	O5B-C20B	1.34(2)
O5A-C21A	1.45(2)	O5B-C21B	1.43(2)
C1A-C2A	1.37(2)	C1B-C2B	1.41(2)
C1A-C5A	1.41(2)	C1B-C5B	1.40(2)
C2A-N2A	1.40(2)	C2B-N2B	1.42(2)
N2A-C4A	1.38(2)	N2B-C4B	1.37(2)
N2A-C13A	1.44(2)	N2B-C13B	1.40(2)
C4A-C5A	1.39(2)	C4B-C5B	1.36(2)
C4A-C20A	1.45(2)	C4B-C20B	1.47(2)
C6A-C7A	1.40(2)	C6B-C7B	1.39(2)
C6A-C11A	1.38(2)	C6B-C11B	1.41(2)
C7A-C8A	1.40(2)	C7B-C8B	1.38(2)
C8A-C9A	1.35(2)	C8B-C9B	1.37(2)
C9A-C10A	1.38(2)	C9B-C10B	1.40(2)
C10A-C11A	1.38(2)	C10B-C11B	1.37(2)
C13A-C14A	1.37(2)	C13B-C14B	1.35(2)
C13A-C18A	1.39(2)	C13B-C18B	1.36(2)
C14A-C15A	1.39(2)	C14B-C15B	1.38(2)
C15A-C16A	1.39(2)	C15B-C16B	1.41(2)
C16A-C17A	1.37(2)	C16B-C17B	1.36(2)
C17A-C18A	1.39(2)	C17B-C18B	1.40(2)
N1A-C3A-C2A	118(1)	N1B-C3B-C2B	119(1)
C3A-N1A-C6A	116(1)	C3B-N1B-C6B	123(1)
C9A-O2A-C12A	118(1)	C9B-O2B-C12B	119(1)
C16A-O3A-C19A	120(1)	C16B-O3B-C19B	115(1)
C20A-O5A-C21A	117(1)	C20B-O5B-C21B	116(1)
O1A-C1A-C2A	124(1)	O1B-C1B-C2B	122(1)
O1A-C1A-C5A	129(1)	O1B-C1B-C5B	130(1)
C2A-C1A-C5A	107(1)	C2B-C1B-C5B	108(1)
C3A-C2A-C1A	128(1)	C3B-C2B-C1B	128(1)
C3A-C2A-N2A	122(1)	C3B-C2B-N2B	127(1)
C1A-C2A-N2A	109(1)	C1B-C2B-N2B	106(1)
C2A-N2A-C4A	107(1)	C2B-N2B-C4B	108(1)
C2A-N2A-C13A	123(1)	C2B-N2B-C13B	122(1)
C4A-N2A-C13A	130(1)	C4B-N2B-C13B	129(1)
N2A-C4A-C5A	109(1)	N2B-C4B-C5B	110(1)
N2A-C4A-C20A	122(1)	N2B-C4B-C20B	122(1)
C5A-C4A-C20A	129(1)	C5B-C4B-C20B	128(1)
C1A-C5A-C4A	107(1)	C1B-C5B-C4B	108(1)
N1A-C6A-C7A	118(1)	N1B-C6B-C7B	117(1)
N1A-C6A-C11A	123(1)	N1B-C6B-C11B	124(1)
C7A-C6A-C11A	118(1)	C7B-C6B-C11B	119(1)
C6A-C7A-C8A	120(1)	C6B-C7B-C8B	120(1)
C7A-C8A-C9A	119(1)	C7B-C8B-C9B	121(1)
O2A-C9A-C8A	124(1)	O2B-C9B-C8B	116(1)
O2A-C9A-C10A	114(1)	O2B-C9B-C10B	124(1)
C8A-C9A-C10A	122(2)	C8B-C9B-C10B	121(1)
C9A-C10A-C11A	119(1)	C9B-C10B-C11B	119(1)
C6A-C11A-C10A	121(1)	C6B-C11B-C10B	121(1)
N2A-C13A-C14A	119(1)	N2B-C13B-C14B	119(1)
N2A-C13A-C18A	120(1)	N2B-C13B-C18B	121(1)
C14A-C13A-C18A	121(1)	C14B-C13B-C18B	120(1)
C13A-C14A-C15A	119(1)	C13B-C14B-C15B	121(1)

