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SYNTHESIS AND REARRANGEMENT OF 5-ISOTHIOCYANATOPYRAZOLINES

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Abstract- 1-(3-Iminoprop-1-enyl)-5-isothiocyanato-2-pyrazolines have been synthesized by reaction of hydrazine derivatives with carbon disulfide. These pyrazoline derivatives are precursors of pyrimidinylpyrazoles.

Hydrazine derivatives 1 are easily obtained by reaction of ketazines with saturated nitriles[1] and are useful precursors in the synthesis of heterocycles.[1,2] On the other hand, the usefulness of carbon disulfide as a synthetic reagent in the preparation of heterocycles and other organic compounds has been widely demonstrated.[3]

A few years ago, we reported that 4-amino-1-azabutadienes react with carbon disulfide to give pyrimidine-2(1*H*)-thiones.[4] Moreover, ethyl chloroformate reacts with these azadienes[4] and with the hydrazine derivatives 1[2] to yield pyrimidine-2(1*H*)-ones. Accordingly, we have thought it of interest to study the reaction of hydrazines 1 with carbon disulfide.

RESULTS AND DISCUSSION

Hydrazines 1 react with carbon disulfide 2 at 80°C (THF, sealed tube) giving 5-isothiocyanatopyrazolines 4 in high yields. The structure of 4 are deduced from their elemental analysis and spectral data; thus, compounds 4 display in their ir spectra a clear absorption at ca. 2000 cm^{-1}, which is assigned to the N=C=S stretching vibration. The ^{1}H-nmr spectra show the methylene group of the pyrazoline ring as a typical AB system with coupling constant of 19 Hz. This methylene carbon is found at ca. 50(t) ppm. in the ^{13}C-nmr; The corresponding carbon resonance of the isothiocyanate group is

not observed because of the large relaxation time of this tipe of carbon atom.

The formation of the pyrazoline 4 can be rationalised in terms of nucleophilic addition of the unsubstituted imine nitrogen atom to the heterocumulene to form the intermediate 3, which leads to the pyrazoline 4 by an intramolecular condensation reaction (see scheme I).

We thought that heterocycles 4 with attached isothiocyanate and azadiene groups should be, in principle, precursors of other heterocycles through simple intramolecular reactions. Surprisingly, pyrazolines 4 are stable in mild acid media. Thus, when these compounds are allowed to react with 1N H_2SO_4 or trifluoroacetic acid at room temperature, the starting heterocycles 4, are recovered. However, with more concentrated acid (5N H_2SO_4, room temperature) other unidentified products are found.

On the other hand, treatment of 4 with butyllithium gives rise to 3*H*-pyrazolo[1,5-a]pyrimidine 5, which is also obtained by hydrolysis of hydrazines 1.[1] The formation of compounds 5 can be explained by an attack of the imine anion to the quaternary carbon.

SCHEME I

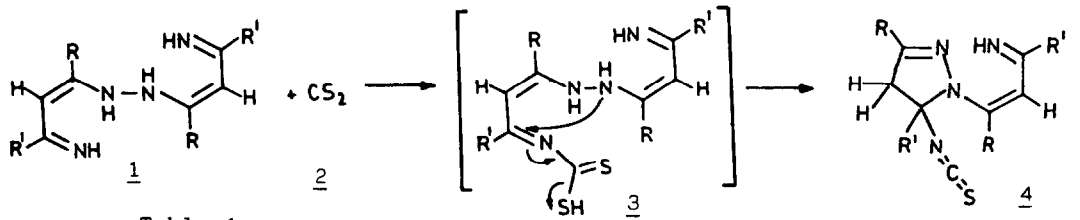


Table 1

Compound	R	R'	Yield %	mp °C
4a	CH_3	C_6H_5	94	195-198
4b	C_2H_5	C_6H_5	92	157-159
4c	CH_3	C_6H_{11}	92	142-144
4d	CH_3	4-CH_3-C_6H_4	93	130-133
4e	C_6H_5	C_6H_5	90	148-151

Then, we studied the effect of heating pyrazolines 4 and found that pyrimidinylpyrazoles 6 are obtained as the major product (51-70 % yield). Thus, treatment of a toluene solution of 4 at 130°C in a sealed tube affords the heterocycles 6 (see scheme II). In some cases, the pyrimidines 7 and the pyrazoles 8 are isolated as side products but with very low yields (see experimental section).

