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The Crystal and Molecular Structures of *N*-Phenyl-4-nitrobenzylamine, *N*-Phenyl-4-nitrophenethylamine, and *N*-Methyl-*N*-*p*-tolyl-4-nitrophenethylamine

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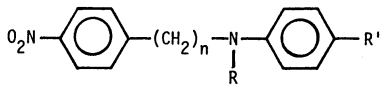
The crystal and molecular structures of *N*-phenyl-4-nitrobenzylamine (**1**), *N*-phenyl-4-nitrophenethylamine (**2**), and *N*-methyl-*N*-*p*-tolyl-4-nitrophenethylamine (**3**) have been determined by the X-ray method. The crystals of **1** are monoclinic, $P2_1/n$, a=16.924(1), b=8.792(1), c=7.642(1) Å, β=91.59(1)°, V=1136.8(1) Å^3, Z=4, D_x=1.334 Mg m^{-3}. **2** is triclinic, $P\bar{1}$, a=15.106(1), b=9.573(1), c=9.427(1) Å, α=113.22(1), β=91.27(1), γ=83.61(1)°, V=1244.7(2) Å^3, Z=4, D_x=1.293 Mg m^{-3}. **3** is trigonal, $P3_1$, a=b=8.435(1), c=17.758(1) Å, α=β=90°, γ=120°, V=1094.2 Å^3, Z=3, D_x=1.231 Mg m^{-3}. The final R values are 0.064, 0.059, and 0.045 for 1625, 3606, and 1131 observed reflections of **1**, **2**, and **3**, respectively. About the amino-methylene N-C bond the phenyl group is trans to C for the molecules of **1** and **2**, while in **3** the phenyl group is gauche to C about the N-C bond. The nitrophenyl plane of **3** is stacked on the *p*-toluidino plane of the neighbouring molecule alternately with the mean distance of 3.40 Å. The presence of the intermolecular CT interaction of **3** has been confirmed by the electronic absorption spectra of these compounds in the solid state.

Intramolecular interactions, especially a charge-transfer interaction, are extensively studied for *N*-[ω-(4-nitrophenyl)alkyl]anilines in which electron donor (anilino) and acceptor (4-nitrophenyl) moieties are bound together by a polymethylene chain.[1] The study with UV-VIS spectroscopy revealed that the solutions of the lower homologs show the presence of an intramolecular charge-transfer interaction, which is also detectable by the pale yellow color of the dilute solutions (ca. 10^{-4} mol dm^{-3}). Since the color persists in solid, even in the higher homologs, we suspected the presence of another type of intramolecular donor-acceptor interaction in the solid state. The crystal structure analysis of *N*-phenyl-4-nitrobenzylamine (**1**), *N*-phenyl-4-nitrophenethylamine (**2**), and *N*-methyl-*N*-*p*-tolyl-4-nitrophenethylamine (**3**) was carried out by the X-ray method in order to determine their molecular conformations and intra- and/or intermo-

Table 1. Crystal Data and Experimental Conditions

	1	**2**	**3**
	$C_{13}H_{12}N_2O_2$	$C_{14}H_{14}N_2O_2$	$C_{16}H_{18}N_2O_2$
Color	Pale-brown	Pale-brown	Orange-red
Mw	228.25	242.28	270.33
Crystal system	Monoclinic	Triclinic	Trigonal
Space group	$P2_1/n$	$P\bar{1}$	$P3_1$
a/Å	16.924(1)	15.106(1)	8.435(1)
b/Å	8.792(1)	9.573(1)	8.435(1)
c/Å	7.642(1)	9.427(1)	17.758(2)
α/°	90.0	113.22(1)	90.0
β/°	91.59(1)	91.27(1)	90.0
γ/°	90.0	83.61(1)	120.0
V/Å^3	1136.8(1)	1244.7(2)	1094.2(1)
Z	4	4	3
D_x/Mg m^{-3}	1.334	1.293	1.231
Radiation	Cu $K\alpha_1$	Cu $K\alpha_1$	Cu $K\alpha_1$
μ/mm^{-1} (Cu $K\alpha$)	0.711	0.677	0.624
Crystal size/mm	0.40×0.35×0.05	0.40×0.40×0.30	0.30×0.35×0.20
Scan range/°	$2<2\theta<130$	$2<2\theta<130$	$2<2\theta<130$
Scan width/°	$1.2+0.5\tan\theta$	$1.2+0.5\tan\theta$	$1.2+0.5\tan\theta$
Max. h, k, l	±19, 10, 9	±17, 11, ±11	9, ±9, 20
No. of Reflections			
measured	2187	4775	2423
unique	1923	4472	1699
observed	1625	3606	1131
refinement	1620	3595	1130
R (refinement)	0.060	0.051	0.041
R_w (refinement)	0.074	0.051	0.043
R (observed)	0.064	0.059	0.045
S	1.003	0.612	0.721

