Structural-chemical transformations during organic self-propagating high-temperature synthesis. Crystal structure of piperazine malonate and its crystal hydrate

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An organic salt, piperazine malonate, was prepared by self-propagating high-temperature synthesis (SHS) in a solid-phase piperazine—malonic acid (P—M) system. Triclinic crystals of piperazine malonate (PM) hydrate (**1**) were isolated from an aqueous solution. Monoclinic crystals of anhydrous piperazine malonate (**2**) were isolated from a solution in DMSO. Crystals **1** and **2** were studied by X-ray structural analysis. Structures **1** and **2** consist of centrosymmetrical piperazinium cations, which are linked to anions of malonic acid through N—H···O hydrogen bonds. In structure **1**, the anion is asymmetrical. The angle between the planes of the carboxyl groups and the plane of the CH_2 groups are 29.2° and 99.9°. In structure **2**, the anion is located on a twofold axis, and the corresponding angles are 81.5°. The N···O distances are in the range of 2.691(4)—2.838(5) Å.

Key words: organic self-propagating high-temperature synthesis; piperazine malonate, piperazine malonate hydrate, crystal structure.

A new method for the synthesis of high-melting inorganic compounds, namely, self-propagating high-temperature synthesis (SHS), has been developed.[1—3] In the course of the preparation of various inorganic compounds by the SHS method, the initial components undergo fundamental structural-chemical transformations to form a number of intermediate phases. Identification of these intermediate phases as well as final products, in particular, by the X-ray powder diffraction method, presents no problems due to the high symmetry of the crystal structures and the extensive structural data base available.

A different situation arises with SHS carried out in mixtures of powdered crystalline organic compounds.[4—6] Crystal structures of organic compounds generally belong to low-symmetry structural classes, and their X-ray diffraction patterns are complicated. Therefore, it is difficult to obtain the data on the existence of intermediate compounds, the phase state of the products, and the mechanism of the process as well as to establish the structure of the final product formed in the combustion wave by the known X-ray powder diffraction methods.

Studies of the autowave reaction in the first model organic solid-phase piperazine—malonic acid (P—M) system demonstrated that the reaction yields an organic salt, namely, piperazine malonate (PM).[4,5] Analysis of the data from physicochemical studies (thermochemical parameters and IR spectra) suggested that a chemical bond is formed through transfer of a proton from the hydroxyl group of the acid to the lone electron pair of the N atom in the amine molecule.[4]

With the aim of obtaining direct evidence for the mechanism of the self-propagating high-temperature reaction and the structures of the products, we carried out an X-ray diffraction study of the piperazine—malonic acid system. The structures of PM and its hydrate were established. The results of crystal-chemical analysis of the salt, which is the first representative of a new class of compounds prepared by SHS, are of interest.

The model reaction of piperazine with malonic acid was studied in more detail. The results of quantum-chemical and electron microscopy studies will be published elsewhere.

Experimental

The reaction of malonic acid with piperazine was studied on a dynamic X-ray diffraction apparatus, which made it possible to obtain a "diffraction cinema picture" from a burning sample in the angle range of 10—40° (see Ref. 7). The parameters of combustion obtained in the experiment agree well with the data published previously.[4,5] The process occurred in one stage. The temperature in the combustion zone was 130 °C. The final organic crystalline product was formed in the reaction front within a period of 1—3 s. We were unable to index the X-ray diffraction pattern of the product.

Previously,[5] it was reported that powdered malonic acid was slow to react with piperazine under mixing. Therefore, X-ray diffraction studies of an equimolar mixture of piperazine and malonic acid were carried out on a DRON-3M diffractometer using a special sealed cell (to protect from atmospheric moisture and CO_2) at room temperature over a period of 10 days. A series of X-ray diffraction patterns (Fig. 1), which were recorded at specific intervals determined

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 979—983, May, 1997.

