Studies on Picrate. VIII.[1] Crystal and Molecular Structures of Aromatic Amine Picrates: Aniline, *N*-Methylaniline, *N*,*N*-Dimethylaniline and *o*-, *m*- and *p*-Phenylenediamine Picrates

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The crystal and molecular structures of the title compounds have been elucidated by X-ray structure analysis. All compounds are formed through ionic and hydrogen bondings in the crystal state. The picrates of *N*-methylaniline and *m*-phenylenediamine have additional π-bondings. The picrates are 1 : 1 complexes except for *o*-phenylenediamine picrate, in which the picrate consists of one *o*-phenylenediamine and two picric acid molecules.

Key words picrate; aromatic amine; crystal structure; X-ray analysis

Picric acid forms crystalline picrates with various organic molecules, and such picrates are convenient for identification and qualitative analysis of the organic compounds. We have investigated the crystal structures of several aromatic hydrocarbon picrates[2-4] and aromatic heterocyclic compounds,[5-7] and it has become clear that the picrates of basic aromatic hydrocarbons are formed through π-bonding, while picrates of aromatic heterocyclic compounds including nitrogen atoms in their skeleton are formed through ionic and hydrogen bonding. Furthermore, in the case of isoquinoline picrate, π-bonding also contributes to the stabilization of the picrate structure. As there is still no report concerning the crystal structure of the picrates of basic aromatic amines, we have carried out X-ray crystallographic analysis of picrates of aniline picrate (**1**), *N*-methylaniline picrate (**2**), *N*,*N*-dimethylaniline picrate (**3**), *o*-phenylenediamine picrate (**4**), *m*-phenylenediamine picrate (**5**) and *p*-phenylenediamine picrate (**6**) to elucidate the crystal structures and the bonding modes of these picrates.

Experimental

Crystals used for X-ray analysis of **1** were obtained from an equimolar mixture of picric acid and aniline in ether. Crystals of **2** and **3** were obtained from an equimolar mixture of picric acid and the corresponding amines in methanol. Crystals of **4**—**6** were also obtained from equimolar mixtures of picric acid and the corresponding amines in methanol. In the case of *o*-phenylenediamine (**4**), the complex was found to be formed with one *o*-phenylenediamine and two picric acid molecules under the above mentioned experimental conditions. Intensity data for **1** and **5** were collected on AFC-4 and those for **2**, **3**, **4** on AFC-5R Rigaku automated four-circle diffractometer using graphite-monochromated CuK_α radiation ($\lambda = 1.54178$ Å). The data for **6** were collected on AFC-5R using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) at 23 °C. The $\omega - 2\theta$ scan mode with a scan rate of 16°/min was employed in the ω scan range of $(1.20 + 0.30 \tan\theta)°$ with 2θ in the range of $6° < 2\theta < 116.3°$, $6° < 2\theta < 120.0°$, $6° < 2\theta < 135.3°$, $6° < 2\theta < 120.3°$, $6° < 2\theta < 120.0°$ and $6° < 2\theta < 60.0°$ for **1**, **2**, **3**, **4**, **5** and **6**, respectively.

The intensities were corrected for Lorentz and polarization effects, but not for absorption and extinction. The structures were solved by the direct method (MULTAN),[8] and were refined by the full-matrix least-squares method. The positions of all hydrogen atoms of complexes **1**, **2**, **3**, **4**, **5** and **6** were located from a difference Fourier synthesis. At the final stage of refinement, non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Unique reflections

Table 1. Crystallographic Details

Picrate	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{12}H_{10}N_3O_7$	$C_{13}H_{12}N_4O_7$	$C_{14}H_{14}N_4O_7$	$C_{18}H_{14}N_8O_{14}$	$C_{12}H_{11}N_5O_7$	$C_{12}H_{11}N_5O_7$
Formula weight	322.24	336.27	350.29	566.35	337.25	337.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/a$	$Pbca$
Size (mm)	0.3×0.2×0.2	0.5×0.2×0.2	0.4×0.5×0.1	0.2×0.2×0.4	0.2×0.3×0.4	0.5×0.3×0.6
Lattice parameters						
a (Å)	11.588 (2)	12.684 (2)	10.932 (4)	21.663 (6)	14.854 (3)	17.200 (5)
b (Å)	16.112 (2)	9.979 (1)	8.497 (3)	8.080 (2)	6.987 (3)	21.972 (3)
c (Å)	7.652 (1)	11.818 (4)	17.970 (3)	14.487 (4)	13.296 (9)	7.190 (5)
β (°)	93.23 (1)	102.53 (2)	103.42 (2)	118.45 (2)	91.13 (3)	
Z value	4	4	4	4	4	4
V (Å^3)	1427	1463	1624	2229	2760	2717
F (000)	636	696	728	1160	656	656
λ (Å)	1.54179	1.54179	1.54179	1.54179	1.54179	0.71069 (Mo)
μ (cm^{-1})	10.337	10.46	9.61	12.48	11.302	0.65
D_x (g/cm^3)	1.501	1.529	1.433	1.687	1.624	1.648
No. observations	1842	2036	2927	1561	2373	2071
Crystal color	Yellow	Dark yellow	Yellow	Orange	Dark yellow	Green
mp (°C)	185	142	161	214 (dec.)	184	205
Diffractometer	AFC-4	AFC-5R	AFC-5R	AFC-5R	AFC-4	AFC-5R
R (R_w)	0.090 (0.090)	0.086 (0.089)	0.073 (0.059)	0.045 (0.060)	0.052 (0.052)	0.050 (0.054)