lecular interactions. The compounds **1** and **2** were chosen because they are the first two members of the homologous series of the most basic group studied so far. The compound **3** was chosen on account of its remarkable orange-red color in the crystals, while the other derivatives studied are all pale brown or yellow in the solid state.



(**1**) n=1 R=H R′=H
(**2**) n=2 R=H R′=H
(**3**) n=2 R=CH_3 R′=CH_3

Experimental

X-Ray Crystal Structure Determination. Crystal data and some experimental conditions are listed in Table 1. Intensities were collected on a Rigaku automatic diffractometer with graphite-monochromated Cu $K\alpha_1$ (λ=1.54051 Å) radiation, using the ω-2θ scan technique with a scanning rate of 4° min^{-1} in 2θ. At both ends of the scan range 10s background counts were taken for each reflection. Three reflections were monitored after every 50 reflections. Variations of intensities of the monitored reflections were within 1, 1.5, and 2% for **1**, **2**, and **3**, respectively. Reflections with $|F_o| \geqslant 3\sigma(F_o)$ were used for structure determination.

The structures were solved by the direct method with the program MULTAN 78.[2] All non-hydrogen atoms were refined by the block-diagonal least-squares with anisotropic temperature factors. Difference maps showed all the hydrogen atoms. During the final stage of the refinement 5, 11, and 1 strong reflections which were seriously affected by extinction were omitted from the reflection data of **1**, **2**, and **3**, respectively. Least-squares refinements with anisotropic temperature factors for the non-hydrogen atoms and iso-