A

B

C14A-C15A-C16A	120(1)	C14B-C15B-C16B	120(1)
O3A-C16A-C15A	123(1)	O3B-C16B-C15B	116(1)
O3A-C16A-C17A	116(1)	O3B-C16B-C17B	125(1)
C15A-C16A-C17A	121(1)	C15B-C16B-C17B	119(1)
C16A-C17A-C18A	120(1)	C16B-C17B-C18B	120(1)
C13A-C18A-C17A	120(1)	C13B-C18B-C17B	121(1)
O4A-C20A-O5A	123(1)	O4B-C20B-O5B	125(1)
O4A-C20A-C4A	126(1)	O4B-C20B-C4B	124(1)
O5A-C20A-C4A	111(1)	O5B-C20B-C4B	112(1)

The bond lengths and bond angles in both molecules **A** and **B** (Figure 1) in general do not differ significantly; the major conformational difference being the dihedral angle between mean planes through the central pyrrole ring C1, C2, N2, C4, C5 and phenyl ring C6, C7, C8, C9, C10, C11. The value of this angle in molecule **A** is 37.7(6)°, as well as 7.7(6)° in molecule **B**. Explanation for this apparent conformational changes lie in the observed short intermolecular contacts of oxygen O2 and hydrogen atoms of the methoxy groups. All calculations were performed with the SHELXS-76 [13] and CSU [14] program packages. The view of the molecule is given in Figure 1.

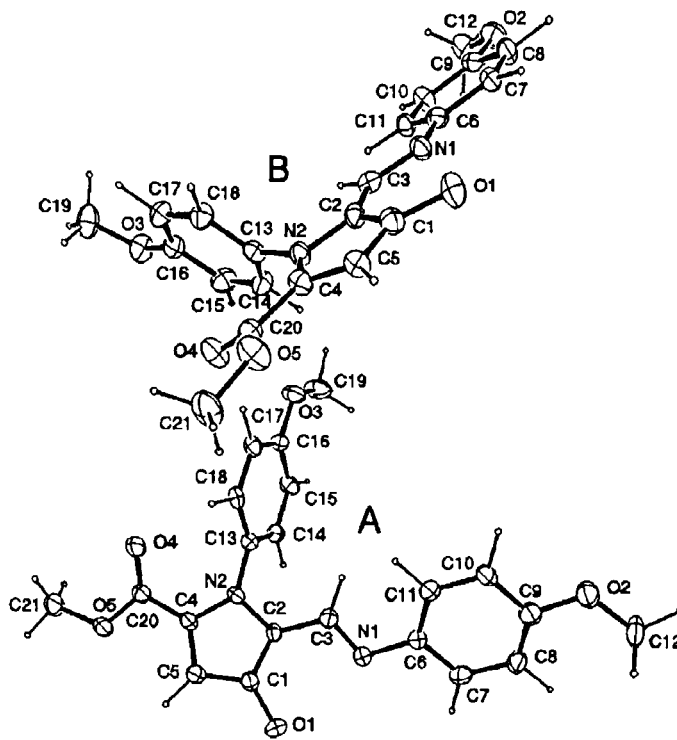


Figure 1. ORTEP [15, 16] view of two crystallographic independent molecules **A** and **B** of compound **2** with the atom labeling scheme. Displacement ellipsoids are drawn at 20% probability level.

Similarly as with **2** the ir spectra of **3** showed azomethyne absorption at 1580 cm⁻¹ but instead of an

ester carbonyl the 2-pyridone carbonyl at 1780 cm⁻¹ appeared. The stretching frequency for a secondary amine appeared at $\nu_{\text{NH}} = 3260 \text{ cm}^{-1}$.

The ¹H nmr spectrum of **3** showed three singlets at 3.82 (s, 3H), 3.92 (s, 3H) and 3.99 ppm (s, 3H) for the protons of the three methoxy substituents on the *p*-methoxyphenyl groups. The H-4 proton of the 2-pyridone nucleus appeared at 6.22 ppm (s, 1H), while the proton of the azomethyne moiety was found at 8.71 ppm (s, 1H). The proton of the hydroxy group was found to be a part of the multiplet at 6.74–7.50 ppm (13H) since after exchange by deuterium oxide a 12H multiplet appeared. The aromatic protons were found as an unresolved multiplet at 6.74–7.50 ppm.

The ¹³C nmr spectra were in full accord with the proposed structure of **3**.

