# Unexpected Formation of a 11*H*-Pyrido[2,1-*b*]quinazolin-11-one Derivative from 5,11-Dihydro-6*H*-pyrido[2,3-*b*]-1,4-benzodiazepin-6-one



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**Dedicated to Professor Ernest Campaigne on the occasion of his 75th birthday**

The unexpected formation of 11*H*-pyrido[2,1-*b*]quinazolin-11-one derivative **6** from 5,11-dihydro-6*H*-pyrido[2,3-*b*]-1,4-benzodiazepin-6-one (**2**) has been observed. Its structure **6** was determined by X-ray crystallography. Detailed nmr study provided a complete set of proton and carbon-13 nmr parameters of compound **6** in solution.

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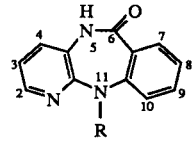
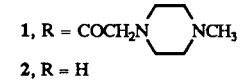
Needing a sample of compound **1** (pirenzepine) as a standard for testing new potential antiulcer agents, Hulinská *et al.* [2] have recently described its synthesis from **2** using methods described earlier in patents. Compound **2**, obtained from *N*-(2-chloro-3-pyridyl)anthranilamide [3], was treated with chloroacetyl chloride in boiling dioxane in the presence of triethylamine [4,5]. An inhomogeneous product, consisting mainly of the wanted **3**, was obtained from which homogeneous **3** could be prepared by uneconomical crystallization. Reaction of the crude product with excessive 1-methylpiperazine in boiling benzene [4,5] gave a mixture of two components which were separated by chromatography on silica gel. The more polar product, obtained in a yield of 87%, was the desired **1**. The less polar component, which was eluted with a mixture of 95% chloroform and 5% of chloroform saturated with ammonia, crystallized from ethanol and melted at 193-195°. It was characterized by analysis and mass spectrum as $C_{19}H_{21}N_5O_2$, *i.e.* an isomer of **1**. Its mass spectrum is similar to that of **1** with a striking difference in abundance of the fragment with m/z 238. The uv spectrum indicated a higher degree of conjugation than expected and found for **1** (*cf.* ref [2]). The ir spectrum showed two carbonyl bands (1640 and 1690 $cm^{-1}$), both of them belonging most likely to the amide region. The $^1H$ nmr spectrum has proven, similarly as in the case of compound **1**, the presence of *N*-methyl piperazine, $-CO-CH_2-N<$ group, one NH proton and seven aromatic protons located on 1,2-disubstituted and 1,2,3-trisubstituted rings, respectively. In addition to the changes in the chemical shifts of aromatic protons the higher mobility of the side chain was indicated by the equivalence of $-CO-CH_2N<$ protons and one multiplet for all piperazine protons unlike from **1**. The $^{13}C$ nmr spectrum has shown the same type of carbon atoms with a significant downfield shift for one of the carbonyl carbons (*ca.* 10 ppm against **1**). From two alternative isomeric structures **4** and **5**, which were suggested for the by-product, the first one could hardly explain the higher conjugation observed (see above) and none of them could be

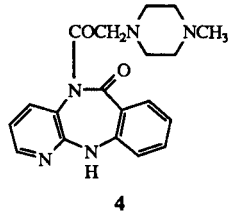




1, R = $COCH_2N$ $NCH_3$

2, R = H

3, R = $COCH_2Cl$



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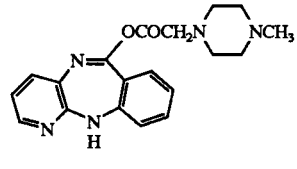

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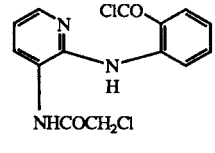
6, R = N $NCH_3$

7, R = Cl



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unequivocally confirmed and/or excluded from $^1H$ and $^{13}C$ nmr spectra. Therefore we have decided to solve the structure of the by-product using X-ray crystallography.