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Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (B_{eq}/Å^2) of Compounds **1**, **2**, **3**, **4**, **5**, and **6** with Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}	Atom	x	y	z	B_{eq}
Aniline picrate (**1**)									
O1	3096 (4)	6699 (3)	2524 (6)	2.3	C2	5128 (6)	6568 (4)	3195 (8)	2.2
O2	4518 (5)	7836 (3)	4287 (8)	4.1	C3	6135 (6)	6125 (4)	3324 (8)	2.5
O3	6127 (5)	7816 (4)	3067 (11)	6.2	C4	6033 (6)	5274 (4)	3049 (9)	2.6
O4	8028 (5)	5104 (4)	3390 (9)	5.2	C5	4986 (6)	4901 (4)	2615 (9)	2.6
O5	6934 (5)	4007 (3)	3257 (8)	4.5	C6	4028 (6)	5397 (4)	2413 (8)	2.2
O6	2555 (6)	4464 (5)	2819 (10)	6.8	C7	863 (5)	7730 (4)	4805 (8)	2.3
O7	2403 (6)	5243 (4)	540 (8)	5.6	C8	577 (6)	6901 (5)	4980 (10)	3.2
N1	5271 (5)	7481 (3)	3536 (8)	3.0	C9	−509 (7)	6705 (6)	5528 (12)	4.6
N2	7082 (6)	4773 (4)	3249 (8)	3.7	C10	−1276 (3)	7314 (7)	5874 (11)	4.0
N3	2916 (5)	5012 (3)	1884 (8)	2.9	C11	−993 (7)	8135 (7)	5864 (11)	5.1
N4	2020 (5)	7948 (3)	4333 (7)	2.5	C12	94 (7)	8362 (5)	5133 (11)	3.8
C1	4009 (5)	6277 (4)	2708 (8)	2.0					
N-Methylaniline picrate (**2**)									
O1	1981 (4)	4434 (7)	3940 (4)	5.1	C2	2406 (5)	3730 (7)	5932 (5)	2.6
O2	3976 (4)	4198 (7)	5248 (5)	4.9	C3	2094 (5)	3623 (7)	6879 (5)	2.5
O3	4060 (4)	4268 (7)	7086 (5)	5.1	C4	1021 (5)	2991 (7)	6775 (5)	2.6
O4	1350 (5)	2264 (8)	8687 (4)	5.6	C5	282 (5)	3041 (7)	5742 (6)	2.6
O5	−288 (4)	2081 (6)	7696 (5)	4.5	C6	620 (5)	3512 (7)	4800 (5)	2.6
O6	−1148 (5)	3401 (8)	3796 (5)	6.3	C7	3021 (5)	5505 (7)	1764 (5)	2.6
O7	31 (5)	3990 (10)	2858 (5)	7.9	C8	1908 (6)	5747 (10)	1412 (7)	4.0
N1	3564 (4)	4087 (7)	6084 (5)	3.4	C9	1467 (6)	5708 (10)	228 (8)	4.9
N2	675 (5)	2396 (7)	7787 (5)	3.7	C10	2099 (7)	5388 (9)	−556 (7)	4.4
N3	−208 (5)	3614 (7)	3720 (5)	3.5	C11	3194 (7)	5133 (9)	−181 (6)	3.9
N4	3492 (4)	5584 (7)	3012 (4)	3.0	C12	3640 (5)	5203 (8)	986 (6)	3.1
C1	1716 (5)	3936 (8)	4796 (5)	2.8	C13	3485 (8)	6970 (10)	3497 (7)	4.6
N,*N*-Dimethylaniline picrate (**3**)									
O1	11863 (5)	3334 (7)	4108 (3)	3.1	C2	9716 (7)	363 (1)	4090 (4)	2.0
O2	10025 (8)	420 (1)	2906 (4)	4.0	C3	8743 (7)	346 (1)	4427 (5)	2.3
O3	8842 (6)	5653 (9)	3329 (4)	4.7	C4	8902 (7)	260 (1)	5090 (5)	2.1
O4	6827 (5)	2908 (8)	5119 (3)	5.1	C5	10038 (7)	188 (1)	5429 (4)	2.1
O5	8055 (6)	1712 (9)	6077 (4)	3.7	C6	11025 (7)	290 (1)	5065 (5)	2.1
O6	12281 (6)	699 (9)	6084 (4)	5.8	C7	14428 (6)	339 (1)	3374 (5)	2.3
O7	13036 (6)	1214 (9)	5106 (4)	4.1	C8	15134 (7)	330 (1)	2848 (5)	2.7
N1	9522 (8)	453 (1)	3384 (5)	2.9	C9	15829 (8)	459 (1)	2735 (5)	3.2
N2	7853 (7)	2382 (9)	5466 (4)	3.1	C10	15818 (8)	593 (1)	3157 (6)	3.7
N3	12197 (7)	124 (1)	5460 (5)	3.1	C11	15126 (8)	599 (1)	3693 (6)	3.8