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors for Non-H Atoms

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
(a) **1**									
O(1)	6260(2)	363(3)	3806(4)	7.7	C(6)	2653(2)	2945(3)	−4748(3)	4.0
O(2)	5611(2)	1424(3)	5830(3)	7.2	C(7)	3807(2)	4264(3)	−864(4)	4.3
N(1)	3595(1)	3342(3)	−2366(3)	4.1	C(9)	4307(2)	3416(3)	470(3)	3.6
N(2)	5733(1)	1189(3)	4300(3)	4.8	C(10)	4883(2)	2389(3)	−17(4)	4.0
C(1)	3080(1)	3943(3)	−3655(3)	3.4	C(11)	5352(2)	1648(3)	1226(4)	4.0
C(2)	2998(2)	5489(3)	−3936(3)	4.0	C(12)	5234(1)	1963(3)	2961(3)	3.7
C(3)	2508(2)	6029(4)	−5278(4)	4.6	C(13)	4670(2)	2965(4)	3499(4)	4.4
C(4)	2084(2)	5041(4)	−6345(4)	4.8	C(14)	4208(2)	3698(4)	2236(4)	4.3
C(5)	2158(2)	3502(4)	−6060(4)	4.5					
(b) **2**									
O(1A)	10831(1)	6407(3)	7832(3)	10.0	O(1B)	5773(1)	3739(2)	7225(3)	7.5
O(2A)	10645(1)	8865(3)	8598(3)	9.8	O(2B)	5951(1)	1289(2)	6376(2)	7.0
N(1A)	5310(1)	7104(2)	6287(2)	4.8	N(1B)	423(1)	2932(3)	8689(2)	6.0
N(2A)	10382(1)	7622(3)	8004(3)	6.9	N(2B)	5508(1)	2519(2)	7028(2)	5.1
C(1A)	4572(1)	7332(2)	7234(2)	3.9	C(1B)	−313(2)	2686(3)	7746(3)	4.5
C(2A)	4593(2)	8006(3)	8830(3)	4.5	C(2B)	−244(2)	2029(3)	6148(3)	5.2
C(3A)	3823(2)	8312(3)	9720(3)	4.9	C(3B)	−1000(2)	1739(3)	5276(3)	5.6
C(4A)	3017(2)	7935(3)	9041(3)	4.9	C(4B)	−1839(2)	2100(3)	5956(3)	5.4
C(5A)	2993(2)	7233(3)	7459(3)	4.7	C(5B)	−1911(2)	2772(3)	7534(3)	5.2
C(6A)	3755(2)	6934(3)	6557(3)	4.4	C(6B)	−1167(2)	3064(3)	8423(3)	5.0
C(7A)	6208(2)	7253(3)	6886(3)	4.7	C(7B)	1325(2)	2663(3)	8058(3)	5.6
C(8A)	6847(2)	7235(3)	5670(3)	5.1	C(8B)	1995(2)	2649(3)	9268(3)	5.6
C(9A)	7782(1)	7340(3)	6244(3)	4.1	C(9B)	2928(2)	2596(3)	8705(3)	4.5
C(10A)	8335(2)	6043(3)	6097(3)	5.2	C(10B)	3287(2)	3938(3)	8937(3)	5.2
C(11A)	9182(2)	6123(3)	6675(3)	5.5	C(11B)	4125(2)	3922(3)	8397(3)	4.9
C(12A)	9471(1)	7535(3)	7399(3)	4.7	C(12B)	4608(1)	2537(3)	7608(2)	4.0
C(13A)	8950(2)	8850(3)	7561(3)	5.3	C(13B)	4282(2)	1176(3)	7344(3)	4.6
C(14A)	8100(2)	8744(3)	6971(3)	4.9	C(14B)	3440(2)	1221(3)	7899(3)	4.9
(c) **3**									
O(1)	14888(4)	4718(4)	589(2)	8.9	C(7)	5406(5)	427(5)	1079(2)	5.8
O(2)	14224(4)	2714(4)	−280(1)	8.0	C(8)	6413(5)	−559(4)	1320(2)	5.4
N(1)	3433(4)	−599(5)	1190(2)	6.6	C(9)	8368(4)	417(4)	1058(2)	4.8
N(2)	13811(4)	3317(4)	262(2)	6.2	C(10)	9666(5)	2040(5)	1403(2)	5.5
C(1)	2337(4)	−2029(5)	712(2)	5.5	C(11)	11442(4)	2990(5)	1143(2)	5.6
C(2)	3006(5)	−2355(5)	44(2)	6.0	C(12)	11910(4)	2311(4)	536(2)	4.8
C(3)	1870(5)	−3728(5)	−447(2)	6.1	C(13)	10681(4)	718(5)	179(2)	5.5
C(4)	25(5)	−4874(5)	−307(2)	6.0	C(14)	8914(4)	−209(5)	445(2)	5.4
C(5)	−626(5)	−4555(5)	357(2)	6.4	C(15)	−1182(6)	−6377(6)	−831(3)	8.2
C(6)	467(5)	−3207(5)	853(2)	5.9	C(16)	2766(6)	−487(6)	1924(2)	6.9

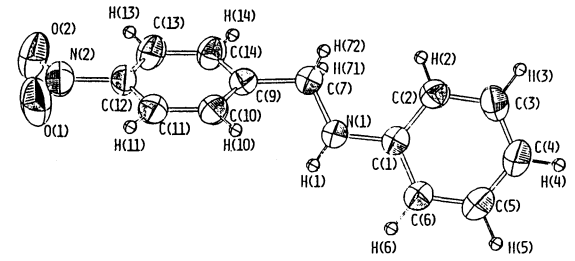
$B_{eq}=4/3\sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.
The e.s.d.'s in parentheses refer to the last digits.

