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Polymorphism of 2,4,6-Trinitro-4'-iododiphenylamine

O. V. Mikhalev, I. V. Fedyanin[a], B. N. Tarasevich, I. G. Il'ina, and K. P. Butin[†]

Department of Organic Chemistry
e-mail: mov@org.chem.msu.ru

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Abstract—The experimental conditions for preparation of four differently colored polymorphs of 2,4,6-trinitro-4'-iododiphenylamine, a picryl autocomplex, have been determined. The specific features of intra- and intermolecular interactions in the resulting polymorphs, one of them being noncentrosymmetric, have been studied by IR spectroscopy and X-ray crystallography.

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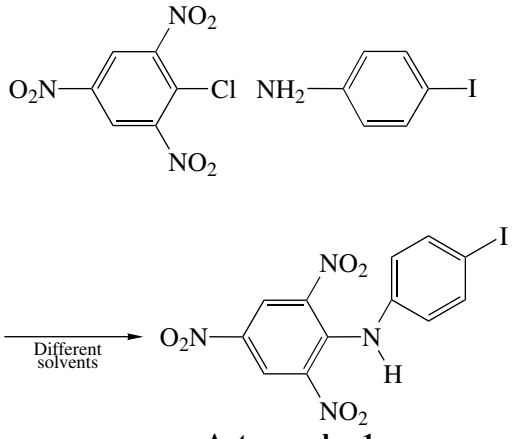
The study of polymorphism is of fundamental significance for an understanding of the general principles of the structure of organic compounds [1, 2]. Polymorphism is inherent in organic compounds with intramolecular charge transfer (ICT), so-called autocomplexes, whose molecules contain both donor and acceptor moieties linked through a bridging group. The bridge can be of different length and contain atoms of different nature, which considerably affects the conformational mobility of the molecule as a whole and ICT in different crystal structures and species. As a rule, heating the less stable form leads to its transformation into the more stable one without signs of melting, and then the latter turns into a liquid [3–4]. For example, nitro derivatives of diphenylamine are known to exist in several differently colored crystalline polymorphs. In particular, three polymorphs with different melting temperatures have been obtained for 2,4,6-trinitro-4'-iododiphenylamine: yellow **1a**, orange **1b**, and pink **1c** [5]. These species have different types of crystal packing: **1b** forms noncentrosymmetric crystals in which the molecules have the same geometry, whereas the crystals of **1a** and **1c** are formed by molecules of two configurations. However, the conditions of mutual transformations of different crystal modifications have been described only briefly, and conditions of their synthesis have not been reported [5]. We are interested in studying the conditions of preparation of compound **1** in different crystal modifications and studying them by physicochemical methods. This problem is addressed in the present work.

EXPERIMENTAL

Autocomplex **1** (Scheme 1) was synthesized by means of nucleophilic substitution of chlorine in picryl chloride under the action of *para*-iodoaniline.



Autocomplex 1

Crystal modifications of **1**:
1a yellow
1b orange
1c pink
1d red

Scheme 1.

Acetone–water (10 : 1), alcohol–water (10 : 1, in the presence of Na_2CO_3), and acetone–acetic acid (10 : 1) mixtures or neat CH_3CN were used as solvents. The reaction mixture was heated to boiling for 10 min and

[†] Deceased.

[a] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

Table 1. Polymorphs of autocomplex **1**, their preparation, notation, and melting points

Precipitate	Solvent for crystallization (temperature, °C)	Precipitate composition after recrystallization	Color after recrystallization	T_m, °C (this work)	T_m, °C [5]
A	Acetone–water 10 : 1	**1a** (major)	Yellow	172–185*	185.5
		1b (minor)		187	181
B	Acetone–alcohol 1 : 1 (50)	**1b**	Yellow-pink	187	181
		1c (1 : 1)		190.5	191
B	Alcohol (70)	**1b** (flat bands)	Orange-yellow	187	181
B	MeCN	**1b** (needles)	Orange-yellow	187	181
B	$CHCl_3$–alcohol 1 : 1 (50)	**1c** (major)	Orange-pink	190.5	191
		1a (minor)			185.5
B	Toluene (100)	**1c** (major)	Orange	190.5	191
		1a (minor)		172–185*	185.5
B	Toluene (0)	**1a** (needles)	Yellow	172–185*	185.5
B	Alcohol (0)	**1a** (flat needles)	Yellow	172–185*	185.5
C	Acetone–alcohol 1 : 1	**1b** (flat needles)	Orange-yellow	187	181
	Crystallization of the melt	**1d** (crystalline mass)	Red	135–145*	–

