Reactions with Diazoazoles. Part VI [1]. Unequivocal Synthesis of 3-Methyl-3*H*-azolotetrazoles. Correction of the Formerly Described 3-Methylazolotetrazoles in Favour of Mesoionic 2-Methylazolotetrazoles

Günter Ege*, Reinhard Heck, Karlheinz Gilbert, Hermann Irngartinger*, Ursula Huber-Patz and Hans Rodewald

Organisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270, D-6900 Heidelberg, West Germany

Received December 7, 1982

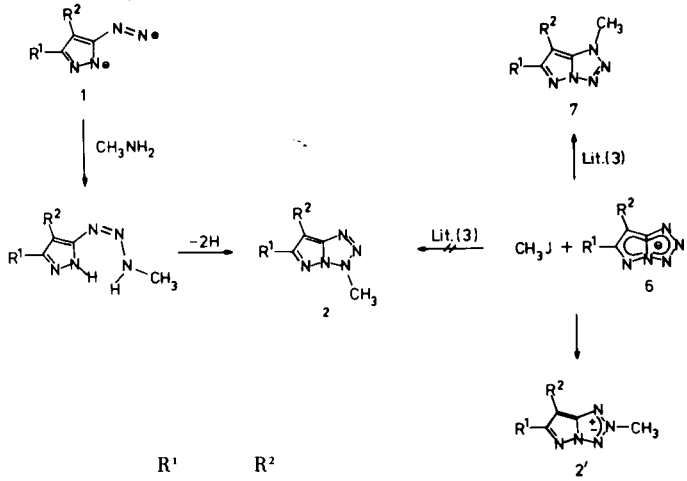
3-Methyl-3*H*-pyrazolo[1,5-*d*]tetrazoles **2** and 3-methyl-6-phenyl-3*H*-1,2,4-triazolo[1,5-*d*]tetrazole (**4**) have been unequivocally synthesized by annulation of the tetrazole moiety to the pyrazole resp. 1,2,4-triazole system. The constitution of some *N*-methyl substituted azolotetrazoles, formerly described as 3-methyl-3*H*-pyrazolo[1,5-*d*]tetrazoles **2**, 3-methyl-6-phenyl-3*H*-1,2,4-triazolo[1,5-*d*]tetrazole (**4**) and 1-methyl-6-phenyl-1*H*-1,2,4-triazolo[4,3-*d*]tetrazole (**5**), has to be revised in favour of the corresponding mesoionic 2-methyl derivatives **2'**, **4'**, **5'**. The structures of 3-methyl-3*H*- as well as of 2-methyl-2*H*-pyrazolo[1,5-*d*]tetrazole derivatives **2a**, **2c**, **2'a** have been determined by X-ray analyses. The azapentalenic system is aromatic in all three measured compounds and mesoionic in the case of the 2-methyl-2*H*- substitution pattern. The phenyl and ester substituents are coplanar with the azapentalene system. 3-, 2-, and 1-Methylpyrazolo[1,5-*d*]tetrazoles exhibit different behaviour when allowed to react with stannous chloride or sodium ethoxide. Azolotetrazoles with a methyl substituent at N-1, N-2 or N-3 of the tetrazole moiety can be distinguished by a combination of ^{1}H and ^{13}C nmr with respect to the chemical shifts of the *N*-methyl group and the bridgehead carbon. Results of semiempirical calculations of the pyrazolo[1,5-*d*]tetrazole anion and of its *N*-methyl derivatives are discussed.

J. Heterocyclic Chem., **20**, 1629 (1983).

In the course of our investigation of the reactions with diazoazoles we found a convenient procedure for obtaining 3-substituted 3*H*-pyrazolo[1,5-*d*]tetrazoles **2** with various substitution patterns [1]. This method consists in coupling of the 3-diazo-3*H*-pyrazoles **1** with primary amines and dehydrogenation of the intermediate triazenes to form the bicyclic system **2**. The reaction sequence outlined in Scheme 1, clearly allows the unequivocal synthesis of 3-alkyl substituted 3*H*-pyrazolo[1,5-*d*]tetrazoles **2**, especially the 3-methyl derivatives **2a-c**, which are supposed to be the only 3-substituted 3*H*-pyrazolo[1,5-*d*]tetrazoles reported in the literature [2,3]. For comparative purposes we became interested in compounds **2a-c**, expecting identical properties when synthesized according to our or to the procedure reported in the literature.

Applying our reaction sequence to methylamine and to the 3-diazo-3*H*-pyrazoles **1a-c** or to the 5-phenyl-3-diazo-3*H*-1,2,4-triazole (**3**) according to methods A-D (see Experimental), we obtained the 3-methyl-3*H*-pyrazolo[1,5-*d*]tetrazoles **2a-c** and the 3-methyl-6-phenyl-3*H*-1,2,4-triazolo-[1,5-*d*]tetrazole (**4**) (Scheme 1 and 2). In the case of the diazo-1,2,4-triazole **3** ring closure does not occur to the solitary triazole nitrogen with the formation of **5** as can be concluded from the ^{13}C nmr (see section Discussion of Spectroscopic Data). Surprisingly the physical data (mp, ^{1}H nmr, ^{13}C nmr) of **2** and **4** were not in agreement with those reported in the literature [2-4] for these compounds (Tables 1, 3, 4). In order to find the reason for this discrepancy it is necessary to examine the reaction paths reported in the literature for **2a-c** and **4** critically.

Scheme 1

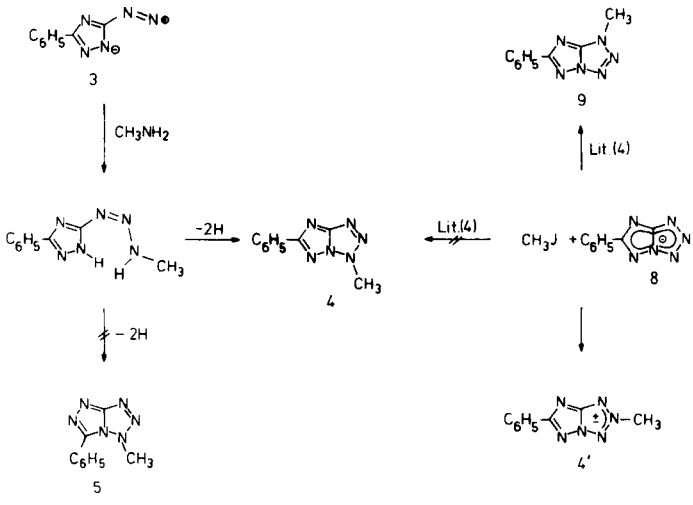


	R^1	R^2
a	H	C_6H_5
b	H	H
c	CH_3	$CO_2C_2H_5$

Previous Results from the Literature.

Alcalde *et al.* [2,3] and Butler *et al.* [4] have studied the methylation of the anion of the pyrazolo[1,5-*d*]tetrazole system **6** as well as of the anion of the 1,2,4-triazolo[1,5-*d*]-

Scheme 2

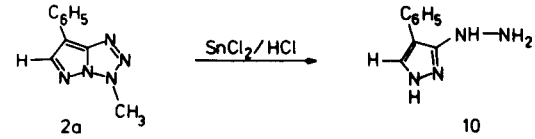


tetrazole system **8**. According to the multivalency of these bicyclic anions, in each case two bicyclic methylation products have been obtained. As structures for the bicyclic methylated compounds on the one hand the 3-methyl- and 1-methylpyrazolo[1,5-*d*]tetrazoles **2** and **7** and on the other hand the 3-methyl- and 1-methyl-1,2,4-triazolo[1,5-*d*]tetrazoles **4** and **9** have been claimed. The structures **2** and **7** or **4** and **9**, respectively, have been assigned mainly on the basis of the empirical rule, valid for both ^1H nmr and ^{13}C nmr, that the *N*-methyl group in a structural unit $=N\text{-}N(CH_3)\text{-}N=$ resonates at lower field than that in the unit $=\overset{|}{C}\text{-}N(CH_3)\text{-}N=$. Supplementary to the structure assignments by means of nmr spectroscopy, the constitution of the 1-methyl compounds **7** was confirmed by X-ray analysis of **7c** [3].

