

Nonclassical *Pschorr* and *Sandmeyer* Reactions in Pyrazole Series

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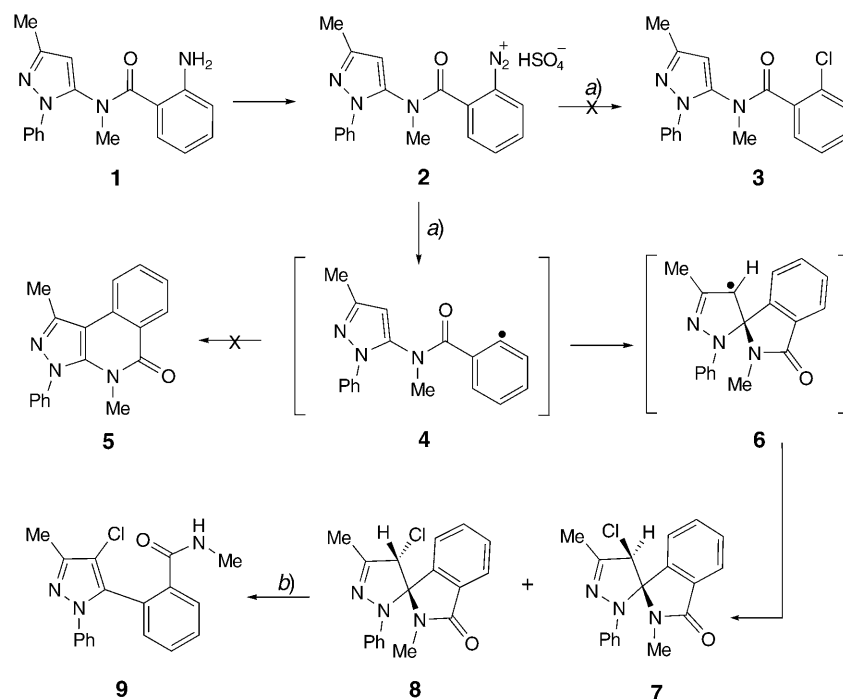
The diazonium salt derived from 4-amino-*N*,1,3-trimethyl-*N*-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-1*H*-pyrazole-5-carboxamide (**14**) was reacted with a mixture of CuSO₄ and NaCl, with ascorbic acid as an initiator to afford the planar derivative 4,6-dihydro-1,4,6,8-tetramethyl-3-phenyldipyrazolo[3,4-*b*:4',3'-*d*]pyridin-5(3*H*)-one (**16**) and its unexpected isomer 4,6-dihydro-3,4,6,8-tetramethyl-1-phenyldipyrazolo[4,3-*b*:4',3'-*d*]pyridin-5(1*H*)-one (**17**), as well as the epimers (3*S*,4*S*)- (or (3*S*,4*R*)-) and (3*S*,4*R*)- (or (3*S*,4*S*)-) 4-chloro-2,4-dihydro-1',3',5,5'-tetramethyl-2-phenylspiro[pyrazole-3,4'(1'*H*)-pyrrolo[3,4-*c*]pyrazol]-6'(5'*H*)-one (**18a** and **b**, respectively). Epimers **18a** and **b** were converted under basic conditions to 4'-chloro-*N*,1,3,3'-tetramethyl-1'-phenyl-[4,5'-bi-1*H*-pyrazole]-5-carboxamide (**19**). The structures of isomers **16** and **17** determined by single-crystal X-ray analysis are also reported. Linear dichroism (LD) measurements for the above isomers suggest that **17** intercalates into DNA, and **17** exhibited antiproliferation activity against human NCI-H460 pulmonary carcinoma cells.

Introduction. – Previously, we reported the transformation of diazonium salt **2**, derived from 2-amino-*N*-methyl-*N*-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)benzamide (**1**). This reaction was carried out with CuSO₄ and NaCl, with ascorbic acid as a reducing agent (*Scheme 1*). The diazonium sulfate **2** afforded neither the chloro derivative **3**, the product of the classical *Sandmeyer* reaction, nor the tricyclic derivative **5**, the expected product of the competitive *Pschorr* ring closure. Instead, we obtained epimers **7** and **8**, the formation of which can be considered examples of consecutive nonclassical *Pschorr* and *Sandmeyer* reactions [1], presumably *via* radical intermediates **4** and **6** (*Scheme 1*). The isomeric product **9** was formed by treatment of the mixture of epimers **7** and **8** with 1*M* alcoholic KOH, with restoration of the aromatic system of the pyrazole nucleus [2].

