JOURNAL OF SOLID STATE CHEMISTRY 113, 229–238 (1994)

Kinetics and Mechanism of Phase Transitions in the Crystals of 2,4,6-Trinitrotoluene and Benzotrifuroxane

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Received June 28, 1993; in revised form December 8, 1993; accepted December 9, 1993

Three polymorphs (I, II, III) of 2,4,6-trinitrotoluene ($C_7H_5N_3O_6$) have been grown under different conditions. A comprehensive X-ray study has been carried out for I and II. The phase transition I–II has been investigated in the temperature range 55–75°C. The three polymorphs are characterized as follows:

(I) $a = 20.041(20)$, $b = 15.013(8)$, $c = 6.0836(5)$ Å, $V = 1830.45$ Å^3, $d_c = 1.647$, $z = 8$, space group $P2_1ca$;

(II) $a = 21.407(20)$, $b = 15.019(8)$, $c = 6.0932(5)$ Å, $\gamma = 111.00(02)°$, $d_c = 1.648$, $z = 8$, space group $P2_1/b$;

(III) $a = 40.0$, $b = 14.89$, $c = 6.09$ Å, orthorhombic crystal system.

In addition, two polymorphic modifications (monoclinic and orthorhombic) benzotrifuroxan ($C_6N_6O_6$) have been obtained under different conditions of synthesis and a comprehensive X-ray study of them has been carried out. The phase transition in benzotrifuroxan is observed in the temperature range 100–135°C. Kinetic parameters of the phase transitions have been determined and peculiarities of the mechanisms of the processes discussed. The two polymorphs are characterized as follows:

(A) $a = 14.661(4)$, $b = 10.219$ (2), $c = 12.032(3)$ Å, $\gamma = 103.72(2)°$, $V = 1751.2$ Å^3, $d_c = 1.911$, $z = 8$, space group $P2_1/a$;

(B) $a = 6.923(1)$, $b = 19.516(3)$, $c = 6.518(1)$ Å, $V = 880.7$ Å^3, $d_c = 1.901$, $z = 4$, space group $P\,na2_1$.

It is well known from the literature that the properties of 2,4,6-trinitrotoluene (TNT) in the range from room temperature to the melting point ($T_m = 82$°C) acquire some specific features, such as the presence of several DTA peaks depending on the sample prehistory near T_m, anomalies of thermal expansion of crystals (1). It is also known that there are several polymorphic modifications of TNT; however, their crystal structure (2–4) lacks a complete solution. To make clear why these specific features appear, we have carried out in the current work a study of the structure of TNT single crystals grown by different methods, as well as of temperature conversions of the phase composition of polycrystalline samples.

The TNT molecule is characterized by a low barrier to nitro group rotation about the C–N bond (2–4 kcal/mol) (5); we consider that the rotations of the nitrogroup planes about the C–N bond in solids are connected with the diversified character of the O ··· O and O ··· N(C) intermolecular interactions and their dissimilar behavior with temperature change (6).

The above factors make available different metastable modifications of TNT (depending on the crystal growth conditions), which may undergo phase transformation while affected by environmental factors. A complete structural investigation was carried out for the first two of the three polymorphs (I,II, III) obtained under different conditions. The single crystals I suitable for X-ray study were crystallized from the gas phase; the crystals II were grown from a TNT solution in dichloroethane, and the crystals III from a TNT solution in benzene.

The unit cell parameters of the first two modifications were refined on a diffractometer for single crystals the parameters of the crystals III were obtained by a photographic technique:

(I) $a = 20.041(20)$, $b = 15.013(8)$, $c = 6.0836(5)$ Å, $V = 1830.45$ Å^3, $d_c = 1.647$, $z = 8$, space group $P2_1ca$;

(II) $a = 21.407(20)$, $b = 15.019(8)$, $c = 6.0932(5)$ Å, $\gamma = 111.005(20)°$, $d_c = 1.648$, $z = 8$, space group $P2_1/b$;

(III) $a = 40.0$, $b = 14.89$, $c = 6.09$ Å, orthorhombic crystal system.

The intensities of 1466 nonzero reflections of I ($0.050 < \sin\Theta/\lambda < 0.590$) with $I > 2\sigma$ and those of 2650 nonzero reflections of II ($0.025 < \sin\Theta/\lambda < 0.603$) with $I > 2\sigma$ were recorded on a three-circle automated diffractometer, CuK_α radiation, absorption ignored. The structures I and II were solved by a direct method using the Rentgen-75 (7) program.

Refinement was carried out by the least-squares technique in a full-matrix anisotropic approximation for nonhydrogen atoms and anisotropic for hydrogen atoms using a weighting scheme. The resulting $R(I) = 0.055$ and $R(II) = 0.061$ (the atomic coordinates for the structures I and II can be received from the authors).

To study the kinetics of phase transition, an X-ray phase analysis was employed for determination of relative proportions of the initial and final phases, using an internal standard.

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In the TNT single crystals, the phase transition I–II proceeded without disintegration: structure registration of the same crystal was carried out in the initial state, and after thermal annealing as well (75°C, for 7 hr). In this case the reverse transition was not observed, which made it possible to investigate the samples at room temperature after necessary thermal treatment.

The phase compositions of TNT crystals obtained by different methods were studied using X-ray powder diffraction patterns.

Identification of reflections was performed based on theoretical powder patterns of modifications I and II calculated by the $[F_g]^2$.

The kinetics of the transition from a TNT orthorhombic phase to a monoclinic one was studied using crystals prepared by water precipitation from a TNT solution in ethyl alcohol (dimensions $5 \times 10 \times 50$ μm^3) after 2 days of drying at room temperature. In the course of isothermal heating the samples (weight 70 mg) were taken from the thermostat at definite time intervals, crushed with a pestle in an agate mortar, and their powder patterns were recorded on an X-ray diffractometer (Cu K_α) at room temperature.

The reflection (511) with $d = 3.27$ Å and the reflection (211) with $d = 4.62$ Å were chosen to determine the relative contents of the orthorhombic and monoclinic phase in the sample, respectively. The relative phase content in the sample was determined by comparing the area of reflections with that of the normalizing peak with $d = 3.86$ Å.