N4	13685 (5)	2003 (7)	3513 (3)	2.4	C12	14407 (7)	470 (1)	3828 (5)	3.2
C1	10975 (7)	301 (1)	4397 (5)	2.3	C13	12741 (7)	149 (1)	2816 (4)	3.9
					C14	14511 (7)	69 (1)	3860 (5)	4.9
o-Phenylenediamine picrate (**4**)									
O1	9406 (8)	−463 (2)	−1987 (1)	2.5	N4	134 (1)	1381 (3)	1430 (2)	2.2
O2	6353 (9)	−1104 (2)	−4035 (1)	3.3	C1	1551 (1)	−826 (3)	−1806 (2)	2.1
O3	1142 (1)	−3396 (2)	−3974 (2)	4.4	C2	1694 (1)	−1675 (3)	−2557 (2)	2.2
O4	3622 (1)	−2726 (3)	−2034 (2)	4.0	C3	2345 (1)	−2141 (3)	−2395 (2)	2.4
O5	4414 (1)	−2085 (3)	−406 (2)	4.1	C4	2919 (1)	−1773 (3)	−1473 (2)	2.4
O6	2685 (1)	554 (5)	815 (2)	9.2	C5	2844 (1)	−971 (3)	−663 (2)	2.6
O7	1607 (1)	676 (5)	−25 (2)	8.4	C6	2187 (1)	−519 (3)	−837 (2)	2.3
N1	1116 (1)	−2088 (3)	−3586 (2)	2.5	C7	68 (1)	2938 (3)	−1983 (2)	2.1
N2	3613 (1)	−2220 (3)	−1279 (2)	2.8	C8	148 (1)	4415 (3)	−1457 (2)	2.7
N3	2155 (1)	323 (3)	25 (2)	3.4	C9	78 (1)	5892 (3)	−1981 (2)	3.1
m-Phenylenediamine picrate (**5**)									
O1	4741 (1)	1402 (3)	8906 (1)	2.3	C1	4381 (2)	1201 (4)	8049 (2)	1.6
O2	2114 (1)	−427 (4)	8439 (2)	3.3	C2	3455 (2)	702 (4)	7831 (2)	1.6
O3	3012 (2)	971 (5)	9481 (2)	4.6	C3	3103 (2)	470 (4)	6873 (2)	1.8
O4	3709 (2)	1264 (4)	4348 (1)	3.9	C4	3638 (2)	827 (4)	6061 (2)	1.9
O5	2504 (2)	−28 (4)	4947 (2)	4.3	C5	4536 (2)	1324 (4)	6185 (2)	1.8
O6	6305 (1)	1116 (4)	7896 (2)	3.4	C6	4889 (2)	1427 (4)	7138 (2)	1.7
O7	6167 (1)	2919 (4)	6575 (2)	3.9	C7	4306 (2)	6094 (4)	6998 (2)	2.1
N1	2830 (1)	396 (4)	8639 (2)	2.2	C8	5041 (2)	6730 (4)	7591 (2)	1.9
N2	3260 (2)	686 (4)	5052 (2)	2.7	C9	4943 (2)	6195 (4)	8614 (2)	1.8
N3	5853 (1)	1852 (4)	7219 (2)	2.4	C10	4161 (2)	6446 (4)	9101 (2)	2.3
N4	4388 (2)	5970 (4)	5967 (2)	3.2	C11	3443 (2)	5763 (5)	8506 (2)	2.6
N5	5701 (1)	7754 (4)	9192 (2)	2.1	C12	3508 (2)	5603 (4)	7473 (2)	2.4
p-Phenylenediamine picrate (**6**)									
O1	274 (1)	1359 (1)	7429 (3)	2.9	C1	338 (1)	1928 (1)	7334 (4)	2.0
O2	−1126 (1)	1672 (1)	8845 (3)	3.4	C2	−250 (1)	2380 (1)	7718 (3)	1.9
O3	−1486 (1)	2604 (1)	8760 (4)	5.7	C3	−126 (2)	2996 (1)	7464 (4)	2.0
O4	136 (1)	4191 (1)	6769 (3)	3.4	C4	584 (2)	3205 (1)	6861 (4)	2.0
O5	1359 (1)	4033 (1)	5284 (3)	3.3	C5	1205 (2)	2803 (1)	6547 (4)	2.0
O6	1804 (2)	1537 (1)	5043 (3)	6.2	C6	1065 (1)	2203 (1)	6785 (3)	1.9
O7	2099 (2)	1640 (1)	7844 (3)	6.5	C7	8280 (1)	393 (1)	2022 (3)	2.0
N1	−1007 (1)	2205 (1)	8460 (3)	2.6	C8	8195 (2)	909 (1)	3129 (4)	2.3
N2	704 (1)	3849 (1)	6620 (3)	2.3	C9	8497 (2)	919 (1)	4911 (4)	2.2
N3	1708 (1)	1768 (1)	6526 (3)	2.4	C10	8895 (1)	420 (1)	5594 (3)	1.8
N4	7997 (1)	386 (1)	178 (3)	2.5	C11	8986 (2)	−96 (1)	4507 (4)	2.0
N5	9217 (1)	442 (1)	7481 (3)	2.0	C12	8677 (2)	−107 (1)	2725 (4)	2.1