Since the results in the literature **6** → **2** [2,3], **8** → **4** [4] are contradictory to our own findings **1** → **2**, **3** → **4** we repeated the procedure in the literature for the methylation of **6a** in order to be able to elucidate the real structure of the compound, originally supposed to be **2a**. The methylation of the bicyclic anion **6a**, obtained from the corresponding 3-azido-1*H*-pyrazole with sodium hydride in tetrahydrofuran, afforded two bicyclic methylation products **2'a** and **7a**, whose physical data are those reported in the literature [2,3], but differ from our 3-methyl-7-phenyl-3*H*-pyrazolo[1,5-*d*]tetrazole (**2a**) [5]. These three *N*-methyl substituted products **2a**, **2'a** and **7a** have now been submitted to chemical degradation reactions.

Reduction of **2a**, **2'a** and **7a**.

Reduction of the 3-methyl derivative **2a**, synthesized according to our procedure, with stannous chloride in hydrochloric acid at 70° for two hours yielded 3-hydrazino-4-phenyl-1*H*-pyrazole (**10**), whereas compound **2'a**, synthesized according to the literature procedure [2,3] on treatment with the same reagent remained unchanged even under reflux for 3 hours. The hydrazinopyrazole **10** could be isolated and characterized as the 4-nitrobenzylidene derivative.



Submitting to similar reduction conditions as in the case of **2a** the other methylation product **7a** [2,3] gave *N*-methyl-4-phenyl-1*H*-pyrazol-3-amine (**11**) in accordance with the 1-methyl structure **7** which has already been determined by an X-ray analysis of the analogue **7c** [3].

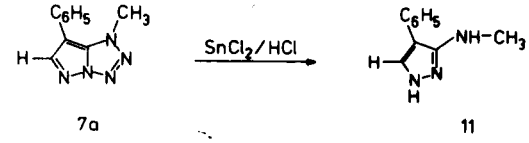


Table 1

Physical Data of 3-Methyl-3*H*-azolotetrazoles **2a-c** and **4**

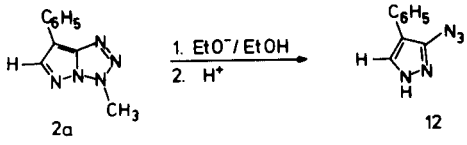
	R¹	R²	Method	Yield (%)	Mp (°C)	Formula	Analyses (%) Calcd./Found C	H	N	Mp (°C) from lit [a]
2a	H	C_6H_5	A	53	152-154 (Ethanol/-benzene)	$C_{10}H_9N_5$ (199.22)	60.29 / 60.32	4.55 / 4.84	35.15 / 34.94	138-139
2b	H	H	B	31	39-40 (Sublimed)	$C_4H_5N_5$ (123.12)	39.02 / 39.13	4.10 / 4.23	56.88 / 56.61	oil
2c	CH_3	$COOC_2H_5$	A	34	94 (Chloroform/-petrolether)	$C_8H_{11}N_5O_2$ (206.21)	45.93 / 46.02	5.30 / 5.48	33.48 / 33.46	—
4	C_6H_5	—	C [b], D	22, 27	200 (Sublimed)	$C_9H_8N_6$ (200.20)	53.99 / 54.03	4.03 / 4.25	41.98 / 41.86	182-184

[a] Supposed structures **2** and **4** from lit [2-4] have to be revised to compounds **2'** and **4'**. [b] When using method C, a by-product at most to 10% yield is formed.

The exo-*N*-methyl structure **11** follows from the ^{1}H nmr with δ = 2.76 for the exo-*N*-methyl group and its coupling (J = 1 Hz) with the adjacent NH. In ring methyl substituted pyrazoles the endo-*N*-methyl groups appear in the region δ = 3.5-4.0 [6].

Treatment of **2a** with Nucleophiles.

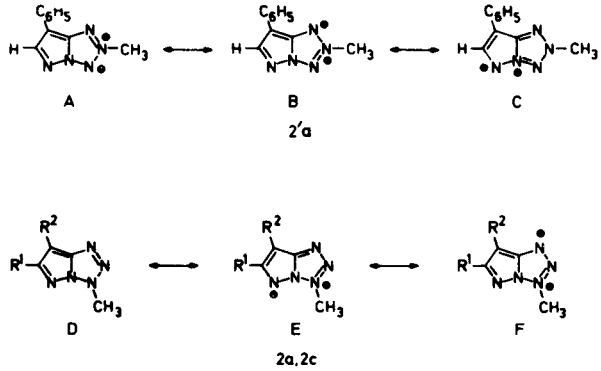
Since the supposed "3-methyl-3*H*-pyrazolo[1,5-*d*]tetrazoles" (**2'**) are formed by methylation of the anions **6** with methyl iodide in ethanol in the presence of a large excess of sodium ethoxide [2,3] we subjected our 3-methyl-7-phenyl-3*H*-pyrazolo[1,5-*d*]tetrazole (**2a**) to similar reaction conditions. After treatment of **2a** with a threefold amount of sodium ethoxide in ethanol under reflux for 60 hours the starting material had disappeared and after acidification the demethylated 3-azido-4-phenyl-1*H*-pyrazole (**12**) could be isolated in 77% yield.



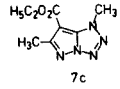
To elucidate the fate of the methyl group in the course of this reaction the demethylation of **2a** was performed with sodium phenolate and afforded methyl phenyl ether in 24% yield in addition to 10% of azidopyrazole **12**. As expected, a similar demethylation reaction with the literature compound **2'a** failed.

From these experiments it follows that under the reaction conditions described in the literature [2,3] the 3-methyl derivatives **2** cannot be obtained, and consequently another structure has to be assigned to the "3-methyl derivatives" **2'** described in the literature. This problem was solved by X-ray studies on the following substances.

Crystal Structure Analyses of Compounds **2'a**, **2a** and **2c**.



	R¹	R²
a	H	C_6H_5
c	CH_3	$CO_2C_2H_5$



According to the bond lengths (Figures 1-3) and the planarity (average deviation ±0.009 Å) the pyrazolo[1,5-*d*]-tetrazole system of compounds **2'a**, **2a** and **2c** are aromatic [7]. Within the experimental error the bond lengths N1-N2 (1.328 Å) and N2-N3 (1.321 Å) of compound **2'a** are equal. Therefore the π-electrons of the tetrazole moiety of **2'a** are delocalized in a mesoionic form as shown by the mesomeric formulas **A** and **B**. On the other hand the corresponding bond lengths in **2a** and **2c** show significant differences. From the N1-N2 distances (Figures 2 and 3a) a

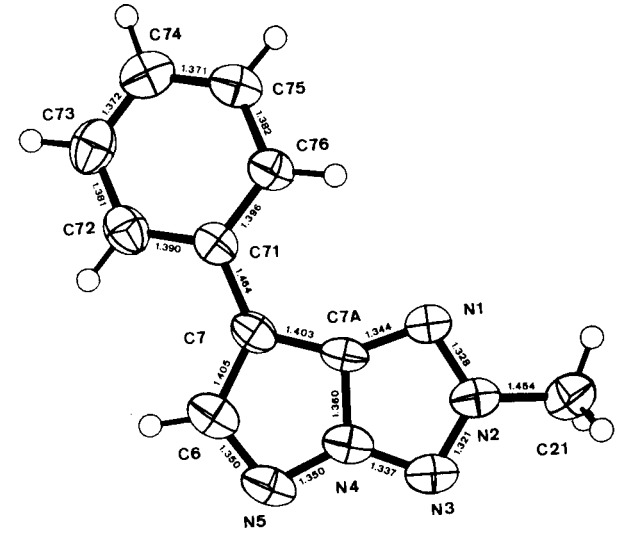


Figure 1. Molecular structure of **2'a** with the numbering scheme and bond lengths [Å]. The mean standard deviation is 0.003 Å.