The theoretical powder patterns obtained from complete X-ray analysis of both the phases, I and II, showed the intensities of the reflections with $d = 3.86$ Å in the two phases to be equal. This fact was confirmed experimentally both for the individual phases I and II and for the samples with their different contents.

The kinetic studies were carried out in the temperature range 55–75°C. The changes in relative content of the orthorhombic (circles) and the monoclinic (triangles) phases with time for various temperatures are shown in Fig. 1.

Experimental kinetic curves show that an increase in phase II lags considerably behind a decrease in phase I. It can be due to two reasons. One of them may be the accumulation of some amount of amorphous nuclei of phase II, another—the selectivity of a chosen method of determining the kinetics of the process exceptionally through reflections of phases I and II, in which it is impossible to discover any metastable transition structure (phase) other than I or II. For this reason, the kinetic parameters were determined only with respect to a decrease in the orthorhombic phase I.

The slope of the kinetic curves corresponds to an autocatalytic process observed for the phase transitions elsewhere (8, 9).

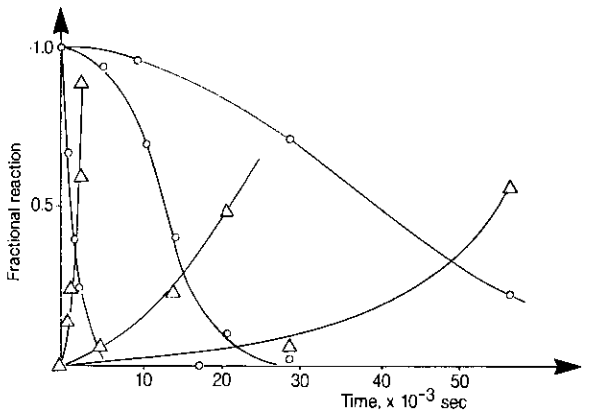

FIG. 1. Time dependence of the extent of phase transition at different temperatures in the TNT crystals.

In our case the autocatalytic equation was given as

$$-dC/dt = K_1 \cdot C + K_2 \cdot (1 - C),$$

where C is the relative content of the orthorhombic phase, K_1, K_2 are the temperature-dependent constants, and t is the time. The values of K_1 and K_2 for different temperatures are given in Table 1. The kinetic parameters for the phase transition were obtained from the Arrhenius equation:

$$\text{for } K_1, E_1 = 86 \pm 10 \text{ kcal/mol}, \log A_1 = 50 \pm 6;$$

$$\text{for } K_2, E_2 = 82 \pm 6 \text{ kcal/mol}, \log A_2 = 48 \pm 4.$$

Reflections with $d = 3.27$ and 4.62 Å had low intensity, which increased an error in the determination of the kinetic parameters. However, the choice of these peaks was connected with the fact that there appeared to be no individual reflections of higher intensity in the theoretical powder patterns.

In the unit cell of polymorphs I and II there are two crystallographically independent molecules with different conformations (Figs. 2, 3). The conformational differences are presented in the dihedral angles between the

TABLE 1
K_1 and K_2 Constant Values at Different Temperatures

T, °C	K_1, sec^{-1}	K_2, sec^{-1}	T, C	K_1, sec^{-1}	K_2, sec^{-1}
55	5×10^{-8}	1.4×10^{-6}	70	6.1×10^{-6}	3×10^{-4}
60	2×10^{-7}	5×10^{-6}	72.5	3×10^{-5}	5×10^{-4}
65	4×10^{-6}	7×10^{-5}	75	1.3×10^{-4}	1.5×10^{-3}
67.5	1.5×10^{-5}	1.5×10^{-4}			

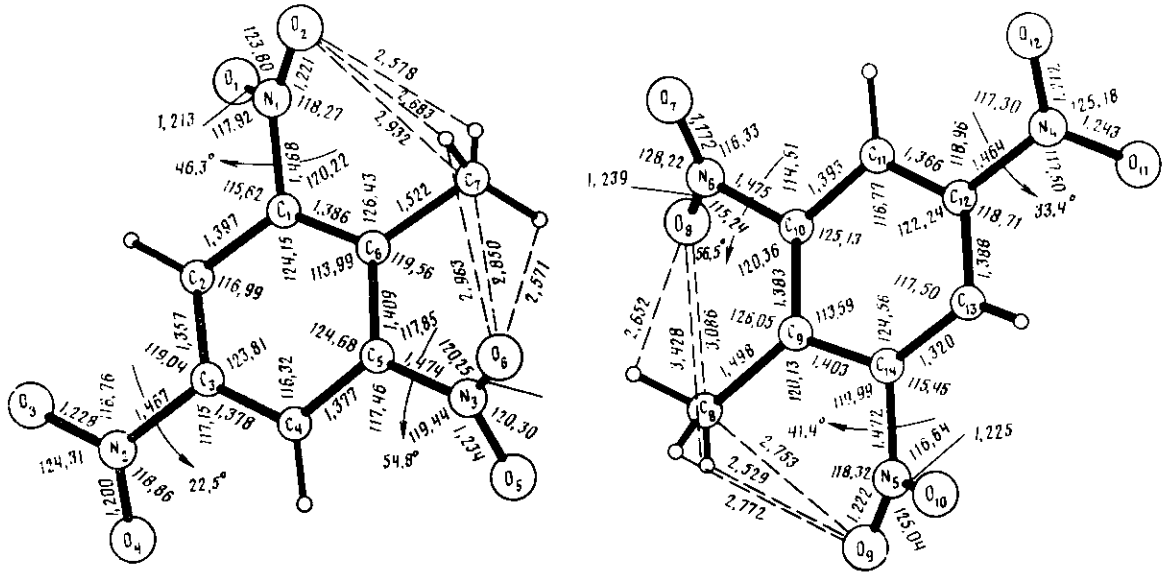

FIG. 2. Crystallographically independent TNT molecules in structure I.

benzene ring plane and appropriate planes of the nitro groups. In both the modifications, the rotation of the nitro group in position 4 of the benzene ring about the ring plane (22–30°) is not large compared to that of the other two nitro groups (positions 2 and 6) adjacent to the methyl group (40–60°). The intermolecular contacts of the nitro groups in positions 2 and 6 with the methyl group occur by "engagement": one of the oxygen atoms from each group fits into the space between two hydrogen atoms of the methyl group, i.e. the rotation of the methyl group is stopped by the position of the two nitro groups on the left and on the right.