* Temperature ranges for phase transitions are given.

cooled, and the resulting crystalline precipitate was separated by filtration. In all solvent mixtures selected for the synthesis, the colors of the precipitates were different, and, as a rule, the latter consisted of several polymorphs. From the acetone–water (10 : 1) mixture, the yellow precipitate of **1a** with an admixture of **1b** (mixture **A**) was isolated; from the alcohol–water (10 : 1) mixture with Na_2CO_3, the orange precipitate of **1b** with an admixture of **1a** and **1c** (mixture **B**) was deposited; the acetone–acetic acid (10 : 1) solvent led to the orange precipitate of **1c** with an admixture of **1b** (mixture **C**); and from acetonitrile, the orange-yellow precipitate of **1b** was obtained. The differently colored crystals were separated under a magnifying glass and used in further studies. The mixtures of crystals were recrystallized from different solvents, including mixed solvents, at different temperatures. These results are summarized in Table 1. The recrystallized samples, as well as mechanically separated crystals, were used in further studies.

Table 2. Assignment of stretching vibration frequencies of some groups in the IR spectra of the polymorphs of **1** according to [6]

Bands	Yellow **1a**	Orange **1b**	Pink **1c**	Red **1d**
NH stretches	3264	3276	3306	3327
			3311	
CH stretches (aromatic)	3089	3073	3065	3063
			3093	3086
				3110
Antisymmetric NO_2 stretches	1624	1621	1620	1616
	1591	1589	1592	1590
	1540	1535	1550	1536
	1518	1518	1529	1500
	1509	1483	1510	1436
	1481		1484	
Symmetric NO_2 stretches	1349 s	1360 w	1352	1351
	1337 w	1337 s	1330 w	1328
	1293	1288	1308	1292
			1290	

FT IR spectra were recorded on a ThermoNicolet IR 200 spectrophotometer. Samples were prepared as KBr pellets and Nujol mulls.

RESULTS AND DISCUSSION

As distinct from the literature data [5], our findings indicate that yellow modification **1a** has no well-defined melting temperature (T_m); rather, it irreversibly transforms into the pink modification in the range 172–185°C. Below 172°C, no visible signs of changes in color or structure are observed. Modification **1b** melts

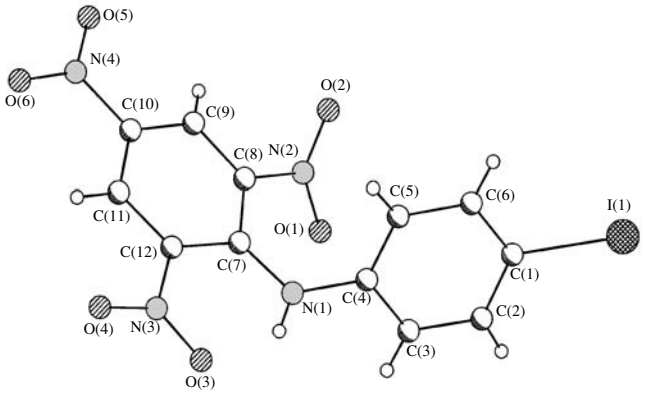


Fig. 1. General view of the molecule of autocomplex **1** with the numbering of atoms according to X-ray crystallography.

at a higher temperature (Table 1) than that reported in [5]. On heating above 170°C up to the melting point, the color of **1b** becomes deeper. Modification **1c** is the only form whose melting temperature (190.5°C) virtually coincides with the reported value. It is worth noting that **1c** has an anomalous thermomechanical behavior. In particular, at 135–145°C, its crystals shatter to form a powder.