The X-ray analysis led finally to structure **6** which was evidently formed *via* **7**. The step in which the ring contraction took place, must have been the chloroacetylation of **2**. This evidently proceeded by attacking the nitrogen atom N-5 (instead of N-11) with acyl exchange (transacylation) under the formation of an intermediate like **8** in which rotation of the pyridine ring around the (pyridine-2-yl)-*N* bond brought the pyridine nitrogen and the newly formed COCl group closely together. The following recyclization, accompanied by shifting of a double bond and elimination of hydrogen chloride concluded the transformation to **7**. The more discrete mechanism of this strange reaction was not investigated.

## Results and Discussion.

### a. X-Ray Crystallographic Studies.

Atomic coordinates are summarized in Table 1 and bond lengths and angles in Table 2. Figure 1 depicts a perspective view of the molecule, the unit cell content is shown in Figure 2.

Table 1

Atomic coordinates (x $10^4$) of non-H atoms with estimated standard deviations in parentheses.

$$U_{eq} = 1/3 \sum\sum \vec{a}_i.\vec{a}_j \; a_i^* \; a_j^* \; U_{ij}$$

| Atom | x/a | y/b | z/c | $U_{eq}$ (x $10^3$), Å$^2$ |
|---|---|---|---|---|
| C1 | 2830(4) | 3216(4) | 3763(1) | 103(1) |
| C2 | 1610(4) | 2959(5) | 3831(1) | 116(2) |
| C3 | 1108(3) | 2409(5) | 4371(1) | 108(1) |
| C4 | 1839(3) | 2137(4) | 4826(1) | 89(1) |
| C4a | 3093(3) | 2372(3) | 4759(1) | 74(1) |
| C5a | 4971(2) | 2325(3) | 5154(1) | 68(1) |
| C6 | 5725(2) | 2033(3) | 5639(1) | 71(1) |
| C7 | 6951(2) | 2275(4) | 5591(1) | 84(1) |
| C8 | 7478(3) | 2820(4) | 5049(2) | 98(1) |
| C9 | 6814(3) | 3076(4) | 4593(2) | 95(1) |
| C11 | 4877(3) | 3171(3) | 4139(1) | 86(1) |
| C11a | 3593(3) | 2904(4) | 4223(1) | 84(1) |
| C1' | 5463(2) | 1261(4) | 6671(1) | 79(1) |
| C2' | 4503(2) | 575(4) | 7093(1) | 82(1) |
| C2" | 2418(2) | -525(4) | 7121(1) | 82(1) |
| C3" | 1211(2) | -214(4) | 6862(1) | 90(1) |
| C5" | 1619(3) | 3127(4) | 6782(1) | 92(1) |
| C6" | 2837(3) | 2828(4) | 7037(1) | 80(1) |
| C7" | -434(3) | 1966(7) | 6738(2) | 134(2) |
| N5 | 3798(2) | 2077(3) | 5224(1) | 69(1) |
| N6 | 5068(2) | 1487(3) | 6132(1) | 71(1) |
| N10 | 5551(2) | 2854(3) | 4638(1) | 78(1) |
| N1" | 3277(2) | 900(3) | 6900(1) | 71(1) |
| N4" | 745(2) | 1699(4) | 6989(1) | 93(1) |
| O11 | 5414(2) | 3617(3) | 3690(1) | 115(1) |
| O1' | 6515(2) | 1510(3) | 6805(1) | 108(1) |

The prominent feature of the structure is the heterocyclic fused 3-ring system which is planar within ± 0.018 Å including its hydrogens, N(6) and O(11). Search of the crystallographic database [6] has shown that this relatively common ring system has not yet been characterized by a crystal structure determination, either as such or as any of its derivatives. In order to relate the established bond lengths and angles to a reasonable chemical model, the

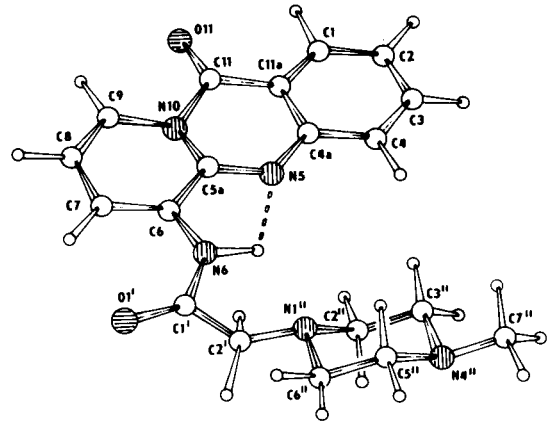


Figure 1. Perspective view of the molecule with atom labelling. Hydrogen atoms are given the numbers of their bonding partners.