tropic ones for H gave the final R values of 0.060, 0.051, and 0.041 for 1620, 3595, and 1130 reflections of **1**, **2**, and **3**, respectively. The quantity minimized was $\sum w(|F_o|-k^{-1}|F_c|)^2$. For **1**, $w=1/(0.41515-0.0188|F_o|+0.0016|F_o|^2)$, for **2**, $w=1$ for all reflections, and for **3**, $w=1/(0.1936+0.0157|F_o|+0.0014|F_o|^2)$. The R values for 1625, 3606, and 1131 observed reflections of **1**, **2**, and **3** were 0.064, 0.059, and 0.045, respectively. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[3] All computations were performed on a HITAC M180 Computer of the Data Processing Center of the University of Electro-Communications with the programs UNICS III,[4] MULTAN 78,[2] and ORTEP II.[5] The final atomic parameters are given in Table 2.[6]

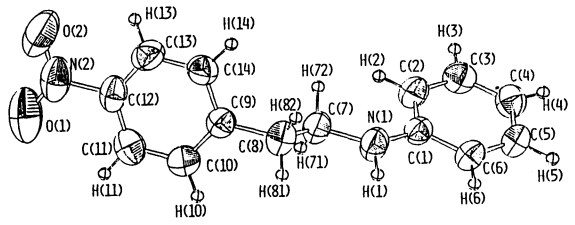
Electronic Spectra. A small amount of crystals of **1**—**3** was melted on a quartz plate (22×13×1 mm³), covered with another quartz plate of nearly the same size, and left to crystallize. No attempt was made to control the thickness of the solid. The absorption spectrum of the plate was recorded on a Hitachi UV-3200 spectrophotometer.

Discussion

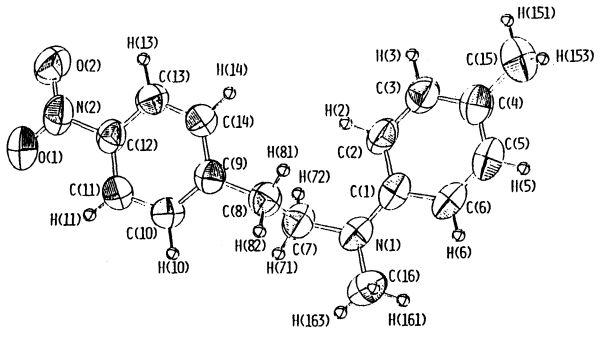
Molecular Structures. The molecular structures with the atomic numbering are shown in Fig. 1. Bond distances and angles are listed in Table 3. Some torsion angles are listed in Table 4. For **2**, there are two crystallographically independent molecules, **A** and **B**, in an asymmetric unit. These two molecules, however, have the same structures within the experimental errors. For **1** the phenyl group is trans to the 4-nitrophenyl group about the N(1)-C(7) bond. The



(a)



(b)



(c)

Fig. 1. Atomic numbering of the molecules. (a) **1**, (b) **2A**, and (c) **3**. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 3. Bond Lengths (l) and Angles (θ)

Distance	**1** l/Å	**2A** l/Å	**2B** l/Å	**3** l/Å
O(1)-N(2)	1.218(4)	1.233(5)	1.221(3)	1.218(5)
O(2)-N(2)	1.211(4)	1.207(4)	1.218(3)	1.219(5)
N(1)-C(1)	1.400(4)	1.387(3)	1.390(4)	1.384(6)
N(1)-C(7)	1.443(4)	1.458(4)	1.455(4)	1.455(6)
N(1)-C(16)				1.441(6)
N(2)-C(12)	1.474(4)	1.477(4)	1.471(3)	1.472(5)
C(1)-C(2)	1.383(4)	1.385(4)	1.386(4)	1.399(6)
C(1)-C(6)	1.399(4)	1.399(3)	1.397(4)	1.404(6)
C(2)-C(3)	1.386(4)	1.385(4)	1.381(4)	1.382(6)
C(3)-C(4)	1.378(5)	1.379(4)	1.378(4)	1.383(6)
C(4)-C(5)	1.376(5)	1.375(4)	1.370(4)	1.382(6)
C(4)-C(15)				1.490(7)
C(5)-C(6)	1.378(4)	1.381(4)	1.373(4)	1.368(6)
C(7)-C(8)		1.509(4)	1.511(4)	1.518(6)
C(8)-C(9)	1.505(4)[a]	1.500(4)	1.506(4)	1.503(5)
C(9)-C(10)	1.386(4)	1.378(4)	1.386(4)	1.396(5)
C(9)-C(14)	1.387(4)	1.382(4)	1.385(4)	1.384(5)
C(10)-C(11)	1.385(4)	1.377(4)	1.371(4)	1.378(6)
C(11)-C(12)	1.375(4)	1.368(4)	1.370(4)	1.369(5)
C(12)-C(13)	1.370(4)	1.364(4)	1.373(4)	1.375(6)
C(13)-C(14)	1.384(5)	1.386(4)	1.376(4)	1.375(6)