We obtained one more crystal modification **1d**; it is bright red in color and, like **1a**, undergoes a phase transition in the solid state, but in another temperature range (135–145°C), to form pink modification **1c**. Modification **1d** is obtained only upon slow crystallization of a supercooled glassy melt in the temperature range 20–100°C. To conclude, we can say, with some reservations, that modifications **1a–1c** are equivalent to, respectively, the yellow, orange, and pink forms described in [5], whereas modification **1d** (red) has not been found previously.

The composition and molecular and crystal structures of these modifications were studied by IR spectroscopy and X-ray crystallography. The IR spectra

Table 3. Selected crystallographic parameters of polymorphs **1a–1c**

Unit cell parameters	Yellow **1a**	Orange **1b**	Pink **1c**
Empirical formula	$C_{12}H_7IN_4O_6$	$C_{12}H_7IN_4O_6$	$C_{12}H_7IN_4O_6$
a, Å	20.684(6)	5.133(1)	14.076(2)
b, Å	5.064(1)	12.102(1)	5.774(1)
c, Å	13.503(4)	22.457(3)	18.321(3)
β, deg	99.771(6)	α = β = γ = 90°	112.475(3)
V, cm^3	1394.0(7)	1395.1(4)	1375.9(4)
Density (d_X, g/cm^3)	2.049	2.048	2.076
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
Number of molecules in the unit cell, *Z*	4	4	4
R	0.0458	0.0433	0.0322
(*D*/*A*) angle	110.9	109.2	115.7
O(3)–N(1)	2.612	2.654	2.614

* The N(1)–H(1) distance is normalized to the ideal X-ray diffraction distance 0.96 Å.

