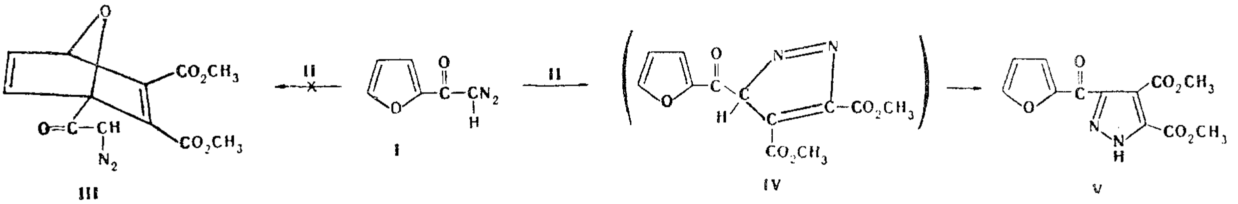
SYNTHESIS AND STRUCTURE OF DIMETHYL 3-(2-FUROYL)PYRAZOLE-4,5-DICARBOXYLATE

Z. G. Aliev, V. G. Kartsev,
L. O. Atovmyan, and G. N. Voronina

UDC 547.778'724.07

1,3-Dipolar cycloaddition to the diazomethine grouping takes place in the reaction of 2-diazoacetylfuran with dimethyl acetylenedicarboxylate. The structure of the crystalline reaction product, viz., dimethyl 3-(2-furoyl)pyrazole-4,5-dicarboxylate, was investigated by x-ray diffraction analysis. The entire molecule, except for one of the two CO_2CH_3 groups, forms a planar conjugated system. The spectral characteristics of the synthesized compounds are presented.

In the reaction of 2-diazoacetylfuran (I) with dimethyl acetylenedicarboxylate (II) one might have assumed that both diene synthesis at the furan ring and 1,3-dipolar cycloaddition to the diazomethine grouping would occur. Nonaromatic structure III with an oxygen bridge and retention of the diazocarbonyl fragment should be formed in the first case. In the second case the final product should have been dimethyl 3-(2-furoyl)pyrazole-4,5-dicarboxylate (V), in analogy with the adduct formed in the reaction of ω-diazoacetophenone with acetylenedicarboxylic ester [1].



Both reactions are well known separately for furan derivatives [2] and diazacarbonyl compounds [1, 3]. The combination in the molecule of these two fragments led to an alternative between I and II in the reaction pathway. One also should not have excluded the possibility of simultaneous reaction via the two pathways. In addition, in the case of the formation of adduct V the conformation of this molecule was not clear *a priori*.

The reaction of diazo ketone I with ester II took place at room temperature in a few days. The final adduct precipitated in the form of large colorless acicular crystals, which were investigated by x-ray diffraction analysis.

Compound $C_{12}H_{10}O_6N_2$ crystallizes in rhombic syngony. The principal crystallographic data are as follows: a = 16.846(8), b = 12.945(6), c = 5.772(3) Å, $d_{x\text{-ray}} = 1.48$ g/cm^3, z = 4, and space group Pna2$_1$.

The x-ray diffraction study showed that the reaction proceeded via the pathway involving 1,3-dipolar cycloaddition. The structure of the molecules is depicted in Fig. 1, which was realized with the ELLIDS program of A. N. Chekhlov. The bond lengths and bond angles are presented in Table 1.

The furoyl group is planar and has an O,O-cis-conformation. The planes of the two heterorings, viz., the pyrazole ring and the furoyl group, form an angle of 10°, which evidently does not exclude conjugation between the aromatic rings. The carbomethoxy group in the 5 position of the pyrazole ring is almost coplanar with it: The angle between the planes is 7°. At the same time, the CO_2CH_3 group in the 4 position deviates from the plane of the pyrazole ring

---

Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka 142432. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 91-94, January, 1982. Original article submitted February 26, 1981.

0009-3122/82/1801-0077$07.50

TABLE 1. Bond Lengths d (Å) and **Bond** Angles ω (deg)