In continuation of our research on pyrazole chemistry, we thought it of interest to investigate the above reaction to establish the role of the aryl-diazonium moiety in the reaction pathway. Here, we describe the CuSO₄/ascorbic acid-catalyzed decomposition in the presence of NaCl of the diazonium sulfate **15**, which bears a pyrazole-diazonium moiety in place of the benzene-diazonium in **2** (*Scheme 2*).

Results and Discussion. – Pyrazolecarbonyl chloride **11**, obtained *in situ*, was reacted with *N*,3-dimethyl-1-phenyl-1*H*-pyrazol-5-amine (**12**) to give nitro derivative **13**, which, in turn, was reduced to the corresponding amine **14**. The pyrazole-diazonium salt **15**, obtained from **14**, was reacted under the same conditions as applied to **2** to afford the tricyclic isomers **16** and **17** and the chlorinated epimers **18a** and **b**

Scheme 1



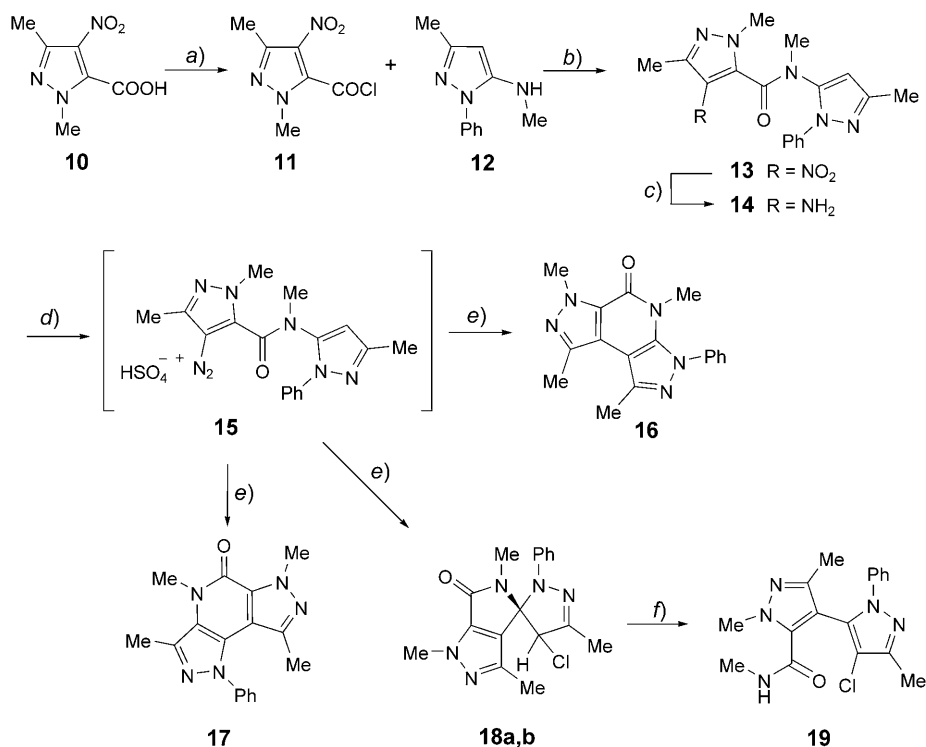
(Scheme 2). The new compounds were characterized by means of analytical and spectral data and, in the case of isomers **16** and **17**, by X-ray analysis.

The ^1H -NMR spectra of **16** and **17** showed signals consistent with four Me groups as shown in the structures. The spectrum of compound **16** showed for the Me groups at 3-positions of the two pyrazole nuclei, two closely spaced resonance signals at δ 2.59 and 2.62, whereas the corresponding Me groups in isomer **17** produced signals at δ 1.47 and 2.69. The high-field signal at δ 1.47 is due to the Me group located in the shielding zone of the Ph ring. Further, the pyridinone Me group of **16** but not **17** exhibited carbonyl diamagnetic anisotropy.

The ^1H -NMR spectra of epimers **18a** and **b** showed signals at δ 5.93 and 5.82, respectively, due to the pyrazoline H-atom, as well as those of the four Me groups at δ 2.19–3.91 and 2.03–3.86, respectively. The relative configuration of the pyrazoline C(5)-atom was not determined. A possible mechanism for formation of isomers **16** and **17** and epimers **18a** and **b** is proposed in Scheme 3.