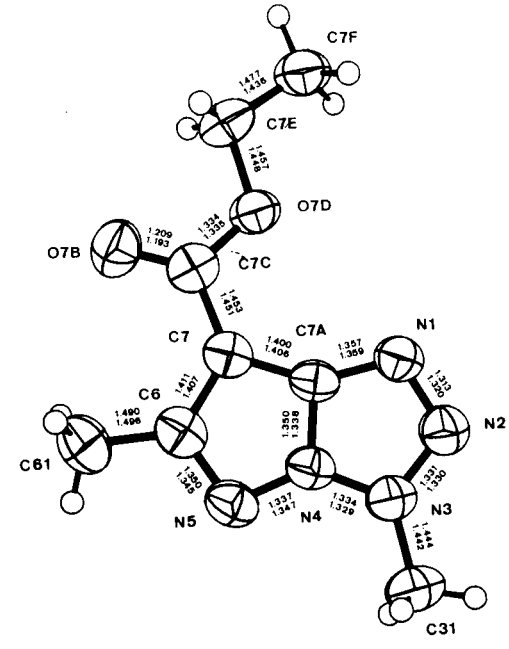


Figure 2. Molecular structure of **2c** with the numbering scheme and the bond lengths [Å]. The first row gives the values of molecule 1 of the two independent molecules in the asymmetric unit. The mean standard deviation is 0.003 Å.

small double bond character can be derived for these bonds. The given mesomeric formulas **A-C** and **D-F** are in accordance with the experimentally determined bond lengths of the 2-methyl compound **2'a** and the 3-methyl compounds **2a, 2c**, respectively.

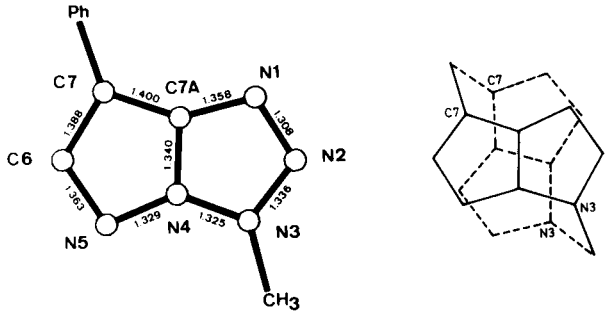


Figure 3a. Molecular structure of **2a** with the numbering scheme and the averaged bond lengths [Å] of the two independent molecules. The mean standard deviation is 0.003 Å. 3b. Disorder of **2a** (see X-ray part in the experimental).

The phenyl rings and the carboxyl group are almost coplanar with the azapentalenic systems (**2'a**: 4.5°; **2a**: 11.6°, 4.0°; **2c**: 10.4°, 8.0°). Because of the steric hindrance of the *ortho* substituents in **2c** (C61...C7C: 3.208(3) Å; C61...O7B: 3.068(3) Å) the methyl group C61 is bent away from the ester group. Compared to the bond angle C61-C6-N5 118.3° the complementary angle C61-C6-C7 127.9° (Table 2) is enlarged to the same extent as was found for the isomeric compound **7c** [3].

Table 2

Bond Angles (°) of **2'a**, **2a** and **2c** With Standard Deviations

Compound **2'a**

N2—N1—C7A	102.3(2)
N1—N2—N3	118.0(2)
N1—N2—C21	121.3(2)
N3—N2—C21	120.6(2)
N2—N3—N4	100.0(2)
N3—N4—N5	132.6(2)
N3—N4—C7A	112.2(2)
N5—N4—C7A	115.2(2)
N4—N5—C6	100.7(2)
N5—C6—C7	115.8(2)
C6—C7—C7A	101.9(2)
C6—C7—C71	131.0(2)
C7A—C7—C71	127.1(2)
N1—C7A—N4	107.5(2)
N1—C7A—C7	146.1(2)
N4—C7A—C7	106.3(2)
C7—C71—C72	122.4(2)
C7—C71—C76	119.9(2)
C72—C71—C76	117.8(2)
C71—C72—C73	121.0(2)
C72—C73—C74	120.7(2)
C73—C74—C75	119.2(2)
C74—C75—C76	120.9(2)
C71—C76—C75	120.5(2)

Table 2 Continued

Compound **2a** Molecule	1	2
N2—N1—C7A	107.0(2)	106.5(2)
N1—N2—N3	110.1(2)	110.1(2)
N2—N3—N4	107.4(1)	107.2(2)
N2—N3—C31	127.2(2)	126.4(2)
N4—N3—C31	125.4(2)	126.4(2)
N3—N4—N5	136.2(2)	135.2(2)
N3—N4—C7A	108.1(2)	108.2(2)
N5—N4—C7A	115.7(1)	116.6(2)
N4—N5—C6	100.8(2)	99.4(2)
N5—C6—C7	115.1(2)	116.1(2)
C6—C7—C7A	102.1(1)	101.4(2)
C6—C7—C71	130.0(2)	130.3(2)
C7A—C7—C71	127.8(2)	128.2(2)
N1—C7A—N4	107.4(1)	108.1(2)
N1—C7A—C7	146.2(2)	145.4(2)
N4—C7A—C7	106.4(2)	106.5(2)
C7—C71—C72	122.2(2)	122.5(2)
C7—C71—C76	120.1(2)	120.0(2)
C72—C71—C76	117.8(2)	117.5(2)
C71—C72—C73	120.8(2)	123.7(3)
C72—C73—C74	120.5(2)	120.0(3)
C73—C74—C75	119.5(2)	120.5(3)
C74—C75—C76	120.4(2)	119.5(3)
C71—C76—C75	120.9(2)	118.8(3)

Compound **2c** Molecule	1	2
N2—N1—C7A	107.6(2)	106.9(2)
N1—N2—N3	109.7(2)	109.6(1)
N2—N3—N4	107.6(2)	107.5(1)
N2—N3—C31	127.2(2)	127.1(2)
N4—N3—C31	125.0(2)	125.3(1)
N3—N4—N5	134.7(2)	134.8(2)
N3—N4—C7A	108.0(1)	108.4(1)
N5—N4—C7A	117.0(2)	116.7(1)
N4—N5—C6	101.2(1)	101.0(1)
N5—N6—C7	113.5(2)	114.0(2)
N5—C6—C61	118.4(2)	118.2(2)
C7—C6—C61	128.0(2)	127.8(2)
C6—C7—C7A	104.0(2)	103.5(2)
C6—C7—C7C	127.2(2)	127.4(2)
C7A—C7—C7C	128.7(2)	128.8(2)
N1—C7A—N4	107.1(2)	107.4(2)
N1—C7A—C7	148.4(2)	147.7(2)
N4—C7A—C7	104.3(1)	104.8(1)
C7—C7C—O7B	124.6(2)	126.1(2)
C7—C7C—O7D	111.5(2)	110.3(2)
O7B—C7C—O7D	123.8(2)	123.6(2)
C7C—O7D—C7E	115.6(1)	115.7(2)
O7D—C7E—C7F	107.6(2)	108.4(2)

The results of our structure analysis of **2'a** are not in agreement with the postulated formula **2a** in the literature [2,3]. Only the revised structure **2'a** with the methyl group in the N2 position is consistent with the results of our X-ray analysis.

Discussion of Spectroscopic Data.