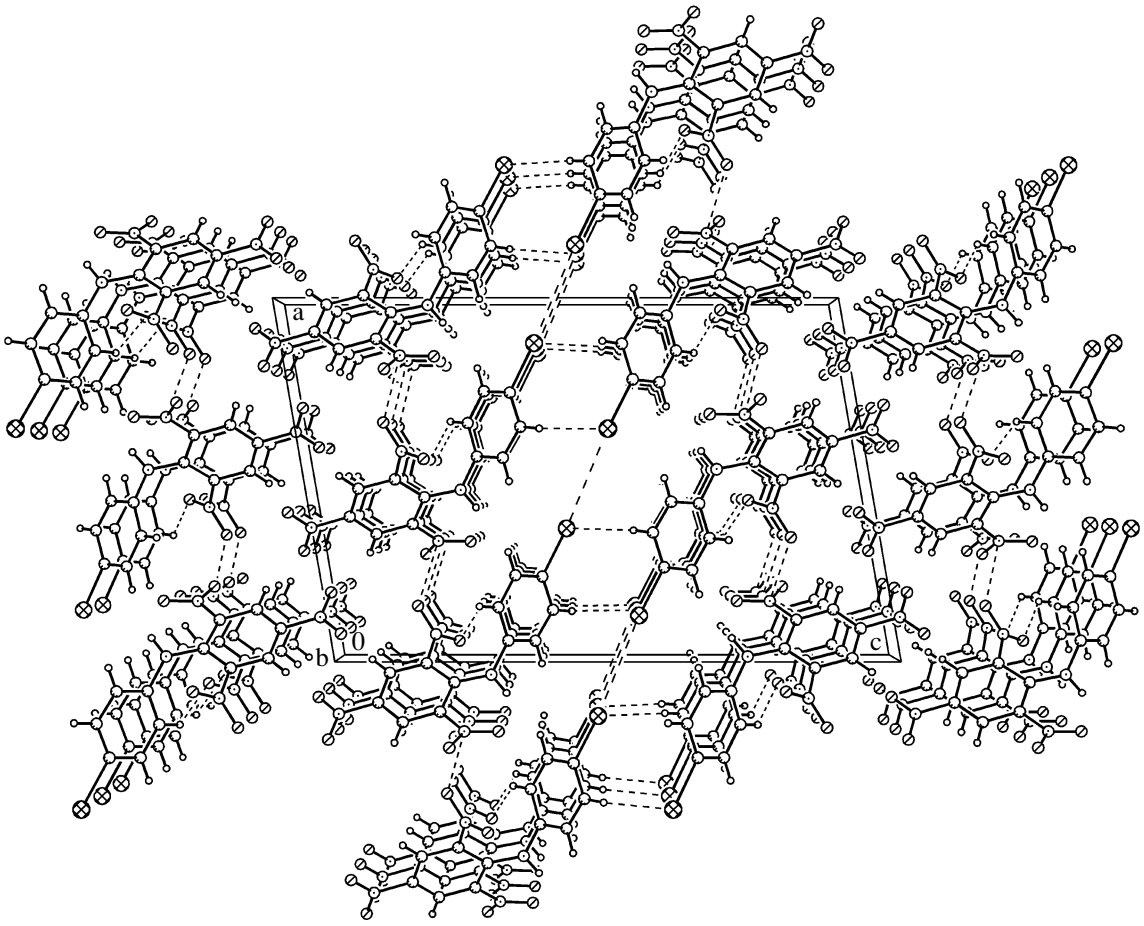


Fig. 2. Yellow form **1a**. General view of the packing motif and the unit cell content (the most important intra- and intermolecular contacts are shown with dashed lines).

recorded in the wide range 400–4000 cm^{-1} show N–H, C–H, and nitro group stretching vibration bands.

For all modifications, the N–H bond stretches are observed in the range 3350–3250 cm^{-1} typical of this type of vibration [6]; however, band positions are different. In the range of aromatic C–H stretching vibrations, these modifications give rise to different numbers of absorption bands (Table 2).

X-ray crystallography for **1a**–**1c** (for **1d**, we failed to obtain suitable crystals) shows that, although they are different polymorphs, their molecular geometries are only slightly different (Fig. 1). In each of these polymorphs, compound **1** has different unit cells and somewhat different conformational parameters (Table 3). As we previously showed for picryl derivatives with other donor moieties [7–9], autocomplexes of this type adopt a conformation with a considerable angle between the donor and acceptor moieties with respect to the bridging nitrogen atom. As distinct from the N(1)–C(4) bond, the N(1)–C(7) bond is shortened, which is evidence of some conjugation between the N(1) atom and the acceptor moiety. All nitro groups deviate from the acceptor ring plane by different angles. One of the *o*-nitro groups is involved in an intramolecular hydrogen bond with the proton of the bridge, whereas the other *o*-nitro group has a shortened contact with the donor ring; i.e., notwithstanding that the plane of this group is not parallel to the plane of the donor moiety, they are spatially close to each other, which renders through-space ICT possible. In addition, the *p*-nitro group is virtually in the plane of the acceptor moiety, which favors charge transfer only along the conjugation chain.

The presence of the iodine atom in **1** prevents the determination of the exact position of the H(1) atom and, hence, the N(1)–H(1) bond length by X-ray diffraction. This causes some problems with unambiguous interpretation of the strength of intramolecular hydro-