SCHEME II

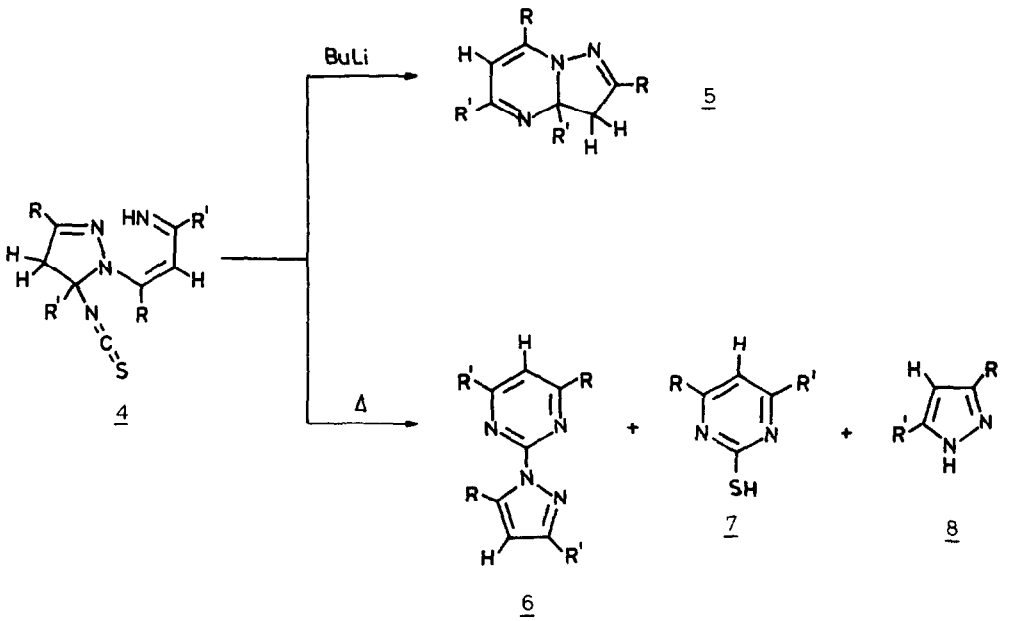


Table 2

Compound	R	R'	Yield %
6a	CH_3	C_6H_5	51
6b	C_2H_5	C_6H_5	61
6c	CH_3	C_6H_{11}	70
6d	CH_3	4-CH_3-C_6H_4	55

Compounds 6, 7 and 8 were characterized on the basis of their elemental analysis, ir, ^{1}H-nmr, ^{13}C-nmr and mass spectral data; the structure of heterocycles 6 was unequivocally established by an X-ray single crystal structure analysis of 6a. It is worth noting the position of R and R' in the pyrazole ring (figures 1 and 2).

Table 3 gives the main geometrical characteristics of the molecule (see Fig. 1). The four rings are so arranged that the two phenyl rings subtend an angle of 49° (see Fig. 2), with the pyrimidine ring slightly puckered in a 11-8 boat form.

The constitution of the pyrimidine and pyrazole rings agree with that found in a search through the CSD.[6] The pyrimidine ring has alternately low values with C6-N11 and C6-N7 shorter than C8-N7 and C10-N11. The pyrazole ring presents angular values at N1 and at C3 higher than the other ones with

the N-C distances of different values due to N1-C5 and N-N distances longer than those reported by CSD.

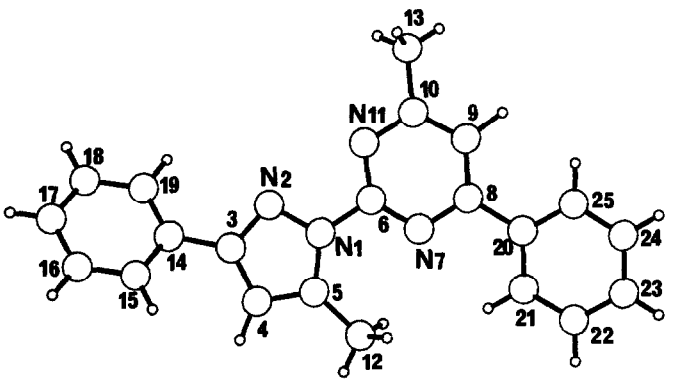


Fig. 1. Molecular structure[5] with the numbering system used in the crystallography work.