On the basis of the experimental results, the radical intermediates **20** and **21** (Scheme 3) are more reactive than the analogous species **4** and **6** (Scheme 1). In fact, in the intermediate **20**, the radical attack at C(4) and C(5) of the pyrazole nucleus takes place to afford the tricyclic system **16** and the radical spiro-species **21**, respectively, whereas the intermediate **4** is transformed to only the spiro-intermediate **6**. Species **21**

Scheme 2



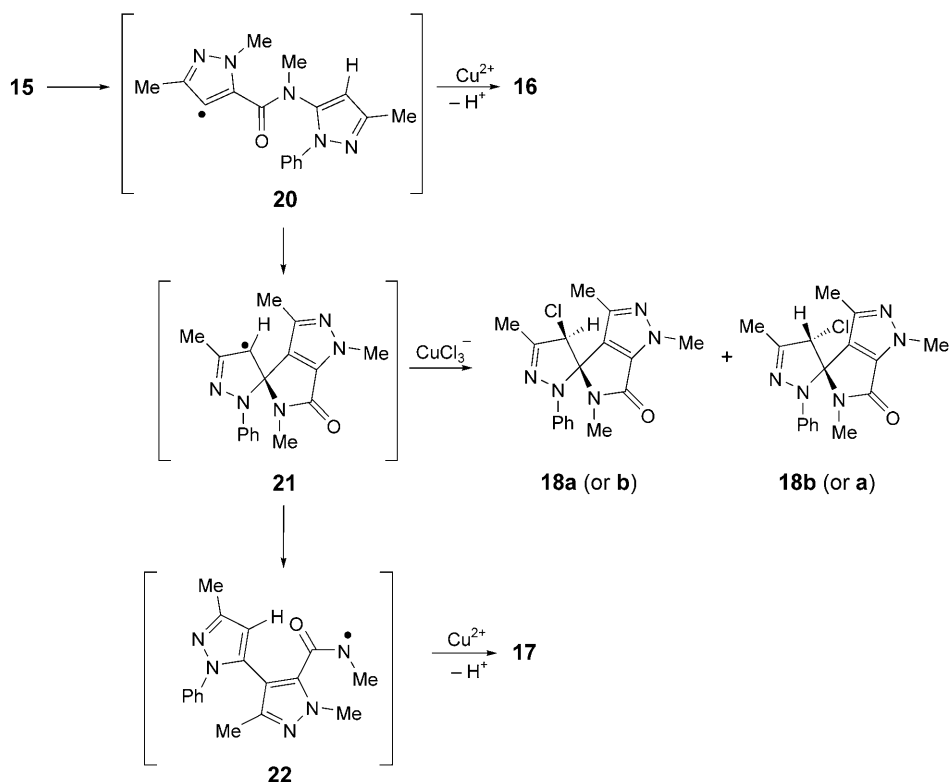
Reagents: a) SOCl₂ reflux. b) Et₃N/CHCl₃ reflux. c) Fe/AcOH. d) KNO₂/H₂SO₄. e) CuSO₄/ascorbic acid/NaCl. f) KOH.

produces both epimers **18a** and **b** and rearranges *via* the *N*-centered radical **22** to form **17**, an isomer of **16**, whereas **6** is transformed only to the epimeric couple **7** and **8**.

Finally, epimer **18a** was reacted with KOH in EtOH solution to give the derivative **19** (Scheme 2). The same result was obtained from reaction of a mixture of **18a** and **b**; conversion of **18b** was confirmed by TLC analysis. The mechanism of the reaction is probably similar to that proposed for the formation of compound **9** from **8** (Scheme 1) [2]. This transformation represents a new way to obtain the 5,4'-bipyrazole system.

ORTEP [3] Views of isomers **16** and **17** are shown in Figs. 1 and 2. The isomers have in common a tricyclic system with the pyrazolo[3,4-*c*]pyridin-4-one moieties equally substituted, but differ in the point of closure of the ring to give the Me- and Ph-substituted pyrazole. In fact, **17** can be thought of as being derived from **16** by a 180° rotation along an ideal axis passing through N(2) and the mid-point of the C(8)–C(9) bond, with exchange of the relative ring-junction atoms.

The crystal structure of **17** is characterized by the presence of a molecule of H₂O of crystallization, which bridges adjacent molecules *via* H-bond interactions involving two N-atoms of pyrazole at the two terminal parts of the tricyclic system with contact distances N(5) ··· O(H₂O) 2.92(1) Å and O(H₂O) ··· N(2') 2.94(1) Å (N(5) ···

Scheme 3. Suggested Mechanism for the Transformation of **15**

H(111)–(H₂O) 1.87 Å, 156(6)° and (H₂O)–H(112) · · · N(2') 2.34 Å, 133(8)°; at 1.5 – x, – 1/2 + y, 1.5 – z). The presence of H₂O gives rise to infinite chains that develop along the *b* axis (Fig. 3), while, in **16**, which has no crystallized H₂O, the molecules are oriented parallel to the (101) plane, as shown in Fig. 4.