Table III

Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\times 10^4$) for Compound **3** (estimated standard deviations are in parentheses)

$$U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{eq}
C1	0.1313(4)	0.0885(6)	0.3879(1)	377(18)
C2	0.1729(4)	0.2225(7)	0.4038(2)	442(22)
C3	0.1576(4)	0.2662(7)	0.4396(2)	482(20)
C4	0.1059(4)	0.1846(6)	0.4590(2)	409(21)
C5	0.0687(4)	0.0379(7)	0.4443(2)	445(23)
O1	0.2181(3)	0.3053(5)	0.3859(1)	577(17)
O2	0.0283(3)	-0.0442(4)	0.4628(1)	539(16)
N1	0.0836(3)	0.0002(5)	0.4101(1)	421(17)
C6	0.0457(2)	-0.1371(4)	0.3952(1)	391(21)
C7	0.0910(2)	-0.2734(4)	0.3983(1)	495(24)
C8	0.0546(2)	-0.4073(4)	0.3830(1)	578(24)
C9	-0.0271(2)	-0.4048(4)	0.3647(1)	600(28)
C10	-0.0724(2)	-0.2684(4)	0.3616(1)	609(28)
C11	-0.0360(2)	-0.1346(4)	0.3769(1)	486(24)
O3	-0.0681(3)	-0.5285(6)	0.3491(2)	879(24)
C25	-0.0260(7)	-0.6733(9)	0.3558(3)	1258(54)
N3	0.0838(3)	0.2221(5)	0.4922(1)	473(18)
C12	0.1047(3)	0.3622(3)	0.5109(1)	438(23)
C13	0.0987(3)	0.5017(3)	0.4924(1)	508(22)
C14	0.1218(3)	0.6364(3)	0.5113(1)	492(23)
C15	0.1509(3)	0.6317(3)	0.5487(1)	495(23)
C16	0.1569(3)	0.4922(3)	0.5672(1)	573(25)
C17	0.1339(3)	0.3574(3)	0.5483(1)	521(25)
O4	0.1769(3)	0.7567(5)	0.5693(1)	733(18)
C26	0.1761(5)	0.9013(8)	0.5515(2)	695(27)
N2	0.1764(3)	0.1343(6)	0.3299(1)	533(19)
C24	0.1340(4)	0.0495(6)	0.3523(1)	468(21)
C18	0.1754(3)	0.1113(5)	0.2918(1)	487(21)
C19	0.1203(3)	0.0133(5)	0.2706(1)	525(24)
C20	0.1232(3)	0.0016(5)	0.2330(1)	567(24)
C21	0.1812(3)	0.0879(5)	0.2166(1)	558(23)
C22	0.2362(3)	0.1859(5)	0.2378(1)	910(36)
C23	0.2333(3)	0.1976(5)	0.2754(1)	789(28)
O5	0.1831(3)	0.0615(5)	0.1801(1)	692(19)
C27	0.2418(6)	0.1383(11)	0.1616(2)	1025(36)
O6	0.0000(0)	0.5553(24)	0.2500(1)	2903(89)
C28	0.0314(13)	0.6703(23)	0.2743(6)	1192(64)

Final proof of the structure was performed by X-ray diffraction measurement on a single crystal of **3**. The structure of **3** was solved by direct methods [11] and refined by bloc matrix least-squares technique [12]. The carbon atoms of the benzene rings are refined as a rigid group. The hydrogen atoms were at a fixed distance from the attached carbon atoms with a fixed isotropic temperature factor for two groupings according to the stereochemical rules for a sp² and a sp³ hybridized carbon atom. The carbon and oxygen atoms of the discrete methanol molecule are refined with the same occupancy factor of 0.5 while the site of the oxygen atom is on the twofold axes and the position of the bonded carbon atom is split into two symmetrically related positions. The hydrogen atoms of the methanol molecule and hydroxyl H atom of the central pyridone ring are not included in refinement. The final R-value was 0.0714 for 284 parameters, $w = 1.7492/\sigma^2 F + 0.002195 F^2$, $(\Delta/\sigma)_{\text{max}} = 0.005$, largest peaks in the final difference map of 0.73 and -0.27 eÅ⁻³. The final atomic coordinates and equivalent isotropic temperature factors for the nonhydrogen atoms are given in Table III. Bond lengths and bond angles are presented in Table IV.