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\alpha_i \cdot \alpha_j$.

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with $|F_o|>3\sigma(|F_o|)$ were used for refinement. The final R (R_w) values obtained were shown in Table 1, where $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}$ in the weighting scheme $w=4F_o^2/\sigma^2(F_o^2)$. Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974).[9] Crystal data and details of the refinement are summarized in Table 1.

The final atomic parameters of **1**, **2**, **3**, **4**, **5** and **6** are listed in Table 2. Calculations for compounds **1** and **5** were carried out on a HITAC M-680H computer at the Computer Center of University of Tokyo using the Universal Crystallographic Computer Program System UNICS III.[10] Calculations for compounds **2**, **3**, **4** and **6** were performed using the TEXSAN[11] crystallographic software package of Molecular Structure Corporation.

No peak larger than 0.40 eÅ^{-3} was found in the final difference electron density map for any of the compounds.

Results and Discussion

Perspective drawings of the molecules with the atomic-numbering system for aniline picrate (**1**), *N*-methylaniline picrate (**2**), and *N*,*N*-dimethylaniline picrate (**3**) are shown in Fig. 1. Those of *o*-phenylenediamine picrate (**4**), *m*-phenylenediamine picrate (**5**) and *p*-phenylenediamine picrate (**6**) are shown in Fig. 2.

As shown in Figs. 1 and 2, the proton of the phenolic hydroxyl group of picric acid migrated to the nitrogen atom of the aromatic amine in all compounds. Thus the structures consist of aniline picrate, *N*-methylaniline picrate, *N*,*N*-dimethylaniline picrate, and *o*-, *m*- and