Finally, we thought it of interest to verify whether the nearly planar heteroaromatic isomers **16** and **17** are able to intercalate into DNA. Due to the very low solubility of the compounds, particularly **16**, only the somewhat more-soluble **17** could be investigated. The interaction of **17** with DNA was evaluated by means of linear dichroism (LD) experiments according to Vedaldi *et al.* [4]. The presence of a small negative band in the 300–350 nm region of the LD spectrum (Fig. 5), corresponding to the maximum absorption range of the compound, was observed, suggesting that the chromophore of the compound lies parallel to the base pairs of the macromolecule, thus indicating intercalation into the macromolecule. Isomer **17** was also active against proliferation of human NCI-H460 pulmonary carcinoma cells with a *IC*₅₀ value of 30 µg/ml. Presumably, the antiproliferation activity is correlated to DNA intercalation.

Conclusions. – The radical intermediate **20** derived from diazonium salt **15** exhibits chemical behavior different from that reported for radical **4** obtained from diazonium

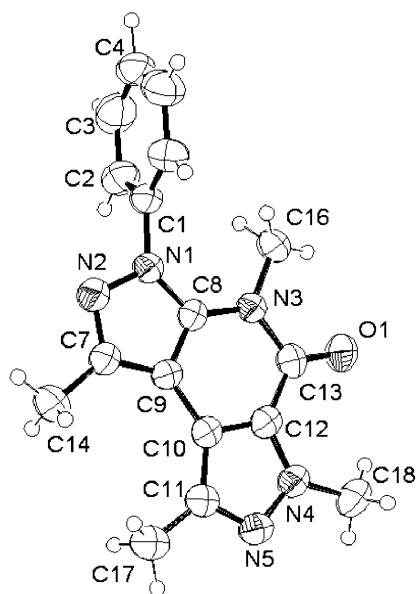


Fig. 1. ORTEP [3] Drawing of the crystal structure of **16** (ellipsoids at 50% probability; arbitrary numbering)

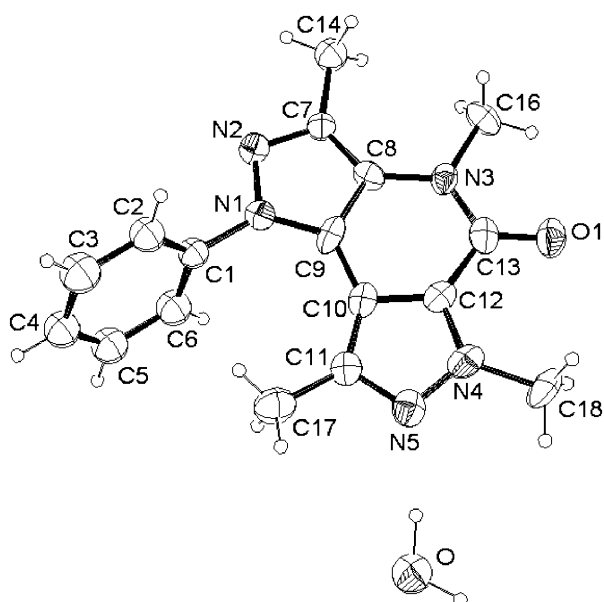
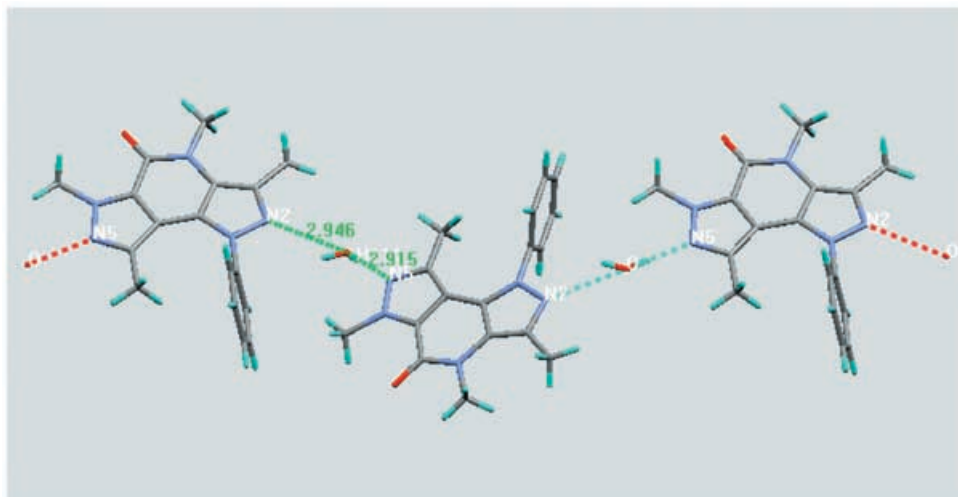
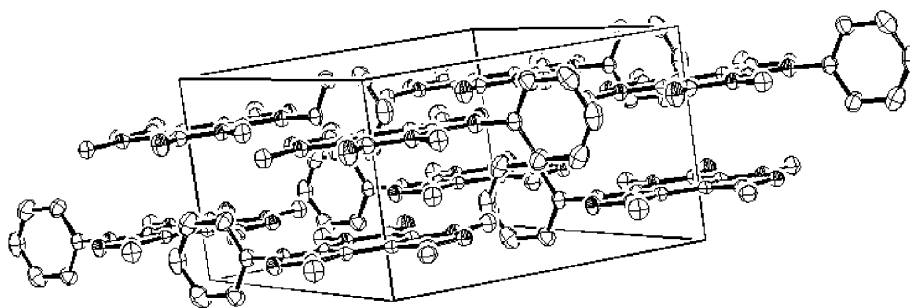