Angle	**1** θ/°	**2A** θ/°	**2B** θ/°	**3** θ/°
C(1)-N(1)-C(7)	119.0(2)	122.0(2)	121.7(2)	120.1(4)
C(1)-N(1)-C(16)				119.9(4)
C(7)-N(1)-C(16)				116.9(4)
O(1)-N(2)-O(2)	123.1(3)	124.5(3)	123.2(3)	123.4(4)
O(1)-N(2)-C(12)	118.0(3)	117.3(3)	118.3(2)	118.1(4)
O(2)-N(2)-C(12)	118.8(3)	118.2(3)	118.5(2)	118.4(4)
N(1)-C(1)-C(2)	122.5(2)	123.1(2)	123.0(2)	122.2(4)
N(1)-C(1)-C(6)	119.0(2)	118.9(2)	119.2(2)	122.1(4)
C(2)-C(1)-C(6)	118.4(3)	117.9(2)	117.8(2)	115.7(4)
C(1)-C(2)-C(3)	120.4(3)	120.8(2)	120.3(3)	121.4(4)
C(2)-C(3)-C(4)	120.9(3)	120.9(3)	121.5(3)	122.6(4)
C(3)-C(4)-C(5)	118.8(3)	118.7(3)	118.4(3)	115.8(4)
C(3)-C(4)-C(15)				122.3(4)
C(5)-C(4)-C(15)				121.9(4)
C(4)-C(5)-C(6)	121.0(3)	121.0(2)	121.1(3)	122.9(4)
C(1)-C(6)-C(5)	120.3(3)	120.6(2)	121.0(3)	121.7(4)
N(1)-C(7)-C(8)	112.6(2)[b]	110.3(2)	110.4(3)	115.0(3)
C(7)-C(8)-C(9)		111.3(2)	110.8(2)	111.9(3)
C(8)-C(9)-C(10)	121.8(2)[c]	120.8(2)	120.4(2)	120.6(3)
C(8)-C(9)-C(14)	119.3(2)[d]	120.8(2)	121.6(2)	121.2(3)
C(10)-C(9)-C(14)	118.9(3)	118.4(2)	118.0(2)	118.1(3)
C(9)-C(10)-C(11)	121.1(3)	121.6(3)	121.6(3)	121.0(4)
C(10)-C(11)-C(12)	118.1(3)	118.3(3)	118.4(3)	118.5(4)
N(2)-C(12)-C(11)	118.7(2)	118.4(3)	118.4(2)	118.6(3)
N(2)-C(12)-C(13)	118.6(3)	119.4(3)	119.3(2)	118.9(3)
C(11)-C(12)-C(13)	122.7(3)	122.2(3)	122.3(2)	122.5(4)
C(12)-C(13)-C(14)	118.3(3)	118.5(3)	118.3(2)	118.1(4)
C(9)-C(14)-C(13)	120.9(3)	121.0(3)	121.4(3)	121.8(4)

For **1**, a) C(7)-C(9) b) N(1)-C(7)-C(9) c) C(7)-C(9)-C(10) d) C(7)-C(9)-C(14).

Table 4. Some Torsion Angles (τ) and Dihedral Angles (ω)

Torsion angle	**1** τ/°	**2A** τ/°	**2B** τ/°	**3** τ/°
C(7)-N(1)-C(1)-C(2)	−25.2(3)	13.4(3)	6.6(3)	−10.8(5)
C(7)-N(1)-C(1)-C(6)	157.3(2)	−169.8(2)	−175.6(2)	171.5(3)
C(8)-C(7)-N(1)-C(1)	175.2(2)[a]	−169.5(2)	−166.4(2)	−74.9(4)
C(8)-C(7)-N(1)-C(16)	36.8(20)[b]	38.2(17)[c]	34.8(22)[c]	85.3(4)
C(9)-C(8)-C(7)-N(1)		−178.3(2)	−171.9(2)	169.2(3)
C(7)-C(8)-C(9)-C(10)	37.3(3)[d]	87.5(3)	88.4(3)	73.7(4)
C(7)-C(8)-C(9)-C(14)	−144.2(2)[e]	−90.7(2)	−89.3(3)	−103.0(3)

a) C(9)-C(7)-N(1)-C(1) b) C(9)-C(7)-N(1)-H(1)
c) C(8)-C(7)-N(1)-H(1) d) N(1)-C(7)-C(9)-C(10)
e) N(1)-C(7)-C(9)-C(14)