A change in the conformation of the molecule must be followed by a synchronous rotation of the methyl group and two nearest-neighbor nitro groups by angles that are multiples of $(2n + 1) \times 60°$.

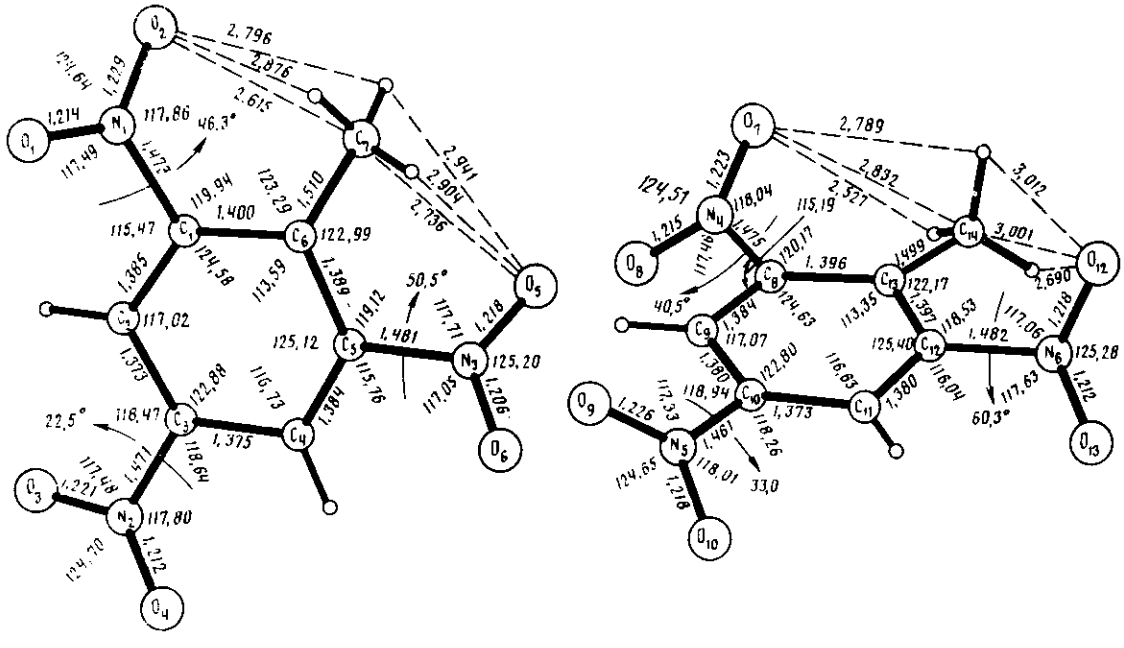

FIG. 3. Crystallographically independent TNT molecules in structure II.

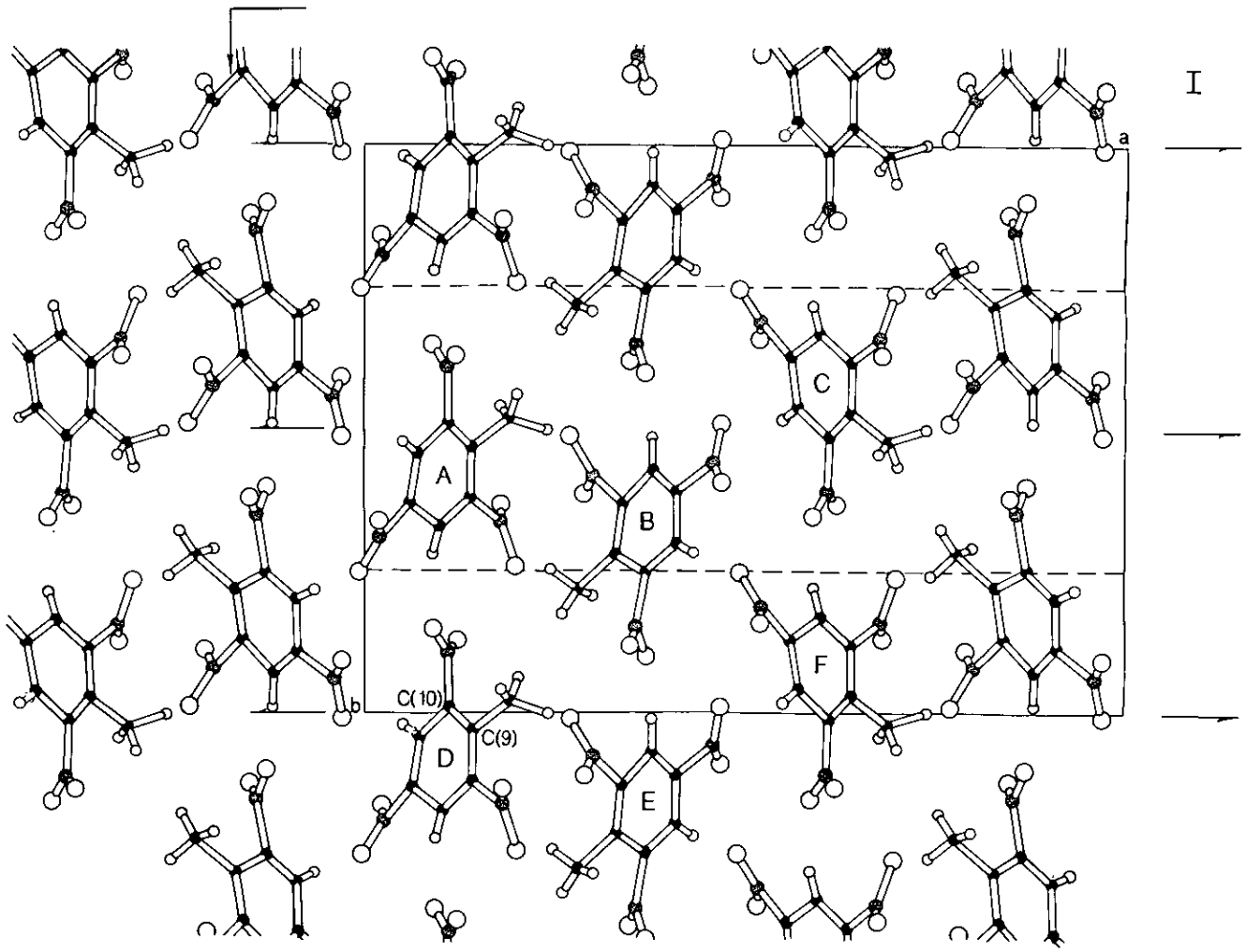

FIG. 4. Projection of structure I onto (*a*, *b*).