The structures of the 3-methyl-3*H*-, 2-methyl-2*H*- and 1-methyl-1*H*-pyrazolo[1,5-*d*]tetrazoles **2a,b**, **2'b,c** and

Table 3

^{1}H NMR Data of 3-, 2- and 1-Methylazolotetrazoles **2**, **4**, **2'**, **4'**, **5'**, **7**, **9**, **13** [a]

	δ, N-CH_3	R^1	R^2
Compounds of type III			
2a	4.40	8.06 (H)	7.15-7.55 (3,4,5-H of C_6H_5), 7.75-7.95 (2,6-H of C_6H_5)
2b	4.44	7.75 (H), J = 2.6 Hz	6.27 (H), J = 2.6 Hz
2c	4.53	2.65 (CH_3)	1.40 (OCH_2CH_3), 4.42 (OCH_2CH_3)
4	4.54	7.4-7.6 (3,4,5-H of C_6H_5), 8.1-8.3 (2, 6-H of C_6H_5)	
Compounds of type II			
2'a [b]	4.46	8.22 (H)	7.08-7.85 (C_6H_5)
2'b [b]	4.43	7.86 (H), J = 2.8 Hz	6.05 (H), J = 2.8 Hz
2'c [c]	4.49	—	—
4' [d]	4.53	7.50 (3H of C_6H_5), 8.15 (2H of C_6H_5)	—
5' [d]	4.60	7.51 (3H of C_6H_5), 8.20 (2H of C_6H_5)	—
Compounds of type I			
7a [b]	4.20	7.93 (H)	7.37 (C_6H_5)
7b [b]	4.11	7.76 (H), J = 2.4 Hz	5.80 (H), J = 2.4 Hz
7c [c]	4.36	2.58 (CH_3)	1.40 (OCH_2CH_3), 4.34 (OCH_2CH_3)
9 [d]	4.20	7.46 (3H of C_6H_5), 8.15 (2H of C_6H_5)	—
13 [d]	4.20	7.52 (3H of C_6H_5), 8.22 (2H of C_6H_5)	—

[a] Measured in deuteriochloroform with TMS as standard. [b] Data from lit [3]. [c] Data from lit [2]. [d] Data from lit [4].

Table 4

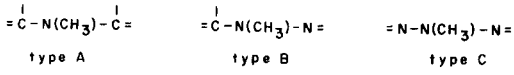
^{13}C NMR of 3-, 2- and 1-Methylazolotetrazoles **2**, **4**, **2'**, **4'**, **5'**, **7**, **9**, **13** [a]

	δ, N-CH_3	C-6	C-7	C-7a / C-3a		Carbons of substituents on C-6 and C-7 [b]
Compounds of type III						
2a	35.85	141.17	104.05	149.33	—	125.00 (7-C-2,6), 126.21 (7-C-4), 128.94 (7-C-3,5), 130.92 (7-C-1)
2b	36.11	145.18	86.58	152.04	—	—
2c	36.25	159.72	92.40	151.04	—	14.29, 14.40 (6-CH_3, $COOCH_2CH_3$), 59.77 ($COOCH_2CH_3$), 162.00 (CO)
4	37.92	167.98	—	161.94	—	126.41 (6-C-2,6), 128.86 (6-C-3,5), 130.35 (6-C-4), 130.66 (6-C-1)
Compounds of type II						
2'a	42.47	143.26	98.94	147.81	—	124.28 (7-C-2,6), 125.41 (7-C-4), 128.88 (7-C-3,5), 131.43 (7-C-1)
2'b [c]	42.4	146.8	80.8	149.8	—	
2'c [c]	42.7	160.8	87.8	149.8	—	
4' [d]	43.2	169.0	—	156.2	—	
5' [d]	43.7	136.9	—	—	164.6	
Compounds of type I						
7a [c]	37.2	144.9	96.7	134.9	—	
7b [c]	35.7	146.9	78.7	138.4	—	
7c [c]	36.7	159.1	87.1	138.5	—	
9 [d]	35.1	168.4	—	150.2	—	
13 [d]	34.4	139.7	—	—	154.5	

[a] Compounds **2a-c**, **2'a-c** and **7a-c** were measured in deuteriochloroform, **4**, **4'**, **5'**, **9** and **13** in deuteriodimethylsulfoxide, in each TMS as standard. [b] For example: 7-C-2,6 denotes the carbons C-2 and C-6 of the substituent on C-7 of the azapentalene system. [c] Data from lit [3]. [d] Data from lit [4].

7a,b result from the X-ray analyzed representatives **2c**, **2'a** and **7c** [3] on account of analogous syntheses and similar ^{1}H and ^{13}C nmr spectra (Tables 3,4).

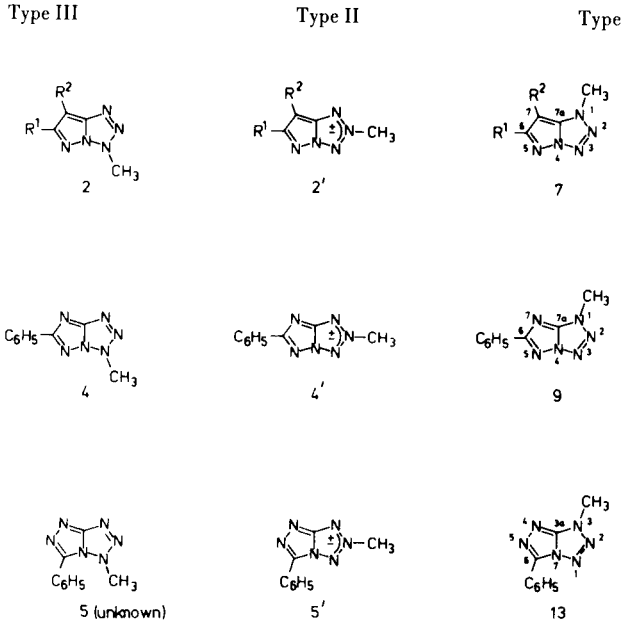
For monocyclic *N*-methyl substituted azoles Butler has established the relationship that the chemical shifts (δ) of the *N*-methyl groups in the ^{1}H nmr [6] as well as in the ^{13}C nmr [8] increases in the following order for the structural units:



These relationships have also been applied to bicyclic azolotetrazoles in order to determine the position of an *N*-methyl substituent in the tetrazole moiety, and structural assignments for the 3-methyl compounds **2** and **4** and the 1-methyl compound **5** as type C, for the 1-methyl compounds **7** and **9** and the 3-methyl compound **13** as type B have been made [2-4,6]. However, the literature assignments concerning the 3-methyl derivatives **2** and **4** and the 1-methyl derivative **5** must be erroneous, because on the one hand they differ from those obtained *via* our unambiguous synthesis (cases **2** and **4** of type III) and on the other hand in the ^{13}C nmr they show similar chemical shifts for the *N*-methyl group as the X-ray analyzed 2-methyl derivative **2'a** (cases **2'**, **4'** and **5'** of type II), but different ones compared to the real 3-methyl- (**2** and **4** of type III) and 1-methyl derivatives (**7** and **9** of type I) and the 3-methyl derivative (**13** of type I) (Table 4, for types I, II, III see Scheme 3).

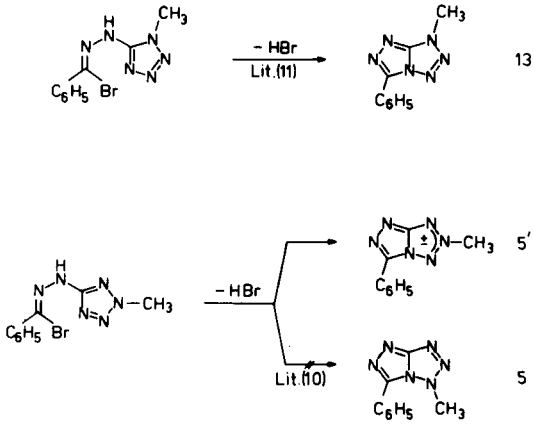
Scheme 3

R^1, R^2 see Scheme 1



In the ^{13}C nmr the *N*-methyl groups of the methyl substituted azolotetrazoles of types III, II, and I are located in the ranges δ = 35-38 (**2**, **4**), δ = 42-44 (**2'**, **4'**, **5'**) and δ = 34-37 (**7**, **9**, **13**), respectively. According to the Butler ^{13}C nmr relationship [8] the azolotetrazoles of type I (Butler type B) should be distinguishable from those of type II (Butler type C) or of type III (Butler type C) by upfield ^{13}C resonance of the methyl group in type I (Butler type B). Contrary to Butler's statement [8] the methyl groups of type I as well as type III resonate in the same upfield region and therefore cannot be distinguished by ^{13}C nmr. However, 2-methyl substituted azolotetrazoles of type II can be discerned from those of type I or III in the ^{13}C nmr because of the downfield shift of the *N*-methyl carbon. Thus, with δ (N-CH$_3$) = 43.7 [4] it is possible to elucidate the kind of ring closure in Scheme 4 by assigning the 2-methyl structure **5'** instead of **5** to the reaction product, contrary to the assignment in the literature [4,6,9,10,11]. To our knowledge, the methyl derivative **5** is hitherto unknown.