Table 1. Interplanar distances (d), relative intensities (I), and indices of the diffraction pattern of compound **2**

d/Å	I	hkl	d/Å	I	hkl	d/Å	I	hkl	d/Å	I	hkl
6.817	1	200	3.505	8	311, $\bar{3}11$	2.910	6	202, $\bar{4}20$	2.513	1	501
5.824	7	101	3.409	1	400	2.810	1	$\bar{2}12$	2.452	6	$\bar{5}11$
5.377	11	020	3.217	5	002	2.756	1	022	2.390	1	032
5.127	100	$\bar{1}11$, 111	3.078	7	012, $\bar{3}21$, $\bar{1}31$, 131	2.684	5	040	2.341	2	402
4.209	26	220				2.588	4	$\bar{3}31$	2.290	3	$\bar{4}12$
3.947	2	121				2.563	8	331, $\bar{2}22$			
3.718	4	301									

by noticeable changes in the X-ray diffraction patterns, demonstrated that at ~20 °C the process was completed in approximately 200 h (the self-propagating high-temperature reaction was completed in a few seconds).The final X-ray diffraction pattern of the sample was in complete agreement with that of the reaction products of SHS.

The product of the self-propagating high-temperature synthesis was dissolved in various solvents to isolate single crystals suitable for complete X-ray structural study. Triclinic single crystals **1** were obtained by slow evaporation of an aqueous solution at room temperature. According to the data of X-ray structural analysis, these crystals contain 1.5 H_2O molecules. Monoclinic anhydrous single crystals **2** were isolated from a solution in DMSO. The X-ray diffraction pattern of **2** was identical to that of the product of SHS (Table 1).

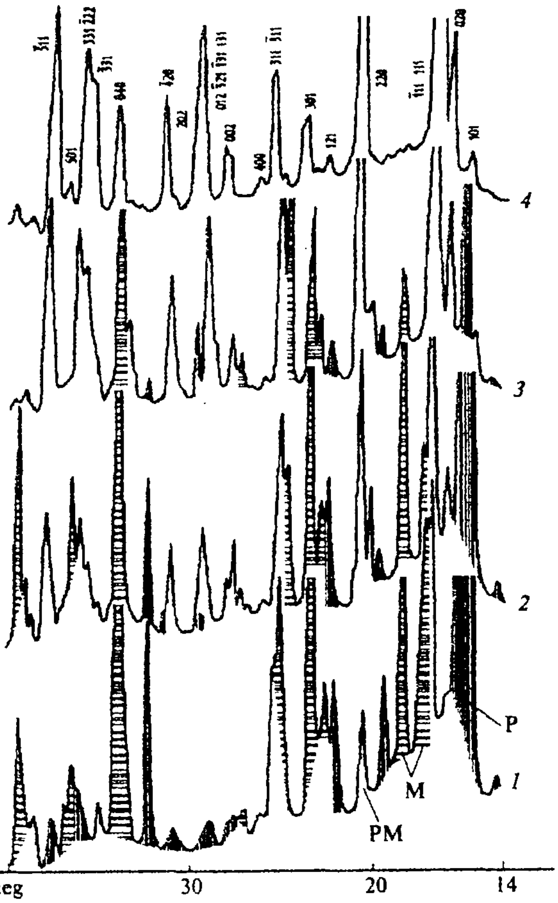

Fig. 1. A series of X-ray diffraction patterns that reflect the course of the reaction at room temperature: *1* is the initial mixture; *2*, after 24 h; *3*, after 4 days; *4*, after 10 days (see Table 1). (P is piperazine; M is malonic acid; and PM is the reaction product analogous to the product of the self-propagating high-temperature synthesis).

The principal crystallographic parameters are as follows: crystals **1** are triclinic, $[C_3H_2O_4]^{2-} \cdot [N_2C_4H_{12}]^{2+} \cdot 1.5H_2O$, a = 8.731(6) Å, b = 8.601(4) Å, c = 7.309(4) Å, α = 101.41(5)°, β = 98.80(4)°, γ = 85.94(3)°, V = 531.3 Å^3, Z = 2, d = 1.36 g cm^{-3}, space group $P\bar{1}$; crystals **2** are monoclinic, $[C_3H_2O_4]^{2-} \cdot [N_2C_4H_{12}]^{2+}$, a = 13.635(3) Å, b = 6.423(4) Å, c = 10.741(3) Å, β = 90.50°, V = 940.6 Å^3, Z = 4, d = 1.33 g cm^{-3}, space group $C2/c$. Intensities of 760 (**1**) and 466 (**2**) independent reflections with $I > 3\sigma(I)$ were measured from platelet-like single crystals of dimensions 0.2×0.2×0.05 mm on a three-circle DAR-UM diffractometer: equi-inclination mode, mixed ω-ω/2ω scanning technique, Cu-Kα radiation (graphite monochromator). Absorption was ignored. The structures were solved by the direct methods and refined anisotropically by the full-matrix least-squares method using the SHELXS program.[8] Positions of H atoms were located from the difference Fourier syntheses. The final refinement was carried out by the full-matrix method with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms to R = 0.028 (**1**) and 0.054 (**2**). The atomic coordinates, bond lengths, and bond angles for structures **1** and **2** are given in Tables 2—5. The projections of structures **1** and **2** are shown in Figs. 2 and 3, respectively.

