0.67 (s, 3 H, 18-Me); 1.03 (s, 3 H, 19-Me); 2.04 (s, 3 H, AcO); 2.22 (s, 3 H, 21-Me); 2.86 (d, 1 H, H(17), J = 10 Hz); 3.36 (m, 1 H, H(16)); 4.61 (m, 1 H, H(3)); 5.40 (m, 1 H, H(6)); for 16β-isomer (**4b**), 0.73 (s, 3 H, 18-Me); 1.03 (s, 3 H, 19-Me); 2.04 (s, 3 H, AcO); 2.34 (s, 3 H, 21-Me); 2.62 (m, 1 H, H(16)); 3.12 (d, 1 H, H(17), J = 10 Hz); 4.61 (m, 1 H, H(3)); 5.40 (m, 1 H, H(6)).

This study was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32404).

References

1. E. Ya. Lukevits, T. K. Gar, L. M. Ignatovich, and V. F. Mironov, *Biologicheskaya aktivnost' soedinenii germaniya* [*Biological Activity of Germanium Compounds*], Zinate, Riga, 1990 (in Russian).
2. K. Asai, *Organic Germanium: A Medical Godsend*, Kogakusha Ltd., Tokyo, 1977.
3. S. P. Kolesnikov, Ph.D. (Chem.) Thesis, Institute of Organic Chemistry of the USSR Academy of Sciences, Moscow, 1965, 110 pp. (in Russian).

Received July 7, 1997;
in revised form September 11, 1997

X-ray diffraction study of 1-[1-benzoyl-2-(2-furyl)vinyl]-2-dicyanomethylene-1,2-dihydropyridine

V. N. Nesterov

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

1-[1-Benzoyl-2-(2-furyl)vinyl]-2-dicyanomethylene-1,2-dihydropyridine was studied by X-ray structural analysis. The compound under study occurs as a Z isomer with respect to the central vinyl fragment.

Key words: 2-dicyanomethylene-1-vinyl-1,2-dihydropyridine, X-ray structural analysis.

As part of continuing studies of the structures of 1,2-dihydropyridines,[1] which contain a strong electron-withdrawing dicyanomethylene substituent at position 2 of the pyridine ring, in this work we studied the molecular geometry of 1-[1-benzoyl-2-(2-furyl)vinyl]-2-dicyanomethylene-1,2-dihydropyridine (**1**) by X-ray structural analysis. The overall view of molecule **1** is shown in Fig. 1. The bond lengths and bond angles are given in Tables 1 and 2, respectively.

As in the case of 1-[1-(4-chlorobenzoyl)-2-ethoxyvinyl]-2-dicyanomethylene-1,2-dihydropyridine (**2**) studied previously,[1] compound **1** occurs as a Z isomer with respect to the virtually planar vinyl fragment (the N(1)—C(7)—C(15)—C(16) torsion angle is −2.1°). In molecule **1**, the 1,2-dihydropyridine ring is planar (the deviations of the atoms from the mean plane are no more than ±0.009 Å), whereas in molecule **2**, this ring adopts a substantially flattened half-chair conformation. The observed π,π-conjugation between the planar

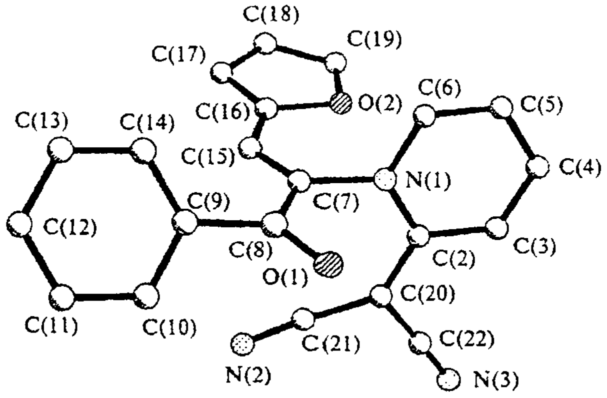


Fig. 1. Overall view of molecule **1**.

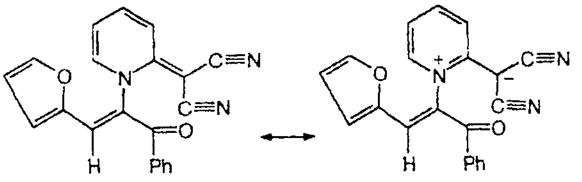
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 181—183, January, 1998.