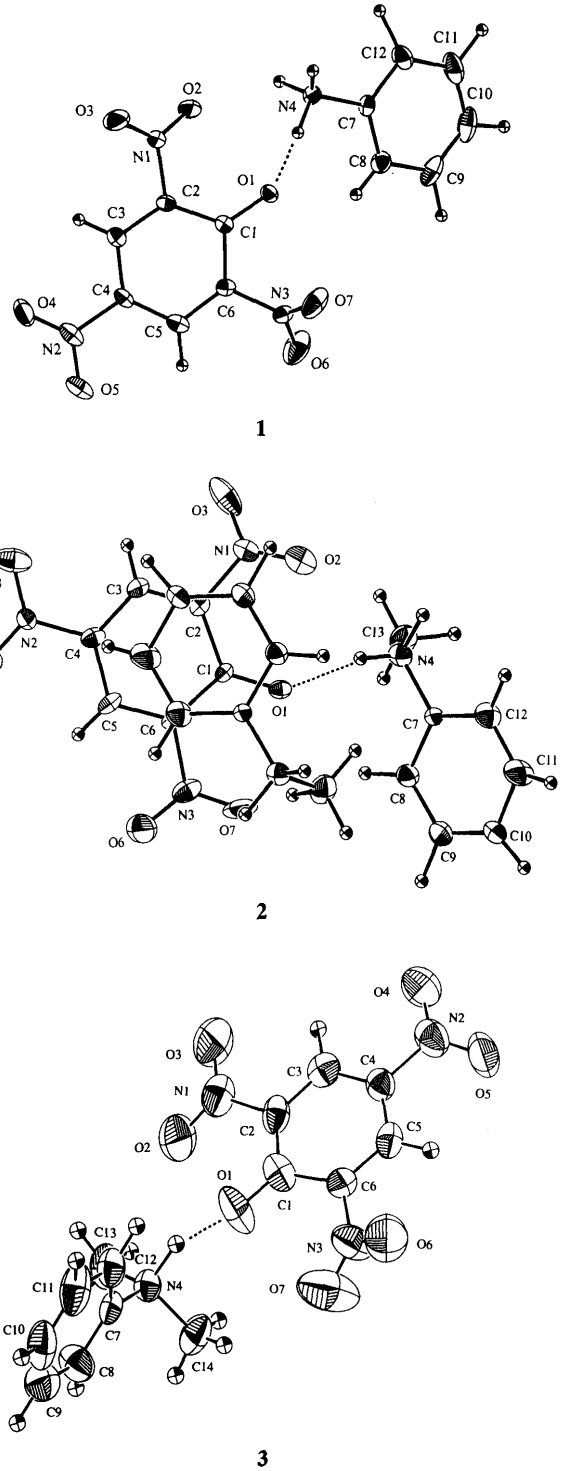

Fig. 1. Perspective Drawings of Compounds **1**, **2** and **3** with the Atomic Numbering System

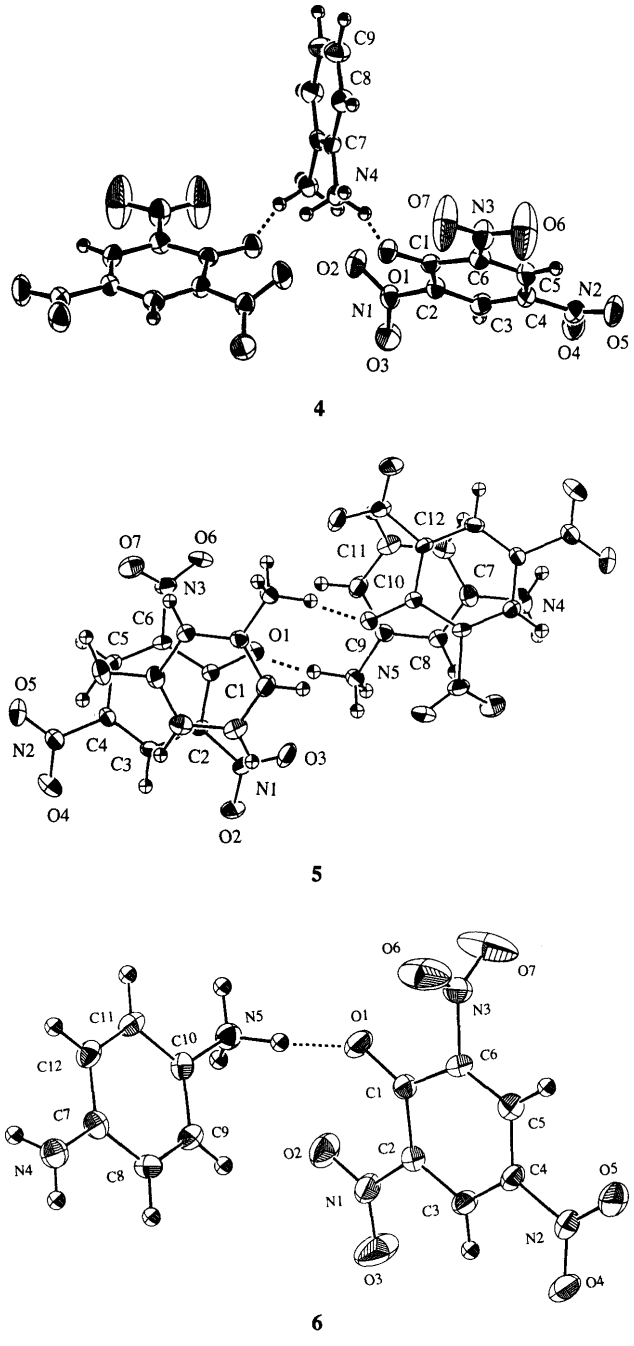

Fig. 2. Perspective Drawings of Compounds **4**, **5** and **6** with the Atomic Numbering System