Table 2

Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

| | | | |
|---|---|---|---|
| C1-C2 | 1.362(6) | C2-C1-C11a | 120.6(3) |
| C1-C11a | 1.410(5) | | |
| C2-C3 | 1.412(4) | C1-C2-C3 | 119.3(3) |
| C3-C4 | 1.375(4) | C2-C3-C4 | 120.6(3) |
| C4-C4a | 1.397(5) | C3-C4-C4a | 120.5(2) |
| C4a-C11a | 1.399(4) | C4-C4a-C11a | 119.0(2) |
| C4a-N5 | 1.379(4) | C4-C4a-N5 | 118.9(2) |
| | | C11a-C4a-N5 | 122.1(2) |
| C5a-C6 | 1.449(3) | C6-C5a-N5 | 118.7(2) |
| C5a-N5 | 1.310(3) | C6-C5a-N10 | 117.2(2) |
| C5a-N10 | 1.393(3) | N5-C5a-N10 | 124.1(2) |
| C6-C7 | 1.364(3) | C5a-C6-C7 | 121.2(2) |
| C6-N6 | 1.390(3) | C5a-C6-N6 | 113.0(2) |
| | | C7-C6-N6 | 125.8(2) |
| C7-C8 | 1.425(5) | C6-C7-C8 | 118.3(2) |
| C8-C9 | 1.331(6) | C7-C8-C9 | 122.1(3) |
| C9-N10 | 1.403(4) | C8-C9-N10 | 120.2(3) |
| C11-C11a | 1.435(5) | C11a-C11-N10 | 114.4(2) |
| C11-N10 | 1.427(4) | C11a-C11-O11 | 126.2(2) |
| C11-O11 | 1.225(3) | N10-C11-O11 | 119.4(2) |
| | | C1-C11a-C4a | 119.9(3) |
| | | C1-C11a-C11 | 119.5(2) |
| | | C4a-C11a-C11 | 120.5(2) |
| C1'-C2' | 1.497(3) | C2'-C1'-N6 | 113.8(2) |
| C1'-N6' | 1.360(3) | C2'-C1'-O1' | 121.9(2) |
| C1'-O1' | 1.228(3) | N6-C1'-O1' | 124.3(2) |
| C2'-N1" | 1.462(3) | C1'-C2'-N1" | 112.7(2) |
| C2"-C3" | 1.502(3) | C3"-C2"-N1" | 109.4(2) |
| C2"-N1" | 1.457(3) | | |
| C3"-N4" | 1.461(4) | C2"-C3"-N4" | 111.2(2) |
| C5"-C6" | 1.508(4) | C6"-C5"-N4" | 111.2(2) |
| C5"-N4" | 1.458(4) | | |
| C6"-N1" | 1.466(4) | C5"-C6"-N1" | 109.5(2) |
| C7"-N4" | 1.462(4) | | |
| | | C4a-N5-C5a | 118.0(2) |
| | | C6-N6-C1' | 128.6(2) |
| | | C5a-N10-C9 | 121.0(2) |
| | | C5a-N10-C11 | 120.9(2) |
| | | C9-N10-C11 | 118.1(3) |
| | | C2'-N1"-C2" | 112.4(2) |
| | | C2'-N1"-C6" | 112.2(2) |
| | | C2"-N1"-C6" | 110.4(2) |
| | | C3"-N4"-C5" | 109.8(2) |
| | | C3"-N4"-C7" | 110.3(3) |
| | | C5"-N4"-C7" | 111.5(3) |

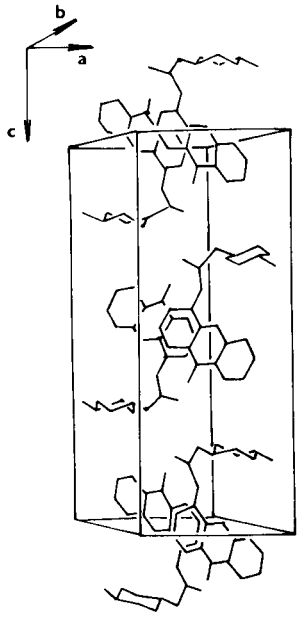


Figure 2. Unit cell content.