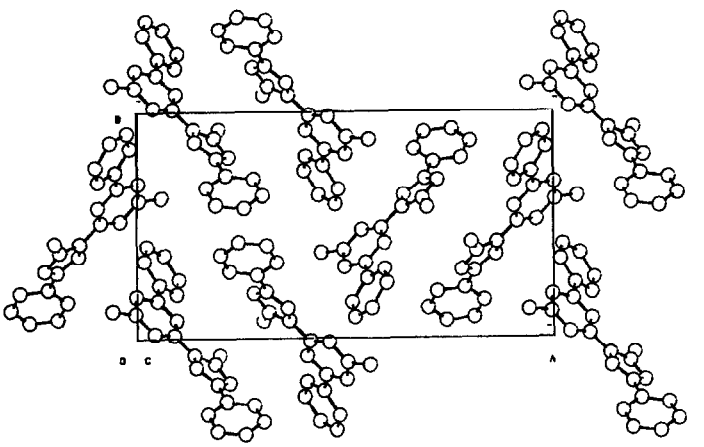


Fig. 2. The crystal packing[5] as viewed down the c axis.

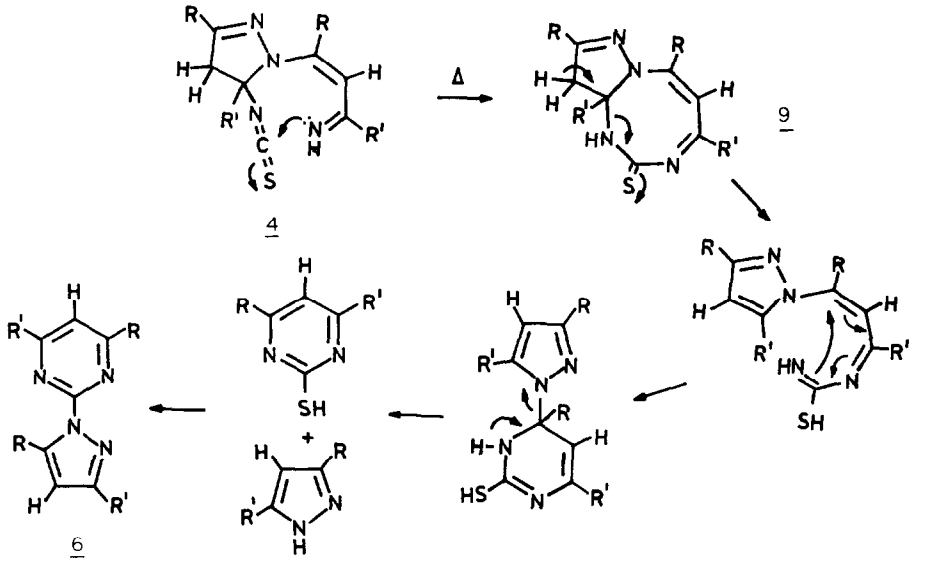
Table 3. Selected geometrical parameters (Å, °)

N1-N2	1.379(3)	N2-C3	1.329(3)
C3-C4	1.409(4)	C4-C5	1.363(4)
C5-N1	1.379(3)	N1-C6	1.416(3)
C3-C14	1.473(4)	C5-C12	1.496(5)
C6-N7	1.322(3)	N7-C8	1.349(3)
C8-C9	1.382(4)	C9-C10	1.379(4)
C10-N11	1.345(4)	N11-C6	1.335(3)
C8-C20	1.479(4)	C10-C13	1.504(5)

C5-N1-C6	129.4(2)	N2-N1-C6	118.2(2)
N2-N1-C5	112.4(2)	N1-N2-C3	103.9(2)
N2-C3-C4	111.7(2)	C3-C4-C5	106.6(2)
C4-C5-N1	105.4(2)	N2-C3-C14	121.4(2)
C4-C3-C14	126.9(2)	C4-C5-C12	127.6(3)
N1-C5-C12	126.9(3)	N1-C6-N11	116.1(2)
N1-C6-N7	115.8(2)	N7-C6-N11	128.1(2)
C6-N7-C8	116.4(2)	N7-C8-C9	120.4(2)
C8-C9-C10	118.1(2)	C9-C10-C11	122.3(3)
C6-N11-C10	114.6(6)	N7-C8-C20	116.6(2)
C9-C8-C20	122.9(2)	C9-C10-C13	121.6(3)
N11-C10-C13	116.1(3)		
N2-N1-C6-N11	-12.9(3)	N2-C3-C14-C19	38.5(4)
C9-C8-C20-C25	15.7(4)	N7-C6-N11-C10	-3.4(4)
N11-C6-N7-C8	1.3(4)	C6-N7-C8-C9	1.9(4)
N7-C8-C9-C10	-2.8(4)	C8-C9-C10-N11	0.6(4)
C9-C10-N11-C6	2.2(4)		