Fig. 2. ORTEP [3] Drawing of the crystal structure of **17** (ellipsoids at 50% probability, arbitrary numbering)

salt **2**. This difference is related to the presence of a dimethyl-substituted pyrazole radical in **20** in place of a phenyl radical in **4**. The transformation of **20** is based on intramolecular attack of the radical moiety on C(4) and C(5) of the phenyl-substituted

Fig. 3. Chain arrangement of the molecules in **17**Fig. 4. Crystal packing of **16**

pyrazole ring. To find **17** among the isolated products was quite unexpected, as it forms as a result of consecutive transformations of **20**. Isomerization of epimers **18a** and **b** to **19** under basic conditions represents a new way to obtain the 4,5'-bipyrazole system. Finally, isomer **17** showed, to some extent, DNA-intercalation, as well as moderate antiproliferation activity against human NCI-H460 pulmonary carcinoma cells.

Experimental Part

General. M.p.: Büchi 530 capillary melting-point apparatus; uncorrected. IR Spectra: Perkin-Elmer Spectrum RXI-FT spectrophotometer; hexachlorobutadiene solns.; ν in cm^{-1} . $^1\text{H-NMR}$ Spectra: Bruker AC-E 250F (250 MHz); in $(\text{D}_6)\text{DMSO}$; δ in ppm rel. to Me_4Si as internal standard. MS: Waters AutoSpec-Ultima orthogonal T.O.F. mass spectrometer; 75 eV; m/z (%). Microanalyses (C, H, N) were performed in the laboratories of the Dipartimento di Scienze Farmaceutiche-Università di Catania. Compound **17** was dried in a cell thermostatted at 150° under vacuum 4 h before analysis.

1,3-Dimethyl-4-nitro-1H-pyrazole-5-carbonyl Chloride (11). 1,3-Dimethyl-4-nitro-1H-pyrazole-5-carboxylic acid (**10**; 1.85 g, 10 mmol) [5] was reacted with SOCl_2 (12 ml) under reflux for 5 h. The soln. was evaporated under reduced pressure and the oily residue obtained was dissolved in abs. benzene (20 ml). The soln. was

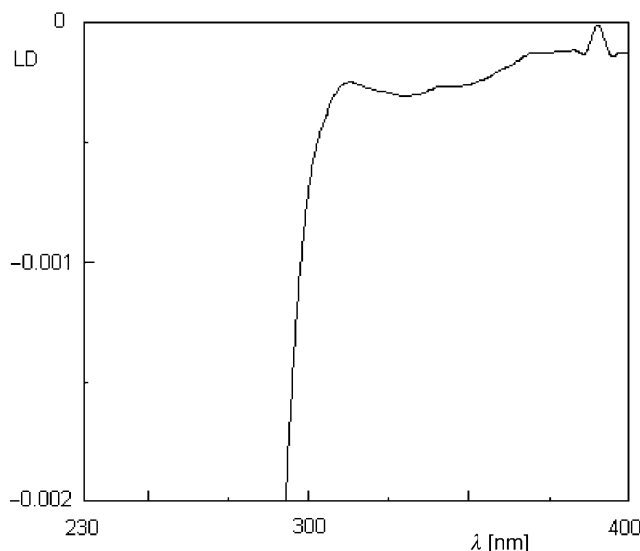


Fig. 5. Linear dichroism spectrum of **17**–DNA complex (optical path 1 mm)

evaporated under reduced pressure. This last part of the procedure was repeated and the oily residue was used in the next step.