3-ring system was approximated as a partial overlap of the more simple quinazolin-4-one and 2*H*-pyrido[1,2-*a*]pyrimidin-4-one fragments, for which 15 and 20 structures respectively were retrieved from the database. After rejecting two of them for the reason of bearing strongly electron-withdrawing substituents which should (and in fact, do) affect drastically the electron distribution within the rings, and after weighted averaging (according to the esd's of individual parameters), a satisfactorily uniform picture of the 3-ring system geometry resulted (Figure 3), characterized by the mean standard deviation of 0.013 Å for bond lengths and 0.9° for bond angles. It is particularly noteworthy that the title structure conforms to this model generally within 1 esd of the individual mean values. An exception is the surrounding of C(6) where substitution by the sterically demanding and hydrogen-bonded side chain occurs. The bond lengths and endocyclic bond angles within the 3-ring system clearly reflect a partial localization of single and double bonds, a feature typical of fused heterocyclic system [7]. Interestingly, this effect is observable even for the carbocyclic part where the deviations from the mean aromatic C–C distance of 1.395 Å exceed, alternatively, ± esd of these bond lengths.

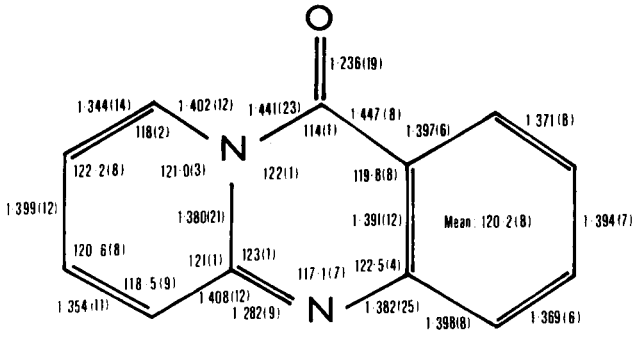


Figure 3. Mean geometry of the 3-ring system deduced from related substructures.

In contrast, the geometry of the 4-methylpiperazinylacetamido substituent is unexceptional. There is only one case where this fragment was subject to a crystal structure determination [8] but the atomic coordinates are not available, preventing a direct comparison to be made. In general, the bond angles, valence and torsion angles of the title structure are as expected [7] for a nearly planar *trans*-peptide group and a chair conformation of the piperazine ring. As shown in Figure 1, there is strong hydrogen bonding between N(6) and N(5) through the amide hydrogen, influencing slightly the geometry of the closest environment and largely determining the orientation of the substituent as a whole relative to the 3-ring system. The parameters of the hydrogen bond are as follows: N(6)-H(6) 0.98(2) Å, H(6)...N(5) 2.18(2) Å, N(6)-H(6)...N(5) 106(1)° and N(6)-H(6)-N(5)-C(5a)-C(6) ring is planar. The hydrogen bond must persist in solution since $\nu$ (NH) ir band in chloroform has a value of 3235 $cm^{-1}$ compared to 3220 $cm^{-1}$ in nujol.

Crystal packing of this structure is also of interest. The planar 3-ring systems of individual molecules are arranged in coplanar stacks along the crystallographic b-axis with a tilt angle relative to the ac-plane of ± 15.6(6)° for the neighbouring stacks (Figure 4). Since the 3-ring systems are mutually related through crystallographic inversion centers, the net result is a nearly eclipsed conformation of the ring atoms and alternating distances of 3.33(1) and 3.42(1) Å within the same stack. These features together strongly indicate that the crystal structure is stabilized by a graphite-like interaction between the heterocyclic 3-ring systems.