There are some other points that support the closeness between the structures I and II. First, there is complete coincidence of the reflections of the type *hk*0, *h*0*l*, 0*kl* for all the modifications; here, only reflections of the *hkl* type are different. Second, the registered transition of a single crystal from I into II occurs without disintegration.

An independent solution of the structures I and II by direct methods and choice of unit cells in space groups $P2_1ca$ and $P2_1/b$ has resulted in the lack of coincidence of the coordinate origin (Figs. 4, 5). The structures I and II coincide with a definite shift (atoms C(1), C(6), C(5) of the structure II coincide respectively with atoms C(14), C(9), C(10) of the structure I). The structure II displaced in the direction **c** by -0.2437×6.09 Å shows the following: in the **a** direction of the orthorhombic crystal to which both the phases are brought there arises a periodical structure formed by layers equal in thickness ($a = 20.041$ Å) arranged perpendicular to this direction and having a molecular stacking that is coincident and noncoincident in the two phases. In the noncoincident layers of the modifications I and II, the positions of the molecular centers of gravity are the same but the molecules themselves are mirror antipodes. Thus the crystallochemical analysis suggests that the structures I and II are polytypes. The structure II for which only the unit cell parameters have been established may be a superposition of the lattices of these phases.

The energies of the structures I and II calculated by a method of atom–atom potentials (10) with allowance made for an electrostatic energy component (atomic charges were calculated using the CNDO/2 method) show that the structure of a monoclinic crystal is 3 kcal/mol more favorable than that of an orthorhombic one, and the phase transition shifts a crystal to a more favorable energy state.

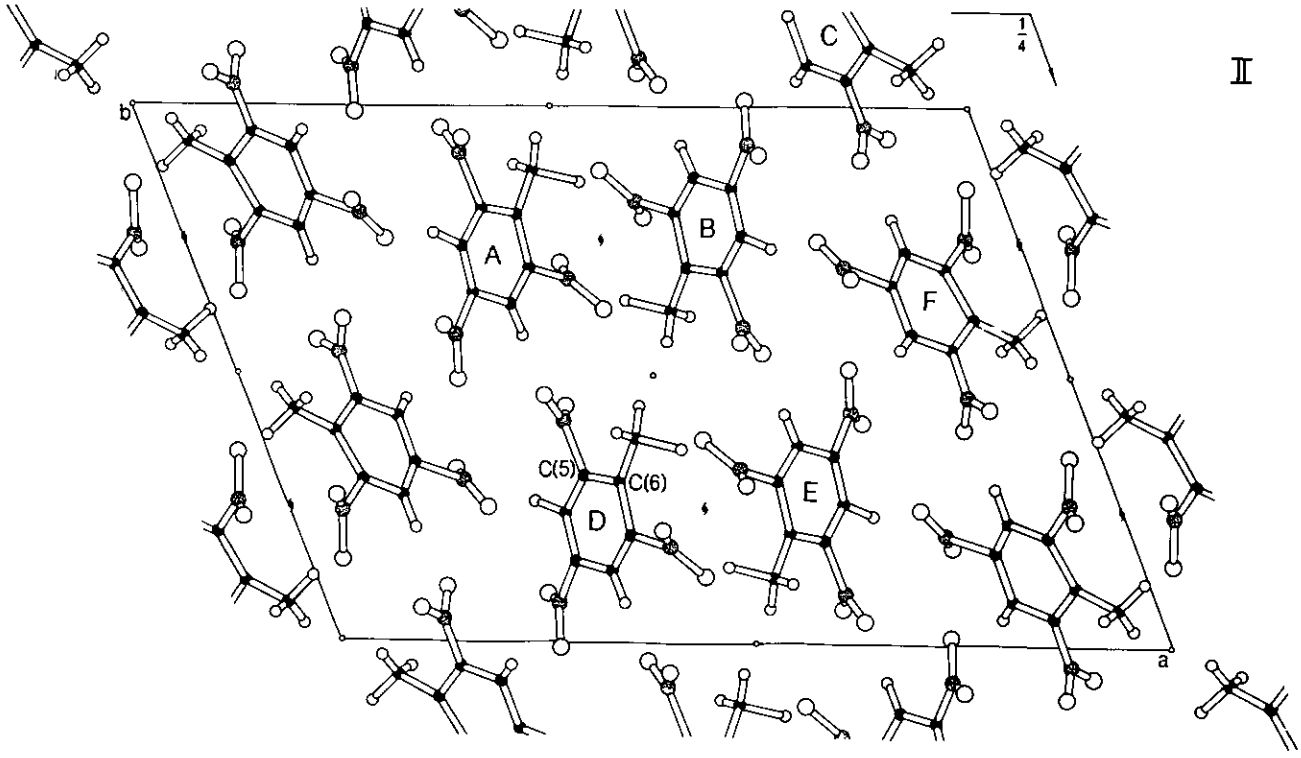

FIG. 5. Projection of structure II onto (*a*, *b*).

An orthorhombic TNT phase at temperatures above 55°C passes to a monoclinic phase. The transition rate depends strongly on temperature. Since the kinetic parameters of constants K_1 and K_2 coincide within experimental error, it is assumed that the temperature dependence of the process rate is, as a whole, characterized by an effective activation energy E_{eff} = 85 kcal/mol. In spite of considerable error in E_{eff} evaluation it apparently significantly exceeds the calculated energy difference of the crystal structures in the monoclinic and orthorhombic phases. The use of other equations to describe the kinetic curves will not lead to a marked decrease in E_{eff}, since the activation energy, as was shown for the solid-phase processes (11), does not depend greatly on the mathematical model chosen.