A tentative mechanism for the formation of 6 is shown in the scheme III. Thus, the intramolecular addition of the imine nitrogen atom to the heterocumulene to form the intermediate 9 takes place first; then, the rearrangement outlined in the scheme would account for the formation of pyrimidinylpyrazole 6. The isolation of pyrimidine 7 and pyrazole 8, although in very low yields, supports the postulated mechanism.

SCHEME III



Pyrimidinylpyrazoles, such as 6, are scarcely known in the literature.[7] Several metabolites with this skeleton have been identified in the human urine.[8] Moreover, pyrimidinylpyrazoles are included in other more complex structures with biological activity.[9]

EXPERIMENTAL

The infrared spectra were recorded on a Pye-Unicam SP-1000 using KBr as support. The ^{1}H-nmr and ^{13}C-nmr spectra were recorded on a Varian FT-80 A and on a Brücker Ac-300 spectrometers in deuteriochloroform, using TMS as internal standard, chemical shifts are expresed in δ(ppm) and the coupling constants, J, are measured in Hz. The mass spectra were recorded on a Hewlett Packard 5897 A and the elemental analysis were performed by Mikroanalytisches Perkin-Elmer 240. All the melting points were determinated on a Büchi apparatus and are uncorrected.

SYNTHESIS OF COMPOUNDS:

1-(3-Iminoprop-1-enyl)-5-isothiocyanato-2-pyrazolines. General procedure. A sample of 1 mM hydrazine derivative 1 was dissolved in 10 ml THF, and 0.6 ml (10 mM) of carbon disulfide were added. The mixture was heated at 80° C for 20 h in a sealed tube. The solvent was removed in vacuo and the product was purified by recrystallization from hot hexane/chloroform.

1-(3-Imino-1-methyl-3-phenylprop-1-enyl)-5-isothiocyanato-3-methyl-5-phenyl-2-pyrazoline (4a). Yield 0.34 g (94 %). Mp. 195-198°C. Ir (KBr): 2040 cm^{-1} (N=C=S). ^{1}H-Nmr: 2.22 (s, 3H, CH_3), 2.70(s, 3H, CH_3), 3.57(d, J=18.9, 1H, CH_2) 4.30(d, J=18.9, 1H, CH_2), 5.76 (s, 1H, CH), 7.30-8.00(m, 10H, aromatic H). ^{13}C-Nmr: 16.21(q), 18.36(q), 53.15(t), 78.56(s), 94.32(d), 123.55(d), 129.01 (d), 129.04(d), 129.04(s), 129.37(d), 129.62(d), 133.62(d), 138.32(s), 155.23 (s), 158.51(s), 166.17(s). Mass spectrum m/e: 360(M^+). Anal ($C_{21}H_{20}N_4S$):found C, 70.10; H, 5.73; N, 15.65; calc. C, 69.70; H, 5.58; N, 15.52 %.

3-Ethyl-1-(1-ethyl-3-imino-3-phenylprop-1-enyl)-5-isothiocyanato-5-phenyl-2-pyrazoline (4b). Yield 0.36 g (92 %). Mp. 157-159°C. Ir(KBr): 2060 cm^{-1} (N=C=S). ^{1}H-Nmr: 1.19(t, 3H, CH_3), 2.19(t, 3H, CH_3), 2.49(q, 2H, CH_2), 3.00 (q, 2H, CH_2), 3.48(d, J=19.0, 1H, CH_2), 3.62(d, J=19.0, 1H, CH_2), 5.84(s, 1H, CH), 7.22-8.00(m, 10H, aromatic H). ^{13}C-Nmr: 10.02(q), 11.24(q), 23.73(t), 25.20(t), 51.46(t), 78.07(s), 92.96(d), 123.26(d), 128.80(d, 2C), 129.13(d), 129.35(d), 129.58(s), 133.31(d), 138.17(s), 158.49(s), 160.03(s), 170.27(s). Mass spectrum m/e: 388(M^+). Anal. ($C_{23}H_{24}N_4S$): found C, 71.18; H, 6.31; N, 14.40; calc. C, 71.10; H, 6.23; N, 14.42 %.