Table IV

Bond Distances (Å) and Angles (°) in Compound **3**
(C₂₇H₂₅N₃O₅ • 0.5 CH₃OH)

C1-C2	1.436(8)	C12-C13	1.395(4)
C1-N1	1.418(7)	C12-C17	1.396(5)
C1-C24	1.360(6)	C13-C14	1.395(4)
C2-C3	1.423(11)	C14-C15	1.395(5)
C2-O1	1.268(8)	C15-C16	1.395(4)
C3-C4	1.364(10)	C15-O4	1.365(5)
C4-C5	1.488(8)	C16-C17	1.395(4)
C4-N3	1.356(8)	O4-C26	1.425(8)
C5-O2	1.231(8)	N2-C24	1.356(7)
C5-N1	1.351(8)	N2-C18	1.414(5)
N1-C6	1.425(6)	C18-C19	1.396(6)
C6-C7	1.394(5)	C18-C23	1.394(7)
C6-C11	1.394(4)	C19-C20	1.394(5)
C7-C8	1.396(5)	C20-C21	1.395(7)
C8-C9	1.394(4)	C21-C22	1.395(6)
C9-C10	1.395(5)	C21-O5	1.367(5)
C9-O3	1.356(6)	C22-C23	1.394(5)
C10-C11	1.395(5)	O5-C27	1.403(11)
O3-C25	1.443(10)	O6-C28	1.397(25)
N3-C12	1.425(5)		
N1-C1-C24	120.3(5)	C9-O3-C25	116.0(6)
C2-C1-C24	121.8(5)	C4-N3-C12	124.8(4)
C2-C1-N1	117.9(4)	N3-C12-C17	118.6(3)
C1-C2-O1	121.5(6)	N3-C12-C13	121.4(3)
C1-C2-C3	118.0(5)	C13-C12-C17	120.0(3)
C3-C2-O1	120.4(6)	C12-C13-C14	120.0(3)
C2-C3-C4	122.2(6)	C13-C14-C15	120.0(3)
C3-C4-N3	126.3(5)	C14-C15-O4	124.3(3)
C3-C4-C5	120.3(6)	C14-C15-C16	120.0(3)
C5-C4-N3	113.4(5)	C16-C15-O4	115.7(3)
C4-C5-N1	116.0(5)	C15-C16-C17	120.0(3)
C4-C5-O2	121.2(6)	C12-C17-C16	120.0(3)
O2-C5-N1	122.8(6)	C15-O4-C26	118.2(4)

Table IV (continued)
Bond Distances (Å) and Angles (°) in Compound 3
(C₂₇H₂₅N₃O₅•0.5 CH₃OH)

C1-N1-C5	125.2(5)	C24-N2-C18	125.6(5)
C5-N1-C6	116.5(4)	C1-C24-N2	121.9(4)
C1-N1-C6	118.3(4)	N2-C18-C23	115.4(4)
N1-C6-C11	120.0(4)	N2-C18-C19	124.5(4)
N1-C6-C7	119.9(3)	C19-C18-C23	120.1(4)
C7-C6-C11	120.0(3)	C18-C19-C20	120.0(4)
C6-C7-C8	120.0(3)	C19-C20-C21	119.9(4)
C7-C8-C9	120.0(3)	C20-C21-O5	115.7(4)
C8-C9-O3	124.5(4)	C20-C21-C22	120.0(4)
C8-C9-C10	120.0(3)	C22-C21-O5	124.1(4)
C10-C9-O3	115.5(4)	C21-C22-C23	120.0(4)
C9-C10-C11	120.0(3)	C18-C23-C22	120.0(4)
C6-C11-C10	120.0(3)	C21-O5-C27	119.8(5)

The molecules in the crystal structure are linked together by hydrogen bonds of 3.025(6) Å realized between N3 and O2 atoms of symmetrically related molecules (symmetry code: $-x, -y, -z + 1$). The contact N3...O2 of 2.674(6) Å suggests also the existence of an intramolecular hydrogen bond. The *p*-methoxyphenyl ring attached to the pyridone moiety is inclined by the dihedral angle 86.3(1)° minimizing H...H electrostatic repulsion. All calculations were performed with the SHELXS-86 [11] and CSU [14] program packages. The view of the molecule is given in Figure 2.