Scheme 4



In the ^{1}H nmr the *N*-methyl groups of the methyl substituted azolotetrazoles of types III, II and I appear in the ranges δ = 4.40-4.53 (**2**, **4**), δ = 4.46-4.60 (**2'**, **4'**, **5'**) and δ = 4.11-4.36 (**7**, **9**, **13**), respectively (Table 3). Here upfield separation of the methyl-range of type I from the others enables structural assignment for the methyl compounds of type I in accordance with the Butler ^{1}H nmr relationship (type B) [6].

The ^{13}C nmr data of the heterobicyclic ring carbons are listed in Table 4. In the pyrazole series **2**, **2'** and **7** the signals for the bridgehead carbon C-7a appear in narrow ranges (δ = 149-152 for 3-methyl derivatives **2**, δ = 147-150 for 2-methyl derivatives **2'**, δ = 135-138 for 1-methyl derivatives **7**) because carbon C-7a is least influenced by variation of the substituents at C-6 and C-7. Since the δ (C-7a)-range for the 1-methyl derivatives is separated from the others, the ^{13}C nmr signal for C-7a can be used for the characterization of 1-methyl derivatives

(type I). The upfield shift of 10 ppm is consistent with the methyl substitution at position 1 [12]. From the ^{13}C nmr is also derivable the kind of ring closure in the dehydrogenation step of the triazolyltriazene of Scheme 2 leading to the 1,2,4-triazolo[1,5-*d*]tetrazole **4** and not to the 1,2,4-triazolo[4,3-*d*]tetrazole **5**. Characteristic for the [1,5-*d*]-annulation is the ^{13}C chemical shift for C-6 located within the range δ = 167-169 as shown for compounds **4**, **4'** and **9** in Table 4. On the other hand in the [4,3-*d*]-annulated compounds **5'** and **13** the ^{13}C chemical shift for the analogous phenyl substituted carbon C-6 is situated in the range δ = 136-140. The value δ (C-6) = 167.98 for the cyclized product **4** in the dehydrogenation reaction in Scheme 2 clearly demonstrates the existence of a [1,5-*d*]- rather than a [4,3-*d*]-annulation (ring closure to **4** and not to **5**).

In summary, in the azolotetrazole series the determination of the *N*-methyl substitution position in the tetrazole moiety is possible by means of nmr: For compounds of type I with δ (NCH_3) in the ^1H nmr and with δ (bridgehead carbon) in the ^{13}C nmr, for compounds of type II with δ (NCH_3) in the ^{13}C nmr, and for compounds of type III with δ (NCH_3) in the ^1H nmr and in the ^{13}C nmr.

Absorptions of the uv spectra of the 3-methyl-3*H*- and 2-methyl-2*H*-azolotetrazoles **2a-c**, **4** and **2'a** are listed in Table 5. A striking difference between the 2-methyl and 3-methyl substituted 7-phenyl compounds **2'a** and **2a** is the bathochromic shift of the longest wavelength absorption of **2'a**, indicating a stronger donor capacity of negatively charged N-3 in **2'a** compared to N-3 in **2a**. A phenyl substituent at C-6 does not contribute to the conjugation in the azapentalenic system as shown by the short wavelength absorptions in compound **4**.

Table 5

Absorptions in the UV Spectra of Compounds **2a-c**, **4**, **2'a**

	λ (ε) [nm (1 mol^{-1} cm^{-1})]
2a	319 (6400), 267 sh (9400), 258 sh (10500), 249 (12400)
2b	283 (3100)
2c	333 sh (1500), 288 (7400)
4	266 (15000), 244 (17000)
2'a	353 (3600), 268 (17000)

Semiempirical Calculations.

MINDO/3 [13] calculations of the pyrazolo[1,5-*d*]tetrazole anion **6** (R^1 = R^2 = H) yield in the following decreasing orders i) the charge densities on the nitrogens responsible for the kinetic control for the methylation reaction: N-5 > N-1 > N-3 > N-2, and ii) the heats of formation of the *N*-methylated products as a measure for their thermodynamic stability: N-1 > N-5 > N-2 > N-3 (Table 6). The yields for the methylation products of the anion **6a** (R^1 = H, R^2 = C_6H_5) correspond with the heats of formation more reliable than with the charge densities in accordance with a thermodynamic control of the methylation procedure. The most unfavourable methylation product *via* thermodynamic control seems to be the 3-methyl compound **2a** in accordance with the fact that it is not obtained either because it is not stable under the reaction conditions (see Section: Treatment of **2a** with Nucleophiles) or it is not formed at all.

Table 6

Charge Densities for Anion **6** Heats of Formation of the *N*-Methylated Products Calculated with MINDO/3 [13]

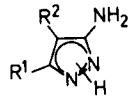
	Charge q_r for **6** [a]	*N*-Methylated Products: Compounds	Heat of formation [a] ΔH_f (kJ/mole)	Yield (%) for R^1 = H, R^2 = C_6H_5
N-1	−0.263	**7**	−32.07	28
N-2	−0.047	**2'**	− 0.23	15
N-3	−0.256	**2**	+ 4.81	—
N-5	−0.353	[b]	−28.25	57

[a] Calculated for R^1 = R^2 = H. [b] 5-Methyl-5*H*-pyrazolo[1,5-*d*]-tetrazole rearranges to 3-azido-1-methyl-1*H*-pyrazole [2,3].

EXPERIMENTAL

Melting points were determined on a Bock-Monoscope and are uncorrected. The uv spectra were taken on a Beckman 25 spectrometer in dichloromethane solution. The ^1H nmr spectra were recorded on a Varian EM 390 spectrometer at 90 MHz, the ^{13}C nmr spectra on a Varian CFT 20 and on a Bruker HFX 90 spectrometer at 22.63 MHz using deuteriochloroform or deuteriodimethylsulfoxide as solvents and TMS as an internal standard. The ir spectra were obtained on a Beckman IR 4240 spectrometer in potassium bromide pellets.

The azolamines corresponding to the diazoazoles **1** and **3** were obtained by procedures from the literature.



R^1	R^2	Lit
H	C_6H_5	[14]
H	H	[15]
CH_3	$COOC_2H_5$	[16]
5-Phenyl-1*H*-1,2,4-triazol-3-amine		[17]

3-Methyl-3*H*-pyrazolo[1,5-*d*]tetrazoles **2a-c** and 3-Methyl-6-phenyl-3*H*-1,2,4-triazolo[1,5-*d*]tetrazole (**4**).

General Procedure.

To an ice-cold solution of azolamine (30 mmoles) in water (60 ml) and concentrated hydrochloric acid (20 ml) in the case of **2a-c** or concentrated nitric acid (60 ml) in the case of **4** was added dropwise a solution of sodium nitrite (2.1 g, 30 mmoles) in water (10 ml) at 0-5°. After stirring at this temperature for 45 minutes ice-cold dichloromethane (100 ml) was added, and the mixture was made alkaline with a saturated solution of sodium carbonate in water.

Method A (**2a**, **2c**).

After neutralisation the organic layer, containing the diazoazole **1**, was separated, dried with sodium sulfate and filtered. To the filtrate powdered methylamine hydrochloride (2 g, 30 mmoles) and then with stirring at

0-5° triethylamine (3 g, 30 mmoles) were added yielding the corresponding triazene within one hour.

Method B (**2b**).

In the case of the water soluble 3-diazo-3*H*-pyrazole (**1b**) the two phase system water/dichloromethane was directly used after neutralisation by adding aqueous methylamine solution (40%, 3.5 ml) at 0-5° yielding the corresponding triazene. After one hour the organic layer was separated, and the aqueous solution was extracted five times with dichloromethane. The collected organic phases were dried with sodium sulfate and filtered.

Method C (**4**).