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p-phenylenediamine picrate ion pair, with the locus of positive charge residing on the primary, secondary and third amino groups of the corresponding compounds.

Conversion of phenol by loss of the hydroxyl proton to phenoxide anion is expected to lead to shortening of the C1–O1 bond of picric acid. The bond length of C1–O1 in compounds **1**, **2**, **3**, **4**, **5**, **6** and isoquinoline picrate[7] ranges from 1.229 to 1.259 Å, being characteristic of a double bond. The bond length of the phenolic hydroxyl group C1–O1 in benzene picrate,[3] phenanthrene picrate[2] and 1,4-naphthoquinone picrate[4] is in the range of 1.299 to 1.340 Å, which is obviously longer than the former range (Table 3). The average C1–O1 bond length (1.250 Å) of the picrate anions is shorter than that of the picric acids and phenols (1.335 Å).[12,13]

Table 3. Bond Lengths of C1–O1 in Picrates of **1**, **2**, **3**, **4**, **5** and **6** with Estimated Standard Deviations in Parentheses

Picrate	C1–O1
Aniline picrate (**1**)	1.259 (8)
N-Methylaniline picrate (**2**)	1.235 (9)
N,*N*-Dimethylaniline picrate (**3**)	1.229 (8)
o-Phenylenediamine picrate (**4**)	1.255 (3)
m-Phenylenediamine picrate (**5**)	1.256 (3)
p-Phenylenediamine picrate (**6**)	1.257 (3)
Isoquinoline picrate	1.250 (4)
Benzene picrate	1.299 (7)
Benzene picrate	1.338 (6)
Phenanthrene picrate	1.340 (6)
1,4-Naphthoquinone picrate	1.332 (5)

Table 4. Bond Lengths (Å) and Angles (°) of O1···H–N in Picrates of **1**, **2**, **3**, **4**, **5** and **6** with Estimated Standard Deviations in Parentheses

Picrate	O1–H	O1–N	O1···H–N
Aniline picrate (**1**)	1.77 (7)	2.73 (3)	175 (9)
N-Methylaniline picrate (**2**)	1.76 (4)	2.67 (1)	158 (3)
N,*N*-Dimethylaniline picrate (**3**)	1.67 (3)	2.72 (1)	154 (3)
o-Phenylenediamine picrate (**4**)	1.90 (3)	2.86 (1)	157 (2)
	1.97 (3)	2.88 (1)	158 (2)
m-Phenylenediamine picrate (**5**)	1.68 (3)	2.69 (1)	158 (3)
p-Phenylenediamine picrate (**6**)	1.68 (4)	2.71 (1)	171 (2)