N,1,3-Trimethyl-N-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-4-nitro-1H-pyrazole-5-carboxamide (13). A soln. containing equimolar amounts of **11** and **N,3-dimethyl-1-phenyl-1H-pyrazol-5-amine (12)**; 1.87 g, 10 mmol [6] in dry CHCl_3 (100 ml) was refluxed for 5 h. After the first hour, Et_3N (1.6 ml) was added in four portions (0.8, 0.4, 2×0.2 ml, resp., with intervals of 1 h between additions). The soln. was evaporated under reduced pressure, and the solid residue was washed with H_2O (2×100 ml) and crystallized from EtOH to afford **13** (1.06 g, 30%). Crystalline colorless solid. M.p. 136–137°. IR: 1664 (CO). $^1\text{H-NMR}$: 2.13 (s, Me); 2.78 (s, Me); 3.53 (s, Me); 6.21 (s, H–C(4) of pyrazole); 7.16–7.57 (m, 5 arom. H). MS: 354 (M^+). Anal. calc. for $\text{C}_{17}\text{H}_{18}\text{N}_6\text{O}_3$: C 57.62, H 5.12, N 23.72; found: C 57.47, H 5.19, N 23.59.

4-Amino-N,1,3-trimethyl-N-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-1H-pyrazole-5-carboxamide (14). A susp. of Fe filings (8 g) in 5% aq. AcOH (10 ml) was heated at ca. 100° under stirring on the water bath of a rotavapor until H_2 evolution ceased. The NO_2 derivative **13** (4.6 g, 13 mmol) was added in four portions, with intervals of 20 min between additions. After the last addition, stirring was continued at 100° for 1 h, then the mixture was cooled to r.t. The pH of the susp. was adjusted to 7–8 with a sat. soln. of NaHCO_3 . The solid was separated by filtration, air dried overnight, and then extracted with boiling CHCl_3 (3×50 ml). The combined extracts were evaporated under vacuum, leaving an oily residue that solidified by addition of a small amount of Et_2O to give practically pure **14** (3.12 g, 74%). Crystalline colorless solid. M.p. 122–124° (Et_2O). IR: 3429–3335 (multiple bands), 1634 (CO). $^1\text{H-NMR}$: 1.89 (s, Me); 2.20 (s, Me); 2.85 (s, Me); 3.36 (s, Me); 3.73 (s, NH_2 (exchangeable with D_2O)); 6.52 (s, H–C(4) of pyrazole); 7.13–7.47 (m, 5 arom. H). MS: 324 (M^+). Anal. calc. for $\text{C}_{17}\text{H}_{20}\text{N}_6\text{O}$: C 62.95, H 6.21, N 25.91; found: C 62.71, H 6.31, N 25.75.

1,3-Dimethyl-5-[[methyl(3-methyl-1-phenyl-1H-pyrazol-5-yl)amino]carbonyl]-1H-pyrazole-4-diazonium Sulfate (15). Pulverized **14** (1.49 g, 4.6 mmol) was dissolved in cooled (0–5°) 5N H_2SO_4 (9.2 ml), and 2.5M aq. NaNO_2 (1.92 ml) was added dropwise to the stirred soln. The soln. was stirred for a further 15 min in an ice bath and then checked for excess HNO_2 with KI-starch paper; excess HNO_2 was destroyed by addition of urea.

(3S,4S)- or (3S,4R)-4-Chloro-2,4-dihydro-1',3',5',5'-tetramethyl-2-phenylspiro[3H-pyrazole-3,4'-(1'H)-pyrrolo[3,4-c]pyrazol]-6'(5'H)-one (18a). To a cold (0–5°) soln. (220 ml) of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ (0.3M) and NaCl (0.75M), first the soln. of **15** obtained from the previous procedure, and then ascorbic acid (205 mg, 1.6 mmol) were added under stirring. The mixture was stirred for 1 h at r.t. and then filtered. The solid product obtained was dried (anh. CaCl_2) for 24 h and then processed by flash chromatography (FC) [7] (external diameter of the column 5 cm, silica gel (0.040–0.063 mm, 170 g), AcOEt/light petroleum ether 6:4 (40–70°)); 50 ml fractions were collected. The initial ten fractions were discarded and Fr. 11–16 were evaporated under reduced pressure

to give 500 mg of a mixture that was crystallized from Et₂O to give **18a** (160 mg). Crystalline colorless solid. M.p. 156–158°. IR: 1708 (CO). ¹H-NMR: 2.19 (s, Me); 2.21 (s, Me); 2.47 (s, Me); 3.91 (s, Me); 5.93 (s, H–C(4) of pyrazole); 6.82–7.21 (m, 5 arom. H). MS: 343 (M⁺). Anal. calc. for C₁₇H₁₈ClN₅O: C 59.39, H 5.28, N 20.37; found: C 59.17, H 5.40, N 20.03.

