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Studies on Picrates. IX.[1] Crystal Structures of *o*-Xylene and *p*-Xylene Picrates

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The crystal structures of *o*-xylene picrate (1) and *p*-xylene picrate (2) have been elucidated by X-ray analysis. In the structure of 1, *o*-xylene and picric acid are arranged alternately along the *a*-axis, making their molecular planes parallel to each other. Two crystallographically independent *o*-xylene:picric acid complexes exist in an asymmetric unit, which are formed through both π–π interaction and hydrogen bonding between neighboring molecules. The *p*-xylene molecule forms a picrate with one of three crystallographically independent picric acid moieties through π–π interaction, but not with the two other picric acid molecules.

Key words *o*-xylene picrate; *p*-xylene picrate; crystal structure; X-ray analysis

Picric acid forms crystalline picrates with various organic molecules, and such derivatives have been very useful for the identification and qualitative analysis of the corresponding organic compounds. Since it is useful to understand the nature of the picrates of basic compounds, we have systematically investigated the crystal structures of picrates of several aromatic amino compounds,[1] aromatic hydrocarbons,[2—4] and aromatic heterocyclic compounds.[5—7] From our studies and literature reports on the crystal structure of picrates,[8—10] it has become clear that the picrates of basic aromatic hydrocarbons are formed through π–π interaction and those of aromatic heterocyclic compounds through ionic and hydrogen bonding or π–π interaction.

In this study, we have carried out X-ray crystallographic analyses of *o*-xylene picrate (**1**) and *p*-xylene picrate (**2**) (Fig. 1) to elucidate their crystal structures in connection with the effect of methyl groups and the bonding mode of the picrates.