Bond	d	Bond	d	Bond	d
O_1—C_{10}	1,185	O_6—C_{17}	1,358	C_{16}—C_{17}	1,479
O_3—C_{12}	1,156	O_6—C_{20}	1,369	C_{17}—C_{18}	1,367
O_5—C_{16}	1,245	C_{10}—C_{13}	1,481	C_{18}—C_{19}	1,423
O_2—C_{10}	1,364	C_{12}—C_{14}	1,535	C_{19}—C_{20}	1,367
O_2—C_9	1,482	C_{13}—C_{14}	1,391	N_7—C_{15}	1,356
O_4—C_{12}	1,370	C_{14}—C_{15}	1,407	N_8—C_{13}	1,352
O_4—C_{11}	1,499	C_{15}—C_{16}	1,485	N_7—N_8	1,317
C_9—H_{22}	1,01	C_{11}—H_{25}	1,01	N_8—H_{21}	0,99
C_9—H_{23}	0,98	C_{11}—H_{26}	1,02	C_{18}—H_{28}	0,99
C_9—H_{24}	1,00	C_{11}—H_{27}	1,02	C_{19}—H_{29}	1,01
				C_{20}—H_{30}	1,03

Angle	ω	Angle	ω
C_9—O_2—C_{10}	112,4	C_{14}—C_{15}—C_{16}	127,2
O_2—C_{10}—O_1	127,3	N_7—C_{15}—C_{16}	122,4
O_2—C_{10}—C_{13}	108,4	C_{15}—C_{16}—O_5	118,6
O_1—C_{10}—C_{13}	124,2	C_{15}—C_{16}—C_{17}	120,6
C_{11}—O_4—C_{12}	113,1	O_5—C_{16}—C_{17}	120,9
O_4—C_{12}—O_3	128,5	C_{16}—C_{17}—O_6	114,4
O_4—C_{12}—C_{14}	106,6	C_{16}—C_{17}—C_{18}	134,1
O_3—C_{12}—C_{14}	124,6	C_{17}—C_{18}—C_{19}	105,1
C_{10}—C_{13}—N_8	118,4	C_{18}—C_{19}—C_{20}	107,3
C_{10}—C_{13}—C_{14}	124,7	C_{19}—C_{20}—O_6	109,8
N_8—C_{13}—C_{14}	106,9	C_{20}—O_6—C_{17}	106,3
C_{12}—C_{14}—C_{13}	128,3	O_6—C_{17}—C_{18}	111,6
C_{12}—C_{14}—C_{15}	127,0	N_8—N_7—C_{15}	105,8
C_{13}—C_{14}—C_{15}	104,4	N_7—C_{15}—C_{14}	110,2
C_{13}—N_8—N_7	112,7		

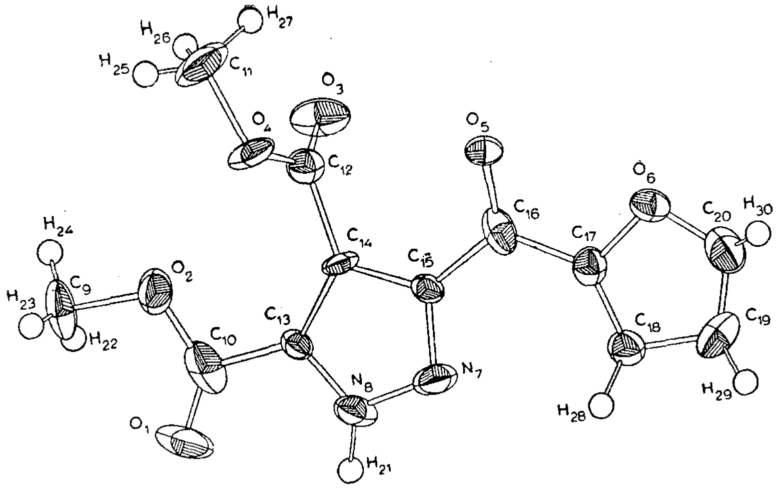


Fig. 1. Structure of the dimethyl 3-(2-furoyl)pyrazole-4,5-dicarboxylate molecule.

forming a dihedral angle of 74°. This is probably determined by an equilibrium between steric and electrostatic interactions of the O_3 and O_4 atoms with the O_2 atom, on the one hand, and with the O_5 atom, on the other. The difference in the C_{13}–C_{10} (1.481 Å) and C_{14}–C_{12} (1.535 Å) distances constitutes evidence for conjugation of the 5-CO_2CH_3 group with the pyrazole ring. Thus in the investigated molecule two heterorings, the bridged carbonyl group, and one of the two carbomethoxy groups form a planar conjugated system. Aromatization of the pyrazole ring is evidently the driving force of the reaction via 1,3-dipolar cycloaddition, while conjugation of it with the 5-CO_2CH_3 and furoyl groups leads to an additional gain in energy. However, conjugation of this sort is absent in the case of adduct III.

It is known [4] that in diazo ketone crystals the diazocarbonyl fragment has a cis conformation. One might have expected that the cis conformation of the OCCN fragment formed by the carbonyl group and the pyrazole CN group should be retained in the cycloaddition product.