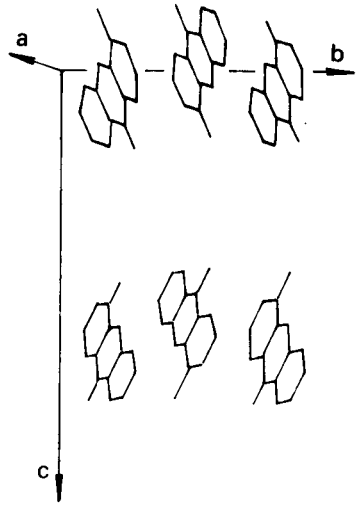


Figure 4. Part of crystal packing showing the arrangement of the 3-ring planes.

Table 3

Proton and Carbon-13 NMR Parameters of Compound **6**

| Proton | δ (H) in deuteriochloroform | J (H,H) [a] | δ (H) in perdeuterioacetone |
|---|---|---|---|
| 1 | 8.42 ddd | J(1,2) = 8.1, J(1,3) = 1.5, J(1,4) = 0.7 | 8.36 |
| 2 | 7.48 ddd | J(2,1) = 8.1, J(2,3) = 6.2, J(2,4) = 2.1 | 7.53 |
| 3 | 7.85 ddd | J(3,1) = 1.5, J(3,2) = 6.2, J(3,4) = 8.3 | 7.94 |
| 4 | 7.79 ddd | J (4,1) = 0.7, J(4,2) = 2.1, J(4,3) = 8.3 | 7.88 |
| N(6)H | 11.21 bs | | 11.19 |
| 7 | 8.55 d | J(7,8) = 7.4 | 8.55 [b] |
| 8 | 6.86 t | J(8,7) = J(8,9) = 7.4 | 7.01 |
| 9 | 8.55 d | J(9,8) = 7.4 | 8.53 [b] |
| 2' | 3.28 s | | 3.24 |
| 2",3",5",6" | 2.73 m | | 2.68 |
| 7" | 2.44 s | | 2.35 |

[a] The same values of J (H,H) were observed in both solvents; in perdeuterioacetone the additional J (7,9) = 1.4 Hz was obtained.
[b] The assignment can be interchanged.

## b. NMR Study.

Proton and carbon-13 nmr spectra were in general agreement with the structure **6**. After the structure **6** was determined from X-ray analysis we could make a complete structural assignment of nmr parameters.

The assignment of proton chemical shifts of 2-(4-methyl-1-piperazinyl)acetamido fragment was straightforward (see Table 3). Downfield position of N(6)H signal (δ 11.21) and its low temperature dependence ($\Delta\delta NH/\Delta T = -1.6 \times 10^{-3}$ ppm) confirm the presence of hydrogen bond N(6)-H(6)-...N(5) in deuteriochloroform solution. On the other hand the singlet of C(2')$H_2$ protons and unresolved multiplet of nearly equivalent piperazine ring protons indicate rather high mobility of this part of molecule in solution. Protons of two aromatic rings could be distinguished by spin systems and corresponding spectra. In the trisubstituted aromatic ring the protons H(9) and H(7) have the same chemical shift in deuteriochloroform (δ 8.55) and only slightly different values in perdeuterioacetone (δ 8.55 and 8.53). It is obviously due to very similar chemical surrounding, especially the orientation of carbonyl groups, as it is seen from Figure 1. In the disubstituted aromatic ring one proton is significantly shifted downfield (δ 8.42), again due to the effect of C(11)-carbonyl group, and can be assigned to H(1). Then, the signals of H(2), H(3) and H(4) can be assigned using coupling connectivities.

The $^{13}C$ nmr spectrum showed 17 signals differentiated by the number of bearing hydrogens in the APT spectrum. The five signals of the acetamidopiperazinyl side-chain