As it has been shown above, during phase transition the positions of centers of gravity in the molecules are not altered and the differences between the orthorhombic and monoclinic phases consist in synchronous rotation of the methyl group and the two neighboring nitro groups. The intramolecular activation barrier of this process is

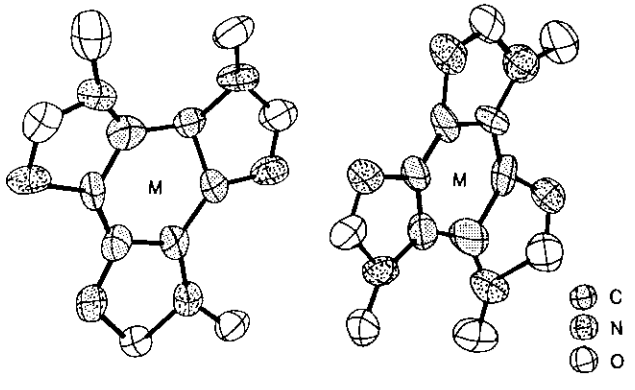

FIG. 6. BTF molecules in the A(M + M) phase.

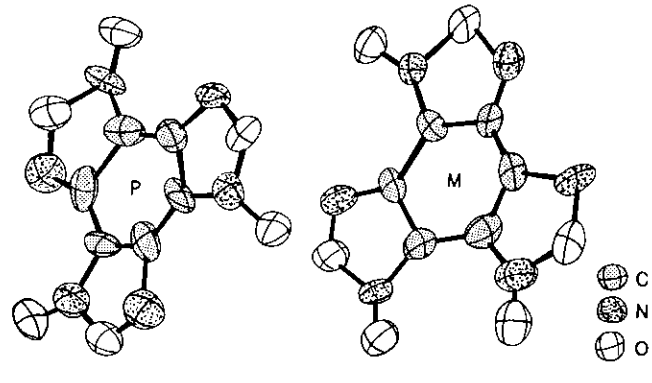

FIG. 7. BTF molecules in the A(M + P) phase.

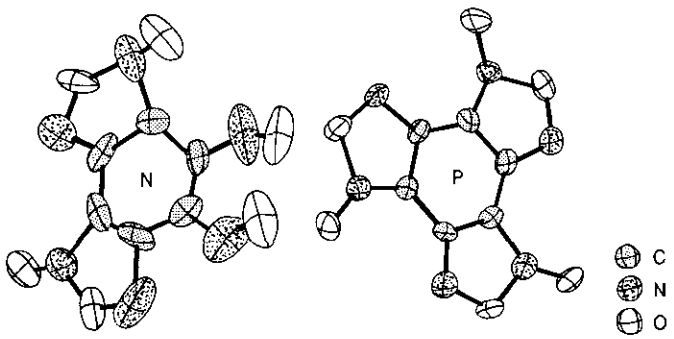

FIG. 8. BTF molecules in the A(P + N) phase.

2–4 kcal/mol and it cannot explain the strong temperature dependence of the phase transition rate. The published work (12) suggests a model that describes the phase transition as proceeding with high activation energy, according to which there is a "gaseous interlayer" between the old and new phases. In this case the molecules sublimate from the surface of the old phase and crystallize on the new one. This scheme for the process must give an activation energy value close to the heat of sublimation, as is often observed in the experiments. Also, if there is a gaseous interlayer, the new phase orients itself in an arbitrary way toward the initial phase, which is also often seen when phase transition is studied (10). However, such a model of the mechanism of phase transition can hardly apply to TNT, as the high magnitudes of the activation energy are seen for the phase transition from single crystal of TNT to single crystal, in which the cyrystallographical orientation of the latter corresponds to the initial structure within experimental error. This and other features of the phase transition in TNT (equal phase volume of both the structures, minor differences between the old and new phases) make us assume that the initial structure (orthorhombic phase) is a matrix according to which and on which a new (monoclinic) phase is built.

The mechanism of phase transition should explain the experimental facts, such as high activation energy of the initial phase decrease and presence of an indefinable phase (phase II mass increase lag). The high activation energy may appear either because of the reverse transition of II–I or because specific features of the process mechanism.

In all the evidence, the II–I transition is absent as under neither conditions is there observed an increase in phase I, but only its decrease. Kinetically also, the phase I and phase II are separated by a stage of a phase which cannot be detected by the chosen method.

Hence it follows that the high activation energies must be determined by the specific features of the process, which are as follows. The differences in the TNT phases are connected with the rotation of the methyl group and two nitro groups by $(2N + 1)$ angles (where N is an integer) and the synchronization of these angles in the alternating layers of the crystal lattice (on retention of the positions of the centers of gravity in the benzene ring).

It may be assumed that stable nuclei of the new phase are formed in the simultaneous cooperative rotation of the methyl group and two nitro groups in the minimum necessary quantity (n) of the TNT molecules. Then, to a first approximation, the probability of formation of a critical nucleus will be given by

$$P_o \sim P_m^n \sim \exp(-nE_m/RT),$$

where $P_m \sim \exp(-E_m/RT)$ is the probability of rotation of one molecule, and E_m is the activation barrier, equal to 2–4 kcal/mol for one TNT molecule. In this case, the effective activation energy is nE_m and it may reach high values.

The minimum number of molecules in such a nucleus, which is 30–40 molecules, can be estimated for the found values of the phase transition activation energy. The formation of nuclei with the changed orientation of the methyl group and nitro groups with respect to the molecules of phase I must decrease the magnitude of the reflections referred to phase I, which is described by the kinetic curve of the phase decrease.

However, the positions of such nuclei in the crystal are arbitrary: hence no reflections referred to phase II have been observed. The phase II reflections will appear after the beginning of the coalescence of such nuclei followed by layer-by-layer phasing of the angles of orientation of the methyl and nitro groups characteristic of phase II. Such a process should lag behind as very high concentration of the initial nuclei is necessary for the coalescence to occur, while the phasing (formation of a layered structure) has its activation barrier.