1066-5285/98/4701-0182$20.00 ©1998 Plenum Publishing Corporation

Table 1. Bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å
N(1)—C(2)	1.367(4)	C(13)—C(14)	1.382(5)
C(2)—C(3)	1.419(4)	C(14)—C(9)	1.384(4)
C(3)—C(4)	1.351(4)	C(7)—C(15)	1.337(4)
C(4)—C(5)	1.405(3)	C(15)—C(16)	1.424(4)
C(5)—C(6)	1.349(5)	C(16)—C(17)	1.355(4)
C(6)—N(1)	1.369(3)	C(17)—C(18)	1.418(5)
N(1)—C(7)	1.451(4)	C(18)—C(19)	1.340(6)
C(7)—C(8)	1.476(4)	C(19)—O(2)	1.370(4)
C(8)—O(1)	1.220(4)	O(2)—C(16)	1.376(4)
C(8)—C(9)	1.500(4)	N(2)—C(21)	1.146(4)
C(9)—C(10)	1.388(4)	C(21)—C(20)	1.421(4)
C(10)—C(11)	1.385(5)	C(2)—C(20)	1.410(3)
C(11)—C(12)	1.376(6)	C(20)—C(22)	1.409(4)
C(12)—C(13)	1.379(4)	N(3)—C(22)	1.150(4)

dicyanomethylene fragment and the heterocycle results in a substantial redistribution of both the exo- and endocyclic bond lengths compared to the average values.[2] However, the bond lengths in compound **1** agree with the corresponding values observed in compound **2** and in the molecule of 2-dicyanomethylene-4,6-diphenyl-6-methyl-1,2,5,6-tetrahydronicotinonitrile whose structure is described by resonance structures with charge redistribution.[3] Therefore, the structure of molecule **1** can be described by resonance structure **A** and **B** as well.



A **B**

The forced shortened nonbonded intramolecular O(1)...C(2) [3.188(4) Å], O(2)...N(1) [2.786(4) Å], O(2)...C(6) [3.016(4) Å], C(7)...C(21) [2.797(4) Å], C(8)...C(21) [3.044(4) Å], C(14)...C(15) [3.182(4) Å], and C(15)...C(21) [3.278(4) Å] contacts (the sum of the van der Waals radii[4] of the O and C atoms is 3.35 Å; the sum of the van der Waals radii of the O and N atoms is 3.22 Å; and the double radius of the C atom is 3.54 Å) cause the twist of the 1,2-dihydropyridine ring and benzene ring with respect to the planar (to within ±0.041 Å) central fragment by 82.6° and 52.2°, respectively, as well as an increase in the N(1)—C(2)—C(20), C(8)—C(7)—C(15), C(7)—C(15)—C(16), and C(2)—C(20)—C(21) bond angles (124.0(2)°, 125.1(2)°, 130.0(3), and 128.2(3)°, respectively). However, the furyl heterocycle is twisted relative to the above-mentioned central fragment by only 4.8°, which does not exclude conjugation between the furyl ring and the adjacent C(15)=C(7) double bond. Thus, the C(15)—C(16) bond length [1.424(4) Å] is somewhat shorter than the typical value of the C(sp^2)—C(sp^2) single bond (1.471 Å)[2], although the C(15)=C(7) double bond [1.337(4) Å] coincides with the standard value of the C(sp^2)=C(sp^2) bond (1.331 Å).[2]

The O(1)—C(8)—C(7)—C(15) torsion angle is 171.3°, which is indicative of a slight twist of the benzene fragment about the C(8)—C(7) bond and does not exclude the possibility of conjugation between the carbonyl group and the C(7)=C(15) double bond. The absence of conjugation between the carbonyl group and the benzene ring is evidenced, on the one hand, by the substantial increase in the C(8)—C(9) bond length [1.500(4) Å] compared to the C(8)—C(7) bond length [1.476(4) Å] and, on the other hand, by the substantial twist of the benzene ring (the O(1)—C(8)—C(9)—C(10) torsion angle is −46.9°).

In the crystal, the following shortened intermolecular nonbonded contacts are observed: O(1)...H(5) $(-0.5 + x, 0.5 - y, -0.5 + z)$, 2.37(3) Å; O(1)...H(18) $(0.5 - x, 0.5 + y, 1.5 - z)$, 2.41(3) Å; N(2)...H(15) $(-x, -y, 1 - z)$, 2.35(3) Å; and N(3)...H(6) $(x - 1, y, z)$, 2.26(3) Å. These bonds can be treated as weak hydrogen bonds, which link molecules in a three-dimensional framework.

Experimental

Crystals of compound **1** are monoclinic, at −80 °C: a = 8.755(2) Å, b = 17.760(4) Å, c = 11.465(3) Å, β =