TABLE 2. Coordinates of the Atoms ($\cdot 10^4$)*

Atom	x	y	z	Atom	x	y	z
O_1	3973 (4)	161 (5)	858 (15)	C_{16}	2534 (5)	3124 (8)	7650 (16)
O_2	4363 (4)	1835 (5)	309 (14)	C_{17}	2006 (5)	2839 (7)	9595 (18)
O_3	4475 (4)	3663 (5)	4960 (14)	C_{18}	1699 (5)	1927 (7)	10382 (18)
O_4	3658 (4)	3843 (4)	1845 (13)	C_{19}	1247 (5)	2196 (9)	12375 (22)
O_5	2716 (4)	4042 (4)	7289 (13)	C_{20}	1306 (6)	3242 (8)	12646 (19)
O_6	1769 (3)	3649 (5)	10923 (13)	H_{21}	463	3870	11780
N_7	2594 (4)	1330 (5)	6097 (0)	H_{22}	596	2038	12876
N_8	2956 (4)	866 (5)	4365 (15)	H_{23}	3898	5968	3725
C_9	4881 (7)	1466 (9)	−1596 (21)	H_{24}	2975	0124	4092
C_{10}	3964 (5)	1048 (9)	1366 (18)	H_{25}	4397	4563	504
C_{11}	4168 (6)	4709 (8)	971 (25)	H_{26}	4151	5100	2650
C_{12}	3933 (6)	3418 (5)	3864 (19)	H_{27}	5352	4554	1569
C_{13}	3482 (5)	1487 (6)	3271 (16)	H_{28}	4664	1526	−2062
C_{14}	3428 (5)	2453 (7)	4321 (18)	H_{29}	4672	1671	−766
C_{15}	2863 (5)	2317 (6)	6091 (15)	H_{30}	573	4351	9632

*The anisotropic temperature factors can be obtained from the authors.

However, a trans configuration of this fragment is realized in the crystal (see Fig. 1). This can be explained by rotation about the C_{15}—C_{16} bond of the nonaromatic pyrazole ring in intermediate IV, which leads to the least strained structure with a subsequent 1,3-sigmatropic shift of hydrogen and aromatization of the pyrazole ring. If this were not the case there would be steric hindrance between the furan ring and the 5-$COOCH_3$ group, which would lead to deviation of one of the heterocyclic rings from the conjugation plane.

EXPERIMENTAL

The IR spectrum of a mineral oil suspension of the compound was recorded with an IR-75 spectrometer. The UV spectrum of a solution of the compound in methanol was obtained with a Specord UV-vis spectrometer. The parameters of the unit cell were determined with an RKOP camera and were refined with a DRON-1 diffractometer. The experimental data, consisting of 614 independent nonzero reflections, were obtained with a DAR-UM automatic diffractometer with monochromatized Cu K_α emission. The maximum sin θ/λ value was 0.5. Absorption was disregarded. The structure was determined by a direct method with a Rentgen-75 program [5]. The hydrogen atoms were revealed from differential synthesis. Refinement by the method of least squares was carried out within the anisotropic (for the nonhydrogen atoms) total matrix approximation up to R = 0.067. The coordinates of the atoms are presented in Table 2.

Dimethyl 3-(2-Furoyl)pyrazole-4,5-dicarboxylate (IV). A solution of 0.408 g (3 mmole) of 2-diazoacetylfuran and 0.426 g (3 mmole) of dimethyl acetylenedicarboxylate in 15 ml of absolute ether was maintained at room temperature for 4 days. The crystalline precipitate was removed by filtration, washed three times with ether, and dried to give 0.8 g (96%) of a product with mp 155-156°C. UV spectrum (in alcohol), λ_{max} (log ε): 210 (4.04), 223 (4.21), and 300 nm (4.18). IR spectrum: 3050-3300 (NH), 1695 (C=O), and 1600 cm^{-1} (C=O, C=N). Found: C 51.6; H 3.6%. $C_{12}H_{10}N_2O_6$. Calculated: C 51.8; H 3.6%.

LITERATURE CITED

1. L. L. Rodina, V. V. Bulusheva, T. G. Ekimova, and I. K. Korobitsyna, Zh. Org. Khim., 10, 55 (1974).
2. H. Kwart and J. Burchuk, J. Am. Chem. Soc., 74, 3094 (1952).
3. A. S. Kather, J. Org. Chem., 38, 825 (1973).
4. E. Fahr, Lieb. Ann., 638, 1 (1960).
5. V. I. Andrianov, Zh. Sh. Safina, and B. L. Tarnopol'skii, Rentgen-75 Programs [in Russian], Chernogolovka (1975).