Table 4

Carbon-13 NMR Parameters of Compound **6** in Deuteriochloroform

| Carbon | δ(C) | $^1J$(C,H) | Long-range J(C,H) |
|---|---|---|---|
| 1 | 127.27 | 164.6 | J(1,3) = 7, J(1,2) ≈ 2 |
| 2 | 125.15 | 164.5 | J(2,4) = 7.7 |
| 3 | 134.68 | 162.0 | J(3,1) = 9.3 |
| 4 | 126.53 | 163.5 | J(4,2) = 6.9, J(4,3) = 1.0 |
| 4a | 146.95 | -- | J(4a,1) ≈ J(4a,3) ≈ 7.3 |
| 5a | 141.19 | -- | J(5a,7) = J(5a,9) = 6.5, J(5a,NH) ≈ 4 |
| 6 | 130.81 | -- | J(6,7) = J(6,NH) = 2.1, J(6,8) = 8.4 |
| 7 | 117.11 | 171.4 | J(7,8) = 1.3, J(7,9) = 8.3, J(7,NH) = 5.3 |
| 8 | 112.45 | 169.3 | J(8,NH) = 3.9 |
| 9 | 119.79 | 190.8 | J(9,7) = 7.5, J(9,8) = 5.5 |
| 11 | 158.47 | -- | [a] |
| 11a | 116.12 | -- | J(11a,2) = 8.5, J(11a,4) = 4.0 |
| 1' | 169.68 | -- | J(1',2') = 5.4 (2x), J(1,NH) = 2.6 |
| 2' | 61.91 | 135.0 | [a] |
| 2",6" | 53.27 | 135.1 | [a] |
| 3",5" | 55.50 | 133.7 | [a] |
| 7" | 46.18 | 132.9 | [a] |

[a] Long-range couplings could not be obtained from unsufficiently resolved signals.