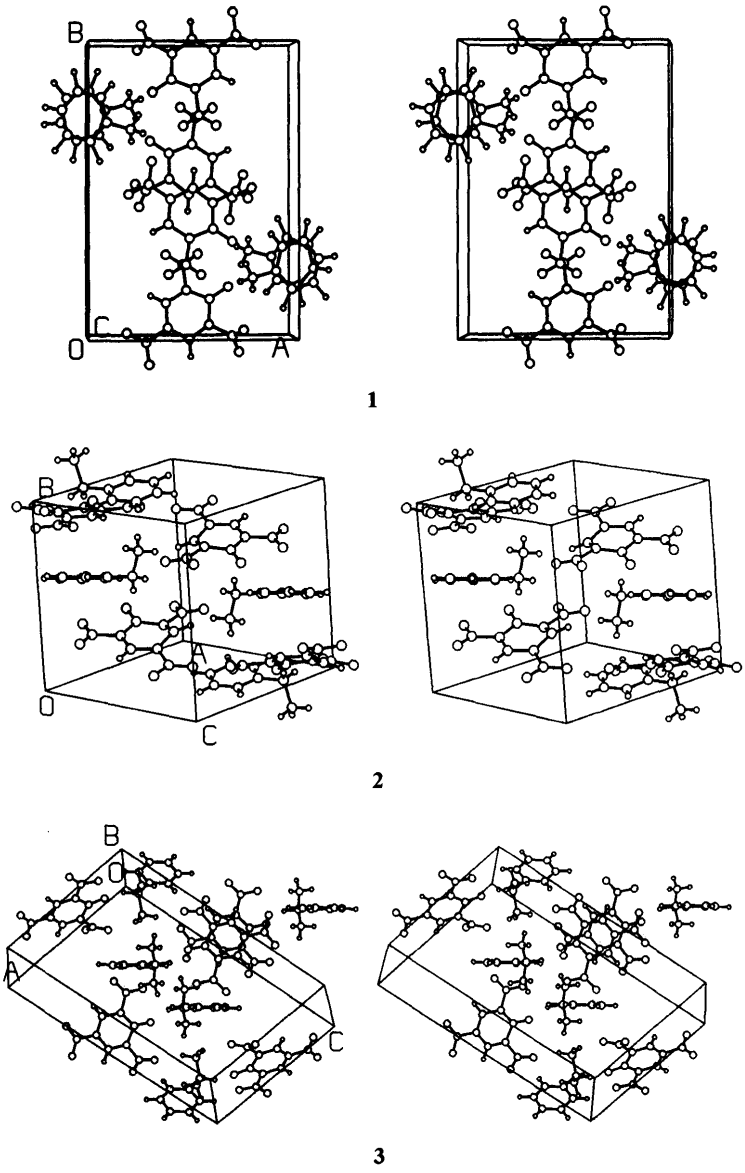

Fig. 3. Stereoscopic Drawings of the Molecular Packing of Compounds **1**, **2** and **3**

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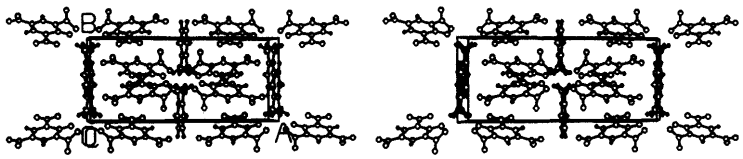
In all these compounds (**1**—**6**), the O1···H and O1–N (in O1···H–N) distances are in the range of 1.68 to 1.92 and 2.66 to 2.80 Å, respectively, which values clearly indicate the presence of ionic hydrogen bonding between picric acid and the corresponding amines. The bond angles of O1···H–N have reasonable values (Table 4).

As shown in Fig. 2, *o*-phenylenediamine picrate (**4**) is composed of two picric acid and one *o*-phenylenediamine with two NH_3^+ groups. In the cases of **5** and **6**, one amino group is in the form of NH_2 and the other is NH_3^+, because these picrates are 1 : 1 complexes with one picric acid and one aromatic amine.

As for *o*-phenylenediamine picrate, two molecules of picric acid form a complex with one molecule of *o*-phenylenediamine. The *m*- and *p*-phenylenediamine picrates are, however, formed from one molecule of the corresponding amines and one molecule of picric acid. We tried to obtain a 1 : 1 complex of *o*-phenylenediamine and picric acid. A molar excess of *o*-phenylenediamine was added to a solution of picric acid in methanol. After evaporation of the solution at room temperature, only the 2 : 1 complex (**4**) was precipitated. When an excess of picric acid was added to a methanol solution of *m*- or *p*-phenylenediamine, only the 1 : 1 complex precipitated.

We have already reported the presence of π-bonding in the crystal of isoquinoline picrates[7] but not in the case of quinoline picrate.[6] In the crystal of **1**, aniline and picric acid molecules form separate columns along the *c*-axis (Fig. 3), and there is no possibility of the presence of π-bonding. As shown in Fig. 4, the crystal structure of **2** is built up from *N*-methylaniline and picric acid molecules alternating in plane-to-plane stacks. The plane of the picric acid ring is at an average distance of 3.40 Å and an angle of 10.1° with the overlapping the plane of the *N*-methylaniline ring. The overlap **2** is 18%, calculated from the overlapping area of the *N*-methylaniline ring and the projection of the picric acid ring on it. These results suggested that the *N*-methylaniline–picrate stacking interaction appears to be of the donor-acceptor (charge–transfer) kind. It is commonly observed that the donor and acceptor molecules are not parallel in cases where one molecule is not completely covered by the second. Furthermore, the *N*-methylaniline molecule stacking with picric acid can form an ionic hydrogen bond with another picric acid molecule. In the crystal of **3**, the *N*,*N*-dimethylaniline and picric acids molecules each form a one-dimensional column along the *b*-axis as shown in Fig. 3, and neighboring *N*,*N*-dimethylaniline and picric acid molecules form side-by-side ionic hydrogen bonds. Thus, complexes **1** and **3** have only ionic hydrogen bonding in the crystals, but **2** also has π-bonding, as is observed in isoquinoline picrate.[7]