5-Cyclohexyl-1-(3-cyclohexyl-3-imino-1-methylprop-1-enyl)-5-isothiocyanato-3-methyl-2-pyrazoline (4c). Yield 0.34 g (92 %). Mp. 142-144°C. Ir (KBr): 2070 cm^{-1} (N=C=S). ^{1}H-Nmr: 0.70-2.00 (m, 22H, C_6H_{11}), 2.20 (s, 3H, CH_3), 2.49(s, 3H, CH_3), 3.57(d, J=19.2, 1H, CH_2), 3.39(d, J=19.2, 1H, CH_2), 5.30 (s, 1H,CH) 11.10(s, 1H, NH). ^{13}C-Nmr: 15.54(q), 18.12(q), 23.93(d), 24.69(t), 24.99(t), 25.04(t), 25.08(t), 25.26(t), 25.60(t), 25.67(t), 30.71(t), 31.05(t), 39.44 (d), 42.31(d), 44.81(t), 80.33(s), 92.55(d), 153.57(s), 164.12(s), 167.69(s). Mass spectrum m/e: 372(M^+). Anal. ($C_{21}H_{32}N_4S$): found C, 67.72; H, 6.85; N, 14.84; calc. C, 67.52; H, 6.63; N, 15.00 %.

1-(3-Imino-1-methyl-3-p-tolylprop-1-enyl)-5-isothiocyanato-3-methyl-5-p-tolyl-2-pyrazoline (4d). Yield 0.37 g (93 %). Mp. 130-133°C. Ir (KBr): 2050 cm^{-1} (N=C=S). ^{1}H-Nmr: 2.22(s, 3H, CH_3), 2.31(s, 3H, CH_3), 2.41(s, 3H, CH_3), 2.64 (s, 3H, CH_3), 3.53(d, J=19.0, 1H, CH_2), 4.26(d, J=19.0, 1H, CH_2), 5.57(s, 1H, CH), 7.16-7.81(m, 8H, aromatic H). ^{13}C-Nmr: 16.22(q), 18.32(q), 20.97(q), 21.55(q), 53.13(t), 78.41(s), 93.88(d), 123.47(d), 126.77(s), 128.96(d), 129.63(d), 130.11(d), 135.29(s), 139.67(s), 144.83(s), 154.87(s), 158.34(s), 165.85(s). Mass spectrum m/e: 388(M^+). Anal. ($C_{23}H_{24}N_4S$): found C, 71.28; H, 6.32; N, 14.37; calc. C, 71.10; H, 6.23; N, 14.42 %.

1-(3-Imino-1,3-diphenylprop-1-enyl)-5-isothiocyanato-3,5-diphenyl-2-pyrazoline (4e). Yield 0.44 g (90 %). Mp. 148-151°C. Ir (KBr): 2050 cm^{-1} (N=C=S). ^{1}H-Nmr: 4.08(d, J=18.5, 1H, CH_2), 4.75(d, J=18.5, 1H, CH_2), 6.17(s, 1H, CH), 7.25-8.29(m, 20H, aromatic H). ^{13}C-Nmr: 49.28(t), 79.29(s), 95.10(d), 123.50(d), 127.63(d), 128.60(s), 128.84(d), 128.93(d), 129.07(d), 129.17(d), 129.35(d), 129.61(d), 129.71(s), 129.88(s), 130.21(d), 132.33(d), 133.09(d), 133.78(d),

138.81(s), 153.98(s), 159.63(s), 162.42(s). Mass spectrum m/e: 484(M^+). Anal. ($C_{31}H_{24}N_4S$): found C, 76.91; H, 5.07; N, 11.37, calc. C, 76.83; H, 4.99; N, 11.56%.