Table 2. Bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(16)—O(2)—C(19)	105.7(3)	N(1)—C(6)—C(5)	121.6(3)	C(10)—C(9)—C(14)	119.7(3)	C(16)—C(17)—C(18)	107.0(3)
C(2)—N(1)—C(6)	122.5(2)	N(1)—C(7)—C(8)	114.1(2)	C(9)—C(10)—C(11)	119.5(3)	C(17)—C(18)—C(19)	106.2(3)
C(2)—N(1)—C(7)	121.3(2)	N(1)—C(7)—C(15)	120.7(2)	C(10)—C(11)—C(12)	120.6(3)	O(2)—C(19)—C(18)	111.3(3)
C(6)—N(1)—C(7)	116.2(2)	C(8)—C(7)—C(15)	125.1(3)	C(11)—C(12)—C(13)	119.8(3)	C(2)—C(20)—C(21)	128.2(3)
N(1)—C(2)—C(3)	115.9(2)	O(1)—C(8)—C(7)	119.7(3)	C(12)—C(13)—C(14)	120.0(3)	C(2)—C(20)—C(22)	118.6(3)
N(1)—C(2)—C(20)	124.0(2)	O(1)—C(8)—C(9)	120.4(3)	C(9)—C(14)—C(13)	120.3(3)	C(21)—C(20)—C(22)	113.0(2)
C(3)—C(2)—C(20)	120.1(3)	C(7)—C(8)—C(9)	119.9(2)	C(7)—C(15)—C(16)	130.0(3)	N(2)—C(21)—C(20)	173.4(3)
C(2)—C(3)—C(4)	121.4(3)	C(8)—C(9)—C(10)	117.6(3)	O(2)—C(16)—C(15)	120.6(3)	N(3)—C(22)—C(20)	178.4(3)
C(3)—C(4)—C(5)	120.8(3)	C(8)—C(9)—C(14)	122.5(2)	O(2)—C(16)—C(17)	109.8(3)		
C(4)—C(5)—C(6)	117.8(3)			C(15)—C(16)—C(17)	129.6(3)		

Table 3. Atomic coordinates (×10^4; for H, ×10^3) in molecule **1**

Atom	*x*	*y*	*z*
O(1)	1049(2)	2276(1)	5777(2)
O(2)	1854(3)	178(1)	9018(2)
N(1)	1326(3)	1575(1)	7897(2)
N(2)	−1806(3)	790(2)	5155(2)
N(3)	−4206(3)	1539(2)	7713(2)
C(2)	−176(3)	1675(2)	8027(2)
C(3)	−350(4)	2086(2)	9052(3)
C(4)	907(4)	2343(2)	9858(3)
C(5)	2433(4)	2221(2)	9696(3)
C(6)	2595(4)	1845(2)	8708(3)
C(7)	1658(3)	1170(2)	6883(2)
C(8)	1567(3)	1637(2)	5805(3)
C(9)	2114(3)	1325(2)	4751(3)
C(10)	1147(4)	1422(2)	3627(3)
C(11)	1643(5)	1176(3)	2625(3)
C(12)	3104(4)	862(2)	2731(3)
C(13)	4072(4)	773(2)	3847(3)
C(14)	3570(3)	995(2)	4857(3)
C(15)	2017(3)	438(2)	6966(2)
C(16)	2192(3)	−60(2)	7960(2)
C(17)	2739(4)	−776(2)	8080(3)
C(18)	2779(5)	−999(2)	9274(3)
C(19)	2223(5)	−415(2)	9793(3)
C(20)	−1506(3)	1385(2)	7229(2)
C(21)	−1590(3)	1044(2)	6095(3)
C(22)	−2985(4)	1476(2)	7508(2)
H(3)	−143(3)	217(1)	914(2)
H(4)	76(4)	262(2)	1054(3)
H(5)	336(4)	240(2)	1032(3)
H(6)	363(4)	173(2)	845(3)
H(10)	6(4)	165(2)	358(3)
H(11)	96(4)	122(2)	187(3)
H(12)	347(4)	72(2)	202(3)
H(13)	517(4)	59(2)	394(3)
H(14)	424(4)	95(2)	565(3)
H(15)	221(3)	18(2)	627(3)
H(17)	312(4)	−106(2)	744(3)
H(18)	323(4)	−146(2)	966(3)
H(19)	199(4)	−32(2)	1062(4)

102.71(2)°, $V = 1739(1)$ Å^3, $d_{calc} = 1.302$ g cm^{-3}, $Z = 4$, space group $P2_1/n$. The unit cell parameters and intensities of 2706 independent reflections were measured on an automated four-circle Syntex P21 diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique to $\theta_{max} = 28°$). The structure was solved by the direct method to locate all nonhydrogen atoms and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 2262 reflections with $I > 3\sigma(I)$. All H atoms were located from difference syntheses and refined isotropically. The final value of the R factor was as follows: $R = 0.043$ ($R_w = 0.043$). All calculations were carried out using the SHELXTL PLUS program[5] (the PC version). The atomic coordinates are given in Table 3 (the thermal parameters can be obtained from the author).

This work was supported by the Russian Foundation for Basic Research (Project No. 97-03-33783a).

References

1. I. A. Aitov, V. N. Nesterov, Yu. A. Sharanin, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 434 [*Russ. Chem. Bull.*, 1996, **45**, 417 (Engl. Transl.)].
2. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
3. V. A. Tafeenko, Yu. T. Abramenko, A. V. Ivashchenko, K. A. Nogaeva, and S. V. Medvedev, *Khim. Geterotsikl. Soedin.*, 1988, 77 [*Chem. Heterocycl. Compd.*, 1988 (Engl. Transl.)].
4. R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.
5. G. M. Sheldrick, *SHELXTL PLUS. PC Version*, Siemens Analytical X-Ray Instruments, Inc., Madison (Wisconsin), 1989.

Received July 8, 1997