In the case of 3-diazo-5-phenyl-3*H*-1,2,4-triazole (**3**) the organic layer was separated after neutralisation, dried with sodium sulfate and filtered. The filtrate was cooled to −40° and at this temperature dry methylamine gas was blown in, upon which the corresponding triazene separated as a solid within a few minutes.

Continuation of the General Procedure.

To the dichloromethane solution or suspension of the corresponding 1-azolyl-3-methyltriazene, lead(IV) acetate (13.35 g, 30 mmoles) was added with stirring at 0-5° (in the case of **4** at −40°). After 15 minutes the solution was neutralised by addition of a saturated aqueous solution of sodium hydrogen carbonate, and the solid was filtered off with suction. The organic layer of the filtrate was separated, dried with sodium sulfate, filtered and then concentrated. The residue was crystallized with ethanol (**2a**) or was filtered through silica gel (**2c, 4**) or alumina (**2b**) (100 g, in each case) with dichloromethane/diethyl ether as eluent yielding the 3-methyl-3*H*-azolotetrazoles **2a-c** and **4**.

Method D (**4**).

The method was performed analogously to the general procedure following Method C with the only variation of using benzyltriethylammonium permanganate [18] (9.9 g, 30 mmoles) instead of lead(IV) acetate.

Yields and melting points of 3-methyl-3*H*-azolotetrazoles **2a-c** and **4** are given in Table 1.

Methylation of the Bicyclic Anion **6**.

Sodium hydride (1.2 g, 50 mmoles) was suspended in dry tetrahydrofuran (30 ml), then 3-azido-4-phenyl-1*H*-pyrazole (**12**) (1.85 g, 10 mmoles) [20] was added in small portions under stirring. After formation of the bicyclic anion **6** (the disappearance of the azido band was checked by ir) a solution of methyl iodide (7.1 g, 50 mmoles) in tetrahydrofuran (20 ml) was added and stirring was continued for an additional hour. The reaction mixture was placed in a polyethylene tube and sealed. The methylation reaction was performed in a high pressure apparatus [19] at 8200 bar and at 27-28° for 18 hours. Thereafter the excess of sodium hydride was hydrolyzed by cautious addition of water, the mixture concentrated under reduced pressure, and the residual mass was taken up in water (100 ml) and neutralised with hydrochloric acid. The solution was extracted with ether (3 × 50 ml portions), the ethereal extracts were dried with sodium sulfate, filtered and evaporated to give 2.0 g (quantitative) of crude methylation products (yields, determined by nmr): 3-azido-1-methyl-4-phenyl-1*H*-pyrazole (57%), 1-methyl-7-phenyl-1*H*-pyrazolo[1,5-*d*]tetrazole (**7**) (28%) and 2-methyl-7-phenyl-2*H*-pyrazolo[1,5-*d*]tetrazole (**2'a**) (15%).

The separation was performed by chromatography on silica gel with dichloromethane as eluent using a fraction collector.

3-Azido-1-methyl-4-phenyl-1*H*-pyrazole.

This compound was the first fraction from the column, 0.8 g (40%) of a light brown oil, which crystallized by scratching in an ice bath. Recrystallization from ethanol gave pale brown crystals, mp 63-65° (lit [3] 70-73°).

1-Methyl-7-phenyl-1*H*-pyrazolo[1,5-*d*]tetrazole (**7**).

This compound was the second fraction from the column, 0.4 g (20%), which was purified by recrystallization from ethanol giving colourless crystals, mp 92-94° (lit [3] 101-103°).

2-Methyl-7-phenyl-2*H*-pyrazolo[1,5-*d*]tetrazole (**2'a**).

This compound was the third fraction from the column, 0.24 g (12%), which was purified by recrystallization from ethanol giving pale green-yellowish crystals, mp 131-133°. This compound was originally viewed as 3-methyl-7-phenyl-3*H*-pyrazolo[1,5-*d*]tetrazole (**2a**), mp 138-139° [3].

The methylation reaction could also be performed by boiling the mixture under reflux for at least 12 hours leading to similar yields of methylated products.

Reduction of Pyrazolo[1,5-*d*]tetrazoles **2a** and **7** with Stannous Chloride in Hydrochloric Acid Solution.

3-Hydrazino-4-phenyl-1*H*-pyrazole (**10**).

To a suspension of **2a** (3.0 g, 15 mmoles) in ethanol (25 ml) a solution of stannous chloride dihydrate (6.75 g, 30 mmoles) in concentrated hydrochloric acid (15 ml) was added. After standing for 18 hours at room temperature the mixture was heated to 60° on a water bath for further two hours. The reaction flask was cooled to room temperature and unchanged starting material (2.3 g) was recovered by filtration. After concentrating the filtrate under reduced pressure 2*N* hydrochloric acid (40 ml) was added, and the mixture was extracted with ether (3 × 30 ml portions) to remove residual starting material. The aqueous solution was alcalized to *p*H 12 with sodium hydroxide and then extracted with ethyl acetate (4 × 50 ml portions). The combined blue coloured organic layers were dried with sodium sulfate and filtered. After evaporation 0.14 g (23%, referred to converted **2a**) of crude 3-hydrazino-4-phenyl-1*H*-pyrazole (**10**) was obtained, identified as 4-nitrobenzylidene derivative, dark red needles with mp 225° (from ethanol-dimethylformamide (2:1)); for a comparison see below.

N-Methyl-4-phenyl-1*H*-pyrazol-3-amine (**11**).

This compound was obtained by reduction of **7a** (1.0 g, 5 mmoles) with stannous chloride dihydrate (2.25 g, 10 mmoles) in the same manner as described for **2a**. A precipitate of unreacted starting material (0.2 g) was recovered. After alcalization the solution was extracted with ether (3 × 20 ml portions). Evaporation of the combined organic layers left an oily residue (0.3 g, 43% referred to converted **7a**), which solidified on scratching and cooling. Recrystallization from diisopropyl ether gave colourless crystals with mp 133-134°; ir: 3440, 3140, 2940, 1612, 1538, 1495, 760 cm^{-1}; nmr (deuteriochloroform): δ 2.76 (d, J = 1 Hz, 3H, NH-CH_3), 3.0-7.0 (broad, 2H, 2 × NH, exchangeable), 7.05-7.65 (m, 5H, C_6H_5), 7.68 (s, 1H, 5-H); the doublet at δ 2.76 changes to a singlet on NH to ND exchange.

Anal. Calcd. for $C_{10}H_{11}N_3$ (173.2): C, 69.34; H, 6.40; N, 24.26. Found: C, 68.99; H, 6.67; N, 24.50.

3-Hydrazino-4-phenyl-1*H*-pyrazole (**10**) from 4-Phenyl-1*H*-pyrazol-3-amine.

4-Phenyl-1*H*-pyrazol-3-amine (8.0 g, 50 mmoles), dissolved in 4*N* hydrochloric acid (100 ml), was diazotized at 0-5° with aqueous sodium nitrite (3.5 g, 50 mmoles). After being stirred for 30 minutes and cooling to 0° the solution was added during 10 minutes to stannous chloride dihydrate (22.5 g, 100 mmoles) in concentrated hydrochloric acid (25 ml). After stirring for further two hours the mixture was covered with ethyl acetate (150 ml) and made alkaline to *p*H 12 with aqueous sodium hydroxide. The organic layer was separated, and the aqueous solution was again extracted with ethyl acetate (3 × 100 ml portions). The combined organic layers were dried with sodium sulfate, filtered and evaporated under reduced pressure. The residue (6.2 g, 71%) was recrystallized from toluene-propanol (10:1) to give pale grey needles, mp 147-148° dec; ir: 3340, 3270, 3180, 3060, 2935, 1641, 1612, 1505, 1485, 1445, 1175, 758, 698; nmr (DMSO-d_6): δ 3.25 (s, broad, 2H, NH_2, exchangeable), 6.4-7.8 (very broad signal, 1H, NH, exchangeable), 6.45 (s, broad, 1H, NH, exchangeable), 7.0-7.6 (m, 5H, C_6H_5), 7.78 (s, 1H, 5-H).

Anal. Calcd. for $C_9H_{10}N_4$ (174.2): C, 62.03; H, 5.79; N, 32.16. Found: C, 62.03; H, 6.06; N, 32.37.