Compounds 5. General procedure. A sample of 0.5 mM isothiocyanatopyrazoline derivative 4 was dissolved in 10 ml THF. The mixture was cooled at 0°C. Then, 0.3 ml of 2.2N butyllithium were added. After being stirred 12h, the mixture was poured into ice-water. The organic layer was extracted with ether and THF and the combined extracts dried (Na_2SO_4), filtered and evaporated. The residue was purified by recrystallisation from hexane. Spectroscopic data of these compounds were reported in reference 1.

Compounds 6, 7 and 8. General procedure. A sample of 0.5 mM isothiocyanatopyrazoline derivative 4 was dissolved in 10 ml toluene. The mixture was heated at 140°C in a sealed tube. The solvent was removed in vacuo and the products 6, 7 and 8 were purified by chromatography (Kieselgel 60, Merck) with chloroform. Some of the compounds 7 and 8 have only been detected in the spectral data of reaction crudes.

5-Methyl-3-phenyl-1-(5'-methyl-3'-phenyl-2-pyrimidinyl)pyrazole. (6a). Yield 0.08 g (51 %). Crystallized from hexane/chloroform. Mp. 127-129°. ^{1}H-Nmr: 2.60 (s, 3H, CH_3), 2.80(s, 3H, CH_3), 6.55(s, 1H, CH), 7.15-8.10(m, 11H, aromatic H), ^{13}C-Nmr: 15.54(q), 24.59(q), 107.04(d), 113.20(d), 126.26(d), 127.20(d), 128.12(s), 128.27(d), 128.85(d), 131.08(d), 132.69(s), 136.21(s), 143.30(s), 152.88(s), 157.57(s), 164.90(s), 170.21(s). Mass spectrum m/e : 326 (M^+). Anal. ($C_{21}H_{18}N_4$): found C, 77.17; H, 5.60; N, 17.14, calc. C, 77.28; H, 5.56; N, 17.16%.

2-Mercapto-6-methyl-4-phenylpyrimidine. (7a). Yield 7.1 mg (7%). Mp. 202-204°C ^{1}H-Nmr: 2.50(s, 3H, CH_3), 6.97(s, 1H, CH), 7.20-8.10(m, 5H, aromatic H). ^{13}C-Nmr: 20.14(q), 107.68(d), 127.10(s), 128.12(d), 128.71(s), 132.27(d), 134.82 (s). Mass spectrum m/e: 202 (M^+). Anal. ($C_{11}H_{10}N_2S$): found C, 65.53; H, 5.15; N, 13.58. calc. C, 65.32; H, 4.98; N, 13.85%.

5-Methyl-3-phenylpyrazole. (8a). Yield 3.9mg (5%). Mp. 126-127°C. Spectroscopic data in reference 10.

5-Ethyl-3-phenyl-1-(5'-ethyl-3'-phenyl-2-pyrimidinyl)pyrazole. (6b). Yield 0.11g (61%). Oil. ^{1}H-Nmr: 1.20-1.60(m, 6H, CH_3), 3.03(q, 2H, CH_2), 3.40(q, 2H, CH_2), 6.33(s, 1H, CH), 7.20-8.45(m, 11H, aromatic H). ^{13}C-Nmr: 12.59(q), 13.28 (q), 22.09(t), 31.11(t), 105.06(d), 111.97(d), 126.24(d), 127.29(d), 128.04 (d), 128.29(d), 128.82(d), 130.99(d), 132.96(s), 136.47(s), 149.53(s), 152.84 (s), 157.70(s), 165.39(s), 174.79(s). Mass spectrum m/e 354 (M^+). Anal. ($C_{23}H_{22}N_4$): found C, 77.99; H, 6.37; N, 15.73, calc. C, 77.94; H, 6.26; N, 15.80%.

3-Cyclohexyl-5-methyl-1-(3'-cyclohexyl-5'-phenyl-2-pyrimidinyl)pyrazole (6c). Yield 0.12g (70%). Oil. ^{1}H-Nmr: 1.03-2.16(m, 22H, C_6H_{11}), 2.30(s, 3H, CH_3), 2.50(s, 3H, CH3), 5.86(s, 1H, CH), 6.56(s, 1H, CH), ^{13}C-Nmr: 11.46(q), 20.61 (q), 24.86-32.06(t), 35.19(d), 43.12(d), 100.22(d), 107.21(d), 113.79(s), 143.43(s), 152.29(s), 164.00(s), 172.35(s), 180.22(s). Mass spectrum m/e: 175 (M^+-163); m/e: 163 (M^+-175). Anal. ($C_{21}H_{30}N_4$) found C, 74.75; H, 8.97; N, 16.79, calc. C, 74.52; H, 8.93; N, 16.55%.