Plane (1) C(1)—C(6) Plane (2) C(9)—C(14)
Plane (3) N(1)-C(7)-C(8) (for **1**, N(1)-C(7)-C(9))

Dihedral angle	**1** ω/°	**2A** ω/°	**2B** ω/°	**3** ω/°
(1) (2)	58.6	71.3	69.1	10.4
(1) (3)	21.9	21.5	19.1	82.2
(2) (3)	36.8	91.0	92.2	72.0

Table 5. Intermolecular Contacts Less than 3.6 Å with Their Estimated Standard Deviations

a) **1**

superscript								
	(none)	x	y	z	(iv)	$x+1/2$	$-y+1/2$	$z+3/2$
	(i)	x	y	$z+1$	(v)	$x-1/2$	$-y+1/2$	$z-1/2$
	(ii)	$-x+1$	$-y$	$-z$	(vi)	$-x+1/2$	$y-1/2$	$-z-1/2$
	(iii)	$-x+1$	$-y$	$-z+1$				

Distance	l/Å	Distance	l/Å
O(1)···O(2^{iii})	3.552(4)	O(2)···C(5^{iv})	3.487(5)
O(1)···N(1^{ii})	3.449(4)	O(2)···C(10^{i})	3.539(4)
O(1)···C(6^{ii})	3.506(4)	O(2)···C(12^{iii})	3.441(4)
O(2)···O(2^{iii})	3.466(4)	N(1)···C(3^{vi})	3.451(4)
O(2)···N(2^{iii})	3.232(4)	N(2)···N(2^{iii})	3.437(5)
O(2)···C(4^{iv})	3.498(5)	C(5)···C(11^{v})	3.565(4)

b) **2**

superscript								
	(none)	x	y	z	(iii)	$-x+1$	$-y+1$	$-z+1$
	(i)	$x+1$	y	z	(iv)	$-x+1$	$-y+1$	$-z+2$
	(ii)	$-x+1$	$-y$	$-z+1$	(v)	$-x+2$	$-y+2$	$-z+2$

Distance	l/Å	Distance	l/Å
O(1)···C(5^{i})	3.503(4)	N(2)···C(3B^{iii})	3.543(4)
O(1)···C(6B^{iv})	3.398(4)	C(3)···O(2B^{iv})	3.560(4)
O(2)···O(2^{v})	3.203(6)	C(3)···N(2B^{iv})	3.558(4)
O(2)···C(13^{v})	3.496(4)	C(6)···O(1B^{iii})	3.441(3)
O(2)···C(3B^{iii})	3.509(4)	O(1B)···C(5B^{i})	3.554(4)
N(1)···N(2B^{iii})	3.471(3)	O(2B)···C(4B^{i})	3.577(4)
N(1)···O(1B^{iii})	3.499(3)	O(2B)···C(13B^{ii})	3.405(3)

c) **3**

superscript								
	(none)	x	y	z	(iii)	$x+2$	$y+1$	z
	(i)	$x-1$	y	z	(iv)	$-y+1$	$x-y$	$z+1/3$
	(ii)	$x+1$	$y+1$	z	(v)	$-y+1$	$x-y-1$	$z+1/3$