Results and Discussion

In both structures, piperazinium cations adopt a chair conformation and occupy inversion centers. The bond lengths, bond angles, and torsion angles for cations **1** and **2** are given in Tables 4 and 5, respectively. The characteristic stereochemical features of the cations agree (to within the experimental error) with the analogous parameters observed previously.[9,10] All N—C bond lengths have close values, which are smaller than the C—C bond length. Three bond angles are virtually identical. The average C(sp^3)—H and N$^+$(sp^3)—H bond lengths are 1.02 Å and 0.98(6) Å, respectively. In structure **1**, the anion is asymmetrical. The angles between the planes of the carboxyl groups and the plane of the methylene groups are 29.2° and 99.9°. In the molecule

Table 2. Atomic coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in structure **1**

Atom	*x*	*y*	*z*
O(1)	7087(5)	2676(5)	4289(6)
O(2)	7459(6)	5267(5)	5083(6)
O(3)	4729(5)	2027(5)	293(6)
O(4)	6935(6)	2776(5)	−321(6)
$O(5)_w$	9670(9)	738(9)	357(1)
$O(6)_w$	89(1)	983(1)	−12(1)
N(1)	4720(6)	10054(6)	−3097(7)
N(2)	8736(6)	4687(6)	−1504(7)
C(1)	6887(7)	4073(7)	4004(8)
C(2)	5824(7)	4360(7)	2222(8)
C(3)	5823(7)	2946(7)	602(8)
C(4)	6267(8)	9552(7)	−3656(8)
C(5)	3873(8)	11173(7)	−4268(8)
C(6)	8953(8)	6322(7)	−359(8)
C(7)	10240(7)	3766(7)	−1614(8)
H(N(1))	579(1)	1069(1)	325(1)
H(N(11))	541(1)	−51(1)	170(1)
H(N(2))	840(1)	466(1)	749(1)
H(N(21))	1208(1)	−400(1)	88(1)
H(2)	593(1)	527(1)	187(1)
H(21)	466(1)	451(1)	263(1)
H(4)	657(1)	867(1)	694(1)
H(41)	674(1)	1044(1)	657(1)
H(5)	433(1)	220(1)	591(1)
H(51)	706(1)	−152(1)	383(1)
H(6)	1210(1)	282(1)	1028(1)
H(61)	1048(1)	318(1)	1101(1)
H(7)	1083(1)	427(1)	749(1)
H(71)	1000(1)	268(1)	773(1)

of malonic acid,[11] the analogous dihedral angles are 13° and 90°, respectively. In structure **2**, the anion is located on a twofold axis. The dihedral angles between the above-mentioned planes are 81.5°.

The bond lengths and bond angles for the anions (Table 6) agree well with each other and with the geometric characteristics of anions of carboxylic acids.[9–11] The value of the four C—O distances in anion **1** and the same distances in **2** is 1.25 Å on the average. This value is intermediate between the C=O and C—O bond lengths, which is indicative of delocalization of the π electrons of the carboxylate groups. The C—C—O bond angles also have close values to within the experimental error and approximate 118°. The IR spectral studies confirmed that the absorption band of the C=O group (1700 cm^{-1})[4] of malonic acid disappeared with the formation of salts **1** and **2**.