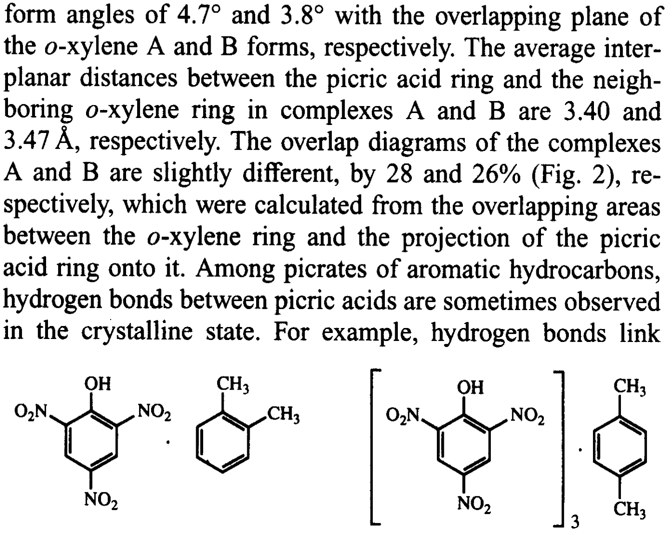
Experimental

Crystal Structure Determination[11] Crystals of **1** and **2** used for X-ray analysis were obtained, respectively, from *o*- and *p*-xylene solutions saturated with picric acid. The melting point of **1** was 83—86 °C (lit.[12] 88.5 °C) and that of **2** was 89—92 °C (lit.[12] 90.5 °C). Crystal data of *o*-xylene picrate (**1**): $C_8H_{10}\cdot C_6H_3N_3O_7$, M.W.=670.54, monoclinic, space group $P2_1$, $a=7.390(1)$ Å, $b=27.709(5)$ Å, $c=7.527(1)$ Å, $\beta=92.72(1)°$, $V=1539.6(7)$ Å^3, $Z=2$, $D_{\text{calc.}}=1.446\,\text{g cm}^{-3}$, μ (CuK_α)=9.71 cm^{-1}. The $R(R_w)$ value of **1** was 0.055 (0.054). Crystal data of *p*-xylene picrate (**2**): $C_8H_{10}\cdot(C_6H_3N_3O_7)_3$, M.W.=793.48, monoclinic, space group $P2_1/a$, $a=10.01(1)$ Å, $b=18.357(5)$ Å, $c=17.383(3)$ Å, $\beta=93.71(3)°$, $V=3188(5)$ Å^3, $Z=4$, $D_{\text{calc.}}=1.653\,\text{g cm}^{-3}$, μ (MoK_α)=1.37 cm^{-1}. The $R(R_w)$ value of **2** was 0.056 (0.046). Crystal and intensity data of both picrates were collected on a Rigaku automated four-circle diffractometer (AFC-5R), using CuK_α radiation ($\lambda=1.54178$ Å) for **1** and MoK_α ($\lambda=0.71069$ Å) for **2**, X-rays were monochromated by a graphite plate. The collected intensities of *p*- and *o*-xylene picrates were corrected for Lorentz, polarization and absorption. Both structures were solved by the direct method (MITHRIL)[13] and refined by the full matrix least squares method. For **1**, 1874 reflections out of 2365 unique reflections with $|F_o|>4\sigma(|F_o|)$ were used and for **2**, 2179 reflections out of 2505 unique reflections with $|F_o|>3\sigma(|F_o|)$ were used. The positions of all hydrogen atoms of **1** were calculated, but those of **2** were obtained from a difference Fourier synthesis. The temperature factor of non-hydrogen atoms was refined anisotropically and that of the hydrogen atoms isotropically. The final R and R_w values obtained were reduced to 0.064 and 0.065 for **1**, and 0.056 and 0.040 for **2**, respectively. Two crystallographically independent *o*-xylene : picric acid complexes are represented by the suffix letters A and B. Three picric acid molecules in an asymmetric unit in **2** are represented by the suffix letters D, E and F. At this stage, no peaks larger than 0.44 and 0.25 eÅ^{-3} for *o*-xylene and *p*-xylene were found in the last difference electron density maps. Scattering factors were taken from the "International Tables for X-Ray Crystallography."[14] All calculations were performed using the TEXSAN[15] crystallographic software package of the Molecular Structure Corporation.

Discussion

Perspective drawings with the atomic-numbering systems of **1** and **2** are shown in Figs. 2 and 3. Dihedral angles of **1** and **2** and the angles between the overlapping planes are listed in Table 1. The average deviation of all the atomic positions from their respective ring planes is only 0.006 Å (0.001—0.010 Å).

In complexes A and B of **1**, the picric acid molecules are differently located, as shown in Table 1. A large conformational difference is found in the dihedral angles of the phenyl ring and the nitro groups (*e.g.*, O6A–N3A–O7A : 23.1°, O4B–N2B–O5B : 16.9°). The picric acid and *o*-xylene components lie approximately in the (100) plane parallel to each other, stacked alternately. As shown in Fig. 4, complexes A and B each form one-dimensional columns along the *a*-axis. The plane of the picric acid ring in the A and B complexes form angles of 4.7° and 3.8° with the overlapping plane of the *o*-xylene A and B forms, respectively. The average interplanar distances between the picric acid ring and the neighboring *o*-xylene ring in complexes A and B are 3.40 and 3.47 Å, respectively. The overlap diagrams of the complexes A and B are slightly different, by 28 and 26% (Fig. 2), respectively, which were calculated from the overlapping areas between the *o*-xylene ring and the projection of the picric acid ring onto it. Among picrates of aromatic hydrocarbons, hydrogen bonds between picric acids are sometimes observed in the crystalline state. For example, hydrogen bonds link



Complex I (**1**)   Complex II (**2**)

Fig. 1. Chemical Structures of Complex **1** and **2**

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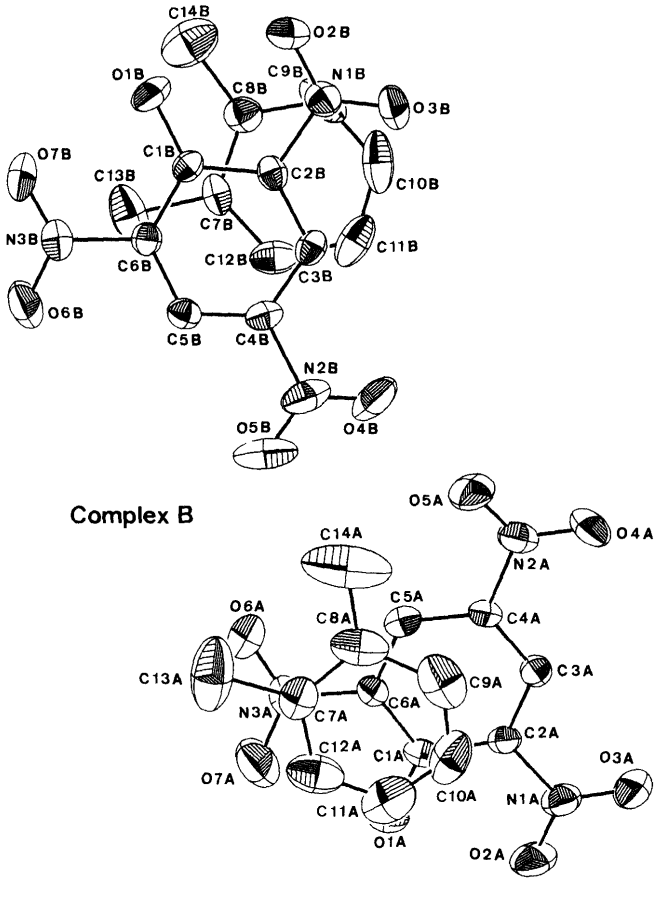