3-(4-Nitrobenzylidenehydrazino)-4-phenyl-1*H*-pyrazole.

To a solution of **10** (1.75 g, 10 mmoles) in ethanol (25 ml) and concentrated hydrochloric acid (1 ml), 4-nitrobenzaldehyde (1.51 g, 10 mmoles) was added. After one hour reflux the red mass was filtered off by suction, and the residue (2.5 g, 81%) was recrystallized from ethanol-dimethylformamide (2:1) to give dark red needles, mp 225°.

Anal. Calcd. for $C_{16}H_{13}N_5O_2$ (307.3): C, 62.53; H, 4.26; N, 22.79. Found: C, 62.62; H, 4.53; N, 22.60.

The ir spectrum of this authentic sample was identical with that of the 4-nitrobenzylidene derivative of **10**, obtained by reduction of **2a**.

Demethylation Reactions of the 3-Methyl-7-phenyl-3*H*-pyrazolo[1,5-*d*]-tetrazole (**2a**) with Nucleophiles (Sodium Ethoxide a) or (Sodium Phenolate b)).

a) 3-Azido-4-phenyl-1*H*-pyrazole (**12**).

The 3-methylpyrazolotetrazole **2a** (1.0 g, 5 mmoles) was treated with an excess of sodium ethoxide (1.05 g, 15 mmoles) in ethanol (20 ml) for 60 hours under reflux. The brown solution was evaporated nearly to dryness, then 30 ml of water was added. The alkaline solution was extracted with ether (3 × 20 ml portions) from which after evaporation starting material (0.09 g) was recovered. The aqueous phase was acidified with 6*N* hydrochloric acid and then extracted with ether (3 × 30 ml portions). The combined ethereal extracts were dried with sodium sulfate, filtered and evaporated to give 0.65 g (77%) brown crystals. Recrystallization from methanol afforded pale brown needles, mp 154-155° (lit [20] 157-158°); ir: 2120 (N_3) cm^{-1}.

b) 3-Azido-4-phenyl-1*H*-pyrazole (**12**) and Methyl Phenyl Ether.

The 3-methylpyrazolotetrazole **2a** (1.6 g, 8 mmoles) was treated with sodium phenolate (2.9 g, 25 mmoles) in dimethylformamide (30 ml) at 140° for 15 hours. The dark solution was concentrated *in vacuo* to 10 ml and poured into ice water (150 ml). The alkaline solution was extracted with ether (3 × 50 ml portions), the combined extracts were dried with sodium sulfate, filtered and freed from solvent. The crude oil was submitted to silica gel column chromatography using dichloromethane-petroleum ether (1:1) as eluent to give 0.21 g (23%) of a colourless, fragrant oil identified by gc (5% carbowax column 20M, 1 = 2.0 m), retention time is identical with an authentic sample of methyl phenyl ether; nmr (deuteriochloroform): δ 3.80 (s, 3H, OCH_3), 6.75-7.45 (m, 5H, C_6H_5).

The aqueous phase was acidified with 6*N* hydrochloric acid and then extracted with ether (3 × 30 ml portions). The combined ethereal extracts were dried with sodium sulfate, filtered and freed from solvent. The crude dark brown oil was submitted to silica gel column chromatography. Using dichloromethane as eluent gave a small amount of phenol as by-product. Subsequent elution with ether afforded a fraction to give after removal of the solvent 0.15 g (10%) of brown crystals, which were purified by recrystallization from methanol giving pale brown needles, mp 148-152° (lit [20] 157-158°); ir: 2120 (N_3) cm^{-1}.

X-Ray Structure Determination and Refinement.

The crystals were grown by cooling saturated solutions (Table 7). The intensities were collected on a computer-controlled diffractometer (CAD4 Enraf-Nonius, Mo Kα radiation, graphite monochromator, $\omega/2\theta$-scan). Crystal data and structure determination parameters are given in Table 7. Lorentz and polarization corrections were applied. Absorption was neglected.

The structures were solved by direct methods. For compound **2a** and **2c** two independent molecules per asymmetric unit have been found. The molecular dimensions of the corresponding independent molecules are in good agreement. Compound **2'a** crystallizes with only one molecule in the asymmetric unit. Despite several attempts disorder effects in compound **2a** could not be avoided. During the refinement of the given data 10% only of the second independent molecule of **2a** was fixed in the disorder position (Figure 3b) with the geometry of the original molecule. The hydrogen atoms of the methyl groups in both independent molecules of **2a** show rotational disorder. Two positions separated by 60° with occupancy factors of 0.5 for each hydrogen atom have been found and refined. Compounds **2'a** and **2c** could be refined smoothly. In the final cycles the C, N and O atoms were refined anisotropically and the H atoms isotropically. The atomic coordinates of the non-hydrogen atoms of **2'a**, **2a** and **2c** are listed in Table 8. All calculations were carried out on the PDP11/44 computer with the SDP programming system of Enraf-Nonius [21,22].

Table 7

Crystal Data and Structure Determination Parameters

	2'a $C_{10}H_9N_5$	**2a** $C_{10}H_9N_5$	**2c** $C_8H_{11}N_5O_2$
M	199.2	199.2	209.2
a	7.887(2)	7.364(2)	8.653(2) Å
b	21.887(4)	8.534(2)	10.496(2)
c	10.999(1)	16.190(2)	11.603(1)
α		97.43(1)°	89.46(1)°
β		97.99(1)°	94.62(2)°
γ		98.83(1)°	103.19(2)°
V	1898.7(10)	983.7(6)	1022.6(6) $Å^3$
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$
Z	8	4	4
D_c	1.39	1.35	1.36 gcm^{-3}
Crystal size [mm]	0.40 × 0.30 × 0.05	0.50 × 0.40 × 0.35	0.30 × 0.40 × 0.50
Solvent	Ethanol	Nitromethane	Petrol ether/-chloroform
Maximum $\sin\theta/\lambda$	0.66	0.60	0.66 $Å^{-1}$
Independent reflections	2291	3747	5263
Unobserved reflections ($F_o^2 < 3\sigma(F_o^2)$)	1112	1145	1431
Final R	0.039	0.048	0.050

Acknowledgement.

We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial support, and to the BASF Aktiengesellschaft for the donation of chemicals. The diffractometer was supplied by the government of Baden-Württemberg. We also wish to thank Dr. M. C. Böhm for the semiempirical calculations and for helpful discussions.

REFERENCES AND NOTES

[1] Part V: G. Ege, K. Gilbert and R. Heck, *Angew. Chem.*, **94**, 715 (1982); *Angew. Chem., Int. Ed. Engl.*, **21**, 698 (1982); *Angew. Chem. Suppl.*, 1508-1514 (1982).

[2] E. Alcalde and R. M. Claramunt, *J. Heterocyclic Chem.*, **13**, 379 (1976).

[3] E. Alcalde, R. M. Claramunt, J. Elguero and C. P. Saunderson Huber, *ibid.*, **15**, 395 (1978).

[4] R. N. Butler, T. McEvoy, E. Alcalde, R. M. Claramunt and J. Elguero, *J. Chem. Soc., Perkin Trans. I*, 2886 (1979).

[5] Under protic conditions, as described by Alcalde *et al.* [2,3], in our hands 3-azido-1-methyl-4-phenyl-1*H*-pyrazole was the main methylation product besides traces of **7a** and **2'a**.

[6] R. N. Butler, *Can. J. Chem.*, **51**, 2315 (1973).