4,6-Dihydro-1,4,6,8-tetramethyl-3-phenyldipyrzolo[3,4-b:4',3'-d]pyridin-5(3H)-one (16). Fr. 21–26 were evaporated under vacuum, and the residues crystallized from AcOEt to give **16** (100 mg): Colorless crystalline solid. M.p. 241–243°. IR: 1649 (CO). ¹H-NMR: 2.58 (s, Me); 2.61 (s, Me); 3.09 (s, Me); 4.18 (s, Me); 7.53 (s, 5 arom. H). MS: 307 (M⁺). Anal. calc. for C₁₇H₁₇N₅O: C 66.43, H 5.57, N 22.79; found: C 66.57, H 5.60, N 22.60.

4,6-Dihydro-3,4,6,8-tetramethyl-1-phenyldipyrzolo[4,3-b:4',3'-d]pyridin-5(1H)-one (17). Fr. 32–38 were evaporated under vacuum, and the residues crystallized from AcOEt to give **17** (90 mg). White crystalline solid. M.p. 220–222°. IR: 1646 (CO). ¹H-NMR: 1.46 (s, Me); 2.61 (s, Me); 3.75 (s, Me); 4.20 (s, Me); 7.57 (br. s, 5 arom. H). MS: 307 (M⁺). Anal. calc. for C₁₇H₁₇N₅O: C 66.43, H 5.57, N 22.79; found: C 66.65, H 5.45, N 22.87.

(3S,4R)- or (3S,4S)-4-Chloro-2,4-dihydro-1',3',5,5'-tetramethyl-2-phenylspiro[3H-pyrazole-3,4'(1'H)-pyrrolo[3,4-c]pyrazol]-6'(5'H)-one (18b). The residue obtained by evaporation of the mother liquors of Fr. 11–16 were processed by FC [7] (external diameter of column 3.5 cm, silica gel (0.004–0.063 mm, 70 g), Et₂O/light petroleum ether 7:3 (40–70°)); 50 ml fractions were collected. The first eight fractions were discarded, and Fr. 17–19 were evaporated to afford a small amount of practically pure **18b**. IR: 1705 (CO). ¹H-NMR: 2.03 (s, Me); 2.20 (s, Me); 2.70 (s, Me); 3.86 (s, Me); 5.81 (s, H–C(4) of pyrazole); 6.70–7.19 (m, 5 arom. H). MS: 343 (M⁺).

4'-Chloro-N,1,3,3'-tetramethyl-1'-phenyl[4,5'-1H-bipyrzole]-5-carboxamide (19). Epimer **18a** (80 mg) was dissolved in 1M KOH in abs. EtOH (5 ml) and the soln. was stirred for 15 h at r.t. The obtained soln. was diluted with H₂O to a volume of 25 ml and then extracted with Et₂O (3 × 25 ml). The combined extracts were dried (Na₂SO₄) and evaporated to afford a solid residue. Crystallization from AcOEt/light petroleum ether (40–70°) gave compound **19** (60 mg, 75%). Colorless crystalline solid. M.p. 111–112°. IR: 3231 (NH), 1671 (CO). ¹H-NMR: 1.67 (s, Me); 2.27 (s, Me); 2.60 (s, Me); 3.84 (s, Me); 7.24–7.41 (m, 5 arom. H); 7.9 (br. s, NH (exchanges very slowly with D₂O)). MS: 343 (M⁺). Anal. calc. for C₁₇H₁₈ClN₅O: C 59.39, H 5.28, N 20.37; found: C 59.60, H, 5.41, N 20.21.

X-Ray Crystallography. The crystal data for **16** and **17** are given in Table 1, and significant bond lengths are listed in Table 2. The intensity data were collected on a CAD4 diffractometer with graphite monochromated MoK_α radiation (λ 0.71073 Å). The cell parameters were determined and refined by least-squares fit of 20 high-angle reflections. The structures were solved by direct methods with Sir-92 [8] and conventional Fourier synthesis (SHELX-97) [9]. The refinement of the structures was made by full-matrix least-squares on F². All non-H-atoms were refined anisotropically. The H-atom positions were detected in a difference Fourier synthesis and refined with isotropic thermal factors. The supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition numbers 253865 and 253866).