The suggested mechanism enables us to explain both the high activation energy and the nature of the indefinable

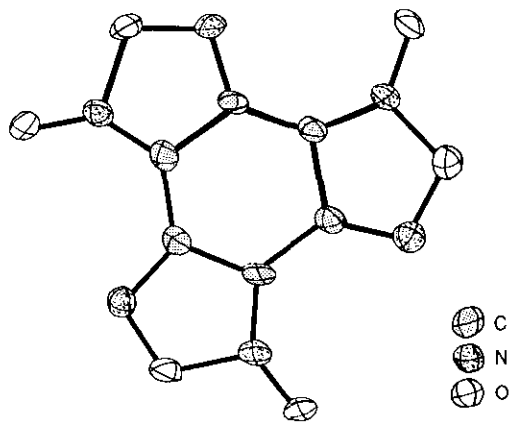

FIG. 9. BTF molecules in the B phase.

TABLE 2
Crystallographic Parameters of BTF Single Crystals in the Monoclinic (A) and Orthorhombic (B) Phases

	Monoclinic (A)					Orthorhom. (B)
Parameter	Freshly prepared crystals	Storage 6 months T = 5°C	Storage 6 months T = 20°C	Warming 12 h T = 80°C	Warming 2 h T = 120°C	After phase transition crystal was grown from acetone
a (Å)	14.661	14.750	14.969	15.055	15.082	6.923
b (Å)	10.219	10.226	10.209	10.168	10.168	19.516
c (Å)	12.032	11.914	11.816	11.714	11.735	6.518
γ (°)	103.72	103.40	102.44	102.20	102.20	
sp. gr.	P $2_1/a$	P $2_1/a$	P $2_1/a$	P $2_1/a$	P $2_1/a$	P $na2_1$
Z	8	8	8	8	8	4
v (Å^3)	1751.2	1748.1	1763.3	1752.8	1759.0	880.7
d (g/cm^3)	1.911	1.915	1.898	1.910	1.903	1.901

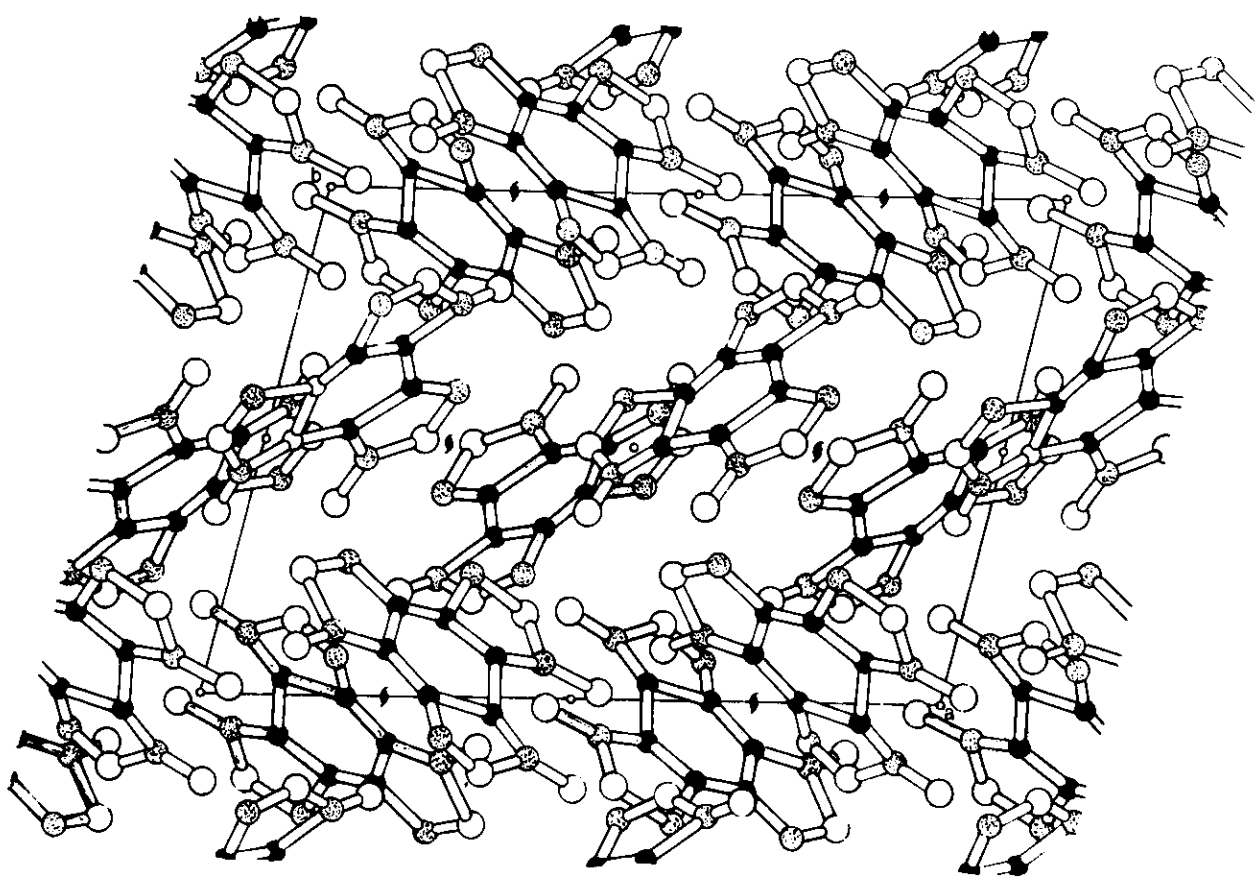

FIG. 10. Projection of the BTF structure in the A(M + M) phase.