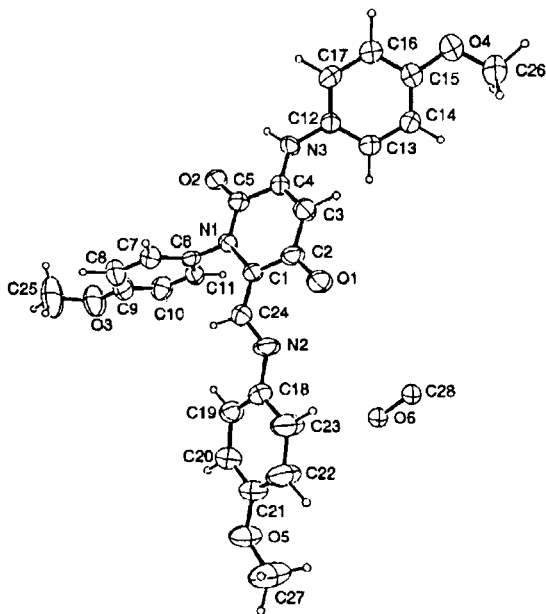


Figure 2. ORTEP [15, 16] view of the compound 3 with the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

EXPERIMENTAL

Melting points were determined on an Original Kofler Mikroheiztisch apparatus (Reichert, Wien) and are not corrected.

Infrared spectra were taken in potassium bromide pellets with a Perkin-Elmer 297 Infracord Spectrophotometer. Ultraviolet spectra were recorded on a Hitachi-Perkin-Elmer Model 124 double beam spectrophotometer. Proton nmr spectra were obtained using Jeol FC 90Q or Varian GEMINI 300 spectrometer with tetramethylsilane as the internal standard. ¹³Carbon nmr spectra were taken on Varian GEMINI 300 instrument at 75 MHz using the APT technique. Mass spectra were recorded on an Extrel FTMS 2001 DD spectrometer by direct insertion probe. The molecular structure was determined by X-ray diffraction using a Philips PW 1100 diffractometer. Methyl comenate, mp 185–186° was prepared according to reported procedure [17].

The Reaction of Methyl Comenate (1) with 4-Anisidine.

To the solution of methyl comenate (1) (0.85 g, 5 mmoles) in glacial acetic acid (8 ml) an excess of 4-anisidine (1.8 g, 17 mmoles) in methanol (8 ml) was added. The reaction mixture was heated under reflux for 2 hours. To the reaction mixture 16 ml of methanol was added. On standing overnight the precipitate was separated and chromatographed on a silica gel column with ethyl acetate. The first fraction gave on evaporation 90 mg of a crude sample of compound 2, the second fraction 160 mg of a crude sample of compound 3.

Further processing of the crude products is indicated in the following paragraphs.

4-Hydroxy-2-methoxycarbonyl-5-[*N*-(4-methoxyphenyl)imino-methyl]-*N*-(4-methoxyphenyl)pyrrole (2).

The first fraction was recrystallized from methanol to give 60 mg (3%) of a pure sample of 2 as red crystals [18], mp 91–93°; ms: (70 eV, electron impact) *m/z* 380 (100, M⁺), 258 (19), 123 (20); ir (potassium bromide): 3110 (m), 2940 (m), 2830 (m), 1710 (vs, C=O), 1660 (s), 1610 (s), 1590 (m, -N=CH-), 1555 (s), 1510 (vs), 1465 (s), 1415 (vs), 1320 (m), 1290 (s), 1250 (vs), 1185 (s), 1170 (vs), 1110 (m), 1030 (s), 1020 (m), 1000 (m), 955 (w), 940 (w), 885 (m), 870 (m), 830 (s), 810 (m), 790 (m), 760 (m), 730 (w), 720 (w) cm⁻¹; uv (methanol, γ = 0.01 g/dm³): λ_{max} (log ε) 227 (4.34), 270 (4.11), 300 (4.05), 370 (4.46), 455 (4.25); ¹H nmr (dimethyl-d₆ sulfoxide): δ 7.96 (s, 1H), 7.33 (d, 2H, *J* = 8.8 Hz), 7.15 (d, 2H, *J* = 8.8 Hz), 7.02 (d, 2H, *J* = 8.9 Hz), 6.91 (d, 2H, *J* = 8.9 Hz), 6.54 (s, 1H), 4.22 (bs, 1H) [19], 3.83 (s, 3H), 3.73 (s, 3H), 3.64 (s, 3H) ppm; ¹³C nmr (dimethyl-d₆ sulfoxide): δ 159.6 (s), 159.0 (s), 157.8 (s), 152.6 (s), 147.2 (d), 141.2 (s), 129.5 (s), 125.3 (s), 121.7 (s), 121.5 (d), 114.6 (d), 113.9 (d), 103.6 (d), 55.3 (q), 51.3 (q) ppm.