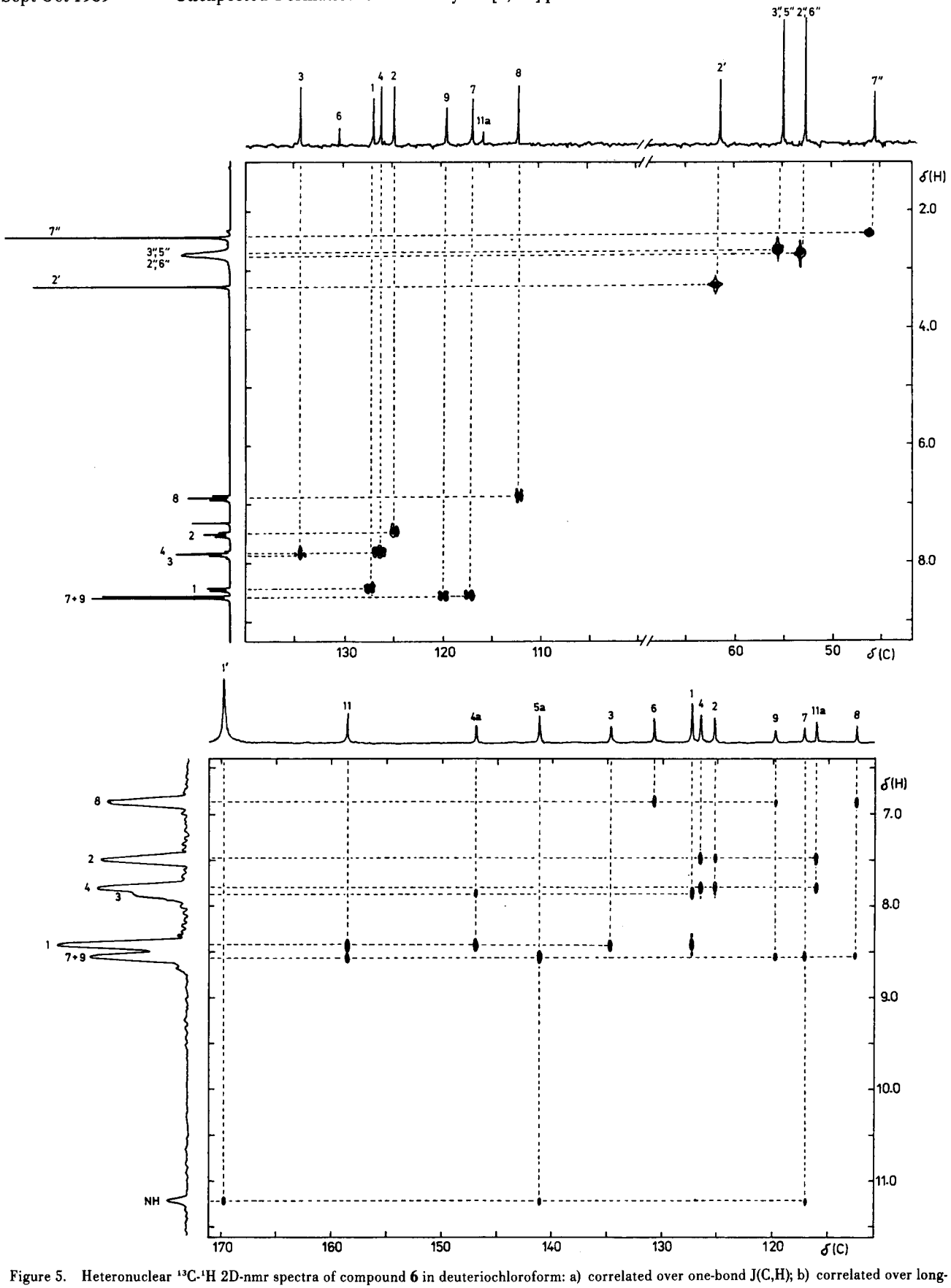


Figure 5. Heteronuclear $^{13}C$-$^{1}H$ 2D-nmr spectra of compound **6** in deuteriochloroform: a) correlated over one-bond J(C,H); b) correlated over long-range J(C,H).

could be easily assigned by means of the chemical shifts and intensities. From 12 signals of the 3-ring aromatic system the signal at δ 158.47 was assigned to amide carbonyl carbon C(11). Its upfield position (compared to the second amide carbon C(1') at δ 169.68) can be explained by the known shielding effect of conjugation (see *e.g.* ref [9]). Seven aromatic CH carbon signals were assigned using heteronuclear 2D nmr spectrum (HETCOR) correlated over $^1J(C,H)$ couplings and already assigned proton signals (see Figure 5a). To distinguish between C(9) and C(7), possessing the same chemical shifts of corresponding protons, we have used one bond J(C,H) values obtained from proton-coupled $^{13}C$ nmr spectrum. Larger $^1J(C,H)$ value of 190.8 Hz must belong to C(9) (the effect of directly bonded nitrogen atom) and smaller value 171.4 Hz belongs to C(7). For the assignment of the residual quaternary aromatic carbon signals we have combined the HETCOR correlated over long-range J(C,H) couplings (see Figure 5b) and proton-coupled $^{13}C$ nmr spectrum. From the last one we could obtain also the most of J(C,H) constants which are given in Table 4.

Table 5

Crystal Data, Measurement and Refinement Details.

| | |
|---|---|
| Formula | $C_{19}H_{21}N_5O_2$ |
| Molecular weight | 351.43 |
| Space group | $P2_1/c$ |
| a,b,c (Å) | 11.04(1), 7.002(3), 23.39(2) |
| α,β,γ (°) | 90, 87.64(7), 90 |
| Cell volume (Å$^3$) | 1806(2) |
| Z | 4 |
| $D_m$, $D_x$ (g.cm$^{-3}$) | 1.30(1), 1.292 |
| Radiation | CuKα, λ = 1.5418 Å |
| Absorption correction | None, μ = 0.673 mm$^{-1}$ |
| F(000) | 744 |
| Temperature (K) | 295(1) |
| Crystal Dimensions (mm) | 0.7 x 0.4 x 0.2 |
| No. of reflections for latt. par. determination | 15 (9.5 < θ < 15°) |
| Diffractometer | Syntex $P2_1$ |
| Scan mode | θ - 2θ |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.55 |
| Standard reflections (variation) | 3 after every 47 (<5 %) |
| Interval h | ‹-12,12› |
| Interval k | ‹0,7› |
| Interval l | ‹0,22› |
| No. or reflections measured | 2418 |
| No. of reflections used (I>1.96σ(I)) | 2144 |
| Resid. electr. density (e.Å$^{-3}$) | 0.22, –0.18 |
| $(\delta/\sigma)_{max}$ for non-H atoms | 0.14 |
| Function minimized | $w(\|F_o\| - \|F_c\|)^2$ |
| Weight | $(\sigma^2(F_o) + 0.0009\|F\|^2)^{-1}$, $\sigma(F_o)$ from counting statistics |
| R, wR | 0.060, 0.079 |

## EXPERIMENTAL

6-(2-(4-Methyl-1-piperazinyl)acetamido)-11*H*-pyrido[2,1-*b*]quinazolin-11-one (**6**).