Distance	l/Å	Distance	l/Å
O(1)···C(5^{iii})	3.542(5)	C(6)···C(14^{i})	3.457(6)
O(1)···C(15^{iv})	3.575(6)	C(7)···O(2^{i})	3.531(6)
N(1)···N(2^{i})	3.560(5)	C(8)···O(2^{v})	3.431(5)
N(1)···C(12^{i})	3.490(5)	C(10)···O(2^{v})	3.452(5)
N(1)···C(13^{i})	3.525(6)	C(10)···C(5^{ii})	3.531(6)
C(1)···C(13^{i})	3.384(6)	C(11)···C(5^{ii})	3.591(6)
C(6)···C(13^{i})	3.439(6)		

torsion angle of C(1)-N(1)-C(7)-C(9) is 175.2(2)°, while the corresponding angle of *N*-(2-bromophenyl)-2-bromobenzylamine is 88.5° because of the existence of large ortho substituents.[7] For **2** the phenyl group is trans to C(8) about the N(1)-C(7) bond and N(1) is trans to the 4-nitrophenyl group about the C(7)-C(8) bond. On the other hand in the case of **3** the phenyl group is gauche to C(8) about the N(1)-C(7) bond and N(1) is trans to 4-nitrophenyl group about the C(7)-C(8) bond. To analyze the planarity of molecular moieties, each molecule has been devided into three fragments: (1) C(1)—C(6) plane of the phenyl or *p*-tolyl groups; (2) C(9)—C(14) of the nitrophenyl groups; and (3) the central chain N(1)-C(7)-C(9) of **1** or N(1)-C(7)-C(8) of **2** and **3**. The dihedral angles of these planes are also listed in Table 4. The phenyl group of **1** and **2** is roughly parallel to the central chain and the 4-nitrophenyl group of **2** is perpendicular to the plane (3). For **3** both six membered rings are almost perpendicular to the central chain, and they are approximately parallel to each other. The nitro group of each compound is nearly coplanar to the phenyl ring. The dihedral angles beween the plane (2) and the nitro group are 3.6, 2.7, 2.6, and 0.4°, for **1**, **2A**, **2B**, and **3**, respectively.

Significant differences are observed about the dimensions of the amino groups between **1** and the other compounds, **2** and **3**. The N(1)-C(1) bond of **1** is longer than those of **2** and **3**, while the N(1)-C(7) bond of **1** is shorter than those of **2** and **3**. The bond angle of C(1)-N(1)-C(7) of **1** is slightly smaller than the corresponding angles of **2** and **3**. The N(1)-C(1) bonds of **2** and **3** show a larger double-bonded character compared with those of anilines. The corresponding length of *N*-benzylideneaniline is 1.460 Å.[8] These features correspond to the difference of the planarity of the amino plane C(1)-N(1)R-C(7) (R=H(1) or C(16)) between the benzyl and phenethyl compounds. The deviations of N(1) from the plane defined by C(1), C(7) and H(1)/C(16) are 0.259, 0.167, 0.125, and 0.145 Å for **1**, **2A**, **2B**, and **3**, respectively.

Crystal Stuctures and Interactions. Crystal structures are shown in Fig. 2 and some intermolecular contacts are listed in Table 5. The packing mode of the molecules in the crystal **2** is approximately $P2_1/c$. There are no special contacts suggesting an intermolecular CT interaction nor an NH ··· O hydrogen bond for **1** and **2**, in spite of the possibility of these interactions. On the other hand in the case of **3** the nitrophenyl plane is stacked on the *p*-tolyl plane of the neighbouring molecule alternately, as shown in Fig. 3.