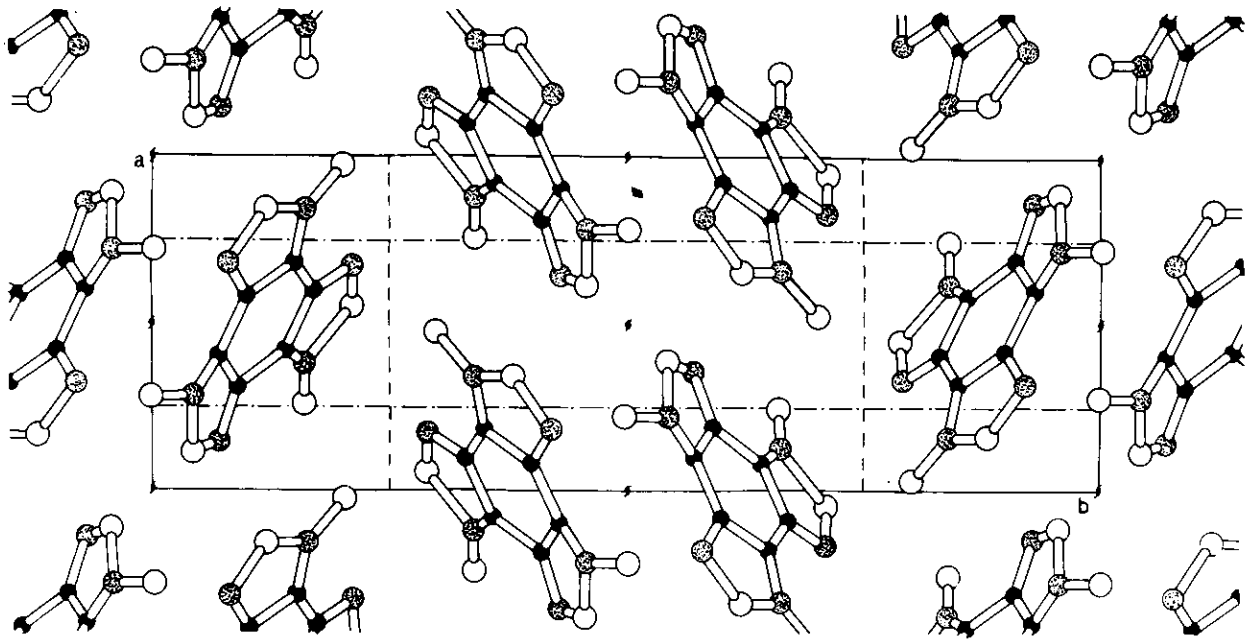

FIG. 11. Projection of the BTF structure in the B phase.

phase (lagging behind the phase II increase) which is a set of nuclei of various sizes without layer-by-layer phasing of the methyl group and the two nitro groups. To confirm this assumption, some additional investigations are needed.

The problem of phase transition in benzotrifuroxan [BTF] suggested itself after Dr. A. V. Morozov kindly provided us with BTF crystals of the monoclinic system [A], the previously known forms of BTF having been orthorhombic [B] (13). Measuring the unit cell parameters of the monoclinic phase crystals for a long period of time and after certain treatments has revealed their considerable change within the same monoclinic crystal system (Table 2).

An X-ray study of freshly prepared crystals of phase A BTF carried out on a three-circle automated diffractometer has shown the presence of two crystallographically. independent molecules with the same conformation (M) (Fig. 6). After 6 months storage at room temperature the unit cell contained two molecules with different conformations (M and P) (Fig. 7).

The BTF crystals of the A phase, after being heated at 120°C for 2 hr, remained in the same monoclinic system, but the unit cell contained two new molecules (Fig. 8): a P, with a local threefold axis and small ellipsoids of thermal vibration, and N, representing an intermediate compound in the transition of molecule-isomers from M to P, with two nitroso groups turned out of the benzene ring plane, which corresponded to the minimum molecular energy (14).

In essence, we have observed three phases, A (M + M), A (M + P), and A (P + N), in the framework of the same orthorhombic crystal system. As is known (13), the orthorhombic B phase contains symmetric BTF molecules whose local threefold axis goes perpendicular to the molecules plane across its center of gravity (Fig. 9); i.e., these are the P molecules. Our quantum chemistry calculations by CNDO/2 and structure energy calculation (10) have shown that the orthorhombic B phase as a whole appears to be more energetically favorable, since the separate P molecule in it lies on a lower energy level as compared to the M molecules in the monoclinic A phase, which compensates for unfavorable molecular packing in the B phase.

Lability of the monoclinic BTF phase is its specific feature manifesting itself in changing the molecule conformation and, consequently, the unit cell parameters, which is proved by X-ray analysis. These facts can be explained through increased conformational "tension" of the freshly prepared A phase containing M molecules, followed by subsequent relaxation.

Considering the conformational transitions as a chemical reaction occurring with energy release (lowering of the energy level of separate molecules), one may assume that the A phase made of M is in endogenic phase transformation from the moment of its formation. Such a process at the initial stage will produce changes in the unit cell parameters in the framework of the invariant crystal structure, and then may lead to crystal disintegration into microblocks with different crystal systems.