Table 3. Atomic coordinates of nonhydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) in structure **2**

Atom	*x*	*y*	*z*
O(1)	511(1)	2024(3)	5652(2)
O(2)	1430(1)	1602(3)	7343(2)
N	1679(1)	−1123(3)	4830(2)
C(1)	702(2)	2350(4)	6770(2)
C(2)	0	3723(6)	7500(0)
C(3)	2703(2)	−326(4)	4831(2)
C(4)	1595(2)	−3018(5)	5602(2)
H(N)	151(2)	140(4)	903(2)
H(N(1))	121(2)	−3(4)	1017(2)
H(2)	36(2)	461(4)	808(2)
H(3)	274(2)	−84(1)	925(2)
H(31)	214(2)	512(4)	930(2)
H(4)	91(1)	352(4)	1054(2)
H(41)	174(2)	256(4)	1149(2)

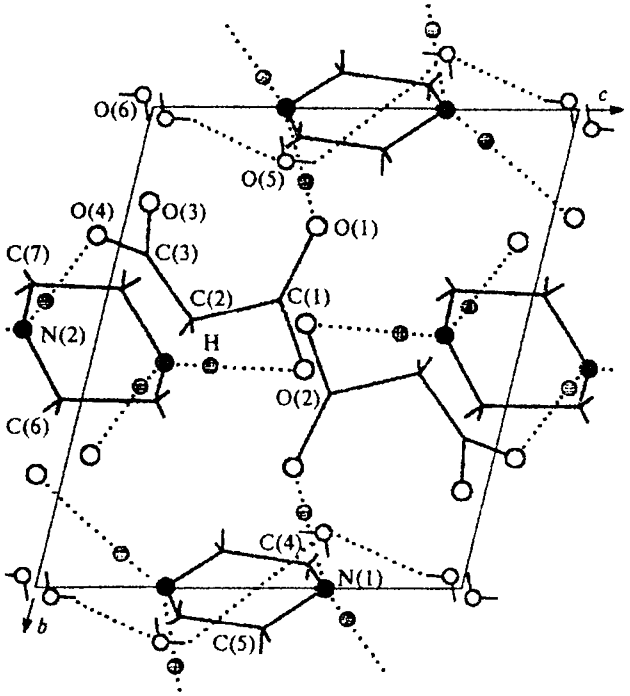

Fig. 2. Projection of structure **1** onto the *bc* plane.

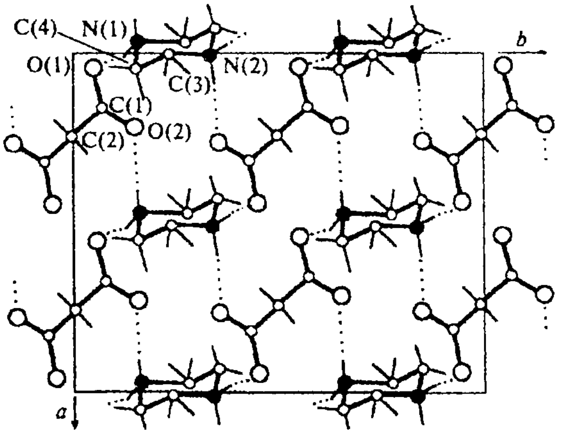

Fig. 3. Projection of structure **2** onto the *ab* plane (N—H···O hydrogen bonds are indicated by dashed lines).

Crystal structure **1** consists of two centrosymmetrical cations and an anion that occupies a general position. The anions and cations are linked through N—H···O hydrogen bonds (Table 7) so that the N(1) cation is

Table 4. Bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the piperazinium cation in structure **1**

Bond	d/Å	Angle	ω/deg	Angle	τ/deg
			1/2 0 1/2		
N(1)—C(4)	1.481(9)	N(1)—C(4)—C(5)	110.8(5)	N(1)—C(5)—C(4A)—N(1A)	55.5(5)
N(1)—C(5)	1.496(8)	N(1)—C(5)—C(4)	111.0(5)	C(4A)—C(5)—N(1)—C(4)	—56.3(5)
C(4)—C(5)	1.512(8)	C(4)—N(1)—C(5)	111.6(5)	C(5)—N(1)—C(4)—C(5A)	—55.9(5)
			0 1/2 0		
N(2)—C(6)	1.496(8)	N(2)—C(6)—C(7)	110.1(5)	N(2)—C(7)—C(6A)—N(2A)	56.6(5)
N(2)—C(7)	1.489(8)	N(2)—C(7)—C(6)	109.8(5)	C(6A)—C(7)—N(2)—C(6)	—57.5(5)
C(6)—C(7)	1.519(8)	C(6)—N(2)—C(7)	111.7(5)	C(7)—N(2)—C(6)—C(7A)	—57.7(5)

Table 5. Bond lengths (*d*), bond angles (ω), and torsion angles (τ) in the piperazinium cation in structure **2**