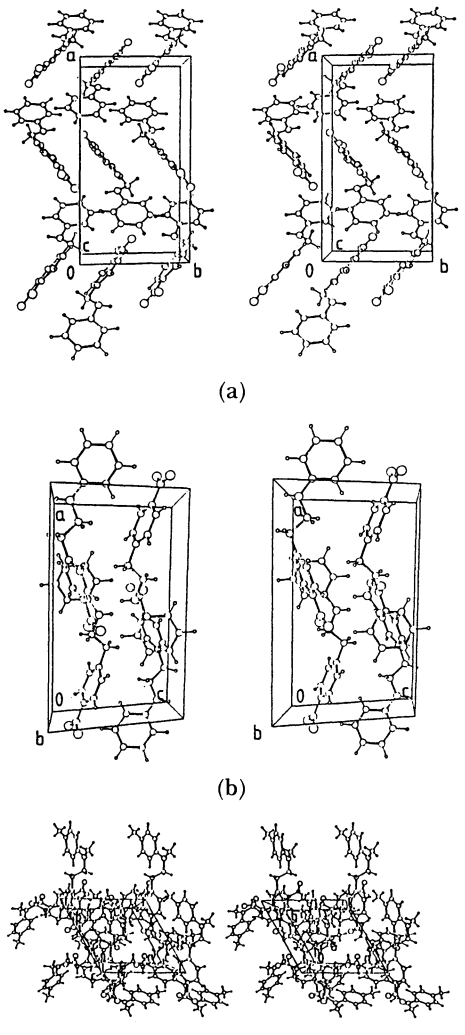


Fig. 2. Stereoscopic view of the crystal structures. (a) **1**, (b) **2**, and (c) **3**.

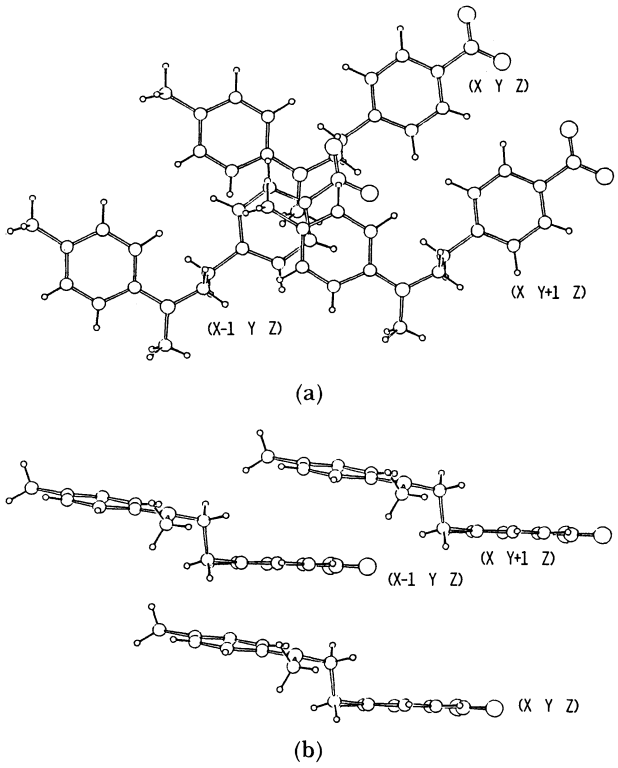


Fig. 3. Molecular stacking of **3**. (a) Projection to the nitrophenyl plane. (b) Side view of the stacking

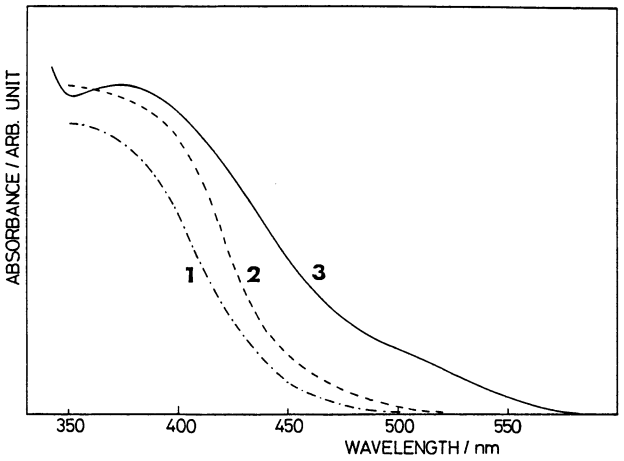


Fig. 4. Electronic spectra of **1**, **2**, and **3** in the solid state. Absorbance is in an arbitrary unit.

The mean distance between these planes is 3.40 Å, which is short enough for π-π overlap or CT interaction and this may relate to the orange-red color of the crystals of **3** compared to pale-brown of **1** and **2**. In order to confirm the presence of the interaction, the electronic absorption spectra of these compounds in the solid state were measured. As illustrated in Fig. 4, **1** and **2** show almost a similar spectral curve. On the other hand **3** has an extra absorption at 400—600 nm region, which is undoubtedly responsible for its orange-red color. Taking into account the molecular arrangement of **3** in the crystals, it is reasonable to conclude that there is an intermolecular CT interaction between 4-nitrophenyl and *p*-toluidino moieties.

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