Complex B

Complex A

Fig. 2. Overlap of Picric Acid and *o*-Xylene Molecules in Sections Parallel to the Picric Acid Ring with Atomic-numbering System

Hydrogen atoms are excluded for clarity.

pairs of picric acid molecules in naphthalene picrate,[4,10] but not in phenanthrene,[3] benzene[4] and anthracene picrates.[9] In **1**, there are hydrogen bonds between picric acids, but not in **2** (Fig. 4).

The structure of **1** results from both van der Waals contacts between neighboring molecules and intermolecular hydrogen bonding between picric acids.

Interestingly, **2** has three picric acids and one *p*-xylene molecule in an asymmetric unit. To our knowledge, amongest picrates of basic aromatic hydrocarbons, **2** is the first case in which the molecular composition is not 1 : 1.

As shown in Fig. 3 and Table 1, *p*-xylene and picric acid D are almost parallel to each other with a dihedral angle of 3.8°. They slightly overlap each other (4%). The average interplanar distance between the phenyl rings of picric acid D and the *p*-xylene is 3.56 Å, and they are reasonably thought to form a π-complex. From the angles between the phenyl rings of *p*-xylene and picric acids E and F (14.0° and 66.6°), we judge that there is no contact among them.

In naphthalene picrate,[4,10] structural disorder is observed, but not in anthracene, phenanthrene and benzene picrates.[3,4,8] In the case of **1** and **2**, disorder is not observed. It is not possible to deduce an important role for the methyl groups in the crystal packing of picrates **1** and **2**. However, crystals of toluene picrate and *m*-xylene picrate could not be prepared under the same conditions as those of the benzene analog. Therefore, the methyl groups of **1** and **2** may affect their packing structure. As shown in Fig. 2, the two methyl groups of *o*-xylene complex A in complex **1** are outside the van der Waals radii of the neighboring molecules, but in complex B, there exists van der Waals contacts between one of the methyl groups (C13B) and atoms (C6B and O6B) in the picric acid molecule. On the other hand, in complex **2**, two methyl groups are in contact with the nitro groups, *i.e.*, one methyl group (C13) of *p*-xylene is in contact with O6D, O7D

