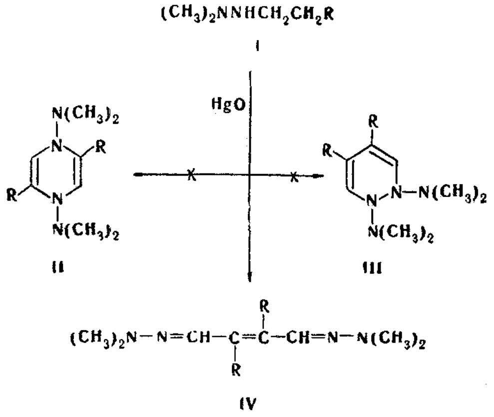
X-RAY DIFFRACTION STUDY OF 1,2-BIS(METHYLIDENE-2,2-DIMETHYLHYDRAZINO)ETHYLENE — PRODUCT OF THE OXIDATION OF 1,1,2-TRISUBSTITUTED HYDRAZINES [1,1-DIMETHYL-2-(2-CYANOETHYL)HYDRAZINE]

Ya. Ya. Bleidelis, A. E. Shvets,
I. Ya. Kalvin'sh, and A. V. Eremeev

UDC 548.737:547.861:543.422.25:542.943

It was established by x-ray diffraction analysis of crystals with the composition $C_{10}H_{14}N_6$ [a = 14.869(2), b = 11.405(2), c = 7.585(1) Å, β = 107.53(1)°, d_{calc} = 1.18 $g\cdot cm^{-3}$, Z = 4, and space group $P2_1/c$] that the molecule has a linear rather than a cyclic structure and is 1,2-bis(methylidene-2,2-dimethylhydrazino)ethylene rather than 1,4-bis(dimethylamino)-2,5-dicyano-1,4-dihydropyrazine as previously assumed.

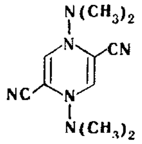
It has been reported [1] that stable pseudoaromatic 1,4-dihydropyrazine (II) and (or) 1,2-dihydropyridazine (III) systems are formed in the oxidation of 1,1-dimethyl-2-(2-cyanoethyl)hydrazine (Ia), 1,1-dimethyl-2-(2-methoxycarbonylethyl)hydrazine (Ib), and 1,1-dimethyl-2-(2-dimethylaminoethyl)hydrazine (Ic) with yellow mercuric oxide in inert solvents.



I–IV a R=CN; b R=COOCH$_3$; c R=CON(CH$_3$)$_2$

This conclusion was drawn on the basis of measurements of the dipole moments, IR and ^{1}H and ^{13}C NMR spectroscopic data, and the results of elementary analysis. However, the systems were found to be very inert. Thus, for example, we were unable to obtain salts of these compounds even with mineral acids, to carry out acid or alkaline hydrolysis of the functional groups, or to prepare quaternary hydrazinium salts by alkylation of the dimethylamino groups; this is not in agreement with the supposed properties of derivatives of 1,4-dihydropyrazines (II) and 1,2-dihydropyridazines (III).

In order to unambiguously solve the problem of the structure of the products of oxidation of 1,1-dimethyl-2-(2-cyanoethyl)hydrazine (Ia) we made an x-ray diffraction study of the supposed [1] 1,4-bis(dimethylamino)-2,5-dicyano-1,4-dihydropyrazine.



Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 541-544, April, 1978. Original article submitted June 7, 1977.

0009-3122/78/1404-0447$07.50

TABLE 1. Coordinates of the Nonhydrogen Atoms

Atom	X	Y	Z	Atom	Y	X	Z
N1	1,537	0,213	0,328	C3	1,389	0,184	0,346
N2	1,456	0,258	0,346	C4	1,307	0,234	0,360
N3	1,237	−0,054	0,345	C5	1,296	0,361	0,373
N4	1,287	0,460	0,384	C6	1,225	0,173	0,359
N5	1,066	0,157	0,367	C7	1,231	0,044	0,354
N6	0,983	0,203	0,380	C8	1,138	0,226	0,378
C1	1,608	0,298	0,327	C9	0,906	0,124	0,341
C2	1,546	0,090	0,281	C10	0,972	0,330	0,381

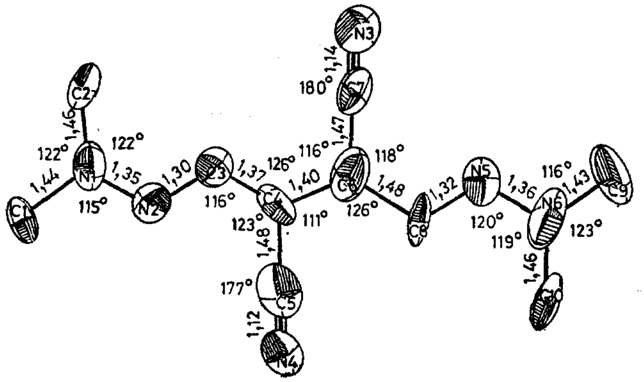


Fig. 1. Interatomic distances and valance angles of the molecule.

The bright-red rhombic crystals with the composition $C_{10}H_{14}N_6$ had the following characteristics: a = 14.869(2), b = 11.405(2), c = 7.585(1) Å, β = 107.53(1)°, V = 1226.65(34) $Å^3$, M = 218.3, d_{calc} = 1.18 $g \cdot cm^{-3}$, Z = 4, $\mu(CuK_\alpha)$ = 6.4 cm^{-1}, space group $P2_1/c$, and F_{000} = 464. The coordinates of the nonhydrogen atoms are presented in Table 1.