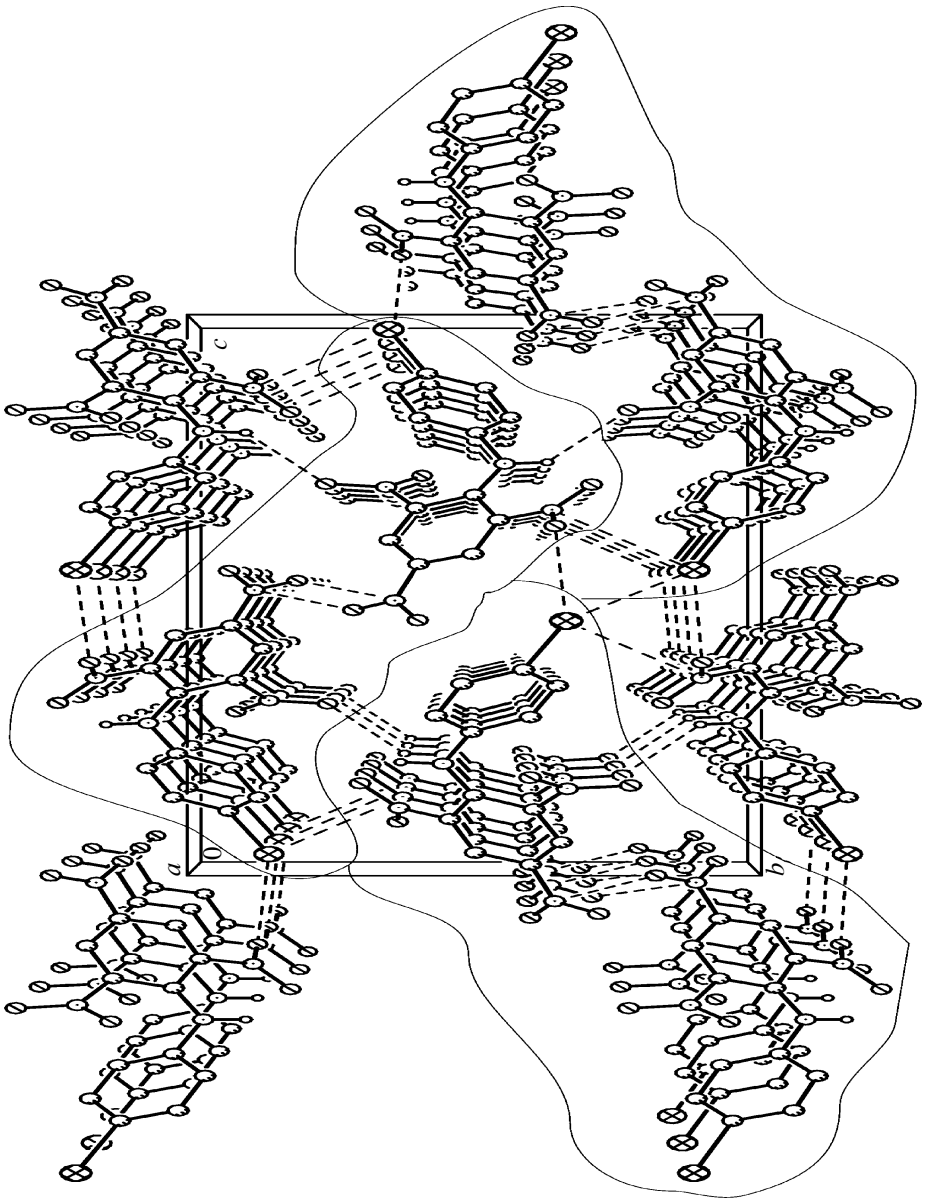


Fig. 3. Orange form **1b**. General view of the packing motif and the unit cell content (the most important intra- and intermolecular contacts are shown with dashed lines).

gen bonds in different modifications of complex **1** if only X-ray diffraction data are used.

At the same time, X-ray crystallography shows that, in addition to the intramolecular hydrogen bond, different intermolecular hydrogen bonds are present in **1a**–**1d**, and some of the latter involve the bridging N(1) atom. It cannot be ruled out that this interaction can be responsible for the composite character of the NH and CH stretching vibration bands in the IR spectra. For example, the IR spectra of **1a** and **1b** show rather strong bands due to the CH stretches at 3089 and 3072 cm^{-1}, respectively. The IR spectrum of **1c** shows two bands (3064 and 3093 cm^{-1}) and that of **1d**, three weaker bands (3063, 3086, and 3110 cm^{-1}). It is worth noting that the first bands in the spectrum of **1d** (3063 cm^{-1}) virtually coincides with the band at 3064 cm^{-1} in the spectrum of **1c**, and the second band at 3086 cm^{-1} is close to the band of the CH stretches of **1a** (3089 cm^{-1}) and not significantly differs from the band at 3093 cm^{-1} for **1c**.

These differences in the IR spectra of **1a**–**1d** can be due to the formation of different mixed dimeric intermolecular structures, which is consistent with the X-ray crystallography data (Figs. 2–4). Results of a more detailed study of this problem and those of a comparative study of the strength of the intramolecular hydrogen bond forming in different modifications of autocomplex **1** will be reported in future papers.