Table 8

Fractional Atomic Coordinates of the Non-hydrogen Atoms of **2'a**, **2a** and **2c** and the Thermal Parameters U_{eq} ($\times 10^3$ Å^2) With Standard Deviations

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Compound **2'a**

Atom	x/a	y/b	z/c	U_{eq}
N1	0.7526(3)	0.0169(1)	0.0137(2)	42(1)
N2	0.7476(2)	−0.0325(1)	0.0837(2)	46(1)
N3	0.8443(3)	−0.0335(1)	0.1818(2)	50(1)
N4	0.9178(2)	0.0214(1)	0.1726(2)	46(1)
N5	1.0313(3)	0.0511(1)	0.2429(2)	56(1)
C6	1.0486(3)	0.1037(1)	0.1801(2)	55(1)
C7	0.9508(3)	0.1086(1)	0.0737(2)	42(1)
C7A	0.8653(3)	0.0524(1)	0.0722(2)	39(1)
C21	0.6336(3)	−0.0829(1)	0.0569(2)	58(1)
C71	0.9349(3)	0.1584(1)	−0.0145(2)	40(1)
C72	1.0164(3)	0.2142(1)	0.0004(2)	51(1)
C73	0.9956(3)	0.2607(1)	−0.0830(2)	57(1)
C74	0.8943(3)	0.2528(1)	−0.1832(2)	54(1)
C75	0.8136(3)	0.1979(1)	−0.1998(2)	52(1)
C76	0.8334(3)	0.1508(1)	−0.1174(2)	46(1)

Compound **2a**

	Molecule 1				Molecule 2			
Atom	x/a	y/b	z/c	U_{eq}	x/a	y/b	z/c	U_{eq}
N1	0.7318(2)	0.2313(2)	0.4619(1)	69(1)	0.2250(3)	0.2436(3)	0.9538(1)	91(1)
N2	0.8531(2)	0.3369(2)	0.5159(1)	77(1)	0.1835(4)	0.1456(3)	1.0071(2)	98(1)
N3	0.7676(2)	0.4129(2)	0.5719(1)	68(1)	0.1704(3)	0.2294(3)	1.0814(1)	86(1)
N4	0.5871(2)	0.3529(2)	0.5524(1)	57(1)	0.2033(3)	0.3834(2)	1.0737(1)	68(1)
N5	0.4332(2)	0.3766(2)	0.5838(1)	73(1)	0.2061(3)	0.5197(3)	1.1234(1)	81(1)
C6	0.3025(3)	0.2672(3)	0.5296(1)	67(1)	0.2481(4)	0.6250(3)	1.0692(2)	78(1)
C7	0.3706(2)	0.1776(2)	0.4663(1)	54(1)	0.2677(3)	0.5578(3)	0.9893(1)	62(1)
C7A	0.5620(2)	0.2395(2)	0.4842(1)	53(1)	0.2352(3)	0.3945(3)	0.9952(1)	64(1)
C31	0.8530(4)	0.5340(3)	0.6432(2)	91(1)	0.1347(5)	0.1643(4)	1.1565(2)	104(2)
C71	0.2720(3)	0.0532(2)	0.3976(1)	54(1)	0.3046(3)	0.6338(3)	0.9158(1)	67(1)
C72	0.0791(3)	0.0236(3)	0.3768(1)	70(1)	0.3277(4)	0.7970(3)	0.9174(2)	87(1)
C73	−0.0102(3)	−0.0938(3)	0.3107(2)	81(1)	0.3530(5)	0.8686(4)	0.8503(2)	111(2)
C74	0.0900(4)	−0.1838(3)	0.2642(1)	82(1)	0.3623(4)	0.7799(4)	0.7759(2)	112(2)
C75	0.2804(3)	−0.1571(3)	0.2841(1)	75(1)	0.3460(4)	0.6161(4)	0.7688(2)	105(2)
C76	0.3712(3)	−0.0400(2)	0.3500(1)	61(1)	0.3174(3)	0.5359(3)	0.8404(2)	82(1)

Compound **2c**

	Molecule 1				Molecule 2			
Atom	x/a	y/b	z/c	U_{eq}	x/a	y/b	z/c	U_{eq}
N1	0.2757(2)	0.7239(2)	0.4710(1)	61(1)	0.0781(2)	0.4074(1)	0.2605(1)	59(1)
N2	0.3326(2)	0.6243(2)	0.5093(1)	66(1)	−0.0018(2)	0.4510(1)	0.3377(1)	61(1)
N3	0.4181(2)	0.6560(2)	0.6097(1)	61(1)	−0.0146(2)	0.5719(1)	0.3109(1)	54(1)
N4	0.4161(2)	0.7794(2)	0.6345(1)	54(1)	0.0594(2)	0.6052(1)	0.2153(1)	49(1)
N5	0.4888(2)	0.8656(2)	0.7170(1)	62(1)	0.0803(2)	0.7103(1)	0.1460(1)	56(1)
C6	0.4423(2)	0.9744(2)	0.6801(2)	59(1)	0.1588(2)	0.6713(2)	0.0625(2)	53(1)
C7	0.3420(2)	0.9553(2)	0.5767(2)	54(1)	0.1867(2)	0.5452(2)	0.0790(2)	50(1)
C7A	0.3283(2)	0.8236(2)	0.5483(2)	52(1)	0.1170(2)	0.5044(2)	0.1824(1)	48(1)
C31	0.5099(3)	0.5777(2)	0.6761(2)	76(1)	−0.0927(2)	0.6541(2)	0.3731(2)	62(1)
C61	0.5039(3)	1.0979(2)	0.7479(2)	82(1)	0.2047(3)	0.7626(2)	−0.0351(2)	72(1)
O7B	0.3104(2)	1.1689(5)	0.5349(1)	74(1)	0.2984(2)	0.5057(1)	−0.0924(1)	80(1)
O7C	0.2767(2)	1.0531(2)	0.5123(2)	58(1)	0.2559(2)	0.4713(2)	0.0004(2)	57(1)
O7D	0.1740(1)	0.9994(1)	0.4247(1)	61(1)	0.2622(2)	0.3547(1)	0.0452(1)	67(1)
C7E	0.1063(2)	1.0904(2)	0.3523(2)	68(1)	0.3184(3)	0.2675(2)	−0.0288(2)	83(1)
C7F	−0.0023(3)	1.0133(2)	0.2606(2)	74(1)	0.2690(3)	0.1364(2)	0.0130(2)	91(1)

[7] J. Elguero, R. M. Claramunt and A. J. H. Summers, "The Chemistry of Aromatic Azapentalenes" in "Advances in Heterocyclic Chemistry", Vol 22, p 183, Academic Press, New York, 1978.

[8] R. N. Butler, T. M. McEvoy, F. L. Scott and J. C. Tobin, *Can. J. Chem.*, **55**, 1564 (1977).

[9] R. N. Butler, *ibid.*, **50**, 1786 (1972).

[10] R. N. Butler and F. L. Scott, *J. Chem. Soc. C*, 1711 (1968).

[11] R. N. Butler and F. L. Scott, *ibid.*, 239 (1967).

[12] A. Parkin and M. R. Harnden, *J. Heterocyclic Chem.*, **19**, 33 (1982).

[13] R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).

[14] E. L. Anderson, J. E. Casey, L. C. Greene, J. J. Lafferty and H. E. Reiff, *J. Med. Chem.*, 7, 259 (1964).

[15] G. Ege and P. Arnold, *Angew. Chem.*, **86**, 237 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 206 (1974).

[16] H. Beyer and H. Wolter, *Chem. Ber.*, **89**, 1652 (1956).

[17] E. Hoggarth, *J. Chem. Soc.*, 612 (1950).

[18] H.-J. Schmidt and H. J. Schäfer, *Angew. Chem.*, **91**, 77 (1979); *Angew. Chem., Int. Ed. Engl.*, **18**, 68 (1979).

[19] D. v.d. Brück, R. Bühler, C.-C. Heuck, H. Plieninger, K. E. Weale, J. Westphal and D. Wild, *Chem. Z.*, **94**, 183 (1970).

[20] E. Alcalde, J. de Mendoza and J. Elguero, *J. Heterocyclic Chem.*, **11**, 921 (1974).

[21] The crystallographic computing package is described by B. A. Frenz in "Computing in Crystallography", edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G. C. Bassi, Delft University Press, Delft, Holland, 1978, p 64.

[22] More information about the crystal structures (atomic coordinates of the hydrogen atoms, thermal parameters of all atoms, individual bond lengths, structure factor tables, intermolecular distances and packing diagrams) may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, FRG, specifying the deposition number CSD 50531, the authors and the journal.