The compound was prepared according to ref [2], mp 193-195° (ethanol); uv (methanol): (Unicam SP 8000) λ max in nm (log ε): infl 274.5 (4.26), 281 (4.34), 360 (4.20), 378 (4.08), 398 (3.86); ir (nujol): (Perkin-Elmer 298) ν cm$^{-1}$ 690, 752, 779, 824 (4 and 3 adjacent Ar-H), 1495, 1550, 1608 (Ar), 1640 (CON), 1690 (CONH), 2780 (N-$CH_3$), 3220 (NH); ms: (MCH 1320 and Varian MAT 311) m/z, % 351 ($M^+$, $C_{19}H_{21}N_5O_2$, 2), 308 (2), 295 (2), 294 (2), 238 (64), 211 (7), 113 (95), 70 (100).

*Anal.* Calcd. for $C_{19}H_{21}N_5O_2$ (mol wt 351.4): C, 64.94; H, 6.02; N, 19.93. Found: C, 65.02; H, 6.03; N, 20.01.

X-Ray Crystallographic Study.

Yellow single crystals were obtained by slow cooling of the hot saturated solution in toluene/heptane (1/1 v/v). The density of the crystals was determined by flotation in an aqueous zinc bromide solution. Crystal data and details of measurement and refinement are summarized in Table 5. The structure was solved by direct methods [10] and refined by full-matrix least squares [11]. Scale factor, positions and anisotropic displacement parameters of non-H atoms and three group ($CH_3$, $CH_2$, aromatic) isotropic displacement parameters of H atoms were refined simultaneously. The C-bonded hydrogens were constrained at idealized positions according to $sp^2$ and $sp^3$ geometry; the amide hydrogen was fixed with coordinates found from a difference map. Secondary extinction correction of type I [12] was applied yielding the refined g-value of 1.4(1) x 10$^{-6}$.

NMR Spectra.

The nmr spectra of compound **6** were measured on a FT NMR Varian XL-200 spectrometer ($^1H$ at 200 MHz and $^{13}C$ at 50.3 MHz, respectively) in deuteriochloroform and/or in perdeuterioacetone at room temperature (24°) with TMS as the internal reference.

Proton chemical shifts and interproton coupling constants were obtained by first order analysis from the expanded parts (2 Hz/cm) of standard $^1H$ nmr spectra. Temperature dependence of NH proton was obtained from deuteriochloroform spectra in the temperature interval 24 to 44°. Carbon-13 chemical shifts were determined from proton noise-decoupled spectrum (spectral width 12 kHz, acquisition time 1 s, pulse width 5μs (flip angle 50°), equilibration delay 1 s). For the "attached proton test" $^{13}C$ nmr spectrum the APT pulse sequence [13] was used with J-modulation time 6.5 ms (corresponds to $^1J(C,H)$ 154 Hz).

Heteronuclear $^{13}C$-$^1H$ correlated 2D-nmr spectra were obtained using a HETCOR pulse sequence [14] (spectral width 7 kHz ($^{13}C$) and 2 kHz ($^1H$), acquisition time 0.146 s, observe $^{13}C$ pulse 8.5 μs (flip angle 90°), proton pulse 68 μs (90°) with decoupler, equilibration delay 2s, 48 transients for each of 256 increments, data matrix 2048 x 512 data points; delay times adjusted using $^1J(C,H)$ 154 Hz for one-bond HETCOR spectrum and/or J(C,H) 5 Hz for long-range HETCOR spectrum). Proton coupled $^{13}C$ nmr spectrum with nOe enhancement was measured using spectral width 8 kHz, pulse width 8.5 μs (flip angle 90°), acquisition time 2 s, 32 K data points, broadband decoupling switched "on" during

2 s before acquisition and switched "off" during the data acquisition, 12 300 transients accumulated.

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Supplementary Material.

Anisotropic thermal parameters, hydrogen atom coordinates and observed and calculated structure factors for compound **6** are available from the author (J.P.) on request.

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