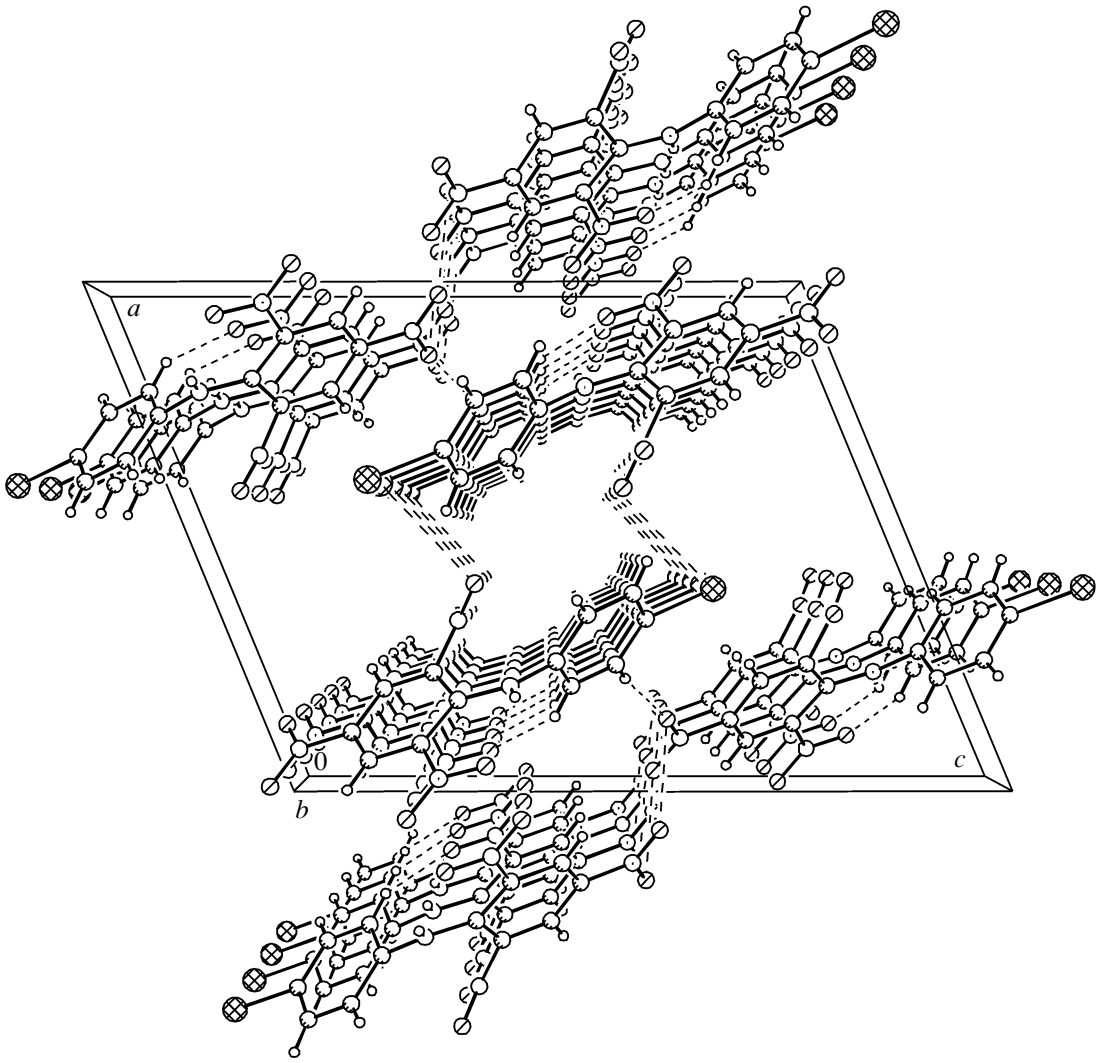


Fig. 4. Pink form **1c**. General view of the packing motif and the unit cell content (the most important intra- and intermolecular contacts are shown with dashed lines).

CONCLUSIONS

Our findings allow us to conclude that autocomplexes are able to form several structures with different crystal packings, in which the molecules not only differ conformationally but also are involved in different intra- and intermolecular interactions whose combination stabilizes a certain modification of a given autocomplex [10, 11].

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