Bond	d/Å	Angle	ω/deg	Angle	τ/deg
N(1)—C(3)	1.487(3)	N(1)—C(3)—C(4)	110.8(5)	N(1)—C(3)—C(4A)—N(1A)	−56.1(5)
N(1)—C(4)	1.478(4)	N(1)—C(4)—C(3)	110.8(5)	C(3A)—C(4)—N(1)—C(3)	−56.3(5)
C(3)—C(4)	1.507(3)	C(3)—N(1)—C(4)	111.1(5)	C(4)—N(1)—C(3)—C(4A)	56.3(5)

Table 6. Bond lengths (*d*) and bond angles (ω) in the anions in structures **1** and **2**

Bond	d/Å		Angle	ω/deg	
	1	**2**		**1**	**2**
C(1)—O(1)	1.255(7)	1.244(3)	O(1)—C(1)—O(2)	125.2(6)	124.4(2)
C(1)—O(2)	1.248(7)	1.259(3)	O(1)—C(1)—C(2)	118.0(5)	117.8(2)
C(3)—O(3)	1.248(8)	—	O(2)—C(1)—C(2)	116.7(6)	117.7(2)
C(3)—O(4)	1.249(8)	—	C(1)—C(2)—C(3)	112.7(5)	—
C(1)—C(2)	1.531(8)	1.524(3)	O(3)—C(3)—O(4)	124.4(6)	—
C(2)—C(3)	1.520(8)	—	O(4)—C(3)—C(2)	117.3(5)	—
			O(3)—C(3)—C(2)	118.3(5)	—

surrounded by four anions, and the N(2) cation is surrounded by two anions. As a result, the molecules are packed in layers parallel to the *bc* plane. The crystal structure contains water molecules which occupy a general position O(5) and disordered relative to the symmetry center at the origin of coordinates position O(6). These water molecules are involved in O—H···O hydrogen bonds (the O(5)···O(6) and O(5)···O(5) distances are 2.452 and 2.623 Å, respectively) to form infinite chains along the *c* axis.

In the crystal structure of anhydrous PM (the product of self-propagating high-temperature synthesis), cations and anions are linked in layers parallel to the *ac* plane through the N—H(11)···O(1) and N—H(1)···O(2) hydrogen bonds. Each piperazinium cation is linked with four adjacent anions, while each anion is surrounded by four adjacent cations (see Fig. 2).

It was believed that analysis of the experimental thermal parameters of the crystal structure fragments of the products would allow conclusions about reaction mobility of the initial components to be drawn. The molecular mobilities of piperazine and malonic acid observed in the crystal structure are characterized by identical mean shifts of atoms and ions as a whole, which is associated with the stabilizing effect of hydrogen bonds and the crystal field, which equalizes the different mobilities of the components.

However, detailed studies of the macromechanism of the transport of reagents demonstrated that during the self-propagating high-temperature synthesis, transfer occurs mainly through capillary spreading of piperazine, which occurs as a melt at the temperature of the process.[5] At room temperature, the general mechanism of the transfer involves the gas-phase diffusion of highly volatile piperazine in the pores of the mixture and, apparently, surface diffusion.

Table 7. Geometry of N—H···O hydrogen bonds in structures **1** and **2**

Structure	Bond	Distance/Å			Angle
		N···O	N—H	H···O	N—H···O /deg
1	N(1)—H(1)...O(1)	2.838(5)	0.78(1)	2.07(3)	168(4)
	N(1)—H(11)..O(3)	2.711(4)	1.04(1)	1.75(3)	152(4)
	N(2)—H(2)...O(2)	2.697(4)	0.74(1)	1.98(3)	163(3)
	N(2)—H(22)..O(4)	2.691(4)	1.15(1)	1.55(3)	168(2)
2	N—H(11)...O(1)	2.725(3)	1.04(3)	1.69(2)	175(2)
	N—H(1)...O(2)	2.715(3)	0.90(2)	1.91(3)	167(2)

Thus, X-ray diffraction studies of the piperazine—malonic acid system demonstrated that self-propagating high-temperature synthesis is a one-stage reaction. The structure of the final product was determined. It was demonstrated that the structural-chemical transformations that occur involve transfer of a proton from the molecule of malonic acid to the piperazine molecule and the formation of a system of hydrogen bonds.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-3284a).

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Received October 21, 1996;
in revised form January 13, 1997