Methyl groups can serve as electron-donors favoring formation of the charge transfer complex of the corresponding amine with picric acid. However, the stereochemistry of the methyl groups in **2** and **3** may hinder charge–transfer complex formation. Methyl groups at the nitrogen atoms in compounds **2** and **3** are almost vertically



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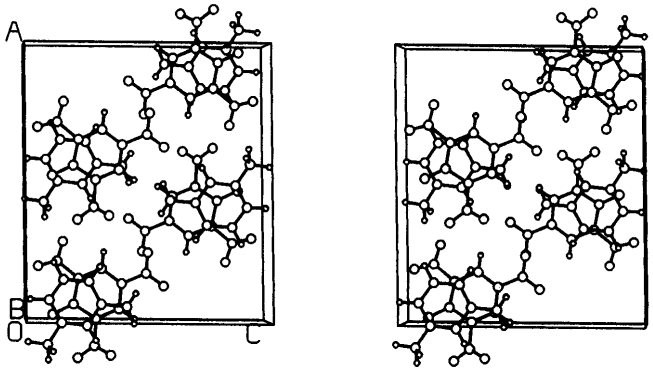

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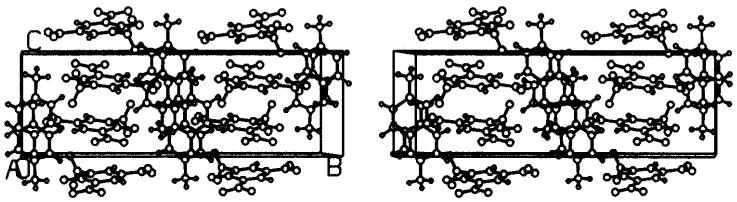

6

Fig. 4. Stereoscopic Drawings of the Molecular Packing of Compounds **4**, **5** and **6**

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Table 5. Dihedral Angles (°) of Nitro Groups to the Plane of the Benzene Ring

Picrate	NO_2 (C2)	NO_2 (C4)	NO_2 (C6)
Aniline picrate (**1**)	12.4	26.5	72.9
N-Methylaniline picrate (**2**)	14.2	6.8	11.0
N,*N*-Dimethylaniline picrate (**3**)	42.3	5.1	19.3
o-Phenylenediamine picrate (**4**)	51.7	9.5	14.5
m-Phenylenediamine picrate (**5**)	17.2	11.3	35.6
p-Phenylenediamine picrate (**6**)	7.6	6.8	89.5
Benzene picrate	6.2	7.9	24.6
Benzene picrate	11.7	8.2	39.0
Phenanthrene picrate	11.5	0.5	2.6
Isoquinoline picrate	34.7	10.8	2.9

oriented from the plane of the benzene ring (Fig. 3). This may be the reason why aniline and *N*,*N*-dimethylaniline picrate do not have π-bonding, whereas *N*-methylaniline picrate does.

As for the crystal structure of *o*-phenylenediamine picrate, the plane of *o*-phenylenediamine is parallel to the *b*–*c* plane, and no stacking is seen in the crystal (Fig. 4). The crystal structure of *m*-phenylenediamine picrate viewed along the *c*-axis is shown in Fig. 4. The *m*-phenylenediamine and picric acid molecules form alternately stacked molecular columns along the *b*-axis and are connected by ionic hydrogen bonds with the nearest-neighbor columns. The angle and mean distance between the rings of picric acid and *m*-phenylenediamine are 8.3° and 3.9 Å, respectively. These facts support the presence of π-bonding in this complex. On the other hand, *p*-phenylenediamine picrate does not have π-bonding in the crystal. The benzene ring of *p*-phenylenediamine is almost normal (93.2°) to that of picric acid. In *p*-phenylenediamine picrate, no stacking was seen in the crystals as shown in Fig. 4.

As found for picrate ions in many other crystal structures, the nitro groups are twisted out of the benzene plane. As shown in Table 5, *para*-nitro groups at C4 are relatively less twisted than *ortho*-nitro groups. The *ortho*-nitro groups at C2 and C6 are twisted from 6.2 to 89.5°. As can be seen in Table 5, the degree of twist in the π-complexes (complexes **2**, **5** and benzene) is less than that of non-π-complexes (complexes **1**, **3**, **4** and **6**).

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