Linear Dichroism (LD) Measurements. The LD spectra of DNA solns. (4 × 10^{−3} M) containing 2 mM NaCl and 1 mM EDTA were measured in the absence and presence of excess **17** on a Jasco J500 CD spectrometer converted for LD according to Wada and Kozawa [10]. Briefly, a quartz cylinder was immersed in a cylindrical cell with two quartz windows. The sample soln. was illuminated with plane-polarized light of incidence perpendicular to the cell axis. When the inner cylinder rotates, the long, stiff DNA molecules are oriented in the flow. The LD spectrum is the difference between the absorption spectra recorded with and without cylinder rotation (i.e., with the molecules oriented randomly or ordered, resp.).

Antiproliferation Assay. Compound **17** was tested *in vitro* for the antiproliferation activity against the human NCI-H460 cell line. Cells were suspended at a density of 4 × 10⁵ cells per ml in minimum essential medium (Eagle MEM, Sigma) supplemented with 10% fetal calf serum (FCS) and antibiotics, transferred (100 µl per well) to 96-well plate and incubated for 4 d at 37° in a humidified atmosphere containing 5% CO₂. After this incubation time, the cells reached confluence, the medium was removed and replaced with RPMI-1640 (without phenol red but with FCS, 0.025% glutamine, and antibiotics) with or without test compound and incubated at 37° for 3 d. At the end of this incubation time, the antiproliferation activity was determined by means of the MTT ((3-(4, 5-dimethylthiazolyl)-2)-5-diphenyltetrazolium bromide; thiazolyl blue) assay [11] and expressed as the IC₅₀ value (test concentration at which the cell proliferation was inhibited to a level 50% of that of the untreated control).

We are grateful to Prof. S. Caffieri (Padova University) for the LD measurements, to Dr. D. Schillaci (Palermo University) for the antiproliferation test and to the Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, Research fund ex 60%) for financial support.

Table 1. *Crystal and Refinement Data for 16 and 17*

	16	17
Formula	C ₁₇ H ₁₇ N ₅ O	C ₁₇ H ₁₉ N ₅ O ₂
Molecular weight	307.36	323.36
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>n</i>
Cell parameters		
<i>a</i> [Å]	10.460(2)	7.226(7)
<i>b</i> [Å]	6.898(2)	20.362(8)
<i>c</i> [Å]	10.820(2)	11.421(4)
β [°]	108.81(5)	96.74(5)
<i>V</i> [Å ³]	739.0(3)	1668.8(9)
<i>Z</i>	2	4
Calc. density [g cm ⁻³]	1.381	1.287
Absorption coeff. (mm ⁻¹)	0.091	0.088
<i>F</i> (000)	324	688
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Crystal size [mm]	0.5 × 0.5 × 1	0.3 × 0.3 × 1
θ range [°]	2.06–24.98	2.00–19.98
Limiting indices	12 ≥ <i>h</i> ≥ –12, 8 ≥ <i>k</i> ≥ –1, 12 ≥ <i>l</i> ≥ –12	6 ≥ <i>h</i> ≥ –6, 19 ≥ <i>k</i> ≥ 0, 10 ≥ <i>l</i> ≥ 0
Refls. collected	1919	1642
Unique refls.	1411	1548
Completeness to θ	99.9%	99.7%
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data, restraints, parameters	1411, 0, 148	1548, 0, 175
Goodness-of-fit on <i>F</i> ²	1.038	0.997
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0508, <i>wR</i> ₂ = 0.1280	<i>R</i> ₁ = 0.0554, <i>wR</i> ₂ = 0.1340

Table 2. *Significant Bond Lengths [Å] for 16 and 17*

	16	17
N(1)–N(2)	1.370(4)	1.352(9)
N(1)–C(9)		1.37(1)
N(1)–C(8)	1.349(5)	
N(2)–C(7)	1.308(5)	1.34(1)
C(9)–C(8)	1.384(5)	1.39(1)
C(7)–C(8)		1.35(1)
C(9)–C(7)	1.400(5)	
N(1)–C(1)	1.426(5)	1.433(8)
N(3)–C(13)	1.408(5)	1.36(1)
C(10)–C(12)	1.389(6)	1.40(1)
C(12)–C(13)	1.445(6)	1.48(1)
C(10)–C(9)	1.443(5)	1.43(1)
O(1)–C(13)	1.212(5)	1.23(1)
N(5)–C(11)	1.333(5)	1.35(1)
N(3)–C(8)	1.378(5)	1.40(1)
N(3)–C(16)	1.452(5)	1.475(9)
N(4)–N(5)	1.344(5)	1.36(1)
N(4)–C(12)	1.354(5)	1.34(1)
C(10)–C(11)	1.403(5)	1.36(1)
N(4)–C(18)	1.454(5)	1.50(1)
C(11)–C(17)	1.468(6)	1.46(1)

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