It is apparent from Fig. 1, in which the geometry of the molecule constructed from the experimentally determined coordinates of the atoms by means of an ORTEP program is presented, that the molecule is not cyclic as proposed in [1] but rather has a linear structure. Consequently, 1,2-bis(methylidene-2,2-dimethylhydrazino)ethylene (IVa) rather than cyclic 1,4-bis-(dimethylamino-2,5-dicyano)-1,4-dihydropyrazine (IIa) is formed in the oxidation of Ia. Since IIa and IVa are structural isomers, it was not possible to draw an unambiguous conclusion regarding the true structure of the product of oxidation of Ia on the basis of an analysis of the IR and NMR spectroscopic data and the elementary composition. Mass spectrometric studies also do not give sufficient information, since fragmentation of both the cyclic and acyclic molecules may proceed extremely similarly.

An analysis of the geometry of the molecule shows that the average value of the C—N bond length of the dimethylamino groups (1.45 Å) corresponds, within the limits of experimental error, to the value in mono- and dialkylamines (1.47 Å), while the average value of the C≡N bond (1.13 Å) corresponds to the value in nitriles (1.16 Å) [2]. The average value (1.47 Å) of the C_4—C_5 and C_6—C_7 bond lengths is close to the average value of the corresponding C—C bond lengths in alkyl and aryl nitriles (1.46 Å) [2, 3]. The average value of the N—N bond lengths (1.35 Å) is considerably shorter than the analogous bond in the hydrazine molecule (1.45 Å) [4]. The difference in the interatomic C_3—C_4 and C_6—C_8 distances is evidently due to a considerable degree to the systematic error that arises because of the imperfection of the single crystal (only 50% of the total number of measured reflections was used in the calculations). However, the elucidation of the possible asymmetry of the electron density distribution in the molecule requires low-temperature experiments. The —C≡N groups are trans-oriented with respect to the chain.

The equation of the plane drawn through the molecule is (−0.0444)x + (0.0536)y + (−0.9976)z − (−3.2683) = 0. The deviations from the average plane of the individual atoms are presented in Table 2.

It is apparent from Fig. 2 that the molecules in the unit cell of the crystal are situated along direction *a* and are parallel to the *a*b plane. Their packing is realized at distances that are no less than the sum of the van der Waals radii of the corresponding atoms.

TABLE 2. Deviations of the Atoms from the Average Plane of the Molecule

Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å	Atom	Δ, Å
N1	0,02	N5	−0,02	C3	−0,04	C7	0,11
N2	−0,03	N6	−0,02	C4	−0,05	C8	−0,09
N3	−0,13	C1	0,04	C5	−0,04	C9	0,24
N4	−0,04	C2	0,24	C6	−0,04	C10	0,08

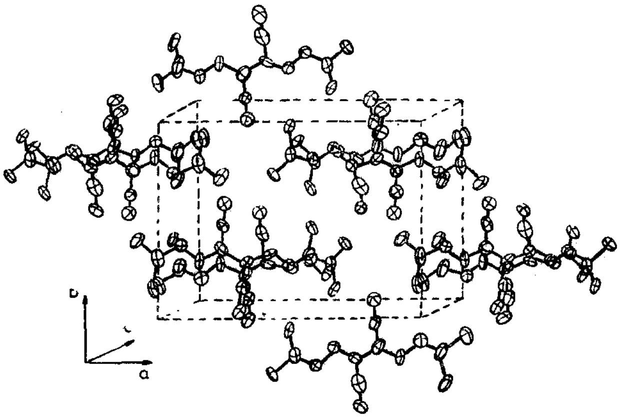


Fig. 2. Packing of the molecules in the unit cell of the crystal.

It follows from the material set forth above that cis or trans derivatives of 1,2-substituted 1,2-bis(methylidene-2,2-dimethylhydrazino)ethylenes or mixtures of them rather than their cyclic isomers — derivatives of 1,4-dihydropyrazines and 1,2-dihydropyridazines — are formed in the oxidation of 1,1,2-trisubstituted hydrazines and 1,1-dimethylhydrazones with yellow mercuric oxide.

EXPERIMENTAL

Compound IVa was obtained by the method in [1] and was purified by sevenfold fractional crystallization from dioxane.

The x-ray diffraction study was made with a $P2_1$ diffractometer with a system for determination of the crystal structure. The intensities of 1392 independent reflections were measured by $\theta/2\theta$ scanning ($2\theta_{max} = 150°$) with monochromatized (graphite) copper emission with a 0.1 by 0.15 by 0.15 mm single crystal. A total of 705 reflections with $I \geq 1.96$ were used in the calculations.

A model of the molecule was found by a direct method with a MULTAN program [5]. Calculation of the electron density distribution by the best phase variant exposed all 16 nonhydrogen atoms. Refinement of the structure by the least-squares method within the total matrix isotropic (R = 0.195) and, subsequently, anisotropic approximations led to a final R value of 0.116. The accuarcy in the determination of the interatomic distances was 0.02 Å, and the accuracy in the determination of the valence angles was 2.0°.

LITERATURE CITED

1. S. A. Giller, A. V. Eremeev, I. Ya. Kalvin'sh, V. G. Semenikhina, Ê. Ê. Liepin'sh, T. M. Kupch, and I. S. Yankovskaya, Khim. Geterotskil. Soedin., No. 3, 396 (1976).
2. A. J. Gordon and R. A. Ford, Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley-Interscience (1973).
3. Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement 1956-1959, London (1965), p. S15s.
4. A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S. I. Mizushima, J. Chem. Phys., 31, 843 (1959).
5. G. Germain, P. Main, et al., Acta Cryst., A27, 368 (1971).