Anal. Calcd. for C₂₁H₂₀N₂O₅: C, 66.29; H, 5.31; N, 7.37. Found: C, 66.15; H, 5.53; N, 7.41.

Crystal Data.

Compound 2, C₂₁H₂₀N₂O₅, *M_r* = 380.43, red crystal of dimensions 0.16 x 0.22 x 0.51 mm, triclinic, space group *P*-1, cell dimensions *a* = 8.660(2), *b* = 11.451(8), *c* = 20.800(5) Å, α = 87.01(2), β = 78.57(2), γ = 80.90(1)°, *V* = 1995.8(15) Å³, *Z* = 4, *D_x* = 1.266 gcm⁻³ and μ(MoK_α) = 0.091 mm⁻¹, θ-2θ scans, range 4-2θ-60°, three standard reflections every 2 hours showed 5.5% statistical variations of intensities, 11477 reflections scanned, 4617 unique data (*h* = -12,12; *k* = -16,16; *l* = 0,29), 2050 ≥ 2.5σ(*I*) retained, used for structure solution and refinement, no absorption correction. For data collection and cell-refinement programs DIF4 and REDU4 [20] were used.

5-Hydroxy-3-(4-methoxyphenylamino)-6-(4-methoxyphenylimino)methyl-*N*-(4-methoxyphenyl)-2-pyridone (**3**).

The second fraction was recrystallized from methanol to give 120 mg (5%) of pure sample of **3** as orange crystals, mp 241-243°; ms (70 eV, electron impact): *m/z* 471 (41, M⁺), 354 (100), 115 (22), 91 (21), 77 (24); ir (potassium bromide): $\nu = 3260$ (m), 2830 (w), 1780 (s), 1625 (s), 1580 (vs), 1550 (s), 1510 (vs), 1460 (s), 1345 (s), 1325 (w), 1300 (m), 1280 (m), 1245 (s), 1230 (s), 1170 (m), 1100 (w), 1030 (m), 970 (w), 925 (w), 830 (m), 800 (w), 790 (w), 770 (w), 740 (w), 710 (w), 690 (w) cm⁻¹; uv (methanol, $\gamma = 0.0125$ g/dm³): λ_{\max} (log ϵ) 224 (4.30), 367 (3.83), 457 (4.41); ¹H nmr (dimethyl-d₆ sulfoxide): δ 12.74 (d, 1H, *J* = 11.3 Hz) [19], 8.71 (s, 1H), 6.74-7.05 (m, 13H), 6.23 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.82 (s, 3H) ppm; ¹³C nmr (dimethyl-d₆ sulfoxide): δ 175.6 (s), 159.0 (d), 156.6 (s), 155.6 (s), 154.2 (s), 143.8 (s), 133.5 (s), 132.8 (s), 131.1 (s), 129.6 (d), 129.3 (s), 124.8 (d), 117.3 (d), 116.9 (s), 115.1 (d), 114.9 (d), 114.5 (d), 102.4 (d), 55.2 (q) ppm.

Anal. Calcd. for C₂₇H₂₅N₃O₅•0.5 CH₃OH: C, 68.97; H, 6.00; N, 8.62. Found: C, 68.82; H, 5.81; N, 8.84.

Crystal Data.

Compound **3**, C₂₇H₂₅N₃O₅•0.5 CH₃OH, *M_r* = 487.53, orange crystal of dimensions 0.12 x 0.18 x 0.21 mm, monoclinic, space group *C2/c*, cell dimensions *a* = 16.046(5), *b* = 8.755(3), *c* = 36.790(9) Å, $\beta = 97.42(2)^\circ$, *V* = 5125(3) Å³, *Z* = 8, *D_x* = 1.264 gcm⁻³, $\mu(\text{MoK}\alpha) = 0.832$ cm⁻¹, ω - θ scans, range 4-2 θ -56°, three standard reflections every 2 hours showed 10% statistical variations of intensities, 10158 reflections scanned, 4608 unique data (*h* = -12,12; *k* = -16,16; *l* = 0,29), 1930 $\geq 2.5\sigma(I)$ retained, used for structure solution and refinement, no absorption correction. For data collection and cell-refinement programs DIF4 and REDU4 [20] were used.

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