5-Methyl-3-p-tolyl-1-(5'-methyl-3'-p-tolyl-2-pyrimidinyl)pyrazole (6d). Yield 0.1g (55%). Oil. ^{1}H-Nmr: 2.30(s, 3H, CH_3), 2.33(s, 3H, CH_3), 2.56(s, 3H, CH_3), 2.73(s, 3H, CH_3), 6.50(s, 1H, CH), 7.10-8.20(m, 11H, aromatic H). ^{13}C-Nmr: 15.49(q), 21.13(q), 21.25(q), 24.44(q), 106.88(d), 112.59(d), 126.03(d), 127.00(d), 128.89(d), 129.46(d), 129.76(s), 133.26(s), 137.77(s), 141.42(s), 143.05(s), 152.72(s), 164.63(s), 169.88(s). Mass spectrum m/e 354 (M^+). Anal. ($C_{23}H_{22}N_4$): found C, 77.97; H, 6.37; N, 15.77. calc. C, 77.94; H, 6.26; N, 15.80%.

2-Mercapto-6-methyl-4-p-tolylpyrimidine. (7d). Yield 5.4 mg (5 %). Oil. ^{1}H-Nmr: 2.33(s, 3H, CH_3), 2.56(s, 3H, CH_3), 7.00-8.00(m, 5H, aromatic H). ^{13}C-Nmr: 13.04(q), 21.26(q), 120.82(d), 126.62(d), 129.36(d), 133.00(s), 138.91(s), 163.78(s), 167.75(s). Mass spectrum m/e: 216 (M^+). Anal. ($C_{12}H_{12}N_2S$): found C, 66.71; H, 5.40; N, 13.03, calc. C, 66.63; H, 5.59; N, 12.95%.

5-Methyl-3-p-tolylpyrazole. (8d). Yield 2.6 mg (3 %). Mp. 122-123°C. Spectroscopic data in reference 10.

X-Ray analysis of compound 6a.

Crystallography analysis is summarized in Table 4 and the final atomic coordinates are presented in Table 5.

Table 4. Crystal analysis parameters at room temperature.

Crystal data	
Formula	$C_{21}H_{18}N_4$
Crystal habit	Transparent prism
Crystal size (mm)	0.67 x 0.23 x 0.17
Symmetry	Orthorombic, $p2_12_12_1$
Unit cell determination:	Least-squares fit from 95 Reflections ($\theta < 45°$)
Unit cell dimensions	20.3985(10), 11.0489(3), 7.6715(2) Å
Packing: V(Å), Z	1733.5(1), 4
Dc($g.cm^{-3}$), M, F(000)	1.251, 326.4, 688
μ (cm^{-1})	5.64
Experimental data	
Technique	Four circle diffractometer Bisecting geometry Graphite oriented monochromator: CuK_α $\omega/2\theta$ scans, scan width: 1.6° Detector aperture 1.0 x 1.0°
Total measurements	Up to 65° in θ
Speed	1 min./reflec.
Number of reflections:	
Independent	1709
Observed	1542 [3 σ (I) criterion]
Standar reflections:	2 reflections every 90 minutes Variation: no
Solution and refinement	
Solution	Direct methods
Refinement	L.S. on F_{obs}, full matrix
Parameters:	
Number of variables	298
Degrees of freedom	1244
Ratio of freedom	5.2
H atoms	Difference synthesis
Final shift/error	0.04
Weigthing scheme	Empirical as to give no trends in $<W\Delta^2F>$ vs. $<\|Fobs\|>$ or $<(\sin\theta)/\lambda>$
Max. Thermal value	U_{11}[C24] = 0.093(3)A^2
Final F peaks	0.11 e. $Å^{-3}$
Final R and R_w	0.037, 0.041
Computer and programs	VAX 11/750 XRAY76 System[11], Multan80[12]
Scattering factors	Int. Tables for X-Ray Crystallography[13]

Table 5. Final atomic coordinates and thermal parameters as in:

$$U_{eq} = (1/3) \cdot \Sigma(U_{ij} \cdot a^*_i \cdot a^*_j \cdot a_i \cdot a_j \cdot \cos(a_i, a_j))$$