Table 2 shows the dependence of the monoclinic phase

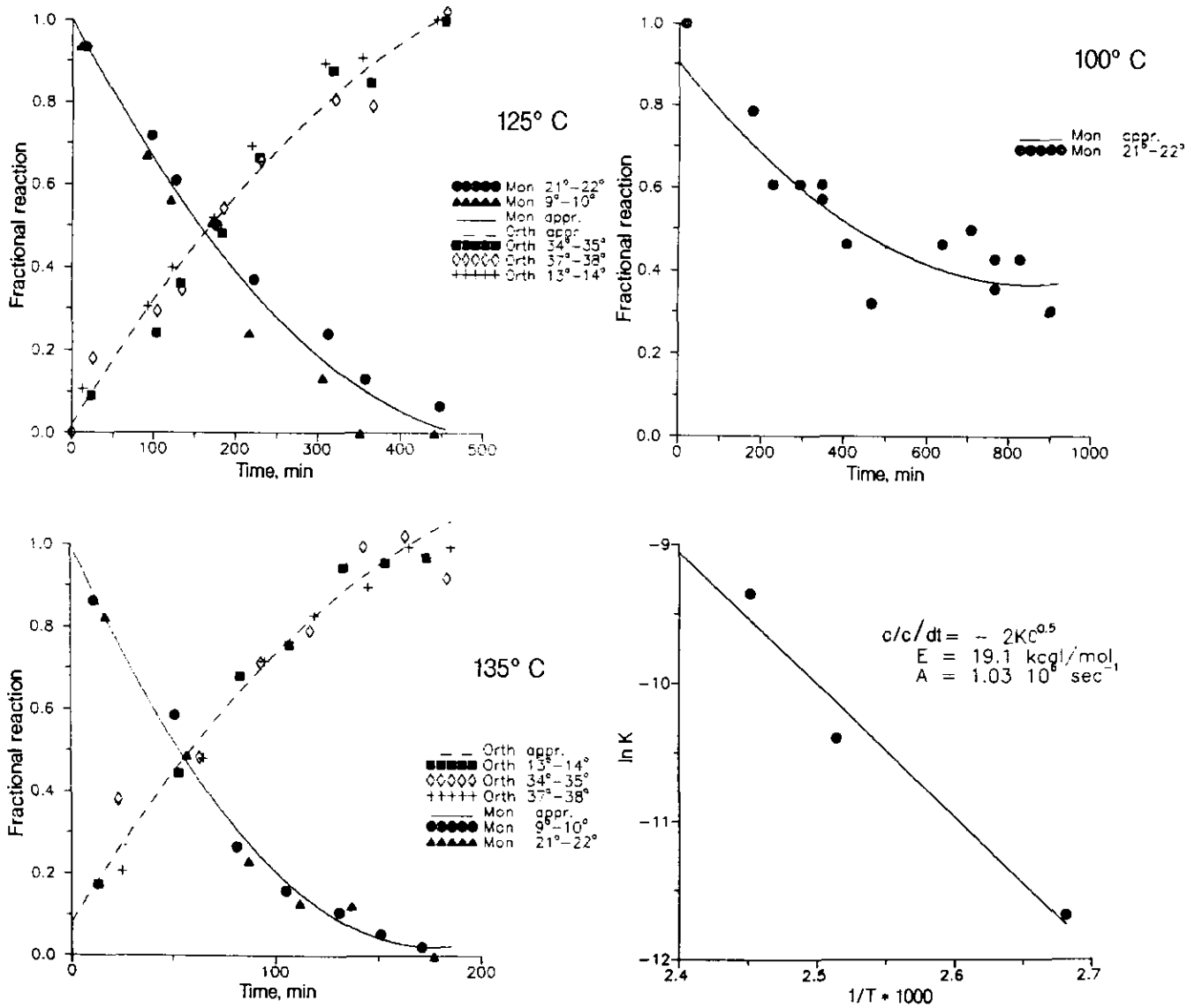

FIG. 12. Time dependence of the extent of phase transition at different temperatures in the BTF crystals.

parameters on the sample prehistory. No variation of the parameters has been observed for the orthorhombic phase, so the table gives the B phase parameters obtained by crystallization from acetone after completion of the A–B phase transition in the BTF crystals.

Decomposition of the monoclinic phase and phase transition are increased with temperature. As this takes place, the observation of the process of phase transition in a hot stage under an optical microscope shows the initial A phase crystal decomposing gradually into blocks with dimensions of a few micrometers. A liquid phase appears in the volume and on the surface of the decomposing crystal. A new orthorhombic B phase forms as numerous needle-like crystals, growing independently both on the surface and in the volume of the initial A phase crystal. The liquid phase presumably provides favorable conditions for both conformation transition and active mass transfer and its appearance must be connected with partial decomposition of the BTF molecules, for example, formation of hexanitrobenzene and other products of decomposition.

An analysis of the packing in both the structures has shown that there is no preorientation of the B phase fragments (Figs. 10 and 11).[10]

The intermediate BTF structures observed by us within the initial monoclinic crystal system and associated with the transformations of the furoxan cycle were apparently stable and accounted for the structural state of the BTF crystals during their lifetimes at different temperatures in the initial stages of conversion (before they entered the

TABLE 3
Kinetic Parameters of Phase Transition in the BTF Crystals

T(°C)	$1/T \times 10^3$	K(min^{-1})	ln K(sec^{-1})	K(sec^{-1})
100	2.881	5.11×10^{-4}	−11.67	8.52×10^{-6}
125	2.513	1.83×10^{-3}	−10.40	3.05×10^{-5}
135	2.451	5.17×10^{-3}	−9.36	8.62×10^{-5}

liquid phase). (The atomic coordinates for the A(M + M), A(M + P), A(P + N), and B structures can be obtained from the authors.)

The investigation of the A–B phase transition kinetics was carried out under isothermal conditions at temperatures of 100, 125, and 135°C on an X-ray diffractometer. Predefined regions of X-ray powder patterns were recorded over a long period of time at constant temperature.

The quantitative phase analysis was performed with several reflections of the initial and final phases using an internal standard. Kinetic curves (time–conversion extent) were plotted by several reflections of the decreasing (monoclinic) phase prenormalized to the inner standard. The experimental curves (Fig. 12) were approximated satisfactorily by the equation $dC/dt = -2KC^{0.5}$, where dC/dt is the process rate, C is the extent of conversion, and K is a temperature-dependent constant. K values for different temperatures are given in Table 3. Arrhenius parameters for the K constant are $A = 1.03 \times 10^6$ sec^{-1}; $E_{\text{eff}} = 19.1$ kcal/mol.

Thus it appears that the effective activation energy of the process is close both to the isomerization energy of the furoxan cycle (14) and to the energy of the BTF crystal structure. With such a relationship between the energies the crystal structure becomes sensitive to environmental effects, this leading to initiation of a chemical reaction in the solid. Chemical conversions in the BTF molecule have low activation energies and some portion of the converted molecules cannot be retained within the initial monoclinic crystal system because of the low energy of this structure.

Similar conversions in the BTF molecules have been observed in the UV spectra for solutions with different polarity and in polycrystalline films prepared from the two BTF modifications (15).

Our studies have clearly demonstrated that the phase conversions taking place in TNT and BTF are in fact followed by chemical conversions which apparently influence the physicochemical properties of these compounds both during their life-time and during ageing, as well as their interaction with other compounds.

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