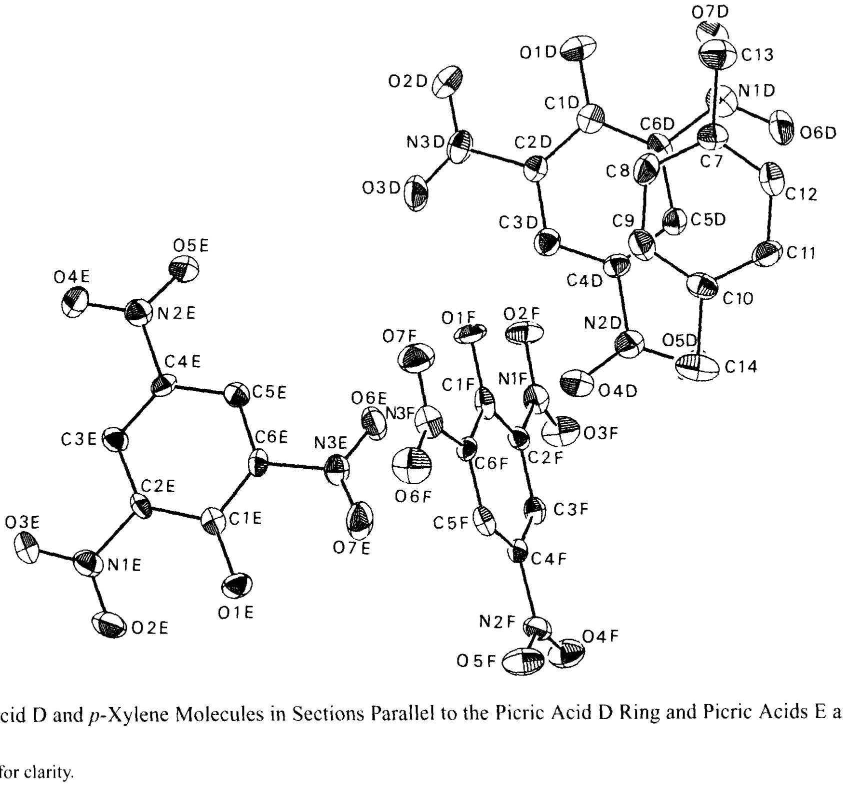


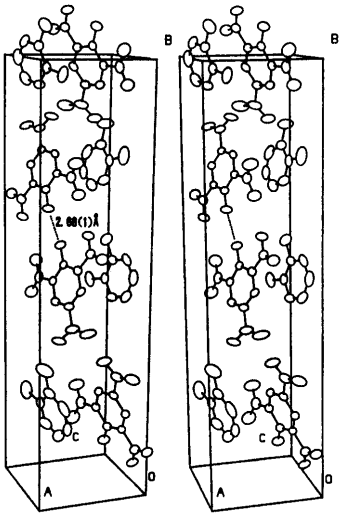
Fig. 3. Overlap of Picric Acid D and *p*-Xylene Molecules in Sections Parallel to the Picric Acid D Ring and Picric Acids E and F with Atomic-numbering System

Hydrogen atoms are excluded for clarity.

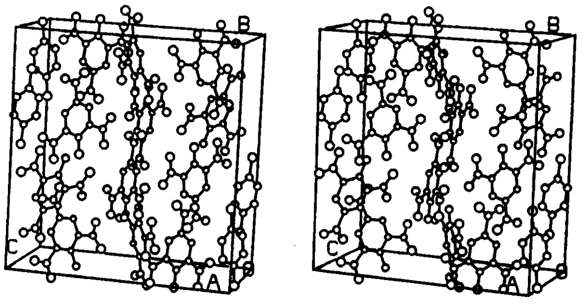
Table 1. Selected Dihedral Angles (°) of *o*-Xylene and *p*-Xylene Picrate and the Angles between Overlapping Planes

Compd.	Plane 1	Plane 2	(°)
o-Xylene picrate	Picric acid ring A	O2A–N1A–O3A	3.7
		O4A–N2A–O5A	8.4
		O6A–N3A–O7A	23.1
	Picric acid ring B	O2B–N1B–O3B	3.4
		O4B–N2B–O5B	16.9
		O6B–N3B–O7B	4.2
	Picric acid ring A	*o*-Xylene ring A	4.7
	Picric acid ring B	*o*-Xylene ring B	3.8
p-Xylene picrate	Picric acid ring D	O2D–N1D–O3D	3.6
		O4D–N2D–O5D	7.3
		O6D–N3D–O7D	1.2
	Picric acid ring E	O2E–N1E–O3E	3.3
		O4E–N2E–O5E	9.8
		O6E–N3E–O7E	18.1
	Picric acid ring F	O2F–N1F–O3F	4.7
		O4F–N2F–O5F	3.3
		O6F–N3F–O7F	4.6
	p-Xylene ring	Picric acid ring D	3.8
		Picric acid ring E	14.0
		Picric acid ring F	66.6

and N1D as is the other methyl group (C14) with O5D and O6D by van der Waals forces. The two picric acids with the suffix E and F stabilize each other by van der Waals forces. Thus, one of the oxygen atoms of the nitro group (O7E) is positioned above the center of the benzene ring of the picric acid with the suffix F within the van der Waals radii. O6E is in contact with O1F, O2F and O7F. Furthermore, O4E is in contact with C10, C11, C12 and C14 . O5F and O2F contact a part of the E and F picric acids.



o-Xylene Picrate



p-Xylene Picrate

Fig. 4. Stereoscopic Drawings of the Molecular Packing of *o*-Xylene Picrate and *p*-Xylene Picrate

Hydrogen bonding is shown with a dotted line.

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