ATOM	x/a	y/b	z/c	$U_{eq} \cdot 10^4$
N1	0.3645(1)	0.0766(2)	0.2171(3)	359(6)
N2	0.3614(1)	0.1317(2)	0.3777(3)	391(6)
C3	0.3099(1)	0.2047(2)	0.3655(4)	366(9)
C4	0.2804(1)	0.1981(3)	0.2001(4)	422(8)
C5	0.3153(1)	0.1152(2)	0.1072(4)	401(8)
C6	0.4130(1)	-0.0131(2)	0.1900(4)	356(7)
N7	0.4062(1)	-0.0791(2)	0.0479(3)	357(6)
C8	0.4517(1)	-0.1659(2)	0.0216(4)	370(8)
C9	0.5009(1)	-0.1849(3)	0.1421(4)	430(8)
C10	0.5036(1)	-0.1094(3)	0.2848(4)	440(8)
N11	0.4601(1)	-0.0199(2)	0.3102(3)	422(7)
C12	0.3044(2)	0.0768(4)	-0.0771(5)	613(12)
C13	0.5566(2)	-0.1217(4)	0.4197(6)	627(12)
C14	0.2885(1)	0.2797(2)	0.5134(4)	385(8)
C15	0.2218(1)	0.2975(3)	0.5412(4)	491(9)
C16	0.1996(2)	0.3680(3)	0.6767(5)	582(11)
C17	0.2433(2)	0.4233(3)	0.7861(5)	643(12)
C18	0.3098(2)	0.4080(4)	0.7587(5)	697(13)
C19	0.3325(1)	0.3358(3)	0.6247(5)	555(10)
C20	0.4468(1)	-0.2349(2)	-0.1426(4)	398(8)
C21	0.4067(1)	-0.1947(3)	-0.2765(4)	455(9)
C22	0.4015(2)	-0.2592(3)	-0.4304(4)	558(10)
C23	0.4359(2)	-0.3657(4)	-0.4507(5)	669(12)
C24	0.4760(2)	-0.4064(3)	-0.3190(6)	711(13)
C25	0.4820(2)	-0.3421(3)	-0.1660(5)	542(10)

Lists of the structure factors, thermal components and hydrogen parameters have been deposited with the Cambridge Crystallographic Database.

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REFERENCES

1. J. Barluenga, L. Muñiz, V. Gotor, J. Chem. Soc., Chem. Commun., 1982, 454.

2. J. Barluenga, L. Muñiz, M. J. Iglesias, V. Gotor, Synthesis, 1985, 1146.

3. M. Yocoyama, T. Imamoto, Synthesis, 1984, 797.

4. J. Barluenga, M. Tomás, V. Rubio, V. Gotor, J. Chem. Soc., Chem. Commun.; 1979, 675.

5. W. D. S. Motherwell (1978) PLUTO. A program for plotting crystal and molecular structures: Cambridge University. England.

6. F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennerd, W. D.S. Narthewell, J. R. Rogers, D. G. Watson., Acta Cryst. 1979, B35, 2331.

7. J. Elguero in "Comprehensive Heterocyclic Chemistry", Vol. 5, Chapter 4.04, 1984, Pergamon Press.

8. R. Dohmori, R. Yoshimura, S. Kitahara, Y. Tanaka, T. Naito, Chem. Pharm. Bull., 1970, 18, 1908; Y. Tanaka, M. Sano, ibid, 1976, 24, 804.

9. K. Ueno, A. Akashi, T. Moroi, T. Yamazaki, H. Kojima, A. Kasahara, Japan. Pat. 42,072 (1973), trough Chem. Abs., 1974, 81, 3933q.

10. J. Barluenga, L. Muñiz, M.J. Iglesias, V. Gotor, J. Chem. Soc. Perkin Trans. I, 1984, 611.

11. P. Main, S. J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J. P. Declercq, M. M. Woolfson, Multan 80 System, 1980. University of York. England.

12. J. M. Stewart, P. A. Machin, C. W. Dickinson, H. L. Ammon, H. Heck, H. Flack, The X-Ray System, 1976. Technical report TR-446. Computer Science Center. University of Maryland. USA.

13. International Tables for X-Ray Crystallography, Vol. IV, 1974, Birmingham. Kynoch Press. England.